

Division of Polymer Chemistry (POLY)

Graphical Abstracts



Submitted for the 255th ACS National Meeting & Exposition

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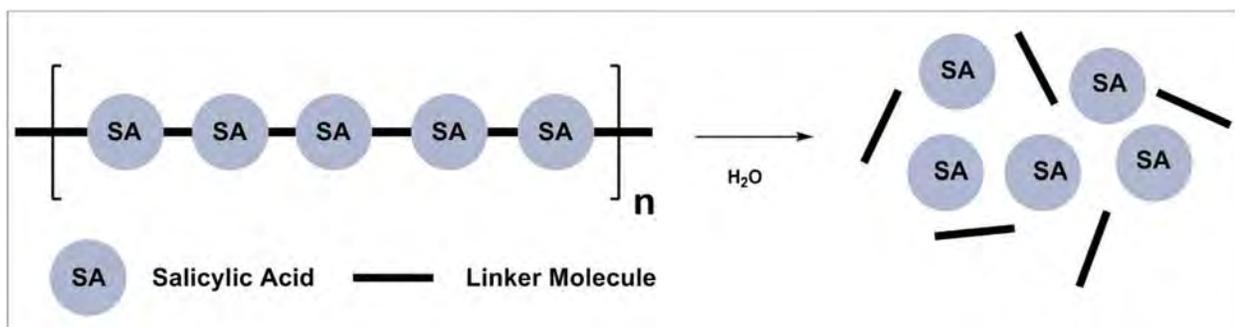
POLY 1: Designing polymers for controlled release applications

Kathryn E. Uhrich, *kathryn.uhrich@gmail.com*. Chemistry, University of California, Riverside, Riverside, California, United States

Our research centers on polymeric bioactives; specifically, the design of biocompatible, biodegradable polymers. While polymeric bioactives were initially designed for drug delivery, the concept has been expanded to include bioactivity delivery – from bioactives that improve the lubricity of engine oils, to bioactives that prevent plaque buildup on tooth enamel, and to bioactives that improve skin appearance. When designing biocompatible and biodegradable polymers, we begin with starting materials that are naturally occurring and generally deemed safe. With these design parameters, we've developed two different classes of polymers - polymers that deliver bioactives and polymers derived from bioactives.

As polymers that deliver bioactives, nanoscale amphiphilic macromolecules (AMs) were initially created to encapsulate hydrophobic drugs and improve drug water-solubility and improve bioavailability. Our current work builds upon the discovery that the demonstrated that the AMs themselves are bioactive – they actively coordinate with binding domains on macrophages to mitigate formation of atherosclerotic plaques. They also display novel mechanisms for mitigating biofilm formation.

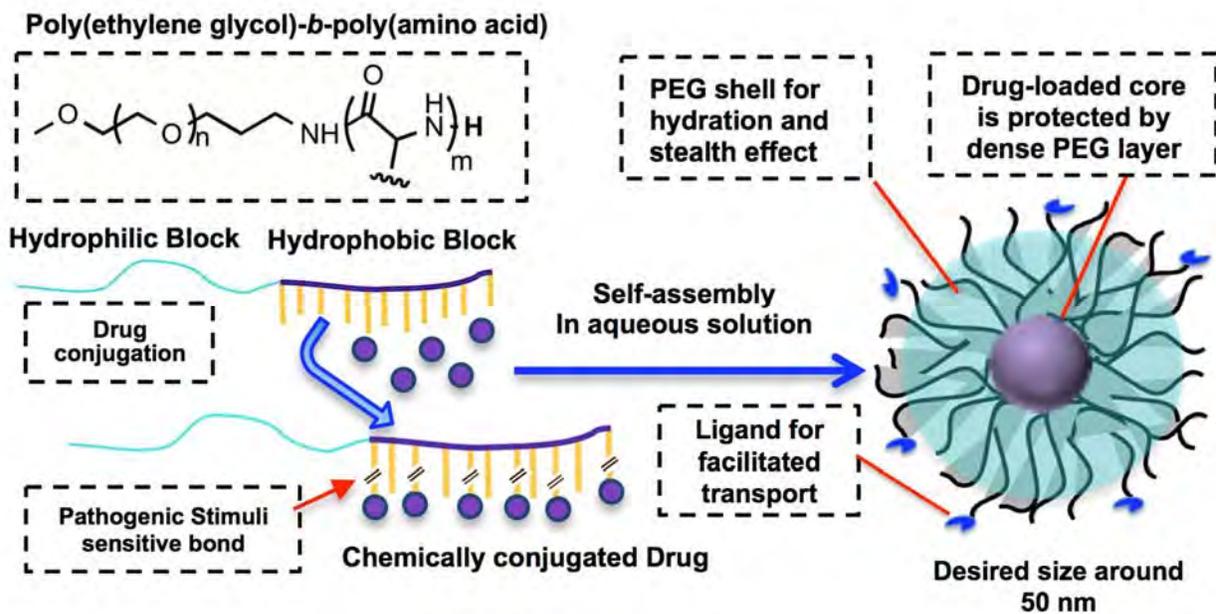
As polymers derived from bioactives, PolyActives are designed to biodegrade into therapeutically useful or bioactive molecules. The first example was a poly(anhydride-esters) that yielded salicylic acid, the active component of aspirin, and nicknamed PolyAspirin. This concept has been expanded to include PolyAntibiotics, PolyAntiseptics and PolyOpiates useful for localized, controlled bioactive delivery for pharmaceutical, personal care, and commercial applications.



POLY 2: Targeting cancer using stimuli-sensitive polymeric micelle.

Sabina Quader¹, *sabina-q@kawasaki-net.ne.jp*, **Kazunori Kataoka**^{2,1}, *kataoka@bmw.t.u-tokyo.ac.jp*. (1) Innovation Centre of NanoMedicine, Kawasaki, Japan (2) Policy Alternatives Research Institute, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, Japan

Nanomedicine has proven to be a safe and efficient alternative to traditional chemotherapeutic approach for tackling a complex and multifaceted disease like cancer. Among different nanomedicines, polymeric micelles, constructed from poly(ethylene glycol)-b-poly(amino acids) (PEG-PAA) copolymers, have already demonstrated significant promise through their clinical translation potential. PEG-PAA copolymers offer unique ability for versatile modifications of the PAA block to engineer stimuli-triggered drug release mechanism that is responsive to tumor microenvironment, while PEG effectively shields the core due to the high degree of hydration, chain mobility, and non-immunogenicity. In this presentation, several examples of stimuli-sensitive polymeric micelle system will be exhibited.

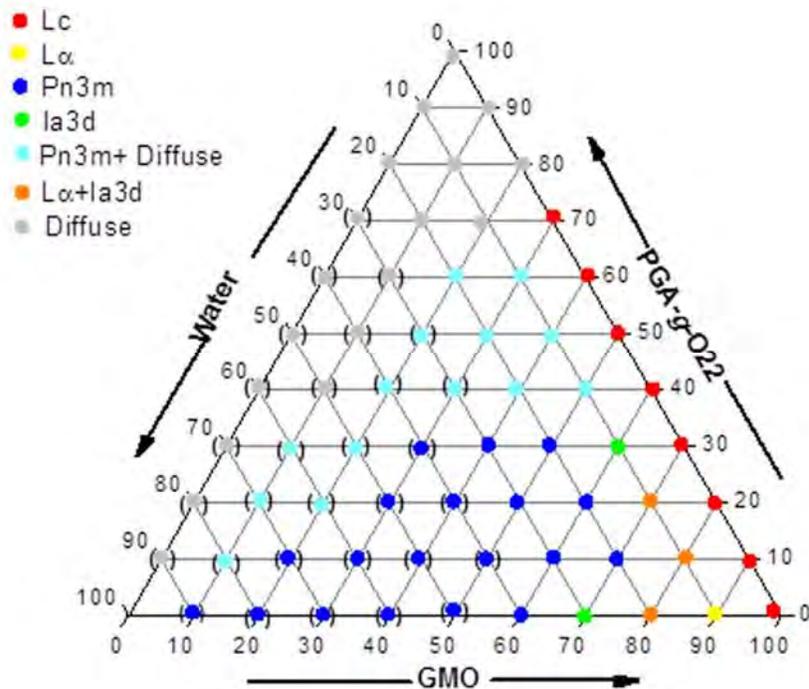


POLY 3: Modification of hydrophilic polyesters with fatty acids for drug release systems

Joerg Kressler, joerg.kressler@chemie.uni-halle.de, Karsten Maeder. Pharmacy, Martin Luther University Halle, Halle (Saale), Germany

Linear hydrophilic polyesters with pendent OH-groups in every monomer unit can be synthesized using lipase B from *Candida antarctica* without employing protecting group chemistry. The less reactive secondary OH-group(s) are usually provided from glycerol or different sugar units and do not react during polycondensation in contrast to the converted primary OH-groups. In order to obtain amphiphilic polymers suitable for the preparation of nanoparticles, the polyesters are partially grafted with saturated or unsaturated fatty acids.

The functional polyesters are biocompatible and non-toxic. They are able to form different nanostructured nanoparticles suitable for drug release purposes. Driving force for the phase separation within the nanoparticles is the ability of the graft chains to crystallize when saturated fatty acids are employed. The graft copolymers are additionally applied for the stabilization of cubosomes formed by glycerol monooleate. In order to have the suitable chain flexibility for cubosome stabilization, it is necessary that the grafting fatty acid is unsaturated as e.g. oleic acid. The present double bond prevents the graft chains from crystallization. Furthermore, poly(glycerol adipate) has been employed for conjugation with the drug indomethacin.



POLY 4: Biomedical applications of nano-sized polymeric micelles and polyion complexes

Alexander V. Kabanov, kabanov@unc.edu. Eshelman School of Pharmacy, University of North Carolina Chapel Hill, Chapel Hill, North Carolina, United States

The lecture will provide a high-level overview of the use of polymeric micelles, polyion complexes, cell mediated drug carriers and exosomes in the therapy of cancer and neurodegenerative diseases. The speaker will try to combine the lessons-learned during over a quarter of century work in the field of nanomedicine and drug delivery along with a vision statement of some trends and future prospective in this field. Several most recent examples from the UNC and MSU laboratories will be presented including high capacity polymeric micelles for single and multiple water-insoluble drugs and computation guided formulation design for cancer therapy. The nanoscale size polyion complexes formed by ionic block copolymers and polypeptides for the delivery of these polypeptide will be also discussed. Examples include antioxidant enzymes (e.g. superoxide dismutase, catalase), stoichiometric and catalytic scavengers of organophosphorus toxins (butyrylcholine esterase, organophosphate hydrolase) and neurotrophins (brain-derived neurotrophic factor, glial cell line-derived neurotrophic factor). The applications include treatments of obesity, stroke, Parkinson's disease (PD), RETT syndrome, organophosphorus toxins poisoning, and some other medical conditions that have been demonstrated using animal models. The application of these complexes in the context of the macrophage carriers for drug delivery to the site of inflammation will be presented. A concept of the use of genetically modified macrophages as natural gene delivery vectors will be stated and illustrated using PD therapy as an example. The role of exosomes in gene and protein delivery and its potential as a true pharmaceutical modality will be also discussed.

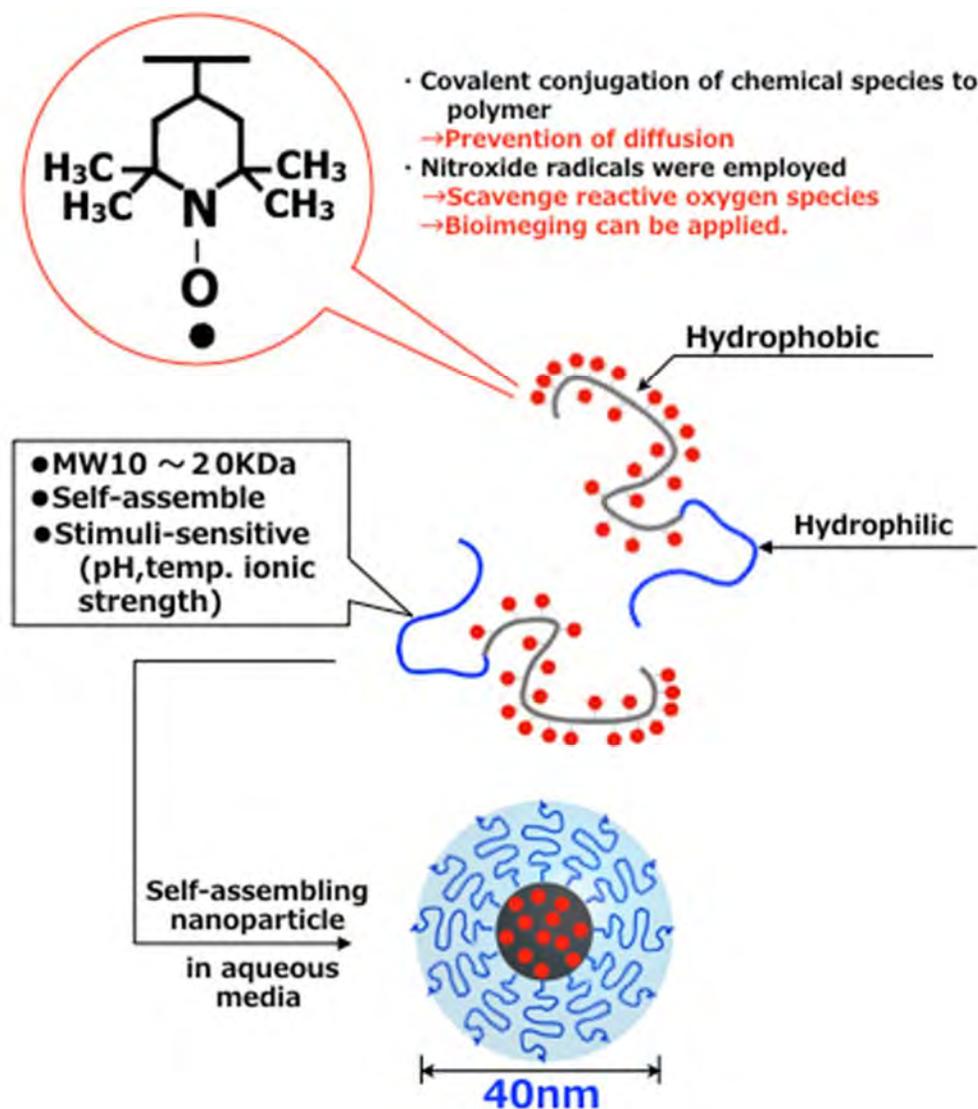


Prof. Sasha Kabanov

POLY 5: Design of antioxidative nanomedicines

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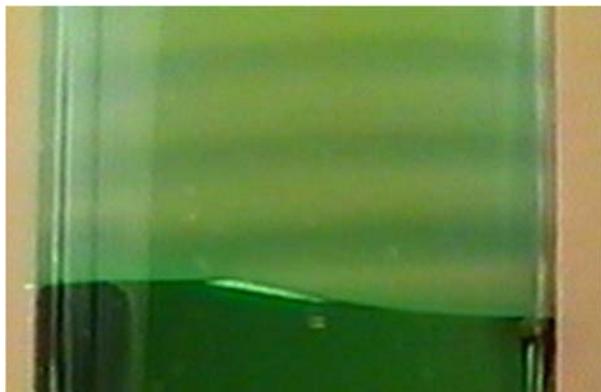
Reactive oxygen species (ROS) are known to play various roles on the occasion of many important events in our body. However, excessive production of ROS causes significant adverse side effects to living body. Low molecular weight antioxidants spread non-specifically to entire body and destroy normal redox reactions after internalization in healthy cells. To improve selective anti-oxidant character in vivo, we have designed redox polymer drugs, which possess self-assembling character in aqueous media (Figure). The author will present detailed design of the antioxidant nanomedicine, which designed in his group.



POLY 6: Nonlinear dynamics and polymer systems: An overview

*Irving R. Epstein¹, **John A. Pojman**², john@pojman.com, Annette Taylor³. (1) MS 015, Brandeis Univ, Waltham, Massachusetts, United States (2) Chemistry, Louisiana State University, Baton Rouge, Louisiana, United States (3) Chemical and Biological Engineering, University of Sheffield, Sheffield, United Kingdom*

This Symposium brings together two fields of science that have, until recently, interacted only relatively rarely. The central role of polymer science in understanding the substances of modern life and, indeed, of life itself is obvious. Nonlinear dynamics is a newer science, but one that has afforded important insights into phenomena in chemistry, physics, mathematics, biology, geology, and even the social sciences. Perhaps because so much of polymer science occurs in an industrial context, where nonlinear behavior such as chaos is typically seen as something to be avoided, even at the cost of suboptimal operating conditions, the amount of cross-fertilization between these areas has been limited. This week, we will learn about the progress that has been made in unveiling and exploiting the nonlinear dynamical aspects of polymer systems.

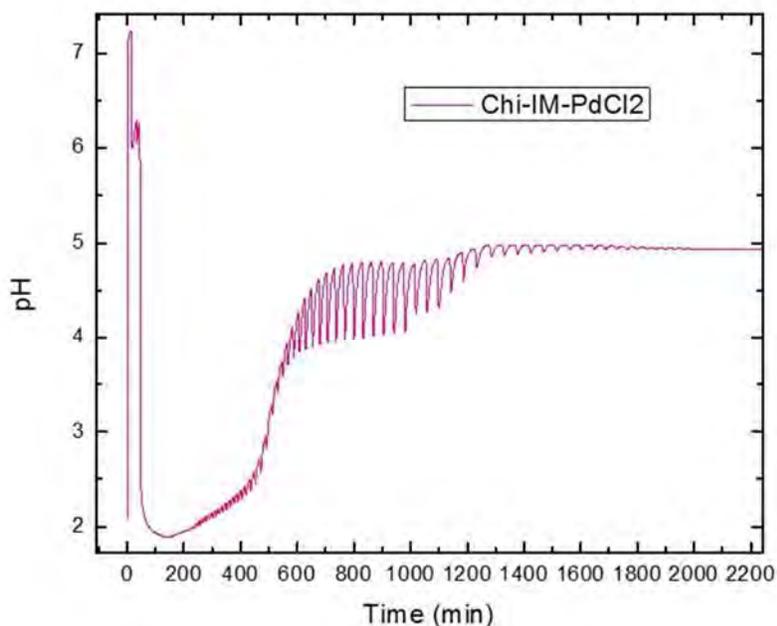


Pattern left by an oscillatory mode of frontal polymerization.

POLY 7: Polymer-based catalysts in oscillatory carbonylation reactions

Anna Isakova, **Katarina Novakovic**, katarina.novakovic@ncl.ac.uk. School of Engineering, Newcastle University, Newcastle upon Tyne, United Kingdom

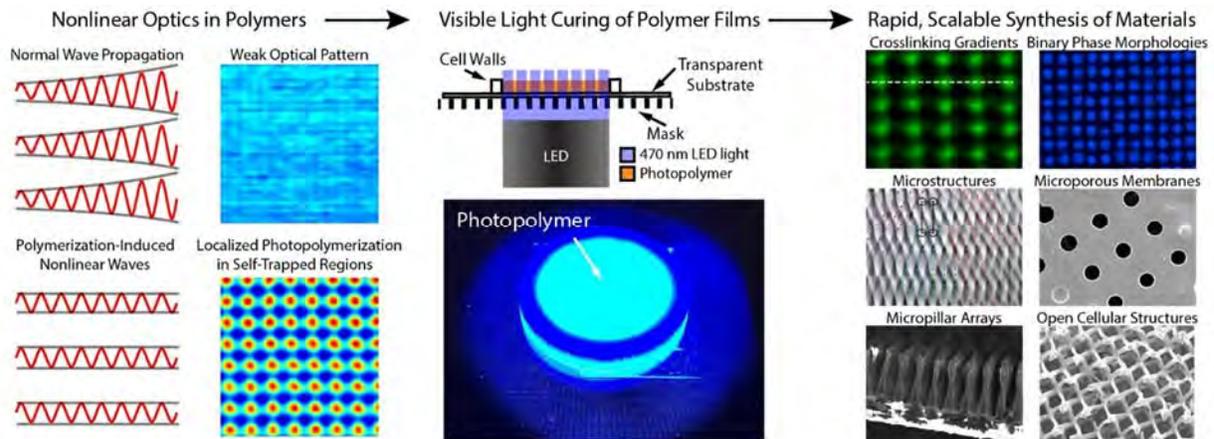
Oscillatory chemical reactions are continuing to attract attention as the driving force for smart materials and, more recently, in the quest for biomedical applications such as pulsatile drug delivery and controlled tissue proliferation. Our group has focused on palladium-catalysed carbonylation of terminal alkynes, reporting reproducible oscillatory behaviour in pH using mono- and di-alkyne terminated polymeric substrates. This is the first and so far only example of a polymeric substrate based oscillatory chemical reaction under laboratory conditions. Paving the way towards an all polymeric oscillatory reaction system we present our study on polymer-based palladium catalysts which produce sustainable oscillations in pH when substituted for the palladium iodide usually employed in this carbonylation reaction. A chitosan based catalyst incorporated in a chitosan-based gel membrane also produces oscillations in a water:methanol mixture (50:50%) while exhibiting controlled release of the reaction product.



POLY 8: Coupling nonlinear optical dynamics to polymer systems for light-directed evolution of morphology

Saeid Biria, **Ian D. Hosein**, idhosein@syr.edu. Biomedical and Chemical Engineering, Syracuse University, Syracuse, New York, United States

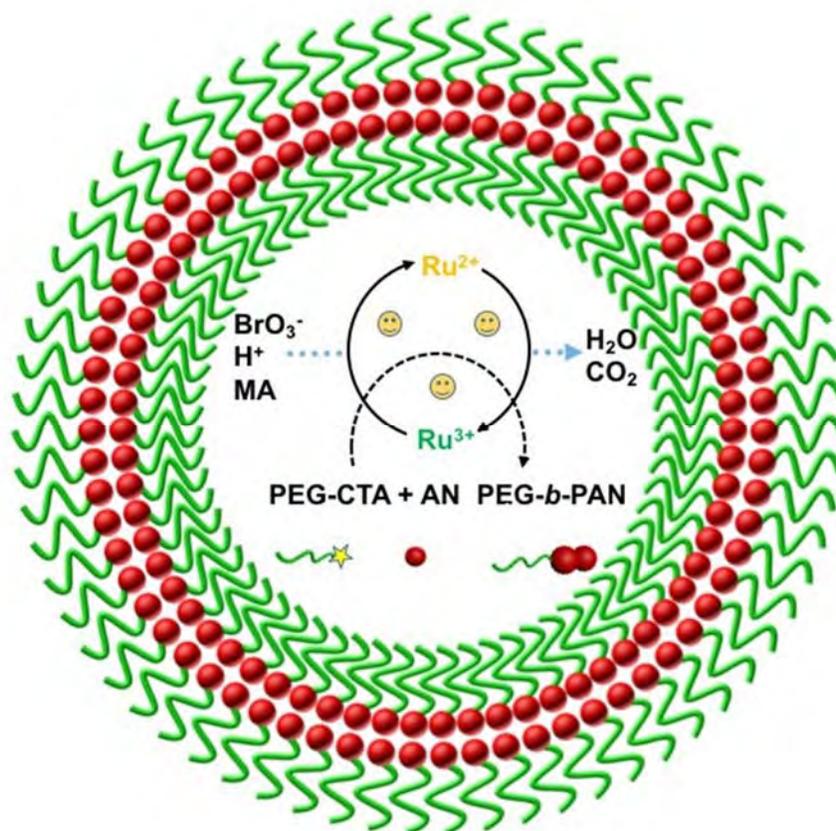
Coupling polymeric systems to nonlinear dynamics offers opportunities to create materials with tailored morphology and function via pattern forming processes. Examples include periodic striations from traveling fronts in thermal polymerization, coalescence of polymer films during dewetting, oscillatory gels, and phase separation. Here, we present a fundamentally new mechanism to organize polymeric materials that couples photopolymerization to the nonlinear dynamics of optical fields. In a new process of optical autoacceleration, a positive feedback mechanism emerges between photopolymerization and transmitted light intensity, whereby a mutual, dynamic interaction emerges between optical field distribution and the underlying morphology of the polymer medium. The input light undergoes Modulation Instability – dividing into a multitude of microscale “self-trapped” beams, which are nonlinear waveforms characterized by divergence-free propagation through polymer medium. As a result, these nonlinear waveforms inscribe permanent microstructure consisting of microscopic “channels” in the polymer. This coupling between optical nonlinearity and morphology evolution will be demonstrated with three examples. First, in a family of photoinitiated polyfunctional acrylates, we demonstrate how crosslinking interacts with the optical instability, whereby it regulates both optical pattern formation and resultant microstructure. Secondly, in a blend of photoreactive monomers, we show how nonlinear waves induce and regulate microscale, spatially-local spinodal decomposition (chemical instability) along their path lengths, leading to a large-scale, multiphase morphology that corresponds to the arrangement of self-trapped beams. Thirdly, microporous materials are produced through nonlinear optical pattern formation in a photopolymer-solvent mixture, wherein the solvent behaves like a porogen and can be removed after the reaction. Harnessing nonlinear optical pattern formation to direct the organization of polymeric materials opens opportunities for studying the fascinating complexity of nonlinear systems, while creating advanced microstructures that can serve functional roles in a host of applications.



POLY 9: Autonomous non-linear chemical control of functional polymer vesicle self-assembly from a 'homogeneous mixture'

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We have addressed the problem of the concurrent vesicle fabrication and encapsulation of an active and functional chemical reaction which is the same reaction that, from a well-stirred mixture, controls and carries out the synthesis of the amphiphilic block copolymers that self-assemble into the polymer vesicles that encapsulate the reaction. We use the chemical energy and radicals provided by the Belousov-Zhabotinsky (B-Z) chemical reaction to synthesize the micrometer- size vesicles enclosing this (active) oscillating chemical reaction inside. The periodically formed radicals from B-Z reaction initiate radical polymerization between a polyethylene glycol based chain transfer agent (PEG-CTA) and acrylonitrile monomers in water. The different chemical environments inside and outside the vesicles contribute to enlarging the area and diameter of the resulting self-assembled vesicles and, in some cases, promote blebbing and division.



Polymerization and self-assembly of amphiphilic block copolymer to form micrometer sized vesicles entrapping an active oscillating B-Z reaction.

POLY 10: Out-of-equilibrium self-assemblies and autonomous material systems with programmable lifetimes

Andreas Walther, andreas.walther@makro.uni-freiburg.de. University of Freiburg, Freiburg, Germany

Living self-organizing systems operate far-from-equilibrium and maintain functions by constant energy dissipation in adaptive steady states, and are orchestrated through feedback loops to allow tailored response in complex sensory landscapes.

In man-made self-assemblies we have mastered to a large extent near-equilibrium structure formation in space, and have gained an increasing understanding to construct very complex, hierarchically structured soft matter with responsive properties. This has allowed to create materials with advanced functionalities and switchability, inaccessible without sophisticated nano- and mesostructuration and delicate control over molecular interactions.

Some of the next steps in self-assembling systems are to approach multicomponent co-assemblies, and to master temporal behavior as well as complex adaptation mechanisms. The latter require new types of internal control mechanisms, such as kinetic control over opposing reactions (built-up/destruction), the integration of feedback mechanisms, or the use of energy dissipation to sustain structures only as long as a chemical fuel is available. This ultimately goes along with a transition towards out-of-equilibrium complex systems, in which multiple components self-assemble dynamically in a non-linear and adaptive fashion.

In this talk I will present concepts for such out-of-equilibrium systems, which allow to program self-assemblies and materials with *lifetimes* via kinetic control mechanisms using of promoter/deactivator pairs, and via the installation of internal feedback systems. This will be showcased for different self-assembling systems (polymers, peptides, DNA), and the connection to hydrogels and photonic materials demonstrates possibilities for new horizons in materials science.



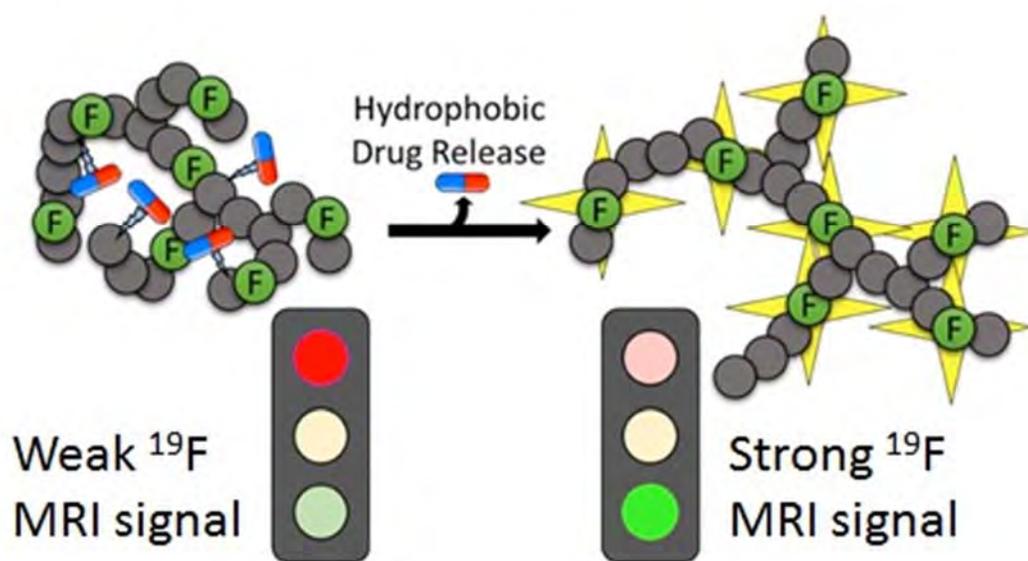
POLY 11: Development of polymeric MRI agents as theranostics

Kristofer Thurecht^{2,3}, k.thurecht@uq.edu.au, **Adrian Fuchs**², **Abhijeet Bapat**¹, **Zachary Houston**⁴. (1) Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, Washington, United States (2) The University of Queensland, Brisbane, Queensland, Australia (3) ARC Centre of Excellence in Convergent BioNano Science and Technology, The University of Queensland, Brisbane, Queensland, Australia

Development of sensitive molecular imaging agents is one of the major challenges for advancing targeted imaging using MRI. The development of imaging agents that can be directly imaged using MRI holds particular interest since these have the potential to increase sensitivity while being able to directly probe a reaction or process that occurs *in vivo*. In general, directly observable MR probes are very sensitive to their local environment and as such, can be manipulated as “switchable” agents in response to a number of endogenous or exogenous stimuli.

In this presentation we report on the development of sensitive hyperbranched polymeric ¹⁹F MRI contrast agents that combine controllable functionality, ability for cell-targeting *in vivo* and low cytotoxicity. More importantly, owing to the strong dependence of the ¹⁹F MR properties on the local environment, such systems are amenable to the development of responsive probes that give real-time assessment of biological function. We demonstrate this effect with some examples of systems that show a change in signal intensity based on its location in the body. Finally, the application of ¹⁹F MRI as a means to potentially quantify drug delivery *in vivo* is discussed, with an example that highlights the potential of this technique, but also the challenges that remain.

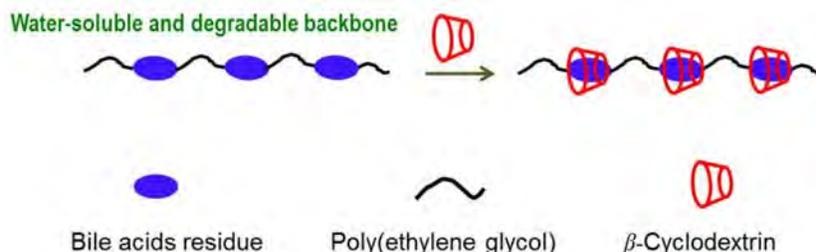
Switchable probe through hydrophobicity



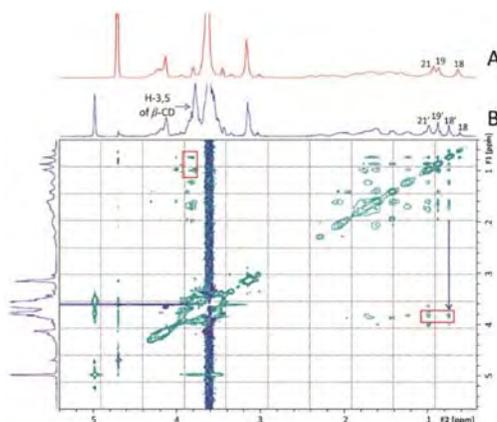
POLY 12: Characterization of hydrogels with NMR techniques

Yongguang Jia, Cédric Malveau, **Julian X. Zhu**, julian.zhu@umontreal.ca. Chimie, Université de Montréal, Montreal, Quebec, Canada

Various NMR techniques can be used in the characterization of hydrogels. The molecular interactions can be studied by 2-dimensional nuclear correlation experiments; diffusion in the gels can be studied by pulsed field gradient NMR experiments and NMR imaging; the gelation process can be followed by the determination of relaxation times. New hydrogels can be made via the formation of dynamic bonds through supramolecular assembly and host-guest interactions of both polymers and small molecules. Such materials may find applications in drug delivery, tissue engineering and cell culture. For example, we prepared polypseudorotaxanes in the form of a molecular necklace by threading β -cyclodextrins (β -CD) onto thermoresponsive polyurethanes derived of bile acids. This can be evidenced by NOESY NMR experiments and visualized by the scanning tunneling microscopy. The polypseudorotaxanes show thermosensitivity in water and the phase transition temperature may be fine-tuned by varying molar ratios of β -CD to the bile acid units. The thermoresponsiveness of the polymers in water can also be studied by variable-temperature NMR experiments. Mixing copolymers bearing cholic acid and cyclodextrin pendent groups induced the gelation of the polymers, resulting in a hydrogel with interesting self-healing properties. The diffusion of linear polymers and dendrimers in polymeric hydrogels can be studied by NMR to elucidate the effects of size and shape of the diffusants.



The preparation of a polypseudorotaxane (a molecular necklace) by threading β -cyclodextrins (β -CD) onto a polyurethane derived of bile acids.

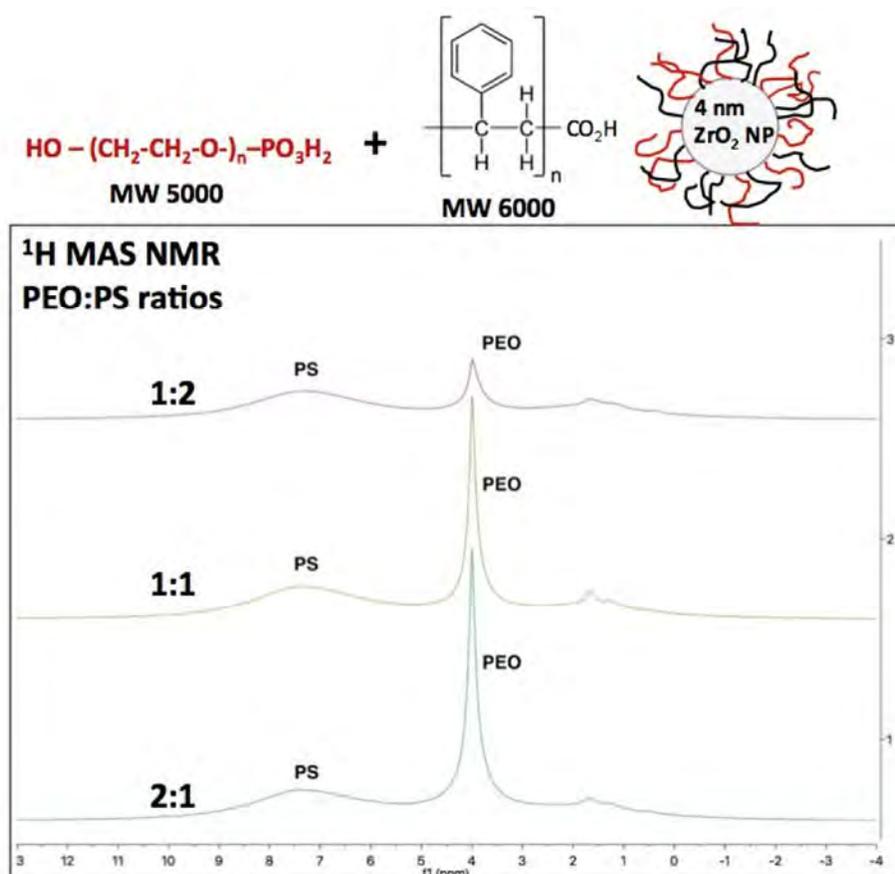


¹H NMR spectrum of the polyurethane containing bile acid and 2D NOESY NMR spectrum of complex of the polymer with β -CD in D₂O.

POLY 13: Characterization of patchy nanoparticles by solid-state NMR

Linda G. Reven, *linda.reven@mcgill.ca*, Brenda Guzman Juarez, Kuenhee Kim, Ahmed Abdelaal, Safiya Allie, Violeta Toader. Chemistry, McGill University, Montréal, Quebec, Canada

“Patchy particles” where the surface is anisotropically patterned through variation in the surface composition, can form different colloidal crystal structures and have applications as interface stabilizers, in catalysis and targeted drug delivery. [1] “Patchy nanoparticles” can be formed by adsorbing two chemically different polymer chains that will spontaneously phase separate. Although there is growing interest in polymer based patchy nanoparticles, the majority of the studies have been theoretical rather than experimental due to difficulties in preparing significant quantities of nanoparticles with controlled polymer ratios. [2] As a model system, metal oxide NPs with polystyrene and poly(ethylene oxide) ligands with different ratios were prepared through a simple exchange process. Solution and solid-state NMR experiments designed to characterize the phase separation on different length scales were applied to characterize the nanoparticles with mixed polymer ligands and their assemblies in response to different solvent mixtures.

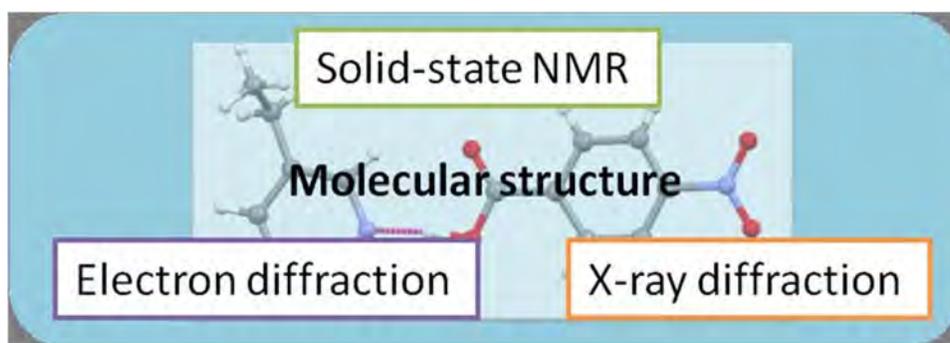


POLY 14: NMR, X-ray and electron crystallography for crystalline polymorphs and salt/cocrystal/continuum issues at natural abundance

Yusuke Nishiyama^{1,2}, nisiyama@pb3.so-net.ne.jp. (1) JEOL RESONANCE Inc, Akishima Tokyo, Japan (2) CLST-JEOL Collaboration Center, RIKEN, Kanagawa, Japan

Salt/cocrystal/continuum: While single crystal X-ray diffraction (SCXRD) is widely used for structure determination of crystalline materials, it is not straightforward to determine the hydrogen positions due to small scattering power of hydrogens. This is problematic especially to distinguish salt and cocrystals, where hydrogen positions play a key role. On the other hand, solid-state NMR (SSNMR) is able to directly observe ^1H (proton) with the aid of technical and methodological progress of very fast MAS. The combination of XRD for structural determination and SSNMR for hydrogen observation gives whole structural picture of small organic molecules. We demonstrate this approach to distinguish salt/cocrystals/continuum in multi-component systems including co-drugs.

Crystalline polymorphs: The same molecule can be packed in crystals with different manners. The different molecular packing results in different ^1H chemical shift anisotropy (CSA) which gives additional insight of molecular structure with a help of quantum chemical calculations. We also demonstrate parallel and anti-parallel arrangement of beta-sheet can be distinguished by 3D $^{14}\text{N}/^1\text{H}$ double quantum (DQ)/ ^1H single quantum (SQ) correlation experiments. Since both ^{14}N and ^1H are naturally abundant nuclei, it provides high-throughput measurements (several hours for each samples). We also demonstrate the use of electron diffraction (ED) for crystalline form determination. Since electron interact to materials 4-5 orders stronger than X-ray, sub-micro to nano-meter sized single-crystals can be used for SCED. This allow us to determine the crystalline form from micro-crystalline samples.



POLY 15: Application of dipolar-filter based time domain NMR for probing molecular motions, polymer crystallization and polymerization kinetics

Eduardo Azevedo, azevedo@ifsc.usp.br. Instituto de Física de Sao Carlos, Universidade de Sao Paulo, Sao Carlos - SP, Brazil

The development of advanced materials with desired properties and functions requires a thorough knowledge of structural and dynamical properties of the molecular systems that comprise them. Time Domain ^1H NMR (TDNMR) at low magnetic field is becoming quite popular for studying organic soft materials, in particular polymer and biopolymer based systems. There are already many TDNMR techniques available, exploring the relaxation phenomena, molecular diffusion and the ^1H - ^1H dipolar interaction. We will show some uses of TDNMR experiments based on the ^1H - ^1H dipolar interaction for investigating organic polymer systems. We build upon dipolar echoes and dipolar filters as tools for detailed characterization of molecular motions in amorphous and semi-crystalline polymers, evaluation and characterization of the slow crystallization kinetics in conjugated polymers and paraffin waxes and probing polymerization reaction in epoxy based resins. We discuss the joint use of ^{13}C NMR spectroscopy and ^1H TDNMR for detailed molecular characterization of intermediate and slow motions in polymers.

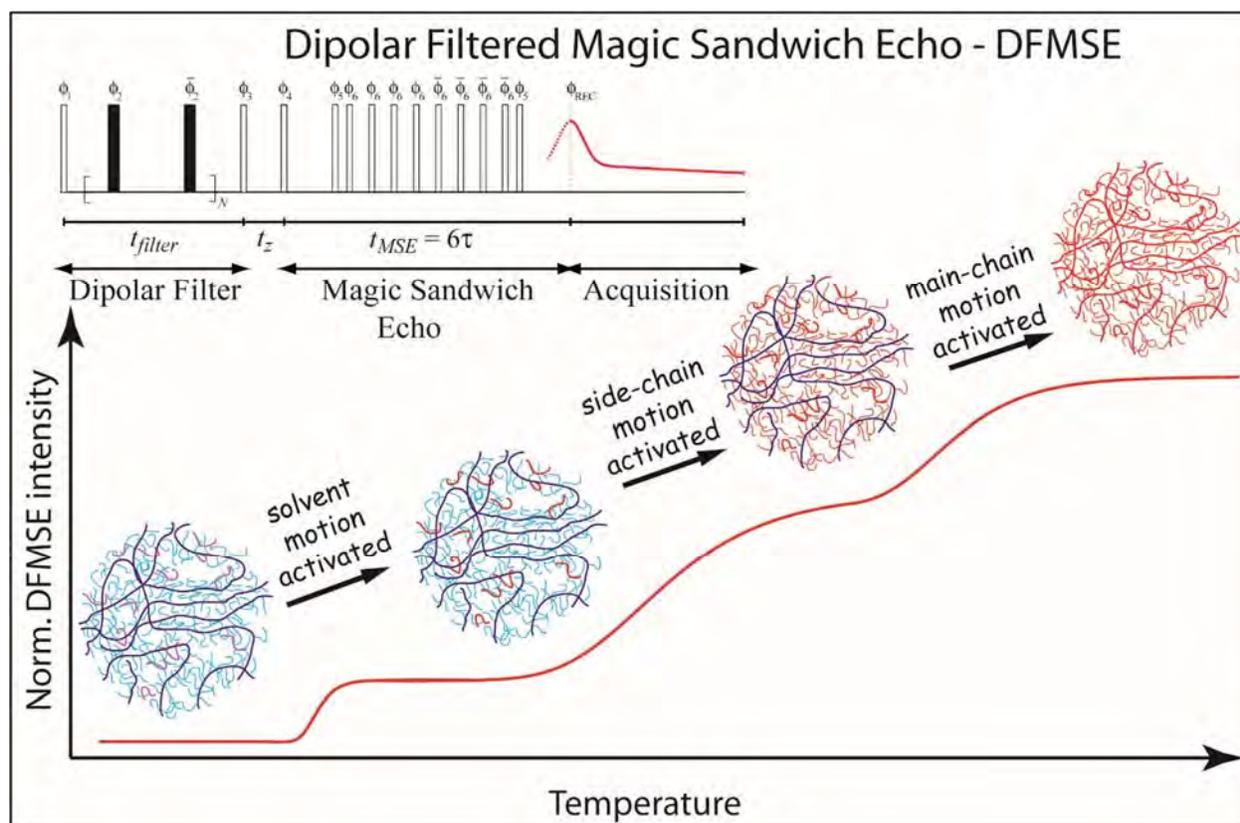
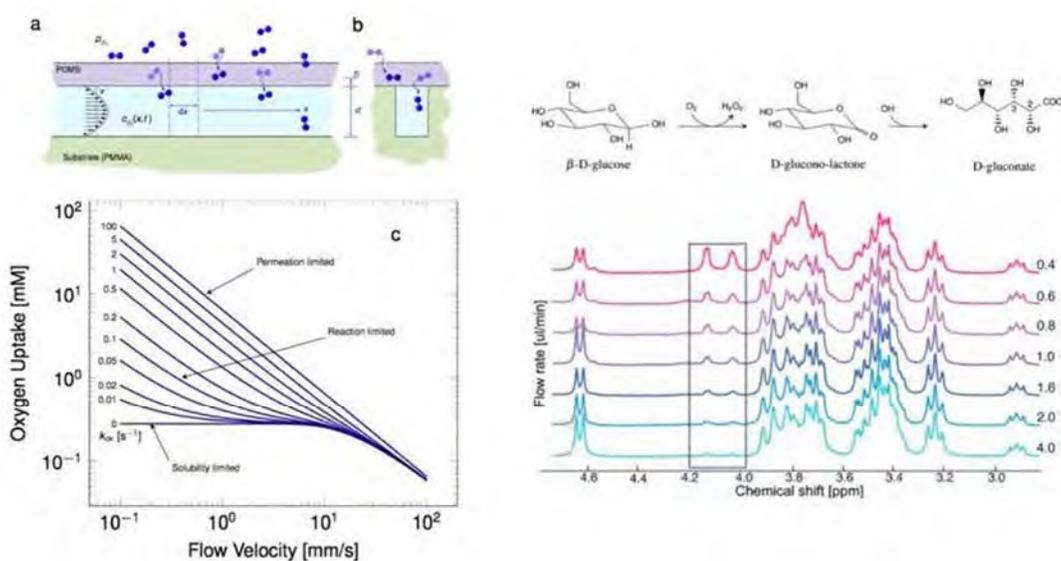


Illustration of the Dipolar Filtered Magic Sandwich Echo (DFMSE) pulse sequence and its use for detecting the onset temperature of different motions in a polymer sample.

POLY 16: Integration of nuclear magnetic resonance spectroscopy with microfluidic devices: Materials and other challenges

Marcel Utz, marcel.utz@southampton.ac.uk. School of Chemistry, University of Southampton, Southampton, United Kingdom

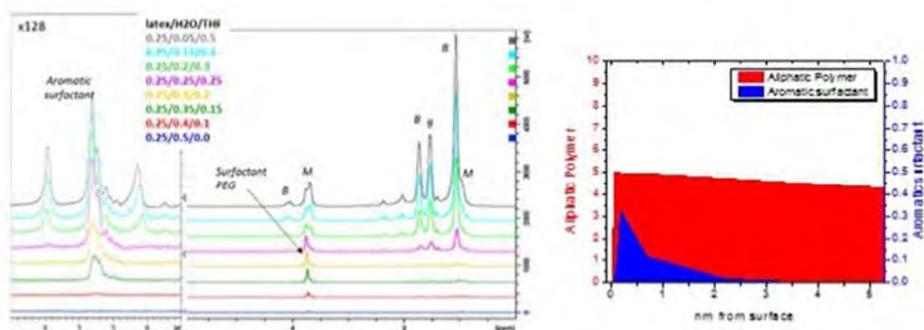
Microfluidic lab-on-a-chip devices are increasingly used in the life sciences. They offer a convenient and cost-effective platform for life science experimentation by enabling detailed environmental control for the culture of life systems, and by providing convenient avenues for highly parallel assays. While currently used devices mostly rely on fluorescence and other optical spectroscopic methods to extract specific information on cultured life systems, our group has focused on integrating high-resolution nuclear magnetic resonance spectroscopy with lab-on-a-chip devices. In contrast to optical methods, which rely on specific molecular markers, NMR spectroscopy can provide system-level information about metabolic processes in a quantitative and non-invasive manner. However, integration of magnetic resonance with microfluidic systems presents a number of technical challenges. On the one hand, sample volumes tend to be at least two orders of magnitude smaller than usual NMR samples. This requires careful design of the NMR detectors. On the other hand, NMR places specific requirements on the materials used in order to avoid unwanted background signals and to maintain the required homogeneity of the static and radiofrequency magnetic fields. Of specific interest to us is the transport of gases through microfluidic substrates. This is of obvious importance for the supply of cultures with oxygen, as well as for hyperpolarised techniques relying on para-hydrogen. The example below shows a study of oxygen permeation into a microfluidic device studied by following GOX mediated oxidation of glucose.



POLY 17: Distribution of functional monomers in latex particles: PFGNMR study

Kebede Beshah, *kbesah@dow.com*. Dow Chemical Company, Spring House, Pennsylvania, United States

Most emulsions use low level functional monomers for targeted end use applications such as adsorption and adhesion, water resistance and ambient crosslinking reactions. The challenge has been to fully characterize the location of these functional monomers in the latex particle. Functional monomers for adsorption property are preferentially placed close to the surface. In this work, we present a novel approach that enables us to probe surfaces as well as deeper into the latex particle for up to about 5-15 nm depending upon the composition of the polymers. The technique involves swelling of the latex particles with mixtures of water and water miscible solvents such as tetrahydrofuran (THF) to hydroplasticize components at the shell of the particle with variable depth based on the amount of THF used. This is followed by T2 (spin-spin relaxation) and diffusion (PFGNMR) filter experiments to remove signals of partially swollen portion of the polymer close to the core of the particle and water soluble species in the aqueous phase, respectively. This leaves only the signals from the hydroplasticized shell of the particle. We have demonstrated the method to probe the location of polymerizable surfactants, aceto acetoxy methacrylate (AAEM) and Diacetone acrylamide (DAAM). While AAEM is distributed throughout the depth we measured (5-10 nm), we detected some portion of DAAM much closer to the surface. We have also shown that changes to synthetic conditions appear to have the ability enhance the amount of DAAM close to the surface. Highly crosslinked latex particles and functional monomers without protonated side group or unique signals may not be accessible by this method.

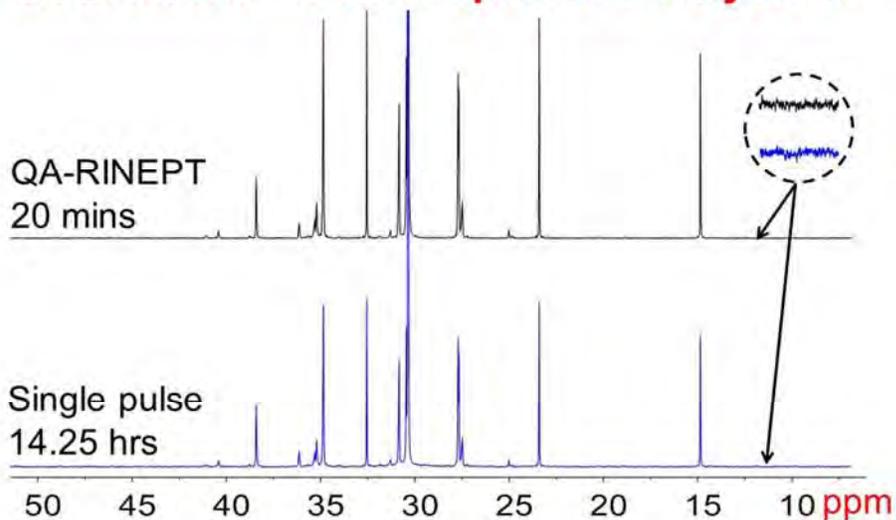


POLY 18: Quantitative analysis of polymers using sensitivity enhanced ^{13}C NMR spectroscopy

Jianbo Hou, JHou@dow.com, Yiyong He, Sam Qiu, Paolo Sabatino. The Dow Chemical Company, Midland, Michigan, United States

We present a novel NMR methodology named quantitative adiabatic refocused insensitive nuclei enhanced by polarization transfer (QA-RINEPT) that allows quantitative analysis of polymeric materials in a fast and robust manner. With the aid of adiabatic pulses, QA-RINEPT enables rigorous and controllable polarization transfer to yield ^{13}C NMR spectra with predictable sensitivity enhancement for quantitative analysis. In this talk, we will use examples to show and discuss the reliability and novelty of QA-RINEPT over other existing polarization transfer based methodologies. In particular, QA-RINEPT demonstrates its remarkable capability with polyolefin materials by saving up to 50-60x experimental time. The ^{13}C NMR spectra obtained have been analyzed and compared with the standard quantitative single pulse method by two individual analysts. Analytical results regarding composition and monomer sequence distribution show excellent agreement between different methods and analysts.

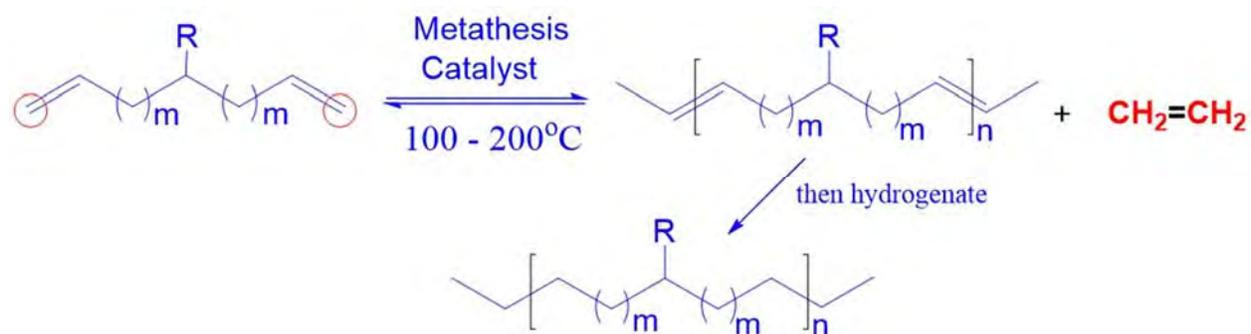
Quantitative ^{13}C NMR Spectra of Polyolefin



POLY 19: High temperature metathesis polymerization: ADMET in the melt state of highly crystalline polymers

Michael H. Bell¹, bellmichael3@gmail.com, **H. Grace Hester**¹, **Valentina Gomez**¹, **Alec Gallman**¹, **Kenneth B. Wagener**². (1) Chemistry, University of Florida, Gainesville, Florida, United States (2) Dept. of Chemistry, University of Florida, Gainesville, Florida, United States

Metathesis polymerization was performed at temperatures up to 200 C in the absence of solvent using a novel ruthenium Grubb's type catalyst. The polymerization temperatures were above T_m of the unsaturated polymer intermediates allowing for metathesis to proceed effectively in the melt state of the highly crystalline polymers. The robust, well-defined catalyst was tolerant to functional groups. The demonstrated high temperature reaction was effective at producing high molecular weight precision polymers via acyclic diene metathesis (ADMET) previously unattainable due to temperature limitations with traditional Grubb's type catalysts.



POLY 20: Synthesis of AB and ABA type block copolymers by ring-opening metathesis polymerization of strained 1,9-paracyclophanedienes

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π -Conjugated polymers have found extensive application as the active layers of optoelectronic and electronic devices such as OLEDs, OFETs, OPVs and sensors because of their flexibility, light weight and easy processability. However, the device performance is greatly influenced by morphology of the active layer. This is generally controlled by the kinetics of thin film formation during device fabrication but greater control is possible by the use of thermodynamic control using the phase separation of conjugated block copolymers to form well defined self-assembled nanostructures. This paper describes the ring opening metathesis polymerisation (ROMP) of strained paracyclophanediene monomers to generate well-defined poly(*p*-phenylenevinylene) (PPV) macroinitiators by end capping with vinyethers containing an α -bromoester radical initiator. The PPV macroinitiators can be utilized in ATRP with MMA to obtain AB and ABA type block copolymers. In addition sequential ROMP of two different cyclophanediene monomers has been investigated to obtain fully conjugated AB and ABA type block copolymers (Figure 1).

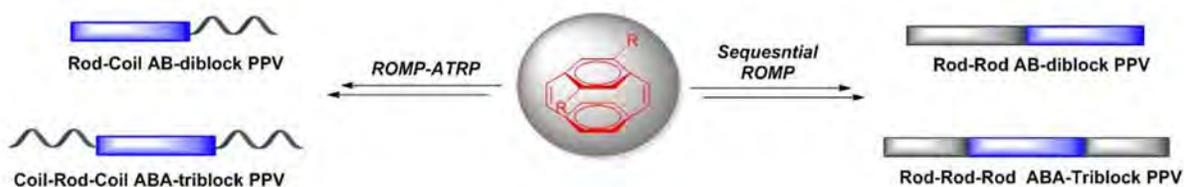
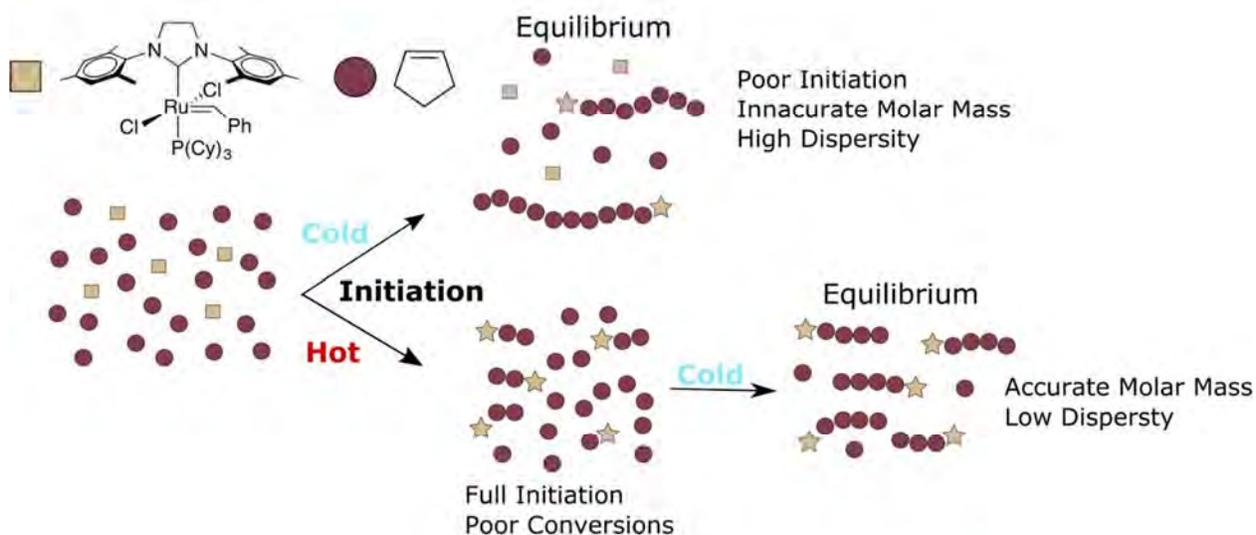


Figure 1: Synthesis of block copolymers by a sequential ROMP and ROMP-ATRP strategy

POLY 21: Variable temperature ring-opening metathesis polymerization of cyclopentene and derivatives

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The synthesis of targeted molar mass, high conversion, and narrow dispersity polymers from ROMP of low ring-strain monomers has been a long standing challenge to polymer chemists. Through careful consideration of polymerization conditions and thermodynamics, we report the synthesis of polymers within 5% of their theoretical molar mass with dispersities of ~ 1.3 and high conversions. Application of these principles to functionalized monomers can lead to new precision polymers for specialty applications and also well-defined segments for use in block polymer systems. With the ability to control the molar mass and dispersity of low strain monomers, new directions towards precision branching and advanced architectures are being explored. Some recent progress will be discussed.



POLY 22: Selective acyclic diene metathesis polymerization: New functional groups to create precise alternating and block polymers

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Beginning with a precise and well-defined monomer and polymer we can control the secondary structure, single chain organization, and the tertiary structure or multi-chain organization. These controlled tertiary structures can then assemble into unique polymer morphologies and have unique behaviors and physical properties. This concept has been applied extensively in homopolymers using acyclic diene metathesis (ADMET) polymerization.

Precise block polymers remain largely unstudied due to synthetic difficulties of creating a precise block polymer with functional groups spaced further than every few backbone carbons. ADMET cannot be used since the double bonds in the polymer backbone remain reactive so can undergo insertion if a new monomer is added (**Figure 1**).

Selective acyclic diene metathesis (SADMET) polymerization is the solution to this. It creates a polymer with nonreactive double bonds in the backbone, allowing for sequential addition of monomers and creating block polymers. Unfortunately, this technique has been limited to only a small number of functional groups, primarily acrylates. The work described aims at addressing this oversight.

We have studied electron deficient olefins such as acrylates, acrylamide, and conjugated ketones as well as sterically hindered olefins with allylic alcohols and methyl groups to find other types of monomers that will undergo SADMET polymerizations. Alternating and block polymers are then created utilizing these functional group, creating some of the first block polymer with precisely placed functional groups utilizing a nonliving, nonchain-growth polymerization mechanism.

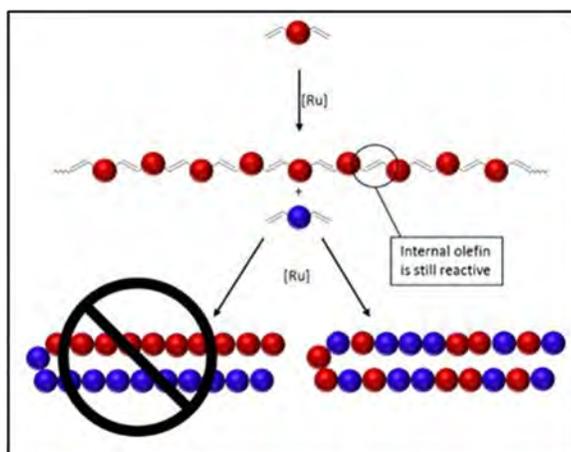
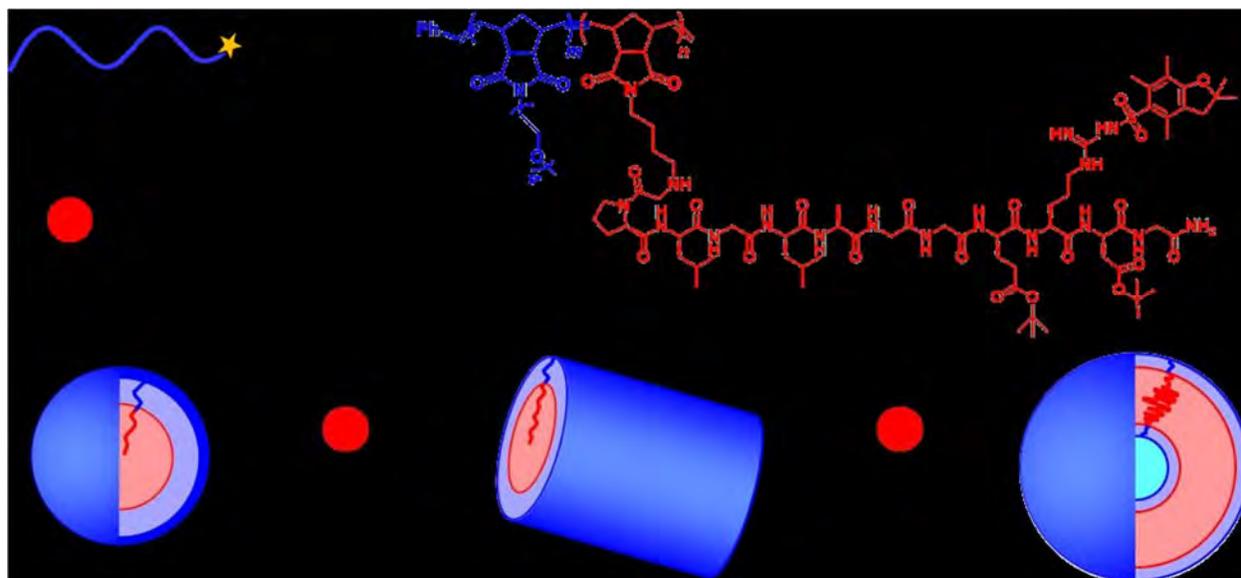


Figure 1: Addition of a second monomer in an ADMET polymerization does not lead to block polymers. Instead a statistical copolymer is formed.

POLY 23: Ring-opening metathesis polymerization-induced self-assembly (ROMPISA) in both aqueous and organic media

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We utilize functional norbornenyl monomers in combination with an oligoethylene glycol based norbornenyl monomer to provide a range of nanostructures at room temperature in both organic and aqueous media via a polymerization-induced self-assembly (PISA) process with ring-opening metathesis polymerization (ROMP) yet at high solids concentrations of 20 wt %. Kinetic evaluation of the polymerizations under mild conditions indicates that the living polymerization is unaffected during the PISA process and high monomer conversion is achieved. The demonstration broadens the scope of the PISA process to a new living polymerization methodology toward the development of easily accessible and highly functionalized nanostructures in situ.



POLY 24: Triblock terpolymers by simultaneous tandem block polymerization

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ABC-type triblock terpolymers of various monomers are typically synthesized by sequential polymerization steps. Herein we demonstrate as an alternative a facile one-pot, single step reaction avoiding potential side reactions due to the transfer of monomers or intermediates into another reaction vessel. A short α,ω -heterobifunctional polymeric linker served to combine initiator and catalytic moieties. After carefully balancing and screening for mutually compatible reaction conditions, two distinct, non-competing polymerization techniques were employed to simultaneously afford chain growth on both ends of the linker. Reactions like ring-opening polymerisation, ATRP and catalytic polymerisations using Grubbs catalysts were applied. Block copolymers of different polarity containing polymers such as polylactides, polynorbornene and PEO were obtained. Structural characterization by H-1-, DOSY-, and H-1,H-1-COSY-NMR revealed well-defined triblock terpolymers. Atomic Force Microscopy (AFM) and Dynamic Light Scattering (DLS) techniques were used to elucidate the self-assembly behavior.

Freudensprung, Ines, Markus Klapper, and Klaus Müllen. 2016. "Triblock Terpolymers by Simultaneous Tandem Block Polymerization (STBP)." *Macromolecular Rapid Communications* 37 (3): 209–14. doi:10.1002/marc.201500568.

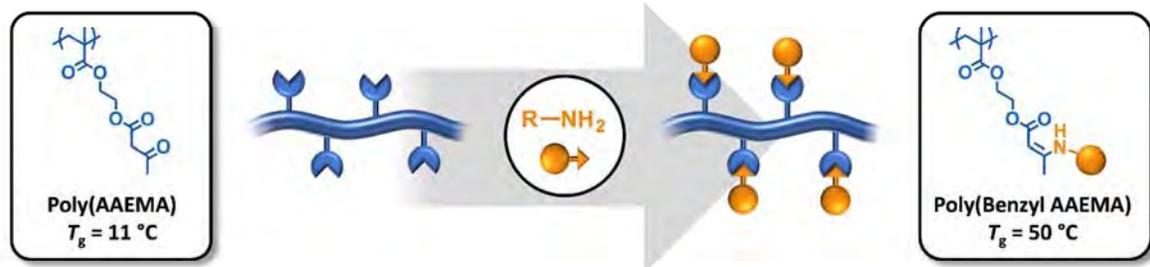


Schematic picture of the tandem polymerization

POLY 25: Modular functionalization of polymeric β -ketoesters via dynamic enamine chemistry

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Department of Chemistry, University of Florida, Gainesville, Florida, United States

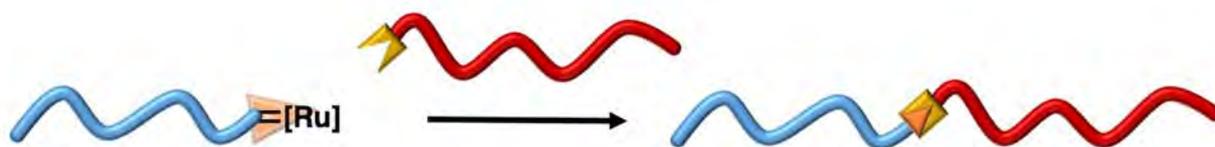
Post-polymerization modification has emerged as a powerful tool for functional polymer synthesis, complementing the suite of controlled polymerization techniques. The recent development of highly rapid, efficient, and mild functionalization reactions has greatly improved the diversity of readily accessible macromolecular structures, and there remains significant interest in further expanding the synthetic toolbox available to polymer chemists. In this work, we outline the utility of the reaction between primary amines and β -ketoesters for post-polymerization modification *via* the formation of robust enamine linkages. Commercially available 2-(acetoacetoxy)ethyl methacrylate (AAEMA) was polymerized under RAFT conditions to yield well-defined polymers bearing pendent β -ketoester moieties. These polymers could then rapidly functionalized with a variety of primary amines under very mild conditions, and the structure of the attached functionality was found to strongly influence the physical properties of the resultant polymers. In a representative example, the functionalization of polyAAEMA with benzylamine resulted in an increase of the glass transition temperature from 11 °C to 50 °C. As enamines are dynamic-covalent linkages, we furthermore investigated the conditions that would enable the exchange of one functionality for another, enabling dynamic modification of the polymers' physical and chemical properties.



POLY 26: Clicking with living ROMP polymers

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Ring-opening Metathesis Polymerization (ROMP) has emerged as one of the leading techniques for polymerizing monomers of unparalleled size and complexity. Despite its established utility in many areas, the power of this chemistry has been restricted by a lack of methods to easily modify the polymer chain-ends, thereby limiting the ability of these polymers to interface with other macromolecular systems. In this presentation, a new approach to directly react and remove the active ruthenium alkylidene employed in ROMP polymerization is described. Utilizing the same general strategy, either end of the polymer structure can be modified to give heterotelechelic polymers with a variety of groups at the termini. This method is fast, quantitative, and powerful enough to even perform polymer-polymer coupling under stoichiometric conditions. Importantly, this approach greatly streamlines the generation of functional ROMP materials because it bypasses the need to go through traditional “click” handles.

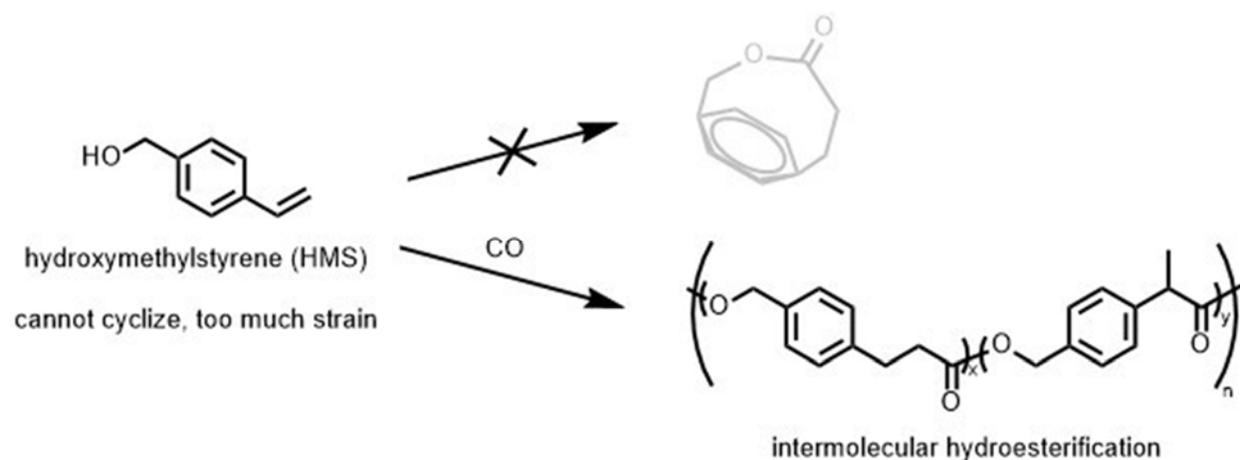


efficient polymer-polymer coupling with living chain-end

POLY 27: Hydroesterificative polymerization of aryl hydroxyl olefins

Tong Wang, wang4384@umn.edu. Chemistry, University of Minnesota, Minneapolis, Minnesota, United States

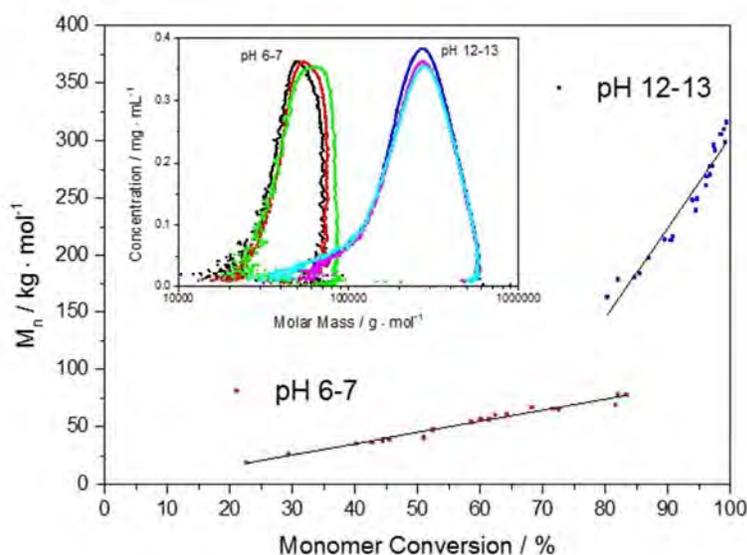
Hydroesterification is metal-catalyzed reaction in which an olefin, an alcohol and carbon monoxide are converted into an ester. Although hydroesterification has been extensively studied, the application of hydroesterification to polymerization reactions remains underinvestigated. In this work, para-substituted aryl hydroxyl olefins were studied as potential monomers in head-to-tail hydroesterificative polymerization reactions. These monomers were chosen because it is difficult for them to undergo intramolecular reactivity, owing to the strain of the resulting paracyclophane product. Herein, we report a highly selective and efficient cationic Pd catalytic system for the hydroesterificative polymerization of (4-hydroxymethyl)styrene (HMS). This is a particularly exciting result because we are able to synthesize a new aromatic polyesters under mild conditions. This new polymerization method also shows the potential to make polyesters from biorenewable molecules such as eugenol or chavicol.



POLY 28: Multivariate study of the synthesis of sodium poly(styrene sulfonate) by aqueous atom transfer radical polymerization

Paul Balding, *pbalding3@gatech.edu*. Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia, United States

The synthesis of sodium poly(styrene sulfonate) via aqueous atom transfer radical polymerization has been demonstrated with control over polymerization kinetics and final polymer properties. This was achieved through an interplay of several reaction variables; addition of nonsolvent, type and concentration of deactivator species, type of ligand, ratio of catalyst to initiator, and pH were explored in order to suppress unwanted side reactions. Kinetic control over the reaction, determined by the rate of monomer conversion, was calculated from ^1H NMR, and both molecular weight and polydispersity were determined by gel permeation chromatography coupled multi angle light scattering. In certain cases an order of magnitude difference was observed in the molecular weight by altering a single reaction variable without changing the monomer to initiator ratio. Kinetic and molecular weight data were correlated, as higher conversions led to larger molecular weights. Polydispersity values ranged from 1.05 to 1.25 for polymers ranging from approximately 2×10^4 to 5×10^5 g/mol which are characteristic values for living polymerizations. Polymer architecture was analyzed by assessing the relationship between R_g and R_h , as well as the dimensionless parameter, ρ , which was found to be on the order of 1.7-1.8, good solvent conditions, and was invariant with molecular weight. Conformation plots showed that ν was 0.65 ± 0.04 , as averaged across all samples, again proof of a linear random coil polymer in good solvent conditions.



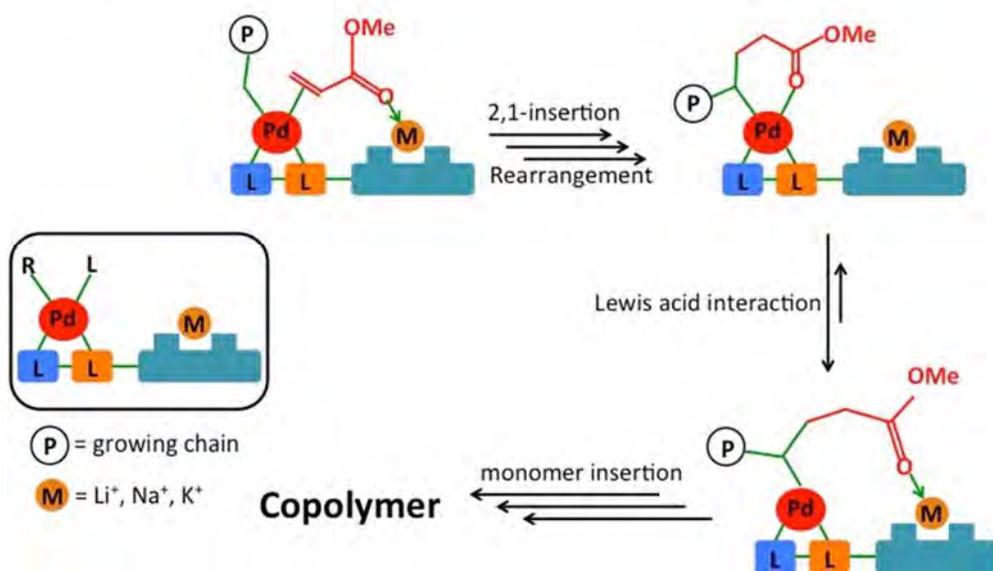
Plot of M_n vs monomer conversion for NaPSS synthesized at both pH 6-7 and pH 12-13 as shown. Linear fits show the living nature of the polymerization. Inset shows concentration vs molar mass plot for three repeatable syntheses of NaPSS at each reaction pH as shown.

POLY 29: Copolymerization of ethylene and polar olefins by heterobimetallic catalysts with phosphine-phosphonate ligands

Zhongzheng Cai, *czhongzheng@163.com*, *Loi Do. Chemistry, University of Houston, Houston, Texas, United States*

Coordination insertion polymerization is an attractive method to synthesize polyolefins due to its ability to give precise control over the polymer microstructure. Pd complexes with phosphine-phosphine oxide ligands can copolymerize ethylene with a variety of polar olefins. However, these polar monomers decrease significantly the catalyst's activity and the polymer molecular weights compared to polymerizations performed using non-polar monomers. It is believed that the formation of metal-monomer chelate complexes prevents efficient copolymerization. To avoid the generation of such intermediates, we designed cationic Pd complexes with polyethylene glycol (PEG) chains that can coordinate with alkali metal cations as secondary metal binding sites. ^1H NMR Job plot studies showed that a 1:1 binding stoichiometry between Pd and alkali ion can be achieved and the tetraethylene glycol group has preference for the coordination of Na^+ over Li^+ and K^+ . The structure of the heterobimetallic palladium-sodium species was confirmed by X-ray crystallography. Our ethylene polymerization studies indicated that the addition of alkali ions to these complexes could enhance their ethylene polymerization activity. The heterobimetallic complexes also exhibit higher copolymerization activity and different polymer morphologies compared to their parent mononuclear complexes.

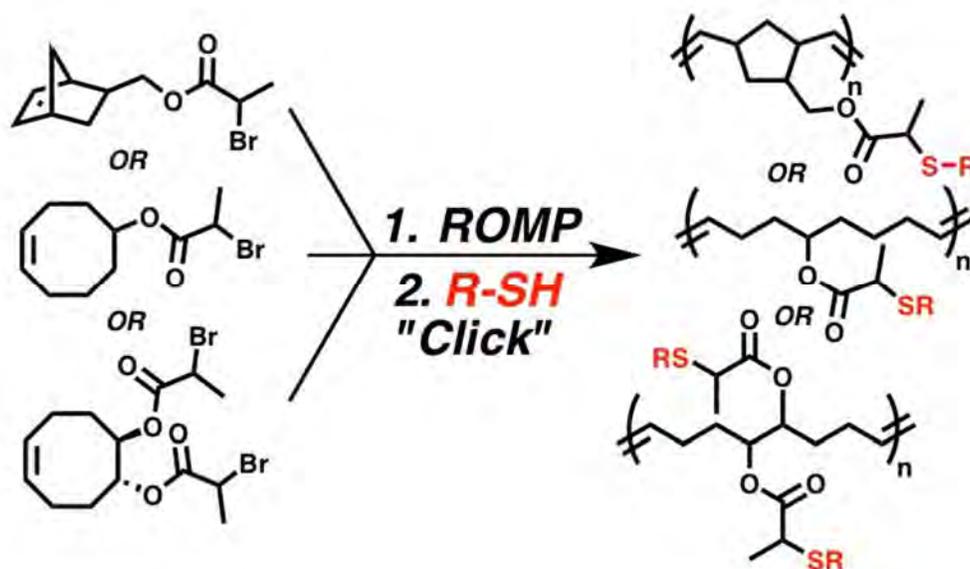
Lewis acid assisted coordination-insertion polymerization



POLY 30: Thio-bromo "click" approach for modifying materials prepared using ROMP

Christopher E. Hobbs, chobbs@shsu.edu. Chemistry, Sam Houston State University, Huntsville, Texas, United States

This talk will describe our current efforts at utilizing a facile, nucleophilic substitution reaction between polymers decorated with α -bromo ester pendant groups and a variety of thiols (so called thio-bromo "click" reaction). We have shown that this is a simple route toward the preparation of polymers that can be used as (i) flame-retardant materials, (ii) drug delivery vehicles, as well as (iii) organo- and hydrogels.



POLY 31: Ion exchange resins in pharmaceutical formulations and FloVibro™ biorelevant dissolution technology: A unique approach to studying biorelevant drug dissolution

Amie Gehris, AGehris@dow.com. The Dow Chemical Company, Collegeville, Pennsylvania, United States

Ion exchange resins have been used in the pharmaceutical industry for over 60 years. The applications for their use include modified release, taste masking, improved bioavailability of poorly soluble materials, stability and abuse deterrence. In recent years, increasing patient compliance, especially in the pediatric and geriatric populations, has driven the direction of drug delivery towards ease of administration and reduced adverse taste. This presentation will demonstrate by loading ionizable active pharmaceutical ingredients (APIs) onto ion exchange resins lend a formulation strategy that works well in suspension formulations and there are several existing examples of this the most well know being Delsym® and Tussionex®.

The ion exchange resin can modify release of the API in the buccal cavity for taste masking or in the GI track for a sustained release effect and in some cases both are achieved with one formulation. Varying product and processing parameters can dial in the desired effect that the formulator is looking for.

FloVibro™ technology is a unique, patented flow through *in vitro* test that evaluates the dissolution of dosage forms under biorelevant conditions. For a given API, the same test method may be used to compare *in vitro* performance of formulations throughout product development. The output of the test is a profile that has the same shape as a plasma concentration-time profile without the need for any mathematical modeling of the raw data. The test conditions include gastric disintegration, gastric dissolution, transfer of dissolved and undissolved materials to intestinal conditions, and intestinal dissolution. It also incorporates aspects of intestinal absorption and systemic clearance.

FloVibro™ applications include:

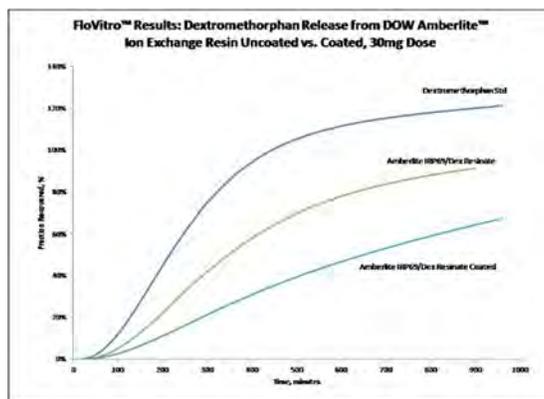
Demonstrating level A *IVIVR* (in vivo/in vitro relationship)

Evaluating innovator equivalence for generic products

Predictive of modified release products based on immediate release profiles

Experimental formulation development where no in vivo data are available

Troubleshooting



POLY 32: Drug delivery to the vessel wall with drug coated balloons

Joram Slager, jslager@surmodics.com. SurModics, Inc., Eden Prairie, Minnesota, United States

Occluded arteries are typically treated by angioplasty and stenting to restore blood flow. However, in some coronary and many peripheral sites stenting may be complicated or contra-indicated. Angioplasty alone, albeit effective in the short term, typically fails to keep vessels patent over time. Without anti-restenotic drug treatment for a prolonged amount of time the trauma from angioplasty usually results in hyperplasia of arterial smooth muscle cells, causing a recurrence of lumen loss and restricted blood flow.

The development of new coating and formulation technologies has enabled the delivery of controlled release depots of anti-restenotic drugs, such as paclitaxel or sirolimus, directly from the surface of a coated angioplasty balloon (deemed drug coated balloons, DCB). Lesions where placement of devices such as drug-eluting stents is less preferred are frequently treated with DCBs.

To effectively treat an occluded vessel with a DCB, the coating must:

- ensure minimal drug loss during navigation of the balloon to the targeted vessel site
- permit transfer of drug to the vessel intima within the timeframe of balloon inflation
- promote retention of the drug depot after balloon deflation and restoration of blood flow

This talk will give an overview of the Surmodics SurVeil™ DCB and discuss mechanisms underlying the drug transfer to arterial vessel surfaces.

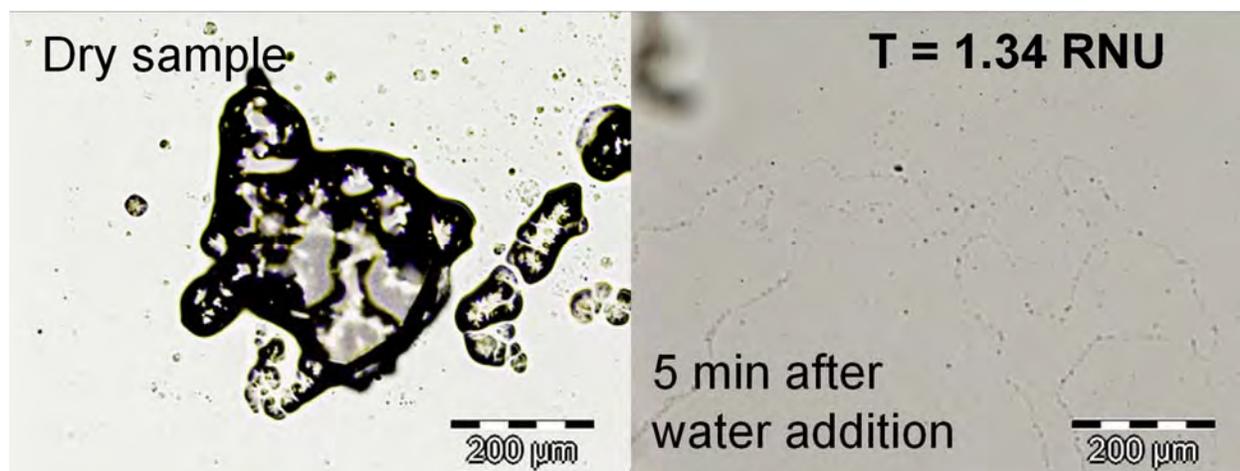
CAUTION SurVeil™ Drug-Coated Balloon is an investigational device. Limited by Federal (or United States) law to investigational use.



POLY 33: Use of high throughput methods in the discovery of novel excipient-solubilizers for drugs with low aqueous solubility

Thomas H. Kalantar¹, kalantar@alum.mit.edu, Jin Zhao², Mladen Ladika¹, Keith Harris¹, Christopher J. Tucker¹, Michael Tulchinsky¹, Steven J. Guillaudeu¹, TC Kuo¹, Bruce Bell¹, Joe Kiefer¹, Shawn Chen¹, Robert D. Krystosek¹. (1) Core R&D, The Dow Chemical Company, Midland, Michigan, United States (2) Dow Food, Pharma and Medical R&D, The Dow Chemical Company, Midland, Michigan, United States

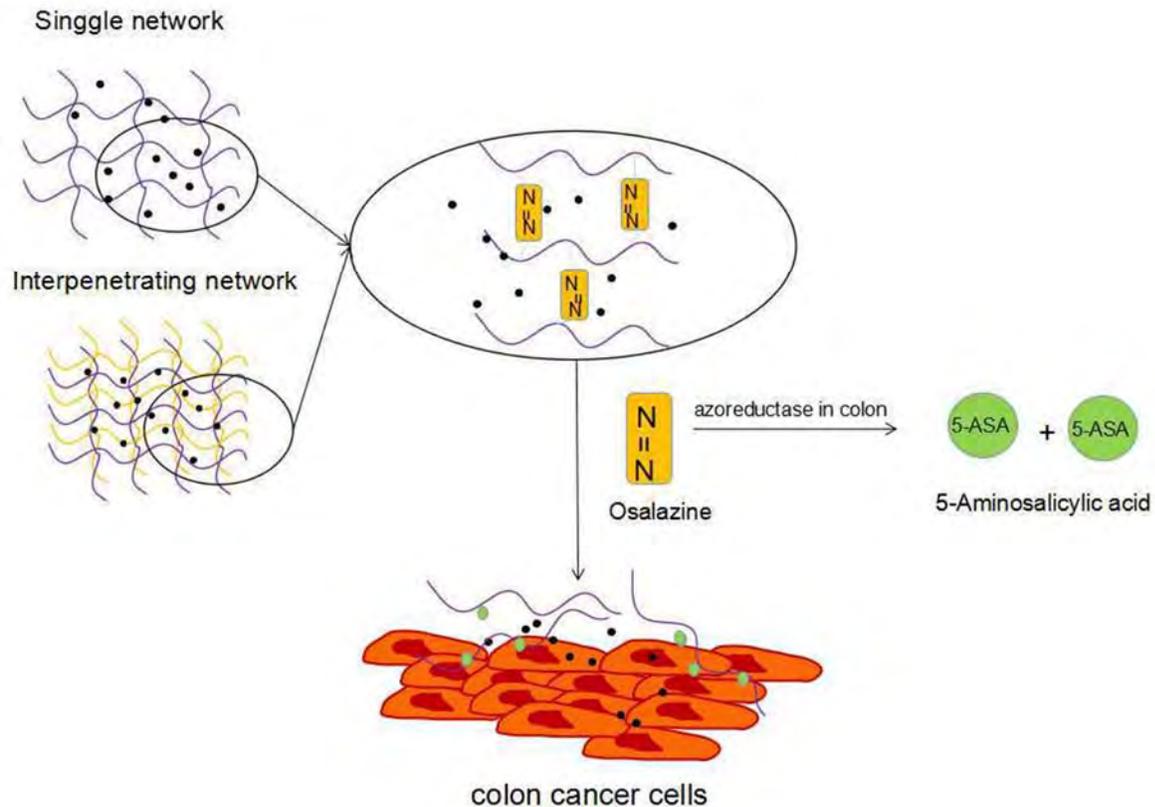
Ca. 40% of new drug candidates suffer from poor aqueous solubility and/or slow dissolution, reducing their bioavailability and efficacy, and even limiting their development and general use. This study explored a solubilization approach using low- T_g alkylated polyoxyalkylene oxide copolymers to enhance drug solubility and dissolution rate, where the drug was combined with the polymeric excipient to form an amorphous solid dispersion. A novel class of alkylated polyols was synthesized using terpene alcohol precursors, which were alkoxyated with butylene oxide (BO) then further with ethylene oxide (EO). The effect of solubilization by these copolymers was studied using model drugs. Raman spectroscopy suggested that several of these copolymers were effective at stabilizing the model drugs in their amorphous form. The aqueous solubility and dissolution rate of model drugs in the presence of these excipients were studied using nephelometry and optical microscopy. Several drug/excipient samples showed a dramatic reduction in turbidity relative to the turbidity of drugs alone in water. Optical microscopy of those drug/excipient samples in water also indicated an increase in drug dissolution. Drug solubility was also measured by an HPLC-based drug assay 30 minutes after dissolution in a phosphate buffer solution. For example, mixtures of probucol and the novel alkyl-BO-EO excipients showed stability of the amorphous condition on aging under ambient conditions for one week and accelerated aging at 40 °C and 75% relative humidity for 4 months. Under both sets of storage conditions, up to 8,000-fold increases in probucol solubility were observed, much higher than that observed using existing polymeric excipients. It is expected that the structure of the alkyl-BO-EO copolymer can be tailored to specific drug structures to enable optimization of solubilization.



POLY 34: Enzyme responsive 5-flurouracil (5-FU) loaded hydrogels based on osalazine derivatives for colon-specific oral drug delivery

Ma Zhengang, zhengangmaxb@163.com, **Ma Rui**, ruimaxb@163.com, **Zhijie Sun***, zhijiesun@hrbeu.edu.cn. Institute of Materials Processing and Intelligent Manufacturing & Center for Biomedical Materials and Engineering, Harbin Engineering University, Harbin, Heilongjiang, China

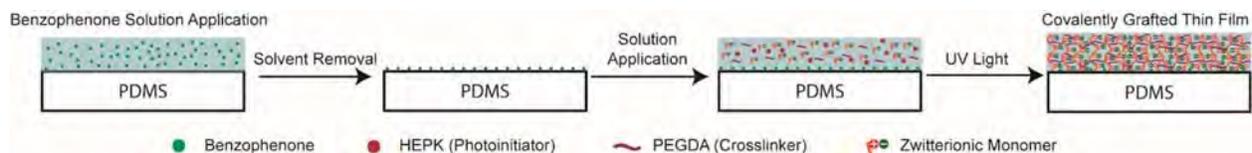
Colon-specific drug delivery systems have shown promise as an effective and convenient therapeutic method. We synthesized an acryloyl chloride modified osalazine as an azo crosslinker which was copolymerized with HEMA, and developed two types of azo hydrogels which contained single network hydrogel and interpenetrating network hydrogel as an enzyme responsive controlled release carrier for colon-specific drug delivery. The structure of the azo crosslinker was characterized by FT-IR and ^1H NMR spectra and the azo hydrogels were analyzed by using HPLC and TEM. The *in vitro* release studies of the 5-flurouracil loaded azo hydrogels were carried out in PBS (PH7.4) ,rat gastric fluid and rat colonic fluid. The drug release profile revealed that 5-FU loaded in azo hydrogels released faster in rat colonic fluid. The results showed that these azo hydrogels could be a potential drug carrier for colon-targeted drug delivery.



POLY 35: Photograftable zwitterionic polymers resist cell and bacterial adhesion

Braden Leigh, *braden-leigh@uiowa.edu*, Marlan Hansen, Allan Guymon. Univ of Iowa, Iowa City, Iowa, United States

Implantable medical devices accumulate significant response from the body weeks to months after implantation. This foreign body response (FBR) can cause significant reduction in performance of neural prosthetics such as the cochlear implant. Engineering surfaces that resist the FBR could lead to enhanced integration with host tissue and improved hearing outcomes. The body's initial step in the FBR is nonspecific protein adsorption which marks the implant as foreign. Thus, coating the surface of cochlear implant materials with polymers that reduce this initial step has the potential to mitigate fibrosis. In this work, a photografting process is used to adhere the zwitterionic polymers sulfobetaine methacrylate and carboxybetaine methacrylate to poly(dimethyl siloxane) (PDMS) surfaces. Zwitterionic thin films were grafted to PDMS by adsorbing benzophenone, a photografting agent and type II photoinitiator, to covalently link the films to the substrate. The adhesion of the crosslinked zwitterionic thin films to PDMS surfaces was characterized through a shear adhesion test. Increasing the surface concentration of benzophenone improved the adhesion of the zwitterionic thin films to PDMS surfaces. To demonstrate the effectiveness of the zwitterionic thin films to resist the FBR, nonspecific protein adsorption was measured with significantly lower levels on zwitterionic-coated samples compared to uncoated controls. Additionally, adhesion of fibroblasts, a cell type prevalent in fibrosis, was reduced dramatically on coated substrates. Bacterial adhesion was also evaluated to demonstrate the ability of these coatings to prevent infection showing low levels of bacteria adhered to zwitterion-functionalized surfaces. These results lay the groundwork for improving neural prosthetic devices by reducing fibrosis and infection.

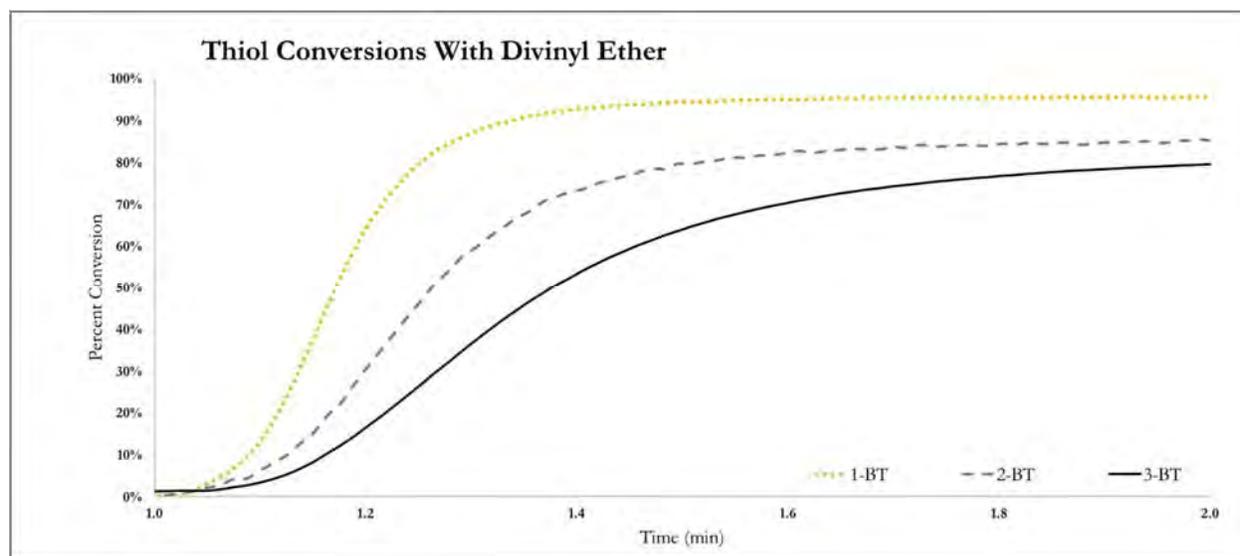


Schematic of the photografting/patterning process.

POLY 36: Kinetic differences between primary, secondary, and tertiary alkyl thiols in thiol-ene reactions

Katelyn Long³, kalo9832@colorado.edu, **Xinpeng Zhang**⁴, **Sijia Huang**³, **Jasmine Sinha**², **Maciej Podgorski**³, **Christopher Bowman**¹. (1) UCB 596, Univ of Colorado, Chemical Biological Eng, Boulder, Colorado, United States (2) Chemical and Biological engineering, University of Colorado, Boulder, Colorado, United States (3) University of Colorado - Boulder, Boulder, Colorado, United States

The thiol-ene addition has been a popular tool for chemists and engineers for applications including dendrimer synthesis, surface and nanoparticle functionalization, (two-stage) optical materials, enhanced-performance coatings, and hydrolytically stable dental resins. However, to date a majority of the research has focused on primary thiols, even though secondary thiols were found to have additional benefits such as reduced odor and reduced likelihood of reacting spontaneously with the alkene in a pre-mixed solution. As such, the effect of the substitution of the thiol was studied by using model system: three isomers of butane thiol and three different alkenes, a vinyl ether, an allyl ether, and a vinyl siloxane. The kinetic rates were observed using FT-IR and NMR analysis was used to confirm conversion. It was concluded that increasing in substitution of the thiol results in a decreased kinetic rate. Reactions typically went to full conversion (85% or higher), regardless of substitution. Novel thiol monomers were then synthesized to observe how the substitution affects the polymerization kinetics as well as mechanical properties.

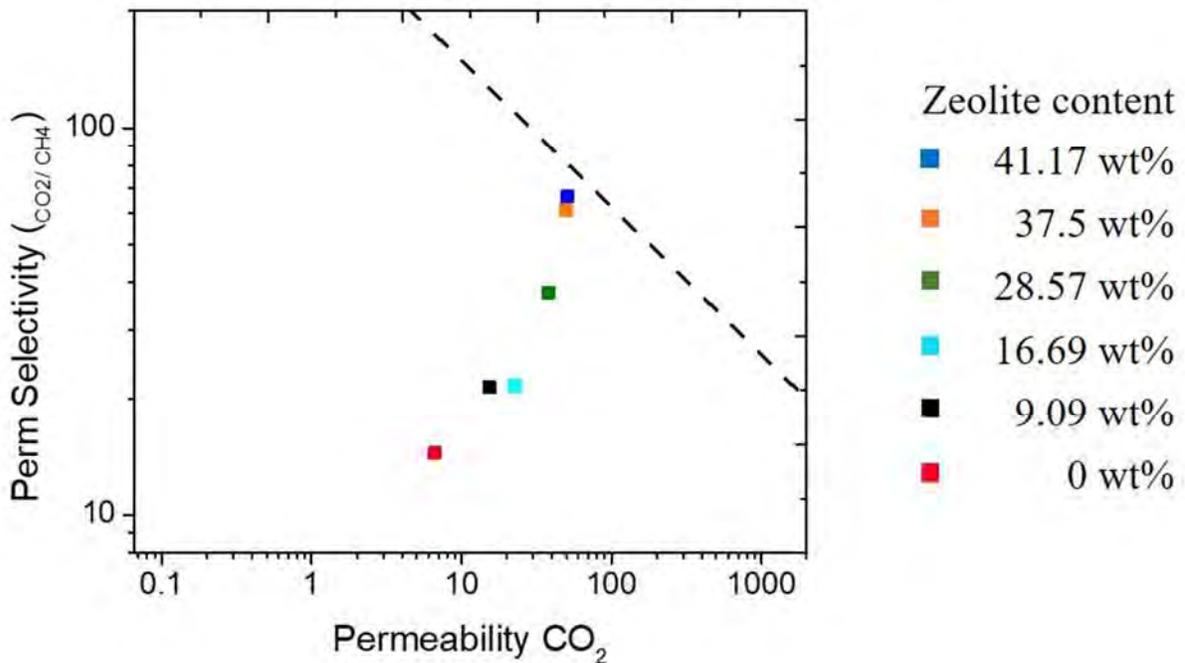


POLY 37: Low energy fabrication of mixed matrix membranes through thiol-ene chemistry

Jacob M. Schekman, jacob.schekman@usm.edu, Vivek Vasagar, Drew Bossier, Sergei I. Nazarenko. School of polymer science and Engineering, University of Southern Mississippi, Hattiesburg, Mississippi, United States

Reduction of cost in material processing heavily relies on facile production methods. Rapid kinetics of thiol-ene “click” chemistry facilitates pure polymer and mixed matrix membrane (MMM) processing. Thiol-ene polymer networks were synthesized to investigate their potential as matrices for MMMs. Characterization of the relationship between zeolitic content and gas permeation was achieved via constant volume/variable pressure analysis. Preliminary studies show improvements in permeability and selectivity (CO_2/CH_4 and CO_2/N_2) of MMMs with moderate zeolite loading (41 wt%) compared to the neat polymer membranes. Results confirm thiol-ene networks as a viable option for easily processed MMMs.

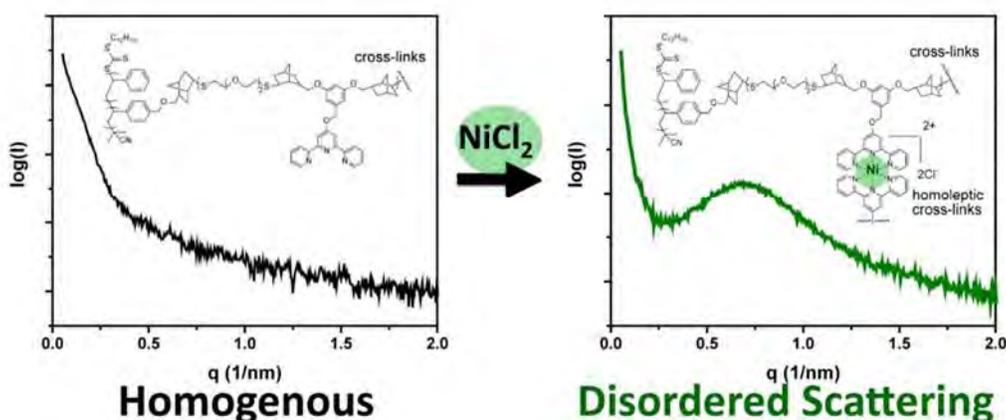
Selectivity plot of CO_2 vs. CH_4



POLY 38: Introducing photoinduced thiol-ene chemistry into metal cation-based anion exchange membranes

Michael Kwasny³, mkwasny476@gmail.com, Liang Zhu¹, Michael A. Hickner¹, Gregory N. Tew². (1) The Pennsylvania State University, State College, Pennsylvania, United States (2) Polymer Science and Engineering, University of Massachusetts, Amherst, South Deerfield, Massachusetts, United States (3) Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, Massachusetts, United States

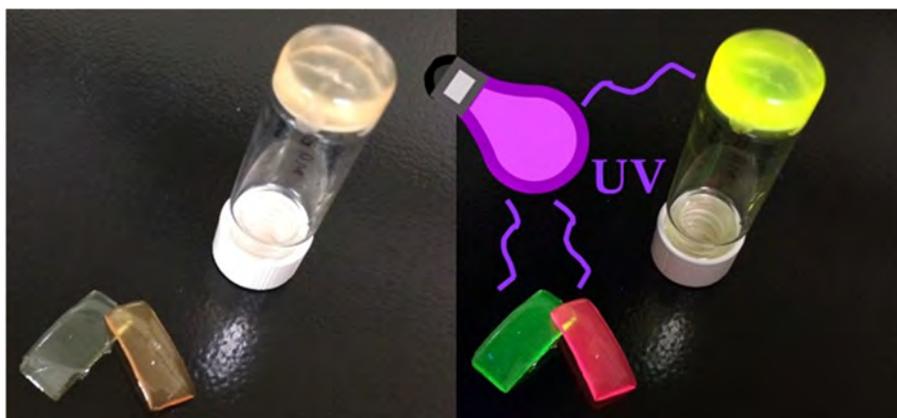
Metal cation-based anion exchange membranes (AEMs) are a unique class of materials that have shown potential to be highly stable AEMs with competitive conductivities. Previously, our group synthesized ring-opening metathesis polymerization (ROMP)-based AEMs featuring cationic ruthenium, nickel, and cobalt complexes. These membranes demonstrated good chemical stability and an enhancement in conductivity for the nickel-based samples over their ruthenium and cobalt counterparts. However, their conductivity and mechanical properties remained limited. Therefore, we expanded upon that work to report the synthesis of crosslinked nickel cation-based AEMs formed using the photoinduced thiol-ene reaction. Using the fast and efficient thiol-ene reaction allowed for the samples to be designed to elicit phase-separation and have simple membrane fabrication. AEMs were first characterized for their morphology, both with and without nickel cations, where the nickel-containing membranes demonstrated a disordered scattering peak characteristic of ionic clusters. The samples were then characterized for their water uptake, chemical and mechanical stability, and conductivity. Despite having excellent chemical stability, they also showed a combination of high water content and weak mechanical properties, which resulted in low conductivity. The weak mechanical properties resulted from large water swelling as well as the need for each nickel cation to act as a crosslinker, necessary with the current nickel-coordination chemistry. Therefore, increasing the ion exchange capacity (IEC) for these types of AEMs, important for enhancing conductivity, also increased the crosslink density. Despite that challenge, however, by using the photoinduced thiol-ene reaction, the encouraging features of ionic clusters, simple membrane fabrication, and excellent stability of the thioethers were observed for the first time in metal cation-based AEMs.



POLY 39: Fabrication of luminescent quantum dot thiol-yne nanocomposites via UV photopolymerization

Darryl A. Boyd, darryl.anthony@gmail.com. *Optical Sciences, US Naval Research Laboratory, Alexandria, Virginia, United States*

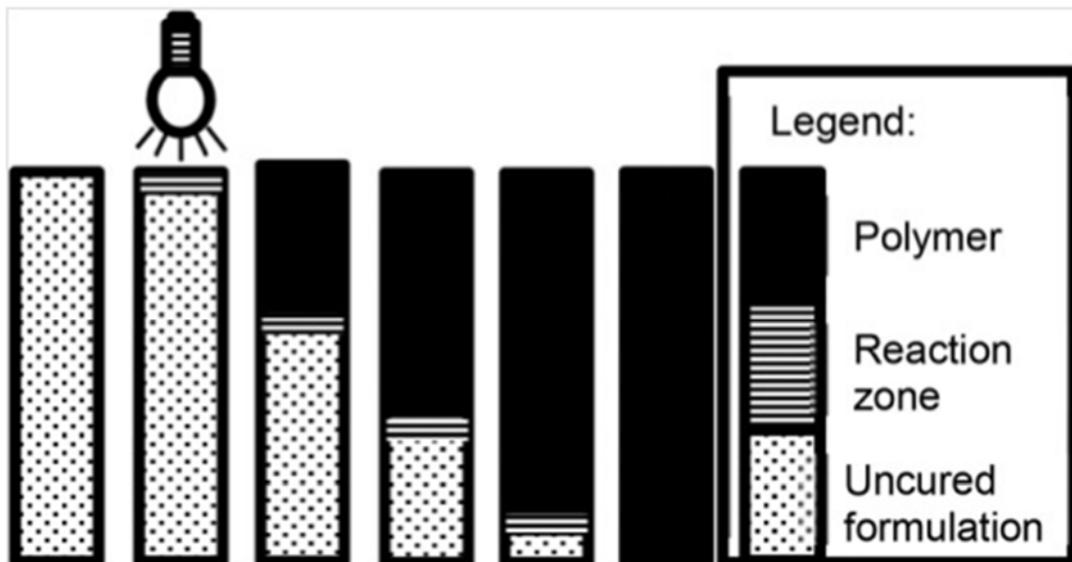
Polymers containing quantum dots were fabricated using thiol-yne chemistry in order to develop durable luminescent materials. To accomplish this, novel ligands were synthesized and used to functionalize quantum dots (QDs) of various diameters. These functionalized QDs were then incorporated into thiol-yne prepolymer matrices. These matrices were subsequently polymerized to form QD thiol-yne nanocomposite polymers. The resulting transparent nanocomposites expressed the size-specific color of the QDs within them when exposed to UV irradiation, demonstrating that QDs can be incorporated into thiol-yne polymers without significantly altering QD expression. With the inclusion of QDs, thiol-yne nanocomposite polymers are promising candidates for use in numerous applications including as waveguides, optical lens materials, and sensor applications.



POLY 40: Successful UV-Curing of epoxy composites

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(1) Applied Science and Technology Department, Politecnico di Torino, Torino, Italy (2) Institute of Applied Synthetic Chemistry, TU Wien, Vienna, Austria

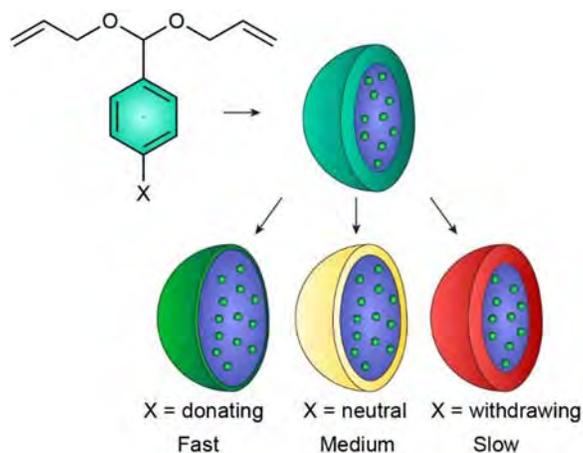
The main limitation of UV-induced crosslinking reactions is related to the hindering of UV-light penetration towards thickness of the formulations, which limits this polymerization technique in the preparation of thick composite materials. This limitation has been overcome by the introduction of a Radical Induced Cationic Frontal Polymerization (RICFP) process¹⁻³. The suggested mechanism put together the so-called Radical Induced Cationic Polymerization (RICP) with Frontal Polymerization (FP). UV-cured bulk epoxy composites were successfully produced by Radical Induced Cationic Frontal Polymerization (RICFP); it was shown that the FP is started by the dissociation of a radical, thermal initiator (RTI) promoted by the heat released during surface UV-induced cationic ring-opening polymerization. Subsequently, the carbon-centred radicals are oxidized to carbocations by the presence of the iodonium salt PAG in a RICP mechanism.



POLY 41: Substituent determined release from polymer microcapsules fabricated via thiol-ene photopolymerization

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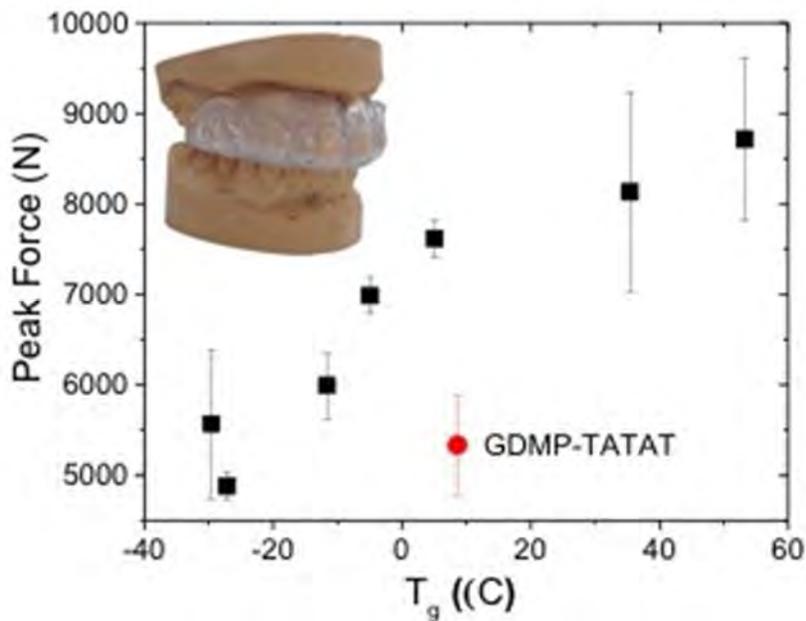
The formulation and delivery of biopharmaceutical drugs poses substantial challenges owing to their broad range of sizes and potential susceptibility to degradation. The development of new capsule platforms which possess tunable degradation, facile encapsulation, and scalability are necessary. Herein, we describe the synthesis of a library of acyclic acetals and their incorporation into a highly-controlled droplet based microfluidic platform via thiol-ene photopolymerization. Specifically, substituted benzaldehydes serve as the molecular basis for tuning the degradation of the acetal-based networks. Degradation rates could be tuned from weeks to years depending solely on the substituent without any differences in network design. To mimic encapsulated drugs, hydrophilic quantum dots were encapsulated and imaged via confocal laser microscopy over a multi-week release study. Additionally, the pH sensitivity of the hydrolytically erodible membranes was also demonstrated via optical microscopy over time.



POLY 42: Modified thiol-ene networks: Tuning the glass transition temperature and energy damping capabilities of photopolymerized networks

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Utilizing thiol-ene photopolymerizations, it is possible to produce thermoset networks that are highly homogeneous and thus exhibit enhanced energy damping capabilities. Such materials can be used in personal protective equipment such as in mouthguards. This talk will present some recent results in the synthesis, characterization and impact testing of modified thiol-ene networks with tunable physical properties. In particular, we synthesize ternary networks containing (1) bulky side-chain substituents, (2) isocyanate functionality, or (3) dual thiol components to improve control over the glass transition temperature and strain at break.



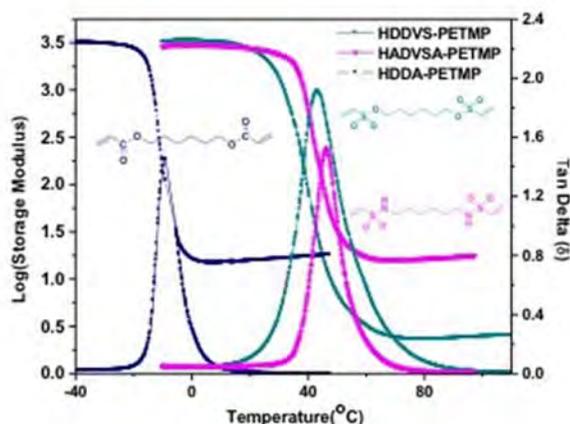
POLY 43: Development of vinyl sulfonate and vinyl sulfonamide: Its implementation in thiol-michael crosslinking polymerization

Jasmine Sinha², *jasmine.sinha@gmail.com*, **Maciej Podgorski**^{3,4}, **Christopher Bowman**¹. (1) UCB 596, Univ of Colorado, Chemical Biological Eng, Boulder, Colorado, United States (2) Chemical and Biological engineering, University of Colorado, Boulder, Colorado, United States (4) Polymer Chemistry, MCS University, Lublin, Poland

A series of vinyl sulfonate and vinyl sulfonamide monomers as Michael acceptors were synthesized and utilized to explore its features by systematic study of the monomer reactivity towards thiol in Photo-base catalyzed thiol-Michael reactions. Furthermore, the multifunctional derivatives were implemented in designing crosslinked polymeric material for improved mechanical properties. Previously, our group has reported the thiol-vinyl sulfone networks containing high weight fractions of sulfone groups which exhibited an improved T_g at ambient temperature. The efficiency and versatility displayed by click Michael type additions to vinyl sulfone prompted us towards vinyl sulfonate and vinyl sulfonamide group.

On investigating the scope of the designed Michael-acceptors with a systematic kinetic study, it demonstrated that the vinyl sulfonate reactivity is significantly higher than acrylate while acrylate exhibited slightly higher reactivity when compared to vinyl sulfonamide. The relative rates of the Michael addition to unsaturated sulfonate, sulfone, ester, and amides could be related to the electrophilicity of the enoyl carbon. The lower reactivity of vinyl sulfonamide as compared to vinyl sulfonate could be attributed to the lower electronegativity of the nitrogen instead of oxygen.

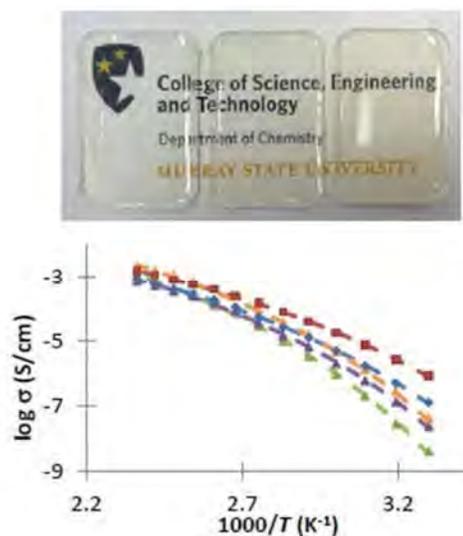
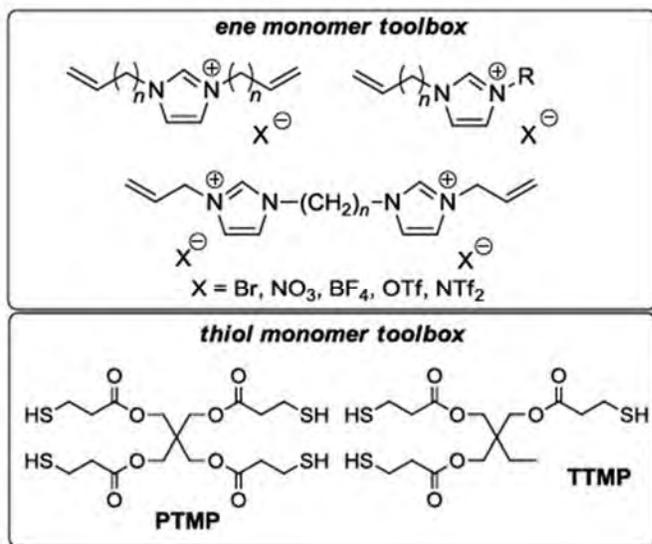
The designed multifunctional derivatives were transformed to form uniform network polymers with the neat stoichiometric mixtures (per functional group concentration) of commercial thiol PETMP and ester free thiol SiTSH. As it is a neat thiol-Michael network polymer, it possess the attributes of step-growth reaction which includes high functional group conversion as well as uniform network structure. Our investigation demonstrated that the thiol-vinyl sulfonamide cross-linked polymers exhibited high glass transition temperatures, along with improved hydrolytical stability, thermal stability and mechanically strengthened material.



POLY 44: Thiol-ene 'click' poly(ionic liquid) networks: Correlating structure with conductive and gas separation properties

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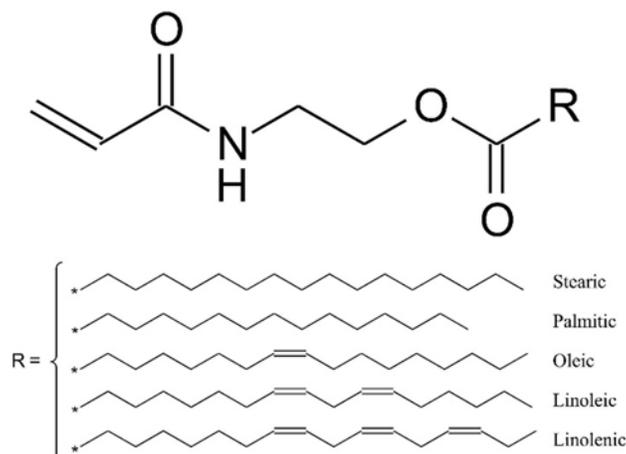
Thiol-ene 'click' photopolymerization has been utilized to prepare imidazolium-containing, covalently crosslinked, poly(ionic liquid) (PIL) networks. Various imidazolium-containing 'ene' monomers were photopolymerized with commercially available multifunctional thiols. Variations in thiol:ene ratio, counteranion and 'ene' functionality were investigated in order to gauge the breadth of mechanical and conductive properties available utilizing this polymerization platform. Thiol-ene PILs with relatively low crosslink densities that employed the [NTf₂] counteranion were found to exhibit the most promising conductivities (10⁻⁶ to 10⁻⁵ S/cm at 30 °C and 30% RH). Dielectric relaxation spectroscopy (DRS) was utilized to determine ionic conductivities of the PIL networks as well as ion transport properties. Additionally, select PIL formulations were examined for their gas separation properties (CO₂, N₂, CH₄) by first photopolymerizing the monomer mixture on a PVDF support and then monitoring the permeability and diffusion of the pure gases.



POLY 45: High biobased content latexes from plant oil-based vinyl monomers in miniemulsion

Zoriana Demchuk¹, Kyle Kingsley¹, Ihor Tarnavchuk¹, Vasylyna Kirianchuk², Oleh Shevchuk², Ananiy Kohut³, Stanislav Voronov², **Andriy S. Voronov¹**, andrejvoronov@hotmail.com. (1) Coatings and Polymeric Materials, North Dakota State University, Reiles Acres, North Dakota, United States (2) National University Lviv Polytechnic, Lviv, Ukraine

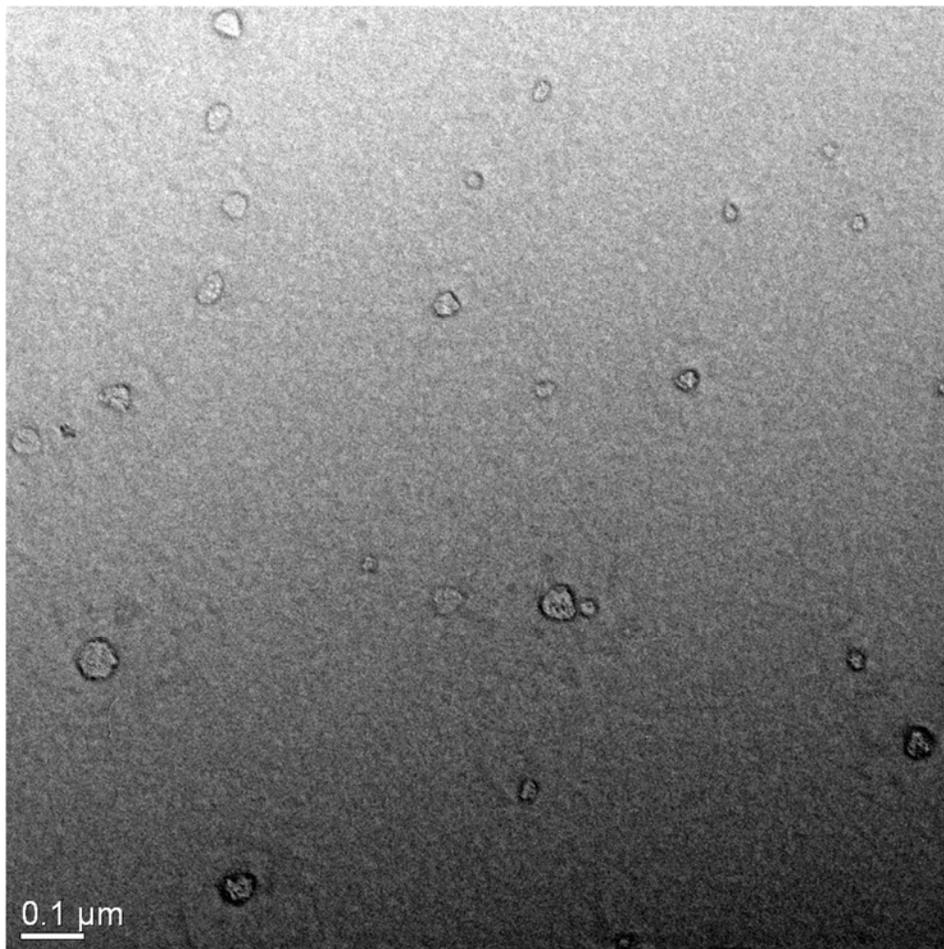
One-step method of plant oil direct transesterification, for synthesis of new vinyl monomers from sunflower, linseed, soybean, and olive oil has been recently developed in our group. Rate of plant oil-based monomers (POBM) homopolymerization, where chain propagation coexists with chain transfer on monomer, depends on the POBM chemical structure, and is determined primarily by unsaturation amount in plant oil triglycerides. Stable latexes containing up to 70 wt% of bio-based content were synthesized using miniemulsion copolymerization of POBM with methyl methacrylate and styrene. This study shows feasibility of latex synthesis with renewable POBMs as basic constituents of the latex polymers, with the improved thermal and mechanical properties. The unsaturation amount in the triglycerides' fatty acids was utilized as a criterion in studying biobased latex properties, including influence of variation in monomer feed unsaturation amount on crosslink density of latex films and, consequently, on polymer properties. In order to vary unsaturation amount in a broader range, new acrylic monomer was synthesized from hydrogenated soybean oil (HSBM, with no unsaturation). Various amounts of HSBM were added into the monomer feed to study if changes in feed unsaturation amount result in variation of crosslink density (network structure), leading to a variation in mechanical and thermal properties of crosslinked latex films. Structural and architectural similarity of HSBM molecules and long-side chain petroleum-based monomers that form polymer crystals (octadecyl acrylate, vinyl stearate, etc.) can be an additional feature in considering the properties of high POBM-based latexes. The observed mechanical properties of latex films can be explained in terms of crosslink density, but also the specifics of chemical structure of saturated HSBM used in combination with POBM and styrene in monomer feed.



POLY 46: Microemulsion preparation of hollow silicone nanoparticles for incorporation in silicone hydrogels

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Silicone hydrogels are widely used as soft contact lens materials due to their good oxygen permeability, wettability, and stable mechanical properties. Wettability is critical for comfort and compatibility of the soft contact lens, and oxygen permeability is important to maintain the normal function of the eye. Insufficiency of oxygen results in hypoxia and increases the possibility of corneal swelling, loss of transparency, and corneal acidosis. In preliminary studies, we demonstrated that foamed silicone sheets showed an order of magnitude increase in oxygen permeability in comparison to solid silicone sheets. Based on this proof-of-concept study, hollow silicone nanoparticles were prepared by micro-emulsion polymerization for dispersion in conventional silicone hydrogel materials. Synthetic methods for producing the nanoparticles will be discussed. Materials were analyzed by dynamic light scattering, FTIR, and transmission electron microscopy.

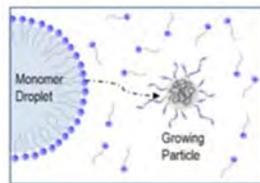


TEM image of hollow silicone nanoparticles

POLY 47: Improved latex stability made by a novel acrylic zwitterionic emulsion polymerization

Ibrahim El-Hedok, *iael-hedok@mmm.com*, *Mafuza Ali*, *Corinne Lipscomb*. *3M Company, Saint Paul, Minnesota, United States*

Acrylic emulsion polymers are widely used in the adhesive industry as solvent-free pressure sensitive adhesive polymers. However, in order to achieve a wider range of performance on more difficult-to-stick-to substrates, formulating the emulsion polymer with tackifiers becomes necessary. This work demonstrates how an unconventional zwitterionic emulsion polymerization chemistry can be used for synthesizing a stable tackifier-containing acrylic emulsion polymer.



POLY 48: Introduction to emulsion polymerization technology: Tutorial

Alvin M. Maurice, *amaurice@dow.com*. Dow Chemical Company, Lansdale, Pennsylvania, United States

Emulsion polymerization is an important process for commercially producing a wide range of polymers for use in multiple applications. In its simplest form, emulsion polymerization requires only four ingredients: water, monomer, surfactant, and initiator. Emulsion polymerization can produce very high molecular weight polymers dispersed in water. Because of the colloidal nature of the polymer dispersion produced, it is possible to obtain systems with relatively high solids and low viscosity. The flexibility of emulsion polymerization processes allow the synthetic chemist to design an almost infinite variety of polymers with a diverse balance of properties. Consequently emulsion polymer dispersions have found broad utility in markets such as coatings, adhesives, personal care, construction chemicals, and floor polish.

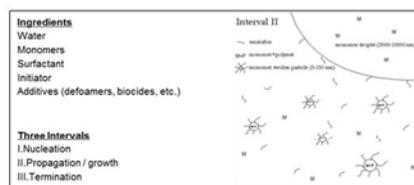


POLY 49: New developments in latex technology for coatings applications

Maqsood S. Ahmed, maqsood.ahmed@nuplex.com, Dirk Mestach, Andreas Steiner, Florian Lunzer. Allnex, Prospect, Kentucky, United States

Acrylic latexes are widely used in coatings for architectural and industrial applications where they are known for their fast dry, good hardness development, and excellent durability. Latex film formation, however, is a complex phenomenon aided by co-solvents and coalescing agents. The quest for near zero VOC limits the use of co-solvents and non-volatile coalescent have their own limitations. Molecular modulation, lowering molecular weight and /or other modifications, is one approach that can be used to enhance the flow and leveling that can improve film formation. This often comes at the expense of hardness development. Coupling this with molecular weight build-up upon application has led to the two pack and self-crosslinking systems. Separating the minimal film-formation temperature (MFFT) from glass transition temperature (T_g) is another approach, which can be brought about by morphological changes and internal plasticization, whereby the lower MFFT can help with film formation without sacrificing the hardness development. Combination of the above two approaches can yet be another approach.

In this paper we will describe some of the work done at allnex consisting of a novel thermoplastic and self-crosslinking core/shell process in which the shell initially functions as a nucleating site and then an in-situ stabilizer. The molecular weight and the acid content of the shell can be controlled to achieve a very fine particle size and good MFFT/hardness balance. In another iteration, the morphology of the core was changed from homogeneous to gradient to multicore while the shell varied in composition from hydrophilic to hydrophobic. Products can be made having a broad range of properties suitable for brushing, roller / dip / curtain coatings, and spray applications. Fundamental considerations as well as performance properties of selected prototypes from these new exciting approaches will be presented.



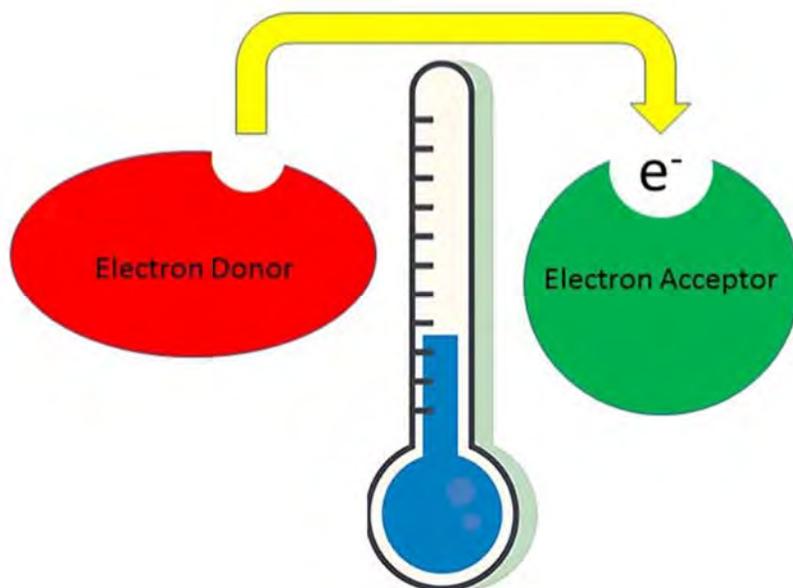
POLY 50: Redox enhanced properties for emulsion polymers

Mike O Shaughnessy, osm@brueggemann.com. BrueggemannChemical U.S., Inc., Charlotte, North Carolina, United States

Redox reactions have been successfully used in emulsion polymerization to reduce free monomer after the main polymerization for decades. New work will be presented highlighting additional valuable benefits of redox chemistry when employed during the main polymerization in conjunction with its use as a post reaction system.

By utilizing the appropriate redox chemistry in the main polymerization, lower polymerization temperatures are possible. This in turn provides the opportunity to further tune the molecular weight of the resulting product improving properties such as scrub resistance and tensile strength among others. The ability to start the polymerization at lower temperature also allows the reaction to heat adiabatically, offering shorter cycle times and cleaner reactions.

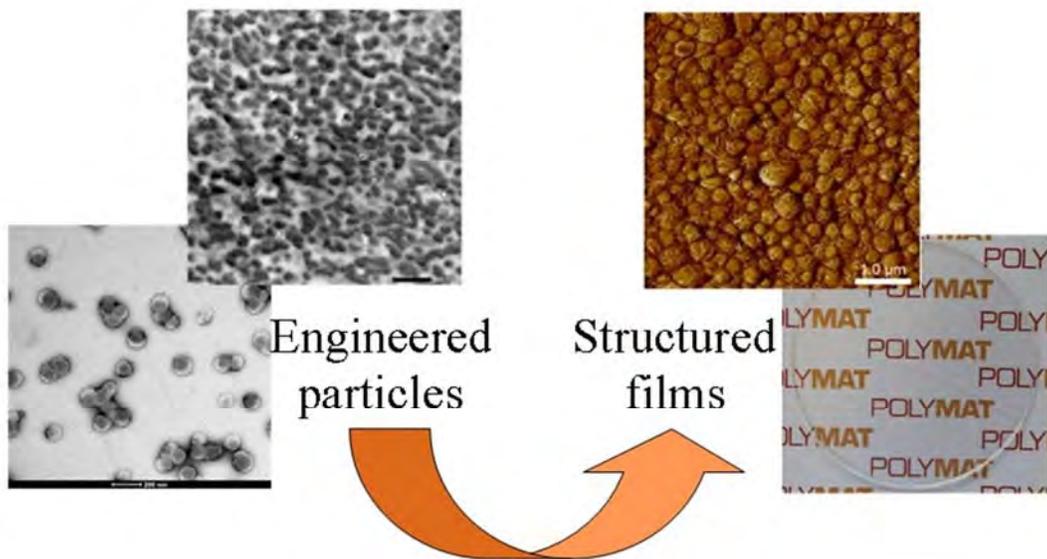
In addition, the polymerizations performed in this manner have produced lower free monomer than conventional thermal polymerizations prior to the monomer chase. After utilizing a redox chase, the residual free monomer in the redox initiated reaction is significantly less than the product in which a thermal initiator was used for the main reaction. This additionally provides lower odor and lower VOC products.



POLY 51: From soft latex particles to hard films: Synthetic routes towards achieving contradictory properties

Nicholas Ballard, *nicholas.ballard@polymat.eu*, José Maria Asua. Polymat-University of the Basque Country, San Sebastian, Spain

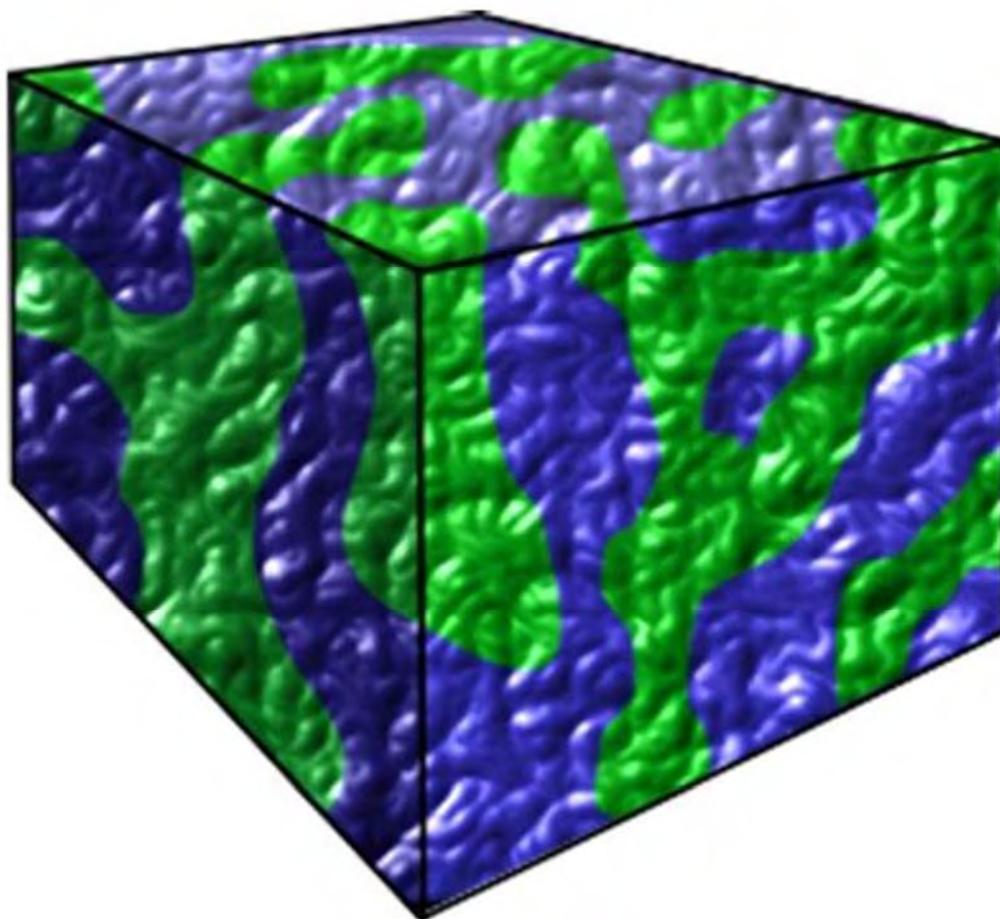
One of the largest areas of commercial application of waterborne polymers is in coatings. However, while latex polymers have many advantages over traditional solvent based polymers the use of latex particles comes at cost. The necessity for a polymer with low enough T_g to form a coherent film inevitably leads to a soft film with poor mechanical properties. Although there are routes to overcome these problems such as through the addition of coalescing agents, increasing concern over the environmental impact has led to the search for new routes to generating hard polymer films from latex particles in the absence of VOCs. In this work, we present results that highlight potential synthetic routes to obtain latex polymers which demonstrate both good mechanical strength as well as the capacity to form a film at ambient temperature.



POLY 52: Bicontinuous amphiphilic polymer co-networks

Gregory N. Tew, tew@mail.pse.umass.edu. *Polymer Science and Engineering, University of Massachusetts, Amherst, South Deerfield, Massachusetts, United States*

Amphiphilic polymer co-networks have gained considerable attention recently. This tutorial talk will outline the history of these materials, recent advances, and future opportunities. Phase-separated and self-assembled co-network materials offer a simple route to bicontinuous-like morphologies, which are expected to be highly beneficial for applications such as ion, charge, and oxygen transport. Despite these potential advantages, the systematic study of co-network structures has not been achieved, largely due to the lack of well-controlled chemistries for their preparation. This talk will also focus on the thiolene addition across norbornene reaction which enables novel co-networks and multi-block copolymers. The thiol-ene end-linking platform enables the systematic investigation of phase-separated networks in terms of the molecular weight and relative volume fractions of precursor polymers.

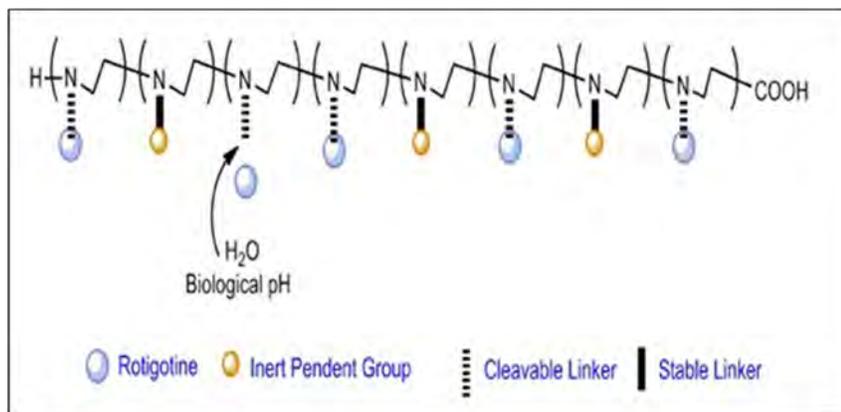


POLY 53: POZ™ –Poly(2-oxazoline) the next generation of polymer therapeutics

Randall Moreadith, *Rmoreadith@serinatherapeutics.com*. Serina Therapeutics, Inc., Huntsville, Alabama, United States

The first poly(2-ethyl-2-oxazoline) (POZ™) polymer therapeutic has completed clinical Phase Ia in patients with Parkinson's disease (PD), and the design, pre-clinical and clinical results of this candidate drug will be reviewed during this lecture. SER-214 is a twenty kDa ten pendent polymer with ten rotigotine molecules attached via copper-catalyzed "click chemistry". In patients that lack sufficient dopamine signaling, continuous drug delivery of a potent dopaminergic agent such as rotigotine might provide continuous dopaminergic tone – a long-sought clinical strategy that would obviate the phasic "peak and trough" profiles of oral agents. This phasic profile underlies the "wearing off" and "dyskinesia induction" that occurs with levodopa. SER-214 may also be an effective therapeutic for restless legs syndrome (RLS) where continuous drug delivery may obviate the need for drugs that are associated with "augmentation".

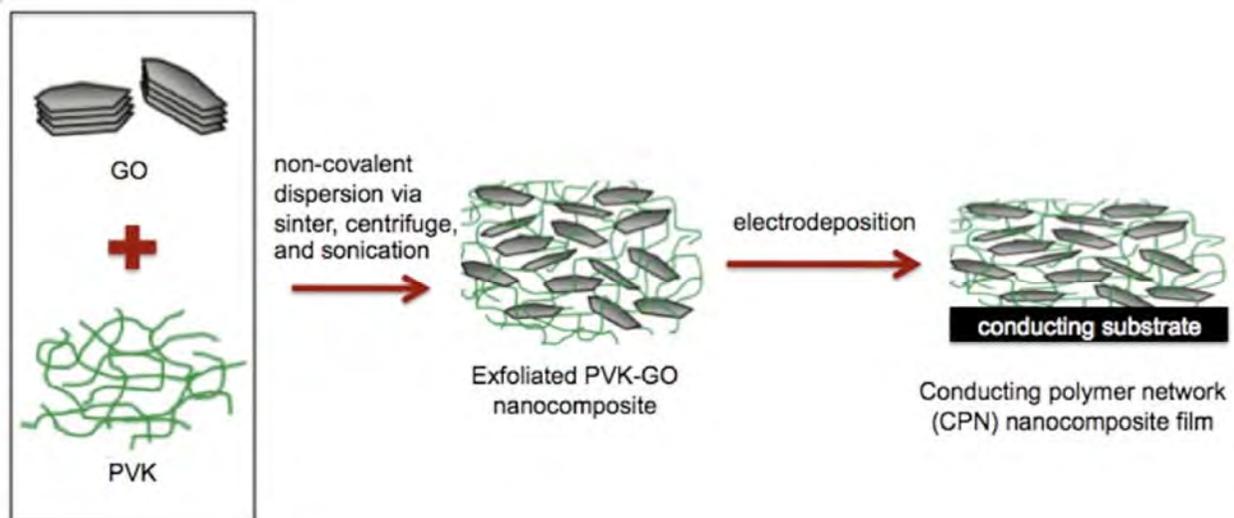
In this lecture I will review the rigorous process we use at Serina to choose a candidate drug, the rationale for development of a molecule that would provide continuous drug delivery, and the landscape of small molecules that would be ideal candidates for such an approach. While Serina's major focus right now is small molecule POZ-conjugates, the technology can readily be applied to proteins – which includes antibody drug conjugates (ADC) to improve the drug antibody ratio.



POLY 54: Polymer surfaces and graphene oxide anti-microbials

Rigoberto C. Advincula, *rca41@case.edu*. *Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio, United States*

Polymers are important from the standpoint of therapeutic and diagnostic applications involving their use as drug delivery vehicles, scaffolds for tissue engineering, and resorbable materials. Along with polymers very important is the use of additives and actives to improve their function and processability. This talk will highlight the preparation of surfaces and use of additives in improving anti-microbial properties against known classes of pathogens. The use of silver nanoparticles and other metal particles for anti-microbials has been the dominant additive for coatings, textiles, and other devices. Here we demonstrate the use of polymer materials and surfaces capable of using graphene and graphene oxide additives for anti-microbial activity such as *E. Coli* and *B. Subtilis* including mitigation biofilm formation. These properties were observed on solution preparation, coatings, and electrodes that have been modified by polymer-graphene composites including preparation as fibers. Modification of graphene oxide further provides chemical functionality that is able to capture heavy metals and their separation.

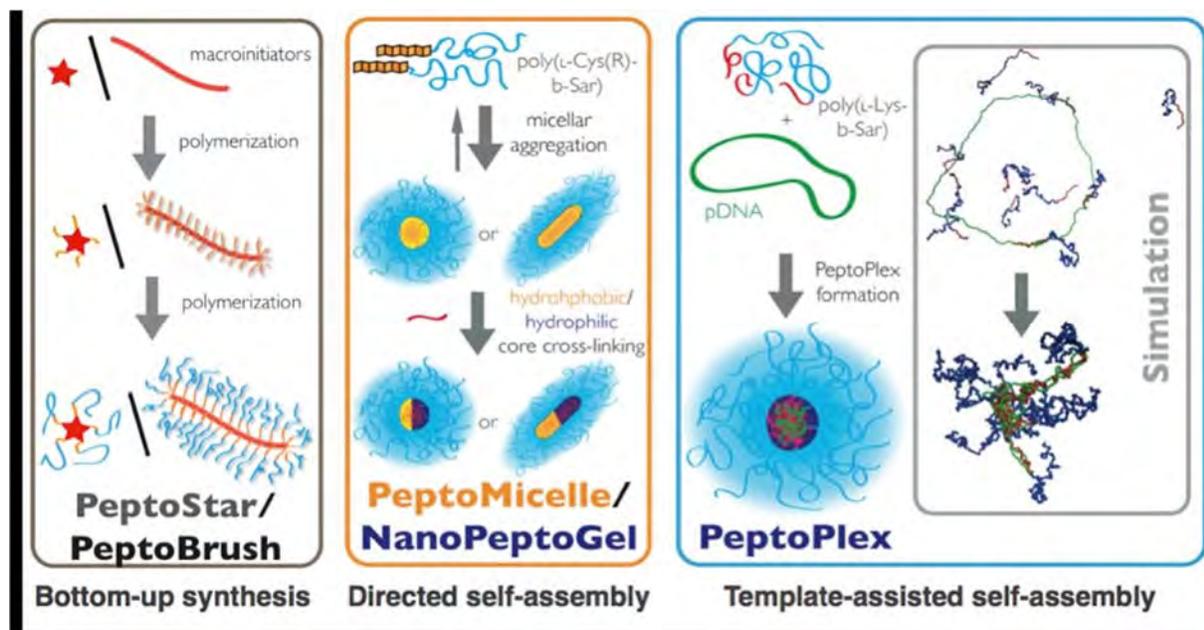


POLY 55: Polypept(o)ides: Tailoring polymer properties for diagnosis and therapy

Matthias Barz, barz@uni-mainz.de. Institute of Organic Chemistry, Johannes Gutenberg-University Mainz, Mainz, Germany

The great potential of polymeric nanoparticles arises from the possibility to combine tailored material properties with compartmentalized functionality. The systems can be obtained either by bottom-up synthesis or solution self-assembly. A class of polymer enabling us to explore the full potential of such materials are polypept(o)ides. These polypeptoid-block-polypeptide copolymers can be synthesized by living ring opening polymerization providing precise control over molecular weights, can be synthesized with low polymer dispersities and high end group integrities. Furthermore, this class of materials is completely based on endogenous amino acids and combines the stealth-like properties of polysarcosine with the multi-functionality of polypeptides.

This toolbox enables the straightforward synthesis of core cross-linked micelles (PeptoMicelles) and nanohydrogels (PeptoNanoGels) by secondary structure-driven self-assembly, bottlebrush polymers (PeptoBrushes), star-like polymers (PeptoStars) and PeptoPlexes, and thus provides synthetic control over particle size, shape and functionality enabling us to tailor material properties to specific needs in diagnosis and therapy of diseases.

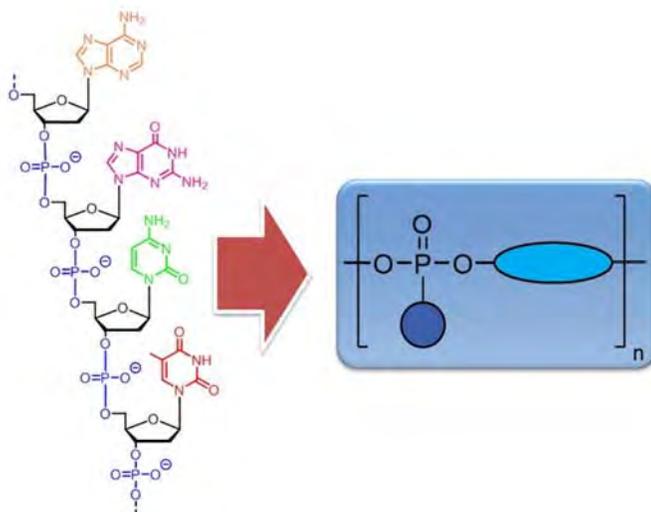


Scheme 1: Synthesis of functional nanoparticles by bottom-up synthesis, secondary structure directed and template-assisted self-assembly for diagnosis and therapy.

POLY 56: Poly(phosphoester)s: History, syntheses, degradation, bio-and flame-retardant applications

Frederik Wurm, wurm@mpip-mainz.mpg.de. Max Planck Institut für Polymerforschung, Mainz, Germany

Nature on planet earth has developed diverse poly(phosphoester)s (PPEs): they structure and determine life in the form of deoxy- and ribonucleic acid (DNA & RNA), and, as pyrophosphates, they store chemical energy in organisms. Polymer chemistry, however, is dominated by the non-degradable polyolefins and degradable polycarboxylic esters produced on a large scale today. Recent work has illustrated the potential of PPEs for future applications beyond flame-retardancy, the main application of PPEs today, and provided a coherent vision to implement this classic biopolymer in modern applications that demand biocompatibility and degradability as well as the possibility to adjust the properties to individual needs. The presentation summarizes synthetic protocols to PPEs, their applications in biomedicine, e.g., as biodegradable drug carrier or in tissue engineering, and their flame retardant properties. History and recent developments that may make phosphorus-based polymers attractive materials for various future applications will be presented.



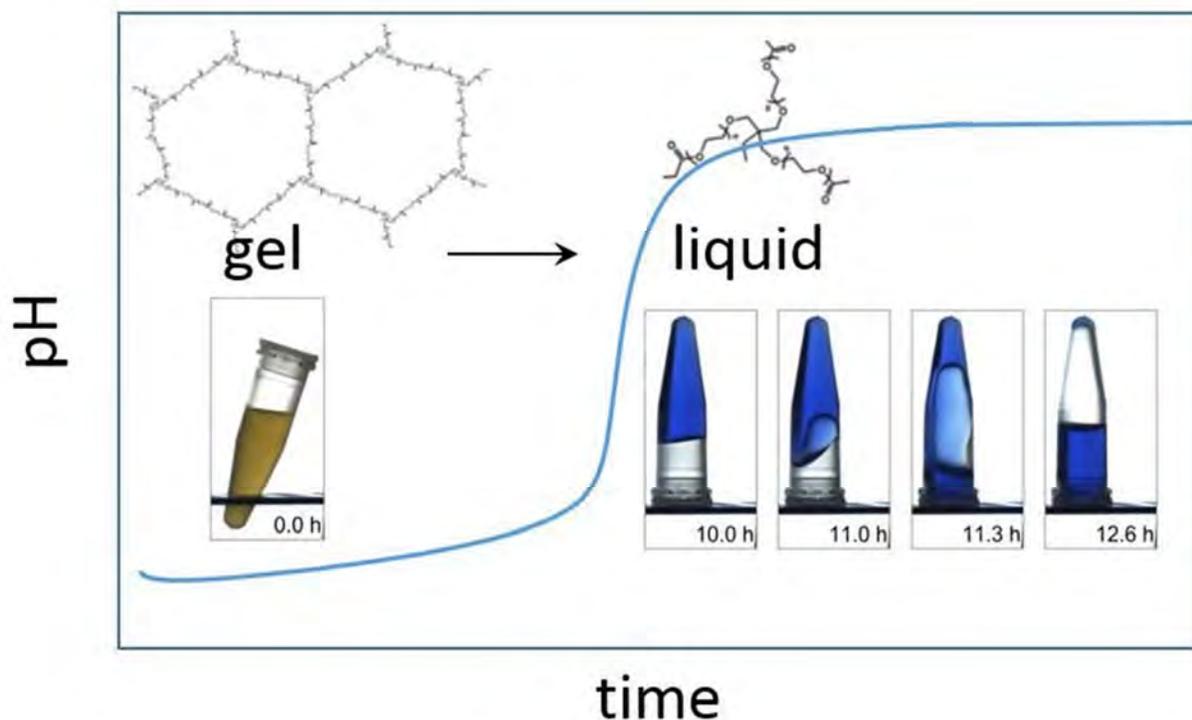
POLY 57: Autocatalysis in depolymerisation: degradation on demand

Annette Taylor, *a.f.taylor@sheffield.ac.uk*. Chemical and Biological Engineering, University of Sheffield, Sheffield, United Kingdom

Autocatalytic reactions can be tuned to display a rapid change in state after a programmable length of time, or be maintained in a low conversion state far-from-equilibrium and then initiated on-demand. These attractive features may be exploited when a material with a certain life-time is required, for example in drug delivery devices or recyclable materials.

One well known example of autocatalysis is in ester hydrolysis where the formation of the acid product can catalyse the hydrolysis resulting in an increase in reaction rate. In the hydrolytic degradation of polyesters such as polylactic acid, the rate acceleration in loss of mass has been attributed to the increasing concentration of terminal carboxylic acid groups. In these heterogeneous environments other factors can also play a role, such as the reaction product enhancing the solubility of the polymer. Tuning the lifetime of such systems can therefore be a complicated process.

We examine the mechanisms of autocatalysis in some depolymerisation processes and discuss methods to programme the time of degradation of the material. We also show how acid/base or enzyme initiated autocatalysis might be used for degradation on-demand in medical or environmental applications.

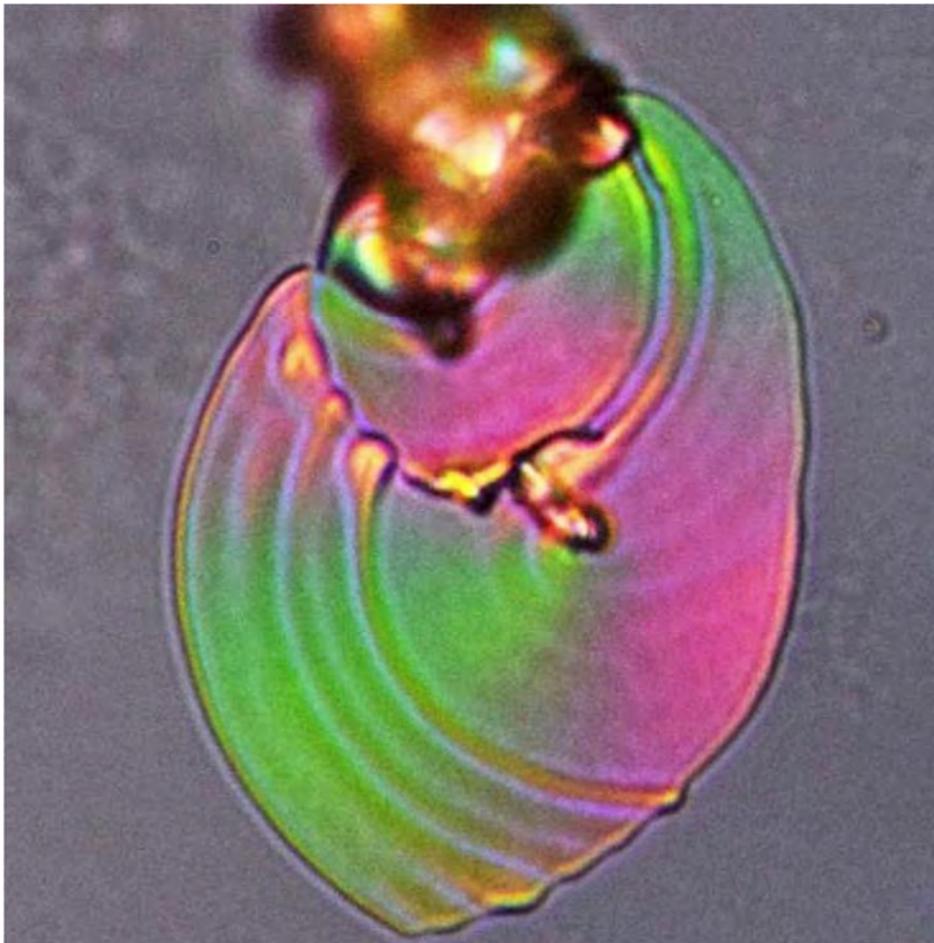


Programmed degradation of a gel

POLY 58: Self-organization in precipitation reactions far from the equilibrium

Oliver Steinbock, *steinbck@chem.fsu.edu*. Florida State Univ, Tallahassee, Florida, United States

Simple rules can create complex patterns and dynamics. This connection is routinely used by living systems to create complex rhythms, spatio-temporal structures, and high-performance materials with design features at meso- and macroscopic length scales that seem to defy their molecular origins. In my talk, I will present several examples that illustrate this point and demonstrate that many phenomena that appear to be unique to life processes actually occur in non-biological, often simple chemical/polymeric systems. Specifically, I will discuss the formation of polycrystalline, micrometer-sized structures that consists of co-aligned arrays of witherite nanorods and amorphous silica. The microshape repertoire includes helices, urns, funnel, and flat sheets. Some of our very recent findings reveal profound links between the shape-generating crystallization fronts and reaction-diffusion fronts in excitable systems that might explain most the observed microshapes. A second, related topic is the production of hollow silica tubes and their possible relevance to prebiotic chemistry.



Biomorph sheet observed with polarization microscopy.

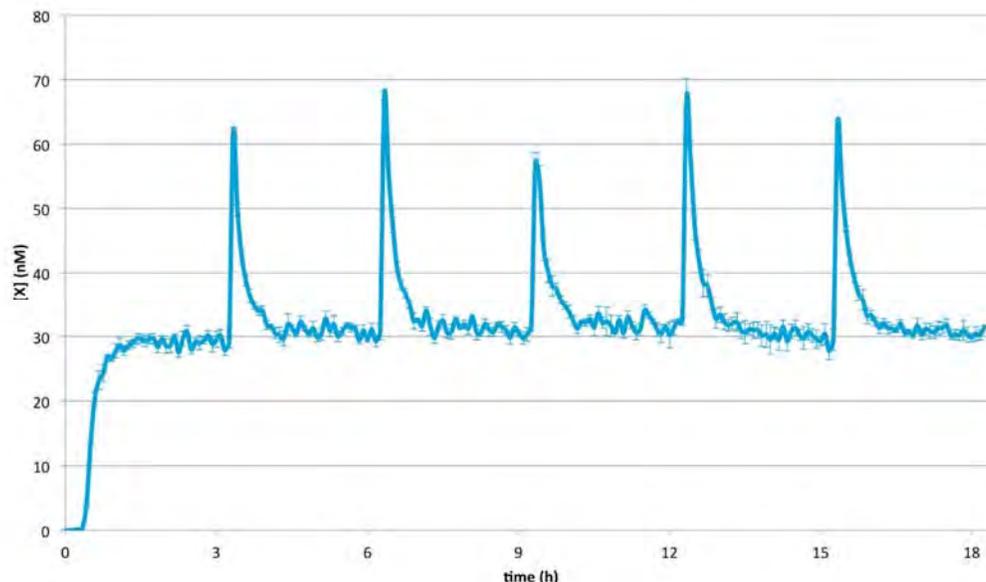
POLY 59: DNA strand-displacement buffers

Dominic Scalise, scalise.dominic@gmail.com, **Rebecca Schulman**. Johns Hopkins University, Baltimore, Maryland, United States

Buffer solutions resist changes to the concentration of a target chemical species. They are commonly used to regulate concentration sensitive systems, such as the human bloodstream, where bicarbonate buffer neutralizes strong acids and bases entering the bloodstream to maintain a constant physiological pH. In cases where the bicarbonate buffer system fails pH can fluctuate freely, which results in a host of ailments collectively referred to as acidemia and alkalemia.

However, there are few mechanisms for buffering chemical species beyond ions. In this study we present a buffer that regulates oligonucleotides, short synthetic sequences of DNA, holding their concentrations constant in the presence of external disturbances. We implement the buffer using DNA strand-displacement (DSD) reactions, programmable interactions between synthetic strands of DNA that enable the design and implementation of *de novo* chemical reaction networks.

A growing library of interface mechanisms exists that enable DSD reactions to control chemical species besides DNA, including proteins, ATP, hydrogels and synthetic nanostructures. These interfaces suggest that under conditions where DNA hybridization occurs normally, DSD buffers could regulate a diverse set of molecules. We will show examples of how DSD buffers could be used to linearize some classes of nonlinear chemical kinetics, and to generate complex reaction-diffusion patterns that are stable over time.

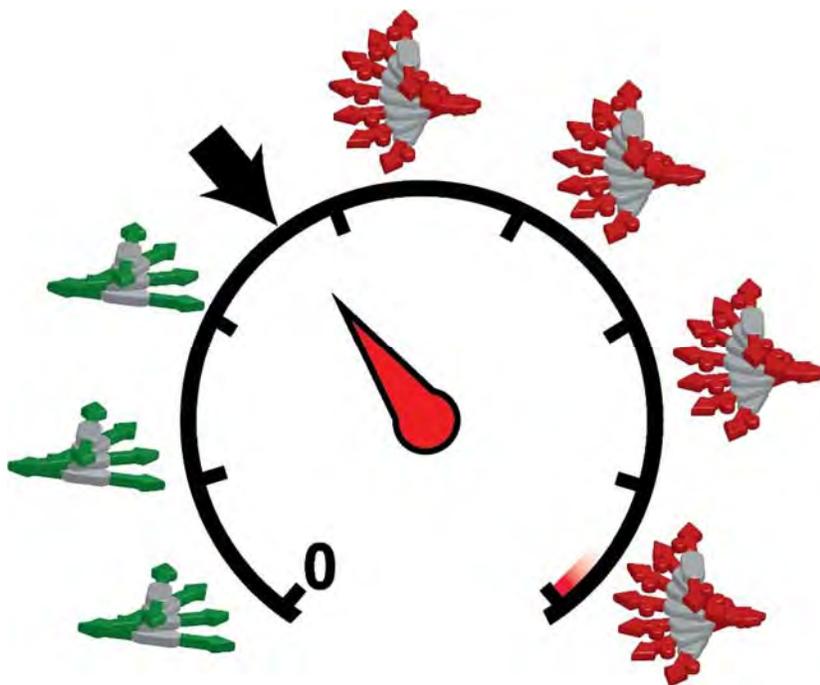


A DNA strand-displacement buffer actively maintaining a target strand of DNA “X” at a constant concentration (~ 30 nM) in the face of five external disturbances where excess X is manually added to the system.

POLY 60: Non-equilibrium steady states in supramolecular polymerization

Alessandro Sorrenti^{2,1}, Jorge Leira-Iglesias², Akihiro Sato², **Thomas M. Hermans²**, hermans@unistra.fr. (1) ETH Zürich, Zürich, Switzerland (2) University of Strasbourg, Strasbourg, France

Living systems use chemical fuel-driven supramolecular polymers such as actin to control important cell functions. Fuel molecules like adenosine triphosphate (ATP) are used to control when and where such polymers should assemble and disassemble. The cell supplies fresh ATP into the cytosol and removes waste products to allow assembly/disassembly cycles to be sustained in steady-states. Artificial fuel-driven supramolecular polymers have been developed in recent years, but keeping them in sustained non-equilibrium steady-states (NESS) has proven challenging. Here we show a supramolecular polymer that can be kept in various NESS, inside a reactor where ATP is added and waste removed continuously. Depending on the ATP concentration the system can be in a dissipative non-equilibrium state that is near equilibrium, or in a far-from-equilibrium state where emergent chemical phenomena can occur. Assembly and disassembly of our polymer is regulated by enzymatic phosphorylation and dephosphorylation, respectively. We believe that our approach can be applied to other stimuli-responsive or transiently dissipative materials to achieve sustained NESS in artificial systems.

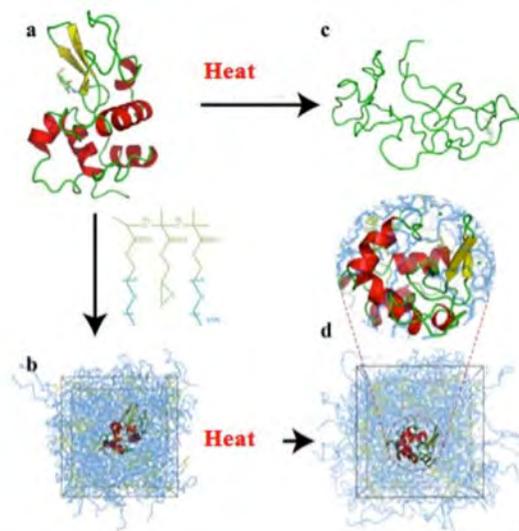


Supramolecular cruise control

POLY 61: Designing highly thermostable biocatalysts

Chandan K. Choudhury¹, Sidong Tu¹, Nataraja Yadavall², Nikolay Borodinov¹, Sergiy Minko², Igor A. Luzinov¹, **Olga Kuksenok**¹, okuksen@clemson.edu. (1) Materials Science and Engineering, Clemson University, Clemson, South Carolina, United States (2) The University of Georgia, Bishop, Georgia, United States

Designing materials functioning in harsh environments is vital for a range of applications. In particular, enhancing thermal stability of various enzymes is beneficial for applications ranging from food processing to deconstruction of biomass for biofuel industry. We show that conjugating lysozymes with a copolymer [poly(GMA-stat-OEGMA)] comprising glycidyl methacrylate (GMA) and oligo(ethylene glycol) methyl ether methacrylate (OEGMA) dramatically increases the thermal stability of these enzymes well above 100°C. This conjugation strategy leads to the formation of cocoons around the enzymes. Using molecular dynamics simulations, we focus on understanding the underlying reasons for the observed thermal stabilization. We represent copolymer with the triads containing the same ratio of GMA to OEGMA units as in our experiments. We conjugated these triads with all the lysine residues of the enzyme, and in addition randomly placed free-floating triads within the simulation box mimicking effects of non-reacted side chains in our experiments. We focus on dynamics of the conjugate at high temperatures and on its structural stability at various copolymer concentrations. We characterize the evolution of the number of the intra-protein hydrogen bonds and the number of contacts between all the species in the system as phase separation and protein unfolding takes place. We also focus on dynamics of the secondary structures within the conjugates. Our simulations show that the water concentration in the close vicinity of the enzyme plays a defining role in maintaining its structural stability at high temperatures; we identify critical water concentration below which a robust stabilization is observed. These results are in agreement with our experimental observations showing densification of the cocoon in the close vicinity of the enzymes.

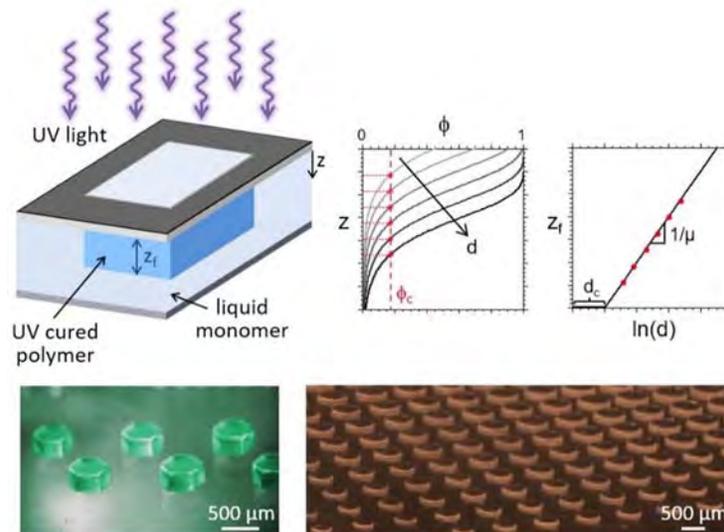


MD simulations of (a,c) native lysozyme and (b,c) enzyme-polymer conjugate at high T.

POLY 62: Controlling the evolution of frontal photopolymerization waves for 3D polymeric patterning

Alessandra Vitale¹, 30126201@acs.org, **Matthew G. Hennessy**², **Omar K. Matar**³, **João T. Cabral**³. (1) Department of Applied Science and Technology, Politecnico di Torino, Torino, Italy (2) Centre de Recerca Matemàtica, Bellaterra, Barcelona, Spain (3) Department of Chemical Engineering, Imperial College London, London, United Kingdom

In this work we describe a general, simple and exceptionally well-controlled patterning approach for photocurable monomers based on frontal photopolymerization (FPP). FPP is a significant case of photopolymerization reaction, where illumination results in the development of a solidification front which propagates in the form of a planar wave, invading the monomer bath. The factors governing the planar solidification process, including front position, profile shape, diffusion and thermal effects, are explicitly investigated and quantified. We find the FPP process to be controlled by tuning selected photopolymerization parameters, such as monomer chemistry, optical properties, temperature, time and intensity of irradiation, in a remarkably general and simple fashion. A minimal descriptive model accurately describes the frontal solidification kinetics, and model extensions were developed accounting for different phenomena occurring during FPP, such as diffusive mass transport, swelling, heat generation and transport, optical attenuation. The predictive capability of the model is applicable to the fabrication of 3D patterned materials from representative radical photopolymerizing systems, showing prescribed dimensions and controlled mechanical properties and stress development.



Schematic of the FPP experimental setup showing the photopolymerization front propagation from the UV illuminated surface and examples of 3D patterns obtained by FPP. The extent of monomer-to-polymer conversion ϕ within the network has a sigmoidal shape profile, while the sample thickness z_f increases logarithmically with exposure dose d .

POLY 63: Potential reactants toward the synthesis of precipitation tubes

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Using reaction conditions far from equilibrium, we investigate the growth dynamics of hollow tubes formed from reactant-loaded seed crystals. The latter crystals are composed of alum and copper(II) sulfate. During the experiment, a single crystal (100 to 1000 mg in mass) is placed in a small volume of sodium silicate such that the formation of precipitation structures is monitored by a time-lapse camera. At low concentrations of sodium silicate (1.0 M), the tube growth is characteristic of the budding regime. For high concentrations of sodium silicate (6.25 M), tubes are directed by a single gas bubble. Using procedures of image acquisition and processing we are able to quantify the spatial and temporal dynamics. Systematic measurements include but are not limited to: tube radius, induction period, and growth velocity. This presentation will discuss both the qualitative and quantitative aspects of the distinct morphologies of precipitation tubes at reactive interfaces. Lastly, results from scanning electron microscopy and infrared spectroscopy will be presented.



Formation of tubular structures in 1.00 M waterglass.



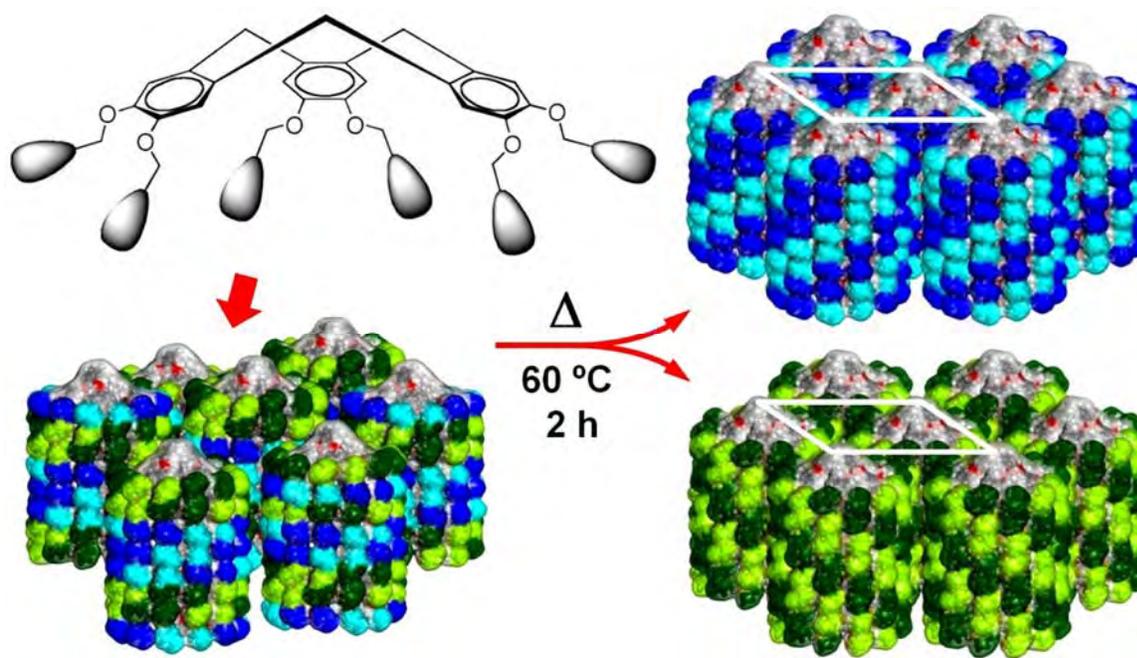
Formation of tubular structure in 6.25 M waterglass.

POLY 64: The role of chirality in supramolecular organization

Hans W. Spiess, *spiess@mpip-mainz.mpg.de*. Max Planck Inst For Polymers, Mainz, Germany

Organic functional materials can be generated via supramolecular organization of carefully chosen building blocks. Secondary interactions such as hydrogen bonding, aromatic pi-interactions, and electrostatic forces are of central importance. Combined with X-ray scattering and quantum chemical calculations, NMR spectroscopy provides unique and highly selective information on structure and dynamics of such systems with atomic resolution.

For use in organic electronics the supramolecular organization has to be as high as possible. In pi-stacks the degree of order not only depends on the packing of the aromatic moieties, but also on the organization of the side groups. In fact, the highest organization achieved so far is achieved by introducing chiral centres in the side groups. NMR spectroscopy can then elucidate the mechanism of self-sorting in mixtures of enantiomers as well as subtle differences in the packing resulting from placing the chiral centres at different positions of dendritic side groups.



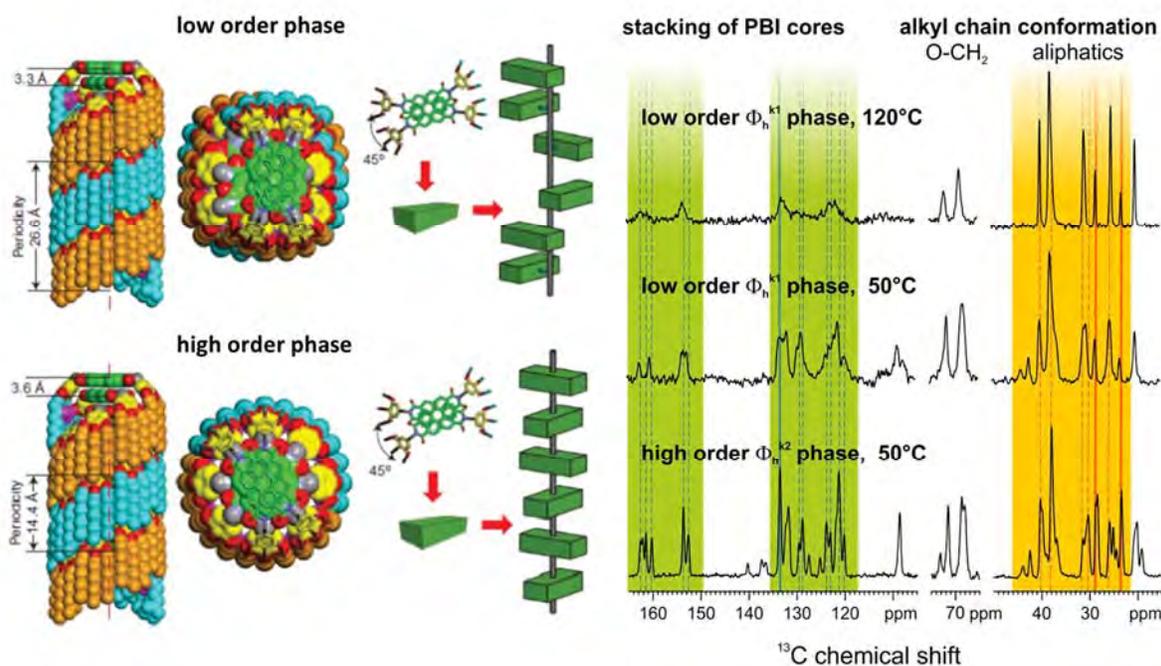
Chiral Self-Sorting During Supramolecular Helical Organization of Hat-Shaped Molecules

POLY 65 Improving precision and stability of self-assembling supra-molecular materials using side chains with chiral centers

Robert Graf, graf@mpip-mainz.mpg.de. Molecular Electronics, Max-Planck-Institute for Polymer Research, Mainz, Germany

The controlled self-assembly of relatively simple molecular building blocks into functional supra-molecular architectures is often used in nature to achieve well defined larger scale structures. For applications in molecular electronics, typically the cores of the supra-molecular building blocks need to have a stable, well defined packing optimized for charge transfer between neighboring building blocks of the supra-molecular material. This required local packing of the cores can be obtained by tailored dendritic side groups of the molecular building block leading to stable helical columnar structures. The quasi-crystalline intra-columnar packing can be directed by the chirality of the outer aliphatic side chains of the dendritic side groups. Remarkably, homochirality of the molecular building blocks is not required to obtain highly ordered columnar structures in supra-molecular systems.

In order to elucidate the mechanism of the supra molecular self-assembly, variable temperature NMR measurements under fast MAS conditions have been performed at different stages of the self-assembly process. In particular the stable, remarkably high conformational order of the side chains as well as the well resolved aromatic signals of the perylene bis-imide (PBI) core and the outer phenyl rings provide detailed information on the supra-molecular self-assembly process.



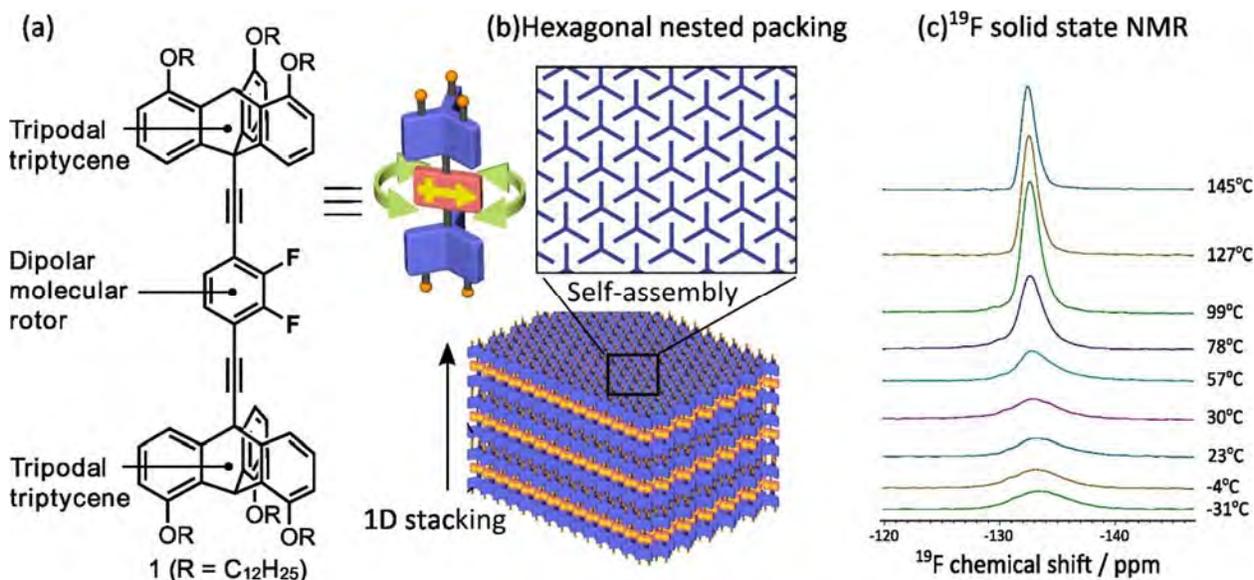
POLY 66: Solid-state dynamics of dipolar molecular rotors incorporated in supramolecular tripodal-triptycene assembly

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Integration and dynamics of dipolar rotor with uniaxial orientation has attracted much attention because of a variety of applications such as thin film memory devices, sensors, and switchable ferroelectrics.

We recently reported that a particular type of tripodal triptycene self-assembles into a macroscopic film with an exceptionally long-range structural order up to the centimeter length scale (Fig.1b). In this study, we incorporate a dipolar rotor into the tripodal triptycene (Fig.1a) and report its self assembling behavior and solid state dynamics of the dipolar rotor.

In order to elucidate the dynamics of the dipolar molecular rotor, variable temperature dielectric and ^{19}F solid state NMR measurements have been performed. While an as-crystallized sample showed no dielectric response and several ^{19}F NMR signals with long T_1 ($> 10\text{s}$) over the measured temperature range (-130 to 150°C), the thermally-treated sample above the melting temperature with hexagonal nested packing structure showed frequency dependent dielectric response and a single ^{19}F NMR signal with much shorter T_1 ($< 1\text{s}$). Moreover, its line-width and T_1 significantly decreased with increasing temperature (Fig.1c). This indicates that the dipolar rotor can flip easily in the hexagonal nested packing structure due to a space volume around the rotors, which was generated by self-assembly of the tripodal-triptycene stator.

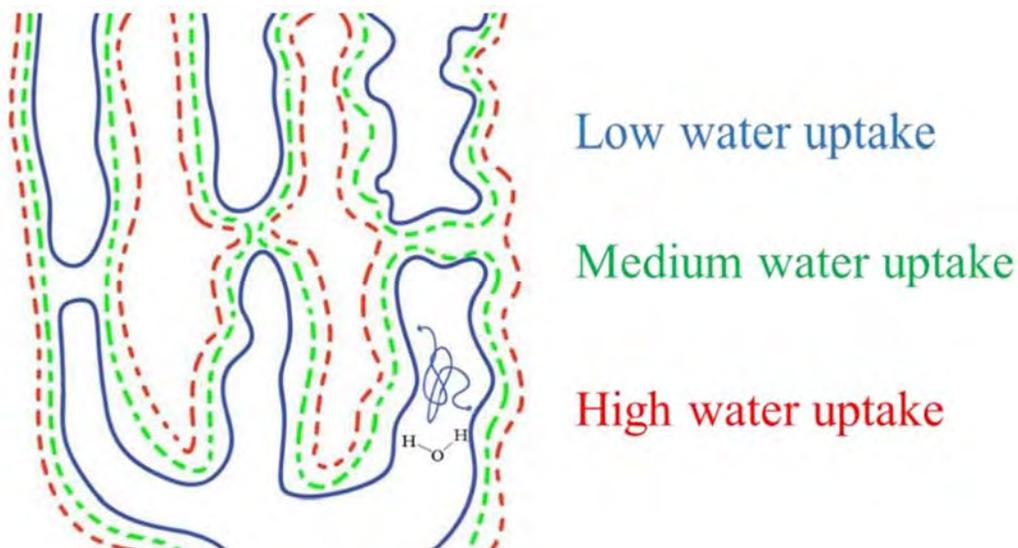


Schematic illustration of assembly of tripodal triptycene with a dipolar rotor **1**. (a) Schematic and chemical structure of **1** and (b) its expected hexagonal nested packing structure. (c) ^{19}F solid state NMR spectra at various temperatures.

POLY 67: Measuring multi-scale tortuosity in polymer membranes

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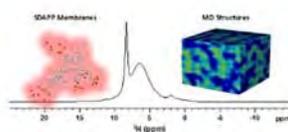
Self-organized polymer membranes conduct mobile species (ions, water, alcohols, etc.) according to a hierarchy of structural motifs that span sub-nm to > 10 microns in length scale. In order to comprehensively understand such materials, our group combines multiple types of NMR dynamics and transport measurements (spectroscopy, diffusometry, relaxation, imaging) with information from scattering, simulations, and microscopy as well as with theories of porous media, electrolytic transport, and oriented matter. In this presentation we will discuss quantification of tortuosity, meaning the restriction of pathways for diffusion through a medium such as a polymer membrane used for molecular separations. We introduce the separate measurement of tortuosity averaged over two distinct length scales – nanometer to bulk and micron to bulk. We present NMR diffusometry measurements of these two quantities on representative systems of hydrophilic-hydrophobic random copolymer polymer membranes including anion-exchange membranes (AEMs), cation-exchange membranes (CEMs) and all-neutral membranes. We also follow multi-scale tortuosity as a function of water uptake (see figure) and discuss associated phenomena. Using knowledge that correlates material structure and morphology with molecular and ionic transport, we seek to give informed feedback on the design of separations membranes for use in, e.g., reverse-osmosis water purification, batteries, fuel cells, and mechanical actuators.



POLY 68: Probing the hydrophilic domain structure and water transport in SDAPP proton exchange membranes

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There is continued effort in developing improved proton exchange membranes (PEMs) targeted to specific energy storage applications including fuel cells and batteries. The PEM performance, including mechanical stability, degradation characteristics and conductivity, are strongly influenced by the local chemical environment and the size and shape of the local domains. In this presentation, we describe a series of both solid-state MAS NMR experiments, along with pulse field gradient (PFG) NMR diffusometry to characterize the sulfonated Diels-Alder polyphenylene (SDAPP) polymer membranes being developed at Sandia. We discuss recent efforts using ¹H double quantum (DQ) NMR spin diffusion (SD) experiments to probe the nanoscale morphologies of the hydrophilic domains created by the hydrated sulfonic acid side groups as a function of water content. The magnetization recovery responses from these NMR spin diffusion experiments were compared directly to recovery curves obtained for structural models based on molecular dynamics (MD) simulations. These results support the emerging description of isolated, “stringy”, poorly connected hydrophilic (sulfonic acid + water) domains at low water concentrations that evolve to larger percolated hydrophilic domains at higher hydration levels. The PFG NMR experiments reveal a significant decrease in the water diffusion rate with decreasing hydration level. The impact the variation in the nanoscale morphology has on the local water transport and proton conductivity in the membrane will be discussed.

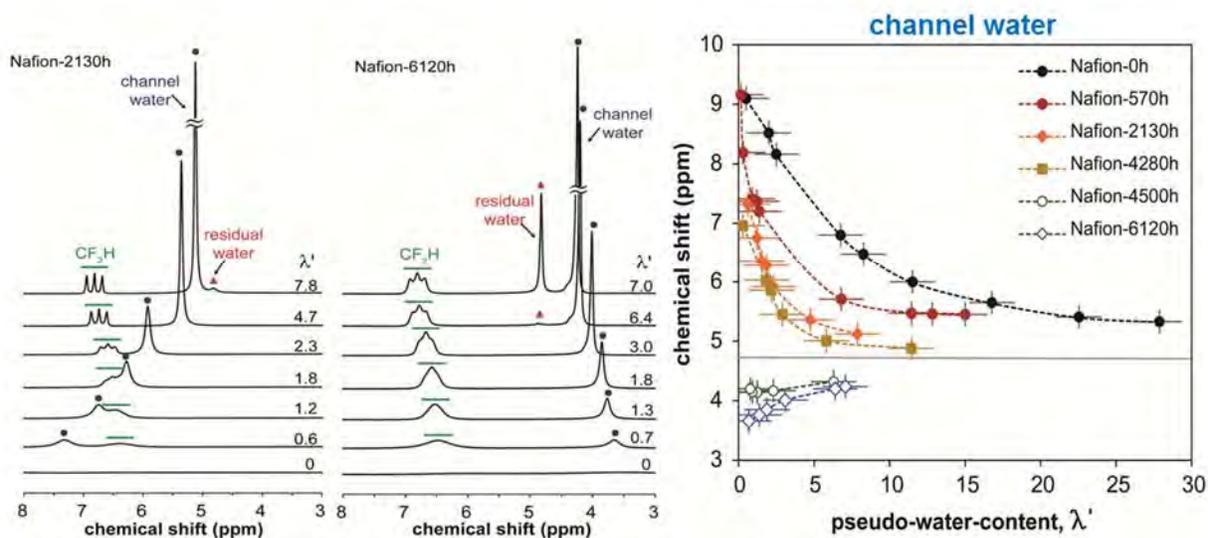


NMR Spin Diffusion Characterization of Domain Structure

POLY 69: Influence of hydrophobicity on dynamics of water in nano-meter scale space of polymer electrolyte membranes

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The ¹H magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra of the Nafion polymer electrolyte membranes thermally degraded with SO₃H groups replaced by H show that the water exposed to more hydrophobic environment moves faster. This agrees with our previous Overhauser dynamic nuclear polarization (ODNP) NMR data indicating that water in the middle of the hydrophilic channel moves slower than those close to the hydrophobic inner walls of the channels. In addition, the MAS NMR data manifest that the chemical shift of channel water reflects not only the number of water per SO₃H group but also the degree of hydrophobicity where water is placed. This finding may open a new door to designing polymer electrolyte membranes with fine control of hydrophilicity/hydrophobicity of channel inner surface in molecular level and to developing hydrophilicity/hydrophobicity measuring methods in molecular level.



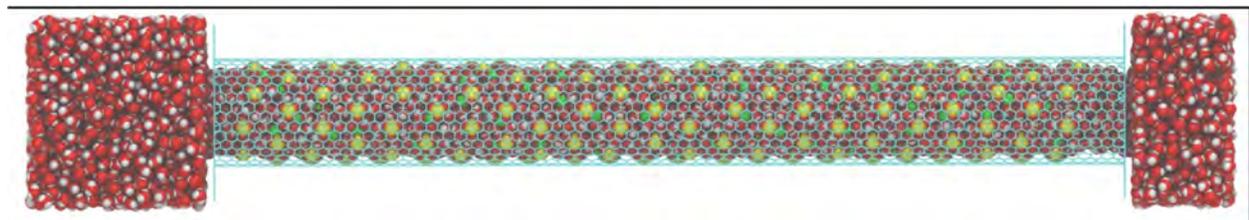
POLY 70: Understanding transport in polymeric separations membranes by combining NMR diffusometry and molecular dynamics simulations

Rui Zhang, ruiz@vt.edu, Diego Troya, Louis A. Madsen. Chemistry, Virginia Tech, Blacksburg, Virginia, United States

Polymer membranes find use in a variety of important applications such as energy storage devices, water purification, and gas separation. Despite the long history of polymer membranes, knowledge about the relationship between their multi-scale structure and macroscopic transport properties is not well developed. This limited knowledge has hindered many practical applications of polymer membranes.

We are investigating lithium-form perfluorosulfonic acid (Nafion) membranes by NMR diffusometry and determine the activation energy of diffusion at various hydration levels for two distinctly different moving species, lithium ions and water molecules.

Combination of these NMR diffusometry experiments with molecular dynamics (MD) simulations as a function of ion-water mole ratio and nanoconfined model representatives of membranes provides insight into the relationship between diffusion behavior and local molecular environment. The MD model (see figure) simulates water and ion diffusion in the Nafion hydrophilic nanochannels. The model consists of a variable-diameter (1 – 3 nm) single wall carbon nanotube with sulfonate groups on the inner wall filled with water and Li⁺ counterions. The synergy between NMR measurements and atomistic simulations affords deeper fundamental understanding of transport processes, and guides the design and optimization of materials for wide-ranging molecular transport and separations applications.

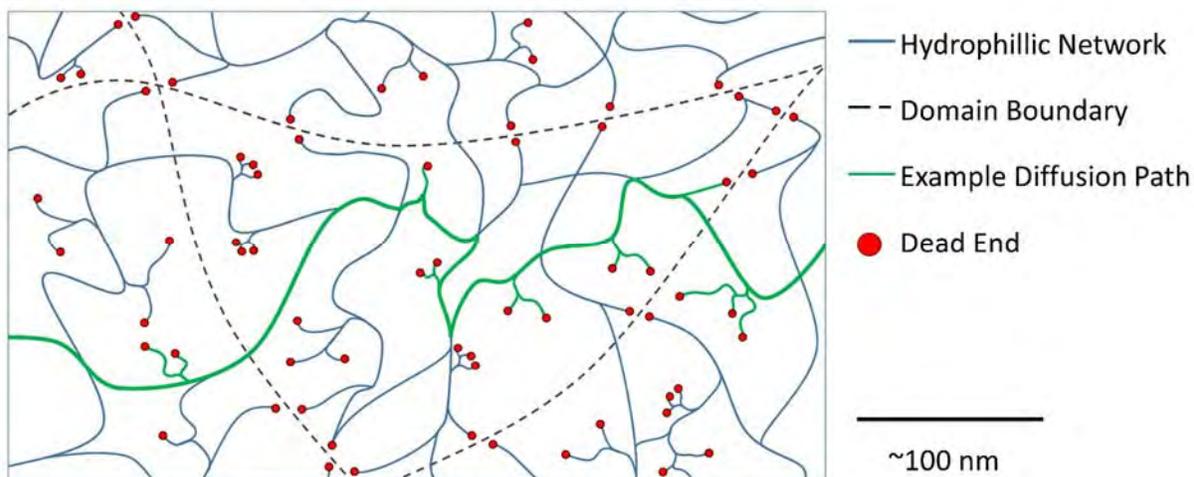


POLY 71: Investigating multi-scale transport in random copolymer membranes for use in molecular separations

Andrew Korovich¹, drewkoro@vt.edu, **Kevin Chang**², **Tianyi Xue**², **William A. Morris**², **Louis A. Madsen**³, **Geoffrey M. Geise**². (1) Chemistry, Virginia Tech, Blacksburg, Virginia, United States (2) Chemical Engineering, University of Virginia, Charlottesville, Virginia, United States

Reverse osmosis (RO) is one of the most efficient means of water purification, however improvements to this process are strongly limited by the polymer membranes used as the separation medium. We will present water transport investigations on two series of neutral random copolymer membranes based on polyhydroxymethylmethacrylate-co-methylmethacrylate (poly(HEMA-co-MMA)), in which $T_g > \text{room T}$ (glassy dynamics), and polyhydroxyethylacrylate-co-ethylacrylate (poly(HEA-co-EA)), in which $T_g < \text{room T}$ (rubbery dynamics).

Using NMR diffusometry we measure water diffusion as a function of polymer composition and diffusion encoding time. Such variable time studies reveal clear micron-scale heterogeneity in these polymers. For the first time, we introduce the quantitative separation of material tortuosity into two regimes, averaged over the nm-to-bulk and μm -to-bulk ranges, which allows for separate insights into the influence of multi-scale morphology on bulk transport. When compared with bulk water and salt uptake measurements, we show that water-salt selectivity, water and salt permeation, and nm-to-bulk tortuosity show dramatic differences between the two membrane series, but the μm -to-bulk tortuosity for these membranes is independent of polymer composition, leading to the conclusion that these properties are influenced by backbone dynamics and nanometer-scale interactions. We propose a model for these membranes in which the hydrophilic network has micron-scale heterogeneous arrangements of nm-scale dead ends (see figure). These studies give new perspectives into the morphology of polymeric materials, and provide a means for guiding design of materials for water purification, fuel cells, and other molecular separations applications.

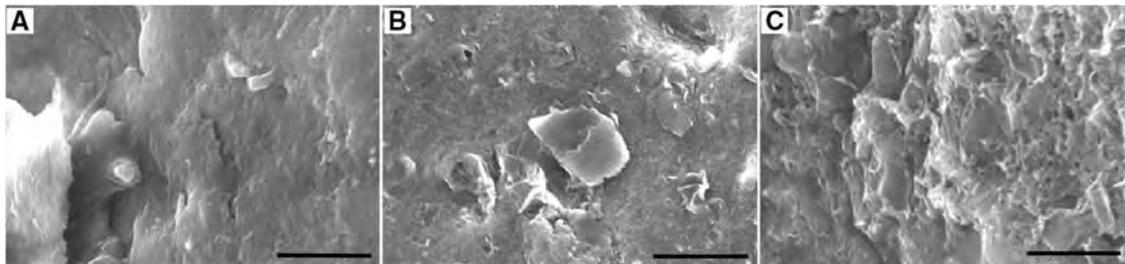


POLY 72: Electrical conductivity/resistivity for copolymers carbon composites at cryogenically low temperature

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Abstract:

The electrical conductivity/resistivity of ethylene vinyl acetate and acrylonitrile butadiene rubber copolymers composites filled with different carbons is determined at cryogenically low temperature, where the composites were prepared by melt mixing technique. Initially, the composites showed NTC behavior of resistivity up to a certain range of temperature and afterwards, PTC behavior of resistivity was observed. The nature of this behavior was dependent on polymer and filler types. Moreover, the conductivity results of the composites were tested by Arrhenius, Kivelson, and Mott's VRH models to check their applicability. It was observed that the models were applicable over a certain range of temperature. The reason behind the non-applicability of these models was discussed by considering their strength, weakness, and limitations.

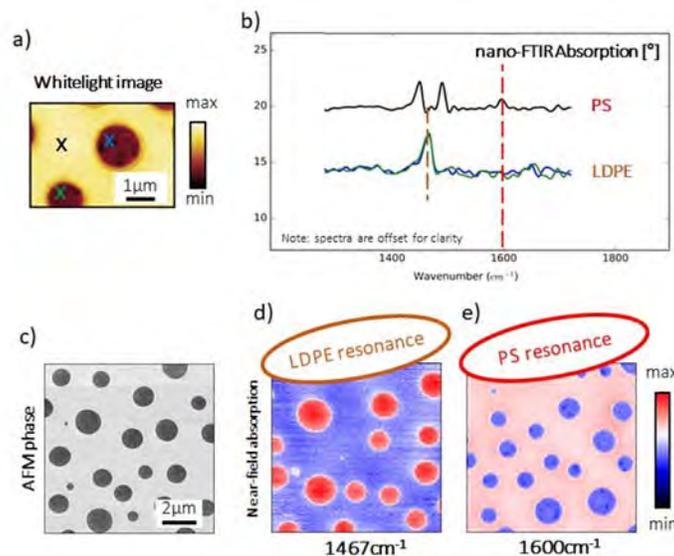


SEM images for copolymers carbon composites .

POLY 73: nano-FTIR: Near-field spectroscopy of polymers at sub200ms per spectrum speed and sub20nm spatial resolution

Philip Schäfer, *philip.schaefer@neaspec.com*, Tobias Gokus. neaspec GmbH, Martinsried, Bayern, Germany

nano-FTIR employs an externally IR-illuminated sharp metallic AFM tip to create a nanoscale hot-spot at its apex. The optical tip-sample near-field interaction is determined by the local dielectric properties (refractive index) of the sample. Detection of the elastically tip-scattered light simultaneous to AFM imaging yields nanoscale resolved near-field images. Utilizing broadband laser sources like a mid-IR supercontinuum laser for tip illumination enables near-field spectroscopic measurements at nanometer scale spatial resolution with unprecedented signal quality. We demonstrate high performance and striking specificity with near-field absorption images of (sub)micron-sized islands of Low-Density Poly-Ethylene (LDPE) in a Poly-Styrene (PS) 50nm thin film. nano-FTIR spectra obtained on different sample regions clearly reveal the material-specific IR spectroscopic signatures of the respective polymers. The exceptional signal to noise ratio obtained for polymeric and even biological samples provides the basis to reduce measurement times by orders of magnitude and to acquire characteristic near-field spectra on the 100-200ms time scale. This allows hyperspectral imaging by recording a full FTIR-spectrum in each pixel of a scanned image with reasonable measurement durations. It enables for instance the elucidation of clustering and localized chemical interactions of polymers in a three-component polymer blend. Besides non-invasive nanoscale resolved material identification, nano-FITR permits quantitative measurements of dielectric values for polymers or the determination of free carrier concentration and mobility in low-dimensional structures.



a) Spectrally integrated whitelight image of LDPE islands in a PS thin film; b) nano-FTIR spectra recorded at spots marked in a, revealing characteristic absorption bands of LDPE and PS; c) AFM image: mechanical phase compared to near-field absorption images scanned at d) LDPE resonance and e) PS resonance.

POLY 74: Applying multi-detector GPC/SEC to complex characterization of drug delivery polymers

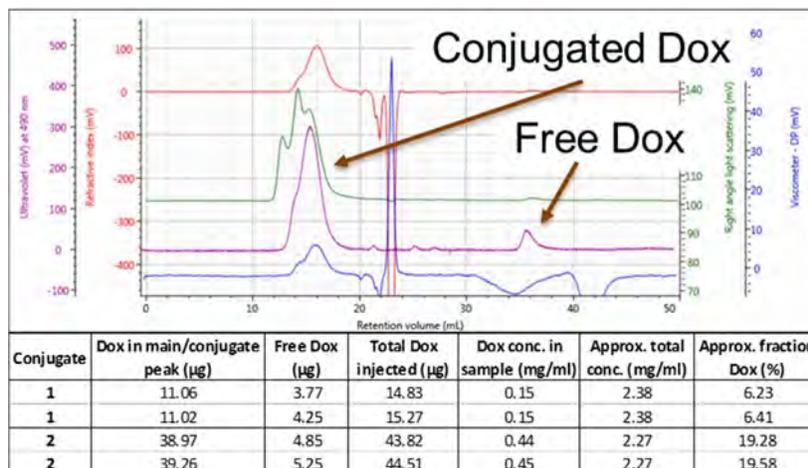
Mark R. Pothecary¹, mark.pothecary@malvern.com, **Carrie Schindler**¹, Guodong Zhang², Haifa Sher². (1) Malvern Instruments, Houston, Texas, United States (2) Department of Nanomedicine, Houston Methodist Research Institute, Houston, Texas, United States

Gel-permeation chromatography (GPC) is widely used for measuring the molecular weight (distribution) of polymers. Historically, the elution volume of an unknown sample was compared with that of known standards to estimate molecular weight. Advanced detection offers *absolute* molecular weight and branching analysis through intrinsic viscosity (IV) or Rg.

In pharmaceutical research, correctly targeting the delivery location and release profile of drugs is a critical challenge and a great many avenues of research are being explored to overcome the challenges of drug delivery. Polymers are playing an increasing role in drug delivery applications as targeted controlled-release mechanisms. One potential solution is to conjugate chemotherapy drugs such as Doxorubicin (Dox) with a delivery polymer such as polyglutamate (PG). Preferential uptake of PG-Dox conjugates by cancer cells and local degradation and drug release could more effectively target cancer cells over healthy cells¹. Advanced GPC can be used to study the conjugated polymer's molecular weight, structure and conjugation levels to measure conjugated and free Dox, to predict efficacy vs toxicity.

Poly(lactic acid) and poly(lactide-co-glycolide) are used in stents, biodegradable sutures and timed-release drug delivery applications. Structural analysis using IV can be combined with absolute molecular weight measurements to characterize the structural changes that accompany the compositional changes.

In this presentation, we will show some novel analysis of PG-Dox polymer conjugate to assess its molecular weight, structure and the presence of free and conjugate Dox to gain additional insight into this conjugated drug delivery polymer. We will also show how IV and the Mark-Houwink plot can be used to characterize PLGA copolymer composition by comparison to known standards. Finally, we will show how these measurements help to understand changes in rheological properties of these polymers.



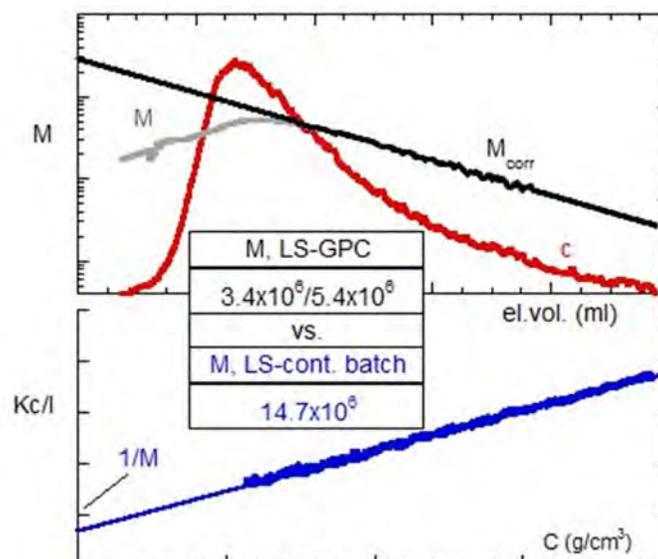
POLY 75: Overcoming challenges in high molecular weight (HMW) polymer characterization

Alina M. Alb, linocika12 @live.com. Kemira Chemicals, Atlanta, Georgia, United States

Ongoing innovations in synthesis of HMW polymeric materials with multiple uses in water purification, oil&mining, require continuous efforts to extend the limits of the analytical techniques, their resolution, selectivity and ability to cover broader range of applications. New characterization routes are sought to enhance knowledge on properties such molar mass, composition, molecular architecture and structure, for better understanding of their impact on performance.

A review of new and existent techniques for HMW polymer characterization is presented, with highlights from selected case studies focused on challenging features. Separation chromatographic techniques are widely utilized tools for polymer characterization. Thus, size exclusion chromatography (SEC) offers valuable information on molecular weight distributions and details on chain conformation and structure. However, limitations due to exclusion limits, interactions with stationary phase, shear degradation led to the development of additional separation techniques, such as field-flow fractionation (FFF), especially useful in applications on HMW and branched polymers. While FFF continues to grow as complementary technique to established separation methods, the high demand for accurate HMW polymer characterization led to the search and development of alternative, non-separation characterization routes. Moreover, in some cases separation is not possible or needed and batch (unfractionated) characterization is a more suitable approach. Thus, introduction of new automated light scattering & viscosity-based methodologies allows a multi-faceted characterization in terms of polymer characteristics and interactions with environment, as well as following time-dependent processes.

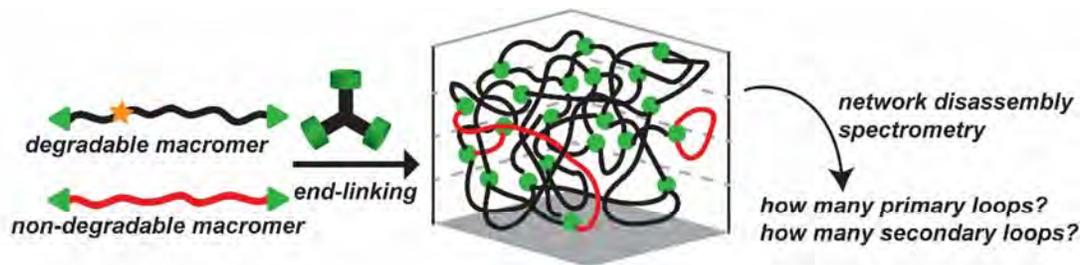
The outcomes of this study are twofold: first, it highlights features of different characterization methods and second, it offers a roadmap for method selection, with the hope that the knowledge gained will lead to increased efficiency and expertise.



POLY 76: Network disassembly spectrometry with a non-degradable tracer: counting primary and secondary loops in polymer networks

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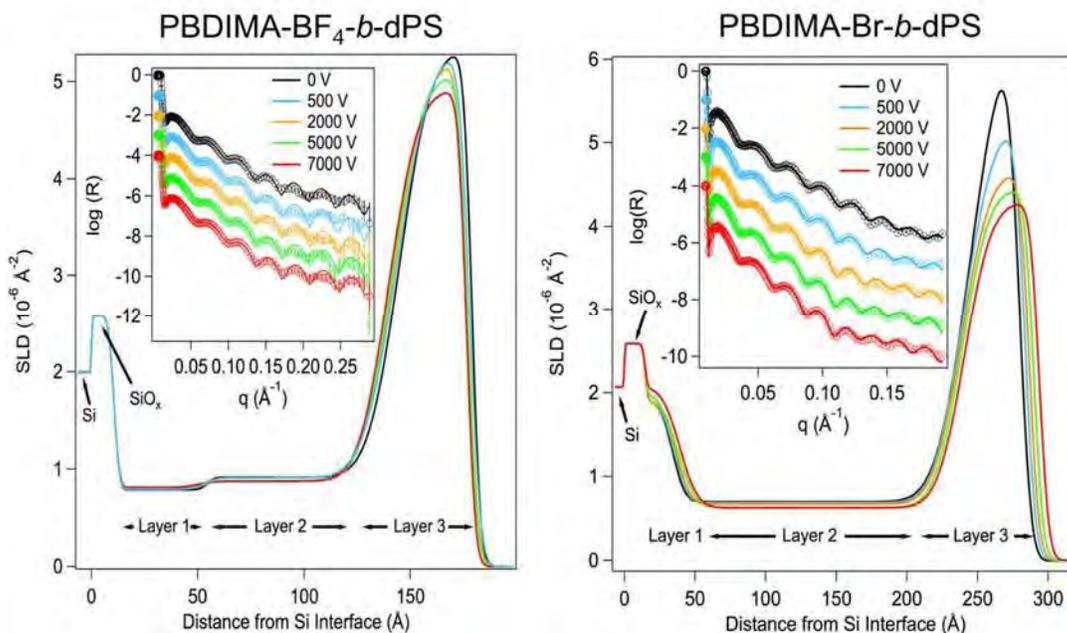
Topological defects in polymer networks profoundly affect the mechanical properties of the materials, and it is therefore pivotal to quantify the amount of defects in the network. While recent work from our group has successfully quantified the primary loops, it has been challenging to measure the fraction of high-order loops, which also significantly affect the mechanical properties of materials. In this work, we demonstrate a method in which a non-degradable tracer is introduced, enabling the direct experimental measurement of both primary and secondary loops. The concentration dependence of the primary and secondary loop fractions matches excellently with that obtained from theories. Semi-batch slow addition technique is applied to the synthesis of the polymer networks and it is found to decrease both primary and secondary loops, compared to the batch mixing method. In addition, with the measured primary and secondary loop fractions, we are able to obtain a close estimation of the elastic shear modulus by conducting the first two order real elastic network theory calculation.



POLY 77: Probing the electromechanical response of ionic block copolymers using neutron reflectometry

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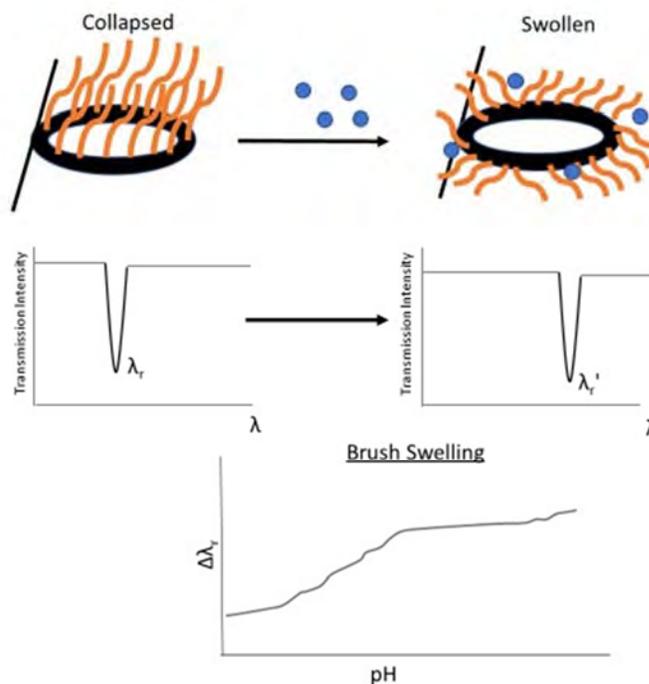
Electroactive polymers have long shown promise to be of use to a variety of fields including energy storage, biomedical and industrial applications, as well microelectronics. In order to better design electroresponsive polymeric systems, a better understanding of how nanoscale interactions contribute to the electromechanical response is needed. The rational synthesis of electroresponsive polymers has the potential to achieve tailored responses by tuning conductivity, rigidity, degree of deformation, or response time all through molecular design. This work describes how counter-anion identity (Br and BF₄) in ionic block copolymers substantially affects the mechanism of electromechanical response, where the propensity of ion dissociation drives whether the film expands (low dissociation) or contracts (high dissociation). In situ neutron reflectometry measurements collected under applied electric fields provide nanoscale resolution of polymer and counter-anion motion and were compared directly to computational models which incorporated applied fields on similar length scales. These results demonstrate not only the impact of counter-anion identity on the mechanism of electromechanical response, but also shows the importance of having experimental and computational experiments converge at a length scale relevant to understanding these processes.



POLY 78: Characterization of polymer brush properties using silicon photonic microring resonators

Shannon Wetzler, swetzler@g.hmc.edu, Ryan C. Bailey. Chemistry, University of Michigan, Ann Arbor, Michigan, United States

Polymer brushes are used often for sensing devices, membranes, or as drug delivery vehicles. Characteristics such as brush thickness and pK_a dictate polymer brush performance and functionality. These properties are currently determined mainly using *in situ* ellipsometry techniques, which require lengthy equilibration periods, meaning analysis times as long as days are often necessary to cover a wide pH range with high resolution. We will demonstrate the advantages of silicon photonic microring resonators, a refractive index-sensitive technique that monitors changes in local environments at the sensor surface, as a faster method to determine brush properties. To assess the platform's performance, pH-sensitive (poly(2-(dimethylamino)ethyl methacrylate) (pDMAEMA), poly(acrylic acid) (PAA)) and non-pH sensitive (poly(methyl methacrylate) (pMMA), poly(2-hydroxyethyl methacrylate) (pHEMA)) polymers were grown to various thicknesses on silicon-on-insulator microring resonators using SI-ATRP. Polymer dynamics were measured in response to both pH and solvent deuteration changes. Relevant pK_a s for polymers were determined with a precision of 0.3 pH units in a period of 4 hours and deuterated solvent comparisons were used to determine brush thicknesses. These results demonstrate that microring resonators could be used as a tool for rapid determination of polymer properties.



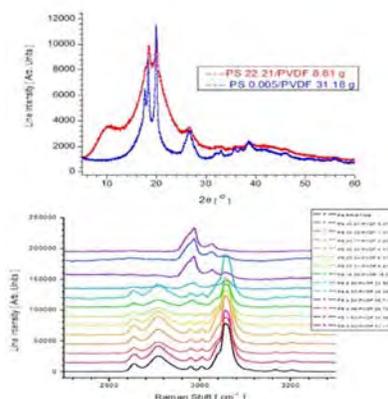
POLY 79: Spectroscopic investigations of PS-PVDF blends

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Blends of polystyrene-polyvinylidene fluoride (PS-PVDF) have been obtained by melt mixing using a Haake mixer. Blends containing various compositions (0%, 1%, 5%, 10%, 15%, 20%, 25%, 30%, 40%, 50%, 60%, 75%, 85%, 90%, 95%, 99%, and 100% weight PS) were obtained using the following parameters for the four-step mixing (step 1 at 175 °C and 40 rotations per minute - RPM - for 5 minutes, step 2 at 190 °C and 60 RPM for 15 minutes, step 3 at 210 °C and 90 RPM for 30 minutes, and step 4 at 180 °C at 60 RPM for 15 minutes).

Blends of PS-PVDF have also been obtained by force spinning. The force spinning used solutions of PS-PVDF blends in dimethylformamide (DMF) of different concentrations and at various rotations (2500, 5000, and 7500 RPM, respectively). The as obtained mats or pellets have been investigated by Raman spectroscopy by using a Raman Renishaw confocal microscope operating at 532 and 785 nm, by UV-Vis spectroscopy using a Bruker Tensor 27/Hyperion system, and by X-Ray diffraction using a Bruker Discovery 8 spectrometer. Optical and electron microscopy were used to determine the average diameter of PS-PVDF nanofibers and the effect of concentration, composition (PS/PVDF), and spinning rate on the diameter of nanofibers. The effect of composition and manufacturing path on the contact angle (using distilled water as fluid) for both melted blends and mats has been analyzed in detail.

The research focuses on the identification of the phase composition of the blends and on the estimation of the ratio between the non ferroelectric phase of PVDF (alpha phase) and the ferroelectric phase(s) (beta and eventually gamma). The research aims to achieve mats and eventually blends of PS-PVDF with enhanced ferroelectric properties.



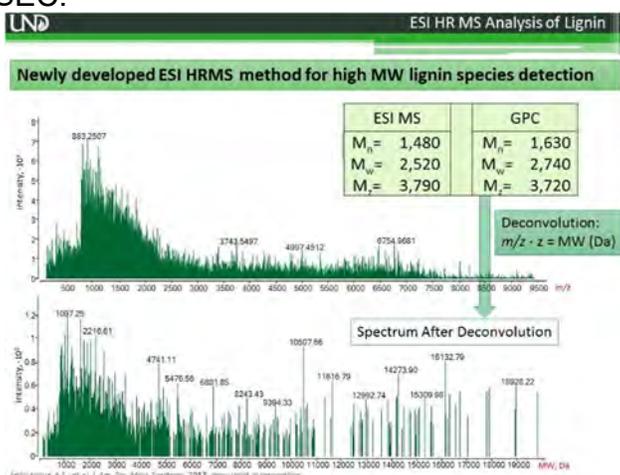
Top: X-Ray spectra of some blends. Bottom: Raman spectra of PS-PVDF blends.

POLY 80: Effective characterization of oligomers and polymers by electrospray ionization with high-resolution mass spectrometry: New tool for lignomics

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Electrospray ionization with high-resolution time-of-flight mass spectrometry (ESI HR TOF MS) was evaluated as a method for polymer molecular weight (MW) distribution determination. The ESI feature of multiply charged ion formation allowed for a successful ionization of high and low MW polymer species. An assessment of MW distribution was performed using the subsequent mass spectrum deconvolution. Unlike size exclusion chromatography (SEC), which is frequently used for polymer analysis, the developed ESI HR MS method allows for determining the polymer repeating unit and the end group structure for regular polymers. The method does not require calibration standards, which is known to be the main limitation of SEC due to the lack of representative standards. Formation of multiply charged ions results in a less pronounced suppression of ionization of high MW species compared to matrix-assisted laser desorption/ionization (MALDI) MS. Therefore a more balanced polymer mass spectrum is recorded when ESI is employed.

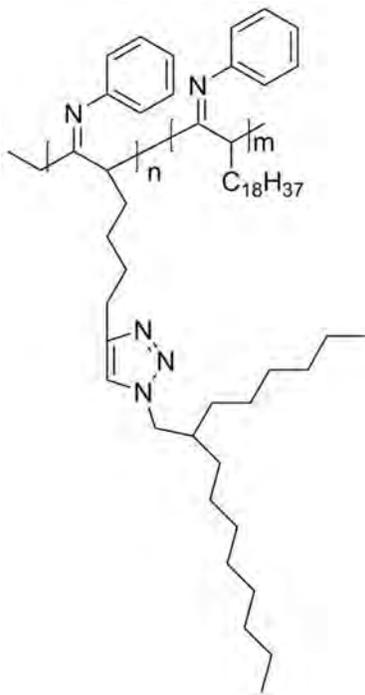
The ESI HR TOF MS method was applied to elucidate the MW of synthetic polymers, e.g., polyethylene glycol, polypropylene glycol and a copolymer of styrene oxide and maleic anhydride. We also evaluated ESI HR TOF MS as a method for lignin analysis via direct infusion targeting the simultaneous detection of low and high MW species. The effect of various ionization conditions on ion formation, including a broad range of electrolytes, was investigated using a range of mono-, di- and triarene lignin model compounds as well as intact lignin. For the first time we have shown an effective ionization of intact lignin in the positive ionization mode with formic acid as an optimal electrolyte resulting in formation of multiply charged species. The presence of multiply charged lignin ions was confirmed with ESI ion mobility HR Q-TOF MS. For both synthetic polymers and lignin, the obtained MW values were in good agreement with those determined by SEC.



POLY 81: Temperature and solvent vapor switching properties of branched carbodiimide polymers

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Polycarbodiimide are helical polymers which show chiroptical switching properties. This is mainly due to the contraction and expansion of the helical conformation in both the solid and solution state. We have studied how these play an important role in the behavior of these polymers. All switching polymers studied thus far have had straight alkane side chains. In this work, we modified the structure of the polycarbodiimides by introducing new alkyne functional group, hexynyl-5-phenylcarbodiimide. We were then able to introduce branching and steric alkyl groups to the side chains by using the click addition reaction. To change the solid-state chain-chain packing of this polymer, hexynyl-5-phenylcarbodiimide was also copolymerized with phenyloctadecylcarbodiimide and the switching properties of these copolymers were studied. Results provided the solution state reversible switching between 2 distinct conformations (state A and state B) observed at different temperatures using infrared spectroscopy (IR). Sensing of volatile organic chemicals (VOC) have also been studied using IR which allowed distinguishing certain hydrocarbons and different polar solvents. Reported here, are the results from Vibrational Circular Dichroism (VCD), Polarized Optical Microscopy (POM), reactIR ATR-FTIR spectrometer and Atomic Force Microscopy (AFM) on these modified materials.



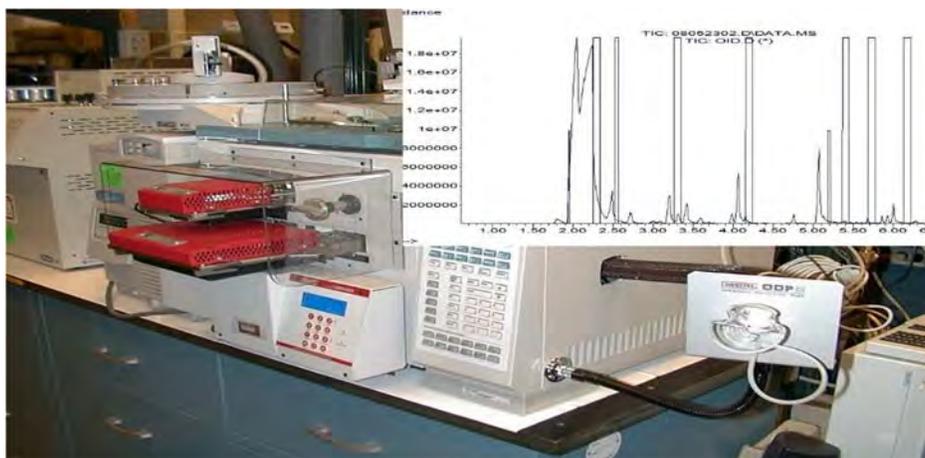
POLY 82: Route to low odor waterborne architectural coatings

James Bohling¹, jbohling@dow.com, Daoshu Lin², Jianming Xu², Jian Zou², Michelle Gallagher¹, Paul Doll¹. (1) The Dow Chemical Company, Collegeville, Pennsylvania, United States (2) The Dow Chemical Company, Shanghai, China

From the 1940's to today, the amount of Volatile Organic Compounds (VOC) found in architectural paint has decreased from over 400 g/L to often less than 50 or even 5 g/L. Environmentally and health conscious consumers, as well businesses that want to minimize "down-time", are pushing the drive for water based low VOC architectural paints with ever lower odor. Many correlate reduced VOC levels with (and expect) a parallel odor reduction though this may not be the case, especially in today's already reduced low VOC coatings.

A range of coatings materials were evaluated through the use of analytical tools such as GC-Olfactory analysis and a number of the malodorants in the headspace of a typical low VOC latex paint have been identified and categorized by potency, functional group and source. These results, combined with an understanding of the human olfactory system, have led to a better understanding of how to develop low odor/low emissions coatings.

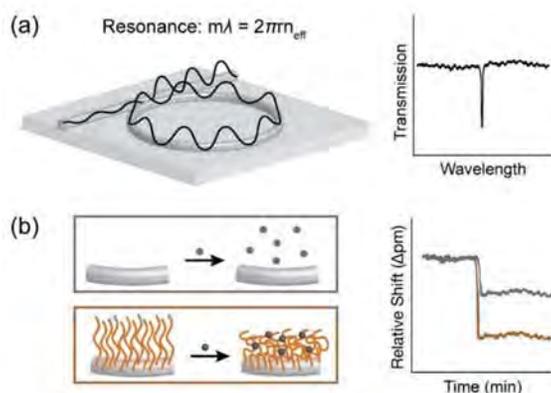
One family of impurities that can be found in some coatings materials are aromatic hydrocarbons which often have a high boiling point and low odor threshold. Aromatic hydrocarbons, such as benzene, toluene, ethyl benzene and xylene (BTEX) are of particular concern. The control of these impurities in the complex matrix of an emulsion polymer without hurting performance or stability has been studied. A variety of adsorbent materials have been evaluated and their removal efficiency has been measured. The regenerability of the adsorbent material has also been studied and will be discussed.



POLY 83: Simultaneous real-time measurement of analyte partitioning and polymer brush conformation using whispering gallery mode sensors

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Polymer thin films are commonly used to tailor material properties, transforming surfaces with sub-micron coating thicknesses. In particular, brushes grown from the surface can drastically change the properties of that surface with just a few nanometers. The unique nature of these ultrathin polymer coatings stems from the dense and extended conformations that are possible at high grafting densities. With applications in wettability, adhesion, biocompatibility, actuation, gating, and detection, many robust techniques have been used to characterize properties such as stimuli-responsive changes in thickness. However, accessible characterization of other polymer properties remains lacking. Herein, we present a new technique for simultaneous measurement of analyte partitioning and polymer brush conformation using whispering gallery mode sensors. Silicon photonic microring resonators were functionalized with several different polymers and their response to changing conditions was monitored in real time. This technique is applied to investigate the kinetics of small molecule partitioning into hydrophobic poly(methyl methacrylate) and hydrophilic poly(2-hydroxethyl methacrylate) brushes as a function of solvent type and concentration. We also investigated the behavior of poly(2-dimethylaminoethyl methacrylate) as a function of pH, with studies that yield evidence for hysteresis upon solvent cycling and vertical phase separation in the vicinity of its pKa. Thus, we demonstrate that our technique allows for accessible characterization of hydrophobic, hydrophilic, and stimuli-responsive polymer layers in the presence of complex analyte-solvent interactions.



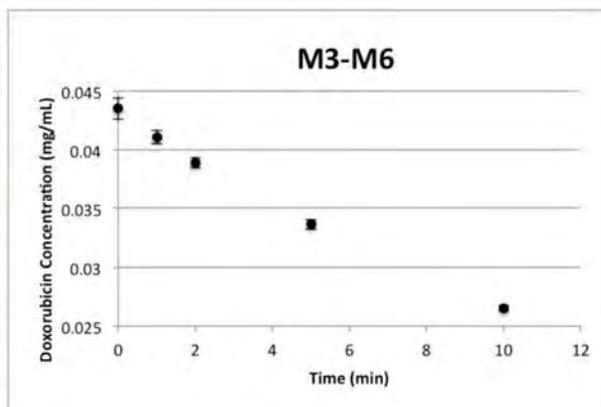
Brush-modified microring resonators are used to interrogate polymer response to complex analyte-solvent interactions. (a) A silicon photonic microring resonator couples light from the waveguide and resonant optical modes are visualized by a dip in transmission intensity. (b) Changes in the resonant mode can be used to visualize small molecule partitioning and brush conformational changes in real-time.

POLY 84: Genomic DNA functionalized 3D printed materials for drug capture

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Since the discovery of nitrogen mustard as an effective anti-cancer agent in the 1940s, and consequently, the concept of chemotherapy, researchers around the world have been actively developing new and more effective chemotherapeutic agents to better treat cancer. Traditionally, chemotherapeutic agents work by interfering with cell division. However, by virtue of their mechanism of action, healthy normal cells can also be targeted and destroyed. As a result, while chemotherapy is an effective way of managing cancer, the resulting side effects limits its use. One approach currently taken to reduce these side effects is to deliver the chemotherapy drugs directly to the tumor via transarterial chemoembolization, or other similar procedures. While this has been effective in reducing systemic toxicity, more can be done to improve this. Ideally, a device that could sequester any unreacted chemotherapy agents could be installed "downstream" of the tumor prior to them entering systemic circulation. Such drug-capture materials have yet to be realized. We report the synthesis of genomic DNA functionalized 3D printed materials that can be used to capture doxorubicin, a commonly used chemotherapy agent. The efficacy of these materials highlight the possibility of utilizing them in a device that can be deployed in the body for drug capture.

3D structuring (Membrane)



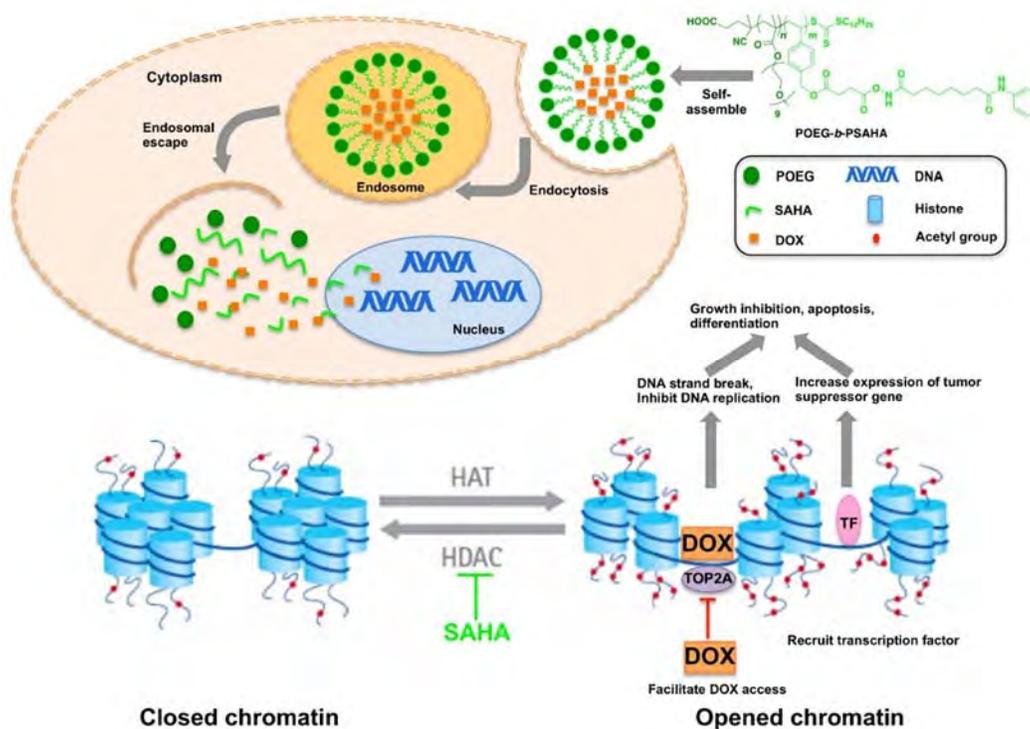
Caltech

Genomic DNA functionalized 3D printed membranes turn red on immersion in a solution of doxorubicin. Concentration of doxorubicin in PBS decreased by approximately 40% over a period of ten minutes. The difference in color of the doxorubicin solution can clearly be seen in the before and after vials.

POLY 85: Pendent HDAC inhibitor SAHA derivatized polymer as a novel prodrug micellar carrier for anticancer drugs

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Suberoylanilide hydroxamic acid (SAHA), a histone deacetylase inhibitor (HDACi) approved by FDA for the cutaneous T cell lymphoma treatment, is a promising anticancer drug for various cancers with a unique mode of action. However, it demonstrates limited clinical benefits in solid tumors as a single drug. In order to achieve enhanced and synergistic co-delivery of SAHA and Doxorubicin (DOX), a cleavable SAHA-based prodrug polymer (POEG-*b*-PSAHA), consisting of hydrophilic poly(oligo(ethylene glycol) methacrylate) (POEG) blocks and hydrophobic SAHA segments, has been developed. POEG-*b*-PSAHA was readily synthesized via a one step reversible addition-fragment transfer (RAFT) polymerization from a SAHA monomer. POEG-*b*-PSAHA prodrug polymer was able to form spherical micelles with a diameter around 60 nm, and well retained the pharmacological activity of SAHA in either inhibiting the proliferation of tumor cells or inducing histone acetylation. DOX formulated in POEG-*b*-PSAHA-based micelles showed a sustained release profile. DOX-loaded POEG-*b*-PSAHA exhibited more potent cytotoxicity towards tumor cells than free DOX and DOX loaded in a pharmacologically “inert” nanocarrier, POEG-*b*-POM. Consistently, DOX/POEG-*b*-PSAHA formulation resulted in a superior therapeutic effect *in vivo* compared to free DOX, Doxil, or DOX formulated in POEG-*b*-POM micelles. These results suggest that SAHA-based prodrug micelles may serve as a dual functional carrier for combination strategies in epigenetic-oriented anticancer therapy.

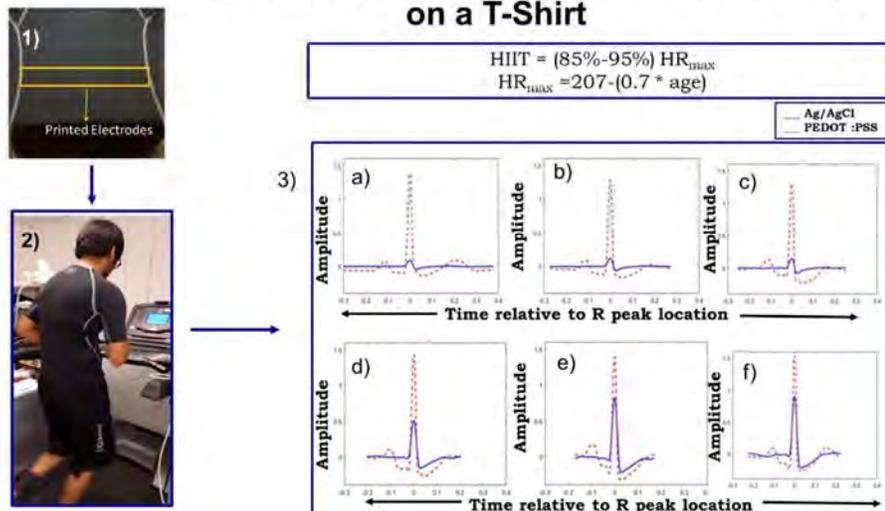


POLY 86: Conducting polymers as materials for wearable electronics and its application as biopotential electrodes

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Wearable electronics has seen a tremendous growth in the recent years. Conducting polymers such as poly (3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) known to be a conductor of both ionic and electric current has been used in applications such as organic transistors, optoelectronic devices and photovoltaic devices. In this study, commercially available PEDOT:PSS has been shown to function as organic wires with current carrying capacities approaching that of copper. Firstly, a simple circuit containing of PEDOT:PSS resistors and PEDOT:PSS wires was fabricated on polyester (PET) nonwoven textile with the measured resistance of the circuit matching with calculated values using Kirchoff's rules. Secondly, to demonstrate the practical application of the PEDOT:PSS wires, electrocardiogram (ECG) signal was measured with screen printed PEDOT:PSS wires with Ag/AgCl electrodes resulting in a signal comparable to Ag/AgCl electrodes connected with copper wires. Thirdly, electrocardiogram signal was recorded with screen printed PEDOT:PSS electrodes on nonwoven PET in dry skin condition without the use of hydrogel or adhesive around the electrode. The obtained signal showed the characteristics of ECG waveform and the amplitude of the ECG signal increased on preparing the skin with common moisturizing lotion. PEDOT:PSS wires were then combined with PEDOT:PSS electrodes and ECG signal was recorded at rest. Finally, a prototype shirt was developed with PEDOT:PSS electrodes for measuring ECG signal under exercise. The signal was recorded in dry skin conditions and showed an increase in amplitude on increase in intensity of exercise as a result of transpiration of water vapor from skin. This easy to fabricate metal free approach of fabrication of organic electrodes finds application in healthcare, gaming and military.

Continuous Monitoring of ECG signal from Electrodes Printed on a T-Shirt



POLY 87: Surface modification of silicone catheters to combat device-associated complications

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Indwelling medical devices such as catheters are a ubiquitous and indispensable component in modern medical practice. However, they can be a cause of healthcare-associated infections contributing to patient morbidity and mortality, and healthcare costs. Other surface-related complications can also arise from interactions of the catheter with biological components in the body. Silicone is commonly used for urinary catheters and peritoneal dialysis (PD) catheters but its highly hydrophobic surface attracts bacteria. A problem frequently encountered in modifying silicone with antimicrobial moieties is hydrophobic recovery caused by reorientation and migration of the hydrophobic silicone segments and the coating polymer. We have developed a microscale coating comprising silver nanoparticles–polydopamine multilayers and an outer poly(sulfobetaine methacrylate-co-acrylamide) layer that reduced in vitro colonization by uropathogens on the urinary catheter by $\geq 99\%$. It also resisted encrustation in artificial urine spiked with *Proteus mirabilis* for 45 days compared to 6 days for the commercial Dover™ silver-coated catheter. However, this strategy is not suitable for the long-term indwelling PD catheter. For PD catheter, crosslinked agarose was grafted on the catheter surface as a microscale coating. This coating reduced in vitro biofilm formation by $\geq 99\%$, and protein adsorption, cell and platelet adhesion by $\geq 90\%$. Reduction of protein adsorption and cell adhesion on the catheter surface is expected to inhibit omental wrapping which is a leading cause of PD catheter outflow failure. The surface modification processes were scaled up for full-length catheters and tested in animal models. The rationale for the selected animal models, results obtained and the challenges of conducting these trials to mimic the actual conditions of application of these catheters will be presented.

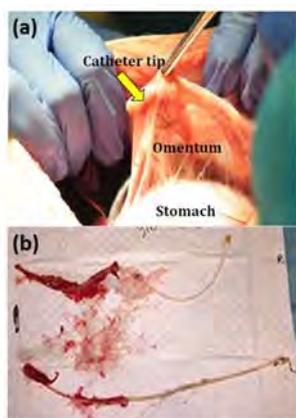
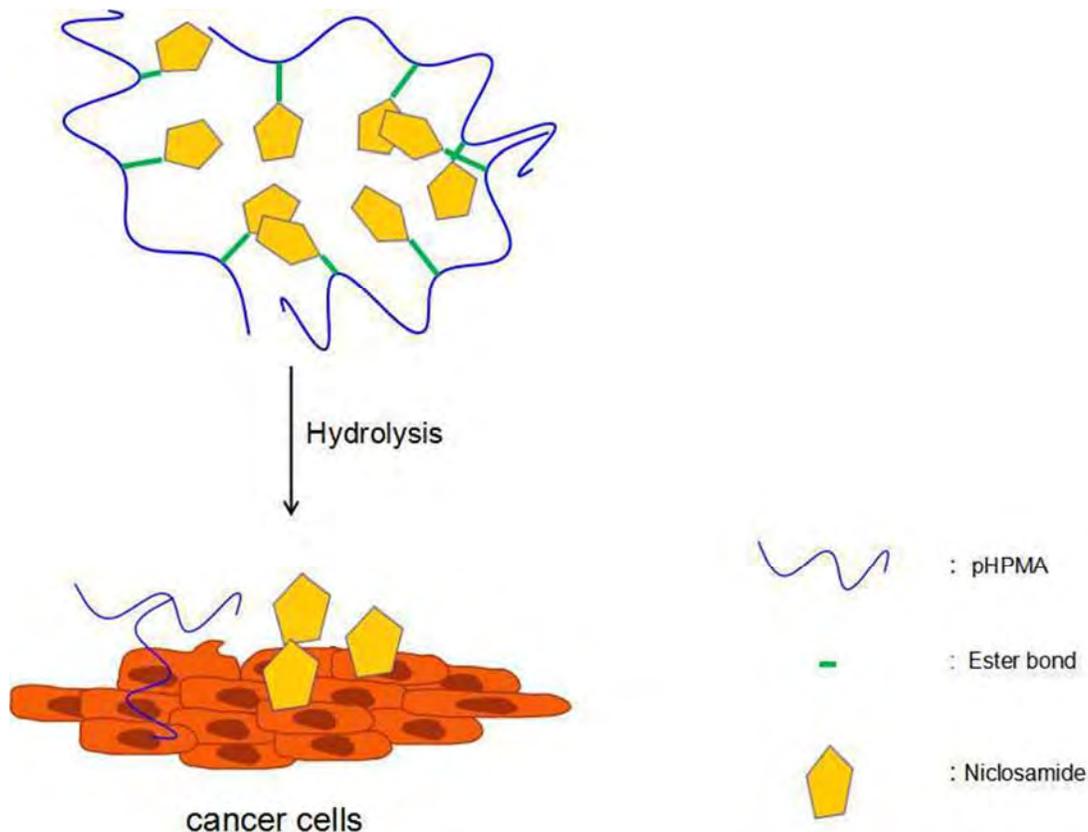


Fig. 1 (a) Omental wrapping around unmodified catheter in pig with catheter failure occurring ~20 days post implantation, (b) comparison of extent of omental wrapping on unmodified (top) and coated (bottom) catheters after 28 days.

POLY 88: Design, synthesis and characterization of HPMA copolymer-nicosamide conjugates and its anticancer effect

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The current study identified nicosamide as a potential anticancer agent. However, its application for cancer therapy was limited due to its low solubility, low bioavailability and low systemic exposure. In order to overcome these limitations, we synthesized the pHPMA-nicosamide polymer. The chemical structure was identified by FTIR and ^1H NMR spectra. The water solubility of nicosamide conjugated in the polymer was increased significantly compared with nicosamide. In this report, the drug loading efficiency and cumulative release in vitro will be described, the anti-tumor effect in vitro of the pHPMA-nicosamide polymer was presented. We conclude that pHPMA-nicosamide polymer could be a promising approach for intravenous delivery of nicosamide.

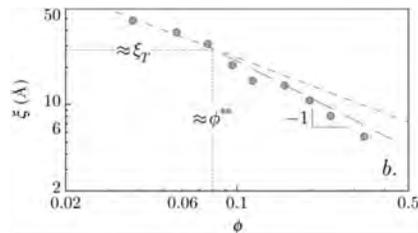


POLY 89: Small angle neutron scattering studies of gelatin as applied to liquid filled gelatin capsules

John Bachert¹, *john.bachertiii@pfizer.com*, **Edwin Chan**², *edwin.chan@nist.gov*, **Bradley Frieberg**², **Ronald L. Jones**², **Benjamin Crawshaw**¹, **E Peter Maziarz**¹, **Xiaojun M. Liu**¹. (1) Global R&D Operations, Pfizer, Richmond, Virginia, United States (2) NIST, Gaithersburg, Maryland, United States

In the prototype development and manufacture of Liquid Filled Gelatin Capsules, numerous capsule defects are encountered such as leaking, softening, body-shape deformation, among others. Encountering these defects during product development and on storage stability require additional batch manufacturing and longer development time. As a result, the potential product launch will be delayed and the cost for correcting these issues will be substantial for the company.

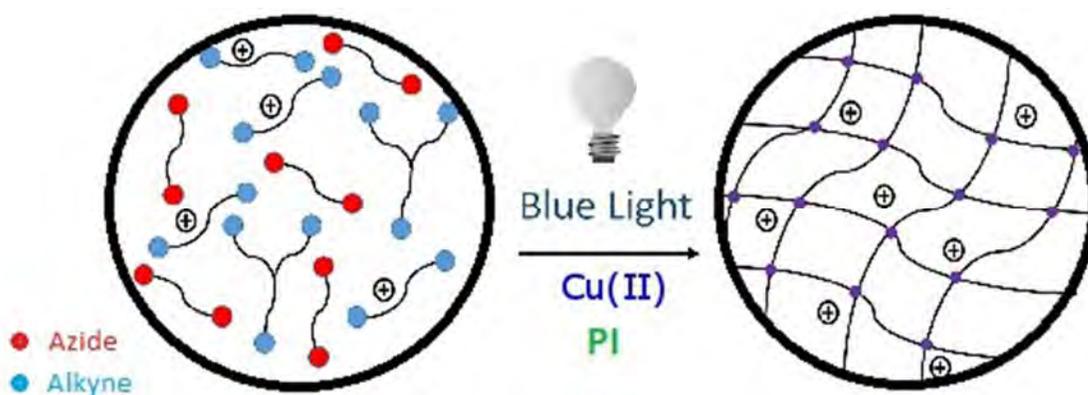
In order to better understand the cause and ultimate mitigation of these defects, we have collaborated with National Institute of Standards and Technology (NIST) to perform systematic studies of gelatin composition variations with the attendant polymer structure variations as probed by small angle neutron scattering (SANS). This will help us better understand and clarify the protein structural changes which occurs leading to the capsule defects cited above. With the knowledge of the product performance and gelatin structure on the molecular level, we can then modify the gelatin composition to favorably design capsules which are resistant to defects that have been historically observed. The detailed experimental designs, technologies used, and experimental results will be presented and discussed.



POLY 90: Photoinitiated copper(I) catalyzed azide-alkyne cycloaddition (CuAAC) reaction for conductive network synthesis

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Click chemistry is a subset of high yielding and selective organic chemical reactions that proceed under simple reaction conditions with limited or easily removable by-products. Many of these reactions afford spatial and temporal control through light activation. In particular, the photoinduced copper(I) catalyzed azide—alkyne cycloaddition (photo-CuAAC) reaction is both photo-initiated and robust enabling its utilization in many applications, including organic synthesis, surface modification, bioconjugation, medicinal chemistry, and polymer synthesis. In the work presented here, we demonstrate that photo-CuAAC chemistries offer a simple monomer crosslinking strategy for the formation of polymer ionic liquids (PILs) under blue light. These charged polymers exhibit rapid network formation (less than 30 minutes of total reaction time) under neat conditions. They can be tailored towards hydroxide exchange networks and yield conductivities >10 mS/cm at low ionic group density. We show that we can photopattern these charged networks and embed them into non-charged polymeric materials, further making these membranes attractive in photolithographic and coating applications.



POLY 91: Photopolymerizable and durable bio-based isosorbide resins for additive manufacturing

Dominika N. Lastovickova, *dominika.lastovickova@gmail.com*. *Weapons and Materials Research Directorate, U.S. Army Research Laboratory, Saylorburg, Pennsylvania, United States*

The development of thermosetting polymers from readily available and affordable sources that feature high thermal and mechanical properties is crucial towards an advancement of current resins used in stereolithography (SLA) 3D printing. Bio-based isosorbide methacrylate has been previously shown to produce thermosets with glass transition temperatures (T_g) of over 200 °C, making it an excellent candidate in an SLA production of durable materials. Building upon these results, we compared isosorbide-based (meth)acrylates to their bisphenol A analogues and commercial vinyl ester resins. Due to the aliphatic core of isosorbide, the corresponding resins displayed viscosities that were 5 and 25 times lower than that of bisphenol A (meth)acrylates and vinyl esters, respectively. Furthermore, the isosorbide resins had higher extents of cure, likely due to their lack of photo-absorbing aromatic rings that are present in the other resin systems. The bio-based isosorbide resins retained their high T_g of over 200 °C, which were significantly higher than that of other tested (meth)acrylate systems, making them very attractive for SLA 3D printing applications. Additionally, we demonstrated that photo-cure times of relatively thick specimens can be shortened from as long as 25 min to less than 30 seconds using a reflective substrate and/or addition of a thermal initiator, while simultaneously enhancing the extent of cure. Lastly, we investigated the effect of partially acrylated epoxy resins on the processing, extent of cure, morphology, thermal properties, and mechanical properties of a variety of photocured and thermally postcured thermoset polymers. Although the epoxy-containing additives increased the viscosity of the resins, significant weight fractions of these components can be used while maintaining adequate T_g and viscosities that are acceptable for additive manufacturing applications.

POLY 92: Photoenforced surface segregation for the synthesis of gradient copolymers

Alessandra Vitale, 30126201@acs.org, *Roberta M. Bongiovanni*. Department of Applied Science and Technology, Politecnico di Torino, Torino, Italy

In this work we describe a facile, single step method for generating gradient polymeric films and for independently controlling their surface and bulk properties. Photocured copolymers are obtained by photopolymerization of polyoxyethylene (meth)acrylates and a low polarity comonomer (i.e., siloxane or perfluoropolyether). These copolymers are found to have a compositional gradient, showing simultaneously the bulk properties of the main hydrogenated monomers and a strong hydrophobic character on the surface. Thanks to the spontaneous migration of the apolar chains towards the free surface and to their segregation induced by the photocrosslinking process, films having a low surface energy are produced using only a small amount (≤ 1 wt.%) of the low-surface energy comonomer (Figure 1a). The factors governing the surface segregation process, including the light intensity used for the photopolymerization reaction (Figure 1b), the film thickness and the monomer functionality, are explicitly investigated.

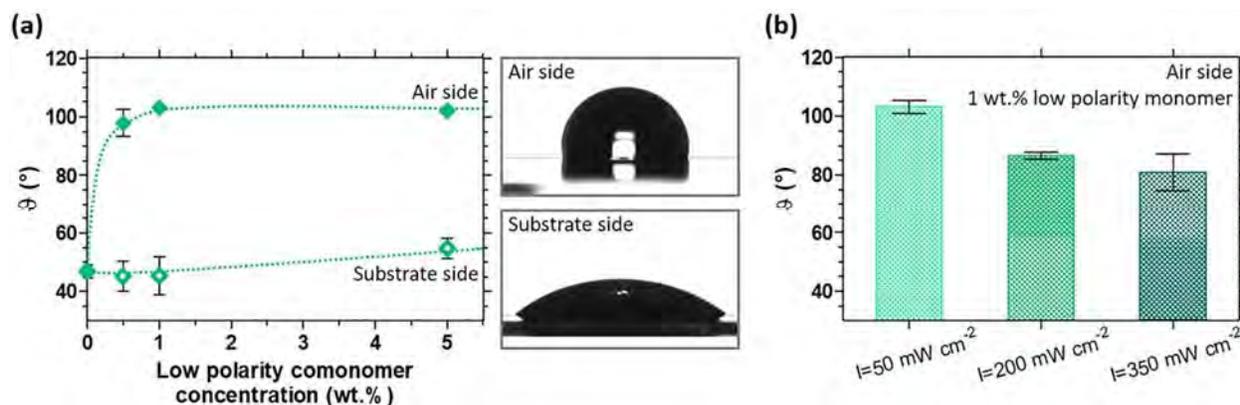
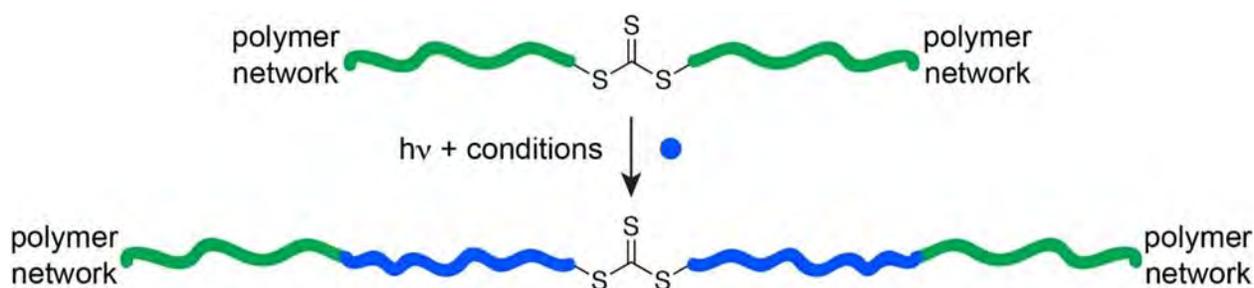


Figure 1. (a) Effect of the addition of a low polarity comonomer into an hydrogenated matrix on surface properties: static water contact angles θ measured on the air and on the substrate side of photocured copolymers. (b) Effect of incident light intensity I on static water contact angles θ of photocured copolymers containing 1 wt.% of the low polarity comonomer.

POLY 93: Living additive manufacturing with trithiocarbonate functionalized polymer networks

Jessica Lamb, Yuwei Gu, Ke Qin, **Jeremiah A. Johnson**, jaj2109@mit.edu. MIT, Massachusetts Institute of Technology, Boston, Massachusetts, United States

We have developed a strategy for the photocontrolled insertion of monomers and crosslinkers into trithiocarbonate-based polymer networks that enables the conversion of parent materials into progeny materials with diversified functionality. To make this concept practical, increasingly robust and efficient photopolymerization methods are required. Using symmetric trithiocarbonates as a testing ground, we have investigated a variety of photopolymerization conditions, using both direct photolysis and photoredox catalysis, in an effort to identify systems that can operate quickly under ambient conditions with minimal termination. This talk will describe these efforts.

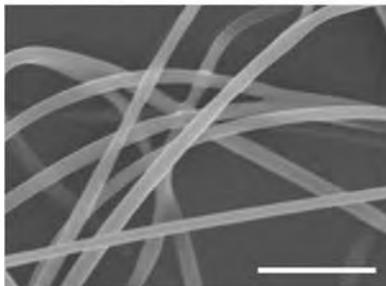


POLY 94: High performance fibers via simultaneous spinning and photopolymerization

Christopher J. Ellison, cellison@umn.edu. *Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota, United States*

Synthetic fibers have been manufactured for decades using organic solvents or heat to reduce the viscosity of pre-formed polymers and promote drawing. However, nature has engineered spiders and silkworms with benign ways of making silk fibers with high strength and toughness that do not require heat or organic solvent. Conceptually, their approach of chemically linking small functional units (i.e., proteins) into long chain molecules and solid fibrillar structures "on-demand" is fundamentally different from current synthetic fiber manufacturing methods. Drawing inspiration from nature, a method will be described that uses light to trigger a thiol-ene photopolymerization to rapidly transform reactive liquid mixtures into solid thread-like structures as they are forced out of a capillary at high speeds. Besides being manufactured without using solvents/volatile components or heat, these fibers are mechanically robust and have excellent chemical and thermal stability due to their crosslinked nature. During processing, the balance between curing kinetics, fiber flight time, and monomer mixture viscoelasticity is essential for the formation of defect free fibers. This work focuses on developing a universal operating diagram to show how the intricate interplay of gel time, flight time, and fluid relaxation time leads to the formation of uniform fibers and other fiber morphologies such as beads-on-string, fused fibers, non-uniform fibers, and droplets. This predictive capability could enable adaptation of this spinning concept to all existing fiber spinning platforms, and customization of monomer formulations to target desired properties.

Average Dia.
 $1.5 \pm 0.3 \mu\text{m}$

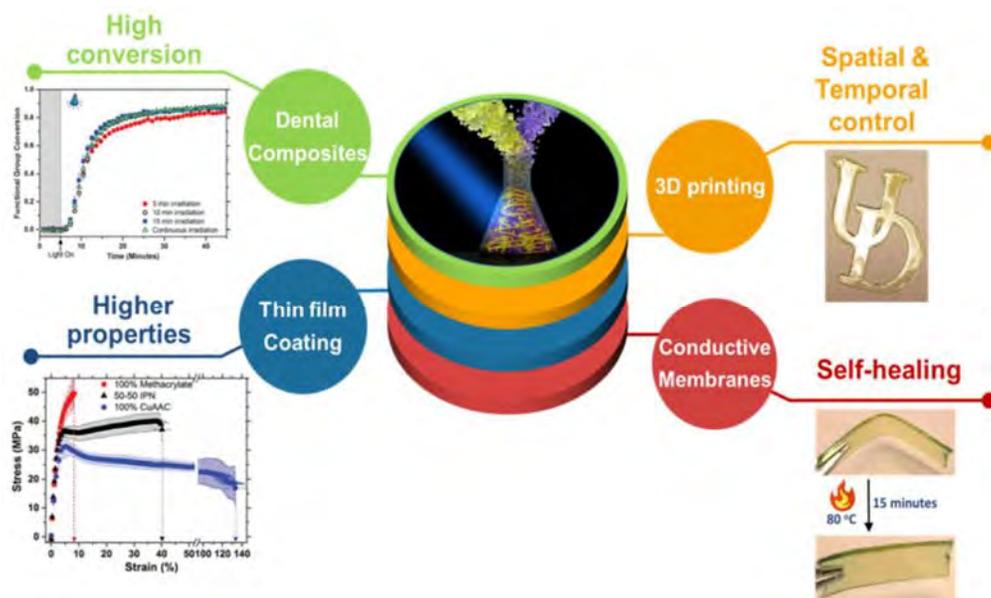


An example of crosslinked fibers made by the simultaneous spinning and photopolymerization process.

POLY 95: Photoinitiated CuAAC–methacrylate-based interpenetrating polymer networks

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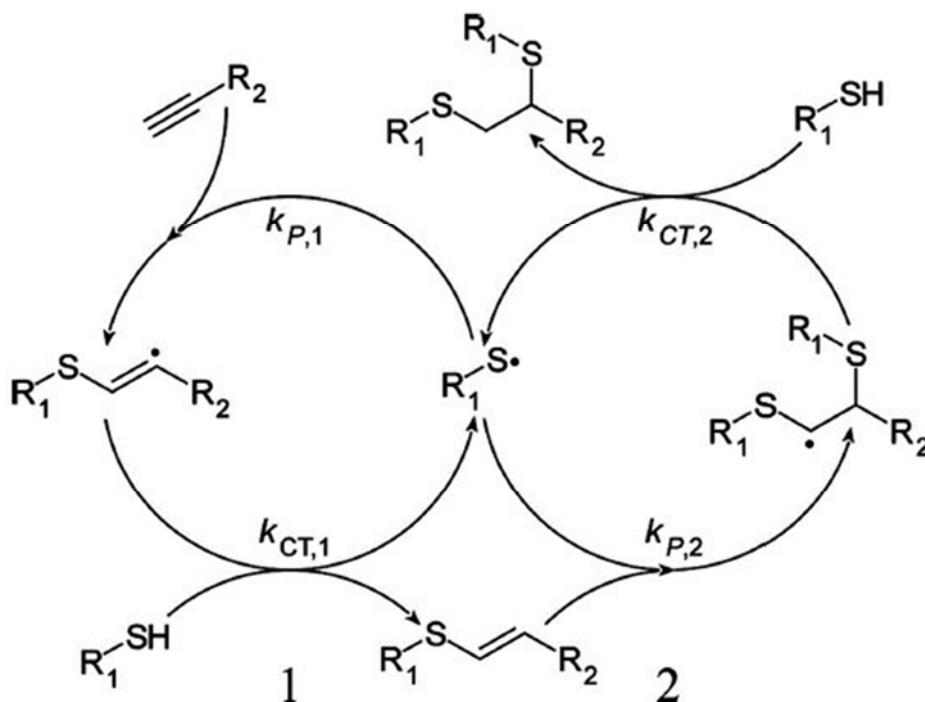
The photoinitiated copper(I)-catalyzed azide-alkyne cycloaddition (photo-CuAAC) reaction enables rapid network formation with a wide range of functional group tolerance. Reaction initiation is achieved by reducing copper(II) to copper(I) via a photogenerated radical species, affording spatio-temporal control over the CuAAC reaction. We have previously shown that a Norrish Type II photoinitiating system (photosensitizer and co-initiating tertiary amine) activated using blue-light can be utilized to produce a glassy (modulus >2GPa), transparent, and defect-free CuAAC-based material. Here we exploit the orthogonal reactivity of the CuAAC and free-radical methacrylate chemistries by simultaneously triggering these reactions to form an interpenetrating polymer network (IPN) in a solventless one-pot scheme. Interestingly, the inhibitory effect of the copper cationic species on the free-radical methacrylate polymerization results in sequential reactions, where the CuAAC step-growth polymerization precedes the methacrylate chain-growth polymerization. The resulting mechanical properties exhibit clear contributions from the two networks: the glass transition temperature and rubbery modulus of the CuAAC network are enhanced by the incorporation of the methacrylate network, and the brittleness associated with the methacrylate is toughened by the CuAAC network. Overall, this work highlights that the functional group tolerance and simplicity of the photo-CuAAC reaction in concert with free-radical chain-growth polymerization, providing an effective route to design and synthesize polymers networks for a variety of applications, including photolithographic resists, 3D printing, coatings, and medical implants.



POLY 96: Light-curable energetic binder synthesis and optimization DOE

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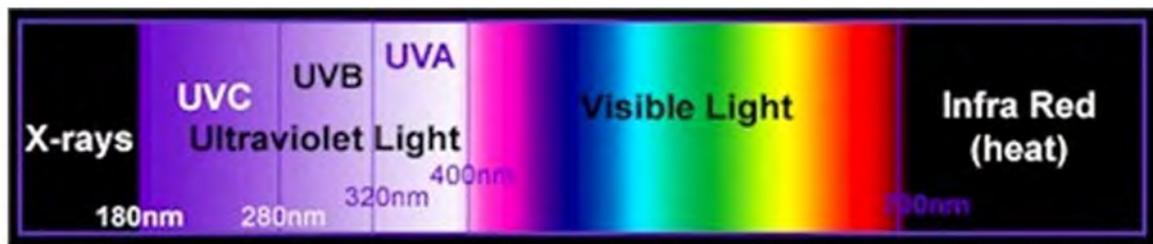
The U.S. Army has established a need for an energetic, light-curable binder system. A known energetic pre-polymer was synthetically modified producing a novel material specifically designed to meet this need. Incorporation of this novel pre-polymer into a functional binder system was investigated through an iterative design of experiments. A screening, half fractional factorial design was followed by an I-optimal augmentation to provide high model fidelity with a minimal number of experimental runs. Factors built into the design included the type and amount of curing agent, quantity of photo-initiator, and intensity of the curing light source. Several analyses were performed before, during, and after curing the binder mixtures to provide an in-depth understanding of the material. This presentation will cover the synthesis process employed to create the pre-polymer as well as neat material characteristics. Initial results from time-lapsed FTIR analyses, viscosities, and mechanical properties from the binder DOE will also be presented. While this system is elaborate and extremely robust, a proposed optimization of the binder ingredients and cure parameters will be discussed.



POLY 97: UV curing technology – benefits, chemistries and trends

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The market for ultraviolet curing technology has been growing at double-digit rates in the last decades. The main reason for such a rapid technological growth of UV curing is its unique process characteristic, which allow UV-coating to be applied on virtually any substrates, including plastic, metal, composite, wood, paper, leather, vinyl, glass and even human teeth. The original driving forces behind the commercialization of UV-technology were energy saving and freedom from solvents. These benefits are complemented by high productivity and subsequently higher profits that can be achieved with the increased line speed, just-in-time benefits and immediate “pack and ship” capabilities. Industries that take advantage of UV curing include medicine, automobiles, cosmetics (for example artificial fingernails and gel nail polish), food, science, education and art. Our presentation gives an overview on the benefits of the UV curing technology, with emphasis placed on relevant chemistries and the latest trends in the UV business.

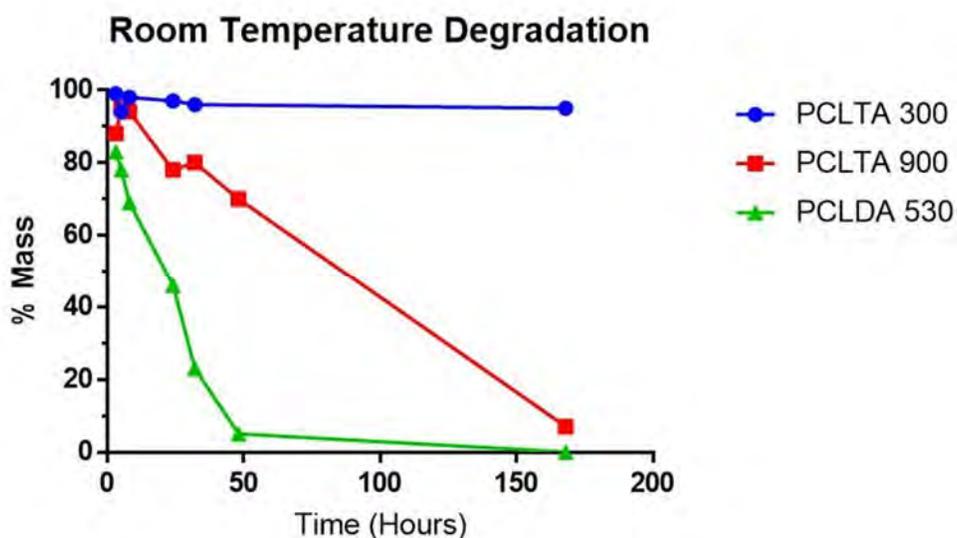


UV Band	Wavelength Range
UV-A	400nm - 320nm
UV-B	320nm - 280nm
UV-C	280nm - 180nm

POLY 98: Effect of molecular weight and degree of functionality on degradation, biocompatibility and 3-D printing of acrylated poly(caprolactone)

Brian Green, brian-green@uiowa.edu, *Jessica Thompson, Kristan Worthington, Budd Tucker, Allan Guymon. University of Iowa, Iowa City, Iowa, United States*

Poly(caprolactone) (PCL) is a degradable polyester that is commonly used in biomedical applications such as drug delivery, sutures, and tissue scaffolds. Linear PCL finds success in these applications due to its biologically favorable rheological and viscoelastic properties that allow it to be easily shaped into structures with a broad range of properties. Additionally, PCL tends to be well tolerated in the body because its slow degradation time does not lead to an increase in the local acidity which is a significant issue with other degradable polymers. One issue that limits the ability of PCL to create effective tissue scaffolds is the lack of 3-dimensional structure control inherent to patterning linear polymers. In this research, we functionalize PCL with acrylate groups that enable photopolymerization and subsequent 3D printing. Five molecular weights of PCL were functionalized with either two or three acrylate groups per prepolymer molecule to understand the effects of molecular weight and prepolymer functionality. Reaction kinetics and functional group conversion were determined using photo-DSC and real-time FTIR, respectively, to determine suitability for 3D photocuring. Additionally, the mechanical properties, degradation profile, and biocompatibility were tested to understand the effect of molecular weight and functionality in cross-linked systems. It was found that lower molecular weights and higher prepolymer functionality exhibited the fastest reaction kinetics, making them particularly well-suited for 3D printing of tissue scaffolds. Due to the cross-linked nature of these photopolymers, the mechanical properties and degradation profile follow the opposite trend of what is expected in linear polymers, where lower molecular weight and higher functionality lead to increased modulus and decreased degradation.



Accelerated degradation of cross-linked polycaprolactone polymerized from prepolymers of different molecular weights and functionalities.

POLY 99: Nanocomposite microgels formed by seeded emulsion polymerization in the presence of radially structured polyelectrolyte microgels

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Unlike spherical polymer particles, non-spherical particles have attracted a great deal of attention in a variety of applications due to their specific properties. Therefore, many types of methods for designing the morphology of polymer particles have been developed. Among these methods, seeded emulsion polymerization (SEP) is drawing attention as one of effective approaches for designing particle morphology. In general, since the particle morphology is determined by the relationship between thermodynamic and kinetics, solid particles such as polystyrene (PS) are used as seeds due to compatibility with hydrophobic monomer. Under such circumstances, we have discovered that a series of raspberry-shaped composite microgels can be synthesized by SEP of styrene using “microgel” containing hydrophilic or amphiphilic polymer chains as a seed (Figure (a)).¹ Microgels are water swelling and hydrophobic substances different from solid particles. Therefore, the relationship between the properties of the local micro-hydrogel environment such as polarity and hydrophobicity, and the function as the nucleation site of the hydrophobic PS was unknown. In this study, we focused on the polarity within the microgels and investigated the effect of the charge distribution in the core microgels on the structure of the resulting composite microgels. In the case of charged microgels in which the carboxyl-groups are located on the center of microgels, the solid nanoparticles formed only the surface of the seed microgels (Figure (b)). Conversely, the microgel cores were occupied by hydrophobic solid particles in the case of charged microgels with carboxyl groups located on surface of microgels (Figure (c)). From these results, it was concluded that styrene monomer may penetrate into the polyelectrolyte hydrogel layer. However, the resultant polystyrene nanoparticles obtained do not like combinations with polyelectrolyte hydrogels.²

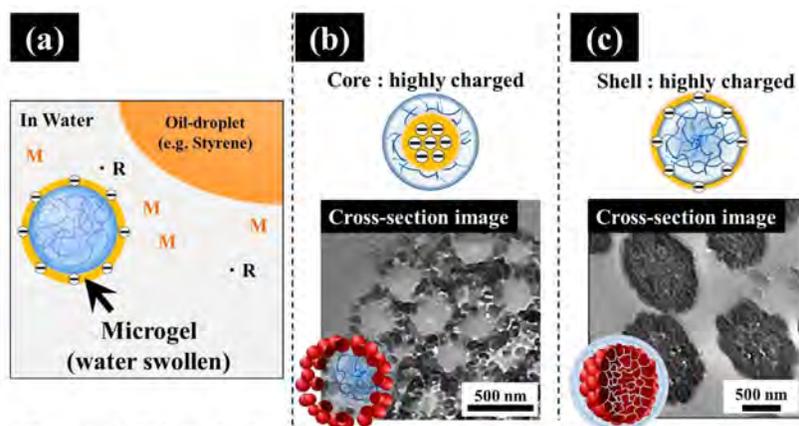
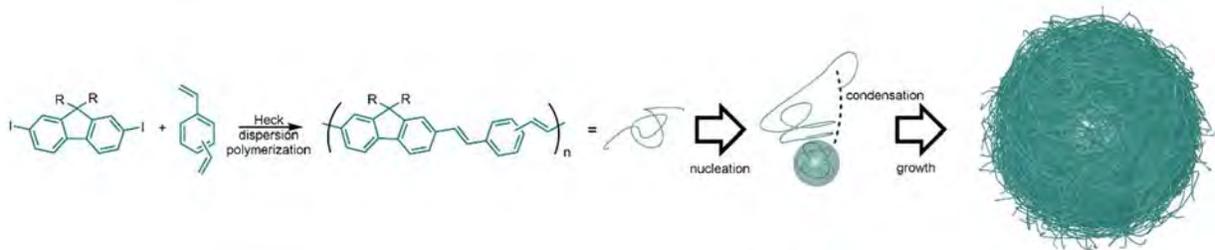


Figure. (a) Schematic diagram of our seeded emulsion polymerization system, and (b, c) results for composite microgels prepared by seeded emulsion polymerization.

POLY 100: Step-growth dispersion polymerization yielding monodisperse conjugated polymer particles for self-assembled organic lasers

Alexander J. Kuehne, kuehne@dwi.rwth-aachen.de. DWI - Leibniz Institute for Interactive Materials, Aachen, Germany, Germany

Conjugated polymers possess high fluorescence yields, optical gain, and low laser thresholds. However, to structure conjugated polymer to impose a resonator grating onto the conjugated polymer film requires nano- and microfabrication techniques. I will present a novel step-growth dispersion polymerization protocol, yielding monodisperse particles completely composed of conjugated polymer. We analyze the polymerization kinetics to understand, which the polymerization yields highly monodisperse particles with excellent tunability of the particle diameter from 200 nm up to several microns. When such a conjugated polymer particle dispersion dries, the particles self-assemble into colloidal crystals, which exhibit a photonic bandgap. The particle diameter can be adjusted so that the fluorescence and the photonic bandgap overlap, leading to optical resonators, which can be used as organic lasers. I will present different syntheses leading to a variety of conjugated polymer architectures as particles and I will present how printed colloidal crystals as well as core shell whispering-gallery mode particles can be used as self-assembled laser resonators.

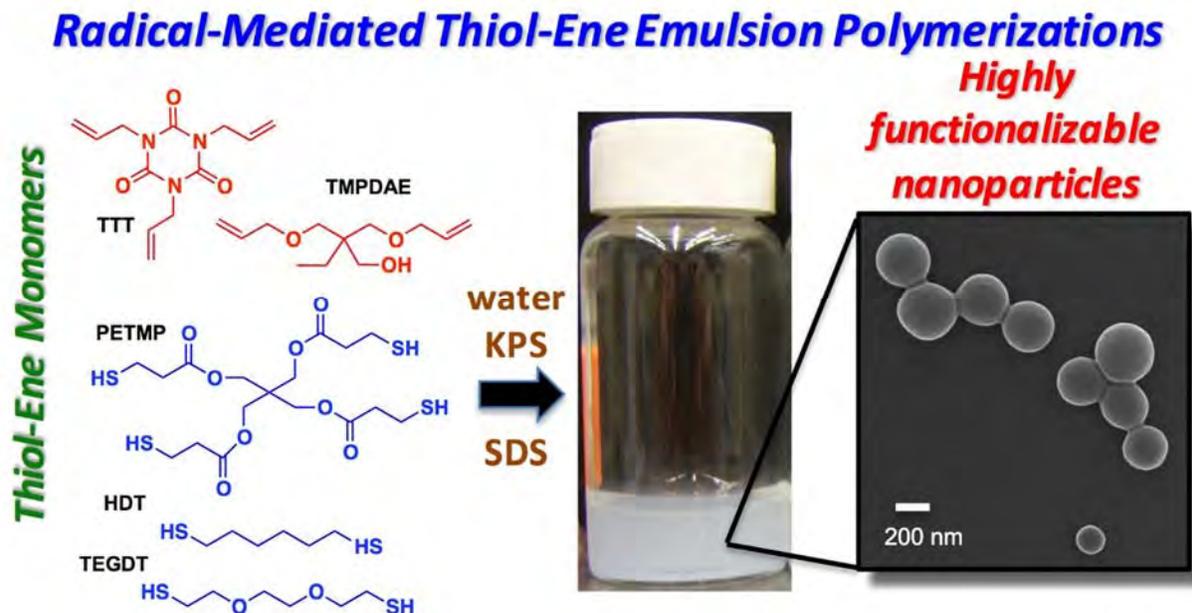


Step-growth dispersion polymerization leads to monodisperse particles fully composed of π -conjugated polymer. When self-assembled into colloidal crystals, the optical gain of the particles allows utilization of the assemblies as organic lasers.

POLY 101: Radical-mediated thiol-ene emulsion polymerizations

Meagan N. Arguien, Kyle J. Cassidy, Dana V. Chapman, Olivia Z. Durham, **Devon A. Shipp**, *dshipp@clarkson.edu*. *Chemistry Biomolecular Science, Clarkson University, Potsdam, New York, United States*

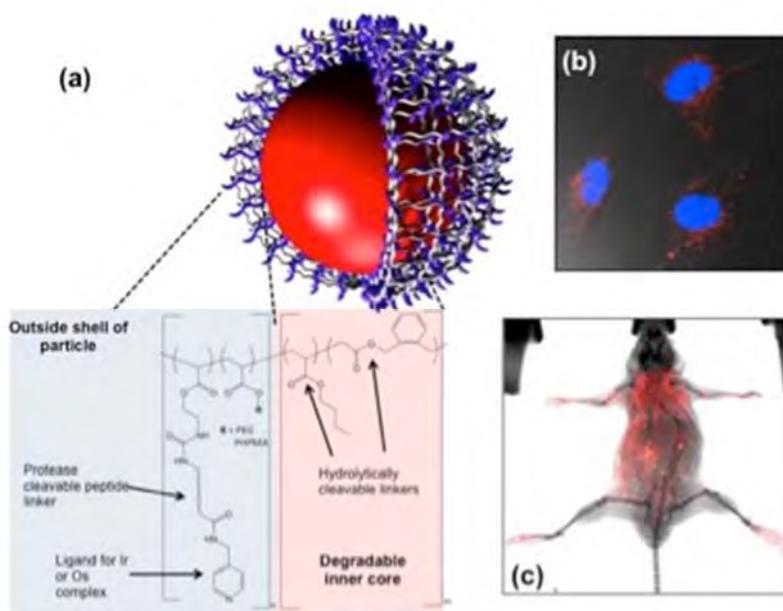
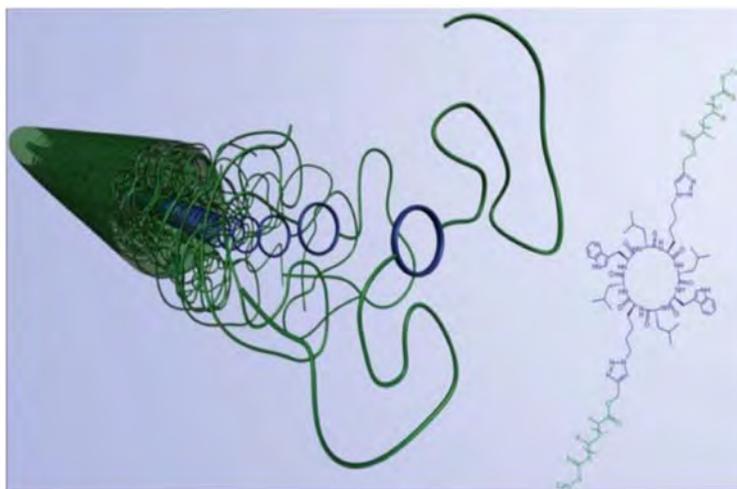
Radical-mediated thiol-ene emulsion polymerizations have recently been developed in our laboratories. Because radical-mediated thiol-ene polymerizations are step-growth polymerizations, they differ to traditional chain-growth (e.g., acrylic or styrenic) polymerizations in several ways. For example, functionalization is readily achieved through simple stoichiometric adjustments of the monomers used in the polymerization. Furthermore, several thiol-based chemistries, which are often categorized as 'click reactions', can be performed post-polymerization in order to introduce specific functionality to the particles. Additionally, the molecular weight growth mechanism in thiol-ene polymerization produces low-stress networks, resulting in narrow glass temperature transitions. Herein we will report on the synthesis and functionalization of nano- and micro-particles made using radical-mediated thiol-ene emulsion polymerizations, and will discuss the use of thiol-ene (and thiol-yne) and other 'click' chemistries for the production of highly functionalized polymer colloids.



POLY 102: Polymer nanoparticles for drug delivery by PISA RAFT polymerization

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We have designed a range of functional nanoparticles using PISA RAFT polymerization¹⁻³ to probe cell mechanisms and to be used as drug delivery vectors. The use of an amphiphilic RAFT agent in water enables the polymerisation of hydrophobic monomers and lead to the formation of nanoparticles. These particles can be precisely tuned to investigate complex cell mechanisms such as uptake pathways, as well as pharmacokinetics and biodistribution. Particles were functionalised with sugars and peptides as targeting ligands, and used for the delivery of organometallic anticancer drugs in vitro and in vivo.



POLY 103: Polymerization-induced self-assembly in aqueous media: Tutorial

Steven P. Armes, *s.p.ames@sheffield.ac.uk*. Univ of Sheffield Dept of Chem, Sheffield, United Kingdom

Polymerization-induced self-assembly (PISA) is a highly versatile, scalable platform technology for the efficient synthesis of a wide range of bespoke diblock copolymer nano-objects in various media. The basic principles of PISA are generic: a soluble precursor 'A' block is chain-extended using a second monomer that forms an insoluble 'B' block in the chosen solvent. As this second 'B' block grows in the reaction mixture, micellar nucleation occurs at some critical chain length, leading to sterically-stabilized nanoparticles. This talk will focus on RAFT aqueous dispersion polymerisation and RAFT aqueous emulsion polymerisation. In the former case, the design rules are now well understood: spheres, worms or vesicles can be obtained for many formulations, with the copolymer morphology being dictated by the relative volume fractions of the two blocks. In the latter case, only kinetically-trapped spheres are widely reported in the literature. Strategies for breaking this restrictive paradigm will be discussed and exemplified.

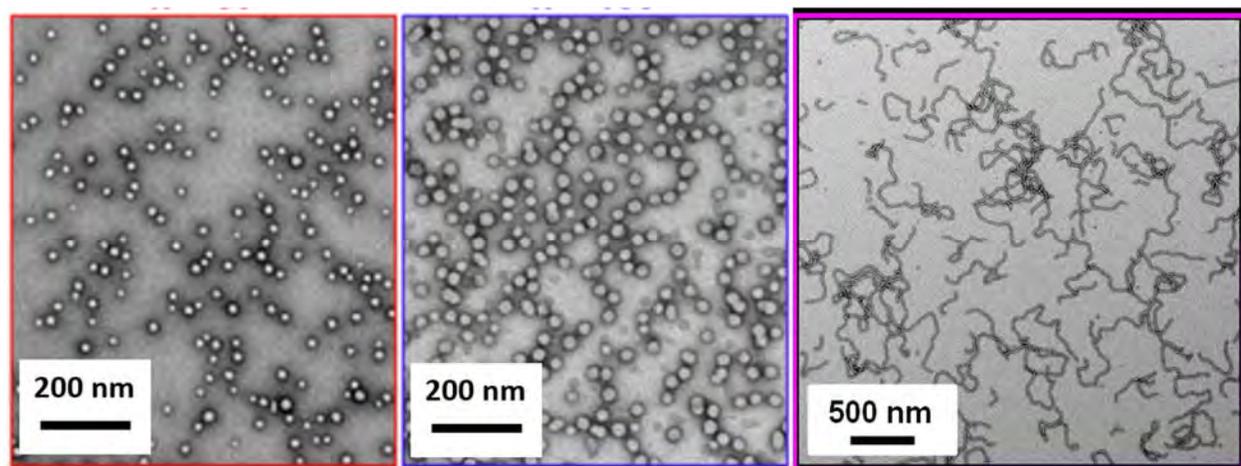
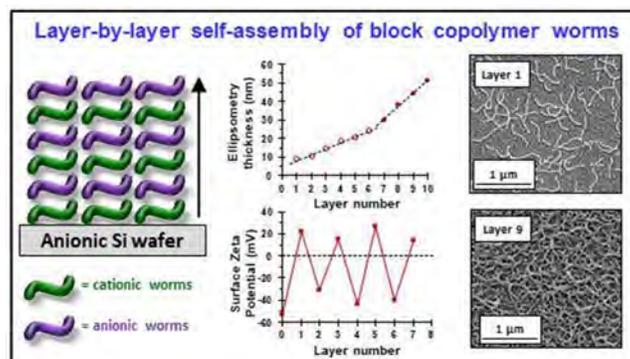


Figure 1 shows three TEM images of diblock copolymer spheres and worms obtained via RAFT aqueous emulsion polymerisation.

POLY 104: Layer-by-layer self-assembly of polyelectrolytic block copolymer worms on a planar substrate

Nicholas J. Penfold¹, *n.penfold@sheffield.ac.uk*, **Andrew Parnell**¹, **Marta Molina**¹, **Pierre Verstraete**², **Johan Smets**², **Steven P. Armes**¹. (1) University of Sheffield, Sheffield, United Kingdom (2) P&G, Strombeek-bever, Belgium

Cationic and anionic block copolymer worms are prepared by polymerization-induced self-assembly (PISA) *via* reversible addition-fragmentation chain transfer (RAFT) aqueous dispersion copolymerization of 2-hydroxypropyl methacrylate (HPMA) and glycidyl methacrylate (GlyMA), using a binary mixture of a non-ionic poly(ethylene oxide) macromolecular RAFT agent and either a cationic poly([2-(methacryloyloxy)ethyl] trimethylammonium chloride) or an anionic poly(potassium 3-sulfopropyl methacrylate) macromolecular RAFT agent. Covalent stabilization of the resulting cationic or anionic block copolymer worms was achieved *via* reaction of the epoxide groups on the GlyMA repeat units with 3-mercaptopropyltriethoxysilane. Aqueous electrophoresis studies indicated a pH-independent mean zeta potential of +40 mV and -39 mV for the cationic and anionic copolymer worms, respectively. These worms are expected to mimic the rigid rod behavior of water-soluble polyelectrolyte chains in the absence of added salt. The kinetics of adsorption of the cationic worms onto a planar anionic silicon wafer was examined at pH 5 and found to be extremely fast at 1.0% w/w copolymer concentration in the absence of added salt. Scanning electron microscopy (SEM) analysis indicated that a relatively constant worm surface coverage of 16% was achieved at 20 °C, for adsorption times ranging from just 2 seconds up to 2 minutes. Furthermore, the successive layer-by-layer deposition of cationic and anionic copolymer worms onto planar surfaces was investigated using SEM, ellipsometry and surface zeta potential measurements. These techniques confirmed that the deposition of oppositely-charged worms results in a monotonic increase in mean layer thickness, with concomitant surface charge reversal occurring on addition of each new worm layer. Unexpectedly, two distinct linear regimes were observed when plotting the mean layer thickness against the total number of adsorbed worm layers, with a steeper gradient (corresponding to thicker layers) being observed after the deposition of six worm layers.



POLY 105: One-pot synthesis of epoxy-functional amphiphilic diblock copolymer nano-objects from a single monomer via polymerisation-induced self-assembly

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Various epoxy-functional amphiphilic diblock copolymer nano-objects have been synthesized from a single monomer, glycidyl methacrylate (GlyMA), via a one-pot protocol. The diblock copolymer nano-objects were prepared via the three-step synthetic route outlined in Fig. 1. This involves: (i) hydrolysis of GlyMA to produce glycerol monomethacrylate (GMA), (ii) polymerization of GMA to form a water-soluble PGMA macro-CTA, and (iii) subsequent chain extension of this PGMA macro-CTA with further GlyMA to give PGMA-PGlyMA diblock copolymer nano-objects via polymerization-induced self-assembly (PISA). An initial aqueous emulsion of GlyMA was converted to an aqueous solution of GMA by heating to 80 °C in air for 9 h. GMA was then polymerized via reversible addition-fragmentation chain transfer (RAFT) solution polymerization in water (pH 3) at 50 °C, using a water-soluble carboxylic acid-functionalized RAFT agent, 4-(((2-carboxyethyl)thio)carbonothioyl)thio)-4-cyanopentanoic acid (CECPA). Chain extension of PGMA using GlyMA was achieved via RAFT aqueous emulsion polymerization (50 °C) to afford an aqueous dispersion of the desired diblock copolymer nano-objects. The solution pH was maintained at pH 3 in order to prevent ionization of carboxylic acid groups on the PGMA stabilizer chain-ends. Fast rates of polymerisation and high final monomer conversions (>99%) could be obtained under these relatively mild conditions when targeting 15% w/w solids. Varying the mean degree of polymerisation of the PGMA stabiliser block and the PGlyMA core-forming block resulted in well-defined nano-objects with either spherical or worm-like morphologies. These epoxy-functional nano-objects could be further derivatized and/or cross-linked directly in water, as previously reported. For example, reaction of 4-amino-TEMPO with the epoxy groups in the core-forming PGlyMA block afforded diblock copolymer nano-objects containing relatively high levels of stable free radicals, which suggests potential energy storage applications.

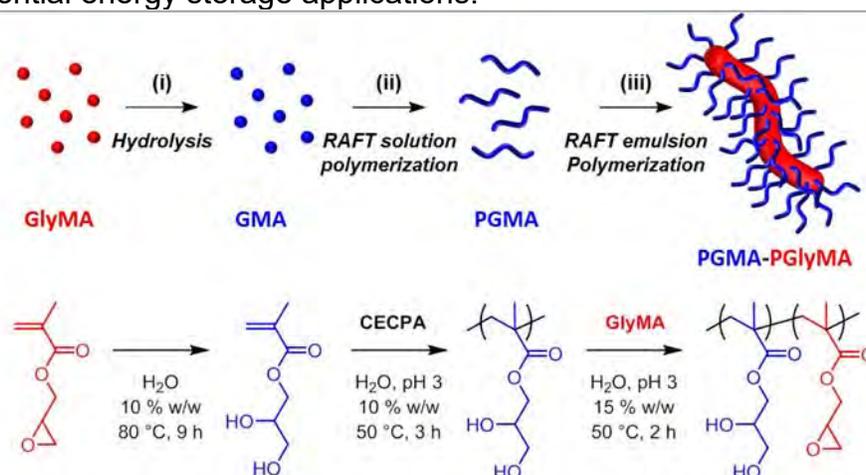


Figure 1. Schematic representation of the one-pot three-step synthesis of epoxy-functional PGMA-PGlyMA diblock copolymer nano-objects using only GlyMA.

POLY 106: Tuning the properties of worm gels prepared by RAFT dispersion polymerization in non-polar media

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Department of Chemistry, University of Sheffield, Sheffield, United Kingdom

Reversible addition-fragmentation chain transfer (RAFT) dispersion polymerization of benzyl methacrylate (BzMA) in *n*-dodecane enables the *in situ* synthesis of diblock copolymer spheres, worms or vesicles. Dispersions of diblock copolymer worms are of particular interest as they form free-standing gels at sufficiently high copolymer concentrations due to multiple inter-worm interactions. Polymerization-induced self-assembly (PISA) occurs when using a soluble poly(stearyl methacrylate)₁₁ (PSMA₁₁) macromolecular chain transfer agent (macro-CTA) to polymerize BzMA monomer to yield an insoluble second block, thus forming sterically-stabilized PSMA₁₁-PBzMA_x diblock copolymer nanoparticles in *n*-dodecane. For a PSMA₁₁-PBzMA_x worm gel, heating to 150 °C results in surface plasticization by hot solvent; this induces a worm-to-sphere morphological transition which results in degelation to form a free-flowing fluid. Utilizing a PSMA₁₁ macro-CTA containing either carboxylic acid or methyl ester chain-ends provides access to PSMA₁₁-PBzMA₆₅ worms decorated with either of these two functional groups. Moreover, the acid/ester molar ratio can be tuned by employing binary mixtures of HOOC-PSMA₁₁ and MeOOC-PSMA₁₁ macro-CTAs for the PISA syntheses. Alternatively, two separate dispersions comprising HOOC-PSMA₁₁-PBzMA₆₅ and MeOOC-PSMA₁₁-PBzMA₆₅ worms can be heated up to 150 °C followed by mixing of the resulting hot free-flowing dispersions of spheres to achieve the desired molar ratio. Subsequent cooling to ambient temperature results in the formation of hybrid worms via sphere-sphere fusion. Interestingly, worm gels with tunable storage moduli, G' , could be obtained using either method, with up to a 25-fold increase in gel strength being observed for the HOOC-PSMA₁₁-PBzMA₆₅ worms compared to the MeOOC-PSMA₁₁-PBzMA₆₅ worms. This suggests the formation of strong hydrogen bonding interactions (e.g. dimerization of carboxylic acid groups) between neighbouring worms in *n*-dodecane.

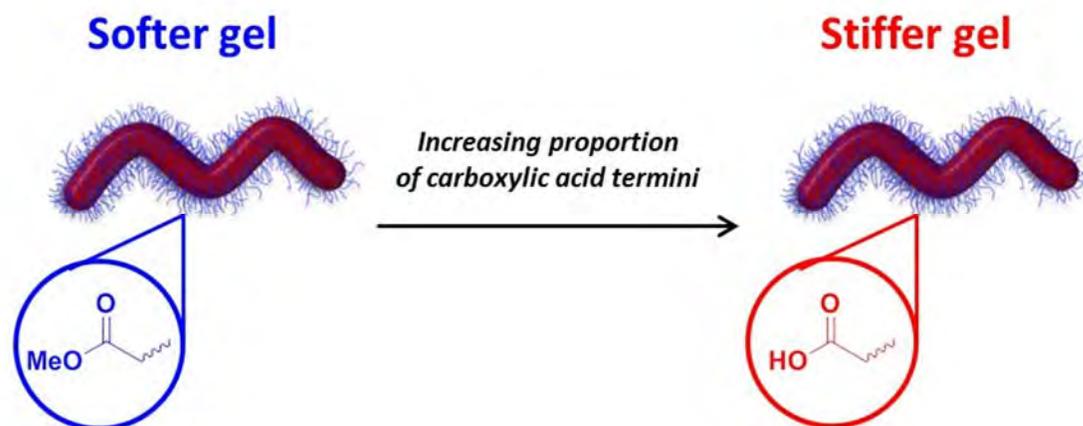
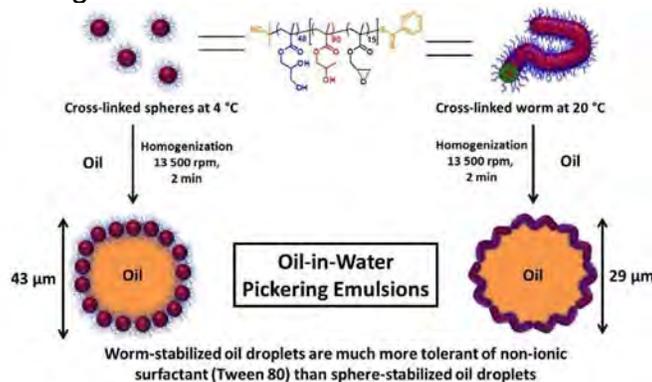


Figure 1. Schematic representation of PSMA-PBzMA worms with tunable gel properties.

POLY 107: Exploring the formation and stability of Pickering emulsions stabilised by cross-linked diblock copolymer nanoparticles

Saul J. Hunter⁴, shunter2@sheffield.ac.uk, Kate Thompson⁵, Joseph Lovett², Fiona Hatton¹, Chris Lindsay⁶, Steven P. Armes³. (1) Department of Chemistry, Sheffield, United Kingdom (2) Dainton Bldg, Univ Sheffield, Sheffield, United Kingdom (3) Univ of Sheffield Dept of Chem, Sheffield, United Kingdom (4) Chemistry, University of Sheffield, Sheffield, United Kingdom (5) School of Materials, University of Manchester, Manchester, United Kingdom (6) Syngenta, Bracknell, United Kingdom

RAFT-mediated polymerization-induced self-assembly (PISA) is used to prepare epoxy-functional PGMA₄₈-P(HPMA₉₀-*stat*-GlyMA₁₅) diblock copolymer *worms*, where GMA, HPMA and GlyMA denote glycerol monomethacrylate, 2-hydroxypropyl methacrylate and glycidyl methacrylate, respectively and the subscripts indicate the mean degrees of polymerization. The epoxy groups on the GlyMA residues can be ring-opened using 2-aminopropyltriethoxysilane (APTES) in order to cross-link the worm cores *via* a series of hydrolysis-condensation reactions. Cross-linked spheres of *precisely the same copolymer composition* can be prepared by cooling the linear worms from 20 °C to 4 °C to induce a worm-to-sphere transition, followed by APTES cross-linking conducted at 4 °C. Aqueous electrophoresis studies indicated that the resulting cross-linked worms and spheres both acquired weakly cationic surface charge at low pH as a result of protonation of APTES-derived secondary amine groups within the nanoparticle cores. The cross-linked worms and spheres were evaluated as Pickering emulsifiers for the stabilization of *n*-dodecane-in-water emulsions *via* high-shear homogenization at 20 °C and pH 8. For both nanoparticle morphologies, increasing the copolymer concentration led to a reduction in mean droplet diameter, indicating that APTES cross-linking was sufficient to allow the nanoparticles to adsorb intact at the oil/water interface, rather than undergo *in situ* dissociation to form surface-active diblock copolymer chains. Moreover, the cross-linked worms required at least a thirty-fold higher concentration of a non-ionic surfactant (Tween 80) to be displaced from the *n*-dodecane-water interface than the cross-linked spheres, indicating that the former nanoparticles are much more strongly adsorbed than the latter. In contrast, colloidosomes prepared by reacting the adsorbed cross-linked worms or spheres with an oil-soluble polymeric diisocyanate remained intact when exposed to high concentrations of this non-ionic surfactant.

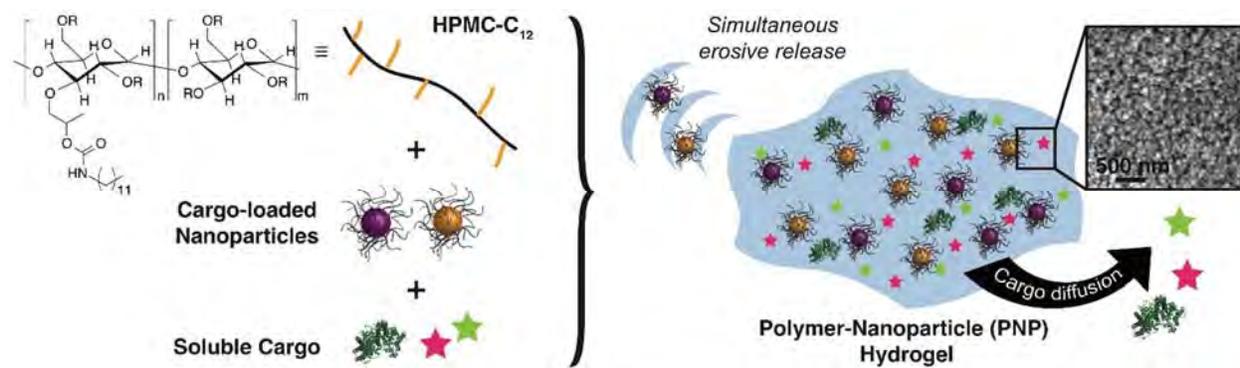


Synthetic route to Pickering emulsions prepared using either spherical or worm-like diblock copolymer nanoparticles.

POLY 108: Supramolecular biomaterials enabling innovations in drug formulation and delivery

Eric A. Appel, eappel@stanford.edu. *Materials Science & Engineering, Stanford University, Stanford, California, United States*

Supramolecular biomaterials exploit rationally-designed non-covalent interactions to enable innovative approaches to drug formulation and delivery. For example, supramolecular interactions can be used to dynamically cross-linking polymer networks, yielding shear-thinning and self-healing hydrogels that allow for minimally invasive implantation in vivo through direct injection or catheter delivery to tissues. Herein, we discuss the preparation and application of shear-thinning, injectable hydrogels driven by non-covalent interactions between modified biopolymers (BPs) and biodegradable nanoparticles (NPs) comprised of poly(ethylene glycol)-block-poly(lactic acid) (PEG-b-PLA). Owing to the non-covalent interactions between PEG-b-PLA NPs and BPs, the hydrogels flow under applied stress and their mechanical properties recover completely within seconds when the stress is relaxed, demonstrating the shear-thinning and injectable nature of the material. The hierarchical construction of these biphasic hydrogels allows for multiple therapeutic compounds to be entrapped simultaneously and delivered with identical release profiles, regardless of their chemical make-up, over user-defined timeframes ranging from days to months. These materials enable novel approaches to immunotherapy, which rely on precise release of complex mixtures of compounds, as well as long-term treatment strategies for a variety of disease targets. Overall, this presentation will demonstrate the utility of a supramolecular approach to the design of biomaterials affording unique opportunities in the formulation and controlled release of therapeutics.

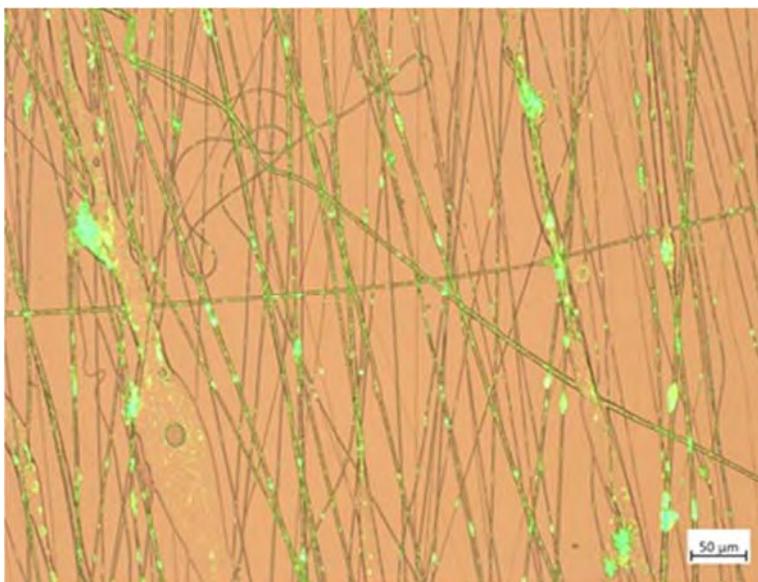


Polymer-nanoparticle (PNP) hydrogels. Dynamic, multivalent interactions between polymers and nanoparticles yield shear-thinning and rapidly self-healing hydrogels allowing for minimally invasive delivery of diverse molecular cargo. Cryogenic scanning electron microscopy of PNP gels demonstrates a homogeneous distribution of NPs within the gel structure. The modular nature of these materials allows for controlled delivery of complex mixtures of compounds with comparable release behavior, regardless of their chemical composition, over time-frames ranging from days to months.

POLY 109: Nanofiber wound-dressings for treatment of multidrug-resistant infections

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The development of bacterial resistance mechanisms to antimicrobial drugs poses a serious threat to the treatment of common infectious diseases and compromises the safety of medical procedures such as surgery. The potential absence of effective antimicrobials has spurred research in both the public and defense sectors. Here, we explore the application of two promising classes of alternative therapeutic agents, antimicrobial peptides (AMP) and lytic bacteriophages, to electrospun nanofibrous wound dressings. Nanofibrous materials are ideal candidates as they have high surface area/volume ratios and have previously demonstrated effectiveness in the delivery of active therapeutic biomolecules. Nanofiber mats, composed of different compositions containing poly(ethylene glycol), polycaprolactone and/or hydrophilic polyurethane elastomer, were optimized for encapsulation and release of active therapeutic agent. Injuries suffered in combat, particularly those which are blast-related, are susceptible to infection and therefore, it is critical that novel therapeutic materials address complications arising from multidrug-resistant (MDR) bacterial infections.



POLY 110: Engineering intelligent hydrogel nanoparticles with tunable release properties

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Lack of specificity in conventional chemotherapy leads to significant dose-limiting toxicities and requires patients to wait long periods between treatments. During this time, cancer cells can recover and develop drug resistance. To improve treatment and reduce toxicity to healthy tissues, we have developed novel, intelligent nanoscale hydrogel carriers (nanogels) for the targeted and controlled delivery of chemotherapeutic agents.

Here we show that the nanogel molecular architecture can be tailored to carry a variety of cargos with varying physicochemical properties, and release can be tuned to a desired stimuli. The nanogels are comprised of: i) hydrophilic, cationic 2-(diethylamino)ethyl-methacrylate, ii) tetraethylene-glycol-dimethacrylate crosslinker, and iii) surface-grafted poly(ethylene-glycol). Impact of nanogel hydrophobicity was investigated through systematic variation of monomer steric bulk and chain length. The physical properties of the resulting nanogels were compared using dynamic light scattering, zeta potential, titration, pyrene fluorescence, and red blood cell hemolysis to elicit the influence of polymer composition on swelling ratio, surface charge, pKa, hydrophile-hydrophobe phase transition, and erythrocyte membrane disruption capability. The delivery capacity was analyzed using multiple agents.

We demonstrated that both the grafted and hydrophobic monomer composition can be varied to enable precise control over the nanogel surface and core characteristics to enable effective, controlled delivery. Varying both chain length and steric bulk allowed for precise control over the thermodynamic response (swelling ratio), dynamic behavior (pKa, membrane disruption), and drug-polymer interaction (delivery capacity). Ultimately, we demonstrated that the tunability of our multicomponent nanogel can be exploited to enable long-circulation and effective transport of the drugs to the tumor site.

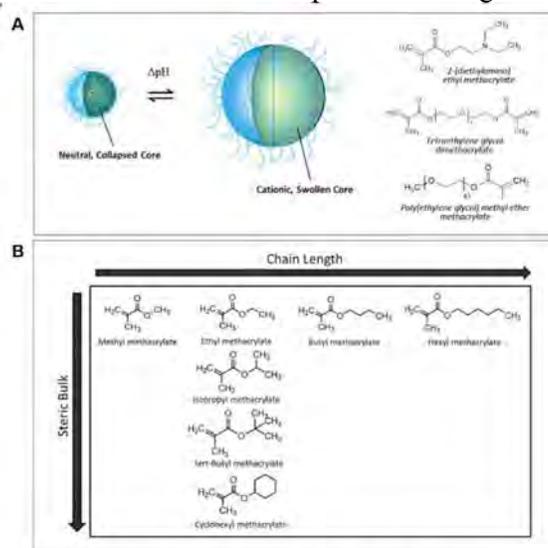


Figure 1. A) Schematic representation of the nanogels which swell in response to acidic pH environments, and structures of the cationic monomer, crosslinking agent, and polyethylene glycol surface graft. The nanogels were designed to have a neutral surface charge and collapsed core at pH 7.4, and a cationic surface charge and swollen core in acidic pH. B) The impact of nanogel copolymer composition was investigated through alkyl methacrylate monomer inclusion and systematic variation of monomer functionality and chain length.

POLY 111: Tunable amino acid based biodegradable polyesteramides for drug delivery

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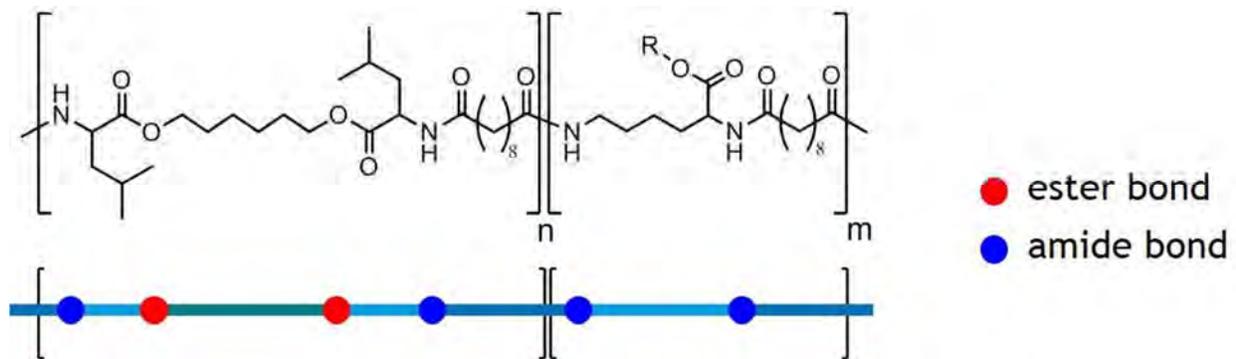
Lysine, leucine and phenylalanine bearing degradable polymers represent the next stage of evolution in degradable polymers from aliphatic polyesters, polyurethanes and polyamides. The pursuit of these changes has been to achieve better control over biocompatibility, degradation and release properties for medical and pharmaceutical applications.

Polyesteramides (PEAs) are based on α -amino acids, aliphatic dicarboxylic acids and aliphatic α - ω diols.

These PEAs allow with minimal chemical modification the tailoring of degradation to be either predominantly enzymatic, hydrolytic and with the introduction of disulphide bearing building blocks even reduction sensitive, triggered degradation. Furthermore, these polymers degrade without a significant lowering of pH an effect known to aggravate inflammation and the foreign body response. The degradation characteristics of PEAs have been optimized so as to achieve better improved in vitro – in-vivo correlation.

The biocompatibility and biodegradation of these bioinspired biomaterials for drug delivery in ocular and vascular setting will be presented as well as recent developments to develop systems for intracellular drug delivery.

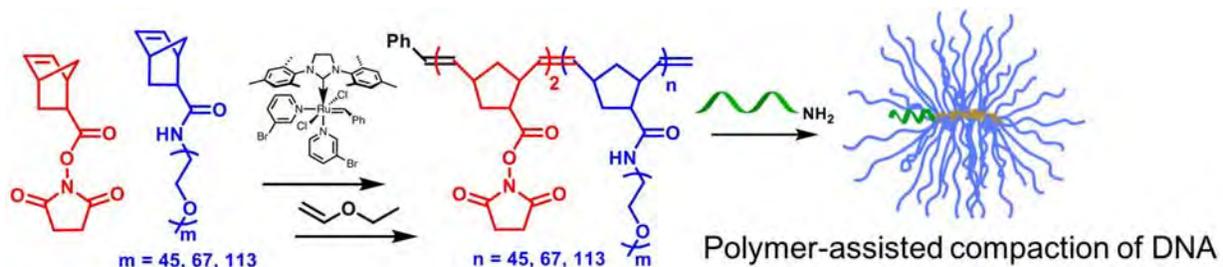
The extensive safety and biocompatibility data on these biomaterials as drug eluting matrices has lead to their first use in humans in a drug eluting stent and new applications pursued in the ocular space.



POLY 112: Brush-architected poly(ethylene glycol) for oligonucleotide delivery

Ke Zhang, *k.zhang@neu.edu*. Chemistry and Chemical Biology, Northeastern University, Boston, Massachusetts, United States

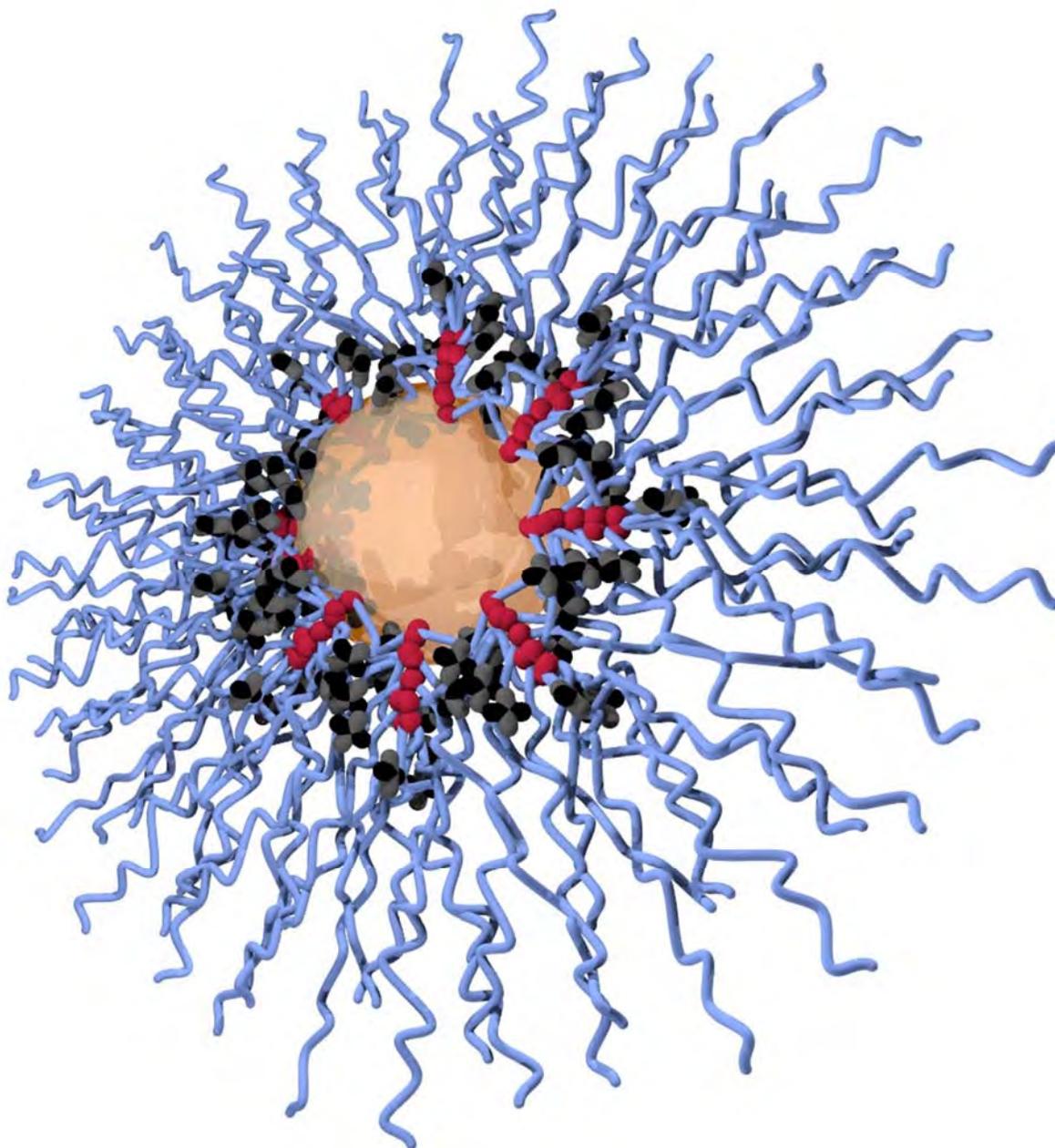
Oligonucleotides hold significant promises as a programmable therapeutic. However, with over 40 years of development, only a handful of oligonucleotide-based drugs reached the market. The lack of greater success is in part due to the poor biopharmaceutical properties of naked oligonucleotides, which require extensive chemical modification and/or the use of an (often toxic) carrier system. This presentation focuses on the development of a new strategy for transferring oligonucleotides to cells using biologically benign polymers. With this approach, oligonucleotides acquire steric selectivity towards complementary strands vs. proteins, which allows it to bypass many of the side effects associated with protein-DNA interactions.



POLY 113: Scalable ROMP polymers with drug delivery applications

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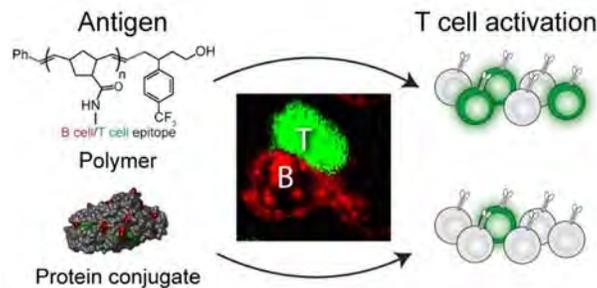
Herein, we leverage convergent ring-opening metathesis polymerization (ROMP) processes, whereby norbornene-based drug-conjugated macromonomers are polymerized, to generate various scaffolds for biomedical utility. We will present synthetic routes to the versatile and modular assembly of these materials. Additionally, we will share some recent applications of our polymers.



POLY 114: Glycopolymer probes to control immunity

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Molecular guidelines to design compounds that selectively augment immune responses (vaccines) or mitigate them (treatments for autoimmune diseases) are needed. Principles have been elusive because many immune system receptors (e.g., the B cell receptor or the lectin DC-SIGN) can transmit signals that lead to either immunity or tolerance. Synthetic conjugates can now be synthesized with exquisite control over antigen structure. We are capitalizing on these methods to elucidate how antigen scaffold structure influences immunity and tolerance. Specifically, features of an antigen's structure (e.g., valency, size, affinity, co-receptor binding) can be altered to optimize its function. By using living polymerization strategies, we are generating polymers and nanoparticles that function as antigens. This presentation will focus on our latest results in generating polymeric antigens that can elicit selective immune signaling pathways.

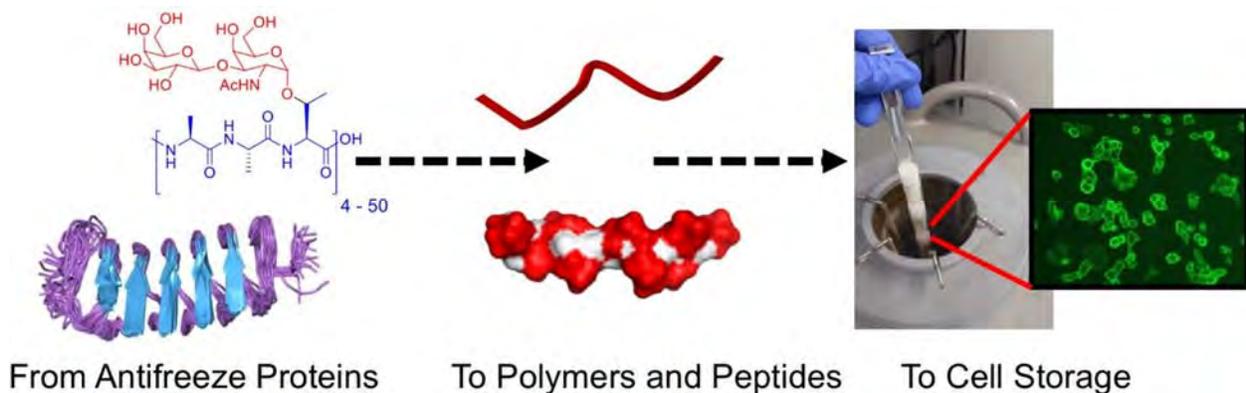


POLY 115: Antifreeze-protein inspired polymers to enable (therapeutic) cell storage and distribution

Christopher Stubbs², Ben Graham², Trisha Bailey², David Fox¹, Peter Scott³, **Matthew I. Gibson²**, *m.i.gibson@warwick.ac.uk*. (1) University of Warwick, Coventry, United Kingdom (2) Chemistry and Warwick Medical School, University of Warwick, Coventry, United Kingdom (3) Department of Chemistry, University of Warwick, Coventry, United Kingdom

All biotechnology, basic biology, drug delivery and regenerative medicine is reliant on high-quality cells and tissue. Continuous culture is not a viable option for most cells, so they must be stored as frozen stocks. Current cryoprotectants are (toxic) organic solvents which do not give 100 % recovery, many cells-types do not fully recover after freezing and the solvents are challenging to remove which can impair translational applications.

To overcome these challenges we have developed a unique class of synthetic polymers which can modulate the formation and growth of ice crystals, inspired by antifreeze (glyco)proteins, AF(G)Ps. We have previously demonstrated the use of poly(vinyl alcohol), PVA, as a (surprisingly) potent ice recrystallization inhibitor, but its underlying mode of action is still not fully understood. Here I will show progress into understanding the function of PVA, using mono-disperse oligomers of precise chain length and introduce our next generation materials. These are designed around the principle of amphipathicity, rather than precision engineering of ice-binding sites, and the concept will be demonstrated with design peptides, polymers and self-assembled entities. The application of these antifreeze-protein inspired polymers to enhance the cryopreservation of a range of challenging cell types will be shown, including adherent cell monolayers, without the need for detachment and processing.

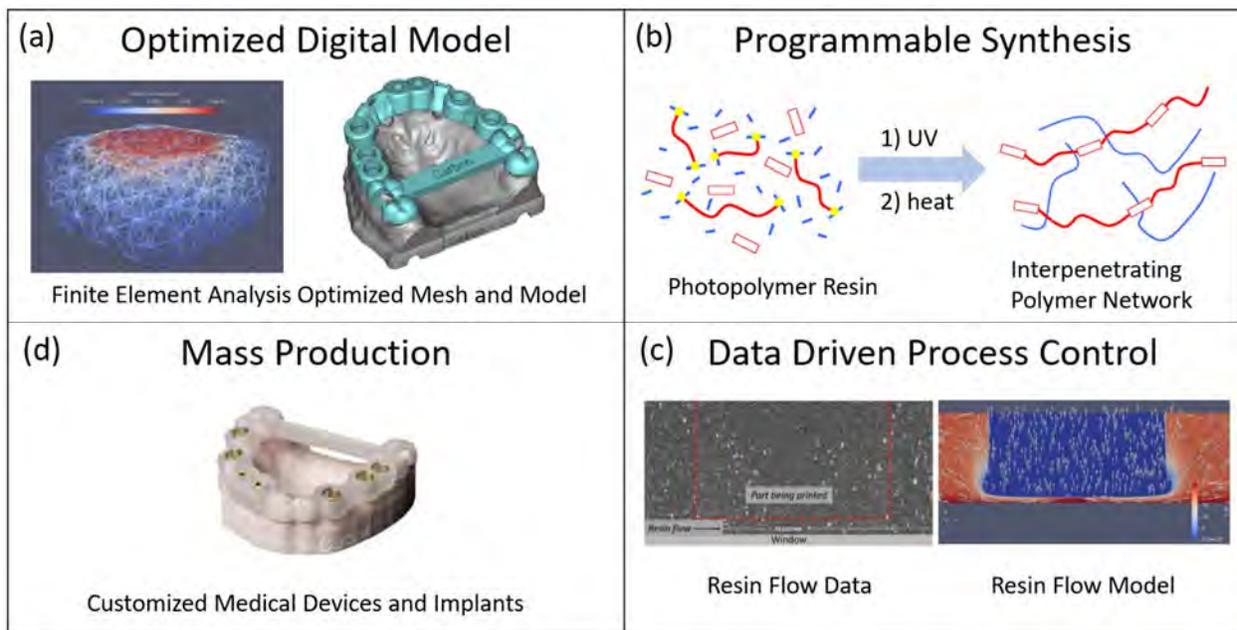


Design concept going from complex antifreeze proteins, to structurally simple polymers and peptides, and applying them to enhance the cryopreservation of cells.

POLY 116: Digital manufacturing for biomedical applications

Justin Poelma, *jpoelma@carbon3d.com*, Jason Rolland, Elle Meyer. Carbon, Inc., Sunnyvale, California, United States

Additive manufacturing (AM) is positioned to become a key technology in an age of personalized medicine and highly targeted therapies. Also known as 3D printing, AM has advantages over traditional manufacturing techniques such as injection molding and thermoforming. Advantages for medical devices and implants include mass customization, on-demand inventory, and the formation of complex geometries. However, material properties and surface quality have mostly limited AM to applications where fit and accuracy are prioritized over performance. In 2015, Carbon, Inc. published continuous liquid interface printing (CLIP) and has since introduced several classes of “dual-cure” photopolymer resins with the goal of achieving economical print speeds with production quality materials. Today, Carbon’s propriety Digital Light Synthesis (DLS) technology governs all aspects of part production from 3D model to final part. This presentation will discuss novel AM materials and processes in the context of biomedical applications.



POLY 117: Polypept(o)ides: A novel class of biocompatible polymers based on endogenous amino acids

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Polypept(o)ides have been introduced by our group as copolymers combining polypeptides with polypeptoids. They can be synthesized by sequential ring-opening polymerization (ROP) of α -amino acid-*N*-carboxyanhydrides (NCA). Whenever the polymerization itself is performed under controlled conditions, precise control over chain length, narrow molecular weight distributions (PDI<1.2) and high end group integrities can be achieved (see figure 1). Although NCA polymerization does not allow control over the primary structure of amino acids, it enables the production of polypeptides, polypeptoids and polypept(o)ide block copolymers in gram to kilogram scale and grants adjustment of chain length, architecture, solubility, functionality, and immunogenic properties. Most importantly, the incorporation of functionalities beyond nature's possibilities can be accomplished.

In most cases, we use polysarcosine (poly(*N*-methylglycine)) as a non-ionic, non-immunogenic and hydrophilic polymer ("stealth"-like) in combination with polypeptides based functional α -amino acids, since amino acids can both be easily transformed into the corresponding NCA by the Fuchs-Farthing method, provide multiple functional groups, and allow copolymerization as well as block copolymer synthesis. In addition, the initiator's valency enables control over the position of functional groups within block copolymers, introduces branching points and thus allows for the adjustment of material properties by bottom up-synthesis (see figure 1). Here we demonstrate how one can tailor polymer properties to yield functional materials for various applications ranging from tissue engineering, drug or gene delivery, diagnostic tools or functional coatings for organic or inorganic surfaces.

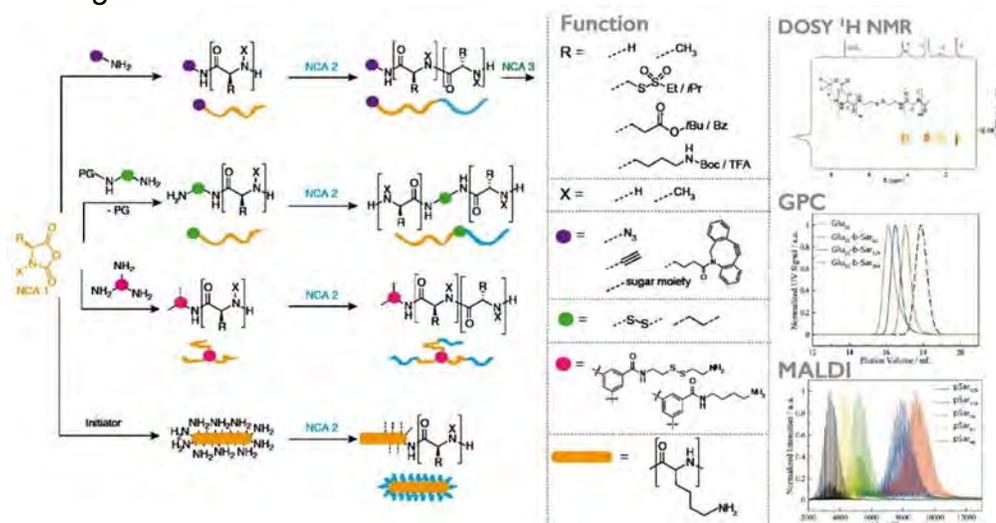


Figure 1: The synthesis of copolymers, multiblock copolymers based on monovalent initiators or functional/stimuli-responsive bi-, tri or multivalent initiators with adjustable end group functionality enables the positioning of functional groups within the polymer and representative analytical data (¹H-DOSY NMR, SEC and MALDI-ToF) for polypept(o)ides.

POLY 118: Incorporating polymer science into the high school science classroom – NSF RET at the University of Southern Mississippi

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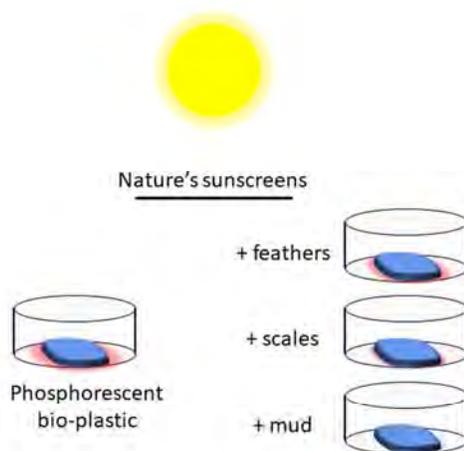
The goal of the RET in Engineering and Computer Science Site for Sustainable Polymer Engineering Research (RET) at the School of Polymers Science and Engineering at the University of Southern Mississippi (USM) is to develop long-term professional relationships between faculty researchers and local teachers by providing meaningful research experiences in relevant polymer engineering research efforts and establishing follow-up activities to extend the impact of the program throughout the school year. To that end, teachers and community college faculty engaged in a six-week summer research and training program in cutting-edge research in sustainable polymer engineering. Integrated with the research experience are education and professional development programs, including team-building workshops, short courses in polymer science, field trips to industry, presentation skills development, and workshops in developing activities for laboratory experiments based on their research. The other primary goal is to schedule interactions throughout the year to maintain engagement with teachers. These will include field trips to USM, visits of faculty and graduate students to teacher classrooms, and presentation of workshops at the Mississippi Science Teachers Association (MSTA) as well as other national conferences. By the end of their research experience, teachers develop classroom lessons and laboratory activities with content based on their own research findings. The lessons are designed to engage students in experiments with relevance to the world around them and that address national science standards. The research-based classroom activities are disseminated through the RET website and publication in *Teach Engineering*. A few research projects that were developed into successful classroom lessons will be highlighted. This presentation will highlight successful tools used to develop lessons and improve the impact of polymer research in the classroom.



POLY 119: Seeing the light in polymer science

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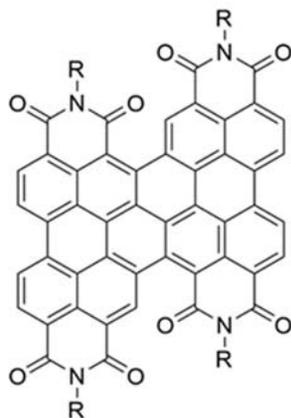
Visual cues are extremely useful in a variety of settings from signal transmission to detection schemes. Polymer scientists have devised many strategies that rely on luminescence as a means to detect specific events ranging from the presence of biologically relevant to the dissociation of bonds. One interesting way to induce bond scission is the use of mechanical force and specifically the elongational flow induced by sonochemical waves. In our project, we focused on the introduction of a variety of weak links or mechanophores capable of generating an optical cue as a result of bond scission. To impart better understanding of optical processes, a lesson plan was designed for eleventh-grade students revolved around harmful UV rays from the sun. Students will be first engaged by learning how sunscreen works and will complete a demonstration applying sunscreen to paper. Students will then explore how animals protect themselves from sunlight without sunscreen. After discussing more natural sunscreen solutions, students will try to mimic animals by combing a phosphorescent bio-plastic with scales, feathers, etc. Finally, the classroom's findings can be assessed and the results will be presented in the present contribution.



POLY 120: Incorporating polymer solar cell research in the high school classroom

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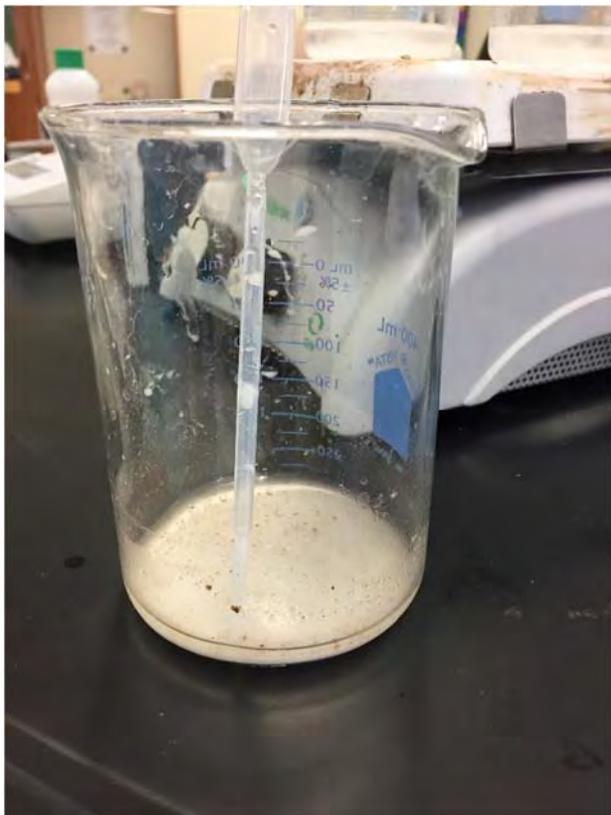
Polymer organic photovoltaic solar cells (OPVs), in contrast to conventional silicon-based solar cells, have the potential to be mass produced at much lower costs through simple methods like spin coating and inkjet printing. However, OPVs exhibit lower efficiencies than conventional cells. There have been many approaches to the improvement of these efficiencies, including new polymer synthesis, varied annealing treatments, and additives like POSS (polyhedral oligomeric silsesquioxane) that act as structuring agents in the active layer of the device. POSS molecules have a tunable organic corona, allowing for addition of photoactive groups like perylene bisimides (PBIs). Perylene bisimides have seen much use in organic electronics due to their high charge mobility, broad light absorption, and their environmental stability. Combining the nanostructuring capability of POSS with the charge transport capability of PBIs has the potential to improve the performance of polymer photovoltaics through simultaneous morphology and charge mobility improvements. The research completed was transformed into a lesson plan for students in the polymers and robotics classrooms. Students will be asked to consider U.S. energy demands and present means of energy production, and how we will meet our increasing needs in future. Focusing on solar energy, students will analyze energy output of readily available, traditional, silicon-based cells. After contemplating the need for solar power and the limitations of traditional cells, students will make their own organic solar cells using pigment dyes in blackberries, and will then visit the polymer labs at USM to see how the OPVs were developed and tested. As a culminating activity, students will write our state congressmen to ask that they continue funding research into alternative energies for Mississippi — especially as it pertains to creating better OPV technologies.



POLY 121: Polymers from potatoes: A Shark Tank challenge

Robin L. Lewis¹, *RLLewis16@gmail.com*, **Rebecca Hooper**¹, *rebeccag.hooper@gmail.com*, **Vivek Vasagar**², **Ramesh Ramakrishnan**², **Sergei I. Nazarenko**². (1) *Science, Laurel High School, Laurel, Mississippi, United States* (2) *School of polymer science and Engineering, University of Southern Mississippi, Hattiesburg, Mississippi, United States*

We present high school Advanced Placement Science students to a laboratory investigation into polymer chemistry. During this lab exploration, students first create a teacher-assisted polymer from potatoes. Students then work as chemical engineers to design, create, and test a plastic made from starch to meet specific criteria. Students will present their product to a panel with the goal to “sell” their design. This lab uses simple, non-inexpensive materials to create polymers. Over the span of five, 50 minute lab days, students create and refine their plastic, test both its quantitative and qualitative properties, conduct background research, and formulate an use and/or a plan for their product. The lesson not only leads students through the chemical engineering and design processes, it also makes them evaluate their plastic’s production costs and environmental effects. Additionally, students learn both written and oral presentation skills as they attempt to “sell” their product to a panel of investors.



POLY 122: Shape memory polymers in the classroom

Laura Ruttig², ruttigl@plainlocal.org, Kevin A. Cavicchi¹. (1) University of Akron, Akron, Ohio, United States (2) Science, GlenOak High School, Canton, Ohio, United States

Shape memory polymers have multiple applications in aerospace, medicine, and robotics. In the 5E lesson plan I will be presenting, students are able to make a shape memory polymer using only 2 ingredients: silicone-1 caulk and polyethylene glycol (widely available as MiraLAX). They will compare the shape memory polymer that they've made to the more common "oogoo" – a mixture of silicone-1 caulk and corn starch – in order to investigate how the properties of the mixture change based on the ingredients. Additional resources will also be shared to help students explore this topic further, including an extension lab activity where students create a sponge-like material from the silicone and MiraLAX. Students can then use the sponge to simulate an oil spill clean-up.



POLY 123: Classroom lesson on polymer molecular weight and dilute solution viscometry

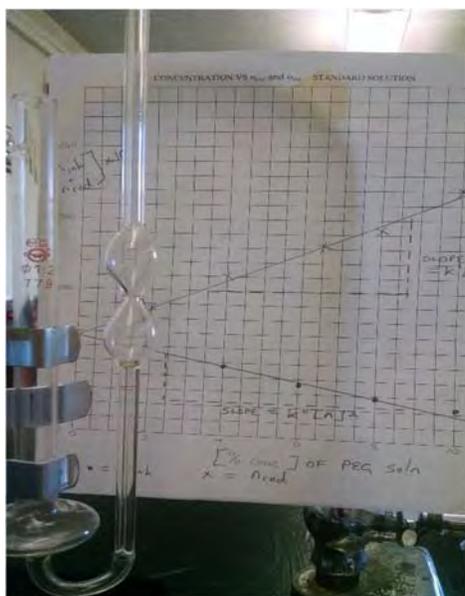
Antonello Cotugno², NCotugno@paduafranciscan.com, **Nicole Zacharia**¹. (1) Dept. of Polymer Engineering, University of Akron, Akron, Ohio, United States (2) Padua Franciscan High School, Parma, Ohio, United States

There are several methods for determining the molecular weight of a polymer. These include size exclusion chromatography (SEC) and dilute solution viscometry (DSV). In this experiment, DSV, which uses relatively simple and inexpensive equipment, is used to determine the molecular weight of different samples of the polymer polyethylene glycol (PEG). PEG has many uses: in toothpaste, as a lubricant, and as an ink solvent in printers. PEG with a molecular weight of 3350 is sold as a laxative under several different brand names.

In this lab activity, the students take on the role of a quality control engineer comparing two bargain brands of PEG 3350 laxative that are being considered as replacements for a more expensive name brand of PEG 3350. DSV is used to measure the viscosity of the name brand of PEG 3350 (the standard) at several dilutions, and the data is graphed in order to determine two constants (k' and a) called the Mark-Houwink constants. After measuring the viscosity of the bargain brands (the unknowns), their molecular weights can be determined using the Mark-Houwink constants and equation. The results are used to determine if the bargain brands of PEG 3350 are acceptable replacements for the more expensive name brand.

The lab activity also has students design and perform an experiment to determine the concentration of an unknown PEG 3350 solution.

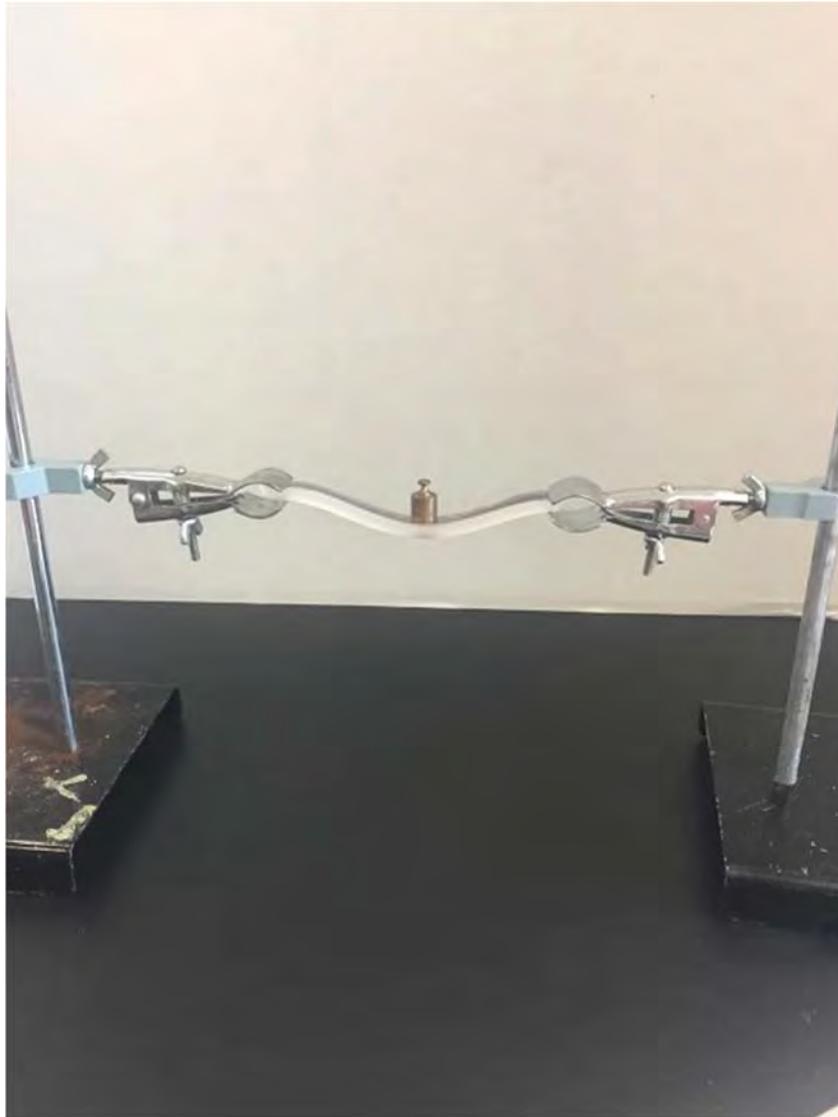
The activity is for use in an AP or first-year university level general chemistry class in order to review important concepts such as graphing and calculating the slope of a line, determining and using constants, using standards in analytical chemistry, statistics, intermolecular forces and experimental design.



POLY 124: Comparing and contrasting science and engineering through epoxy bridge building

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The lesson plan created was titled "The Chemistry of Coatings" a scientific inquiry investigation utilizing the scientific method and engineering design matrix. The lesson had a class of students broken down into two groups, one using the scientific method to examine the best ratio of epoxy to hardener to create the strongest resin bridge. The other half of the class used the engineering design matrix to decide the best epoxy hardener ratio that would be the strongest and most cost effective. This lesson was an engaging experience which gave a good example of the similarities and differences between the two processes and how using both benefit each other.



POLY 125: Effect of the size and temperature of silver nanoparticles on their conductivity

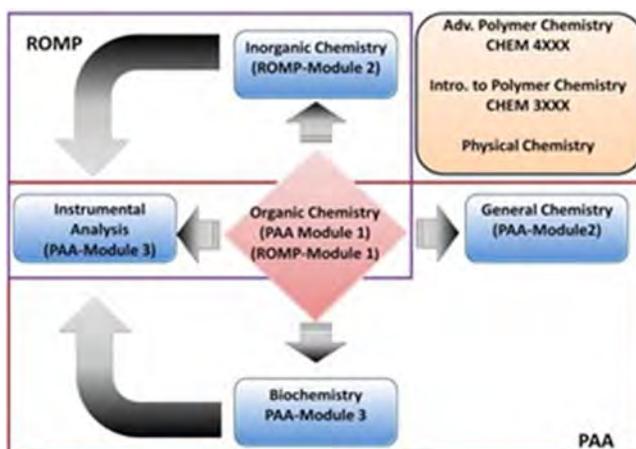
Elif Polat¹, polat@horizoncleveland.org, Alamgir Karim². (1) Horizon Science Academy, Cleveland, Ohio, United States (2) Dept of Polymer Engineering, University of Akron, Akron, Ohio, United States

The purpose of the experiment is to see how different size of Ag nanoparticles conductivity will vary under different temperature with using 2 methods. The first method was Flash Sintering. 10 nm Ag nanoparticles were exposed to 1.6 kV, 2.7 kV, and 3.8 kV. The second method that I used was thermal sintering. 10 nm, 50 nm, and 100 nm Ag nanoparticles were kept in an oven for 30 minutes, 60 minutes, and 90 minutes, under 180 Celsius, 200 Celsius, and 220 Celsius, to measure the conductivity of the samples. As a result of the experiment, the samples that were exposed to the highest pulses and the highest temperature were electrically conductive. The 10 nm Ag nanoparticles had higher conductivity than others.

POLY 126: Cross-linking the curriculum with polymer chemistry: A strategy to enhance polymer chemistry instruction in ACS-Certified Programs

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The recent changes to the 2015 American Chemical Society (ACS) guidelines for ACS-Certified bachelor's degrees dictates that adequate instruction on polymers, macromolecules, and large aggregates be provided. In an effort to satisfy this mandate at Armstrong State University, Savannah GA (ASU), the chemistry and biochemistry faculty began integrating polymer concepts into the laboratories of several courses with a central theme of "cross-linking" the curriculum, whereby materials prepared in one course would be utilized in other courses. Some previous, narrowly focused, laboratory exercises were replaced with polymer-based experiments that also investigate concepts relevant to the primary purpose of the course. These experiments involved Poly(aspartic acid) (PAA) and Ring-Opening Metathesis polymerization (ROMP). Stand-alone polymer courses, experiments, and capstone projects were implemented to provide a deeper understanding of polymer chemistry, including excursions into contemporary literature. A schematic depiction of the flow of materials are shown in the graphical abstract. The ACS polymer chemistry inclusion mandate will affect chemistry departments nationwide. Our proposed curriculum changes may serve as a model for other institutions with comparable chemistry departments to ASU to help satisfy the polymer chemistry component for ACS-certification. Herein, we provide a summary of our strategy and our efforts to date.



POLY 127: Preparing students for an industrial environment in a master's-level graduate internship program in polymer science

David R. Tyler¹, dtyler@uoregon.edu, Stacey E. York². (1) Chemistry and Biochemistry, University of Oregon, Eugene, Oregon, United States (2) University of Oregon, Eugene, Oregon, United States

The Master's Industrial Internship Program at the University of Oregon has been running successfully for nearly 20 years. The program offers an M.S. in Chemistry with a focus in Polymer Science. The polymer program's curriculum focuses on polymer synthesis, thermomechanical analysis and processing of materials. Hands-on labs are structured in a manner that recreates industrial environments, allowing students to practice relevant technical and soft skills. Students typically have undergraduate degrees in chemistry or chemical engineering and are able to complete their degree requirements within 12-15 months. The program starts with a week of professional development followed by an intensive 16 credits of coursework in the summer. Following the successful completion of their summer coursework, students interview with corporate partners and national labs to gain 9-month internships. Within 3-months of gaining their M.S. degrees, 90% of students are employed. In this talk, best practices learned over 20 years will be described.



Students in the graduate internship program in polymer science

POLY 128: INTERFACE: The National Science Foundation Graduate Research Traineeship Program at The University of Southern Mississippi

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The vision of the *NRT: Training Next-Generation Scientists with Experimental, Theoretical, and Computational Competencies for Complex Interfaces (INTERFACE)* at the School of Polymer Science and Engineering at the University of Southern Mississippi is to train the next generation of materials researchers through an interdisciplinary and integrated research, education, and professional development program designed to equip graduates with the theoretical, computational, and experimental skills needed to address the grand challenges of the 21st century. Through NRT, graduate students are immersed in a new model of graduate training that combines theory with experiment, employs a common vocabulary, and develops expertise in both computational and experimental techniques. Our goal is to provide students with the skills needed in industrial, academic, and national labs to drive competitiveness and enable advanced materials innovation. To that end, graduate students in Departments of Biochemistry, Chemistry, Physics and Polymer Science and Engineering participate in a program which incorporates computer modeling and simulation, experimental and computational methodologies for complex interfaces, interdisciplinary workshops, oral and written communication skills, proposal development, and career path experiences. This presentation will highlight successful computational initiatives, professional skills workshops, and student internship experiences.



THE UNIVERSITY OF
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INTERFACE

A National Science Foundation Research Traineeship



POLY 129: Expanding horizons: National Science Foundation NRT graduate student experiences at the University of Southern Mississippi

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The University of Southern Mississippi-National Science Foundation Research Traineeship (USM-NRT) provides training at the *INTERFACE* of experimental, theoretical, and computational competencies for the next generation of scientists. Two participants in NRT: INTERFACE will provide personal insight toward the experiences that have helped to develop these integrated scientific and communication skills. The USM NRT program has *expanded horizons* by affording personal and professional growth opportunities that otherwise are not emphasized in traditional STEM graduate programs. Two distinct internship experiences, one abroad at Aston University in Birmingham, England and the other at Johnson and Johnson Vision in Jacksonville, Florida, will be discussed, with reference to advancing graduate research, developing new collaborations, and exploring alternative careers. This presentation will also highlight collaborative endeavors that have resulted from visiting seminar speakers, computational workshops, and internal seed proposal competitions.



POLY 130: Reflections and experiences of current and past NSF NRT Interface Trainees at the University of Southern Mississippi

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The University of Southern Mississippi's National Science Foundation Research Traineeship (NRT) encompasses the development of next-generation STEM graduate training through interdisciplinary data-driven research, outreach, educational opportunities, and professional development skills. The mission of NRT seeks to equip graduate students with a training in computational methodologies, effective communication skills, creative problem solving, team-building, among many others. This presentation will highlight a few recent experiences of NRT graduate trainees in professional development activities ranging from boot camps to internship experiences at other academic institutions and discuss how the beneficial skills learned from NRT played a role. Lastly, outreach and engagement activities performed by NRT trainees at local high schools in Mississippi will be discussed.



POLY 131: Soft materials for life sciences: A National Science Foundation Graduate Traineeship Program

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The NRT Program in Soft Materials for Life Sciences (SMLS) engages faculty and students at the University of Massachusetts - Amherst in exploring a new graduate education model for training students in T-shaped skills--capability for breadth across professional skill areas and other technical areas, and depth in one area of specialization--that will serve master's and doctoral students well in the science and engineering workforce after graduation. The program aims to directly impact 74 students in the disciplines of polymer science and engineering, immunology, food science, and several engineering fields through a multi-year training program. The research theme of applying polymeric materials to technical challenges in the life sciences such as drug delivery methods and personalized health monitoring devices enables an excellent ground for meaningful interdisciplinary collaboration. The educational program features an intensive "Year Two Experience" that combines an interdisciplinary course in technical topics related to the research theme, professional development workshops and training activities, and interdisciplinary lab training modules. Students also take a graduate course in scientific and engineering management, attend a seminar series featuring invited speakers and NRT trainee presentations, and take an elective associated with the program.

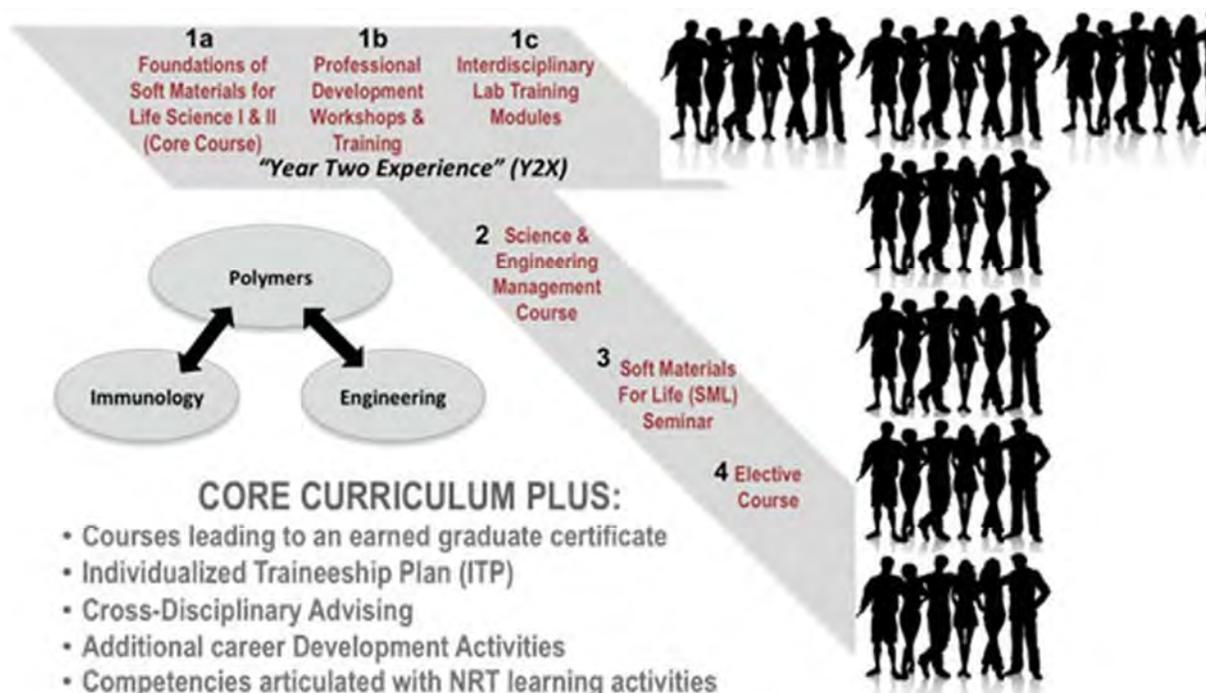


Figure 1. Overview of Soft Materials for Life Sciences NRT Program Theme and Key Programmatic Elements

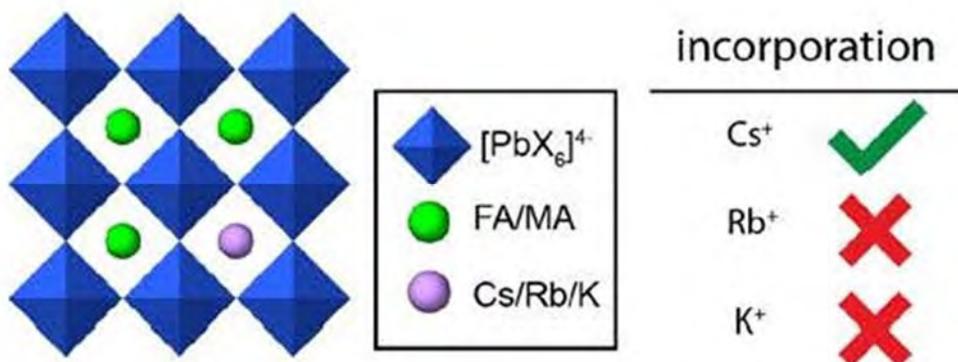
POLY 132: Solid-state NMR approaches to inorganic materials: From lead-halide perovskites to gallium phosphide

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We will discuss new approaches to studying highly technologically relevant materials that have so far been difficult to address using high-resolution multi-dimensional NMR methods.

One example will be the study of hybrid (organic-inorganic) multi-cation lead halide perovskites which hold promise for a new generation of easily processible solar cells. We show how low temperature (~100K) NMR allows us to obtain the first quantitative, cation-specific data on cation reorientation dynamics in hybrid mixed-cation formamidinium/methylammonium lead halide perovskites. We use ^{14}N , ^2H , ^{13}C and ^1H solid-state MAS NMR to elucidate cation reorientation dynamics, microscopic phase composition, and the MA/FA ratio, in $(\text{MA})_x(\text{FA})_{1-x}\text{PbI}_3$ between 100 and 330 K. The reorientation rates correlate in a striking manner with the carrier lifetimes previously reported for these materials and provide evidence of the polaronic nature of charge carriers in PV perovskites. The methods also allow us to obtain rapidly spectra with high sensitivity to elucidate the atomic level nature of Cs and Rb incorporation into the perovskite lattice of formamidinium-based materials. We use ^{133}Cs , ^{87}Rb , ^{39}K , ^{13}C and ^{14}N solid-state MAS NMR to probe microscopic composition of Cs-, Rb-, K-, MA- and FA-containing phases in double-, triple- and quadruple-cation lead halides in bulk and in a thin film. Contrary to previous reports, we find no proof of Rb or K incorporation into the 3D perovskite lattice in these systems.

Another example will address the challenge of how to obtain enhanced sensitivity in bulk inorganic materials, which are often difficult to study because of prohibitively long T_1 s. We will describe an approach to significantly increase NMR sensitivity in bulk oxides, and we demonstrate it with examples of gallium phosphide.



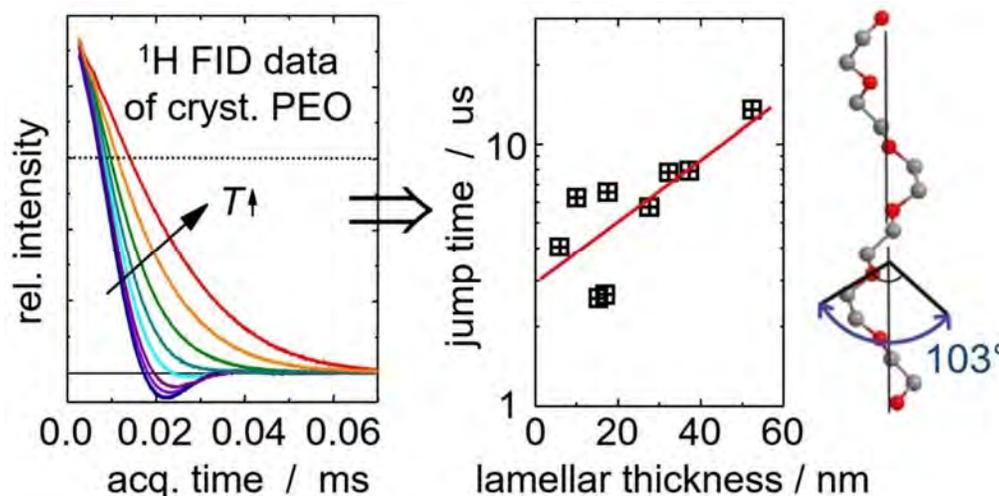
POLY 133: Relations between amorphous and crystalline chain motions and the morphology of semicrystalline polymers

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In recent years, more and more evidence has been accumulated that calls into question the popular Lauritzen-Hoffman model explaining the formation of crystalline lamellae in semi-crystalline polymers. The still open question is why a specific lamellar thickness is chosen during crystallization of long entangled linear polymers. Here, we address this question by considering explicitly entanglement constraints as well as the as yet underestimated potential influence of intra-crystalline chain mobility [1].

We compare the crystallization of poly(ethylene oxide) (PEO) and poly(ϵ -caprolactone) (PCL) as representative cases of crystal-mobile [2] and crystal-fixed [3] polymers, resp. An intermediate case is represented by poly(oxymethylene) (POM). We study the morphology of the samples in terms of the thicknesses of the crystalline and amorphous domains as determined by small-angle X-ray scattering, including the newly developed option to also extract the width of the thickness distribution [4]. We find that, contrary to conventional wisdom, in PEO it is the amorphous rather than the crystalline thickness that is well-defined. NMR investigations of the timescale of intra-crystalline chain motion in PEO demonstrate that the lamellae re-organize already on the timescale of the attachments of stems.

The morphology further depends on the crystallization conditions, where we distinguish slow and fast crystal growth as compared to the terminal relaxation time of the chains in the melt, again with qualitative differences between PEO and PCL. Finally, we use modern NMR techniques to assess the entangled structure [5] within the amorphous domains, and present correlations with the different morphologies.



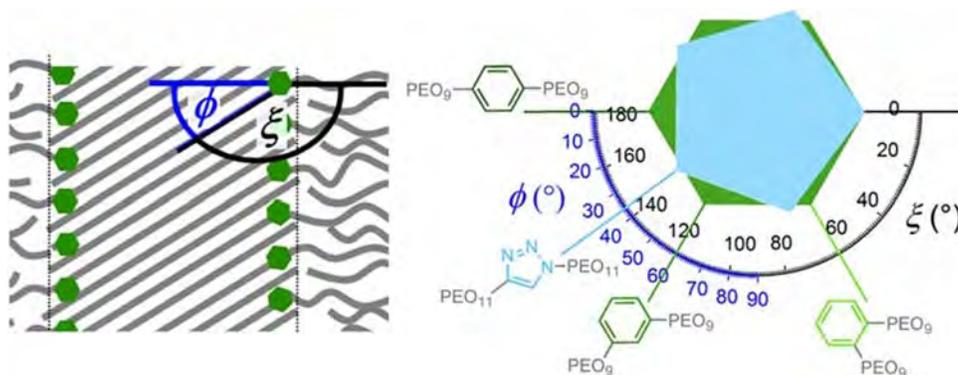
POLY 134: Chain tilt and crystallization of ethylene oxide oligomers with mid-chain defects

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Point defects in polymer chains received increasing attention in the past. On the one hand, they might be introduced on purpose to control the properties of polymer materials. On the other hand, chain defects might be a result of attempts to create specific chain architectures, as connecting precursors to form well-defined branches, stars or networks. Their effect on the crystalline structure and mobility can be conveniently studied by Solid-State NMR.

The studies on short linear poly(ethylene oxide) (PEO) with a triazole ring in the middle of the chain (PEO-TR-PEO) show that such well-defined point defects can be incorporated into the crystalline lamellae after a temperature-induced phase transition. The crystal structure is thereby stabilized by the attractive interactions between the triazole rings. It was shown by means of ¹H FID analysis and ¹³C CODEX exchange experiments that the chain dynamics in the crystalline regions of PEO-TR-PEO (helical jumps) is significantly slowed down as compared to the neat PEO.

Next, we replaced the triazole rings by benzene rings (PEO-BZ-PEO) on the crystallization process. We show that the incorporation of defects into the crystalline lamella of PEO-BZ-PEO depends essentially on the substitution pattern of the aromatic unit and thus on the chain tilt of the chains in the crystalline lamellae. A model recently proposed by Schmidt-Rohr et. al with tilted polymer chains in the crystallites was thus confirmed for the case of PEO.



POLY 135: Physical structures of semi-crystalline polymers in relation to their functional properties

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The physical and mechanical properties of semi-crystalline polymers are significantly influenced by morphology, phase composition and molecular mobility in different phases. Therefore, a quantitative characterization of these meso-/nano-scopic characteristics of semi-crystalline polymers is of great importance to advance our understanding of their properties. Time-domain proton NMR is a sensitive and robust method for determining phase composition and chain motions in complex multiphase polymers in cases when the motion of chain segments in the different phases differs significantly. The method allows us to detect small difference in segmental mobility in amorphous phase caused by difference in molecular structure of polymers, processing conditions, thermal history and deformation. A few examples of the use of this information for understanding the functional properties of semi-crystalline polymers will be provided.

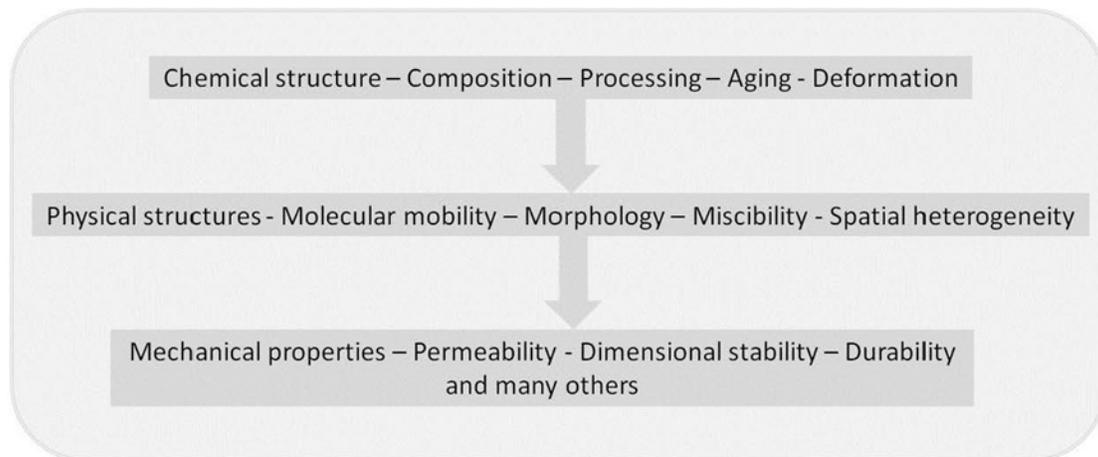


Figure 1. Route from material development to applications. Time-domain ^1H NMR is a reliable and accurate method for characterization of phase composition, domain sizes and chain mobility in different phases of semi-crystalline polymers. This information is valuable for better understanding of functional properties and provides hints for their improvement.

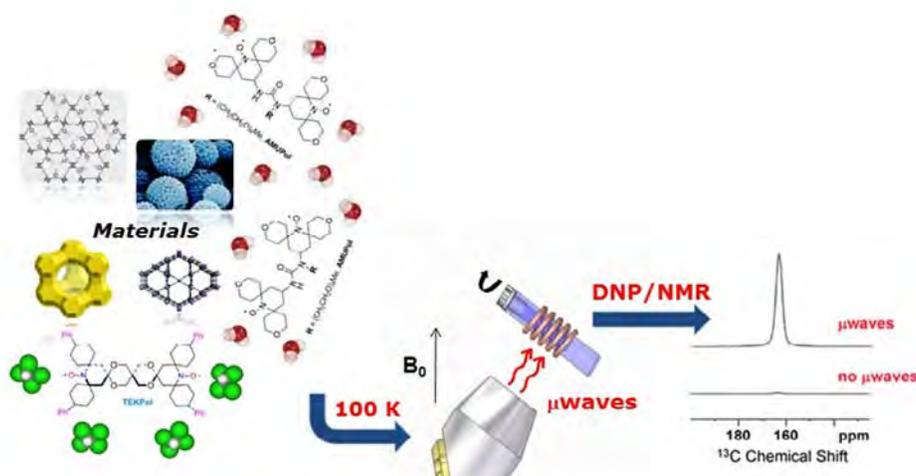
POLY 136: Solid state dynamic nuclear polarization for materials study

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Solid-state Nuclear Magnetic Resonance (SS-NMR) is a powerful spectroscopic technique offering unique information about the structure and the dynamics of materials at a molecular scale. This method is frequently used to characterize various types of materials for energy storage, catalyst, health and construction. As non-invasive method, SS-NMR is especially suitable to study materials in different states: amorphous (polymers, glasses), disordered (battery materials), soft (liquid crystals, gels, pastes) or heterogeneous (catalyst, nanomaterials). However, SS-NMR suffers of a low sensitivity of detection due to a low nuclear spin magnetization at thermal equilibrium. The lack of sensitivity of SS-NMR is a major limitation to solve important questions for materials chemistry.

In this respect, different strategies have been developed to boost the NMR sensitivity. It mainly concerns methods that enhance the nuclear polarization such as the Dynamic Nuclear Polarization (DNP). DNP is a hyperpolarization technique that increases the signal intensity in NMR by several orders of magnitude. The basic principle is to transfer the high electron spin polarization to surrounding nuclear spins by sample irradiation at a frequency close to the EPR transitions. The material of interest is mixed with a solvent containing a source of electron, then SS-NMR Magic Angle Spinning (MAS) experiments are performed at high magnetic field and at low temperature (100 K) under microwave irradiation. The solid state DNP approach enables to obtain new structural and dynamical insights into materials, performing multi-dimensional SS-NMR experiments which were unrealizable because of sensitivity limitation. It opens a new avenue to explore the structural properties of materials.

In this communication, we will present a selection of recent examples of DNP applications for the characterization of different types of materials (synthetic polymers, battery material and bio-materials).



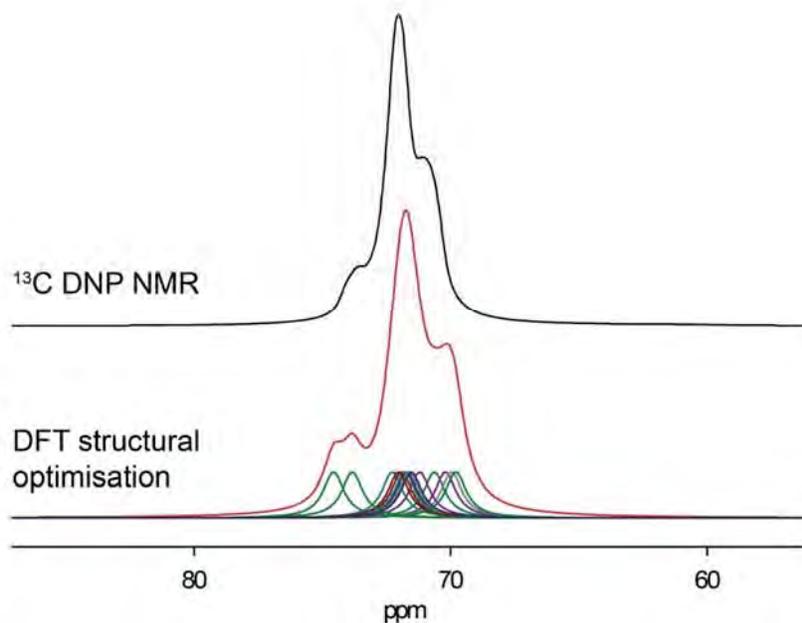
The material sample is mixed with a solvent containing a source of electron, then SS-NMR MAS experiments are performed at low temperature (100 K) under microwave irradiation with enhanced sensitivity.

POLY 137: Solid-state DNP NMR studies of crystalline polymer domains by copolymerisation with radical monomers

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Dynamic nuclear polarisation (DNP) NMR offers a method to probe polymer structures with greatly improved sensitivity. It requires the presence of unpaired electrons, usually in the form of nitroxide radicals, and the location of these species within the structure is crucial. While the radicals act as the source of polarisation enhancement, they will also cause significant broadening of the NMR peaks from nuclei in close proximity, effectively quenching the signal. Moreover, the ability to control the location of the radical can allow selective enhancement of a particular region such as the material's surface, or allow the measurement of domain sizes, which can be particularly useful in studies of multi-component polymers. Many options exist for the incorporation of radicals into polymer structures, including film casting, glass forming, incipient wetness impregnation or covalent functionalisation.

Herein, we report a DNP NMR study of a polyurethane system consisting of poly(ethylene oxide) and TEMPO-based monomers with hexamethylene diisocyanate linkers. At the low temperatures at which the DNP NMR experiments are carried out (approximately 100 K), the materials consist of crystalline PEO domains with the nitroxide radicals located at the interface. This structuring allows the measurement of the PEO domain size by modelling the spin-diffusion mediated polarisation transfer process. DFT calculations are also used to refine the PEO crystal structure and show excellent agreement with experimental data.



POLY 138: Organic light-emitting diodes (OLEDs): Design-synthesis-fabrication, multiscale simulation, and DNP-NMR

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In 2017, large-screen OLED televisions have been widely commercialized from several companies. A new iPhone equipped with OLED, called iPhone X, will also come out commercially soon. However, this is just the start of the commercialization of OLEDs and further developments will be needed. In this work, we will show our newly designed light-emitting compounds for OLEDs and the performance of the resulting device [1-5], together with our recently developed multiscale charge transport simulations based on the combined use of quantum chemical calculations, molecular dynamics, and kinetic Monte Carlo simulations [6,7]. This year, we will install a DNP-NMR spectrometer (Fig. 1), the first such instrument installed in Japan. I would like to show our first results on the DNP-NMR of an organic device material [8].

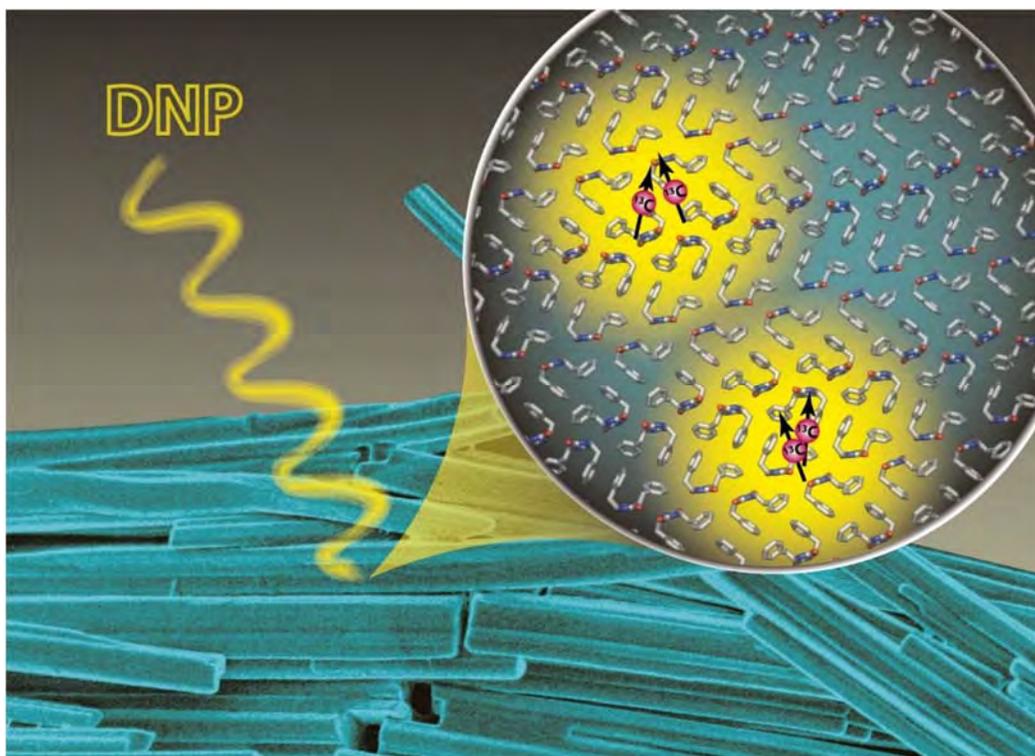


POLY 139: Structure determination of organic assemblies by magic angle spinning dynamic nuclear polarization

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NMR crystallography of small organic molecules faces great challenges owing to the low natural isotopic abundance (NA) of the key nuclei ^{13}C and ^{15}N , and the limited possibilities of isotopic labeling of such molecules. Thanks to tremendous progress in the field of magic angle spinning dynamic nuclear polarization (MAS-DNP), these limitations in sensitivity have now begun to be overcome, enabling the acquisition of ^{13}C - ^{13}C and even ^{15}N - ^{13}C 2D correlation spectra at NA that can be used to perform *de novo* resonance assignment (DFT-free).^{1,2}

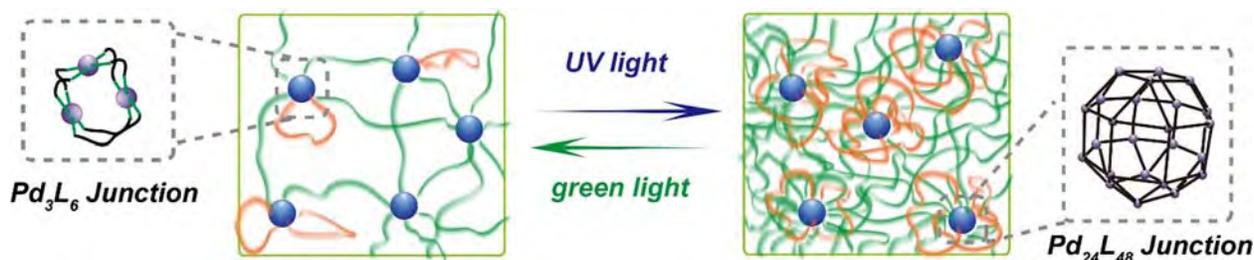
Here we advance beyond this point and employ MAS-DNP for structure determination based on ^{13}C - ^{13}C and ^{13}C - ^{15}N distance information from dipolar recoupling experiments at NA. The features and benefits of structural studies at NA are demonstrated on the self-assembled cyclic diphenylalanine peptide.³ Experimental buildup curves reflecting ^{13}C - ^{13}C and, for the first time, ^{13}C - ^{15}N polarization transfers at NA are presented, alongside with a detailed analysis showing excellent agreement with simulations based on the known crystal structure of cyclo-FF. Notably, a multitude of intermolecular distances of up to ~ 7 Å contribute to the buildup curves, meaning that they contain valuable information on the supramolecular assembly of cyclo-FF. This makes these buildup curves a great probe for full crystal structure determination. Finally, we show that they can indeed be used - in combination with powder X-ray diffraction data and computational modeling - for *de novo* structure determination of cyclo-FF.



POLY 140: Reversible control of polymer network topology using external light

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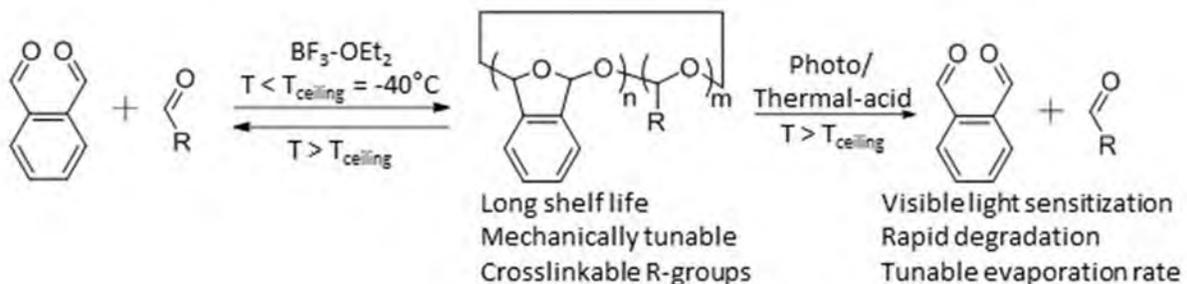
The properties of polymer networks are highly dictated by how network strands are connected topologically (e.g., branch functionality, cyclic defects). Herein we reported a metal-organic-cage based polymer network (polyMOC) wherein external light trigger was used to reversibly induce the rearrangement of network topology. The system was therefore capable to interswitch between two topological states that have different branch functionality. The two states were shown to have largely different mechanical properties (e.g., stiffness, relaxation, junction fluctuation, self-healing properties).



POLY 141: Utilizing polyaldehydes in designing optically degradable systems for transient technology

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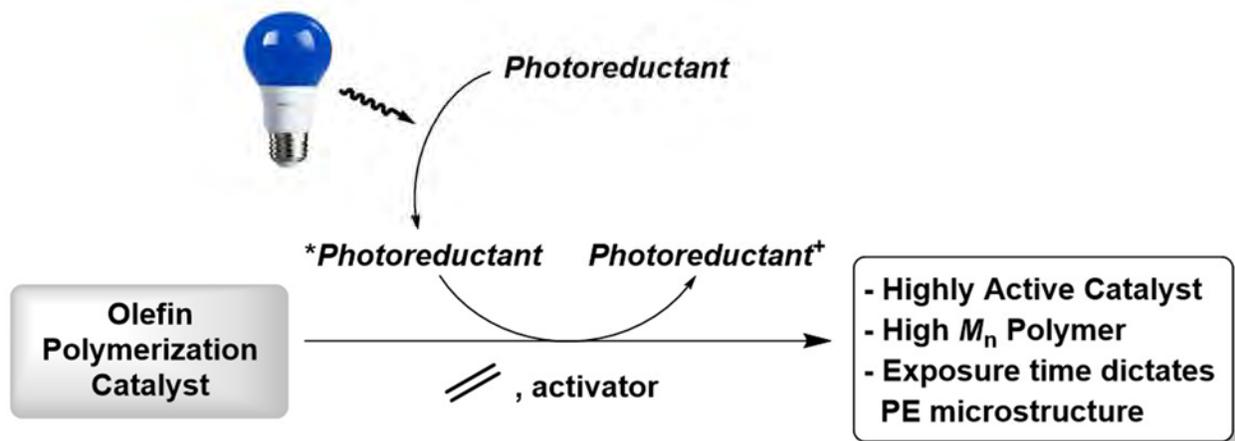
The difficulties surrounding polyaldehyde utilization stem from their low ceiling temperature (T_c), the temperature at which the polymerization and depolymerization are in equilibrium. Typical polyaldehyde T_c values are below 20°C , making them thermodynamically unfavorable at ambient temperatures. Using polyaldehydes above T_c requires the polymer chains to be kinetically stabilized via end caps or cyclization. Applications like transient technology can take advantage of these thermodynamic properties to create rapidly degradable devices that can evaporate to leave behind minimal residue. Cationically grown polyphthalaldehyde (pPHA) has proven to be a robust material that can rapidly degrade with catalytic amounts of acid. Copolymers of pPHA with aliphatic aldehydes offer a route to modify the processing and mechanical properties, as well as modifying the evaporation rate of the depolymerized materials after the device has been triggered to degrade. These copolymers have moduli on the order of 1 GPa and improved elongation-to-break by 60-200% compared to pPHA homopolymer, which makes polyaldehydes suitable for structural materials in transient devices. Post-polymerization modification has been carried out by crosslinking p(PHA-co-4-pentenal). Presence of a higher volatility monomer helps the degradation products depress crystallization and evaporate at a faster rate than decomposed pPHA. A series of synthesized polycyclic aromatic hydrocarbons with a photoacid generator have been shown to photosensitize the degradation of polyaldehyde films across the visible spectrum. The Rehm-Weller equation is used to quantify the feasibility of the photo-induced electron transfer. Films hundreds of microns thick have been shown to completely depolymerize upon exposure to sunlight for 10 minutes.



POLY 142: Photochemical regulation of redox-active catalysts: Controlling polyethylene microstructure with visible light

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Redox-active catalysts are a next-generation tool capable of achieving enhanced *in situ* polymerization control. By employing traditional redox chemistry, we can now access different polymerization activities using a single catalyst, as well as generate diverse polymer microstructures. While we continue to use this fundamental process to advance polymer chemistry, the field of redox chemistry has emphasized the importance in externally stimulated and/or regulated processes. The ability to manipulate a polymerization via external stimuli, such as light, is potentially advantageous to the production and application of polymers. Initially in the polymer field, photo-active molecules were only used to influence initiation events, but recent reports demonstrate how light can also control propagation and termination events. Though these methods demonstrate improved catalytic control, we noted that they typically have no effect on polymer microstructure. Herein, we demonstrate the ability to use photoredox chemistry to control the behavior of an olefin polymerization catalyst. With the addition of a photoreductant, we can modulate the branching content of polyethylene generated by a redox-active catalyst. GPC, ^1H NMR, and quantitative ^{13}C NMR analyses were used to verify the change in polymer branching content and the identity of the branches.



POLY 143: Material property evolution and mechanics during photopolymerization

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Photopolymerization is a process that changes liquid monomer solution into solid polymer by using the light activated chemical reaction, which has been widely used in many engineering fields such as coating industry, dental restoration and 3D printing process. The physical properties of the cured polymer change dramatically during the polymerization process. Due to the absorption of solution, the light intensity is not uniform in the curing material, which will cause the non-uniform conversion of the monomer and nonhomogeneous material properties in the cured part. And the volume shrinkage is often observed in the photopolymerization process. The internal stress caused by the volume shrinkage could be a severe problem which may cause the warpage of the polymerized part. Therefore investigating the mechanics and material property evolution is very important for the application of photopolymerization. Here we investigated the photopolymerization reaction kinetics and material property evolution during curing process by theoretical modeling and experiments. The model employs the first order chemical reaction equations to characterize the reaction kinetics. The degree of conversion of monomers is used to characterize the mechanical properties of cured polymer at different curing states. The multi-branch model is used to capture the viscoelastic and nonlinear viscoelastic deformation behavior of the cured polymer. The internal stress of a photopolymerized sample caused by the volume shrinkage during curing is investigated by the FEM simulation. The bending curvature of the cured sample induced by the internal stress are investigated by experiment and modeling. The results indicate that the model is able to capture the internal stress during photopolymerization.

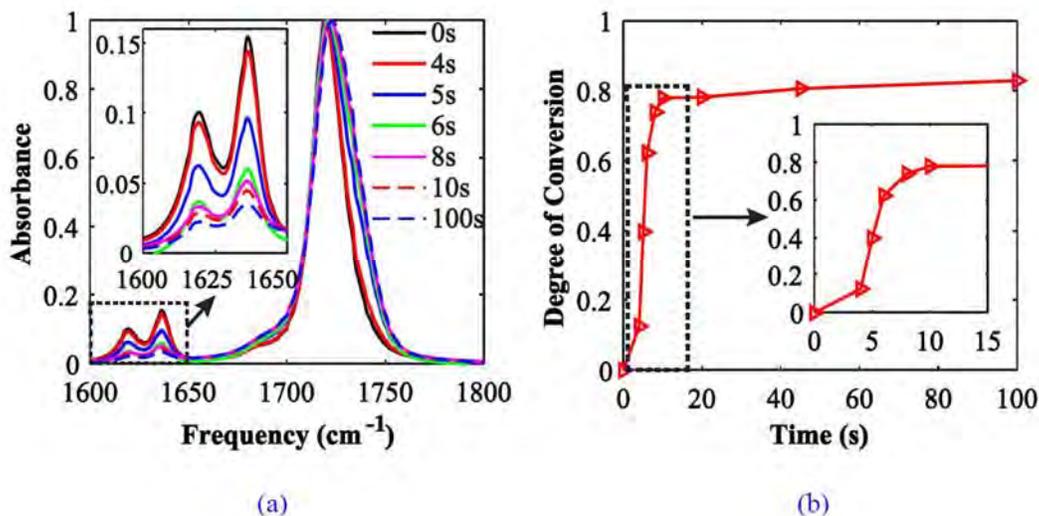
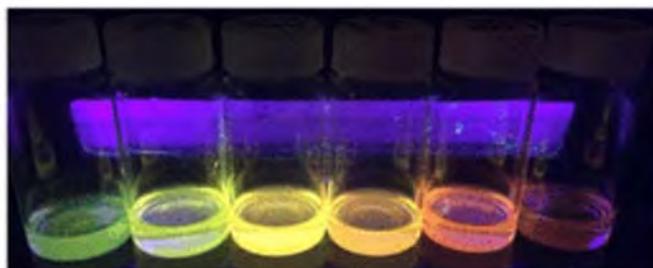
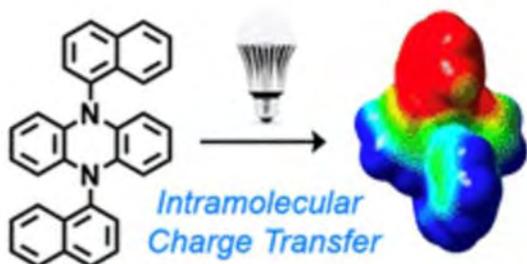


Fig. 1. Measured degree of conversion of the cured polymer at different curing time. (a) FTIR absorbance spectra. (b) The calculated degree of conversion as a function of time.

POLY 144: Mechanism-driven catalyst design for organocatalyzed atom transfer radical polymerization

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Organocatalyzed atom transfer radical polymerization (O-ATRP) has emerged as a powerful method for the synthesis of precision polymeric materials, driven by visible light. The development of successful *N,N*-diaryl dihydrophenazine and *N*-aryl phenoxazine photocatalysts (PCs) provides access to polymers with dispersities lower than 1.10 and controlled molecular weights in a polymerization with quantitative initiator efficiency. Insights provided by quantum chemical calculations enabled the design of PCs with photophysical properties rivaling those of the common iridium and ruthenium polypyridyl complexes. The roles of specific PC properties have been explored in context of different polymerization conditions, namely solvent polarity and irradiation intensity. These mechanistic insights, from a combination of computational, physical, and synthetic chemistries have enabled next-generation catalyst design for accessing highly active PCs in an economical fashion.



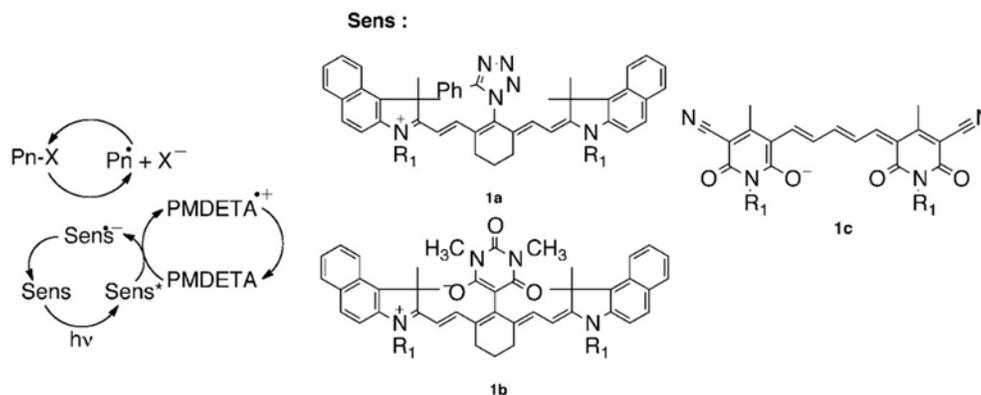
POLY 145: Visible and NIR light photoinduced metal-free atom transfer radical polymerization

Ceren Kütahya³, cerenkutahya@gmail.com, Yusuf Yagci², Jochen Gutmann¹, Bernd Strehme³. (1) NETZ, DTNW gGmbH, Duisburg, Germany (2) Istanbul Technical Univ, Maslak Istanbul, Turkey (3) Chemistry, Niederrhein University of Applied Sciences, Krefeld, Germany

Among the controlled radical polymerization methods, Atom Transfer Radical Polymerization (ATRP) has been the most-widely used method as it has demonstrated high tolerance towards many functional groups available in the initiator and monomer structure. The major drawback associated with the ATRP process is the requirement of the low oxidation state copper halide catalysts, which are hard to remove from the polymers obtained. The residual inorganic materials in these polymers prevent the application of these materials especially in medical or bioapplications. In addition, these are thermal processes and application of photochemical strategies were sometimes connected with problems. Thus, additional innovative research is required due to the insufficiency of adaptation of light into the present technologies. It is therefore important to realize the syntheses of telechelic polymers, block, graft and star copolymers by light induced approaches as they provide low-energy requirements and simpler experimentation procedures. Recently, it has been demonstrated that some controlled polymerization techniques can be performed in the absence of inorganic catalysts by the use of light being the smallest reagent[1].

We employed NIR-acting photoinitiating system as new metal-free photo-ATRP systems comprising cyanines as sensitizers with the same number of methine groups. For this purpose, we used NIR-LEDs emitting at 790 nm and halogen lamp to initiate photo-ATRP. These sensitizers exhibit either a positive charge (**1a**), negative charge (**1c**) or neutral substitution pattern (**1b**). **1b** and **1c** resulted in initiation of radical polymerization of methacrylates in combination with an alkyl halide and an amine. However, **1a** did not show any action in the polymerization process applying NIR-LED exposure. This may be explained by an oxidation mechanism based on singlet excited states because the electron-rich canines **1b** and **1c** would follow this route.

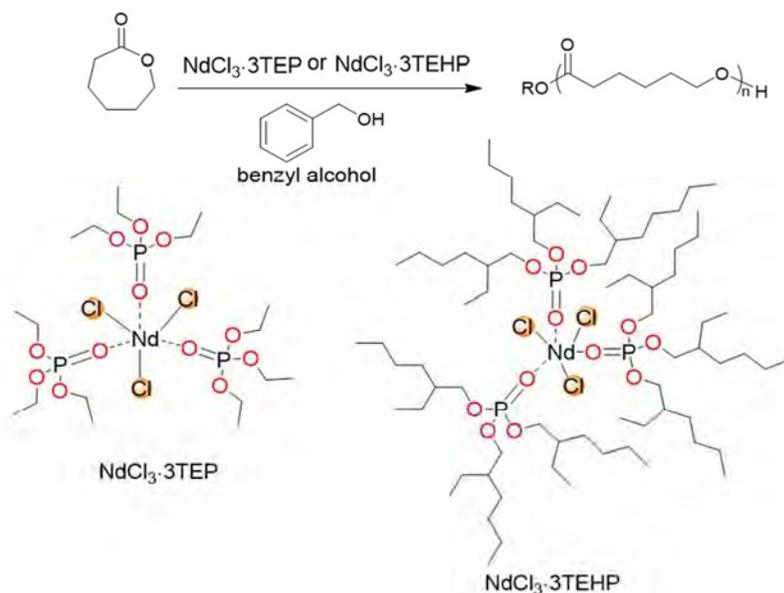
Our contribution can be seen as a new approach to initiate radical photopolymerization. Furthermore, exposure experiments resulted in polymers which were characterized with GPC.



POLY 146: Neodymium-based catalysts $\text{NdCl}_3\cdot 3\text{L}$ (L = triethyl phosphate (TEP) or tris(2-ethylhexyl) phosphate (TEHP) for ring opening polymerization of ϵ -caprolactone

Yixin Ren, *yxr140330@utdallas.edu*, Ruvanathi Kularatne, Katherine E. Washington, Michael C. Biewer, Mihaela C. Stefan. Dept of Chemistry, University of Texas at Dallas, Richardson, Texas, United States

Neodymium-based catalysts bearing phosphate ligands $\text{NdCl}_3\cdot 3\text{L}$; L = triethyl phosphate (TEP) or tris(2-ethylhexyl) phosphate (TEHP) were successfully synthesized. These Nd catalysts were tested for the ring opening polymerization (ROP) of ϵ -caprolactone (ϵ -CL) in the presence of various initiators (benzyl alcohol, pentaerythritol, and poly(ethylene glycol) methyl ether) to generate polymers with relatively narrow polydispersity indices (PDI = 1.22 to 1.55) and tunable molecular weights. An important result from the kinetic studies revealed that the catalyst with the sterically bulkier ligand TEHP gave a higher rate of polymerization and lower amount of the transesterified product. The livingness of this catalytic system was demonstrated by kinetic studies and by successful synthesis of the block copolymer poly(ϵ -caprolactone)-*block*-poly(L-lactide) by sequential monomer addition. The *in situ* NMR studies were also performed by monitoring the reaction of $\text{NdCl}_3\cdot 3\text{TEP}$ and benzyl alcohol at room temperature. The result from the mechanistic studies has indicated that the ROP reaction takes place through a coordination-insertion mechanism.



POLY 147: Molecular design of olefin block copolymers and the impact on elastic performance in health and hygiene

Kyle Anderson, *kdanderson1@dow.com*, Jong-Young Lee, Aleksandar Stoiljkovic, Jeff Munro, Lisa Madenjian. *The Dow Chemical Company, Houston, Texas, United States*

Dow olefin block copolymers (OBC) are unique polyethylene materials that combine hard and soft segments into a single molecule and offer a variety of unique properties. These materials can be effectively used as elastic engines in applications such as diapers, providing clean, easy-to-process and consumer-friendly materials. The unique structure of the material and the ability to control the block structure allow the elastic performance of the material to be tailored to meet market needs. OBC materials are composed of both hard and soft segments of polyethylene which can be modified during production. The hard segments act as anchor points while the soft segments provide elasticity to the final film. Variations in the ratio of hard to soft segments can change the expected performance of the elastic film and bring elastic performance to sensitive hygiene applications where chemistry, performance and sensory experience are important. Elastic films utilizing OBC technology have the ability to power some of the most sensitive hygiene applications driven by ground breaking molecular designs.

POLY 148: Demands of the food industry for ever increasing material performance to meet the needs of today's consumers

Mark R. Watts, mark_watts@campbellsoup.com. *Science & Technology, Campbell Soup Company, Camden, New Jersey, United States*

Consumers are demanding food products to deliver real food experiences, clean label ingredients, removal of preservatives, longer shelf life. At the same time there are expectations of packaging materials to be sustainable, recyclable, Polymers are now needed to perform beyond natural barrier characteristics for water, oxygen and light transmission. Growth of e-commerce, expansion of the health and wellbeing and snacking markets will push towards better solutions in transparency, thermal performance, microwaveability and barrier performance.

High performance, passive, active and interactive packaging will be the future to deliver these demands, as food waste, artificial additives, fresh food solutions and food safe materials become ever increasingly scrutinized by the consumer and through legislation.



POLY 149: Development of a fully automated small scale emulsion polymerization reactor

Ralph Even³, *REven@Dow.com*, **Gregoire Cardoen**¹, **Lisa Rhodes**². (1) Home and Personal Care, The Dow Chemical Company, Collegetown, Pennsylvania, United States (2) Dow Coating Materials, The Dow Chemical Company, Collegetown, Pennsylvania, United States (3) Core Research - Formulation Science, The Dow Chemical Company, Collegetown, Pennsylvania, United States

Developed through a partnership between Formulation Science (Core R&D at The Dow Chemical Company) and Freeslate™, the Large Volume Semi-continuous Parallel Pressure Reactor (LVScPPR) was designed to miniaturize and automate highly complex emulsion polymerization recipes. The tool is composed of an array of four “independent” reactor modules having ~60mL working volume each. Temperature can be controlled from room temperature to 150 degrees C, pressure from 0 to 100 psig. Each reactor can be programmed independently from the others with respect to temperature control, agitation, raw materials, and reaction time. Moreover, each module is fitted with 13 addition ports, two of them being solely dedicated to a single unit. The instrument has 12 syringe pumps which are shared between all four modules. This setup enables the instrument to run complex, multi-staged emulsion polymerization processes. Design philosophy and details will be discussed along with presentation of data validating the performance with regard to reproducibility both batch-to-batch and versus more traditional larger scale methods.



POLY 150: Controlled aesthetics in thermoplastics: Modifying surface gloss of vinyl products

Kevin Yocca, *kevin.yocca@arkema.com*. Arkema Inc., King of Prussia, Pennsylvania, United States

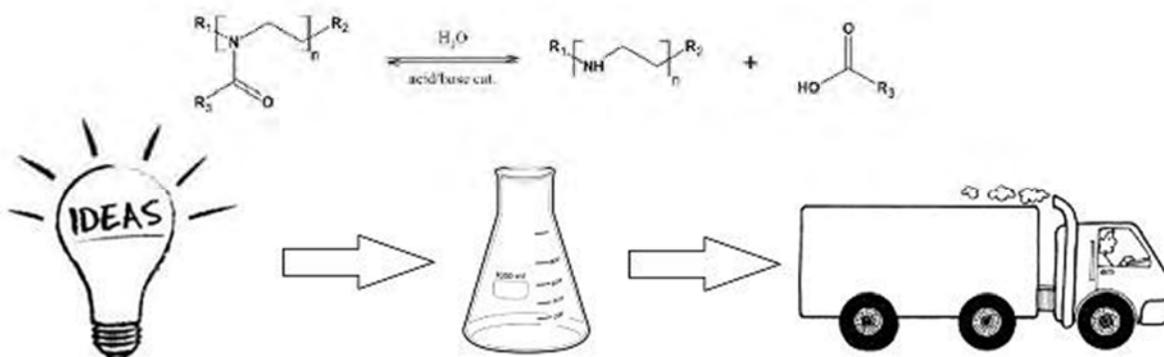
The work included in this presentation explores novel methods for changing aesthetics in polymer resins, specifically vinyl resin, through manipulation with polymer additive chemistry. The new additive technology was developed to specifically target and modify specular gloss in extruded vinyl formulations. These changes were achieved by utilizing emulsion polymerization. Historically, achieving low gloss values in vinyl applications requires a trade-off between appearance and mechanical properties. The technology presented here shows that gloss, or surface quality, can be modified without compromising mechanical integrity.



POLY 151: A path to industry

Benjamin Zarin, zarin@email.arizona.edu. Polymer Chemistry Innovations Inc., Tucson, Arizona, United States

As a research chemist for a company that employs less than fifty people overall, and with a dedicated R&D staff of around 10% percent of the company, my daily routine is often far from routine. Working in a collaborative environment for Polymer Chemistry Innovations (PCI) has greatly expanded my knowledge of polymer science through hands-on experience of numerous diverse polymer classes, and by exposure to novel synthetic strategies that arise from consulting and development type projects. I have been both a project manager and lead chemist on projects as varied as gram scale quantities to large pilot plant scales, where process and equipment modifications are not uncommon. The challenges that present themselves are often unique and require out of the box thinking and a means for implementation. I attribute my success in industry to establishing a solid foundation in chemistry and chemical engineering while in college. This foundation provides the tools necessary to thrive in this industry and meet the ever-changing customer and consumer demands.



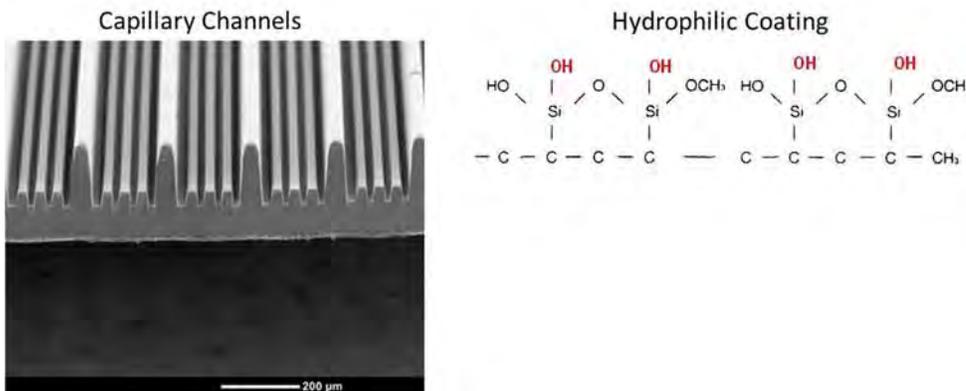
POLY 152: Extrusion replicated microcapillary film for managing condensation in food processing facilities

Kurt Halverson¹, kjhalverson@mmm.com, **Steven Swanson**¹, **Caleb Nelson**¹, **David Slama**¹, **Jayne Stratton**², **Bismarck Martinez**². (1) 3M, St. Paul, Minnesota, United States (2) University of Nebraska-Lincoln, Lincoln, Nebraska, United States

Wet sanitation of food processing equipment is performed daily in cooled USDA inspected facilities. The first step in the process is the removal of residual solids using copious amounts of hot pressurized water. This procedure generates warm, moist air in the environment which condenses on the cool surfaces inside the facility. Condensation accumulating on horizontal surfaces coalesces to form large hanging drops, which can fall on to underlying equipment or product. The presence of residual moisture is associated with an increased risk of microbial proliferation, therefore hanging drops must be removed from overhead surfaces prior to returning to production. This is currently achieved manually using mops, squeegees, or compressed air.

We have developed a film designed to adhere to overhead surfaces that increases the evaporation rate of condensation. The film surface contains a series of parallel nested microchannels (see figure). The channels are formed in LDPE utilizing a roll-to-roll extrusion replication process. Following replication a conformal, hydrophilic organosilane coating is deposited on the microchannels via continuous plasma enhanced chemical vapor deposition (PECVD). Finally, a hot melt pressure sensitive adhesive is coated on the back side followed by converting to slit rolls of film.

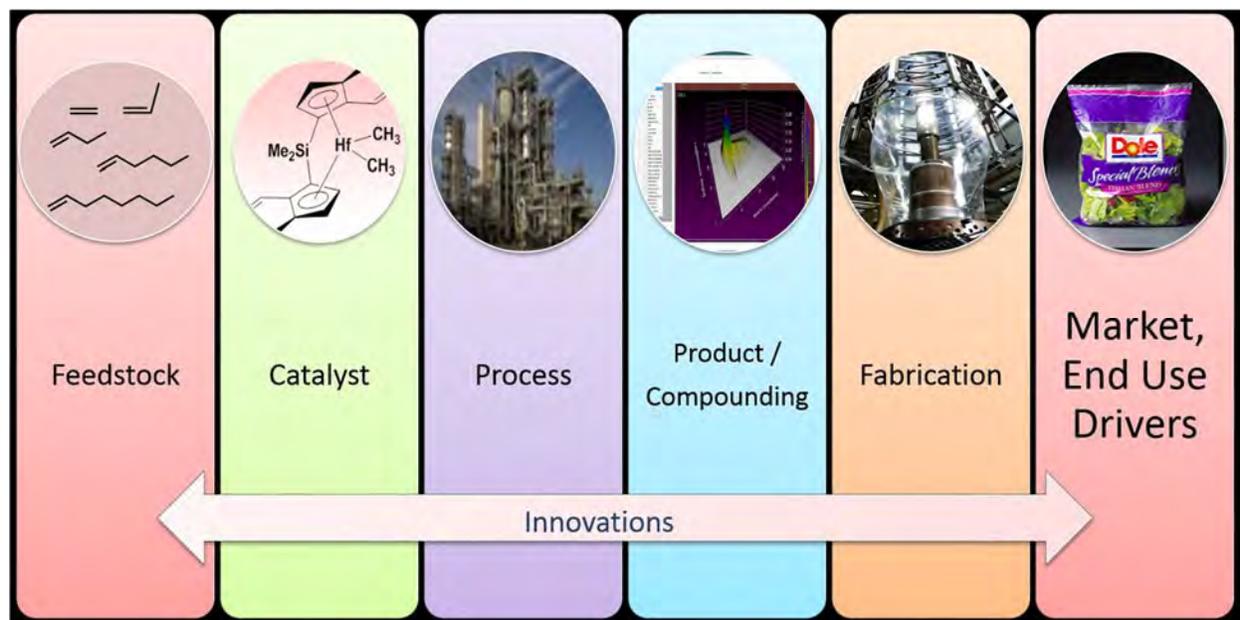
During use, condensation formed on the film surface is spread by capillary action along the microchannels. This spreading increases the surface to volume ratio of the condensate relative to a hemispherical hanging drop of equivalent volume. This increase in surface area increases the evaporation rate by a factor of 8, eliminating the need to mop or squeegee the surface prior to returning to production. Bacterial survivability studies conducted using *Listeria innocua* in a model system, and surface swabs for aerobic bacteria obtained during in-plant trials demonstrated no increase in microbial counts on the film relative to control surfaces. To maintain a hygienic surface over time the film is periodically removed and replaced. The increase in evaporation rate and hygienic benefit of periodic replacement eliminates the need for manual intervention in managing overhead condensation.



POLY 153: Polyolefin contributions and new opportunities to meet societal and environmental needs

Patrick Brant, pat.brant@exxonmobil.com. Exxonmobil Chemical Company, Baytown, Texas, United States

Today, polyolefins comprise well over 60% of all polymers manufactured in the world. Their share of polymer manufacture has increased almost 1% a year since the beginning of this century. And their robust growth continues. In the United States especially, production growth is stimulated by abundant and low cost natural gas for olefin production. The reasons for this growth are found in their myriad cost-effective solutions, created along the Polymer Delivery Chain, to evolving societal and environmental needs in food, energy, and water. Polyolefins now broadly compete or work together with metals, glass, wood and other polymers in meeting these fundamental needs and improving quality of life around the world. In this presentation we will share examples of the history and ongoing successes, as well as future opportunities and challenges of polyolefins in this continuous endeavor. Special attention will be given to aspects of sustainability.



Polyolefin Delivery Chain

POLY 154: Visible-light driven RAFT polymerization accelerated by amines

Michael Allegrezza, allegrml@miamioh.edu, Alex Kloster, Zach DeMartini, Zachary Digby, Dominik Konkolewicz. Department of Chemistry and Biochemistry, Miami University, Oxford, Ohio, United States

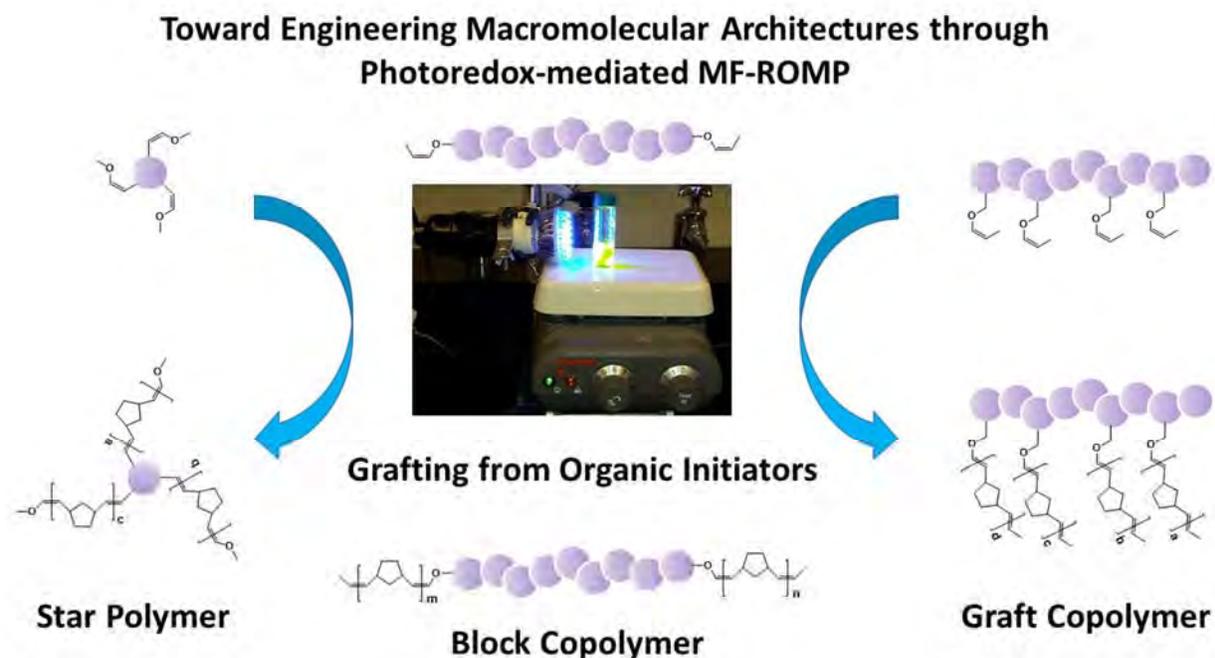
In recent years, reversible addition-fragmentation chain transfer polymerization (RAFT) has become an increasingly promising polymerization technique due to its ease of use and the control over molecular weight that it affords. Photochemical RAFT processes have been gaining increased attention, due to the fact that these allow the polymerization to be switched on and off and limit it to certain regions by the light source. This technique relies on photochemical processes that will generate a radical when excited by a light source, as opposed to a thermally generated radical source in a traditional RAFT process. Recent research has shown that trithiocarbonate (TTC) compounds act as both the RAFT agent and radical initiator in the presence of a tertiary amine and UV light. This technique is interesting, as it eliminates the need for an added photocatalyst. In this study, the kinetics of photochemical dithiobenzoate-mediated RAFT polymerization in the presence of triethylamine is explored. The effects of light source, RAFT chain transfer agent concentration, and amine concentration are also investigated to understand the kinetic contributions of each component and possible mechanism of this process. We have found that this technique can reach high monomer conversions and offers good control over chain length and molecular weight distribution.



POLY 155: Toward engineering macromolecular architectures of polymers through photoredox-mediated metal-free ring-opening metathesis polymerization

Pengtao Lu, pl24@uw.edu, Andrew J. Boydston. Chemistry, University of Washington, Seattle, Washington, United States

Toward the preparation of polymers without residual metal contamination, metal-free ring-opening metathesis polymerization (MF-ROMP) utilizing organic photoredox mediators has emerged as an alternative to traditional metal-based ROMP. Instead of using metal-based initiators, the photoredox-mediated MF-ROMP protocol uses vinyl ethers as organic initiators. Since vinyl ether moieties can be easily installed via simple organic transformations, we believe that the photoredox-mediated MF-ROMP, aside from its inherent metal-free merits, can also provide opportunities to develop expedient synthetic approaches toward controlling macromolecular architectures. This is crucial in shaping both physical and chemical properties of the obtained polymers. Herein, we describe our recent efforts in preparing polymers with various macromolecular architectures by photoredox-mediated MF-ROMP grafting from both multifunctional small molecular initiators and macroinitiators. The research began with the study of bidirectional MF-ROMP, which could have either inward or outward polymer growth depending on different relative orientation of alkoxy moieties in divinyl ethers. Based on the evaluation of inward-growing polymers versus outward-growing polymers, the incorporation of monomers was successful both at chain-end and chain-centered active site. The use of macroinitiators derived from PPG, PEG and polystyrene also allows the rapid access to acid-cleavable copolymers, which might be useful for future application.



POLY 156: Photoredox ring-opening polymerization of O-carboxyanhydrides to synthesize stereoblock polyesters

Rong Tong, rtong@vt.edu. MIT, Cambridge, Massachusetts, United States

Poly(α -hydroxy acids) are important biodegradable polymers with wide applications. Attempts to synthesize them from O-carboxyanhydrides (OCAs) with pendent functional groups have been plagued by uncontrolled polymerization. We have recently developed an effective protocol that combines photoredox Ni/Ir catalysis with the use of a Zn-alkoxide for efficient ring-opening polymerization (ROP), allowing for the synthesis of isotactic polyesters with expected molecular weights (>140 kDa) and narrow molecular weight distributions ($M_w/M_n < 1.1$).¹ Herein, expanding from our initial discovery, we present a general approach for the synthesis of new stereoblock polyesters using photoredox ROP of OCAs (Fig. 1).

We investigated zinc-based complexes to high activity of zinc alkoxide for photoredox ROP polymerizations of OCAs. We previously found that sterically bulky β -diiminate Zn complexes did not initiate controlled polymerization of L-1 at a DP of 300, whereas a less bulky tridentate Schiff base ligand (**NNO-1**) did (Fig. 1a). We discovered that within 4 h at -15 °C under irradiation, the photoredox ROP mediated by (**NNO-1**)ZnEt ([L-1]/[D-1]= 150/150) resulted in a product with a M_n of 45.7 kDa, which is close to the expected MW (44.5 kDa), and a narrow polydispersity of 1.05; whereas the similar reaction mediated by (**NNO-2**)ZnEt had less controlled polymerization. Analysis of the microstructure of this polymer using homonuclear decoupled ¹H NMR in the methine region ($\delta \sim 5.2$ ppm) revealed a high degree of isotacticity as evidenced by the large mmm tetrad peak (Fig. 1b). The probability of *meso* dyads (i.e., isotactic enchainment, P_m) was up to 0.97 calculated from homonuclear decoupled ¹H NMR.

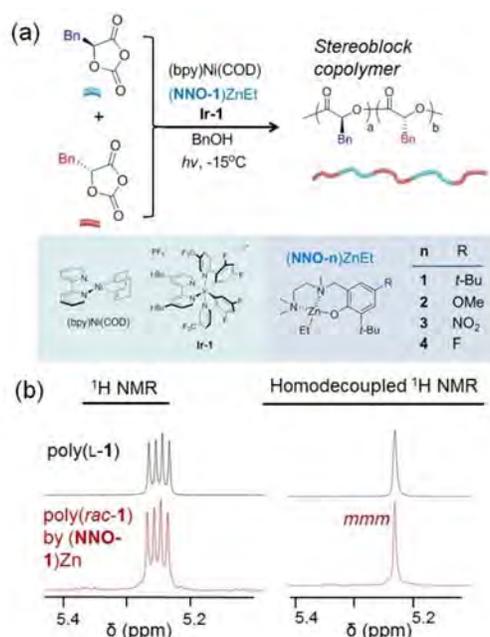
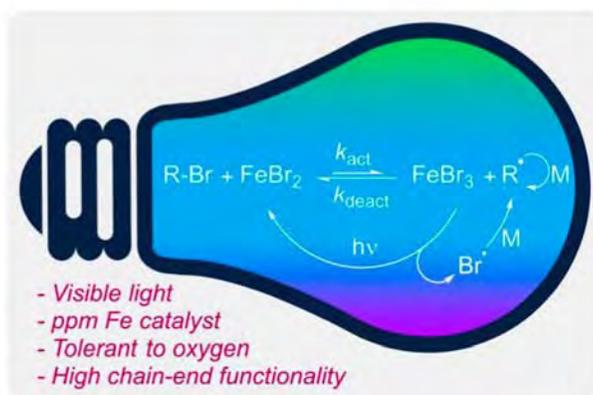


Figure 1. (a) Scheme of stereoselective photoredox ROP of racemic OCAs by Zn/Ni complexes. (b) ¹H NMR of poly(L-1) and poly(*rac*-1) prepared by (NNO-1)Zn via the photoredox ROP.

POLY 157: Photochemical control in ATRP

Krzysztof Matyjaszewski, *km3b@andrew.cmu.edu*. CMU, Pittsburgh, Pennsylvania, United States

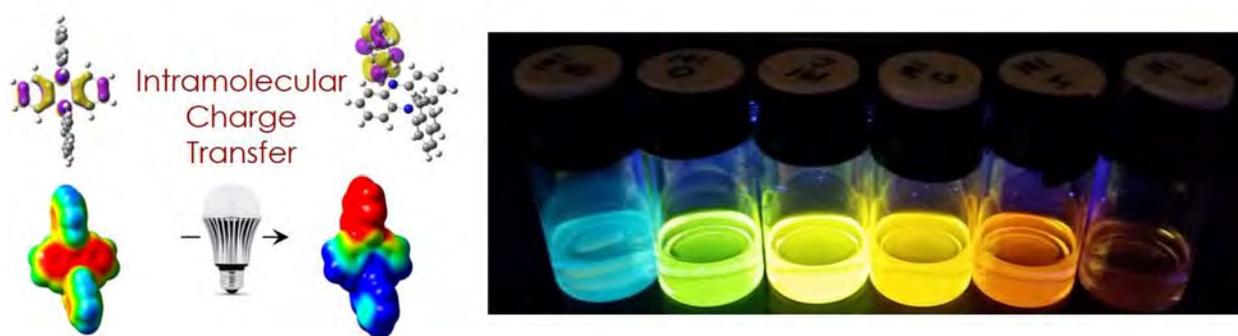
Atom transfer radical polymerization (ATRP) can be successfully controlled by light using Cu based and Fe based catalytic systems. Also light has been successfully applied to the metal free (organocatalyzed) systems.



POLY 158: Intramolecular charge transfer in organic photoredox catalysts for organocatalyzed atom transfer radical polymerization

Garret Miyake, garret.miyake@colostate.edu. Chemistry, Colorado State University, Fort Collins, Colorado, United States

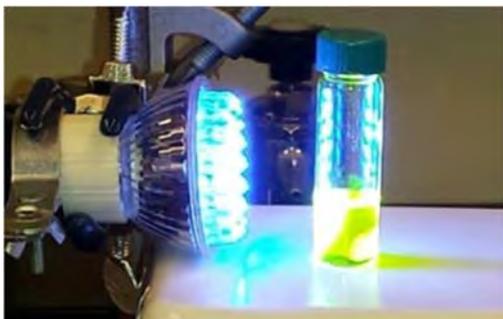
Strongly reducing organic photoredox catalysts have been developed for use in organocatalyzed atom transfer radical polymerization. The most successful catalysts display the characteristic of photoinduced intramolecular charge transfer (CT). This presentation will discuss catalyst design to promote CT as well as the importance of CT in catalysis.



POLY 159: Mechanistic studies on photoredox-mediated metal-free ring-opening metathesis polymerization

Andrew J. Boydston, *boydston@chem.washington.edu*. Chemistry, University of Washington, Seattle, Washington, United States

We recently discovered a method for conducting ring-opening metathesis polymerization (ROMP) using organic vinyl ether initiators and photoredox catalysts in combination with strained cycloalkene monomers. The approach takes advantage of the reactivity of vinyl ether radical cation intermediates and offers unique synthetic and kinetic landscapes in comparison with most metal-mediated approaches to ROMP. Expanding the scope of compatible functional groups and monomer classes has been a focal point of our research since the initial discovery of the metal-free ROMP reactivity. We will discuss updates on mechanistic investigations and specific applications that are enabled from recent breakthroughs.



POLY 160: Using PET-RAFT for polymerization in low volume

Cyrille Boyer, *cboyer@unsw.edu.au*. Chemical Engineering, UNSW, Sydney, New South Wales, Australia

The emergence of visible light regulated living/controlled radical polymerization adds a new layer of control over polymerization. Visible light mediated polymerizations afford simple and facile route to modulate polymerization rate through manipulation of light intensity, wavelength and by switching on/off the light source. However, these techniques present a major limitation as polymerizations are they are not usually oxygen tolerant. In the last 2 years, we have developed new approaches to overcome this limitation, which allows to perform polymerization in the presence of air (in open and closed vessel). This talk will be dedicated to the presentation of these strategies. Our recent approaches allow to perform polymerization with 10 μL volume without the need of specialized equipment and loss of control to produce around 1 microgram of polymer. We have successfully exploited this approach to produce library of polymers.

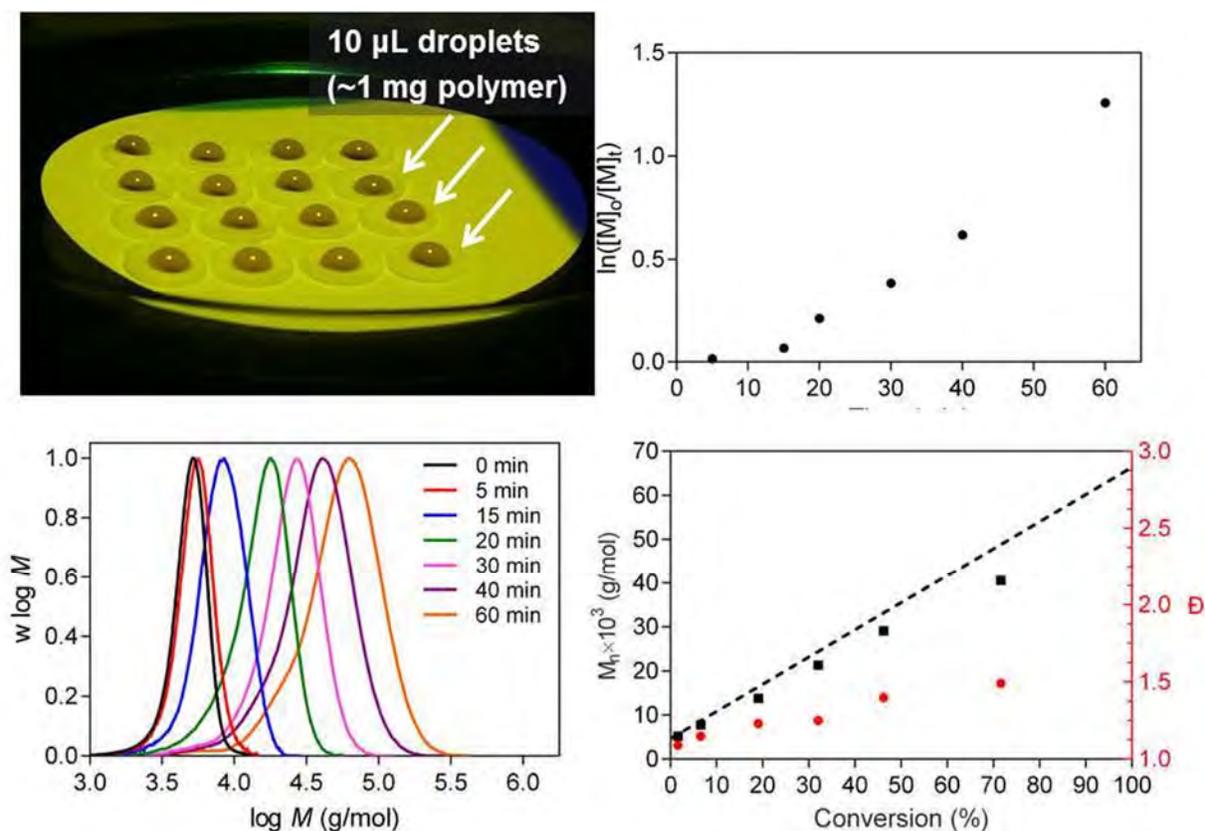
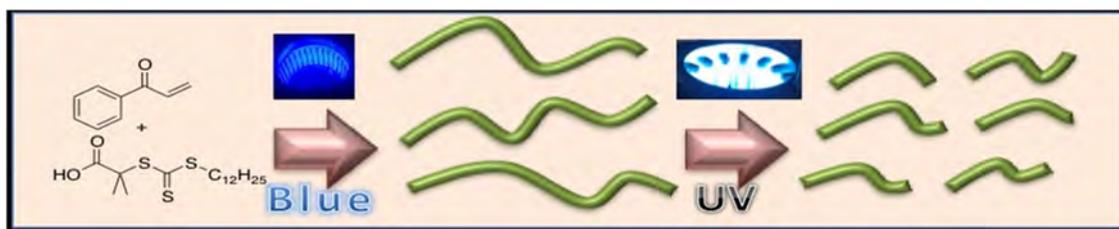


Figure 1. Reaction set-up for PET-RAFT for low volume polymerization and polymerization kinetics of diethylacrylamide under green light.

POLY 161: Rise and fall: Poly(phenyl vinyl ketone) photopolymerization and photodegradation under visible and UV radiation

Jennifer A. Reeves, *kingslja@miamioh.edu*, Michael Allegrezza, Dominik Konkolewicz.
Department of Chemistry and Biochemistry, Miami University, Oxford, Ohio, United States

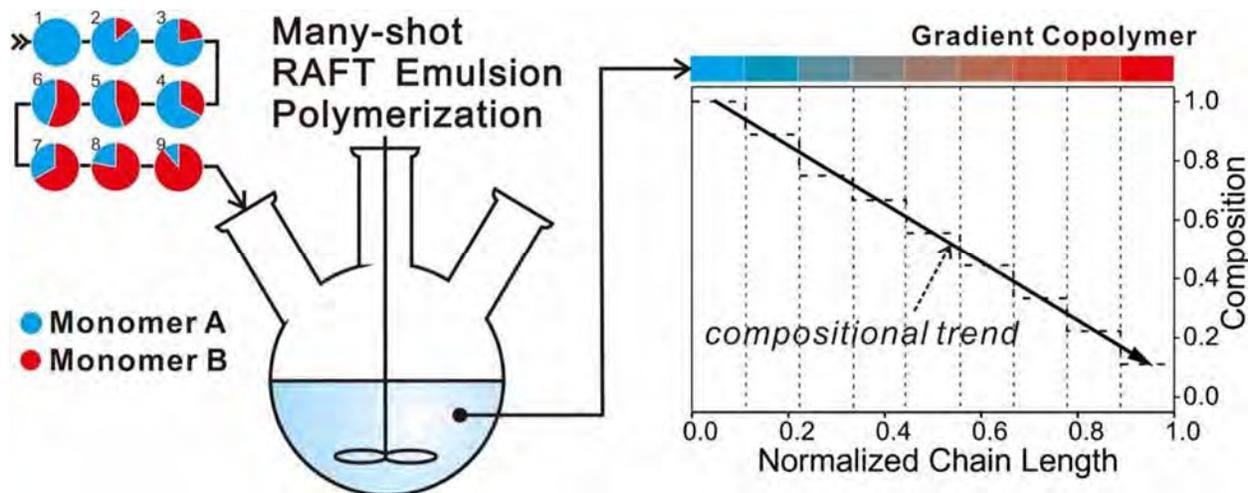
Vinyl ketone polymers, including poly phenyl vinyl ketone (PVK), are an important class of polymers due to their degradability when irradiated with ultraviolet light. This ability to be degraded makes them useful for a wide variety of applications, including “green” materials and plastics. However, traditional radical methods for synthesizing PVK polymers give rise to poor control or are unable to produce block copolymers. Photopolymerization is an attractive technique due to the ability of photochemistry to give access to high energy intermediates, which allows for reactions to occur under mild conditions. Light is an attractive source of external stimuli because it is readily available and offers simple and tunable control over both the temporal and spatial domain of polymerization. This work uses reversible addition-fragmentation chain transfer polymerization (RAFT) and photochemistry to polymerize PVK. When visible blue radiation of 440 ± 10 nm is used as the light source for the photopolymerization, rapid polymerization and well-defined polymers are created. This RAFT method uses PVK as both monomer and radical initiator, exciting the acetophenone portion of the PVK monomer by irradiation with 440 ± 10 nm, avoiding the use of an additional radical initiator. Once the polymer is synthesized, it is stable against degradation by blue light (440 ± 10 nm), but upon exposure to UV radiation (310 ± 20 nm) a significant decrease in molecular weight is observed. The degradation is observed for all poly(PVK) materials synthesized.



POLY 162: RAFT emulsion polymerization: fundamentals and emerging materials

Yingwu Luo, yingwu.luo@zju.edu.cn. chemical and biological engineering, Zhejiang University, Hangzhou, China

Controlled/living radical polymerizations (CLRPs) have been developed into a powerful tool to synthesize well-defined (co)polymer with complex microstructures like block copolymer and gradient copolymer. Emulsion polymerization is not only a commercially desirable process but also fundamentally important for CLRP. It is a great challenge for CLRPs to synthesize high molecular weight polymer due to the existence of irreversible termination. The irreversible termination could be much suppressed thanks to the radical segregation effect, which is particularly significant in RAFT emulsion polymerization. However, RAFT emulsion polymerization is much more complicated than we thought due to the heterogeneous nature. Colloidal instability and lost control over molecular weight had been often observed. In this talk, we are going to touch on how the RAFT reactions interplays with the heterogeneous nature. We will summarize our fundamental understandings on following aspects: (1) The cause for colloidal instability and lost control over molecular weight; (2) Polymerization kinetics at extremely low initiation concentrations; (3) Particle activation/deactivation effects. We will demonstrate that how these understandings help to develop successful techniques to synthesize highly living polystyrene with molecular weight over 500 kg/mol and high molecular weight triblock and gradient copolymer. RAFT emulsion polymerization is opening up many opportunities to tailor-make the multi-functional materials of multi-block and gradient copolymers, which is not accessible previously.



POLY 163: Polymer-modified cellulose nanocrystals prepared by nitroxide-mediated polymerization and their use as CO₂-switchable Pickering emulsifiers

Joe Glasing², joe.glasing@queensu.ca, **Jean Bouchard**¹, **Philip G. Jessop**⁴, **Pascale Champagne**⁵, **Michael F. Cunningham**³. (1) FPInnovations, Pointe-Claire, Quebec, Canada (2) Chemical Engineering, Queen's University, Kingston, Ontario, Canada (3) Dept Chem Eng, Queens Univ, Kingston, Ontario, Canada (4) Dept of Chemistry, Queens Univ, Kingston, Ontario, Canada (5) Civil Engineering/Chemical Engineering, Queens University, Kingston, Ontario, Canada

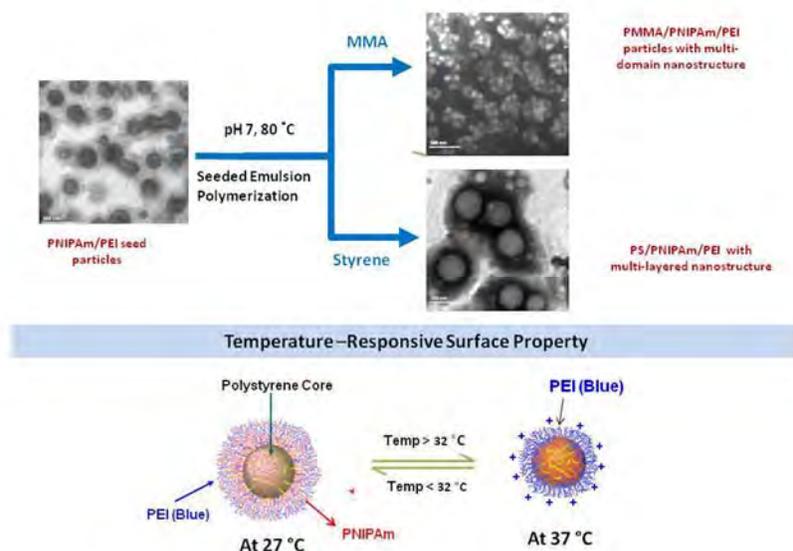
We have studied the use of a bio-sourced Pickering emulsifier based on cellulose nanocrystals (CNC) grafted with less than 25% of synthetic, CO₂-responsive polymer for the reversible emulsification/demulsification of oil and water. Following functionalization of the CNC surface with glycidyl methacrylate, CO₂-switchable poly(*N,N*-(diethylamino)ethyl methacrylate) (PDEAEMA) and poly(*N*-3-(dimethylamino) propyl methacrylamide) (PDMAPMAM) macroalkoxyamines with low dispersities, high livingness and chain end functionalities were grown through nitroxide-mediated polymerization (NMP) and grafted to the nanocrystals. Two different tertiary amine polymers were selected to investigate how differences in their pK_{aH} and T_g affected the final properties of the graft-modified CNC and the resulting Pickering emulsions. The graft molecular weight and graft density were shown to have an influence on the surface and interfacial properties of the Pickering emulsifiers, which were characterized by surface and interfacial tensiometer measurements. The resulting droplets obtained from oil in water emulsions were visualized using optical microscopy. The emulsification/demulsification process was found to be responsive to N₂ and CO₂, reversible and easily repeatable. The Pickering emulsifiers could be recovered after application, which would make this technology particularly interesting for oil water separation and enhanced oil recovery. The pK_{aH} of the grafted polymer and the polarity were correlated to the CO₂ bubbling time required to break the emulsion and to the emulsion stability (lifetime). The effects of chain length of the grafted polymer, graft densities, total amount of CO₂-switchable groups on the CNCs surface, and concentration of Pickering stabilizer on the properties of emulsions were investigated.



POLY 164: Synthesis of multi-component polymer particles with stimuli-responsive properties through a controlled semi-batch emulsion polymerization

Pei Li, pei.li@polyu.edu.hk, Chun Ho Yam, Cheng Hao Lee, Yuen Shan Siu, Kin Man Ho. Hong Kong Polytechnic Univ, Hung Hom Kowloon, Hong Kong

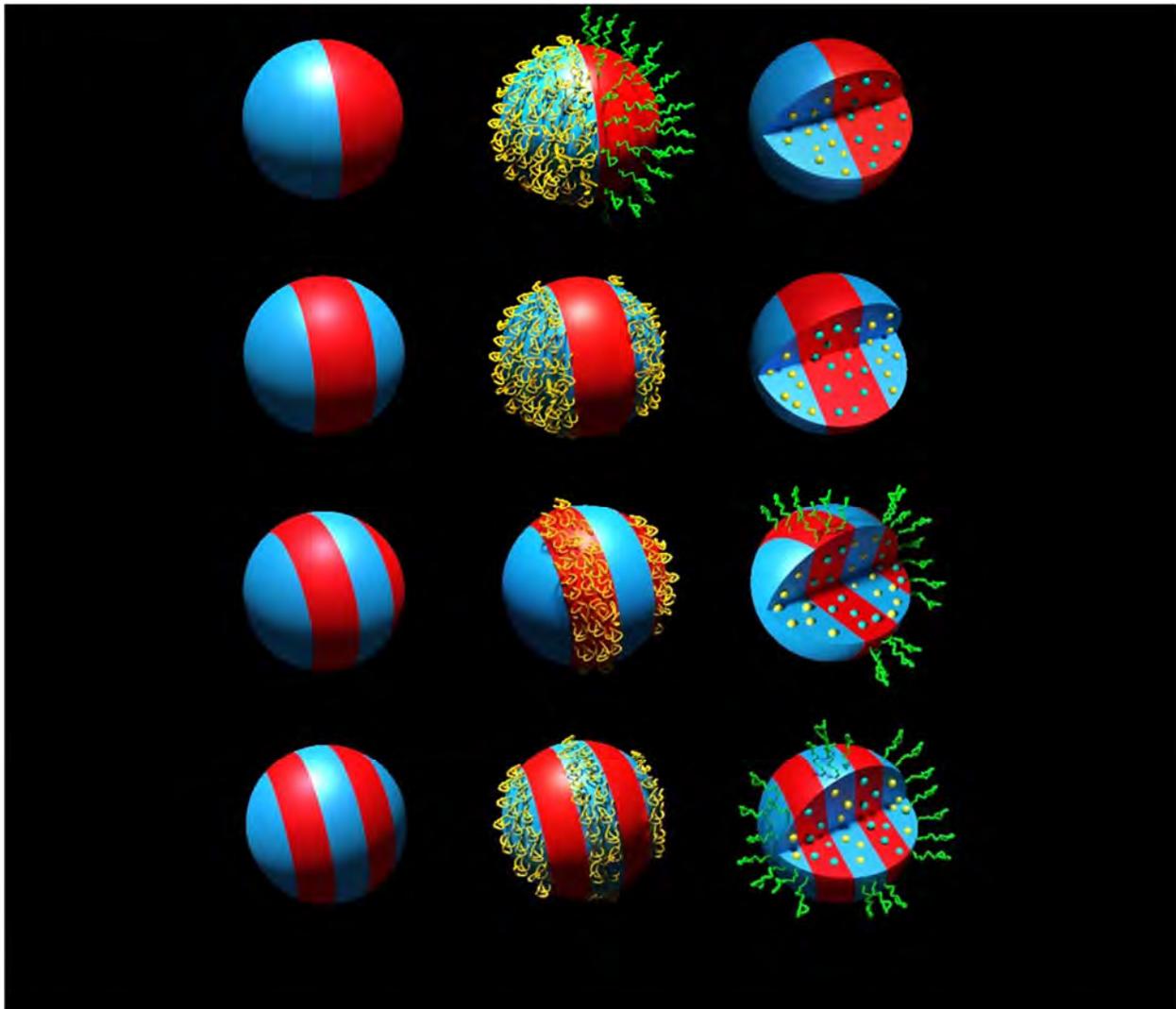
Multicomponent polymer (MCP) particles have received increasing attention because of their multiple functionalities, intriguing hierarchical nanostructures and synergistic properties due to their different chemical components. In this presentation, synthetic strategies to prepare dual stimuli-responsive amphiphilic particle that consists of a hydrophobic component, a pH-sensitive poly(ethyleneimine) (PEI) and a temperature-sensitive poly(*N*-isopropyl acrylamide) (PNIPAm) will be discussed. This type of smart multi-component polymer particles was prepared through a controlled semi-batch emulsion polymerization. It involved an initial formation of PNIPAm/PEI core-shell nanogel particle via a graft copolymerization of *N*-isopropyl acrylamide from PEI, followed by the seeded emulsion polymerization of methyl methacrylate or styrene. Properties of resultant MCP particles including particle composition, size, size distribution, surface charge, and morphology are described. Our studies show that morphologies of the MCP particles are strongly dependent on the crosslinking degree of the seed nanoparticle and chemical structure of the hydrophobic monomer. The addition of the MMA monomer in the second stage seeded emulsion polymerization generated PMMA/PNIPAm/PEI particles with the multi-domain nanostructure. On the other hand, the use of styrene resulted in multilayered polystyrene/PNIPAm/PEI particles. Variation of PNIPAm composition in the multilayered MCP particles could provide charge shielding and temperature tunable surface properties. The unique feature of temperature-dependent surface charge enables thermally triggered intracellular uptake of the nanoparticles into HeLa cells through varying temperatures at 27 and 37 °C. These results provide new insights into the design of future stimulus-responsive nanoparticle-based therapeutics.



POLY 165: Stimuli-responsive nano-colloids: Tutorial

Marek W. Urban, mareku@clemson.edu. *Material Sci Engineering, Clemson University, Clemson, South Carolina, United States*

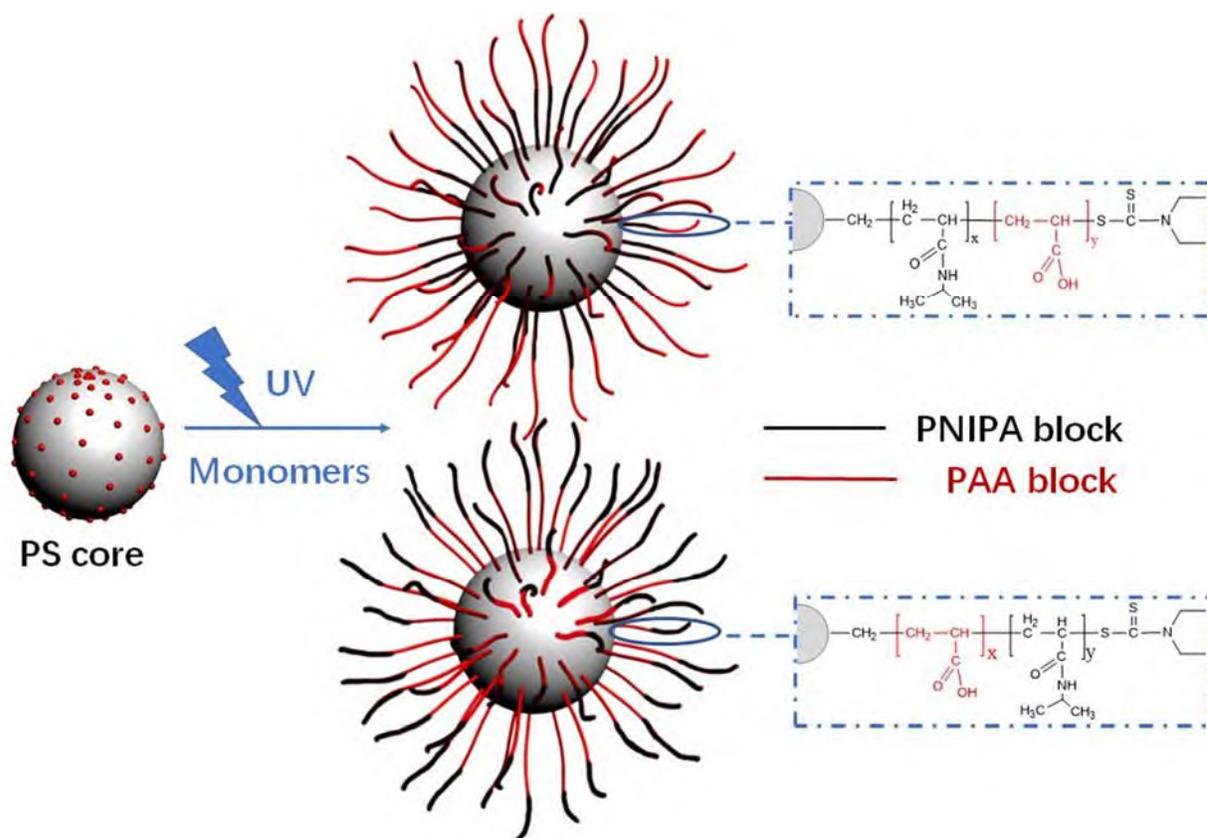
There is an increasing evidence that stimuli-responsive nanomaterials become significantly important components of modern materials developments. This Talk will outlines recent advances in synthesis and fabrication of stimuli-responsive polymeric colloids with built-in stimuli-responsive components and surface modifications of functional nanoparticles that facilitate responsiveness. The synthesis and construction of stimuli-responsive spherical, core-shell, concentric, hollow, Janus, gibbous/inverse gibbous, and cocklebur morphologies with the focus on shape, color, or size changes resulting from external stimuli will outlined. Selected surface reactions that lead to responsiveness achieved by decorating nanoparticles with stimuli-responsive polymers will be presented in the context of synthetic approaches facilitating controllable recognition, signaling, or sequential responses.



POLY 166: Temperature and pH responsive colloidal diblock copolymer brushes prepared via SI-PIMP

Lan Cao², Kaimin Chen¹, **Xuhong Guo**^{2,3}, guoxuhong@ecust.edu.cn. (1) College of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, Shanghai, China (2) School of Chemical Engineering, East China University of Sci and Tech, Shanghai, China (3) School of Chemistry and Chemical Engineering, Shihezi University, Shihezi, China

Temperature and pH responsive diblock copolymer brushes were synthesized via surface initiated photoiniferter mediated polymerization (SI-PIMP). In this work, N-isopropylacrylamide (NIPA) and acrylic acid (AA) were grafted from the PS cores by UV irradiation with the help of photoiniferter to prepare two different diblock copolymer brushes (PS@PNIPA-b-PAA, PS@PAA-b-PNIPA). FT-IR spectra and element analysis confirmed the diblock copolymer structure in the brush layer. TEM and SAXS were used to characterize the morphologies and structure of the two diblock brushes. And, data of dynamic light scattering and zeta potential studies showed that the diblock copolymer brushes responded to pH and temperature stimulations very well.

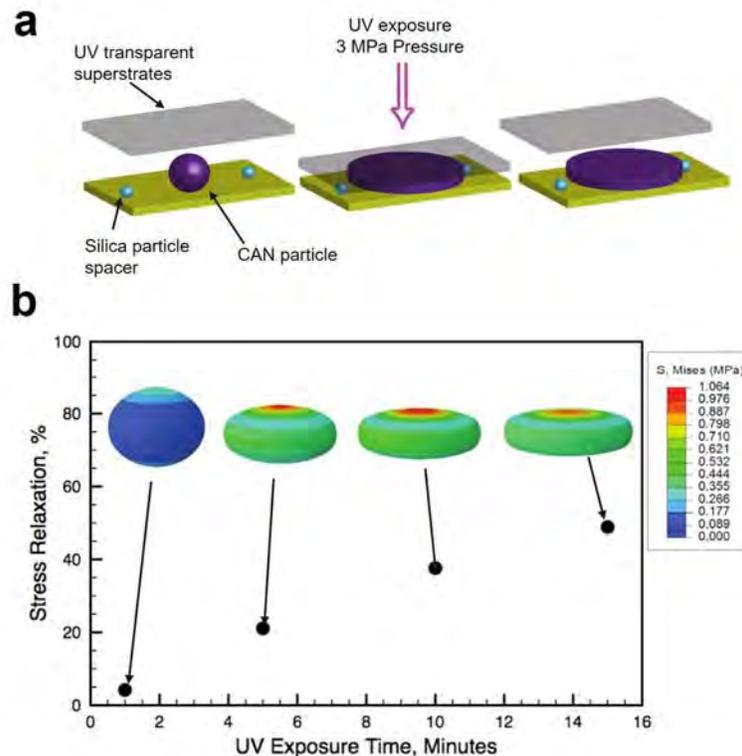


Preparation of colloidal diblock copolymer brushes.

POLY 167: Light-stimulated permanent shape reconfiguration in crosslinked polymer surfaces and microparticles

Lewis Cox^{1,2}, lewis.cox@nist.gov, **Xiaohao Sun**^{3,1}, **Chen Wang**⁴, **Nancy Sowan**⁴, **Jason Killgore**², **Jianliang Xiao**¹, **Rong Long**¹, **Hengan Wu**³, **Christopher Bowman**⁴, **Yifu Ding**¹, yifu.ding@colorado.edu. (1) Dept. Mechanical Engineering, UCB427, Univ. of Colorado, Boulder, Colorado, United States (2) NIST, Boulder, Colorado, United States (3) University of Science and Technology of China, Hefei, China (4) Chemical and Biological Engineering, University of Colorado, Boulder, Colorado, United States

Reconfiguring the permanent shape of chemically crosslinked polymers has been impossible due to the incapability for plastic deformation in these materials. Recent progresses in covalent adaptive network (CAN) chemistry can overcome this limitation. CANs are cross-linked polymer networks that are capable of reconfiguring their network topology, which enables stress relaxation and shape changing behaviors while maintain the degree of crosslinking. In this presentation, we show that CAN polymers based on reversible addition-fragmentation chain transfer (RAFT) mechanism can effectively allow us to permanently reconfigure the polymer surface topography as well as the overall shapes of CAN-based microspheres. The shape-reconfiguration process is carried out using a combined UV and thermal-embossing nanoimprinting lithography, where the polymer network rearrangement is triggered by UV radiation under controlled thermo-mechanical deformation. We demonstrate that the degree of shape reconfiguration can be reliably controlled by the NIL-process parameters and the composition of the CAN polymers.



POLY 168: Control of particle shape and internal morphology: Polymer self-assembly and monomer feed based approaches

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This presentation will comprise two different parts: (i) Synthesis of non-spherical particles using polymerization-induced self-assembly (PISA) based on conventional (non-living) radical polymerization, and (ii) synthesis and characterization of gradient polymer particles for coating applications.

PISA based on AFCT: The PISA technique to date depends on controlled/living radical polymerization (CLRP) approaches, most notably RAFT polymerization. A solvophilic block is chain extended with a monomer that yields a solvophobic block, resulting in generation of an amphiphilic diblock copolymer that subsequently self-assembles into polymer particles of a wide variety of morphologies depending on a number of experimental factors. This presentation will be concerned with a novel approach towards PISA, whereby diblock copolymers are generated in situ via conventional “non-living” addition-fragmentation chain transfer (AFCT) radical polymerization. This approach may have the potential to significantly expand the scope of PISA for synthesis of polymeric (nano)particles of a wide range of morphologies.

Gradient polymer particles: Many paints and coatings applications are based on waterborne latexes produced by emulsion polymerisation. Over the last decades, industry has pushed forward to develop novel speciality latexes to improve film properties and to remove volatile organic solvents. Gradient particles are nano-sized polymer particles where the composition of the polymer continuously varies as a function of the radius from the centre of the particle. Until recently, it has been challenging to experimentally confirm the existence of such internal morphologies. We have developed an approach based on X-ray photoelectron spectroscopy (XPS) that has allowed us to quantify the internal morphology and experimentally demonstrate the existence of such gradient nanoparticles.

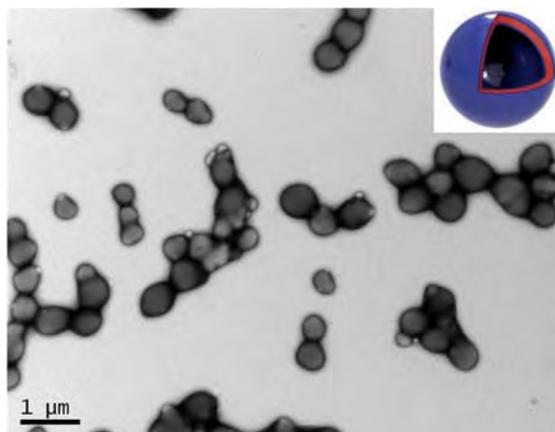
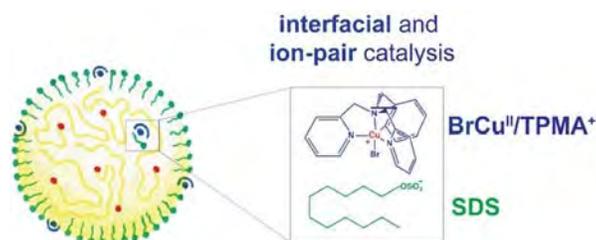


Fig. 1. Vesicles obtained by polymerization-induced self-assembly (PISA) based on a conventional (non-living) radical polymerization system.

POLY 169: *Ab-initio* emulsion ATRP by interfacial and ion-pair catalysis

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Pennsylvania, United States

A new ion-pair catalyst for (mini)emulsion atom transfer radical polymerization (ATRP) is presented. The ion-pair complex controlled a (mini)emulsion ATRP from both the inside and the interface of monomer droplets, allowing for the preparation of complex polymeric architectures with only part per billion (ppb) of residual copper. Conditions for *ab-initio* emulsion ATRP are discussed: initiation occurred exclusively in the continuous aqueous phase, followed by micellar nucleation. Size and rheology of droplets were tuned by changing type of surfactant and polymerization initiator.

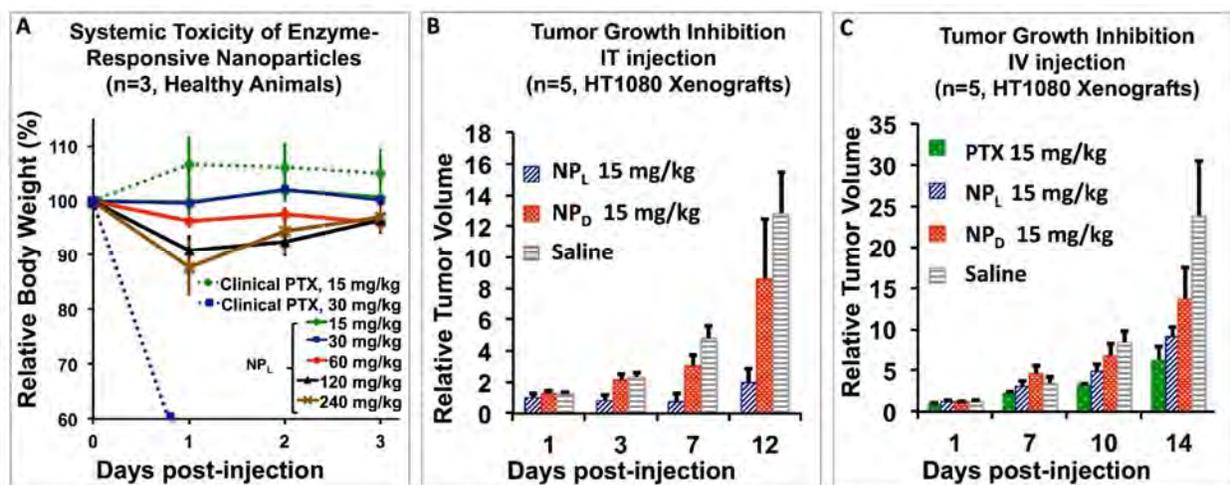


POLY 170: Seek, destroy and heal: Enzyme-responsive nanoparticles as *In vivo* targeted delivery systems

Nathan C. Gianneschi, ngianneschi@ucsd.edu. Chem M/C 0343, University of California, San Diego, La Jolla, California, United States

The goal of targeted therapeutics and molecular diagnostics is to accumulate drugs or probes at the site of disease in higher quantities relative to other locations in the body. To achieve this, there is tremendous interest in the development of nanomaterials capable of acting as carriers or reservoirs of therapeutics and diagnostics *in vivo*. The general goal is that particles will either target passively via the enhanced permeability and retention (EPR) effect, actively by incorporation of targeting groups, or by a combination of both. Nanoparticle targeting strategies have largely relied on the use of surface conjugated ligands designed to bind overexpressed cell-membrane receptors associated with a given cell-type.

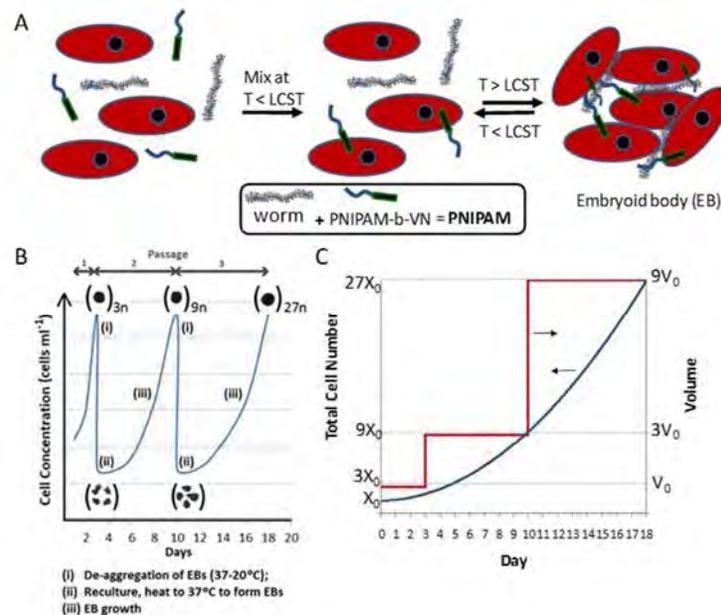
We envisioned a targeting strategy that would lead to an active accumulation of nanoparticles by virtue of a supramolecular assembly event specific to tumor tissue, occurring in response to a specific signal. The most desirable approach to stimuli-induced targeting would be to utilize an *endogenous* signal, specific to the diseased tissue itself, capable of actively targeting materials introduced via intravenous (IV) injection. We present the development of nanoparticles capable of assembling *in vivo* in response to selective, endogenous, biomolecular signals. For this purpose, we utilize enzymes as stimuli, rather than other recognition events, because they are uniquely capable of propagating a signal via catalytic amplification. We will describe the preparation of highly functionalized polymer scaffolds, their development as *in vivo* probes and their utility as a multimodal imaging platform and as drug carriers capable of targeting tissue via a new mechanism. Furthermore, we will describe new methods and approaches for characterizing this kind of dynamic material at the nanoscale, including by liquid cell transmission electron microscopy and combined isotopic and optical



POLY 171: Thermoresponsive worms for expansion and release of human embryonic stem cells

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The development of robust suspension cultures of human embryonic stem cells (hESCs) without the use of cell membrane disrupting enzymes or inhibitors is critical for future clinical applications in regenerative medicine. We have achieved this by using long, flexible and thermoresponsive polymer worms decorated with a recombinant vitronectin subdomain that bridge hESCs, aiding in hESC's natural ability to form embryoid bodies (EBs) and satisfying their inherent requirement for cell-cell and cell-extracellular matrix contact. When the EBs reached an optimal upper size where cytokine and nutrient penetration becomes limiting, these long and flexible polymer worms facilitated EB breakdown via a temperature shift from 37 to 25 °C. The thermoresponsive nature of the worms enabled a cyclical dissociation and propagation of the cells. Repeating the process for three cycles (over eighteen days) provided a >30 fold expansion in cell number while maintaining pluripotency, thereby providing a simple, non-destructive process for the 3D expansion of hESC.

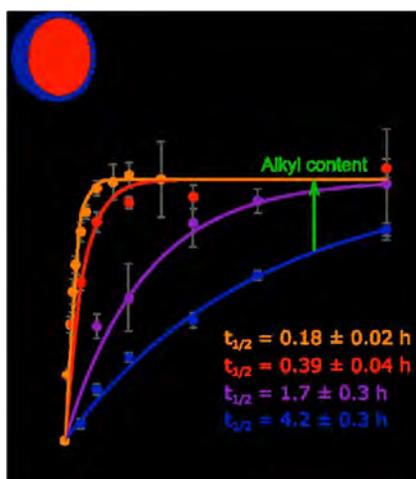


3D expansion of hESC using thermoresponsive worms. (A) Proposed mechanism for temperature reversible hESC 3D clustering (EBs) and release using PNIPAM-b-VN and pBridges (the combination of which is denoted as PNIPAM). (B) Schematic representation for expansion and aggregation breakdown of hESC EBs using PNIPAM-b-VN and pBridges. (C) Representation for hESC expansion with de-aggregation based on the process in graph B: total volume increases 3-fold on each passage.

POLY 172: Tuning release of signaling molecules by controlling mobility in a micelle core

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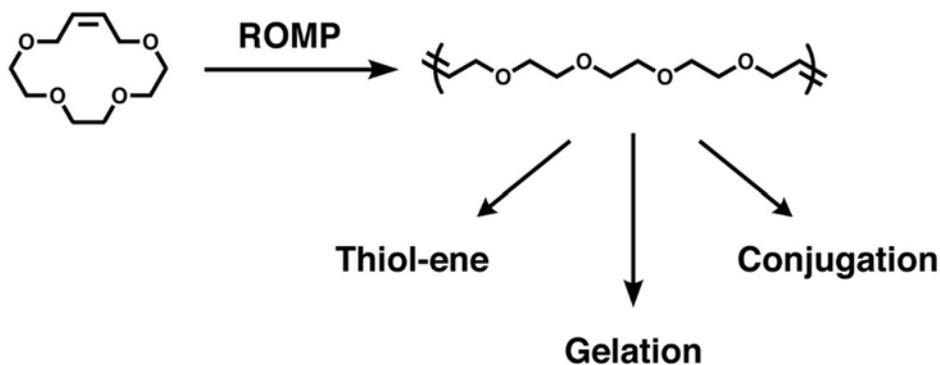
Drug delivery from polymer micelles has been widely studied for decades, but methods to precisely tune rates of drug release from micelles are limited. Here we use the mobility of the hydrophobic micelle core to tune the rate at which a covalently bound drug is released. Our drug of interest is hydrogen sulfide (H₂S), a signaling gas with therapeutic potential. In this system, we appended thiol-triggered H₂S donor molecules onto the hydrophobic block. Because release of H₂S is triggered by cysteine, diffusion of cysteine into the hydrophobic micelle core controls the rate of release. Here we show how the careful tuning of the glass transition temperature of the core block can be used to tune the release rate of H₂S over nearly an order of magnitude.



POLY 173: ROMP PEG (rPEG): Synthesis and functionalization of a versatile PEG analog

Emma Pelegri-O'Day, epelegrioday@gmail.com, Nicholas Matsumoto, Eric Raftery, Uland Lau, Heather D. Maynard. UCLA, Los Angeles, California, United States

Poly(ethylene glycol) (PEG) is widely used in biomaterials, but the synthesis of PEG using ionic polymerization requires rigorous conditions and limits functionalization of the polymer to the end-groups. Herein we report the synthesis of a versatile PEG analog using ring-opening metathesis polymerization (ROMP). A series of polymers with aldehyde end-groups were prepared with varying molecular weights. The ROMP PEG (rPEG) polymers were conjugated to proteins via reductive amination. In vitro experiments showed that rPEGs were non-cytotoxic up to 1 mg/mL and were biocompatible. Additionally, the backbone alkenes were modified with various mercaptans using highly efficient and functional group tolerant thiol-ene chemistry. Organogels could also be easily synthesized by using dithiols. This approach enables the functionalization of PEG polymers with a wide range of side chains and presents a novel family of PEG analogs that can be used in the development of next-generation protein-polymer conjugates.



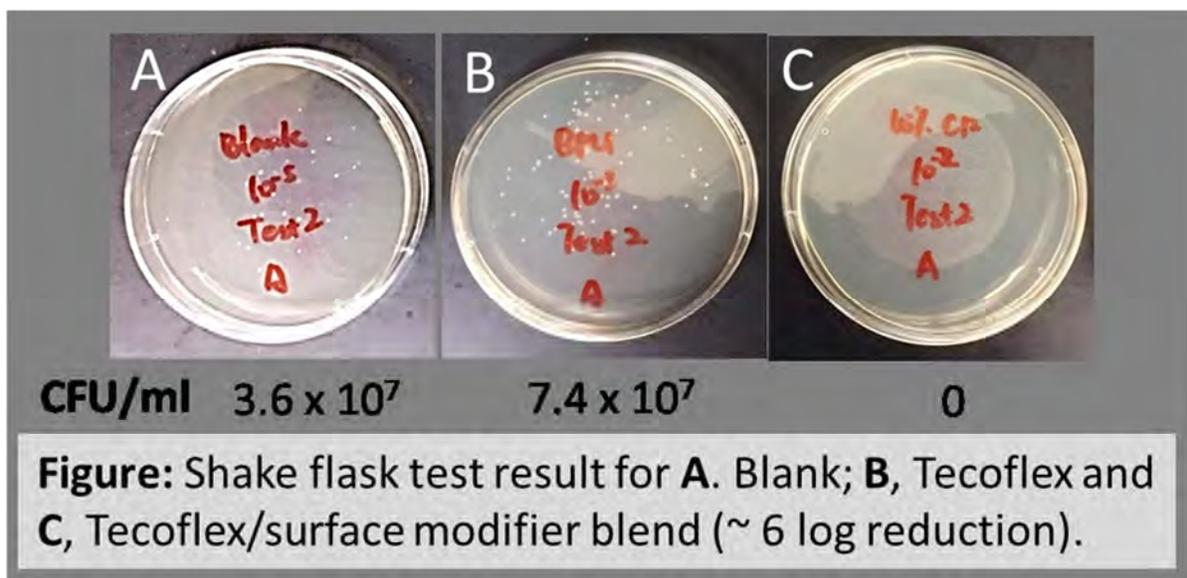
POLY 174: Nanostructural design, synthesis and characterization of antimicrobial and cytocompatible polymer surfaces

Kenneth J. Wynne¹, kjwynne@vcu.edu, **Chenyu Wang**¹, **Olga Y. Zolotarskaya**², **Xuejun Wen**¹, **Daniel Johnson**³. (1) VCU Dept of Chem Engr, Richmond, Virginia, United States (2) Chemical & Life Science Eng, Virginia Commonwealth U, Richmond, Virginia, United States

Soft surface science and engineering in the context of this work emphasizes coatings (~50 nm, bulk) rather than nanofilms. Nanosurface (1-2 nm) modification is obtained by a blend approach using a commodity bulk polymer and a tailored polymer surface modifier. Targets for this work are antimicrobial effectiveness with cytocompatibility, stability, and economy. These criteria are essential for transformation of conventional polymers into “soft” biomaterials for biomedical applications.

Polyurethanes with brush-like soft blocks having PEG and quaternary side chains are used to modify conventional polyurethanes. One physical criterion is stability of nanosurface quaternary charge density monitored by zeta potentials. Interestingly, the zeta potential for the modified coating is about 100 mV higher than the control polyurethane. Following these measurements an ASTM E2149 - 13a Standard Test Method for Determining the Antimicrobial Activity of Antimicrobial Agents Under Dynamic Contact Conditions was carried out (Figure). A >5 log reduction was typical against challenges of *E. coli*. An *in vitro* test in the presence of a human cell line demonstrated good biocompatibility.

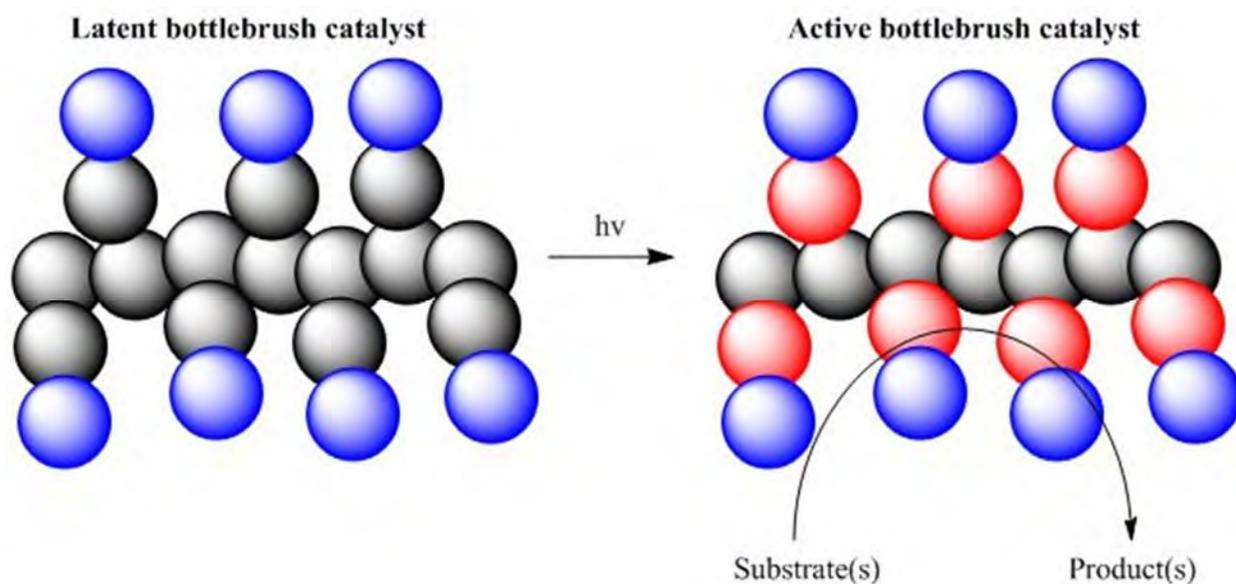
Taken together, a body of evidence is being acquired to support our model for development of Antimicrobial-But-Cytocompatible (ABC) nanosurfaces on conventional polymers used in biomedical applications. The significance of this work lies in a new approach that avoids antibiotic and biocide resistant bacteria or “super bugs”. In this regard, a challenge of future work is showing that bacteria do not develop resistance to ABC modified nanosurfaces.



POLY 175: Bottlebrush nanoreactors for In situ synthesis

Jeffrey Foster, jeff23@vt.edu, Rachel K. O'Reilly. Dept of Chemistry, University of Warwick, Coventry, United Kingdom

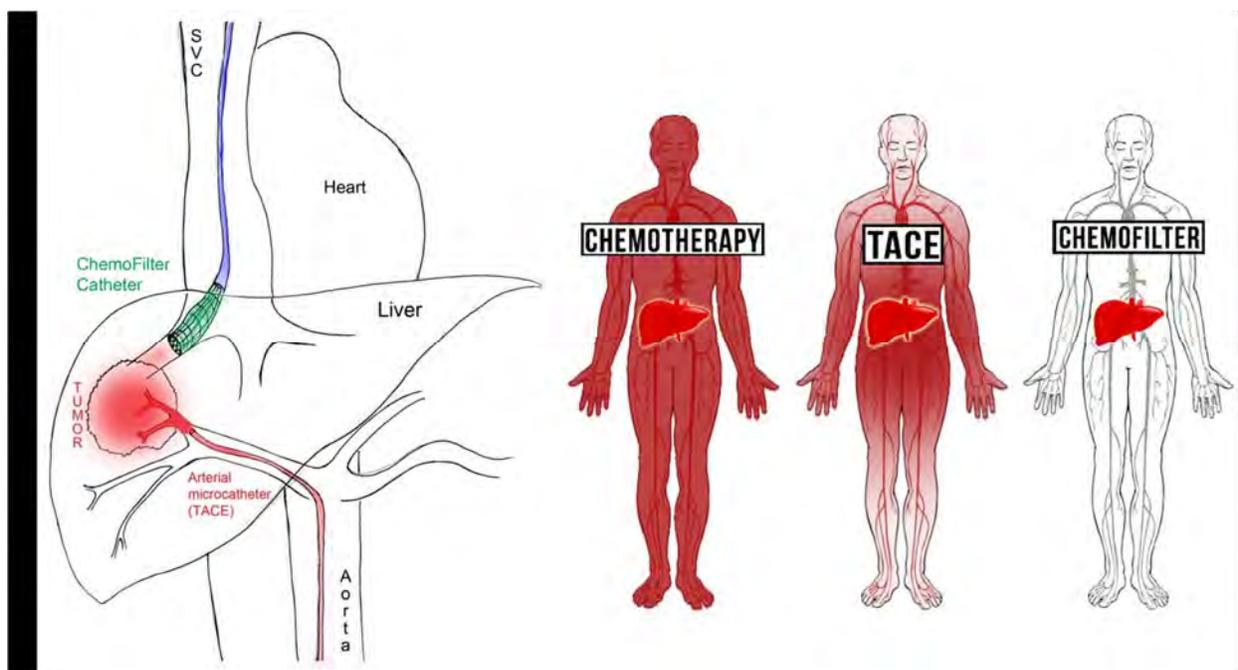
Bottlebrush polymers are shape-persistent, single macromolecules consisting of a polymer backbone functionalized with many polymer sidechains. This rich polymer topology is unique because bottlebrush polymers differ from their linear analogues in their size, shape persistence, cylindrical nanostructure, and their inability to interact through chain entanglement. Despite this versatility, to date, the applications of bottlebrush polymers remain largely unexplored. Here, we utilize bottlebrush polymers as nanoreactors—a novel application which takes advantage of their shape-persistent nature. Core-shell bottlebrush polymers were prepared that contained latent catalyst residues. Upon UV irradiation, these bottlebrush nanoreactors catalysed reactions between encapsulated molecules to generate compounds in situ triggered by an external stimuli.



POLY 176: Materials for drug capture: An approach to reducing the off-target toxicity of chemotherapy

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(1) Chemistry, Virginia Tech, Blacksburg, Virginia, United States (2) Radiology, University of California, San Francisco, San Francisco, California, United States

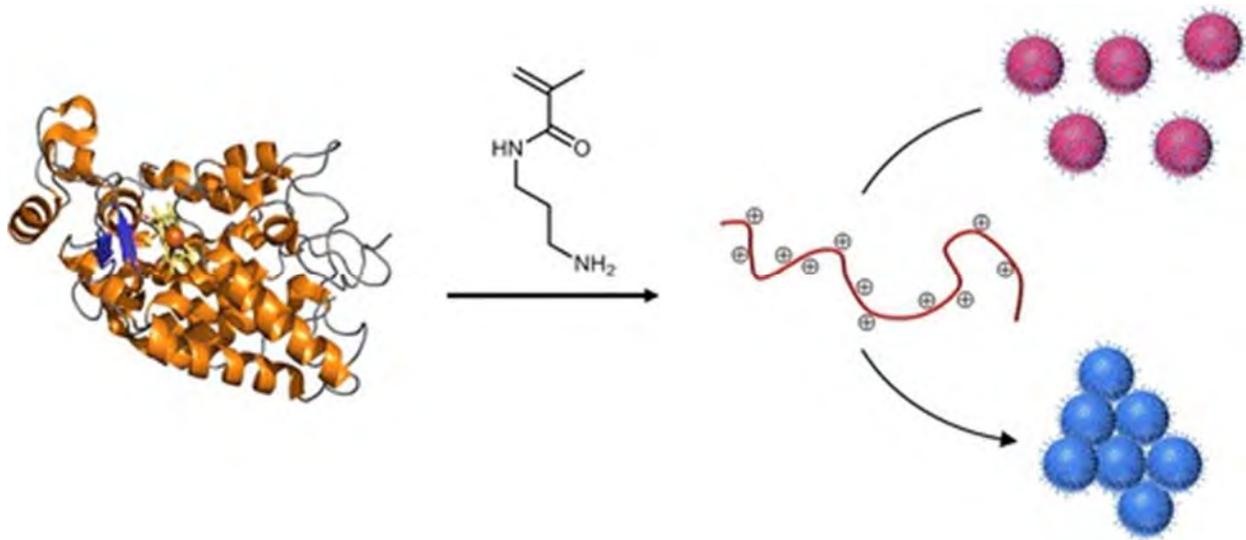
The off-target toxicity of chemotherapy is a well-known problem in oncology. To overcome this challenge, many approaches have been developed to selectively deliver chemotherapy directly to the tumor. One such approach is transarterial chemoembolization (TACE), in which chemotherapy is introduced via catheter directly into the tumor vasculature. Despite this site-specific delivery, however, about half of the chemotherapy dose passes through the tumor, enters systemic circulation, and causes off-target damage. To address this problem, we are developing materials that are capable of capturing this residual chemotherapy from the bloodstream. Ultimately, these materials will be used to construct a device (a "chemofilter") that can be deployed via catheter "downstream" from the tumor, enabling excess chemotherapy to be intercepted and sequestered before entering systemic circulation. Our approach involves the covalent attachment of genomic DNA to surfaces, which enables the capture of DNA-targeting chemotherapy agents. We have explored several methods of achieving DNA attachment and have investigated the ability of different materials to remove chemotherapy agents from biologically relevant solutions. We have observed effective drug capture from solution at clinically relevant concentrations and timescales, indicating that drug capture is a viable strategy for mitigating the harmful side-effects associated with chemotherapy.



POLY 177: New polymer based approaches for biosensing and regenerative medicine

Molly Stevens, *m.stevens@imperial.ac.uk*. *Materials and Bioengineering, Imperial College London, London, United Kingdom*

Bio-responsive nanomaterials are of growing importance with potential applications including drug delivery, diagnostics and tissue engineering. A disagreeable side effect of longer life-spans is the failure of one part of the body – the knees, for example – before the body as a whole is ready to surrender. The search for replacement body parts has fuelled the highly interdisciplinary field of tissue engineering and regenerative medicine. This talk will describe our research on the design of new materials to direct stem cell differentiation for regenerative medicine. This talk will also provide an overview of our recent developments in the design of materials for ultrasensitive biosensing. We are applying these biosensing approaches both in high throughput drug screening and to diagnose diseases ranging from cancer to global health applications.

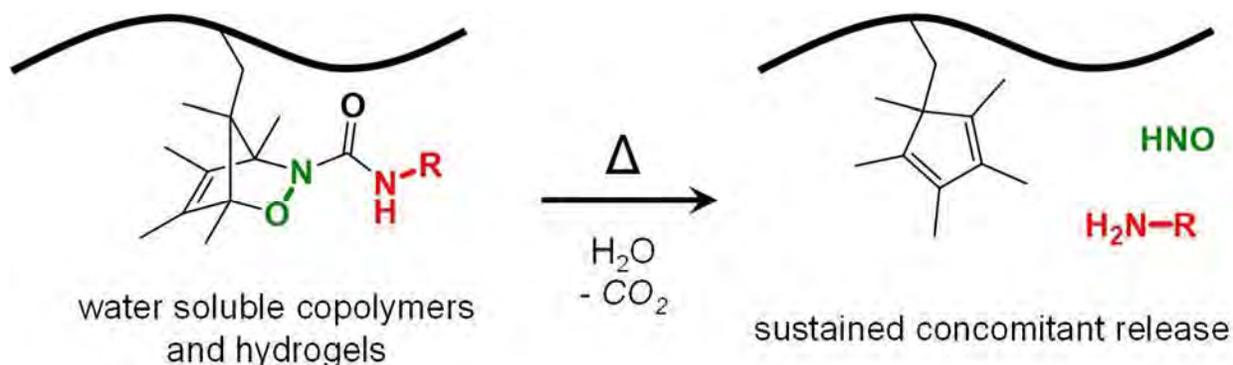


Polymerization Amplified Detection for Nanoparticle-Based Biosensing

POLY 178: Investigation of 1,2-oxazines: Dynamic covalent chemistry and structure-dependent thermal activation

Andrew J. Boydston, boydston@chem.washington.edu, Chang-Uk Lee, Derek Church. Chemistry, University of Washington, Seattle, Washington, United States

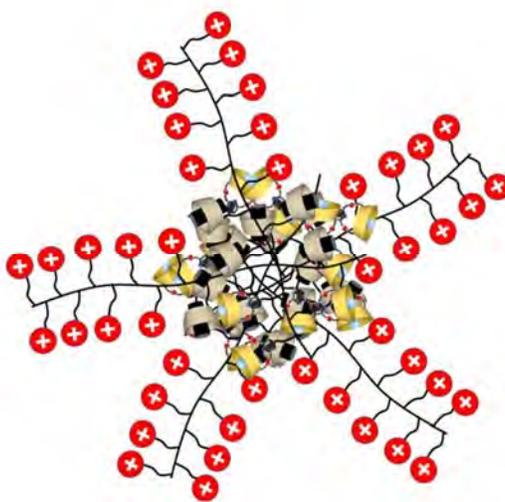
We are studying the structure-reactivity profiles of oxazines derived from carbamoylnitroso species and various 1,3-dienes. The oxazines exhibit structure-dependent isomerization via cycloaddition/cycloreversion pathways. Notably, the carbamoyl moiety strongly influences the rate of isomerization as well as the propensity for hydrolysis. The oxazine building blocks may find application as thermally-activated crosslinkers for formation of covalent adaptable networks or stimuli-responsive carriers of HNO. Both the cycloreversion and hydrolysis rates are key to directing the potential utility of these systems, as is their incorporation into suitable macromolecular frameworks



POLY 179: Supramacromolecular strategy to combat multidrug-resistant bacteria

Jonathan Barnes¹, jcbarnes@wustl.edu, Xuesong Li³, Abby Delawder². (1) Chemistry, Washington University, St. Louis, Missouri, United States (2) Chemistry, Washington University in St. Louis, St. Louis, Missouri, United States

The continual rise of antibiotic resistance – coupled with the shrinking pipeline of new antibiotics – poses a major threat to global health. The traditional approach to solve this growing problem typically relies on developing structural analogs of existing antibiotics, pursuing new leads, or even revisiting previous compounds that were at one point considered very toxic. Combination therapy that combines multiple small-molecule antibiotics into one treatment is also a common strategy to overcome resistance in bacteria, however, it can also be quite toxic. In recent years, these approaches have not only been outpaced by the onset of resistance, but the situation is exacerbated by the fact that the number one reason most antibiotics fail is due to a lack of solubility in water and their inability to permeate bacterial cell membranes. In my presentation, I will describe a different strategy that my laboratory is currently investigating; one which involves precise supramolecular receptors built into a polymer platform, where each receptor can be loaded with different combinations of antimicrobial agents, depending on the type of multidrug-resistant bacteria that is to be treated. Moreover, this platform is easily converted into larger nano-based structures, which stabilize the loaded drugs and allows for selective targeting of bacteria through specific cell surface-based interactions. Since no pro-drugs are involved, the mechanism of action of each agent is unperturbed and each undergoes slow release in a predictable manner. Lastly, I will discuss *in vivo* efficacy studies against different drug-resistant bacterial strains, and how our next-generation platform is an ideal material for sustained protection that may prove useful in wound healing applications, among others.



POLY 180: Frontal polymerization for art and rapid repairs

John A. Pojman, john@pojman.com. Chemistry, Louisiana State University, Baton Rouge, Louisiana, United States

The goal of cure-on-demand polymerization is to create one-pot systems that have a long shelf life but will react rapidly when curing is desired. We demonstrate that frontal polymerization can be used to create a cure-on-demand putty for filling holes in wood, marble, and sheet rock. The putty has a months-to-years shelf life, is a one-pot formulation, can be applied leisurely and then cured rapidly with a heat source. We also demonstrate frontal polymerization can be used to create an adhesive for wood and plastic-wood composites that cures rapidly and has impressive shear strength. Finally, we will explore current efforts to commercialize “3P QuickCure Clay” for the art market and “3P QuickCure WoodFiller” for home repair.



Sculpture (by Shelby Prindaville) made with a cure-on demand material, QuickCure Clay.



a cure-on demand wood repair

POLY 181: Dual-cure initiating systems for photoinduced frontal cationic polymerization: application to carbon composite

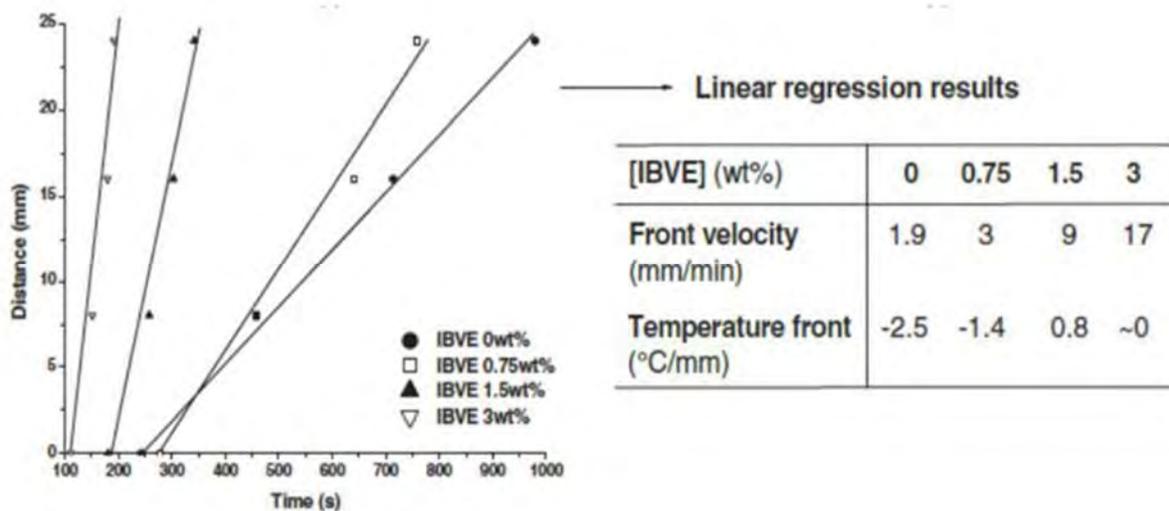
Xavier Allonas, *xavier.allonas@uha.fr*, **Maxime Lecompère**, **David Maréchal**, **Adrien Criqui**. *University of Haute Alsace, Mulhouse, France*

Dual-cure initiating systems have emerged as promising alternatives to perform fast and on-demand curing of thick polymers. From that perspective, photoinduced frontal polymerization appears as an attractive technology for the fabrication of fiber-reinforced polymers in a fast time scale. Recently, a system based on pyrylium salt/hydroperoxide has been reported to be efficient in the polymerization of epoxide resins [1-2]. The chemical mechanisms involved were studied by ESR, laser flash photolysis and fluorimetry. It was found that the interaction between pyrylium salts and hydroperoxide releases a proton that could initiate the polymerization reaction at room temperature as well as under UV light. The combination of both methods allows the polymerization of a thick sample by photoinduced thermal polymerization.

Further evolution of the technology has led to the consideration of vinyl ethers as coinitiators for dual-cure initiating systems based on pyrylium salts [3]. Both photochemical and thermal initiation of oxirane monomers was found to be possible when using isobutyl vinyl ether (IBVE). The combination of both possibilities allows the curing of thick samples through photoinduced frontal polymerization with front speeds ranging from 1.9 to 17 mm/min (Figure 1).

On the basis of quantum calculations and photochemical experiments, some clues are given about the reaction mechanisms involved. Interestingly, a sequential kick-starting effect is observed in the presence of vinyl ether enabling the curing of oxetane monomers.

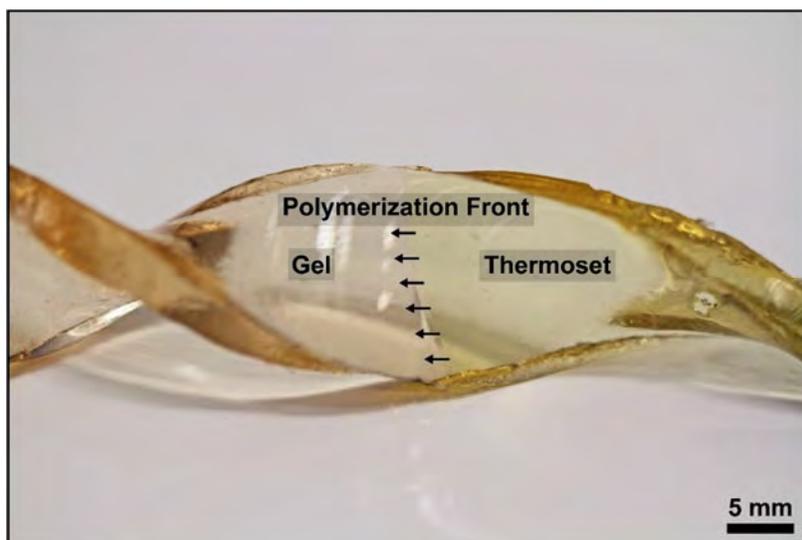
Finally, these dual-cure initiating systems were used to create thick carbon fiber reinforced polymers using a robotized irradiation under LED at 395 nm.



POLY 182: Frontal polymerization of gels derived from dicyclopentadiene

Evan M. Lloyd^{1,3}, elloyd3@illinois.edu, Leon M. Dean^{1,2}, Edgar B. Mejia^{1,4}, Nancy R. Sottos^{1,2}, Jeffrey S. Moore^{1,5}, Scott R. White^{1,6}. (1) Beckman Institute for Advanced Science and Technology, Urbana, Illinois, United States (2) Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States (3) Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States (4) Mechanical Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States (5) Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States (6) Aerospace Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States

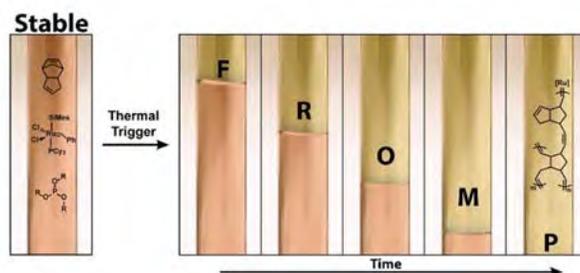
Alkyl phosphite inhibition of the frontal ring opening metathesis polymerization of dicyclopentadiene catalyzed by 2nd generation Grubbs catalyst has revealed a slow bulk polymerization at room temperature. The bulk polymerization did not result in spontaneous frontal polymerization, as with previous frontal polymerization chemistries, but instead, manifested as a liquid to gel transition. By tuning the concentration of alkyl phosphite, a variety of rheological profiles, including high-viscosity fluids and free-standing elastomeric gels, were obtained within several hours. The high-viscosity fluid was utilized for 3D printing via extrusion through a cooled print head onto a heated platform, which initiated the frontal polymerization. The elastomeric gels could be shaped, stamped with macro- and micro-patterns, or cut and joined before frontal polymerization. Frontal polymerization of the gel resulted in a structural thermoset fixed with the chosen morphology. To better understand the liquid to gel transition and optimize the preparation of frontally polymerizable gels, the degree of cure, shear storage and loss moduli, and polymerization front velocity in reactive formulations were tracked over time. The mechanical properties of the obtained thermosets were found to be independent of the amount of time the reactive formulation was aged, provided that frontal polymerization was sustained. The functional lifespan of the gels, the interfacial strength of gel-fused thermosets, and the applications of frontally polymerizable gels in on-demand production of complex structural parts will also be discussed.



POLY 183: Frontal ring-opening metathesis polymerization for rapid curing of fiber-reinforced composites

Leon M. Dean, *lmdean2@illinois.edu*, Ian Robertson, Mostafa Yourdkhani, Polette Centellas, Douglas Ivanoff, Jeffrey S. Moore, Scott R. White, Nancy R. Sottos.
University of Illinois Urbana-Champaign, Champaign, Illinois, United States

Frontal ring-opening metathesis polymerization (FROMP) is a promising technique for rapid, energy-efficient production of materials. The highly exothermic FROMP reaction is driven by the release of ring strain in dicyclopentadiene (DCPD) monomer during polymerization in the presence of a ruthenium-based second generation Grubbs' catalyst (GC2). A local thermal stimulus activates latent catalyst in neat DCPD, initiating polymerization and releasing heat, thus activating additional catalyst. This chain reaction results in a self-propagating polymerization front which rapidly converts all available monomer into a fully cured cross-linked polymer. One of the principal limitations of previous FROMP systems was pot life. We recently discovered that alkyl phosphites serve as effective inhibitors for GC2 in the FROMP of DCPD, increasing pot life up to 140× while still allowing frontal polymerization at relatively high frontal velocities. The increased working time has enabled significant advances in the manufacturing of polymers and composites via frontal polymerization. Fiber-reinforced polymer composites with mechanical properties comparable to conventionally manufactured aerospace-grade bisphenol A epoxy composites were manufactured with significantly less energy and time input. FROMP manufacturing can reduce the energy required to fully cure large components by more than ten orders of magnitude while simultaneously reducing the curing time by more than two orders of magnitude. Experimental and computational studies are ongoing to elucidate the physical and chemical factors that affect the required energy input and curing time.

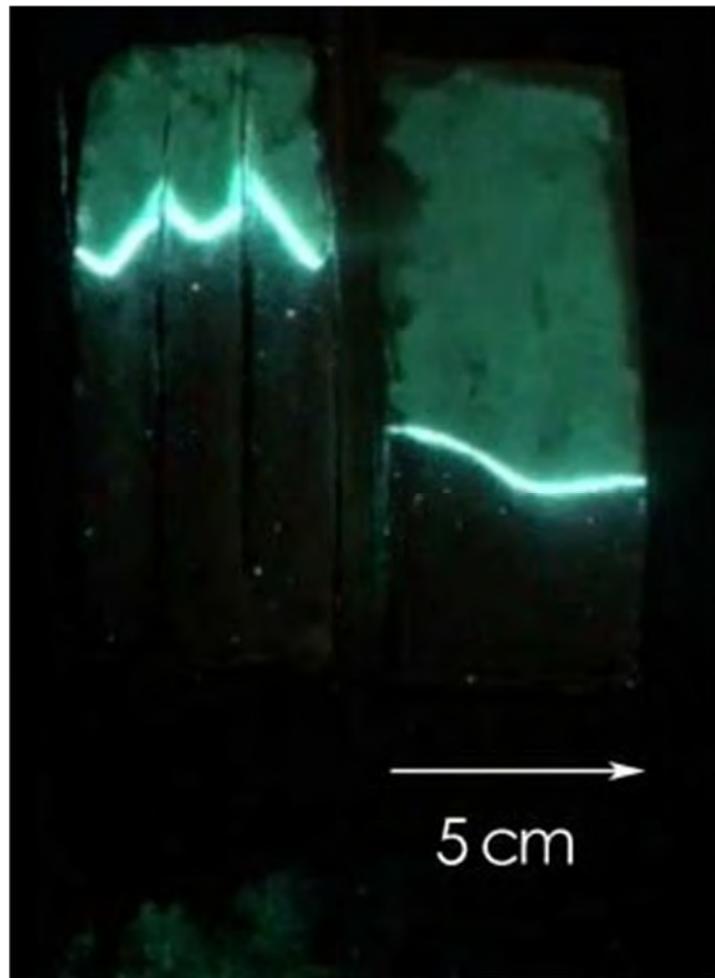


Liquid resin containing DCPD, GC2, and an alkyl phosphite inhibitor remains stable for up to 30 h. An on-demand thermal trigger initiates FROMP, transforming the liquid resin (pink) into a solid cross-linked polymer (yellow).

POLY 184: The effect of conductive material to modulate front velocities in self-propagating thermal frontal polymerization systems

*John A. Pojman, **Corey Weber**, cweber2@lsu.edu. Chemistry, Louisiana State University, Gonzales, Louisiana, United States*

Thermal frontal polymerization is a process whereby an initiator and monomer are heated to the extent of generating a front. We used trimethylol propane triacrylate with an initiator (Luperox 231), and kaolin to create a moldable medium for frontal polymerization. We used thin copper strips and wires to increase the front velocity and affect the direction of propagation. To visualize the front position, we used a europium-based phosphorescent powder.



A view of the effect of thin copper strips conducting heat to advance thermal fronts (left), versus an identical medium with no influence of copper (right).

POLY 185: Frontal polymerization: A valuable method for obtaining functionally gradient materials

G Malucelli³, giulio.malucelli@polito.it, Alberto Marian², Daniele Nuvol², Valeria Alzar², John A. Pojman¹. (1) Chemistry, Louisiana State University, Baton Rouge, Louisiana, United States (2) Dept of Chemistry Pharmacy, University of Sassari, Sassari, Italy (3) Applied Science and Technology, Politecnico di Torino, Alessandria, Italy

Functionally gradient materials (FGMs) show gradual and continuous changes of their properties in one or more dimensions: this peculiarity justifies the growing interest they are obtaining, both from academics and industries. The manufacturing of these materials with an accurate control of the gradient, especially when the gradient is non-linear, is not easy. In this work, frontal polymerization (FP) was utilized for synthesizing polymeric FGMs. An ascending FP with continuous feeding of monomers with computer-controlled peristaltic pumps was exploited for obtaining FGMs with programmed gradients. In particular, copolymers made from triethyleneglycol dimethacrylate/hexyl methacrylate with linear and hyperbolic gradient in composition were synthesized and thoroughly characterized.

A linear dependence of the T_g values on the FGM composition was observed, in agreement with the theoretical trends calculated by the Fox equation. Conversely, the other properties (Shore A hardness measurements, compression tests and swelling studies) exhibited different and peculiar behaviors as a function of the compositional gradient.

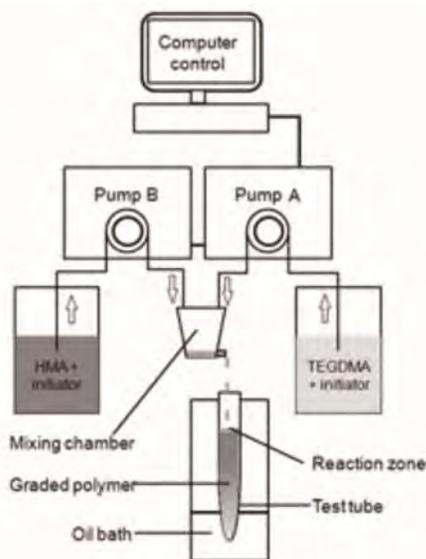


Figure 1. Scheme of the apparatus utilized for preparing gradient polymeric materials.

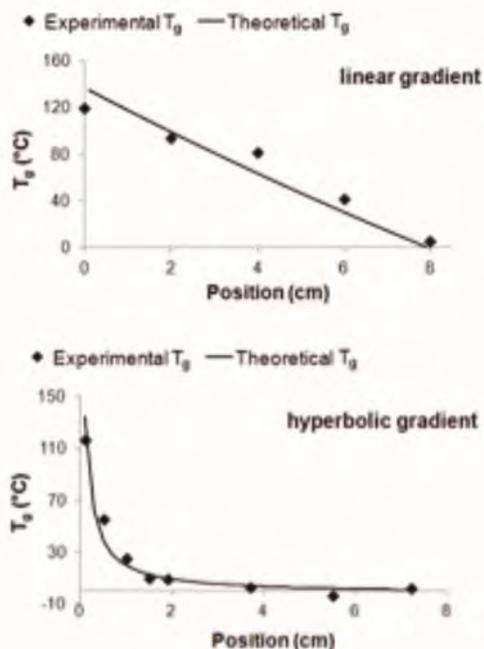
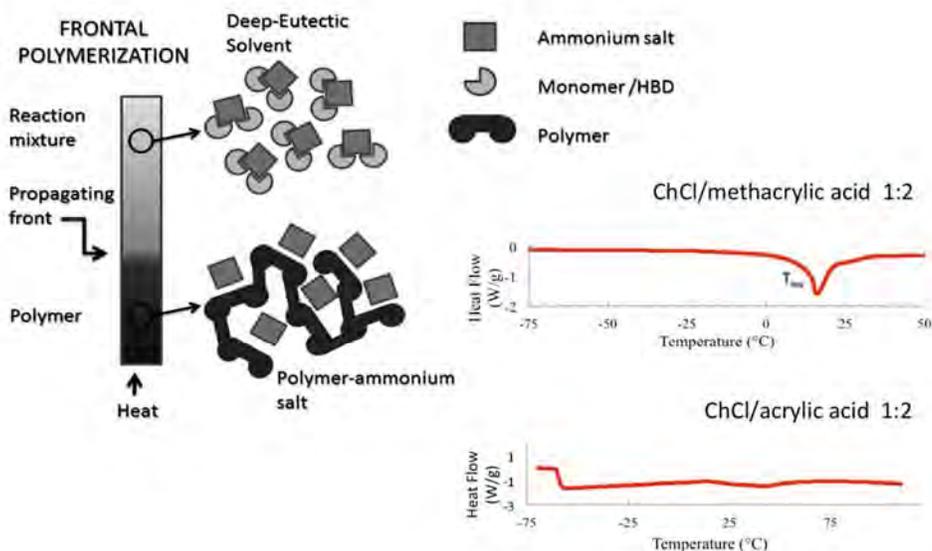


Figure 2. Experimental T_g values as a function of position and theoretical T_g trend determined by the Fox equation for the two types of gradient.

POLY 186: Behavior of acrylates forming deep-eutectic solvents in thermal frontal polymerizations by free radicals

Josue D. Mota-Morales², *jmotam@fata.unam.mx*, **Kylee F. Fazende**¹, **John A. Pojman**¹.
(1) Chemistry, Louisiana State University, Baton Rouge, Louisiana, United States (2) Centro de Física Aplicada y Tecnología Avanzada, Universidad Nacional Autónoma de México, Querétaro, Querétaro, Mexico

Frontal polymerization (FP) is the type of polymerization that relies on a localized reaction zone that propagates through an unstirred medium, due to the coupling of thermal transport and the Arrhenius dependence of an exothermic polymerization. FP is normally performed with neat monomers but can be also accomplished in solution. In this contribution the behavior of acrylates such as acrylic acid and methacrylic acid forming deep eutectic solvents monomers in FP, will be discussed. The deep eutectic solvents (DESs) are binary mixture of ammonium salts (acting as hydrogen-bond acceptors, HBAs) and nonionic hydrogen-bond donors (HBDs) whose composition corresponded to a eutectic point. DESs are considered as a subclass of ionic liquids, *i.e.* they contain ions (coming from the ammonium salt) associated with a second component, so that the resulting mixture is in liquid phase at temperatures below 100°C. The most common HBA used for the preparation of DESs is the ammonium salt choline chloride (ChCl). The experimental evidence has shown that adding an inert filler of the same mass fraction that the HBA in the DES (*e.g.* ChCl), does not lower the front temperature as much as a comparable amount of ChCl. Thus, the thermodynamics and kinetics of polymerization of acrylates are strongly influenced by existing in a DES monomer.



POLY 187: Polymerization fronts in deep eutectic solvents

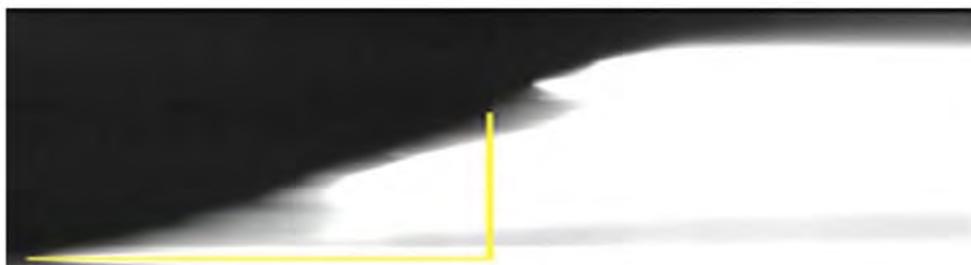
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Nowadays, the polymeric industry should become more environment friendly as any other important industry. In particular, ethylammonium acrylate, a deep eutectic solvent (DES) formed by an ammonium salt and a carboxylic acid share many green properties with ionic liquids and can be used to polymerize acrylic acid by frontal polymerization. In conventional solvents, frontal polymerization of acrylic acid is highly exothermic, producing vapors and burning the already formed polymer. These undesirable phenomena can be attenuated and controlled carry on this polymerization using ethylammonium acrylate as a solvent, where a polymerization front at 100°C has been achieved in contrast to 200°C in conventional medium.

A spatially and thermally controlled front is highly desirable from a technological point of view because it allowed a molecular weight distribution narrower and a homogeneous polymer network can be obtained.

It is evident that a chemical reaction is only possible if all the chemicals involved are available in the same environment. When an ionic liquid is attempted to use as a reactive media, the non-polar/polar structures that form the liquid can be chosen to dissolve polar and non-polar molecules or to segregate water or oil phases.

To study the distribution of the components in the frontal polymerization of acrylic acid in a Deep eutectic solvent two different systems were proved. A simply mixture between the DES and the initiator (Luperox 231) and; an microemulsion of SDS in water; with Luperox inside the micelles. The fronts were followed using an infrared sensor, the properties of the polymers obtained were monitored by viscometer and was chemically characterized by infrared spectroscopy.

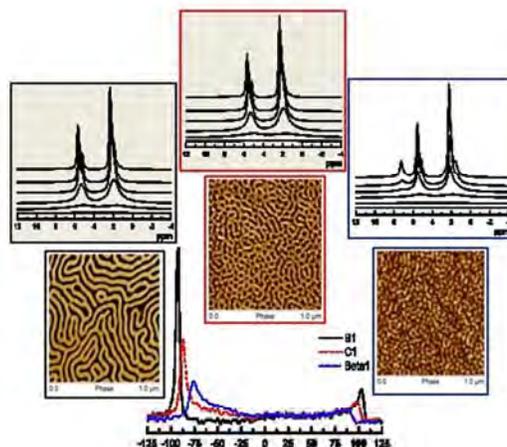


Thermal advance of a polymerization front in ethylammonium acrylate

POLY 188: Simple solids NMR experiments reveal routes to tailored interfaces in copolymers

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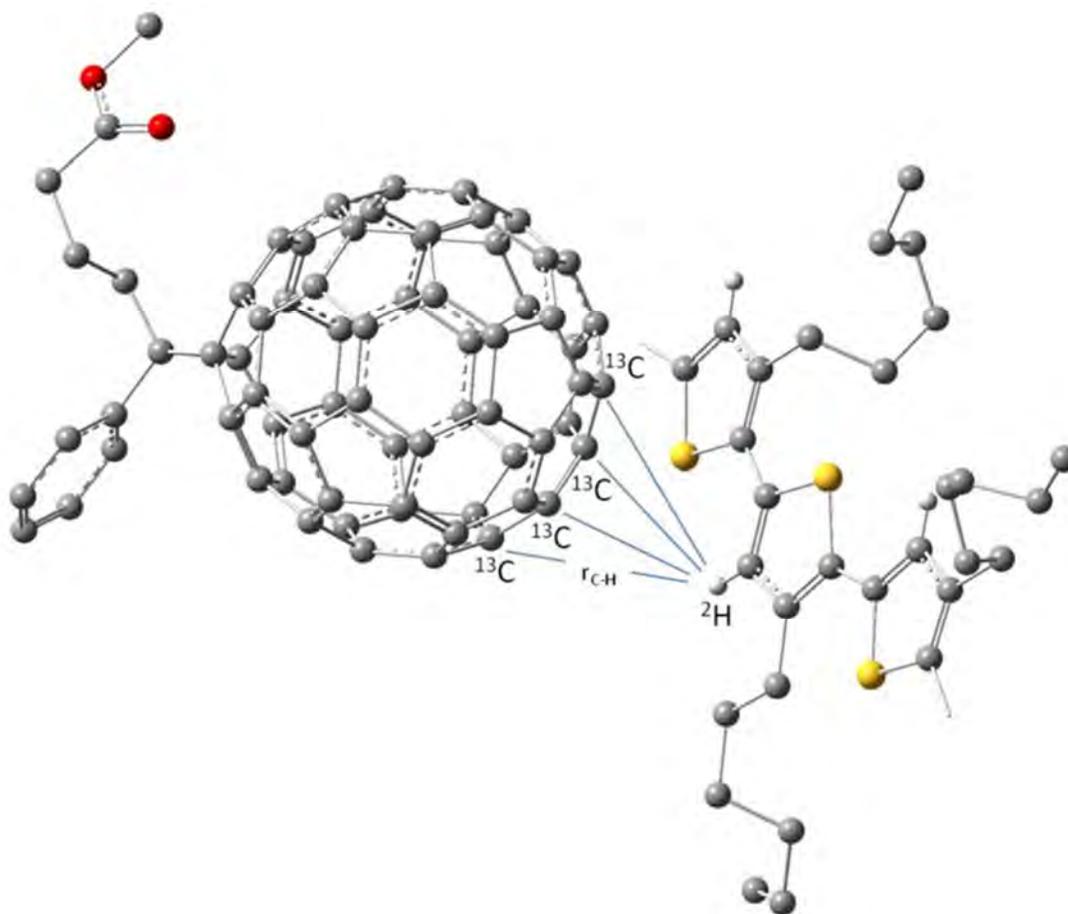
Simple solid-state ^1H NMR methods are applied to the design of tailored chain architectures that maximize interfacial contacts in block copolymers whose individual chemical components have a T_g difference equal to 200 K. Using a combination of variable temperature static, MAS, and spin-diffusion measurements, quantitative determination of bulk rigidity, the amount of low- T_g component partitioned in both soft and hard phases, and the amount of high- T_g component partitioned in each phase is possible. We show that the synthesis conditions can be changed to vary the partitioning of each gradient copolymer component in a systematic way by introducing variations in chain topology, and propose that the interphase between the hard and soft domains is responsible for differential partitioning.



POLY 189: New insights in bulk heterojunction interfacial structure from REDOR NMR

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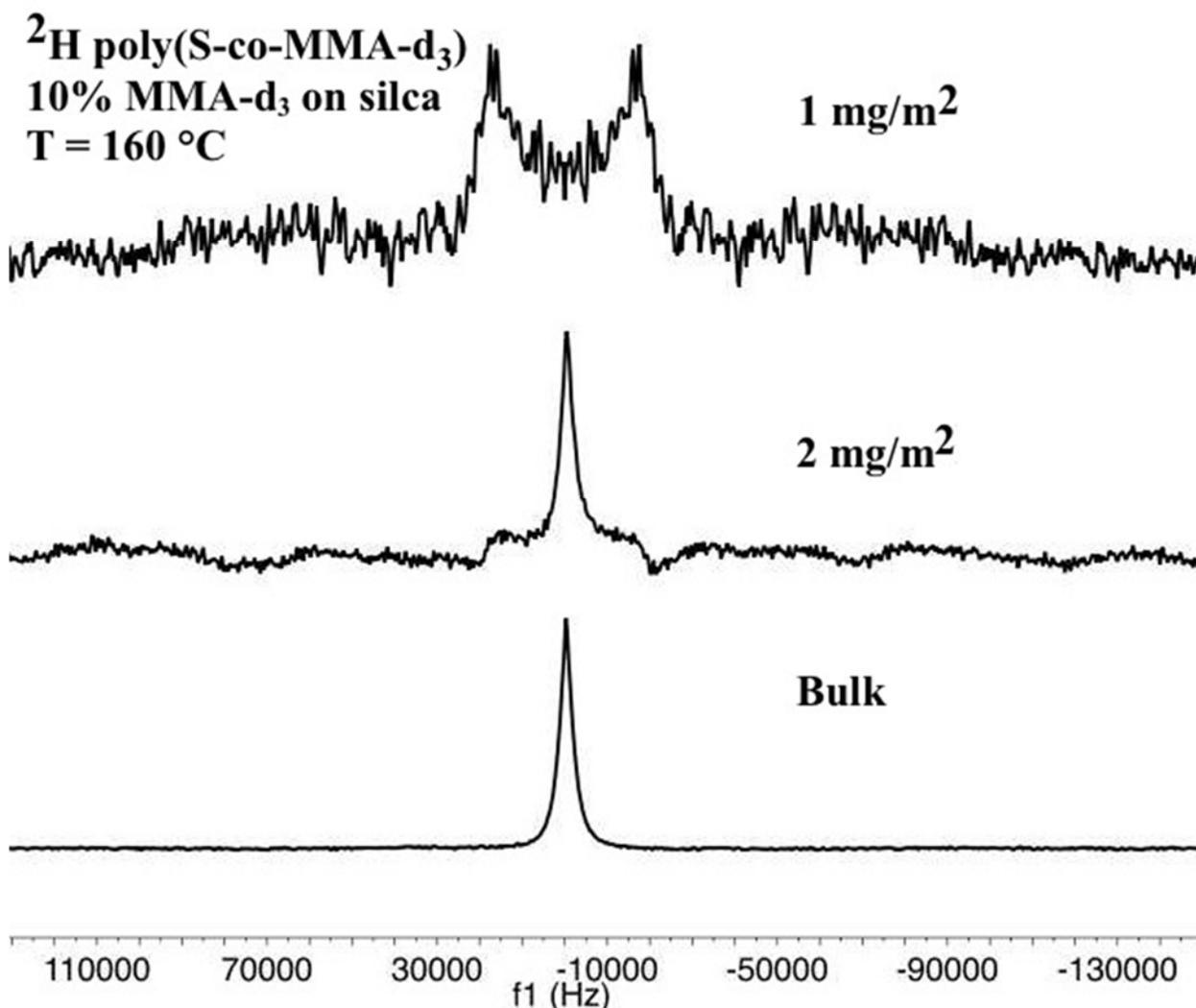
Robust relationships between structure and function are generally lacking in organic photovoltaic (OPV) thin film active layers. To predict performance there exists a need for tools that can measure structure on length scales fine enough to be relatable to inter-molecular energy transfer. Electron microscopy lacks sufficient spatial resolution due to a lack of electron density contrast, and scattering curves can be ambiguous because there typically is not a unique fitting model. In this talk, I will give highlights of recent ^{13}C $\{^2\text{H}\}$ REDOR measurements to characterize the donor/acceptor interfaces in bulk heterojunction thin films. Heteronuclear couplings are measured between ^{13}C nuclei on the acceptor C_{60} cage and thiophene hydrogens on the donor main chain, which has been isotopically enriched with ^2H . I will discuss models of the interface that are used to fit the REDOR dephasing curve, and the constraints that these models have on local composition and packing. We will also show that the REDOR measurements can help solve the mystery of which model to use in fitting small angle neutron scattering curves.



POLY 190: Behavior of poly(styrene-co-methyl methacrylate-d₃) on silica

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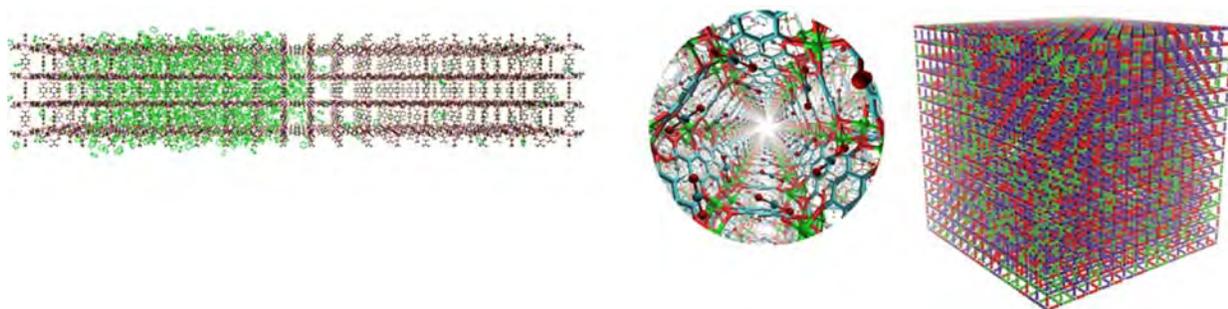
We have extended our studies of the dynamics of the random copolymer, poly(styrene-co-methyl methacrylate-d₃) on silica to smaller adsorbed amounts. Modulated scanning differential calorimetry and deuterium quadrupole-echo NMR were used. Comparisons of bulk and adsorbed polymers were complicated by the changes in glass transition temperature with composition. Nevertheless, using the T_g 's of the bulk polymers as a baseline, several conclusions were made: i) carbonyls from the MMA generally found their way to the silica surface at all copolymer compositions. ii) the fraction of tightly-bound polymer decreased with increased MMA content and iii) the fraction of immobile MMA segments for the adsorbed copolymers also decreased with increased copolymer adsorbed amounts.



POLY 191: NMR assessment of structure and dynamics within metal organic frameworks

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Coordination compounds such as MOFs and their analogy, COFs, exhibit regular structures decorated by spatially varying functional groups. Elucidating the spatially vary parts of their structures is an ideal platform for solids NMR methods. Not surprisingly, these materials are not the static "Tinker-Toy" structures our cartoons suggest: they are fluctuational and these fluctuations are not unrelated to their desirable technological properties. Further, guest molecules embided within them expereince unusual confinements and thereby present unusal thermodynamic properties. Each of these three issues will be presented in this lecture.

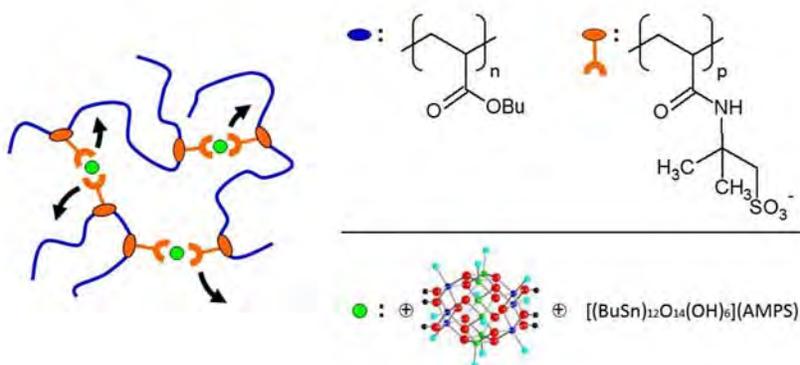


POLY 192: Dynamical processes in self-healing hybrid polymer networks: A solid-state NMR study

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The integration of supramolecular interactions in macromolecular architectures offers the opportunity to design a great variety of self-healing polymers. Such systems are important in the context of the development of sustainable materials. Here, we will consider dynamic polymer networks, in which the chemical bonds between the polymer chains and the cross-links, occurring in conventional polymer networks, are replaced by electrostatic interactions. More precisely, n-butyl acrylate and 2-acrylamido-2-methyl-1-propanesulfonate anions (AMPS) were copolymerized while AMPS forms electrostatic interactions with butyltin oxo-cluster macrocations, $[(\text{BuSn})_{12}\text{O}_{14}(\text{OH})_6]^{2+}$ (Figure 1).

For such materials, the description of the mechanical behavior requires the characteristic lifetime of the ionic interactions between the polymer chains and the hybrid cross-links to be determined. The segmental dynamics of the polymer chains and their interactions with the oxo-cluster macrocations will be investigated by ^1H and ^{13}C solid-state NMR. These motions will be probed over a time scale of tens of microseconds, but the dynamical processes involved will also be monitored over a longer time scale (1 ms – 1 s). The fraction of elastically active chain portions will be determined using ^1H double-quantum experiments. The networks will be first studied *in the molten state*. In this case, temperature will allow to modulate the characteristic lifetime of the ionic interactions. In a second step, the same networks will be swollen *in a good solvent* (chloroform) and small amounts of another good solvent (DMSO), characterized by a higher dielectric permittivity ϵ , will be progressively added. This latter is another parameter allowing the characteristic lifetime of the ionic interactions to be varied. The evolution of the dynamical processes within the networks will be investigated as a function of the permittivity of the solvent mixture.

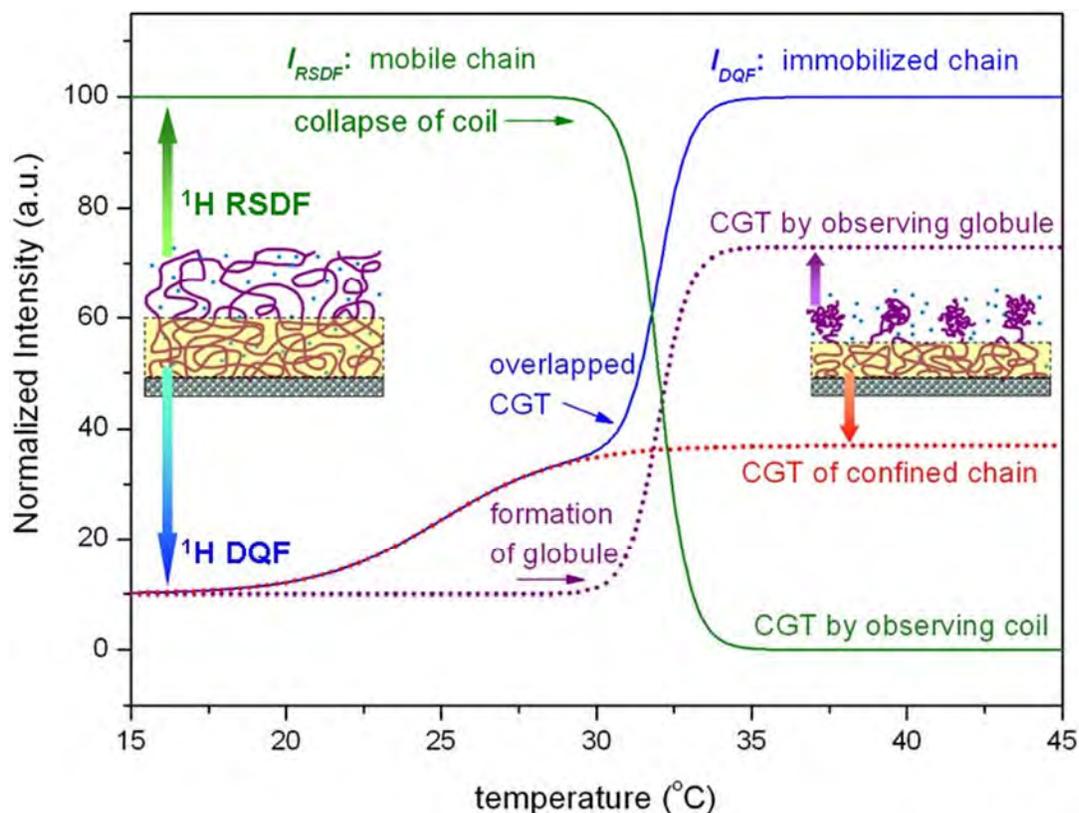


Schematic representation of the hybrid networks investigated

POLY 193: Confined coil-to-globule transition of thermoresponsive polymers as revealed by solid-state NMR

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The coil-to-globule transition (CGT) exhibited by thermoresponsive polymers has attracted significant attention in the past decades due to the unique function and properties of these smart materials. However, a molecular-level detection and understanding of the CGT behavior of nanoscale confined thermoresponsive polymers remains a great challenge. In this work, we report a new and general strategy combining dynamic-editing ^1H solid-state NMR techniques to directly detect the CGT of confined thermoresponsive polymer chains near and far from the grafted interface, whereby the coil collapse and globule formation can be independently monitored at the molecular level. This new strategy was successfully applied to detect the complex CGT of poly(N-isopropyl acrylamide) under different extents of confined environments, and unique confined CGT behavior were revealed for the first time. Compared to free chains far from the grafted interface in both PNIPAM-grafted gold nanoparticles and PINPAM/Laponite nanocomposite hydrogels, it was found that confined chains near the grafted interface underwent CGT at lower temperatures instead of higher temperatures as reported by most previous experimental and theoretical works.

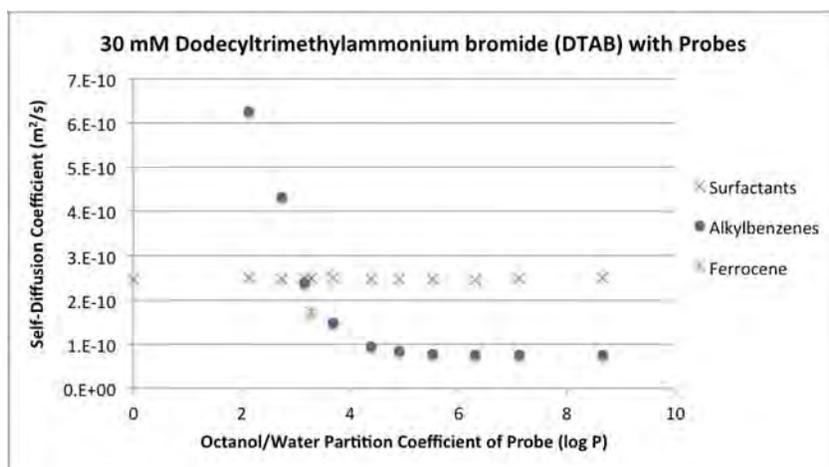


POLY 194: Probe molecules for pulsed-field-gradient diffusion NMR experiments on micelles

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Surfactants continue as a rich area of scientific inquiry. A common method for characterizing surfactant micelles is nuclear magnetic resonance (NMR) spectroscopy, and a wealth of information can be obtained from pulsed-field-gradient (PFG) NMR measurements of diffusion. The diffusion coefficients of the micellized surfactant are commonly used to determine micellar size, which is important knowledge for many applications. In micelle systems, the surfactant molecules exchange between the micelle and bulk solution much faster than the NMR timescale, and the NMR diffusion coefficient (D_{obs}) is a weighted average of the aggregate diffusion (D_{mic}) and the diffusion of surfactant molecules freely dissolved in solution (D_{free}). D_{free} can be easily obtained by measurements below the critical micelle concentration, but accurately determining D_{mic} is more difficult. A commonly accepted way to measure D_{mic} is to add a hydrophobic probe molecule to the solution, assuming that the probe will stay confined inside the micelle. Unfortunately, the probe molecule also exchanges rapidly between the micelle and bulk solution, which may adversely affect experimental values. This suggests that the choice of probe molecule for these applications is important, yet underappreciated.

To illustrate the role of the probe molecule, we present PFG NMR diffusion of common surfactants with probe molecules of varying hydrophobicity. We use a series of alkylbenzene molecules as probes to systematically vary probe hydrophobicity. PFG NMR data for DTAB with varying probes are shown in the figure. We also compare our results with electrochemical measurements of diffusion using ferrocene probes, to gauge the reliability of these techniques. Our results show that probes with an octanol/water partition coefficient with $\log P_{\text{ow}} > 5.5$ most accurately reflect micelle diffusion, and that NMR and electrochemical diffusion measurement agree well.



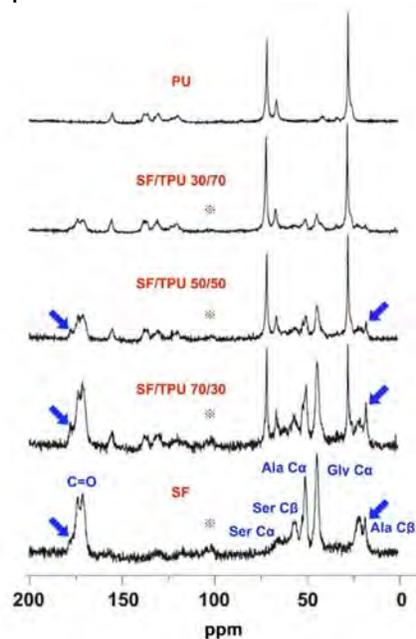
POLY 195: Compatibility evaluation of non-woven composite sheet based on silk fibroin and synthetic polymers for tissue engineered material

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Silk fibroin (SF) has notably favorable characteristics for tissue engineering. However, there is a need of adjustment on the mechanical properties for some cases. For instance, soft tissues such as circulatory system is standing with higher elastic properties from tissue engineered materials. Polymer blends are one of the simple methods that having possibilities to provide materials with extended useful properties. To achieve this, we developed a non-woven SF blend sheets with several synthetic polymers such as thermoplastic polyurethanes (TPU) and biodegradable polycarbonate. Solid-state NMR method used to evaluate structure and polymer miscibility of SF and TPU composite sheet. The miscibility discussed by proton spin-lattice relaxation times in the laboratory frame (T_{1H}).

From the results of ^{13}C CP/MAS NMR spectrum, there is no peak shift observed neither pure samples and blended one (Figure 1). The T_{1H} measurement clearly revealed that, the molecular chains of SF and TPU are under very close circumstance within several ten nm and behave as micro-phase separation. In addition, SF/TPU sheet showed excellent adhesive and biocompatible properties in *in vivo* studies which this results supports of that T_{1H} evaluation.

We consider that the micro-phase separation structure gives high ability to use SF/TPU composite for cardiac repairing. Also, time course evaluation of other silk based degradable composite will be present in further.



^{13}C CP/MAS NMR spectra of SF / TPU composite sheets in wet conditions.

POLY 196: Self-assembly of Pluronic triblock copolymers in a protic ionic liquid and polymerization to create wearable electronics

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A new class of ultra-stretchable and highly ion conductive hierarchical structured iono-elastomer, a subset of ion gels, is developed for use in emerging technologies involving wearable electronics and smart textiles, with potential applications as stretchable batteries, motion sensors, and integrated circuits. Fabrication of such materials usually requires the use of hybrid technology that mixes metals, polymers and conductive materials, to tie the system together electronically. Unlike other manufacturing strategies of current elastomeric composite materials that involve sophisticated and complex integration of elastomeric substrates with micro- or nano-structured organic or inorganic electronic materials via multi-step and often costly processes, fabrication of this material is a facile simplified synthesis process by hierarchical self-assembly of concentrated solutions of end-functionalized commercially available, in-expensive triblock copolymer in a protic ionic liquid, followed by micelle corona crosslinking to generate elastomeric iono-elastomers. The resulted materials exhibit an unprecedented combination of high stretchability, high ionic conductivity and mechano-electrical response. Importantly, the materials conductivity increases with extension, a unique and non-trivial material response, whose origin is postulated to be the microstructural rearrangement of the micelles under uniaxial deformation using *in situ* Sentmanat Extension Rheometer-small angle neutron scattering (SER-SANS). Based on the unique material invention, the first large strain amplitude, stretchable resistive strain sensor patch prototype was developed for customers (e.g., athletes, patients undergoing physical therapy, biomechanicians, etc.) to accurately track motion and performance of specific joints and/or muscles on their smart phone, tablet or computer via Bluetooth wireless communication, with applications in motion capturing, sports performance tracking and rehabilitation monitoring.

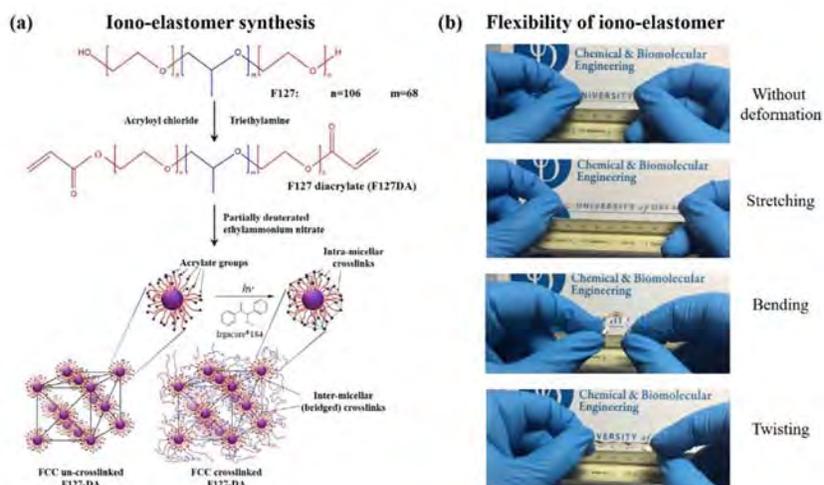


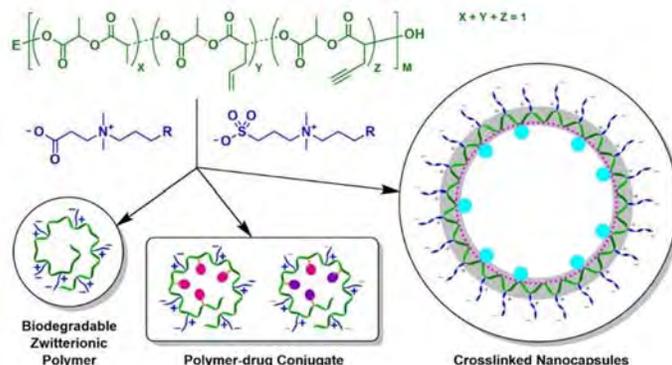
Figure: (a) Step-wise demonstration of iono-elastomer synthesis. (b) Photos of iono-elastomer at rest and post stretching, bending and twisting.

POLY 197: Biodegradable zwitterionic polylactide-based delivery systems for cancer treatment

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Polymer-based therapeutics show great promise in the treatment of cancer due to their versatile and tunable structures, which allow for sophisticated control over their properties and functions. Zwitterions have been widely investigated as alternatives to poly(ethylene glycol) (PEG) for enhancing water solubility and prolonging circulation time of therapeutics. A new class of polymeric biomaterials has been developed in our laboratory by incorporating extremely hydrophilic zwitterions with biodegradable functional polylactides (PLAs). In particular, zwitterionic polymer-drug conjugate (PDC) has been studied for sustained delivery of paclitaxel (PTX). Zwitterionic sulfobetaine (SB) and anticancer drug PTX were functionalized with thiol groups respectively, and then conjugated with PLA backbone by thiol-ene reactions with an allyl-functionalized PLA. The resulting PDC could form stable nanoparticles in aqueous solution. Complete enzymatic degradation and pH-sensitive hydrolytic sustained release of PTX were confirmed. *In vitro* studies demonstrated high anticancer efficacy and effective cellular uptake.

Currently our research efforts on this project focus on development of other biodegradable zwitterionic polymer-based delivery systems for cancer therapy and diagnosis *via* multi-functionalization strategy. Both allyl-functionalized PLAs and acetylene-functionalized PLAs are adopted to serve as the precursors of polymer backbones. New types of hydrophilic zwitterions including SB and carboxybetaine (CB) are employed as solubilizing residues. The zwitterionic moieties and other functional groups such as anticancer drug, dye, targeting moieties, are grafted onto the functionalized PLAs *via* thiol-ene or azide-alkyne click chemistries. The resulting polymer conjugates could be used to develop nanoparticles, micelles, and nanocapsules for delivery of therapeutic agents and/or imaging agents. The integration of functional PLAs with hydrophilic zwitterions and other biomedical-relevant functionalities will generate a variety of novel biomaterials with significant application potentials in drug delivery, gene delivery, drug-gene co-delivery and imaging.

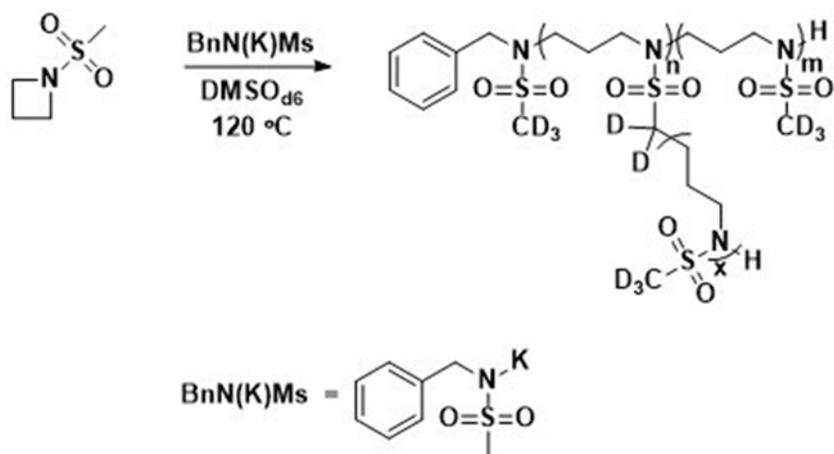


POLY 198: Anionic ring-opening polymerization of azetidine

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Although similar to many anionic ring-opening polymerization (AROP) capable monomers, cyclic amines do not undergo anionic polymerizations. For example, aziridine and azetidine only polymerize through cationic ring-opening polymerization (CROP) and produce hyperbranched polymers with broad molecular weight distributions.

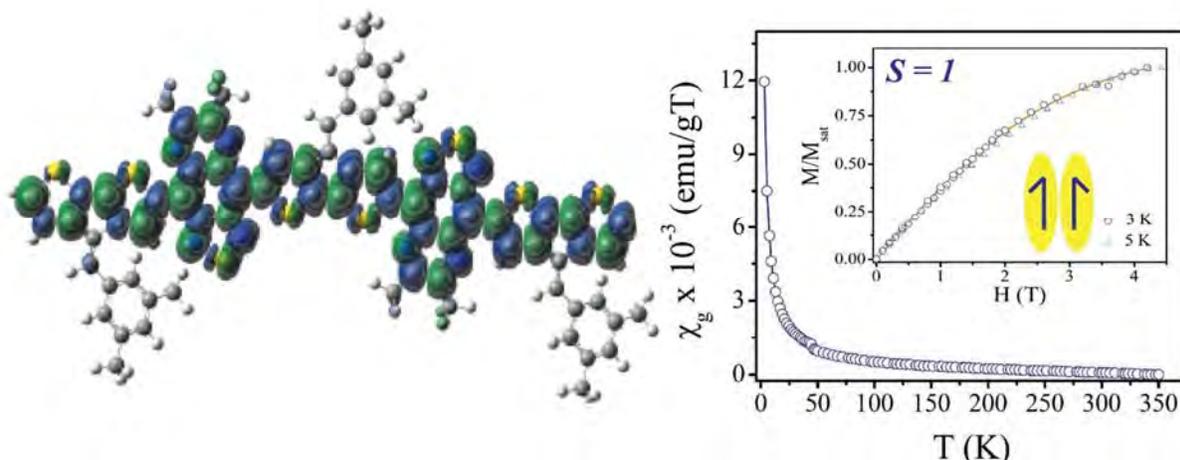
Building upon the progress made with *N*-(sulfonyl)aziridine polymerizations, we now report the first example of the AROP of an activated azetidine. *N*-(methanesulfonyl)azetidine (**MsAzet**) undergoes anionic polymerization at high temperature (>100 °C) in DMSO to form p(MsAzet). However, unlike the sulfonylaziridine systems, light branching of p(MsAzet) does occur, although the mechanism for branching is very different from what occurs in CROPs of aziridine and azetidine. The kinetics of the polymerization of **MsAzet** are also studied.



POLY 199: High-spin ($S = 1$) conjugated copolymer with a paramagnetic ground-state

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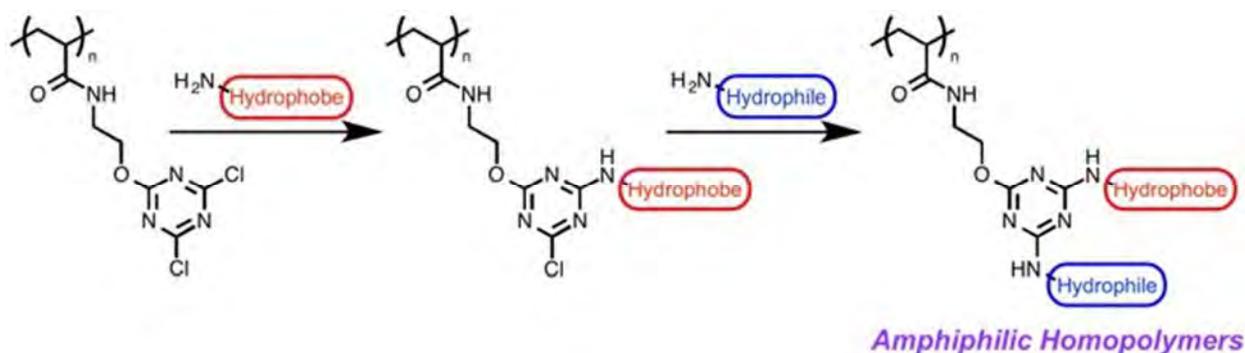
The intrinsic instability of high-spin ($S \geq 1$) organic molecules precludes their practical utility/application. Enabling emergent magnetic, spintronic, and quantum phenomena requires new design principles that overcome instability, enables synthetic manipulation, and combines the electronic and optical properties associated with organic semiconducting materials. Here, we demonstrate the synthesis and characterization of a narrow bandgap, solution-processable, donor-acceptor copolymer that is a ground-state triplet ($S = 1$) in its neutral form. The extended π -system in conjunction with cross-conjugated ferromagnetic coupling units along the polymer backbone results in open-shell character and an inversion of the singlet-triplet energy levels. Electron spin resonance (ESR) and superconducting quantum interference device (SQUID) magnetometry indicate a small high-to-low spin energy gap ($\Delta E_{ST} = 9.30 \times 10^{-3}$ kcal mol⁻¹) with positive exchange coupling ($J = 1.62$ cm⁻¹). Our results demonstrate new molecular design guidelines toward stable, high-spin organic semiconductors with unique spin-spin interactions and magnetic properties.



POLY 200: Successive and chemoselective post-polymerization modification strategy

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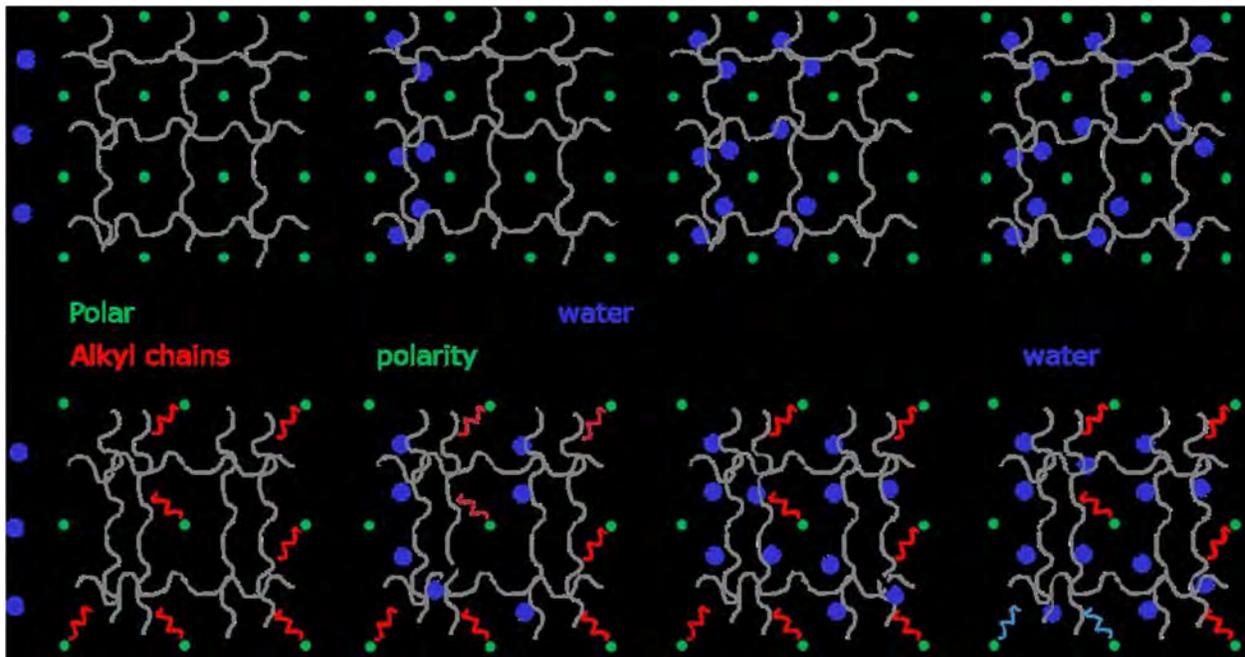
Post-polymerization modification techniques can allow for preparations of polymers with complex architectures and/or with various functions, thus extending the range of attainable, useful materials. Efficient and concise route to side-chain heterodifunctional polymers was developed using 2,4,6-trichloro-1,3,5-triazine (TCT). By leveraging TCT's controlled electrophilicity, which was corroborated through small molecule model studies, we demonstrated the straightforward synthesis of otherwise laboriously prepared polymers bearing multiple functionalities in each repeat unit. This TCT-based synthetic strategy was applied for the modular preparation of amphiphilic homopolymers, in which hydrophobic and hydrophilic groups were sequentially incorporated within side chains of polymers. Formation of self-assembled nanostructures was indicated via light scattering measurements, while amphiphilic properties were demonstrated via fluorescence measurements of encapsulated hydrophobic dye and water-oil interfacial tension studies.



POLY 201: Controlling the diffusion and solubility of water in epoxy/amine thermosetting polymers

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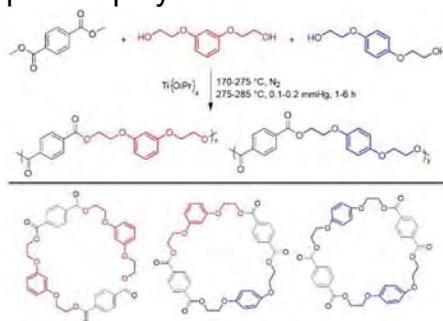
Fundamental studies aimed at elucidating the key contributions to corrosion performance are needed to make progress toward effective and environmentally compliant corrosion control. Epoxy/amine systems are typically employed as barrier coatings for corrosion control, however, the curing agents used for coating applications can be very complex, making fundamental studies of water and oxygen permeability challenging to carry out. Creating model building blocks for epoxy/amine coatings is the first step in carrying out these studies. This work demonstrates structure-property relationships of several model building blocks in relation to a proposed governing relationship between material parameters and the diffusion and solubility of water.



POLY 202: Structure-property relationships of novel (co)polyesters: From advanced packaging materials to the influence of regiochemistry on cyclics and properties

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Identifying novel polymer platforms to combine high barrier properties with thermal stability and mechanical strength is crucial for a competitive polymer platform to replace bisphenol A polycarbonate (BPA-PC) and poly(ethylene terephthalate) (PET). Unique bibenzoate dimethyl esters enabled the synthesis of novel polyesters containing linear 4,4'-bibenzoate and kinked 3,4'-bibenzoate repeat units. Thermal analysis confirmed thermal transitions approaching that of BPA-PC. Melt rheology studied flow behavior, and time-temperature superposition revealed distinct flow relaxations providing insight into fractional free volume, flow activation energies, and entanglement. Positron annihilation lifetime spectroscopy (PALS) supported free volume trends and oxygen transmission testing offered insight into gas permeability and packaging applicability. The resulting polymer platform combining high barrier properties with high temperature and mechanical properties offers a competitive platform for BPA-PC and PET replacement. Size exclusion chromatography (SEC) confirmed high molecular weight and advanced permeation chromatography (APC) elucidated multiple low molecular weight peaks. Step-growth polymerizations produce cyclics in equilibrium with linear polymer chains. Structural alterations, such as regiochemistry, influences the quantity, molecular weight, and dispersity of the produced cyclics. These small molecule cyclics impact processing and influence barrier performance. Thus, understanding the influence of monomer regiochemistry on cyclic formation allows for predicting cyclic quantity and size, while altering properties. Analytical techniques offer avenues to characterize the size and shape of the cyclics, while controlling cyclic weight percent incorporation investigates the impact of cyclics in rheological, mechanical, and barrier properties. Through systematic studies to quantify and predict cyclic formation during polymerization, the development of structure-property relationships enables key understandings to design improved polyesters.

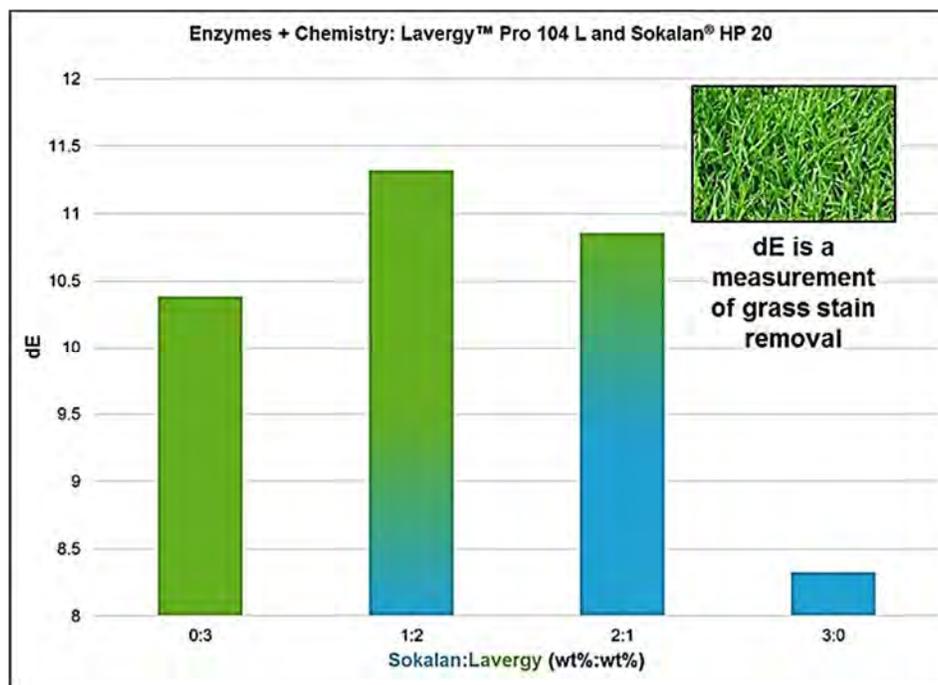


POLY 203: Enzyme/polymer synergies: An innovative approach to sustainable detergents

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Home Care Development, BASF Corporation, Wyandotte, Michigan, United States

New formats and claims toward compaction, convenience, and sustainability are at the forefront of the changing liquid laundry detergent market. One of the most potentially impactful claims intends to alter consumer behavior by encouraging washing in cold water and conserving energy. Consumers agree that setting their washing machine dials to cold is a step toward reducing their energy consumption, keeping money in their pockets, and mitigating their carbon footprint. However, they perceive that washing with cold water reduces stain removal and overall efficacy of their detergents.

One way to achieve adequate cleaning performance at low temperatures is by using enzymes. Enzymes are active at low temperatures and have the ability to break down complex stains such as grass and blood. BASF has developed a new solution for enabling consumers to choose cold water detergents as a sustainable solution without having to compromise on cleaning performance: Lavergy™ Pro 104 L. BASF's new protease Lavergy™ Pro 104 L supplies the power to achieve superior efficacy, differentiation at low temperatures, and broad formulation compatibility to customers who expect sustainable, high-performing solutions. Additionally, BASF is now moving towards developing innovative polymer chemistries to enhance enzyme performance on complex stains. Recent findings have demonstrated favorable synergistic effects between BASF's protease and identified polymers such as our polyethyleneimine copolymer Sokalan™ HP20. The combination of enzymes and synthetic polymers is leading the way for more sustainable detergent solutions.



POLY 204: Chronicling a sustainability journey in durable water repellent technology within the textile market segment

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Chemours™ offers a broad range of additives and finished products that contribute to a wide-range of desirable surface properties – including but not limited to low coefficient of friction, non-stick, anti-fouling, and both oil and water repellency – which are critical to a range of markets for both consumer and industrial applications.

The aim of this talk is to chronicle the technological hurdles within the textile market segment and illustrate the unique solutions that embody short-chain repellents, which offer equivalent and in some cases superior performance and runnability to alternative technology. In addition, the talk will introduce an innovation platform that continues to broaden the product portfolio available in the area of durable water repellent (DWR) textiles through the use of novel non-fluorinated technology derived from renewably-sourced precursors.



Teflon EcoElite finish for durable water repellency and water-based stain protection.
teflon.com/ecoelite

Teflon® Shield and Clean Portfolio for water, oil and stain protection.
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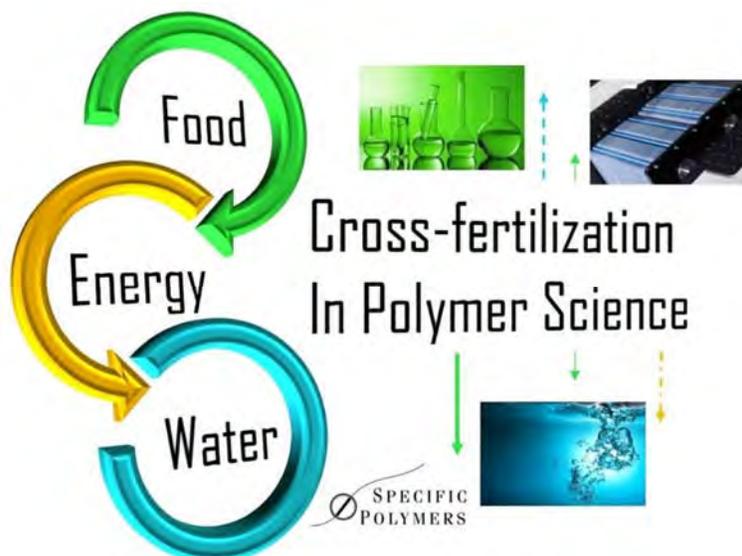
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POLY 205: Industrial R&D in functional polymer science: Cross-fertilization and food-water-energy nexus

Alain Grailot, **Cedric Loubat**, cedric.loubat@specificpolymers.fr. SPECIFIC POLYMERS, CASTRIES, France

SPECIFIC POLYMERS (SP) is dedicated to research and development in functional polymer and materials sciences. SP support academic and industrial partners to develop tomorrow's materials in all fields of research. Being involved in such a variety of projects, SP has acquired an overview of the industrial use of functional polymers and it finally appeared that cross-fertilization is the main driver of SP success. The food, water-energy nexus well illustrates cross-fertilization in polymer science. Instead of using food industry consumables to produce energy (bioethanol from sugar cane), SP directs its research toward the valorization of wastes from the food-industry and the biomass. One significant example is the chemical modification of tannins, lignin or cardanol to produce biobased epoxy resins. The latter are of interest in various sectors since it exhibits outstanding mechanical properties. Recently, they were used to develop biobased composite materials for a drastic reduction of aircraft weights and fuel consumption by substituting current heavy metal alloys. But the issue is not only to save energy but also to store it. Thus, SP also develops solid/gel polymer electrolyte for lithium batteries and fuel cells. Chemistry developed here is based on phosphonic or sulfonylimide moieties that can allow cationic species transport at liquid, gel or solid state. The affinity of such moieties for cationic species was also used for wastewater treatment, especially from nuclear and mining plants. Aqueous effluents of such sector contain a high concentration of cationic species that need to be removed before returning to the natural environment. In this context, SP worked on a variety of (macro)molecules bearing selective sorption groups that can sorb and remove cationic pollutants using various treatment processes. Inspired by these processes, SP is targeting new materials and membranes for water desalinization and potabilization, blue gold being one of the major topics of the 21st century.

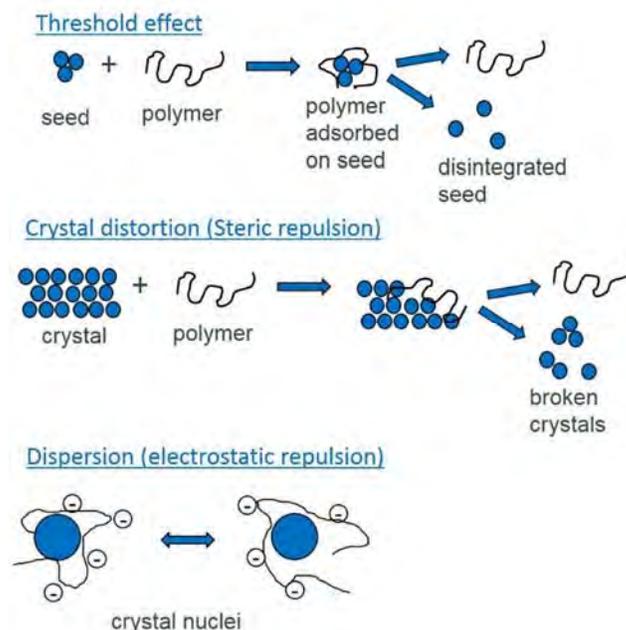


POLY 206: Polymeric-based scale inhibitors for industrial water treatment applications

Kaylie Young, *klyoung1@dow.com*. Oil, Gas & Mining, The Dow Chemical Department, Lake Jackson, Texas, United States

Fouling in water-intensive applications is one of the most problematic issues facing industrial processes today as it often leads to shutdown time and increased process costs. This is especially true in the current environment of global water supply shortages and more stringent environmental regulations. Foulants generally encountered in industrial water systems can be classified into two types: mineral scales and deposits, such as colloidal and suspended matter, including biological growth. Mineral scale deposits are a type of foulant that occurs when inorganic salts are present in excess of their solubility in the respective fluid. Common mineral scales encountered include calcium carbonate, calcium sulfate, barium sulfate, calcium phosphate, silica, and metal silicates. Mineral scale deposits form in practically all processes using water including boilers, heat exchangers, cooling towers, pipes, especially those carrying turbulent water, and RO membranes.

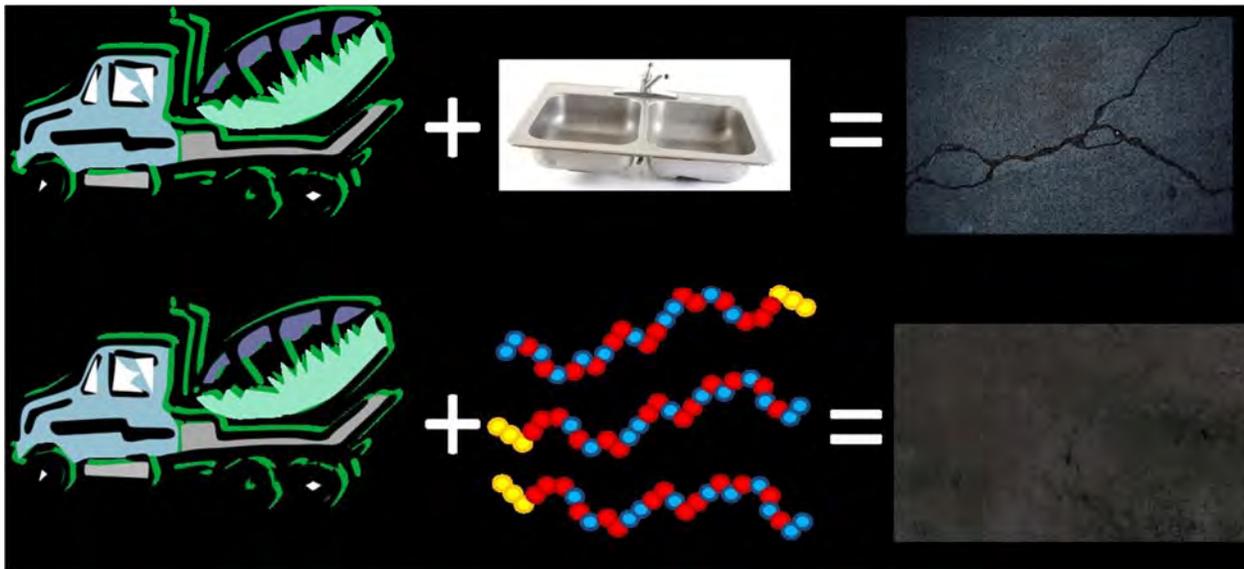
Several methods have been developed to control the formation and deposition of mineral scales including the use of chemical additives that act as scale inhibitors or scale dispersants in addition to removal or reduction of the scale-forming species and removal by mechanical and/or chemical means. The two main classes of scale inhibitors are phosphonates and polymers. Although phosphonates are low cost and well established in the water treatment industry for calcium carbonate, polymer-based scale inhibitors have gained popularity due to their higher temperature stability, improved divalent ion tolerance, and greener environmental profile. This talk will highlight acrylic acid- and maleic acid-based polymers and their use as scale inhibitors in industrial water treatment applications.



POLY 207: Utilizing polymer chemistry to do more with less: Strategic approaches for more efficient oil well cementing

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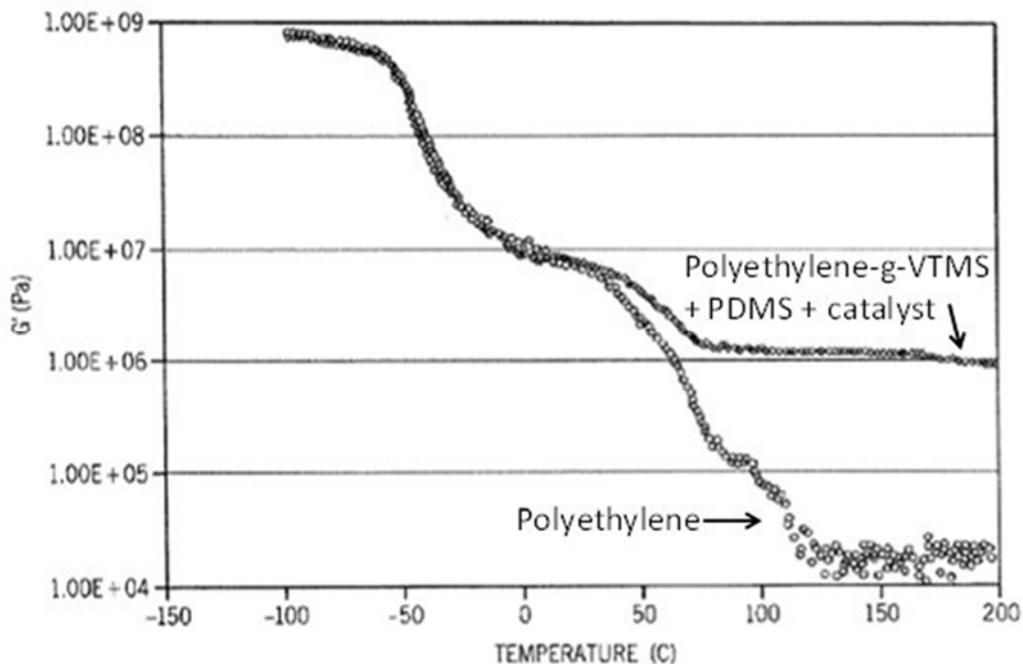
Over the last couple of years, oil prices have declined drastically. In July of 2014 WTI crude oil was at almost \$105 per barrel. Within six months, this was cut in half. By February of 2016 the price was a little under \$28 per barrel, a nearly 75% drop within a year and a half. Needless to say the oil and gas market was suffering drastically. To make oil production profitable was seemingly impossible. The question throughout the industry became “how can we do more with less?” With respect to oil well cementing, a new strategy surrounding this ideology was adopted. Typically in a cement slurry design, a number of different additives are utilized to give the proper performance desired. Some typical classifications of additives include dispersants, retarders, fluid loss preventers, suspension agents, extending agents, mechanical property enhancers and gas migration controllers. Some cement designs could comprise of up to 15 different components. As an innovative approach to address the issue, unique polymer chemistry was utilized to create an advanced cement additive that can provide multiple functions within the cement slurry helping to decrease the total additive count and still give the desired performance.



POLY 208: Improving efficiency of making thermoset polymers: A new method for ambient cross-linking of polyethylene without heat, radiation, or moisture

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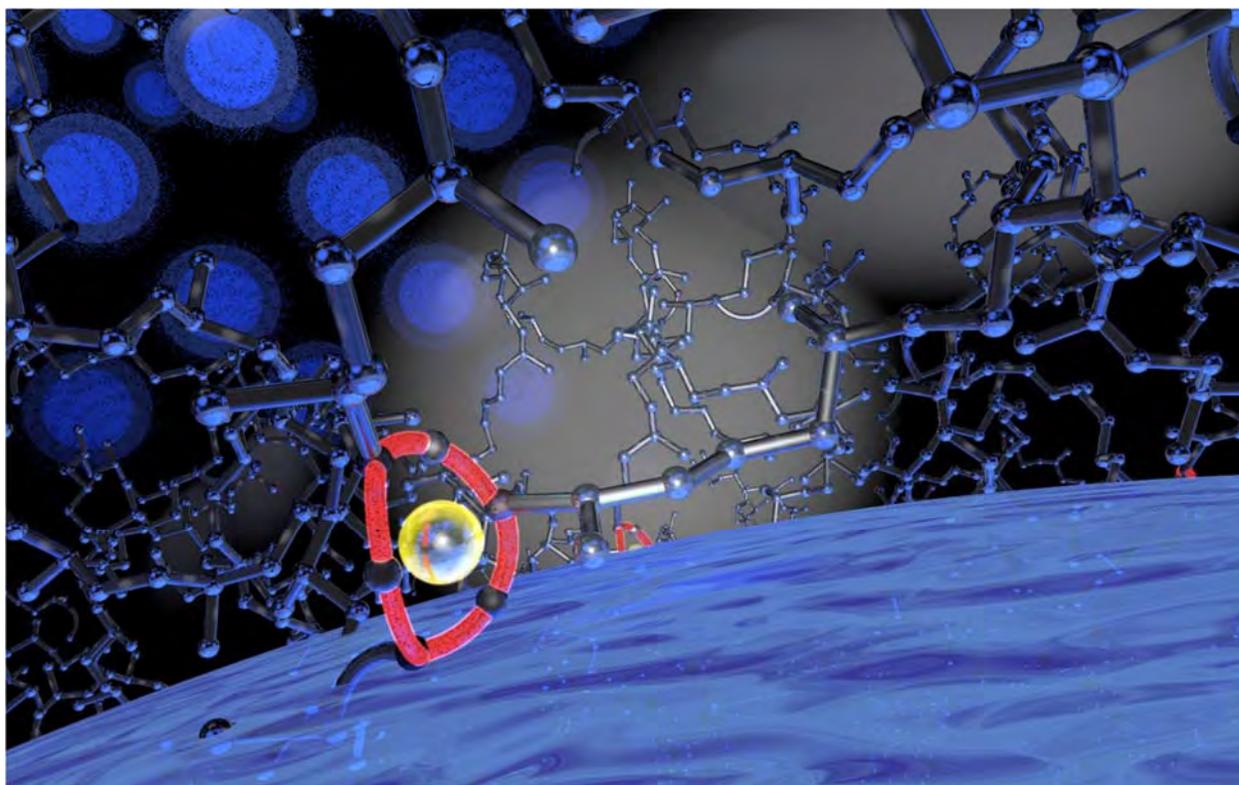
Thermoset polymers are often used as materials of choice in infrastructure applications due to their superior thermo-mechanical and fluid resistance properties. Industrial polymers such as polyethylene (PE) are commonly used to manufacture these thermoset products through cross-linking. By far the most widely used methods for cross-linking of PE are those based on peroxide-initiated free radicals, moisture cure of ethylene-silane reactor or graft copolymers, or irradiation, each of which are energy intensive and possess unique challenges and limitations. For example, peroxide and moisture cure methods require diffusion of heat and/or moisture through thick articles, which can be time consuming and can limit production rates. A new method for cross-linking PE has been developed that overcomes these limitations while still achieving competitive cross-linking levels. A thermoplastic PE (or post-reactor modified PE) polymer and key cross-linking additives can be melt processed (extruded, molded, etc.) to form an article without significant cross-linking. Upon storage at ambient conditions after fabrication, the article undergoes thorough cross-linking without the need for external moisture, heat, or radiation. This method will be discussed in detail, including a proposed chemical mechanism, results of material science-based assessment of cross-linking and use of the new technology in two energy-related infrastructure applications.



POLY 209: Constitutionally dynamic polymers as oil well construction materials

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Dynamic polymers assembled through hemiaminal and aminor functionalities reversibly fragment upon binding to trivalent metals. Gels produced with these dynamic polymers are broken down to liquids after the addition of metal salts. Nuclear magnetic resonance (NMR) spectroscopy studies of intermediates and density functional theory (DFT) calculations reveal that the presence of these metals causes shifts in the energetic landscape of the intermediates in the condensation pathway to render stable non-equilibrium products. These non-equilibrium products are liquids that remain stable liquids at room temperature but convert to gel upon heating. Thermal activation causes the fragmented ligands to transform catalytically into closed-ring products which are macroscopically observable as new gels with distinct physical properties. The interplay between equilibrium and non-equilibrium gels and liquids and the ligands responsible for these transformations has been observed rheologically to offer controlled gel times dictated by the thermodynamics and kinetics of the system. This constitutionally dynamic macromolecular system offers the possibility of harnessing an equilibrium / non-equilibrium system in tandem with its inherent self-healing and triggered release properties. These non-aqueous gels also display superior temperature tolerance to many existing aqueous-based gel systems.

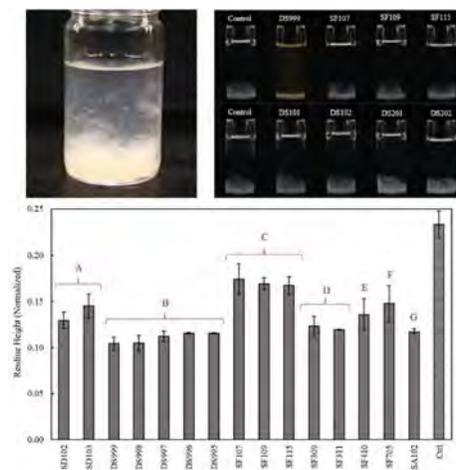


POLY 210: Development of chemistries to improve Guar Gum efficacy in hydraulic fracturing applications

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Hydraulic fracturing consists of pumping water with chemical additives and sand (proppant) at high pressures into rock formations to break open fractures creating increased surface area for the production of hydrocarbons. Available for decades, recent technological innovations enabled widespread use of this technology, particularly in the US. One main component is guar gum, a naturally occurring polysaccharide which provides high viscosity. At the end of the fracturing treatment, the viscous fluid breaks down to water-like viscosity to facilitate its removal from the proppant pack. When guar breaks, however, it generates insoluble residue that clogs the pores of proppant packs. The hydraulic conductivity of the fracture path can be reduced by more than 60%.

A collaboration between an oil service provider and a chemical company aimed at reducing the impact of this natural polymer on fracture conductivity. A suite of characterization techniques, including size-exclusion chromatography, thermogravimetric, elemental and particle size analyses, was used to analyze the chemical composition of guar gums and residue. The data provided critical insights into the development of new chemical additives that minimized the amount of guar residue. A novel experimental workflow was then developed to enable high-throughput testing of a wide range of chemicals, based on quantitative image analysis coupled with analytical characterization. The new workflow enabled screening of hundreds of chemicals in a short time thus significantly improving the product development process for the oil and gas industry. The study resulted in a high performance multifunctional additive, which passed the full cycle of laboratory validation and is currently in the field testing phase in North America.



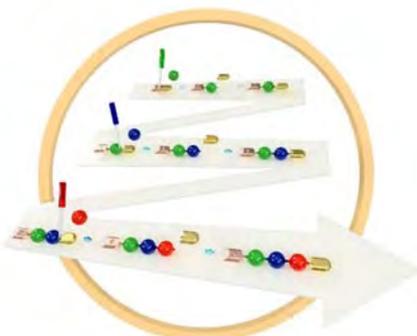
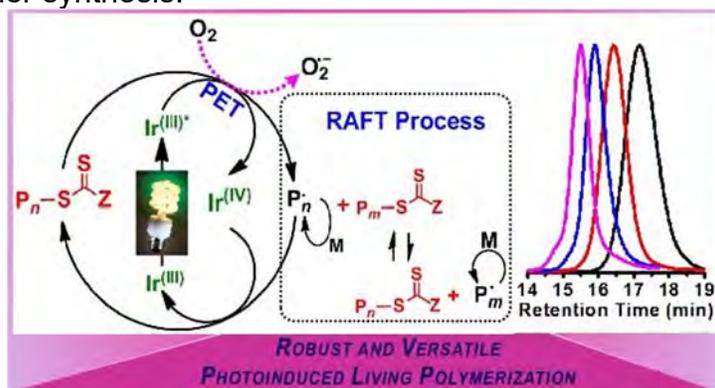
Top left: insoluble guar residue in broken guar; top right: samples in high-throughput automated method, and bottom: residue volume quantification.

POLY 211: Photoinduced living polymerization for precision polymer synthesis

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The use of visible light photoredox catalysis in organic chemistry has enabled the synthesis of known chemical compounds through novel synthetic routes, eliminating side reactions and complex purification procedures. Recently, we have successfully implemented photoredox catalysis in polymer chemistry leading to the development of novel light-induced polymerizations, namely PET-RAFT technology, which involves the reversible deactivation of thiocarbonylthio compounds (RAFT agents) by photoredox catalysts via a photoinduced electron or energy transfer (PET) process. In this technology, ppm amount of photoredox catalyst is employed to catalyze RAFT agent and generate radicals for subsequent polymerization, instead of external radical initiator in the traditional RAFT formulation. The RAFT agent plays the role of initiator, chain transfer agent and termination agent.

Although this technology was developed from traditional RAFT polymerization with minor changes in formulation, it presented different reaction mechanism and offered a number of significantly “green” attributes to living radical polymerizations, including: (1) low energy consumption and mild reaction conditions, (2) spatial and temporal control on radical polymerization, (3) high oxygen tolerance, (4) versatile photocatalysts and (5) selective polymerization activation. In this talk, these benefits from PET-RAFT technology will be summarized and demonstrated by our recent results. This technology is contributing to the development of green chemistry and sustainable polymer manufacturing, but also providing opportunities for the innovation of new methods of organic and polymer synthesis.



POLY 212: Exploiting light to push the limits of controlled radical polymerization

*R. N. Carmean, Charles A. Figg, Georg Scheutz, Tomohiro Kubo, Michael B. Sims, Troy Becker, **Brent S. Sumerlin**, sumerlin@chem.ufl.edu. Department of Chemistry, University of Florida, Gainesville, Florida, United States*

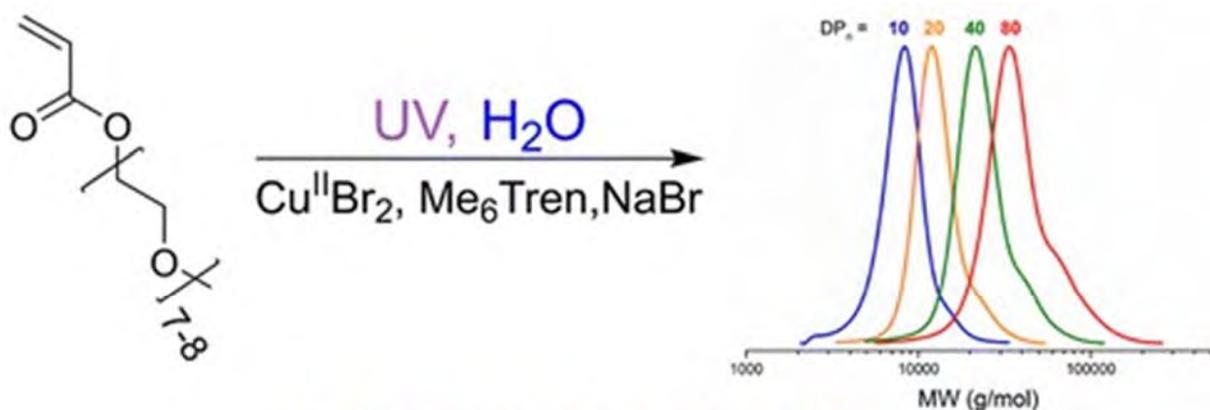
Relying solely on mild ultraviolet irradiation of thiocarbonylthio compounds in the presence of vinyl monomers, a new avenue to well-defined ultrahigh molecular weight (UHMW) polymers has been developed. Through the use of aqueous conditions, well-controlled polymers with high molecular weights that are unprecedented for controlled radical polymerizations have been achieved. This photomediated polymerization approach reaches number-average molecular weights in excess of 8.00×10^6 g/mol with degrees of polymerization above 85,000, making these, to our knowledge, the highest molecular weight polymers ever achieved via reversible-deactivation radical polymerization. In many cases, well-defined UHMW polymers can be obtained in minutes. The utility of the technique is further demonstrated through the synthesis of block copolymers, enabling access to a new field of well-defined UHMW materials.



POLY 213: Developments in aqueous copper(II) photoinduced polymerization of acrylates

David M. Haddleton, *D.M.HADDLETON@WARWICK.AC.UK*, Glen Jones, Richard Whitfield, Athina Anastasaki. *Chemistry Department, University of Warwick, Coventry, United Kingdom*

Photoinduced metal-mediated radical polymerization is a rapidly developing technique which allows for the synthesis of macromolecules with defined molecular weight and narrow molecular weight distributions, although typically exhibiting significant limitations in aqueous media. Herein we demonstrate that the presence of alkali metal halide salts, in conjunction with low copper concentration and UV irradiation, allows for the controlled polymerization of watersoluble acrylates in aqueous media, yielding narrow molecular weight distributions and high conversions. Despite the aqueous environment which typically compromises polymer end group fidelity, chain extensions have also been successfully performed and different degrees of polymerization were targeted. Importantly, no conversion was observed in the absence of UV light and the polymerization could be switched "on" and "off" upon demand, as demonstrated by intermittent light and dark periods and thus allowing access to spatiotemporal control.

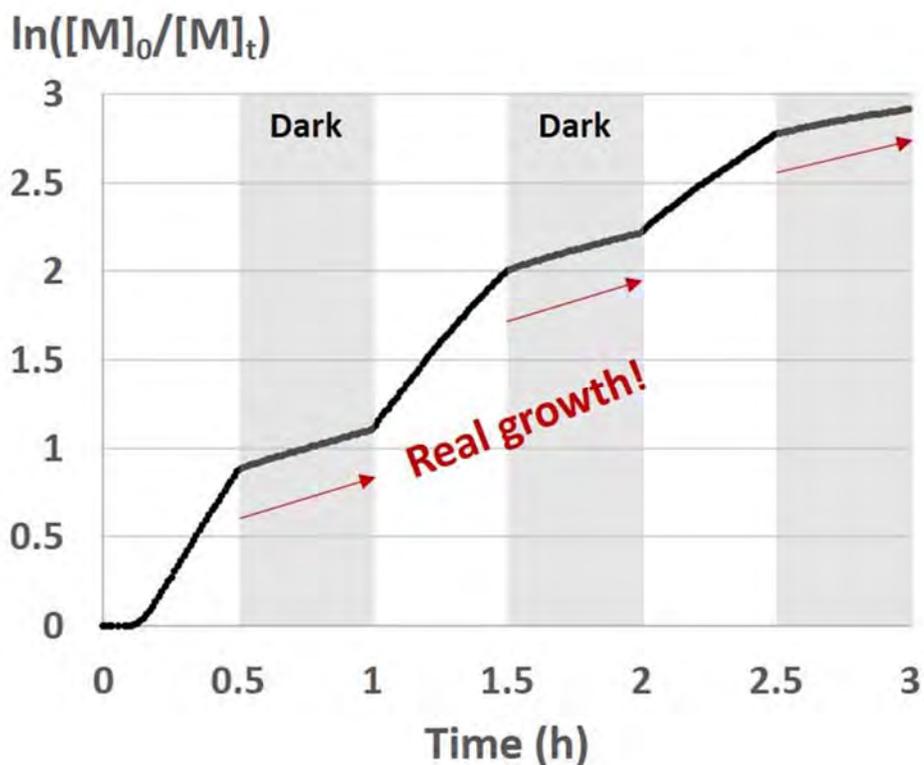


Low [Cu] + NaBr :
Controlled polymerization in Water

POLY 214: Shedding a light on state of the art photo-mediated controlled polymerizations

Athina Anastasaki², *ath.anastasaki@gmail.com*, Neil Dolinsk², In-Hwan Lee², Craig J. Hawker¹. (1) Univ of California, Santa Barbara, California, United States (2) University of California, Santa Barbara, Coventry, United Kingdom

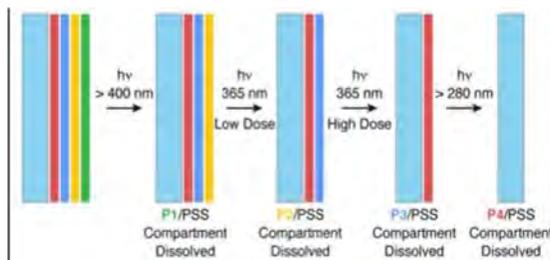
Perhaps the most attractive characteristic of photo-mediated controlled polymerizations is their capability for temporal control. However, in many reported systems a small, yet reproducible, percentage of conversion can be observed during the dark periods. This small percentage has been attributed to either error during sampling or inaccuracy of the NMR measurement. In this talk, the state of the art photo-mediated controlled polymerizations will be compared in order to identify their real behavior during the dark period. In situ NMR monitoring will be used as a simple and modular method to study the polymerization kinetics revealing the best “on-off” photo-polymerization systems and providing with invaluable information with respect to the mechanism of each approach (e.g. ATRP, PET-RAFT etc.)



POLY 215: Photodisruptable layer-by-layer films

Samuel W. Thomas, *sam.thomas@tufts.edu*. Chemistry, Tufts University, Medford, Massachusetts, United States

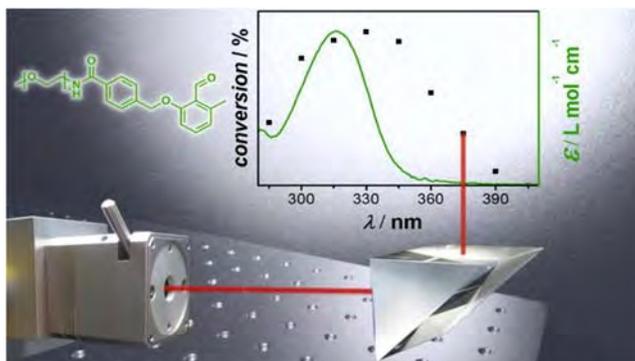
This talk will describe layer-by-layer photoresponsive polyelectrolyte multilayer films that become soluble upon irradiation with visible or ultraviolet light due to photolysis of photolabile side-chains. Irradiation with the appropriate wavelength of light cleaves the side chains from the polymer backbones resulting in increased hydrophilicity and reduced electrostatic attraction of cationic and anionic layers, enabling their dissolution in aqueous solutions. By combining up to four different photocleavable groups, we have demonstrated multi-height photopatterning and sequential, wavelength-selective release of guests. Incorporation of photocleavable groups with good two-photon cross-sections enables film dissolution with near infrared light. Stimuli-responsive, free-standing polyelectrolyte multilayer films can also be fabricated using this approach.



POLY 216: Controlling macromolecular synthesis with different colors of light

Christopher Barner-Kowollik^{1,2}, christopher.barnerkowollik@qut.edu.au. (1) School of Chemistry, Queensland University of Technology, Brisbane, Queensland, Australia (2) Institute for Polymer Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany

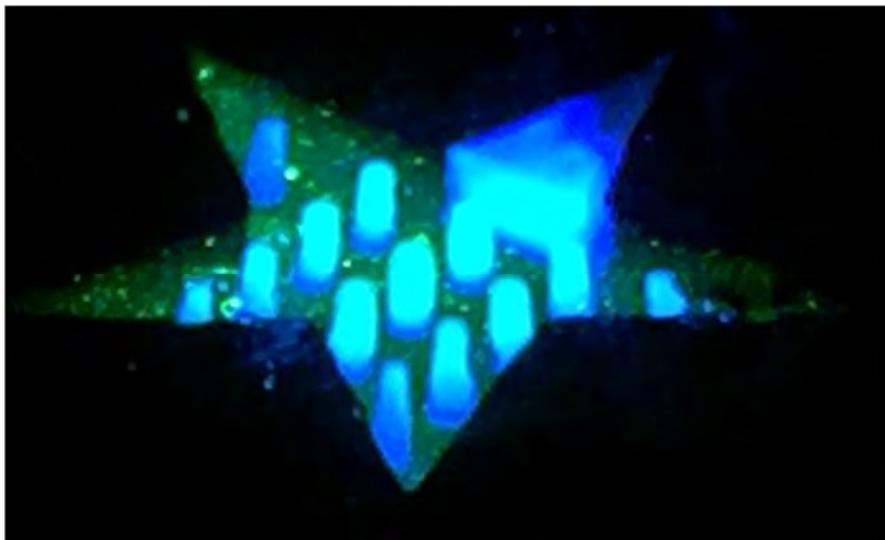
Installing chemical functionality at precise locations within complex macromolecules as well as onto three dimensional direct laser written constructs in the mildest possible fashion (visible light) and without any catalyst becomes possible with efficient light driven, λ -orthogonal, quantitative ligation protocols.¹⁻⁷ Advanced light-induced processes enable the parallel encoding of multiple molecules onto predefined locations on 3D microstructures in one step⁸ as well as the wavelength dependent addressing of specific parts of a macromolecule for its highly orthogonal functionalization (λ -orthogonal photochemistry).⁹ The lecture will highlight how macromolecular ligations can be directed in their selectivity by different colors of light and, critically, how different colors of light can be used to control chemical reactivity and even completely hold thermal reaction channels.¹⁰ Such color guided reaction manifolds can be exploited as a orthogonal triggers in macromolecular chain folding,¹¹ the synthesis of sequence defined macromolecules¹² or diffraction unlimited laser lithography.¹³



POLY 217: Wavelength selective photochemistry for simultaneous multi-material printing

Zachariah A. Page⁴, zapage@mrl.ucsb.edu, Neil Dolinsk², Ben Callaway², Fabian Eisenreich¹, Ronnie Garcia⁴, Roberto Chavez⁴, David Bothman⁵, Stefan Hecht PhD¹, Frank Zok², Craig J. Hawker³. (1) Dept Chemistry Hu Berlin, Berlin, Germany (2) Materials, UCSB, Santa Barbara, California, United States (3) Univ of California, Santa Barbara, California, United States (4) University of California Santa Barbara, Goleta, California, United States (5) Mechanical Engineering, University of California Santa Barbara, Santa Barbara, California, United States

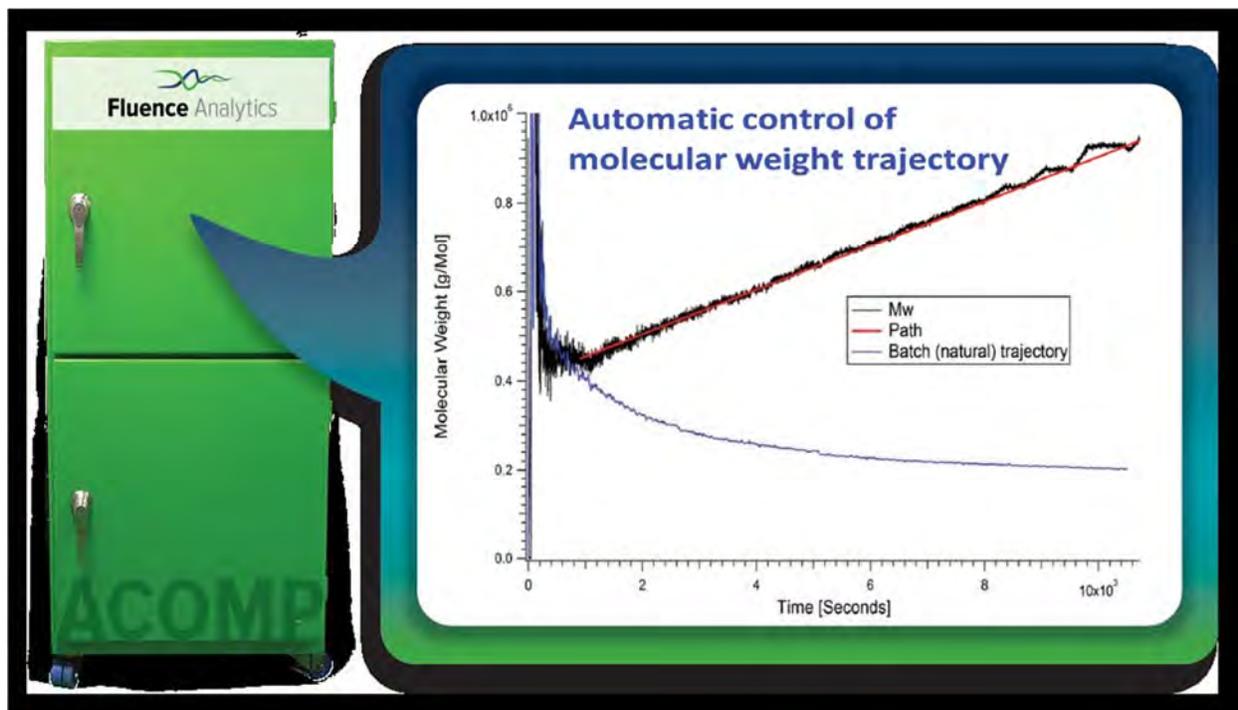
Printing polymer composites with chemically and mechanically distinct domains will provide access to designer plastics that are well-suited for a wide variety of applications, from biomedical implants to trusses. However, state-of-the-art methods to 3D print multi-material objects utilize layer-by-layer processes, which leads to intrinsic defects at the dissimilar interfaces. Here we present a continuous wavelength selective photochemical curing methodology that removes the issues related to layering, while simultaneously providing multi-material objects with spatially resolved features.



POLY 218: Monitoring of emulsion polymerization with ACOMP and early results on control

Aide Wu¹, Rick D. Montgomery², Michael F. Drenski², Terry McAfee¹, **Wayne F. Reed¹**, wreed@tulane.edu. (1) Physics Dept, 2001 Stern Hall, Tulane University, New Orleans, Louisiana, United States (2) Fluence Analytics, New Orleans, Louisiana, United States

Early results are presented for control of conversion kinetics in free radical inverse emulsion polymerization of acrylamide using the ACOMP/CI (automatic continuous online monitoring of polymerization reactions with control interface). Recent work in automatic control of simultaneous molecular weight and copolymer composition trajectories for non-emulsion systems is shown as a prelude to similar control in emulsion polymerization. Initial results on coupling of a 60 MHz process NMR to the ACOMP detector train in order to control terpolymer composition during synthesis are discussed. A dual stream approach has also been taken with inverse emulsion polymerization in which one stream is inverted and broken with surfactants to measure conversion and reduced viscosity, and a second stream uses dilution with oil for simultaneous measurement of emulsion size distributions using Mie scattering. Implementation of ACOMP on full scale industrial inverse emulsion reactions has begun in the past few years, which includes the ability to monitor the approach of reactions to low level ppm residual monomer setpoints, while also continuously monitoring reduced viscosity. The outlook for near term industrial implementation of ACOMP/CI in the industrial sector is discussed.

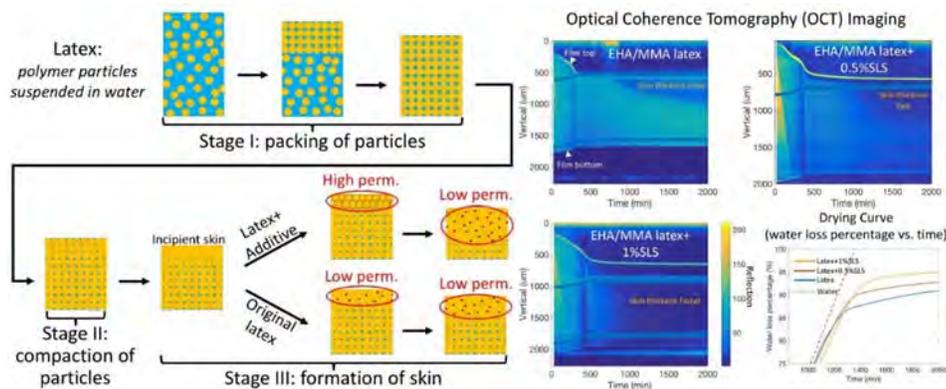


POLY 219: Mechanism of skin layer formation during drying of latex films

Hao Huang¹, *hah213@lehigh.edu*, **Daniel Ou-Yang**², **Willie Lau**³, **Mohamed S. El-Aasser**¹. (1) Department of Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, Pennsylvania, United States (2) Department of Physics, Lehigh University, Bethlehem, Pennsylvania, United States (3) Beijing Oriental Yuhong Waterproof Technology Co., Ltd, Beijing, China

Waterborne latex coatings for protection and waterproofing purposes require film thicknesses in the millimeter range. During drying of such thick latex films, the top surface of the film get dried early and form a transparent polymer skin while beneath it is still wet and opaque. Skin layer impedes water evaporation and extends the film drying time considerably. To study the mechanism of skin layer formation, optical coherence tomography (OCT), analytical balance and video camera were integrated together (called “OCT-Gravimetry-Video” method) to simultaneously monitor the film’s thickness and internal microstructure, the weight loss by water evaporation, and the visual appearance of film as a function of drying time. Three drying stages for skin layer formation were observed: I) packing of particles, II) compaction of particles and III) formation of skin. In Stage I, particles accumulate and become packed from the top to the bottom of the film; the drying rate during this stage is equal to that of pure water. In Stage II, packed particles become further consolidated or compressed while the drying rate is still close to that of pure water. In Stage III, particles on the top of the film become deformed and coalesced into a transparent skin, whose thickness increases slowly with about square root of time until the film is totally dried; the drying rate during this stage is dramatically reduced and determined by the permeability and thickness of skin.

In coating applications, it is anticipated to lose as much water as possible before the skin impedes the drying rate. Some water-soluble additives (such as surfactants, that were mixed with latex) were found to lower the water content trapped in film beneath the skin. OCT also showed that surfactant additive can accelerate growth of skin thickness and the whole film becomes transparent earlier. We propose that: an additive, which can retard coalescence between deformed particles, makes the skin permeable in the initial short time of skin formation. This allows more water evaporation before deformed particles become fully coalesced. This study is expected to provide a guideline in additive selections and synthesis designs to solve the drying problem of thick latex films.



POLY 221: Analysis of polymer colloids: Tutorial

Wei Gao, *weigao@dow.com*. Analytical Sciences, Core R&D, The Dow Chemical Company, Collegeville, Pennsylvania, United States

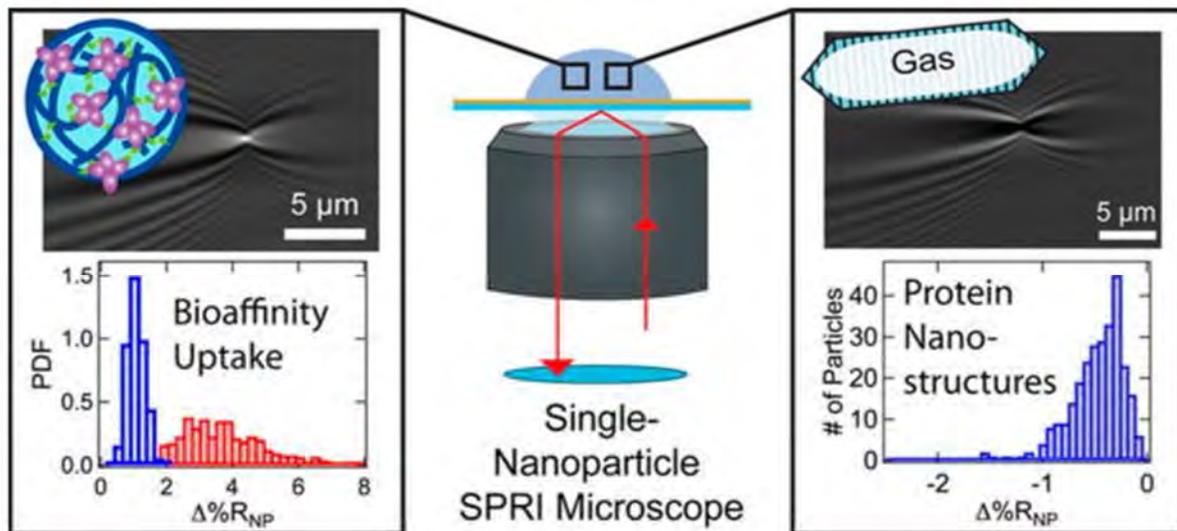
A polymer colloid is usually defined as a dispersion of submicron polymer particles in a liquid (typically aqueous) medium. Besides the traditional lyophobic systems, the association colloids involving amphiphilic polymers are also important systems of polymer colloids. A wide variety of processes are used to prepare polymer colloids. The most often utilized method is emulsion polymerization, which is the basis of a massive global industry. By 2020 the global demand for emulsion polymers alone is forecasted to be 12,500,000 MT with a value of \$37.2 billion. In addition to financial value, the shift from solvent to waterborne dispersions has yielded large and measureable sustainability benefits. The research interest in this area still continues to grow, with emerging applications in biomedical, biotechnology, energy, and other fields.

The analysis of polymer colloids is important to fundamental research, new product development and industrial production. The analysis of polymer colloids can be very complicated based on the level of the information being sought. There are many techniques being commonly used or recently developed for the analysis of polymer colloids. Many polymer characterization techniques have been used for the characterization of polymers made by emulsion polymerization or used for making polymer colloids, but there are many challenges due to the unique nature of these polymers, such as ultra high molecular weight, amphiphilic chemical composition, broad chemical composition distribution, and complexity of polymer chain architecture, etc. Besides polymer molecular structure, the colloidal property is another important aspect for the analysis of polymer colloids. This tutorial will review the analytical techniques with particular emphasis on how to provide molecular insight into emulsion polymerization and many colloidal phenomena, how to characterize the physical and colloidal properties, how to obtain particle morphology information, and how to probe the interactions that determine the properties of colloidal systems.

POLY 222: Detection and characterization of single polymeric nanoparticles with surface plasmon resonance imaging microscopy

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Surface plasmon resonance imaging (SPRI) is a well-established method for the multiplexed bioaffinity detection of protein and nucleic acids via refractive index. We have recently developed a near infrared SPRI microscope for the detection and characterization of single nanoparticles. Single nanoparticles are detected via interference patterns in the differential reflectivity image created by the interaction of the single nanoparticle refractive index with the traveling surface plasmon polariton waves. Single nanoparticle SPRI can be used to measure the refractive index of various types of single polymeric nanoparticles. We have used these single nanoparticle SPRI measurements to monitor to measure particle size distributions of polystyrene nanoparticles, porous hydrogel N-Isopropylacrylamide (NiPAM) nanoparticles, liposomes and gas-filled protein vesicles. We have also monitored the uptake of peptides and proteins into NiPAM nanoparticles, and the lectin-induced aggregation of carbohydrate NiPAM nanoparticles.

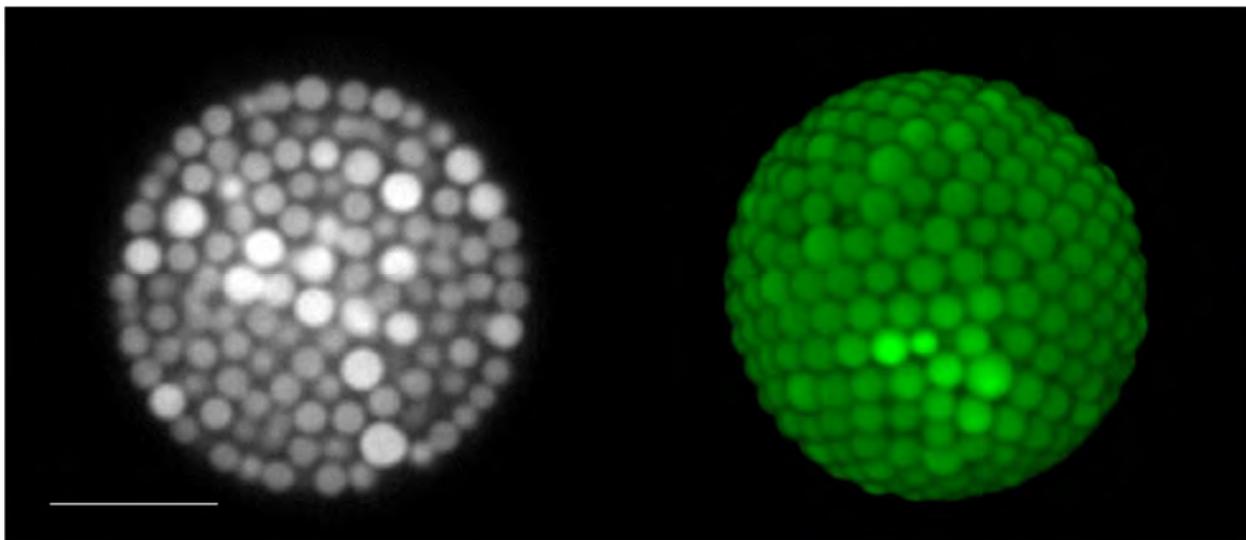


Single Nanoparticle Surface Plasmon Resonance Imaging

POLY 223: Finding order in glasses: Structures and dynamics of glass-forming polymer colloidal liquids under confinement

Bo Zhang, **Xiang Cheng**, xcheng@umn.edu. University of Minnesota, Minneapolis, Minnesota, United States

When a liquid is quickly quenched below its melting temperature, it can avoid crystallization and form an amorphous solid—the glass transition occurs. Although ubiquitous and technically important, the glass transition still eludes a universally accepted theoretical description. Recent theories proposed that when a supercooled liquid approaches the glass transition, particle clusters with a special “amorphous order” nucleate within the liquid, which lead to static correlations dictating the dramatic slowdown of liquid relaxation. Here, we study confined polymer colloidal liquids in both 2D and 3D systems, where a layer of colloidal particles is fixed at the circular or spherical boundary. Using the confined systems of different dimensionalities, we capture the amorphous-order particle clusters and demonstrate the development of a static correlation. Moreover, by investigating the dynamics of spherically confined samples, we reveal a profound influence of the static correlation on the relaxation of colloidal liquids. We propose a simple relation for the change of the configurational entropy of confined colloidal liquids, which quantitatively explains our experimental findings and illustrates a divergent static length scale during the colloidal glass transition. We also explore the effect of confinement on both the translation and rotation of asymmetric polymer colloids.

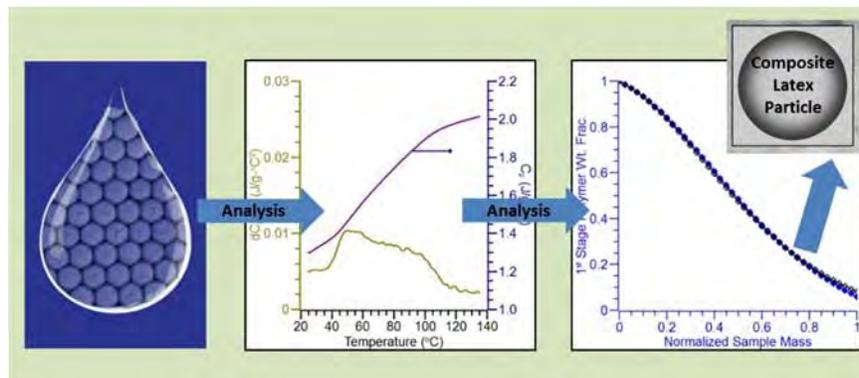


Supercooled liquids made of polymer colloids. The colloidal liquids are confined in a spherical cavity of diameter 14.0 μm .

POLY 224: Utilization of DSC for polymer colloid morphology analysis

Amit K. Tripathi², aka25@wildcats.unh.edu, John Tsavalas^{2,1}. (1) Materials Science, University of New Hampshire, Durham, New Hampshire, United States (2) Chemistry, University Of New Hampshire, Durham, New Hampshire, United States

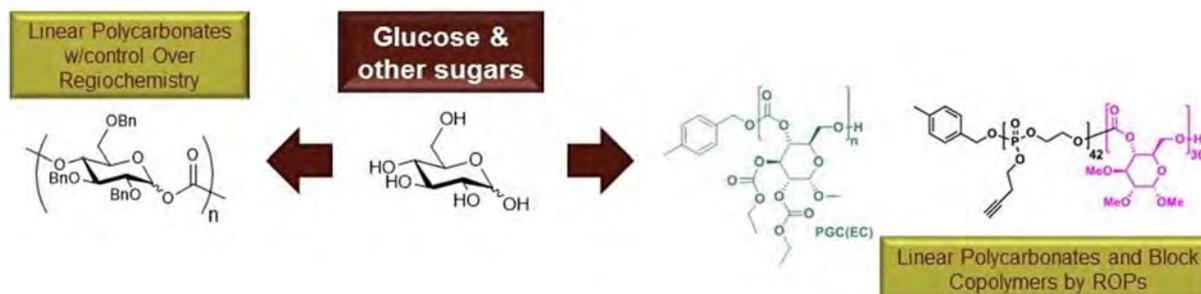
The complex morphology obtained from multiphase emulsion polymerization requires careful analysis using multiple analytical techniques. Differential scanning calorimetry (DSC) has traditionally been used for analysis of individual polymer properties, such as glass transition temperature. However, the DSC analysis of a multiphase latex polymer includes signal corresponding to various mixed phase states within the sample; consequent to the morphology at hand. Here we demonstrate an approach to utilize DSC for complete quantitative analysis of phase mixing within a latex sample towards a better understanding of particle morphology. The sensitivity and cost-effectiveness of this technique make this a useful tool for composite polymer sample analysis. In addition, while most DSC analyses are performed on samples in the dry state, the polymer particle morphology is created when fully hydrated within the continuous aqueous phase. It is thus critically important to understand the role of hydroplasticization in latex particle morphology development. Hydroplasticization of each of the polymer phases within a particle can also be directly measured using DSC, impacting the ability of the phases to diffuse and rearrange, which will also be discussed here.



POLY 225: Transformation of natural products into functional polymer systems, with guidance by biomedical application targets

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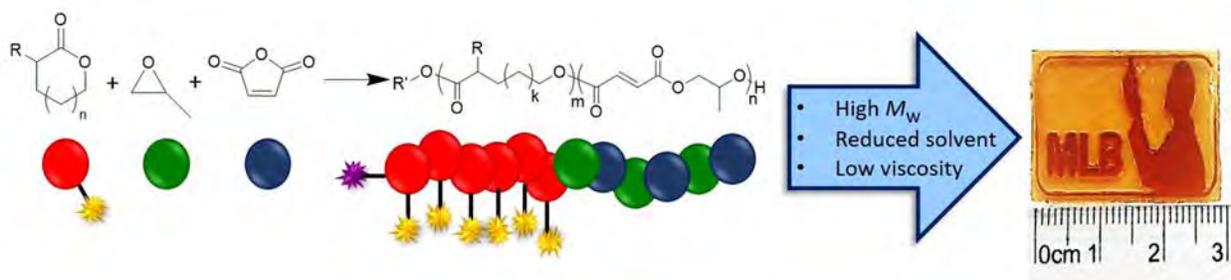
A primary interest in the Wooley laboratory is the production of functional polymers from renewable sources that are capable of reverting to those natural products once their purpose has been served. The inherent stereochemical and functional diversities of natural products provide opportunities to expand the scopes and complexities of polymer materials, by utilizing fundamental synthetic organic chemistry approaches. This presentation will highlight synthetic strategies for the development of polymer materials, which can be produced by relatively simple approaches from complex polyhydroxyl natural products and can be made to exhibit a range of properties, based upon the monomeric building blocks and, typically, carbonate or phosphoester linkages. A focus of this presentation will be on the transformation of D-glucose and other sugars into well-defined polymers with investigation of those materials as nanoscopic drug delivery devices in direct routes of administration for the treatment of osteosarcoma lung metastases or recurrent urinary tract infections.



POLY 226: Block copolymers of polylactones and poly(propylene fumarate) for 3D printed biological scaffolds

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Poly(propylene fumarate) (PPF) has been extensively studied for use in additive manufacturing and *in vivo* applications as a consequence of its alkene photo-crosslinking ability and degradation into bioresorbable products upon hydrolysis of the ester linkage. A one-pot ring-opening polymerization of a lactone followed by a ring-opening copolymerization of maleic anhydride and propylene oxide has been used to produce poly(lactone-*block*-propylene fumarate) copolymers. This method allows for the introduction of chain functionalities that can be modified post-polymerization or post-printing using 'click'-type addition reactions in order to attach proteins to the surface and improve biocompatibility. A series of copolymers were created using various lactones in order to tune the thermal, mechanical, and degradative properties. Resins of these block copolymers were able to be printed to make high resolution objects using continuous digital light processing with a higher molecular weight polymer and less solvent than previously reported.



POLY 227: Development of new polymers for biofabrication: Hydrogels for 3D printing and resins for DLP

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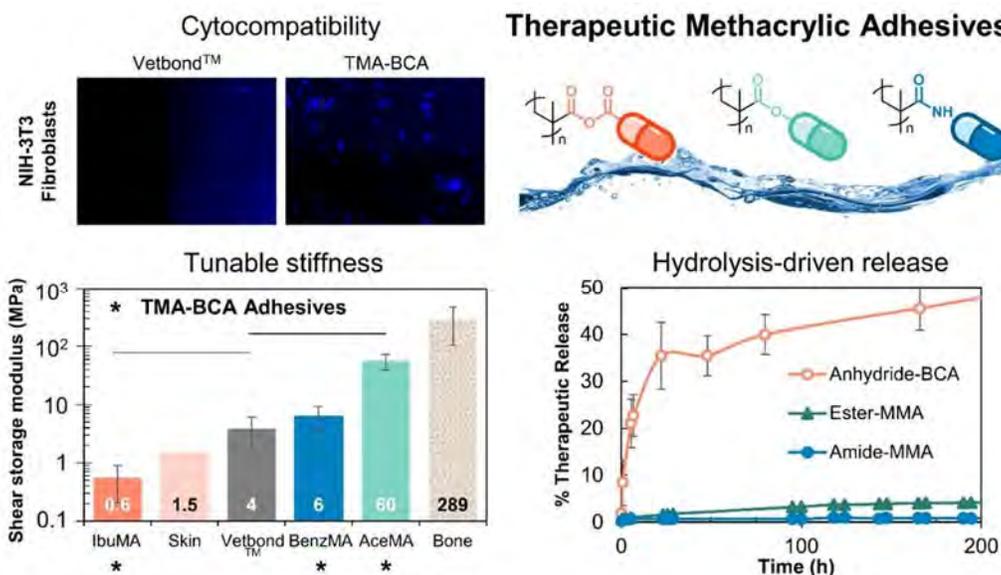
Biofabrication methods provide great potential to go beyond 2D tissue engineering towards 3D functional tissues and organs for application in regenerative medicine strategies. However, despite this promise, the library of materials suitable for fabrication strategies remains relatively small and poorly customizable. Towards expanding the materials and strategies for biofabrication, two examples of customized polymers will be presented. Firstly, in order to facilitate 3D bioprinting of cell laden constructs, we have recently developed a synthetically modified alginate based “bioink” that can support cell growth, proliferation, and the extrusion based fabrication of 3D structures via light activated thiol-ene conjugations. This hydrogel’s material properties can be rationally tuned and can support the creation of constructs with multifunctional bioactive cues. Secondly, a simple example of customized resins for digital light processing (DLP) of culture environments and biofabricated objects will be presented. These poly(ester)urethane acrylate resins provide control over the mechanical properties and cell adhesion of the fabricated construct, while allowing high-fidelity feature production. Both platforms presented are developed towards the future creation of dynamic and stimuli-responsive 3D constructs aimed at investigating the effect of material and construct dynamics on engineered tissues.



POLY 228: Hydrolysis-driven controlled drug delivery and tunable adhesive properties via novel therapeutic methacrylic monomers

Zoe Wright, zwright@andrew.cmu.edu, Stefanie A. Sydlik, Brian Holt. Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States

Medical adhesives have the potential to eliminate the need for unpleasant mechanical fixations such as sutures, staples, and screws, but face challenges to widespread implementation due to brittleness and cytotoxicity. To overcome these limitations, we designed therapeutic methacrylic (TMA) monomers that impart tunable mechanical properties, decreased formaldehyde release, and covalently-controlled bioactivity to commercial medical adhesives. Small molecule therapeutics including NSAIDs, analgesics, and other cell-instructive compounds have been covalently tethered to the carbonyl of methacrylate using bonds of varying stability to hydrolysis. The resulting TMA monomers are compatible with both cyanoacrylate-based (skin) and methacrylate-based (bone) medical adhesives, co-polymerizing with these adhesives on contact with tissue to form polymers with enhanced adhesive properties. For example, when an anhydride-tether TMA was incorporated into 3M's Vetbond™, a butyl cyanoacrylate (BCA) skin adhesive, the resulting TMA-BCA material delivered therapeutic on the same order of magnitude and time scale as topical medications, where ester- and amide-tether TMA-BCA adhesives could sustain delivery of a lower dose of therapeutic over several weeks. In addition to the hydrolysis-driven controlled release, TMA adhesives also inherit new mechanical properties based on the structure of their therapeutic payloads, enabling specific functionality to be programmed directly into the polymer backbone of adhesives. For example, TMA materials carrying therapeutics capable of hydrogen bonding created stiffer and tougher (less brittle) adhesives, while those carrying bulky therapeutics with flexible segments created adhesives that recapitulate the softness of skin. Overall, TMAs represent a platform technology that can be used to build adaptable, bioactive adhesives through principles of molecular design and polymer chemistry.

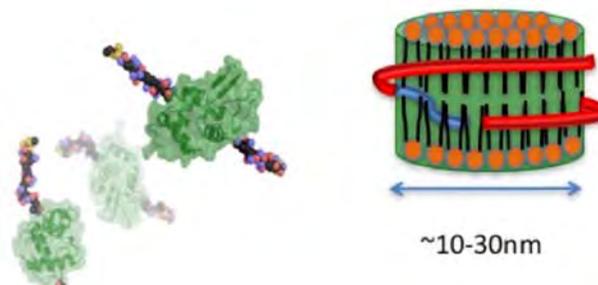


POLY 229: Proteins and polymers: Synergies in bioconjugates and structures

Dominik Konkolewicz², d.konkolewicz@gmail.com, Richard C. Page², Gary Lorigan², Indra Sahu², Kevin Burridge², Melissa Lucius², Thaiesha Wright², Emily Clark², Andrew Craig², Jason Berberich¹, Jamie Stewart², Henry Fischesser². (1) Chem, Paper, Biomed Eng, 64 Eng Bldg, Miami University, Oxford, Ohio, United States (2) Department of Chemistry and Biochemistry, Miami University, Oxford, Ohio, United States

Polymers have been various biological applications, ranging from biocompatible scaffolds, to delivery vectors. Polymer bioconjugation, where a synthetic polymer is connected to an enzymatic or therapeutic protein has been shown to be particularly beneficial since the attached polymer can stabilize the protein against proteases, aggregation and immune responses. However, the connection between polymer structure and protein stability and activity is poorly understood. Using reversible deactivation radical polymerization, a wide library of polymer structures can be synthesized with flexibility over chemical functionality. Here we use two model enzymes, lysozyme from hen egg white, and cellulase from *Fervidobacterium nodosum* to study the impact of polymer structure on enzymatic activity and structural stability in functional polymer bioconjugates. In particular, polymers that have beneficial non-covalent attractions to substrates can dramatically enhance enzymatic activity, enabling polymer modification to be a new avenue for enzyme activation. Further, high molecular weight polymers and larger degrees of polymer modification can enhance protein structural stability.

Synthetic polymers can also interact beneficially with lipids, creating optimized environments for studying membrane proteins. Membrane bound proteins represent 1/3 of all proteins, yet they represent only a small fraction of all known structures. Using well-defined copolymers of styrene and maleic acid enable well-defined nanoscale lipid discs to be created. In particular, the size of these discs can be varied by polymer composition, and they enable membrane protein encapsulation. This enables structural studies of these membrane proteins to be performed, and creates a versatile platform for structural biological studies.



POLY 230: Elastin-like peptide nanoparticles for drug delivery to the brain

Jan Pille^{1,2}, mail@janpille.org, **Lisanne van Oppen**^{3,4}, **Sanne van Lith**⁵, **Ilia Vialshin**¹, **René Raave**⁵, **Danny Gerrits**⁵, **Sandra Heskamp**⁵, **William Leenders**³, **Otto Boermann**⁵, **Roland Brock**³, **Jan Smeitink**⁴, **Jan van Hest**^{1,2}. (1) *Bio-Organic Chemistry, Eindhoven University of Technology, Eindhoven, Netherlands* (2) *Bio-Organic Chemistry, Radboud University, Nijmegen, Netherlands* (3) *Department of Biochemistry, Radboud Institute for Molecular Life Sciences, Nijmegen, Netherlands* (4) *Department of Pediatrics, Radboud Institute for Molecular Life Sciences, Nijmegen, Netherlands* (5) *Department of Radiology and Nuclear Medicine, Radboud University Nijmegen Medical Centre, Nijmegen, Netherlands*

Treating neurological disorders often demands overcoming the blood-brain barrier. Hijacking the active transport mechanisms of this tight, selective endothelial cell layer shows great promise in administering therapeutic agents to the brain.

A potential carrier system needs to be well-defined, bio-compatible and able to display functional moieties for transcytosis. We designed and characterized temperature-responsive elastin-like peptide (ELP) nanoparticles that are highly monodisperse and stable.

We have characterized ELP nanoparticles using multi-angle light scattering coupled to size-exclusion chromatography to determine their absolute molecular weight and aggregation number. The resulting micelles had hydrodynamic radii of 24.2 ± 0.7 nm and consisted of 250 ± 9 monomers with a total molecular weight of 12.0 ± 0.4 MDa. We showed that the surface density of various ligands and targeting groups can be controlled by combining different ELPs prior to temperature-induced micelle formation. This affected cell binding, (endosomal) cell uptake and activity of attached groups. Both cell-penetrating peptides as well as nanobodies were reliably displayed on the micellar surface in combination with e.g. fluorophores and photosensitizers.

We used the peptide G23, known to bind the ganglioside GM1b, resulting in transcytosis across the blood-brain barrier, as a targeting group to direct ELP nanoparticles to the brain. We show *in vitro* and *in vivo* results of G23-modified ELP nanoparticles and their ability to overcome the blood-brain barrier.

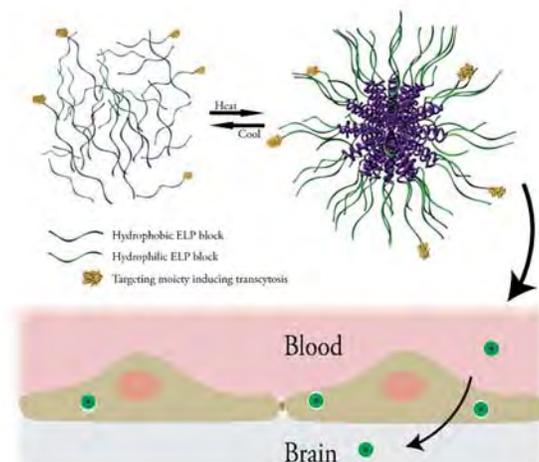
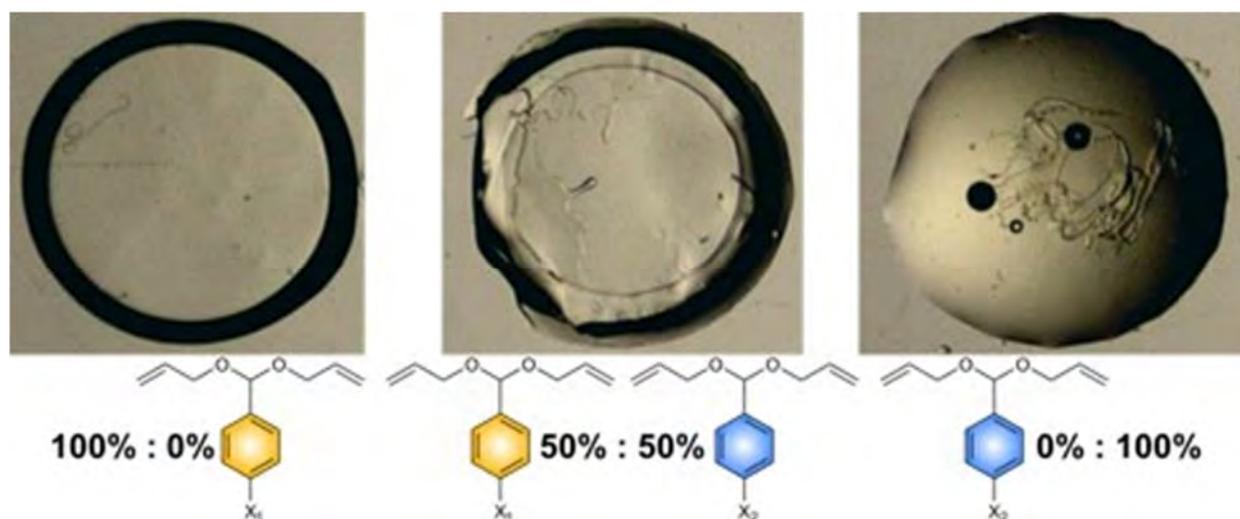


Figure 1: Schema of nanoparticle formation and transcytosis across the blood-brain barrier. Mixed micelles displaying targeting groups are created by co-assembly of dissolved species upon reaching physiological temperature. The resulting particles specifically recognize the blood-brain barrier and are transported by transcytosis.

POLY 231: Bioerodible poly(acetal)-based networks as controlled release matrices

Dahlia N. Amato, dahlia.amato@usm.edu, Douglas V. Amato, William Martin, Sarah Swilley, Michael Sandoz, Derek L. Patton. School of Polymer Science & Engineering, University of Southern Mississippi, Hattiesburg, Mississippi, United States

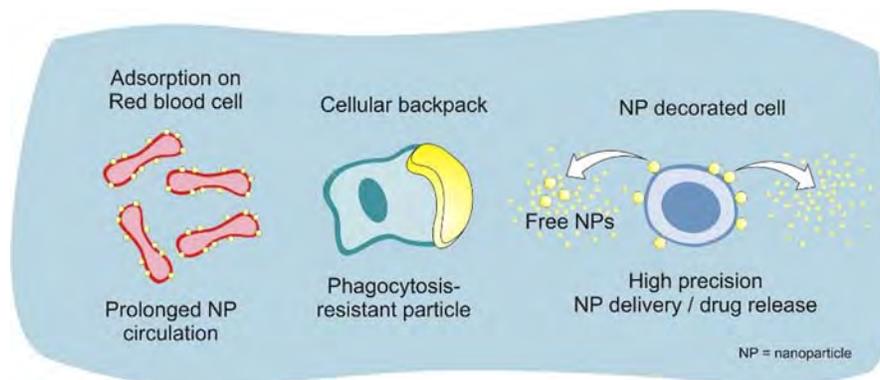
Crosslinked poly(acetals) based on a variety of aromatic and aliphatic aldehydes were developed as bioerodible matrices for controlled delivery applications. The hydrolytic reactivity of the acetal linkage provides an intrinsic advantage over other classes of bioerodible polymers in versatility and control of degradation rates. We have found that the degradation rates of acetal-based polymer networks can be tuned over a dramatic range (days, weeks, months, years) via substituent effects of para-substituted benzaldehydes. Additionally, we found that intermediate degradation rates can be obtained via copolymerization of multiple acetal linkers. The resulting polymer networks were characterized by infrared (IR), differential scanning calorimetry, and optical microscopy. Degradation kinetics were obtained via ^1H NMR spectroscopy and GC-MS over several months. The combination of time lapse imaging and multiple pH environments suggest a release mechanism that is dominantly degradation controlled. Degradation of these poly(acetals) was observed to be pH sensitive, being enhanced in low pH, and became more stable in basic conditions.



POLY 232: Surface modification of living cells with synthetic polymer nano- and microparticles

Harm A. Klok, *harm-anton.klok@epfl.ch*. STI-IMX-LP, EPFL, Lausanne, Switzerland

Cells provide attractive opportunities to develop innovative drug delivery systems. Red blood cells e.g. are uniquely designed to circulate in the bloodstream for extended periods of time. Immune cells, in particular lymphocytes from the adaptive immune system, are attractive as they potentially provide possibilities to home in to the disease site in a highly selective manner. Modifying the surfaces of these cells with synthetic polymers or polymer nanoparticles provides manifold opportunities to further enhance their functionality. Successful polymer cell surface engineering, obviously, requires conjugation chemistries that proceed under biological conditions and in high yields and without compromising cell viability and function. This presentation will discuss various polymer cell surface modification strategies and compare these different approaches in terms of the possibilities they offer to modify cell surfaces as well as their impact on cell viability and function. It will be shown that under appropriate conditions live cells can be surface modified with synthetic polymers while retaining their viability and functional properties.

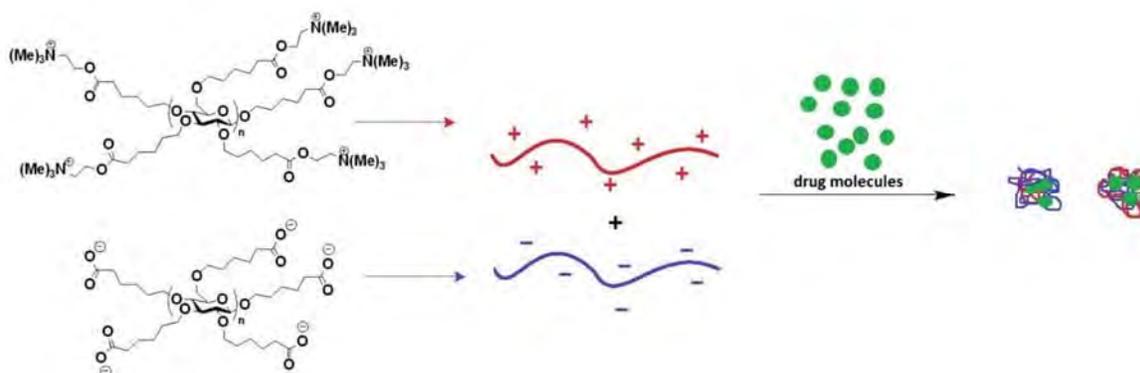


POLY 233: Charging up cellulose and curdlan: Expanding the potential of polysaccharide based polyelectrolytes for therapeutic delivery applications

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Polyelectrolytes are of increasing interest in delivery applications involving charged and peptide drugs due to their ability to form polyelectrolyte complexes (PECs). Drug delivery systems composed of these complexes can avoid the need for chemical crosslinking while achieving desired physicochemical properties and maintaining high biocompatibility. Natural biomaterials such as cellulose and curdlan are extremely attractive for this application due to renewability, biocompatibility and non-toxicity. Chemical modifications of cellulose to append ionic and pH sensitive groups is a promising route to novel delivery biopolymers. However, extensive introduction of highly charged groups to polysaccharide backbones is challenging due to charge repulsion and basic reaction conditions.

We have utilized olefin cross metathesis as a synthetic strategy to eliminate the impediment of charge repulsion to synthesis of cellulose based polyelectrolytes. Olefin cross metathesis (CM) has proven to be a mild and efficient synthetic approach to impart a wide range of functionality to both cellulose esters and ethers. We have been able to utilize this strategy to fully modify cellulose and curdlan (DS 3) with pH-responsive carboxyl groups that permit strong polymer-drug interactions. We expect these interactions to lead to the enhancement of drug solubility and bioavailability. The high functional group tolerance of CM has allowed us to reach the maximum charge content possible in both cationic (quaternary ammonium) and anionic (carboxylate) polyelectrolytes with promise for controlled release of charged and poorly soluble drugs through the formation of polyelectrolyte complexes. This method also allows us to probe the structure-property relationships between chain length and morphology of highly charged polysaccharides. We report the synthesis, characterization and physical properties of these hypercharged polymers and initial findings of their potential in PEC drug delivery systems.

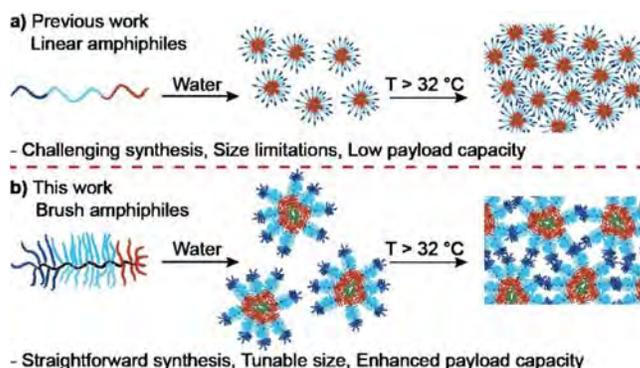


POLY 234: Thermoresponsive copolymers for immunotherapy applications

Farrukh Vohidov¹, fv4@rice.edu, Jeremiah A. Johnson². (1) Chemistry, MIT, Arlington, Massachusetts, United States (2) MIT, Massachusetts Institute of Technology, Boston, Massachusetts, United States

Efficacy of approved small molecule anticancer medicines and immunomodulators, as well as of the drug candidates currently in clinical development is often restricted by several important limitations. Because of their low water solubility and short circulation life-times, many chemotherapeutics are injected intravenously in repeated fashion, often in conjunction with an encapsulating agent to improve their solubility. The systemic administration and importantly narrow therapeutic window, are associated with severe side-effects. An alternative to systemic dosing is the use of drug-loaded delivery vehicles that can be directly injected at the tumor site allowing local drug release. We have developed a thermoresponsive delivery system that enables a single dose administration and maximizes concentration of drug molecules at tumor site for prolonged periods, at the same time minimizing unwanted exposure to healthy tissues, thereby reducing serious side-effects.

We describe a thermoresponsive three block copolymer that can serve as a versatile platform for local delivery of anticancer medicines. The copolymer is an amphiphile that self-assembles into micelles enabling solvation of hydrophobic drugs into water and at room temperature provides straightforward administration using a syringe for direct injection at the tumor site. We achieve efficient loading of three widely used chemotherapeutics: Paclitaxel, Gemcitabine, and SN-38. The drug-loaded micelles demonstrate rapid gelation when heated to 37 °C and in vitro experiments confirmed formation of a local reservoir for sustained release of medicines. We show that upon intratumor injection of combination drug-loaded hydrogel resulted in eradication of A549, human lung cancer cells, in mice. We further used the copolymer for immunochemotherapy, delivering Paclitaxel and Resiquimod, an important immunomodulator, intratumorally achieving significant inhibition in proliferation of aggressive colon cancer cells, CT-26. To best of our knowledge this is the first report of a platform that can be used for delivery of immunomodulator and along with a chemotherapeutic for combination therapy.

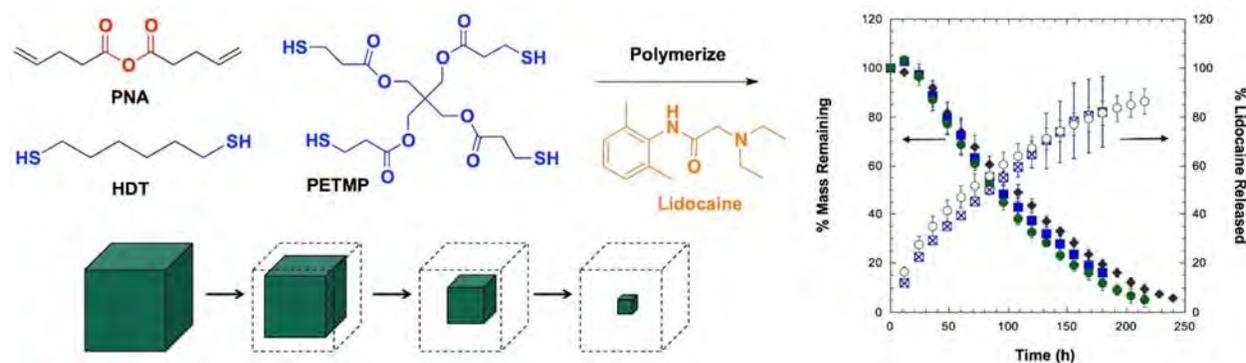


POLY 235: Surface-eroding polyanhydrides from thiol-ene polymerizations: A versatile synthetic material for bio-applications

Kelly R. Tillman, Katie L. Poetz, Ana Witkowski, Rebecca Meacham, **Devon A. Shipp**, dshipp@clarkson.edu. Chemistry Biomolecular Science, Clarkson University, Potsdam, New York, United States

Polyanhydrides have found a niche in the degradable polymer field, largely because they often undergo surface erosion, but demanding synthesis conditions have held them back from widespread use. To address this problem, we have developed novel polyanhydrides that are based on radical thiol-ene 'click' polymerization, an easy to conduct step-growth mechanism of polymerization that can be applied to make materials that have relatively uniform network structure. Further, thiol-ene 'click' polymerization is robust, can be photo-, redox- or thermally-initiated and may use a wide variety of monomers. Thus, these have real potential in a variety of applications, including orthopedics and drug delivery.

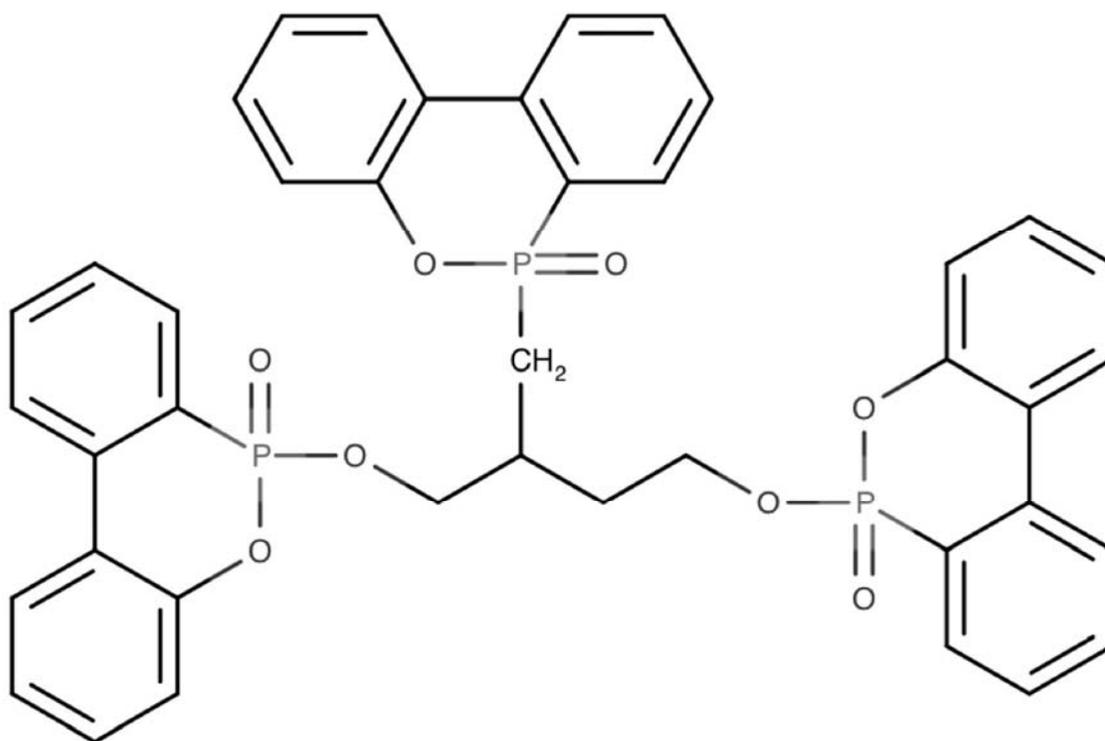
Discussed in this presentation will be the synthesis of elastomeric and semi-crystalline polyanhydrides that have controllable degradation rates, and how this approach to network polyanhydrides can provide significant flexibility in tailoring characteristics such as crosslink density, functionality and hydrophilicity. In particular, it will be shown that polyanhydrides can be used in applications such as drug delivery, can also behave as shape memory polymers, exhibit self-healing properties and can be produced as nanoparticles.



POLY 236: Nontoxic oligomeric flame retardants from the bioacid, itaconic acid

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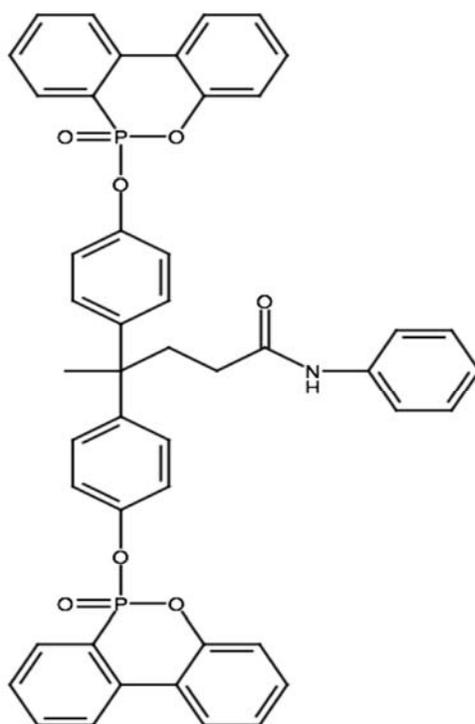
Itaconic acid is a four-carbon diacid containing a methylene group at the 2-position and is readily available from biosources. Michael addition of phosphites to the methylene group provides a route to a variety of phosphorus compounds. Treatment with borane provides the corresponding diol. This compound may serve as a source for a number of compounds of interest as a polymer additive. Direct esterification or Atherton-Todd reaction provides phosphorus esters containing a high level of phosphorus. Polymerization using a variety of carboxylic acids should provide additives with little tendency to migrate from a matrix. These compounds should function as effective flame-retarding additives in a variety of polymers.



POLY 237: Flame retardant properties of phosphorous esters from biobased diphenolic acid

Harrison A. Fulco, *fulco1ha@cmich.edu*, **Bob A. Howell**, *Chemistry and Biochemistry, Central Michigan University, Mt. Pleasant, Michigan, United States*

Development of nontoxic polymer additives has become of utmost importance through recent concerns about sustainability and environmental quality. In particular, non-halogen materials that do not bioaccumulate and are not stable in the environment are being sought. Additives that are generated from renewable biosources are particularly attractive. Generally, they are less toxic and more biodegradable than their petrochemical counterparts. Additionally, the cost of these materials are independent of fluctuations in the petrochemical markets. Diphenolic acid [4,4-di(hydroxyphenyl)pentanoic acid] may be generated from biomass-derived levulinic acid and contains functionality to be readily converted to a variety of phosphorous esters with flame-retarding potential. Treatment with thionyl chloride followed by aniline provides the corresponding amide. The resulting diol is then treated with appropriate phosphorous reagents to generate difunctional phosphorous esters. The resulting compounds contain both phosphorus and nitrogen, which should display good flame retardancy in a variety of polymeric materials.

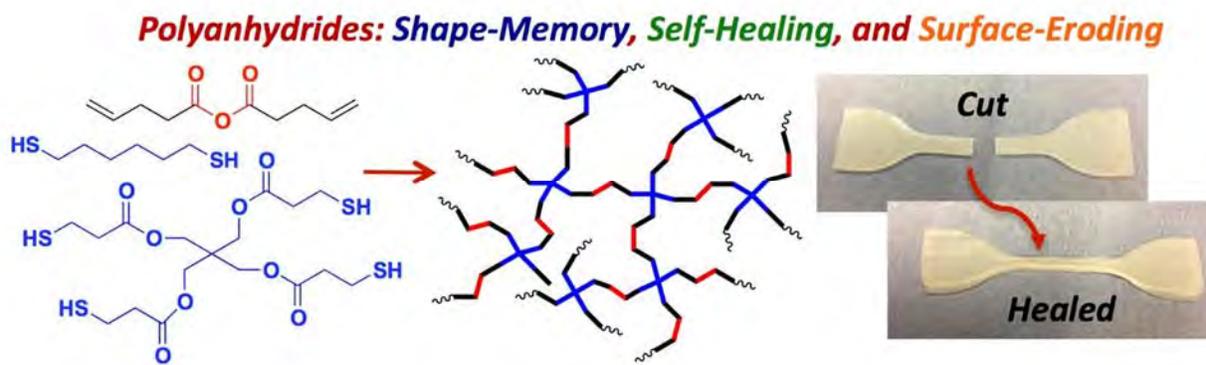


bis-DOPO Ester of N-Phenyl-4,4-di(4-hydroxyphenyl)pentanamide

POLY 238: Shape-memory and self-healing polyanhydrides

Ana Witkowski, *witkowam@clarkson.edu*, **Rebecca Meacham**, **Kelly R. Tillman**, **Devon A. Shipp**. *Chemistry Biomolecular Science, Clarkson University, Potsdam, New York, United States*

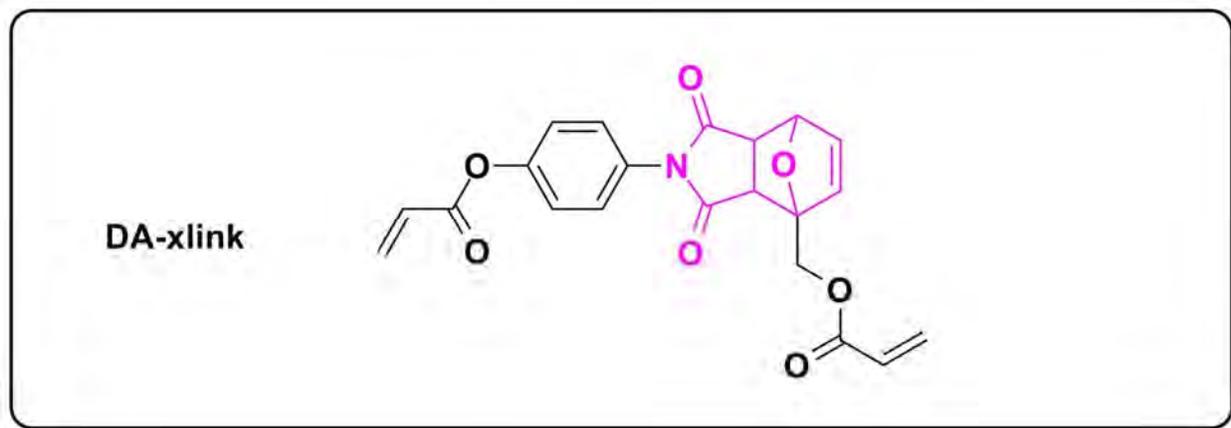
In recent years, shape-memory and self-healing polymers have become increasingly popular. Here we demonstrate the shape-memory and self-healing characteristics of thiol-ene polyanhydrides when heated above and then cooled below the crystalline melt temperature (T_m) of the polymer. Previous work has shown that polyanhydride-poly(ϵ -caprolactone) composites are capable of exhibiting shape memory properties, although dynamic covalent exchange between anhydride moieties occurs at temperatures above ~ 50 - 60°C . This allows for permanent shape reconfiguration of the crosslinked polymer. In this work we aim to create an all-anhydride reconfigurable shape-memory polymer made using thiol-ene monomer combinations that produce a semi-crystalline polyanhydride with a T_m of approximately 30 - 40°C in order to form a polymer that will successfully exhibit shape memory behavior. Self-healing is evident at elevated temperatures because of anhydride dynamic covalent exchange. Additionally, polyanhydrides undergo surface erosion, allowing the mechanical strength of the material to remain intact. This leads to the possibility of using polyanhydrides that have shape memory properties and a predictable erosion profile that can be tuned to allow use of the material as drug delivery vessels.



POLY 239: Controlling polymer solubility with Diels-Alder chemistry and LCST

Emily Wilborn, ewilborn@calpoly.edu, Cecilia G. Gregory, Philip J. Costanzo.
Chemistry, California Polytechnic State University, San Luis Obispo, California, United States

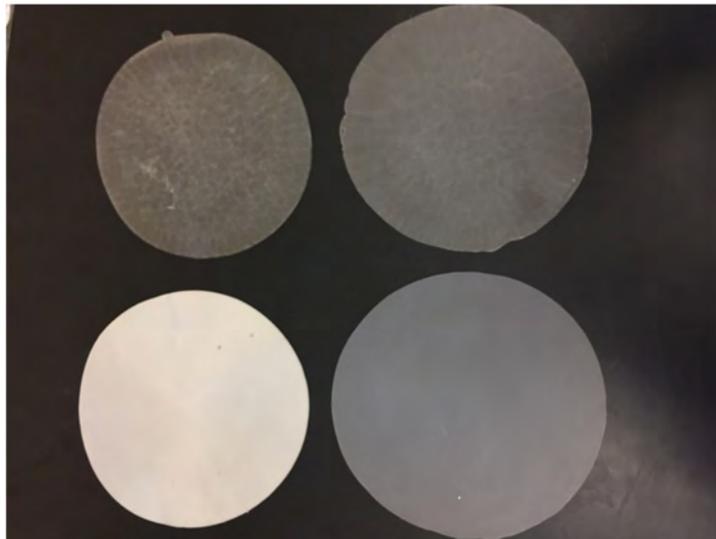
Thermally-responsive materials have been prepared in a multitude of ways for a wide variety of applications. One aspect not previously exploited is the ability to induce changes in polymer architecture. Diels-Alder (DA) chemistry and RAFT polymerization techniques were employed to prepare star-like structures with DA linkages at a central core. Upon the application of a thermal stimulus, the retro-DA was induced and star-like structures were reduced to a linear topology. This had significant impact upon the LCST and provided opportunity to tune the LCST based upon the polymer topology.[figure1]



POLY 240: Microstructural changes in polyolefin thermoplastic elastomers affect elastic recovery and energy dissipation

Leslie A. Maynard¹, *madair@vt.edu*, **Barbara DeButts**², **Justin R. Barone**³. (1) *Chemical Engineering, Virginia Tech, Blacksburg, Virginia, United States* (2) *Macromolecules Innovation Institute, Virginia Tech, Blacksburg, Virginia, United States* (3) *Biological Systems Engineering, Center for Soft Matter and Biological Physics, and Macromolecules Innovation Institute, Virginia Tech, Blacksburg, Virginia, United States*

Polyolefin elastomers (POEs) are a class of thermoplastic elastomers (TPEs) that can be easily processed. POEs have broad applications from the automobile industry to the footwear industry, but for highly customizable materials the POEs must be altered on the microstructural scale. In this work, a systematic study of how thermal processing affected the ability of ethylene octene copolymers to store and dissipate energy was undertaken. Ethylene octene copolymers with different degrees of crystallization were compression molded and slow cooled, quench cooled, or annealed. Copolymer blends were mixed, varying the ratio of high crystallinity copolymer to low crystallinity copolymer. Tensile testing of the cooled samples showed that the crystallinity correlated to the Young's modulus and hysteresis behavior. The higher crystallinity samples exhibited higher hysteresis and higher modulus than the lower crystallinity samples. The blends were immiscible but exhibited physical behavior between the two components. This study showed that thermal processing and blending of POEs can result in microstructural changes that affect the elastic recovery and energy dissipation at a macroscopic level. Microstructural control will allow for the optimal design of elastomeric components where controlled stiffness while still maintaining high extensibility and elastic recovery is desirable.

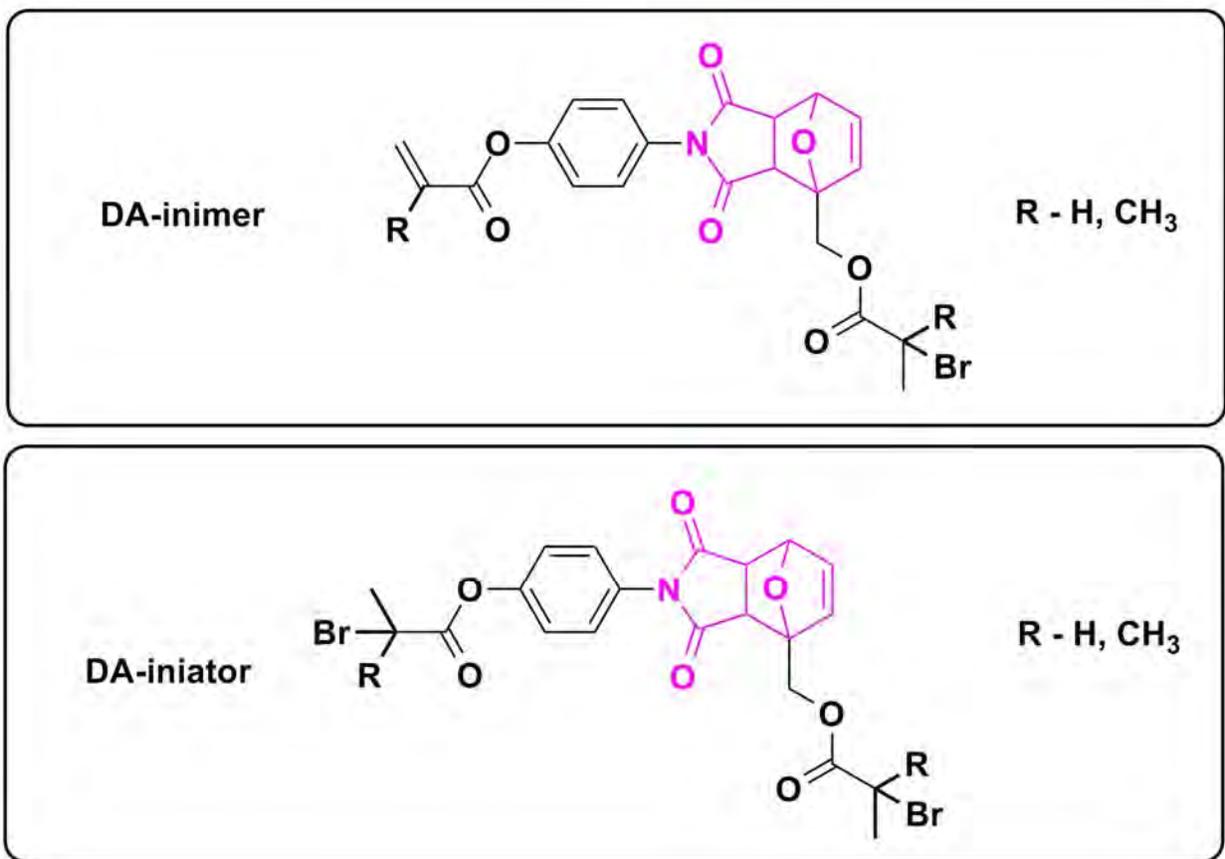


Some samples after they underwent compression mold and thermal processing. 50:50 mixed immiscible blend of high and low crystallinity samples (top left). Low crystallinity sample that underwent quench cool (top right). High crystallinity sample that underwent slow cool (bottom left). Low crystallinity sample that underwent slow cool (bottom right). All show differing miscibility of the samples.

POLY 241: Manipulation of molecular topology and composition using Diels-Alder chemistry

Marianne S. Meyersohn, mmeyersohn@gmail.com, Sierra Gosting, Tyler Colt, Ryan Rhoads, Kyle Barcus, Miles Markmann, Philip J. Costanzo. Chemistry, California Polytechnic State University - San Luis Obispo, Valley Village, California, United States

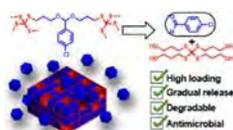
Thermally-responsive materials have been prepared in a multitude of ways for a wide variety of applications. One aspect not previously exploited is the ability to induce changes in polymer architecture. Diels-Alder (DA) chemistry and light-activated ATRP was utilized to incorporate DA linkages at a central core. By utilizing different DA linkages, polymer composition and topology were controlled upon the application of a thermal stimulus, including inversion of composition and variation in topology.[figure1]



POLY 242: A pro-antimicrobial network via degradable acetals (PANDA) prepared via thiol-ene photopolymerization

William Martin¹, *William.B.Martin@usm.edu*, **Dahlia Amato**¹, **Douglas V. Amato**¹, **Olga Mavrod**², **Sarah Swilley**¹, **Keith Parsons**¹, **Dmitri Mavrod**², **Derek L. Patton**¹. (1) School of Polymer Science and Engineering, University of Southern Mississippi, Hattiesburg, Mississippi, United States (2) Department of Biological Sciences, University of Southern Mississippi, Hattiesburg, Mississippi, United States

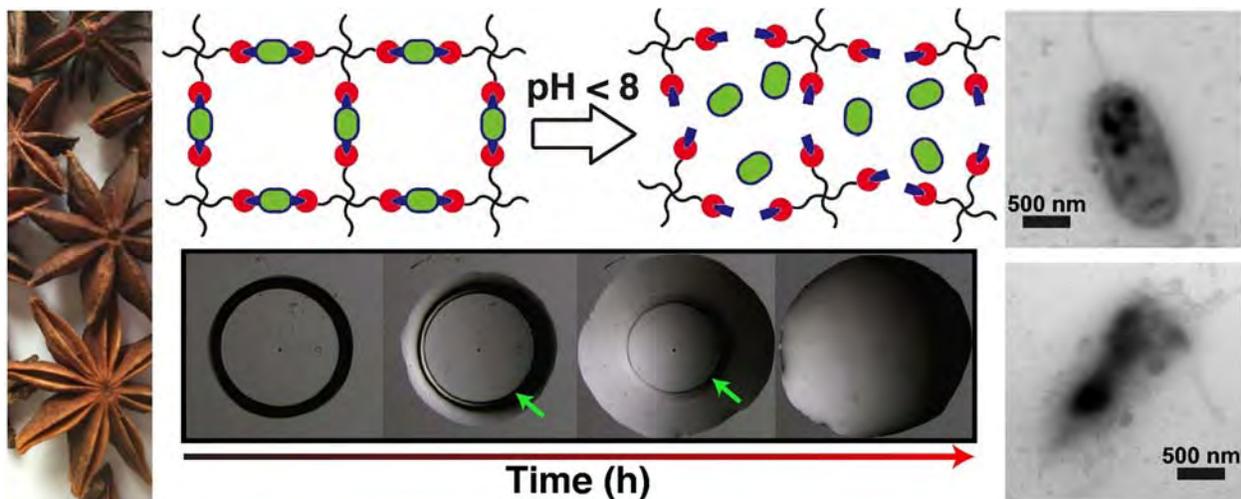
Antimicrobial agents that are dispersed throughout a polymeric network traditionally suffer from unwanted leaching, low loading, and uncontrolled burst release. In this work, we describe the synthesis of a new acetal containing monomer derived from an antimicrobial p-chlorobenzaldehyde (pCB). Upon polymerization, pCB is fully incorporated within a stable thiol-ene network. However, exposure to aqueous environments results in rapid degradation and release of pCB in its active form. Herein, we demonstrate the synthesis of the monomer, photopolymerization kinetics, degradation kinetics, and antimicrobial evaluation of both the monomer and polymerized films. The antimicrobial activity is shown to increase with increasing concentration of the acetal monomer for gram-positive (*S. aureus*) and gram-negative (*E. coli*, *P. aeruginosa* and *B. cenocepacia*) bacteria. This thiol-ene system represents a new approach for tailoring the release of antimicrobial agents from crosslinked polymeric materials.



POLY 243: Bio-based pro-antimicrobial networks synthesized via thiol-ene photopolymerization

Sarah Swilley¹, *Sarah.Swilley@usm.edu*, **Douglas V. Amato**¹, **Dahlia N. Amato**¹, **Logan Blancett**², **Olga Mavrod**², **William Martin**¹, **Michael Sandoz**¹, **Glen Shearer**², **Dmitri Mavrod**², **Derek L. Patton**¹. (1) School of Polymer Science and Engineering, University of Southern Mississippi, Hattiesburg, Mississippi, United States (2) Department of Biological Sciences, University of Southern Mississippi, Hattiesburg, Mississippi, United States

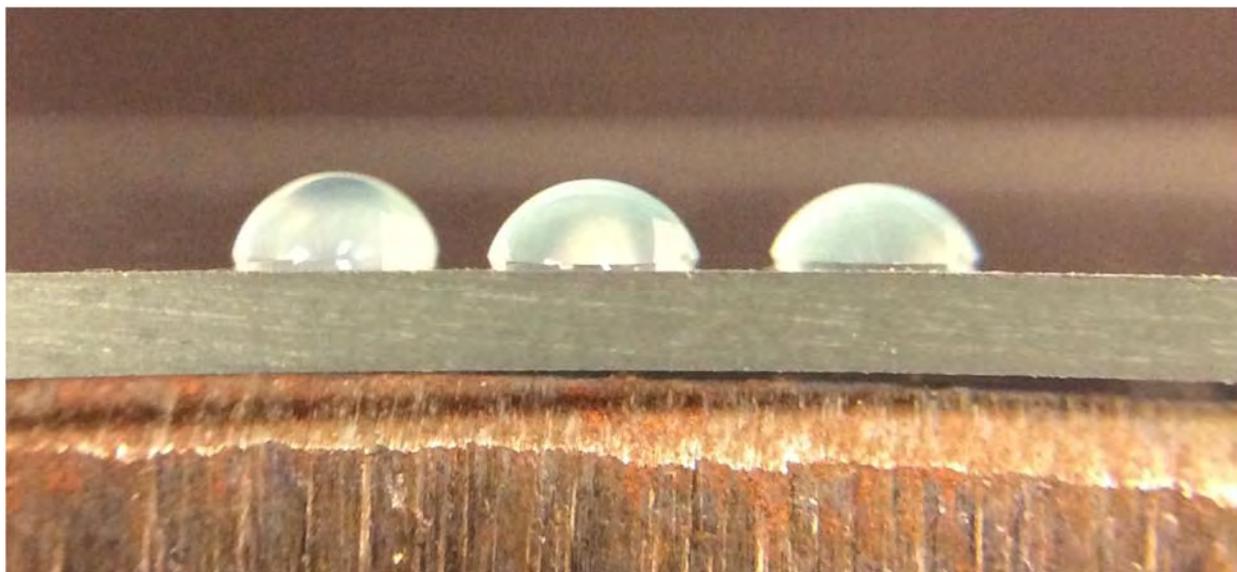
The synthesis of a fully degradable, bio-based, sustained release, pro-antimicrobial polymer network comprised of degradable acetals (PANDA) is reported. The active antimicrobial agent – p-anisaldehyde (pA) (an extract from star anise) – was converted into a UV curable acetal containing pro-antimicrobial monomer and subsequently photopolymerized into a homogenous thiol-ene network. Under neutral to acidic conditions (pH < 8), the PANDAs undergo surface erosion and exhibit sustained release of pA over 38 days. The release of pA from PANDAs was shown to be effective against both bacterial and fungal pathogens. From a combination of confocal microscopy and transmission electron microscopy, we observed that the released pA disrupts the cell membrane. Additionally, we demonstrated that PANDAs have minimal cytotoxicity towards both epithelial cells and macrophages. Although a model platform, these results point to promising pathways for the design of fully degradable sustained-release antimicrobial systems with potential applications in agriculture, pharmaceuticals, cosmetics, household/personal care, and food industries.



POLY 244: Surface free energy characterization of biofilm resistant monomers

Verena Ghebraniou, *vnghebraniou@mail.lipscomb.edu*, Jasmine Carlisle, Spencer Oskin, Emily B. Henry, Wenting Wei, Thomas B. Cavitt. Department of Chemistry and Biochemistry, Lipscomb University, Nashville, Tennessee, United States

Biofilms, found in various surfaces, are the habitat of 95% of the earth's bacteria and successfully protect bacteria from many antibiotics. Biofilms cycle in several steps: 1) primary colonization, 2) quorum sensing, 3) glycocalyx formation, 4) secondary colonization, and 5) release and dispersal of free bacteria. Primary colonization depends on the complex interaction of the binding adhesins to the substrate. Coating surfaces with a biofilm resistant substrate would provide a means by which bacterial adhesion via primary colonization could be hindered. Previous research indicates that formulations incorporating halogenated phenyl acrylate derivatives produce effective biofilm resistant substrates. Analyzing the surface free energy of the homopolymers of the halogenated phenyl acrylate derivatives allows for a method by which a surface is predicted to be more effective in inhibiting biofilm formation. Upon measuring the contact angles of biofilm resistant monomers using the sessile drop method, the surface free energy was determined using the Owens-Wendt and van Oss-Chaudhury-Good equations calculated via the matrix method. Results indicate that effective biofilm resistant coatings were all 1,4-disubstituted halogenated phenyl acrylate homopolymers with a low surface free energy ($\gamma_s < 30 \text{ mJ/m}^2$) and also formed very smooth coatings. Therefore, primary colonization may be inhibited by modifying the surface free energy of the substrate with a smooth coating.

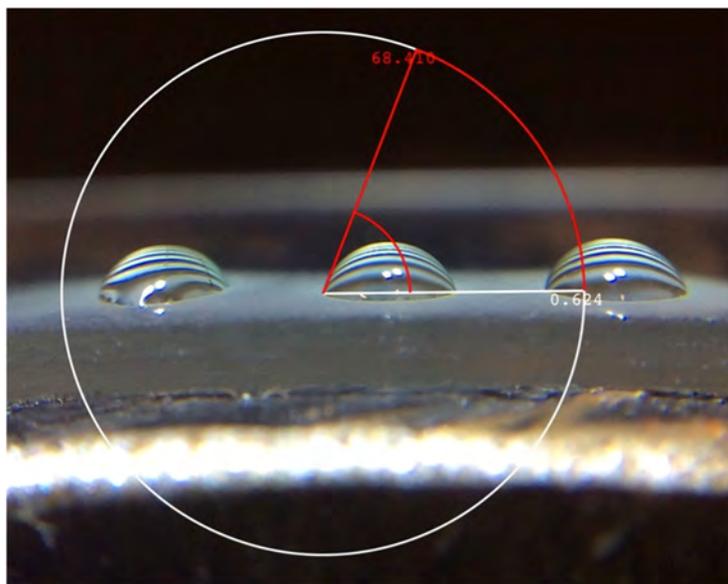


Contact angle of liquid on a polymer coated glass slide captured with an iPad equipped with a macrolens.

POLY 245: Surface free energy characterization of an adhesin protein

Spencer Oskin, *dsoskin@mail.lipscomb.edu*, Jasmine Carlisle, Verena Ghebranious, Thomas B. Cavitt. *Chemistry and Biochemistry, Lipscomb University, Nashville, Tennessee, United States*

Collagen is the most abundant protein found in animals and is also utilized by many bacteria as an adhesin to adhere to different substrates. Previous studies have characterized components of collagen's surface free energy (γ_s^{LW} , γ_s^{AB} , and γ_s) using the Owens-Wendt equation, but the separate acid-base components (γ_s^+ and γ_s^-) remained uncharacterized. The surface free energy of the isolated hydrophilic portion of collagen used by bacteria to adhere to substrates also had not been determined. The present study was designed to determine the full surface free energy profile (γ_s , γ_s^{LW} , γ_s^{AB} , γ_s^+ , and γ_s^-) of collagen's hydrophilic portion to find a suitable surface coating capable of preventing bacterial adhesion and colonization. Glass slides were surface functionalized to produce a nonpolar surface onto which soluble and insoluble collagen was solvent cast onto the slides. The sessile drop method for determining contact angles was used with three fully characterized solvents (e.g., α -bromonaphthalene, formamide and deionized water) whereupon the surface free energy components of the collagen-coated slides were determined via the Owens-Wendt and van Oss-Chaudhury-Good equations. The results, calculated via the linear algebraic matrix method, showed comparable surface free energy values to previous studies for the insoluble collagen. The soluble collagen also had comparable values meaning that the hydrophilic portions of the collagen had not oriented correctly. Though the surface free energy for the hydrophilic portion of collagen remains uncharacterized, the acid (γ_s^+) and base (γ_s^-) components of collagen's surface free energy were determined using the van Oss-Chaudhury-Good equation.

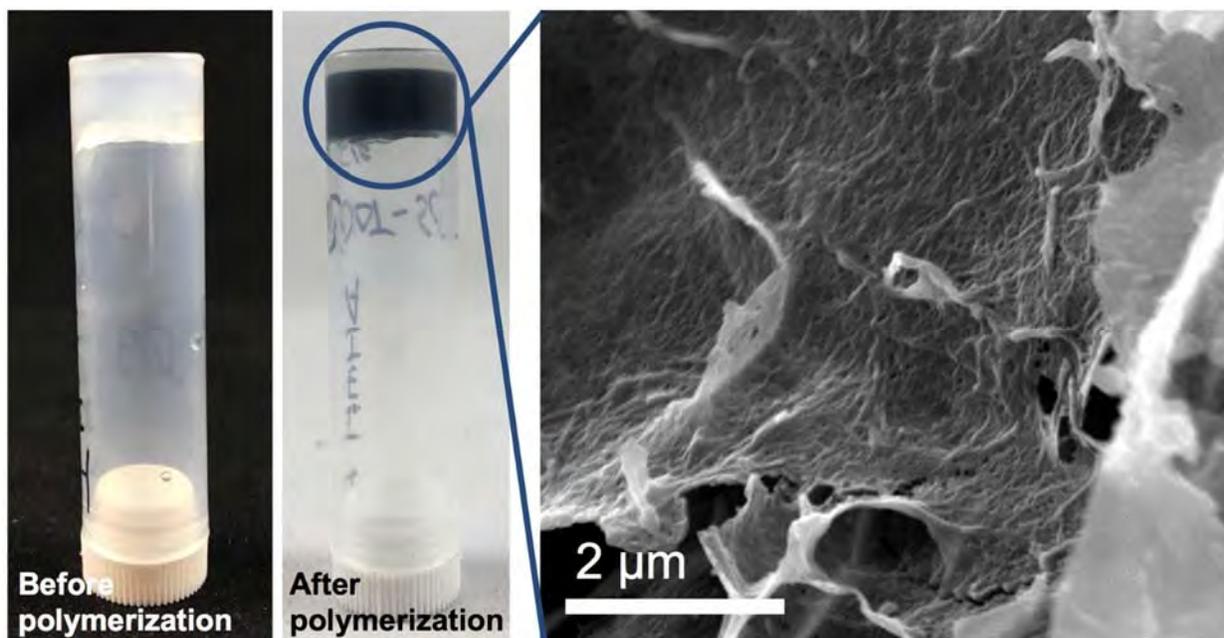


Contact angle of DMSO on OTS coated glass slide using an iPad equipped with a macrolens and using the Photo Protractor V2.6 app.

POLY 246: Controlling nanoscale organization of thiophene-based conductive polymers with self-assembling peptides

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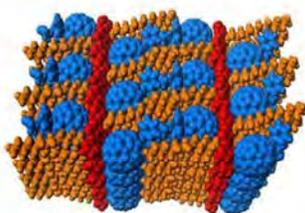
To create nanostructured conductive polymer materials with controlled morphology and robust mechanical properties, we are exploring a bottom-up approach to polymer design. A small library of peptides containing alternating or grouped hydrophobic and hydrophilic residues was synthesized and the peptides were covalently attached to a thiophene-based monomer. Peptide sequences that could self-assemble into stable hydrogels in water were identified and the physical and mechanical properties were evaluated. Synthesis of the monomers and characterization of the gels before and after polymerization will be presented, demonstrating that this method can be exploited to create hybrid peptide-polymer materials in aqueous media.



POLY 248: Molecular-level order, disorder, and interactions in conjugated polymers and blends from solid-state NMR

Bradley Chmelka¹, *bradc@engineering.ucsb.edu*, Manjunatha Reddy¹, Matthew Idso¹, Matthias Junk¹, Denis Andrienko², Michael Ryan Hansen³. (1) Chemical Engineering, University of California, Santa Barbara, Santa Barbara, California, United States (2) Max Planck Institute for Polymer Research, Mainz, Germany (3) Institute of Physical Chemistry, Westfälische Wilhelms-Universität Münster, Münster, Germany

The properties of conjugated polymer materials depend on complicated compositional and architectural features that influence the structures and interactions of their backbones, sidechains and interactions with intercalated species, such as those in organic photovoltaic (OPV) materials. In particular, the presence, causes, and consequences of local order and disorder in such systems are often subtle and have been challenging to establish. Nevertheless, advances in syntheses and molecular characterization of conjugated polymers increasingly enable molecular-level features to be measured and correlated with their macroscopic physicochemical properties. Solid-state NMR spectroscopy, especially two-dimensional techniques, provide improved resolution that yields detailed information on the local environments, interactions, and distributions of backbone, sidechain, and intercalated moieties in conjugated polymer materials. NMR analyses, together with X-ray scattering, molecular modelling, and macroscopic property measurements, yield insights on pi-pi interactions, backbone conformations, sidechain interdigitation, and structure-function relationships associated with bulk-heterojunction OPV materials. Results will be presented for conjugated polymer and conjugated polymer-fullerene blends, with emphases on the molecular interactions and distributions of compositional or structural order and disorder that influence the properties and performances of devices based on these materials.

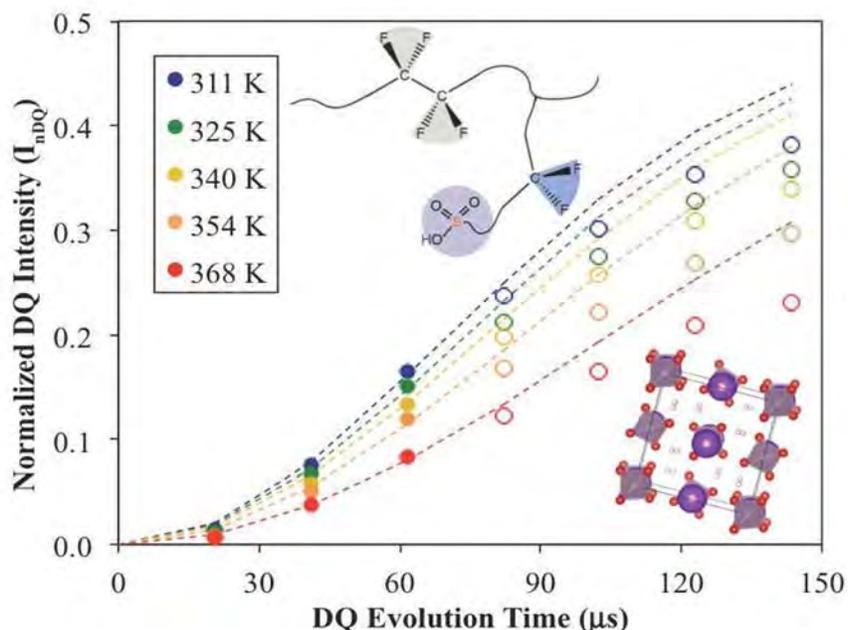


Schematic diagram of an organic photovoltaic material comprised of a conjugated polymer with alkyl sidechains and intercalated fullerene molecules

POLY 249: Structure and dynamics of proton-conducting materials *via* solid-state NMR

Z. B. Yan², Gabrielle Foran², Adam R. MacIntosh², Alan P. Young³, Darren H. Brouwer¹, **Gillian R. Goward²**, goward@mcmaster.ca. (1) Chemistry Department, Redeemer University College, Ancaster, Ontario, Canada (2) Chemistry and Chemical Biology, McMaster University, Hamilton, Ontario, Canada (3) Research and Development Division, Ballard Power Systems, Burnaby, British Columbia, Canada

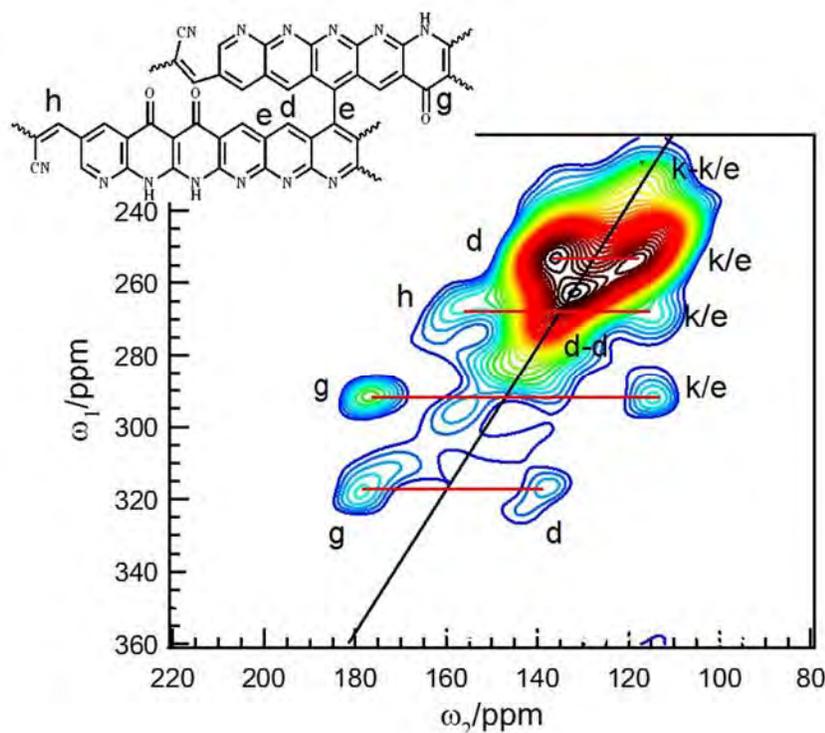
Solid acids are considered reliable electrolyte materials in intermediate temperature fuel cells, as they can be employed over a broad range of temperatures without flooding or drying.^[1] Phosphate solid acids have been studied as a class of solid state proton conductors, which are known to undergo superprotonic phase transitions resulting in significant increase in proton conductivity.^[2] Site specific proton dynamics analysis using double quantum (DQ) filtered ssNMR spectroscopy has been applied by quantifying the ¹H dipolar coupling interaction in various solid-acid species. This NMR approach has also been applied and validated to the perfluorosulfonic acid (PFSA) materials to understand the molecular physicochemical properties *via* ¹⁹F DQ NMR.^[3] The local dynamics information has been separated and analyzed in terms of fluorine interactions with respect to different temperatures and hydration levels. From the *in operando* cyclic voltammetry measurements of the membrane electrolyte assemblies obtained at Ballard Power Systems, the H₂ crossover values have been extracted. There is a strong correlation between the H₂ permeability and the PFSA side chain local dynamics extracted from the NMR analysis. As the side chain mobility increases, an increase in the H₂ permeability is observed. The link between the fundamental dynamics study and the PFSA performance analysis provides insight into gas transport mechanisms in this type of material.^[4]



POLY 250: Elucidation of stabilization pathways of atactic-polyacrylonitrile by solid-state NMR spectroscopy

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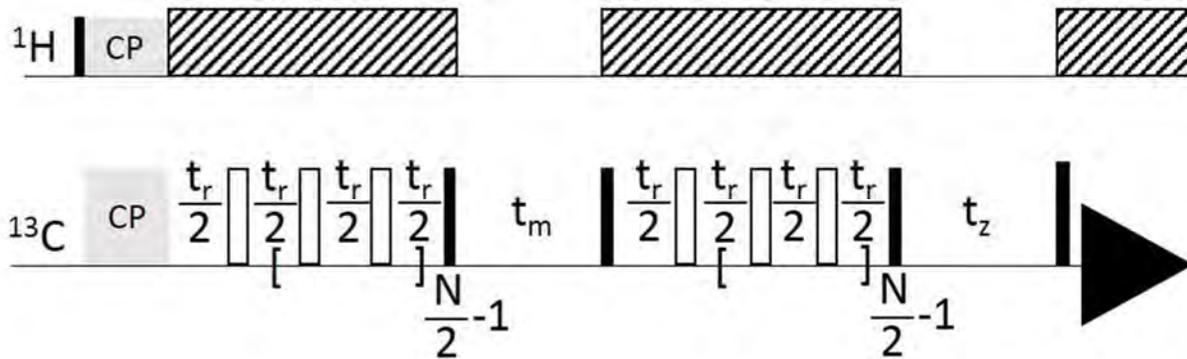
Atactic-polyacrylonitrile (*a*-PAN) is used as major precursor to produce carbon fiber. From *a*-PAN to Carbon fibers, several heat treatment processes including stabilization, carbonization and graphitization are involved. During stabilization, linear polymer structure is believed to convert to ladder structure, which makes it able to survive during further heat treatment at even higher temperature. For the past decades, several experimental approaches including FT-IR, DTA, TGA, etc., have been applied to characterize chemical structures of stabilized PAN. However, due to experimental limitations, stabilization process was still not well understood at the molecular level. In this talk, we report a solid-state NMR strategy to characterize *a*-PAN stabilized as a function of stabilization temperature and stabilization time by two dimensional ^{13}C - ^{13}C and ^1H - ^{13}C correlation NMR techniques.^{1,2} Through-bond correlation of stabilized *a*-PAN was successfully obtained to identify different chemical structures with the change of stabilization temperature. Improved spectral resolutions of 1 and 2D NMR data for the first time will reveal different stabilization pathways for PAN stabilized under air and nitrogen. Meanwhile, degree of stabilization can also be calculated through quantified 1D NMR spectra, which was also plotted as a function of stabilization temperature and time, respectively.



POLY 251: Characterizing the structure and dynamics of the rubber and tackifier in pressure sensitive adhesives

Mark McCormick¹, markmccormick2001@yahoo.com, **Yongqian Zhang**². (1) 3M, Minneapolis, Minnesota, United States (2) Chemistry, University of Wisconsin, Madison, Madison, Wisconsin, United States

Pressure Sensitive Adhesives (PSAs) are a key component to many of 3M's products. One class of PSAs can be made from mixing a tackifying resin into an otherwise homogenous rubber. This works equally well for hydrocarbon and silicone systems. Tuning the properties of the PSA is vital to ensure that it will perform as desired under its exposed conditions. Relaxation methods and Centerband Only Dynamic Exchange (CODEX) are employed to probe the behavior of the PSA and its component ingredients. These methods are used in addition to classic rheology and thermal characterization typically used by product designers.

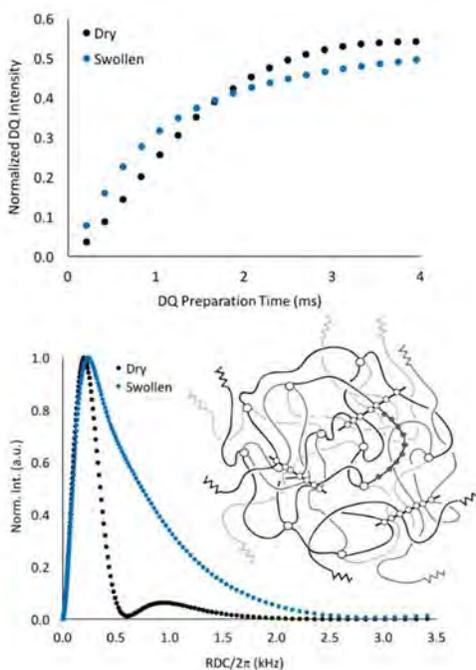


POLY 252: Characterization of network structural motifs in siloxane elastomers using magnetic resonance

April M. Sawvel¹, sawvel4@llnl.gov, Sarah C. Chinn², Matthew Gee¹, Amitesh Maiti¹, Harris Mason¹, Robert S. Maxwell¹, James P. Lewicki¹. (1) Lawrence Livermore National Laboratory, Livermore, California, United States (2) Lawrence Livermore Natl Lab, Livermore, California, United States

The versatile cross-linking chemistry of poly(dimethylsiloxane) (PDMS) based materials affords a large research space in which polymers with widely varying elastomeric properties can be synthesized. Parameters such as PDMS chain length, cross-link density, cross-link functionality, filler content, and PDMS chain chemistry can all be modified to produce materials with specific physical and mechanical properties. These elastomers are generally intractable, which makes the precise characterization of these networks problematic. While advancements in analytical techniques have enabled improved insight into the network structure of model PDMS systems, substantial gaps in the fundamental understating of structure-property relationships persist. We report the application ¹H DQ NMR spectroscopy to determine the network topology of a series of mono-modal and bimodal, model PDMS networks. Analysis of elastomers swollen in deuterated toluene exposes complex network structure even within mono-modal samples that is not revealed through more traditional characterization techniques. This data, combined with solvent uptake and mechanical analysis, provides an in-depth description of the network level structural motifs that govern the macroscopic material properties of siloxanes.

Prepared by LLNL under Contract DE-AC52-07NA27344. LLNL-ABS-728816.



¹H DQ NMR on Swollen PDMS Networks Reveals Structural Complexity.

POLY 253: Structure of crosslinking junctions of network polymers through rubber state NMR spectroscopy

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Rubber state NMR spectroscopy was applied to investigate the structure of crosslinking junctions of crosslinked natural rubber and crosslinked chloroprene rubber. The crosslinked rubbers were prepared with sulfur and various accelerators in the presence of ZnO and stearic acid. The NMR measurements were performed by field gradient magic angle spinning solid state NMR spectroscopy. Intensities of small signals in ^1H -NMR spectra and ^{13}C -NMR spectra were related to the crosslink density of the crosslinked rubbers. Correlations with mechanical properties were investigated in terms of not only crosslink density but also intensities of the signals.

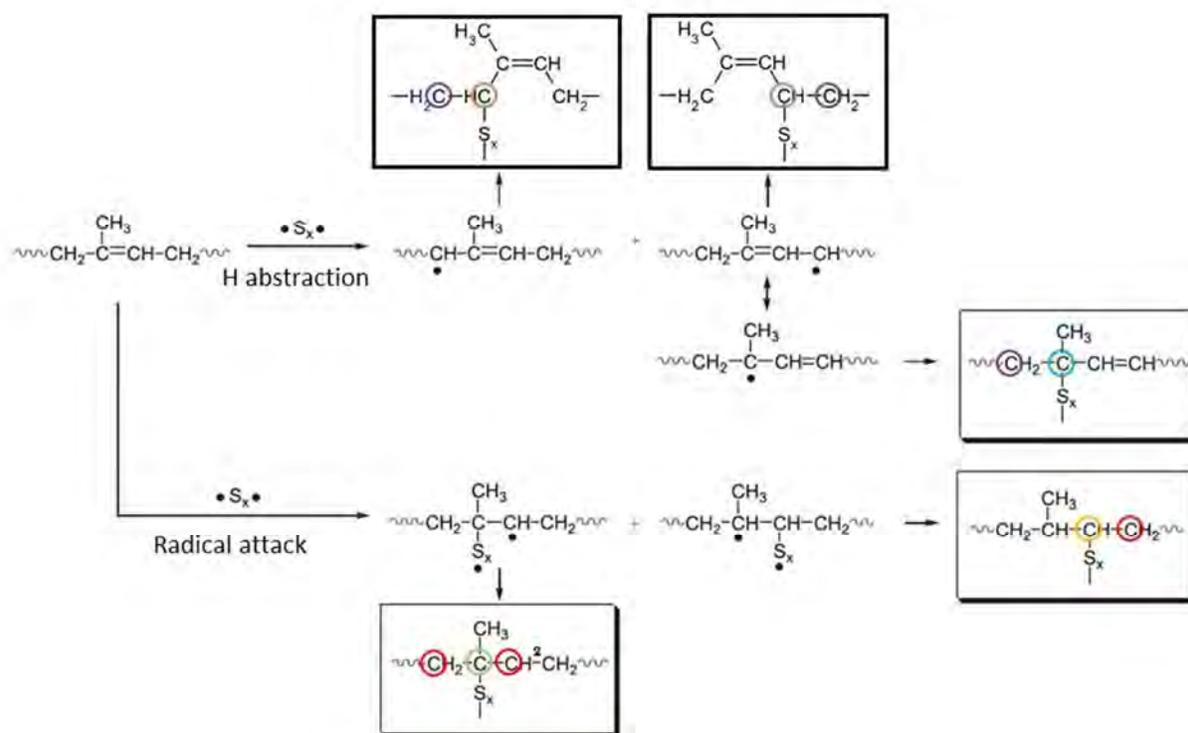
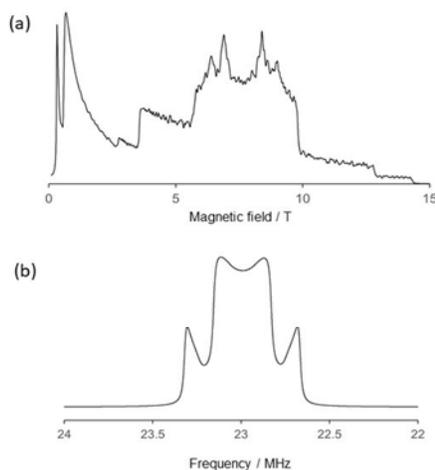


Figure 1. Scheme for the reaction of natural rubber with sulfur

POLY 254: Sulfur-33 NMR of organosulfur compounds and polymers

Kazuhiko Yamada, *kyamada@kochi-u.ac.jp*. Kochi university, Nankoku, Japan

Experimental and theoretical aspects of solid-state ^{33}S Nuclear Magnetic Resonance (NMR) in [^{33}S]-enriched organosulfur compounds and polymers, by using variable superconducting magnets, are presented. For ^{33}S NMR experiments, stepwise-field-swept NMR and/or frequency-swept types in lower magnetic fields were carried out to obtain ^{33}S NMR parameters including quadrupole coupling constants (C_Q value) more than 30 MHz. For spectral simulations, the direct diagonalization method, in which the combined Zeeman and quadrupole Hamiltonian is numerically calculated to obtain probabilities for each transition, was used to obtain ^{33}S NMR parameters. It is found that ^{33}S NMR parameters are highly sensitive to the local molecular structures such as dihedral angles, suggesting that solid-state ^{33}S NMR becomes one of the best methods to investigate cross-linked structures in a rubber at atomic level. Towards the detection of ^{33}S NMR spectra of a rubber without [^{33}S]-isotope enrichment, a high-temperature superconducting (HTS) coil, whose Q value is more than 10,000, and optomechanics NMR, in which the FID signal can be converted into a laser signal via a micro-condenser consisting of two thin films, are being developed. Effectiveness of these high-sensitivity technologies are described.

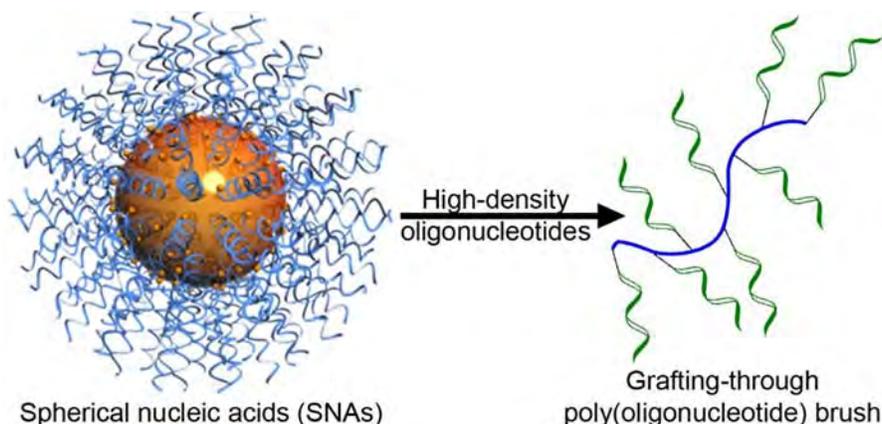


Theoretical results for (upper) field-swept solid-state ^{33}S NMR spectrum, irradiated at 25 MHz, and frequency-swept NMR spectrum at 0.05 T. These calculations were carried out using typical ^{33}S NMR parameters in organosulfur compounds.

POLY 255: Synthesis of high-density molecular DNA brushes by direct grafting-through polymerization of oligonucleotides

Xuyu Tan², tan.xuy@husky.neu.edu, Hao Lu², Yehui Sun², Xiaoying Chen², Dali Wang¹, Ke Zhang¹. (1) Chemistry and Chemical Biology, Northeastern University, Boston, Massachusetts, United States (2) Chemistry and Chemical Biology, Northeastern university, Boston, Massachusetts, United States

Naked and unmodified oligonucleotides are rarely used in gene regulation due to challenges in intracellular delivery and stability. Spherical nucleic acids (SNAs), which consist of oligonucleotides covalently attached to the surface of a rigid structure, typically gold nanoparticles, exhibit enhanced nuclease stability and increased cell uptake. Many side effects associated with traditional polycationic gene carriers, such as toxicity and immunogenicity, can thus be alleviated by utilizing this polyanionic structure. It has been shown that the beneficial properties of SNAs stem from the dense packing and orientation of oligonucleotides, and are unrelated to the core material of the SNA. Therefore, it is possible to synthesize molecular SNA-type structures based on a polymeric backbone via graft-through methodology, given that the densities of the DNA are sufficiently high in the brush form. To reach these high densities, we have attempted direct grafting-through polymerization of natural oligonucleotides, which are modified at the 5' or 3' with a polymerizable monomer. However, the negatively charged character and hydrophilicity of oligonucleotides make them impossible to become solubilized in any solvent other than water to a reasonable degree for polymerization. Furthermore, the electron-rich bases are incompatible with traditional living polymerization methods. Here, we have synthesized non-charged, protected oligonucleotide precursors as macromonomers, which are soluble in the organic phase. The protected strands also make the chemistry compatible with ring-opening metathesis polymerization (ROMP), which yields brush-type poly(oligonucleotides) that can then be deprotected after polymerization. These DNA brushes can be fractionated down to molecular purity, which allows us to study interactions between polyvalent DNA and cells and other living systems.

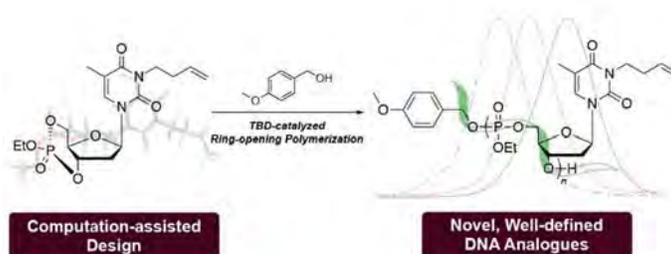


POLY 256: Synthetic, functional thymidine-derived polydeoxyribonucleotide analogues from a six-membered cyclic phosphoester

Yi-Yun T. Tsao, *cm759250@gmail.com*, Travis H. Smith, Karen L. Wooley. 3255 TAMU, Texas AM University, College Station, Texas, United States

A grand challenge that crosses synthetic chemistry and biology is the scalable production of functional analogues of biomacromolecules. We have focused our attention on the use of deoxynucleoside building blocks bearing non-natural bases to develop a synthetic methodology that allows for the construction of high molecular weight deoxynucleotide polymers. Our 6-membered cyclic phosphoester ring-opening polymerization strategy will be demonstrated, herein, by an initial preparation of novel polyphosphoesters, comprised of butenyl-functionalized deoxyribonucleoside repeat units, connected *via* 3',5'-backbone linkages. Computational modeling of the 6-membered 3',5'-cyclic phosphoester ring derived from deoxyribose indicated strain energies at least 5.4 kcal/mol higher than the 6-membered monocyclic phosphoester. These calculations supported the hypothesis that the strained 3',5'-cyclic monomer can promote ring-opening polymerization to afford the resulting polymers with low dispersities.

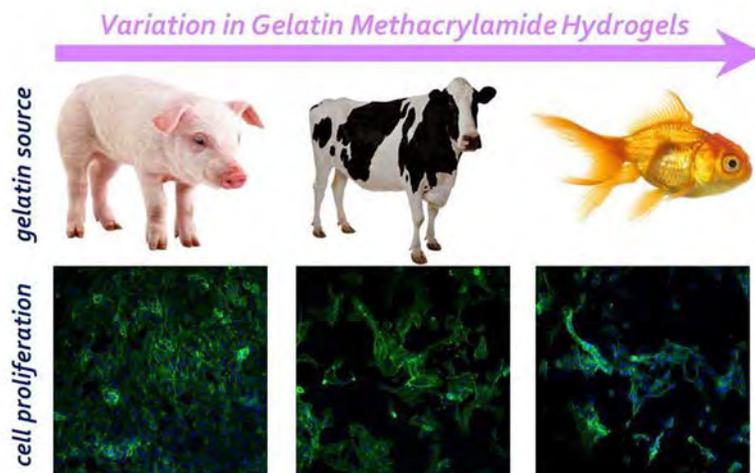
Regioregularity is a crucial property in these DNA analogues, as natural DNA is synthesized exclusively in 5' to 3' direction. The regioisomeric preference was investigated by the synthesis of model compounds of 3',3'-, 3',5'-, and 5',5'-linkages. ³¹P NMR spectra revealed the major connectivity in the polymer backbone to be 3',5'-linkages, with ≤30% of other isomeric forms. Model reactions employing a series of alcohol initiators imparting various degrees of steric hindrance, to mimic the increased steric hindrance of a propagating alcohol, yielded the corresponding ring-opened unimer adducts. ¹H-³¹P HMBC spectroscopy showed ethanol and 4-methoxybenzyl alcohol initiation to yield only the P-O5' bond cleavage product, whereas isopropyl alcohol initiation afforded both P-O3' and P-O5' bonds cleavage products, supporting our hypothesis that the increased steric hindrance of the propagating species during polymerization dictates regioselectivity of P-O bond cleavage. Overall, this work combines the merits of natural product-derived materials and functional, degradable polymers to provide a new platform for functional, synthetically-derived polydeoxyribonucleotide-analogue materials.



POLY 257: Correlating animal source to physical and functional properties of gelatin methacrylamide hydrogels

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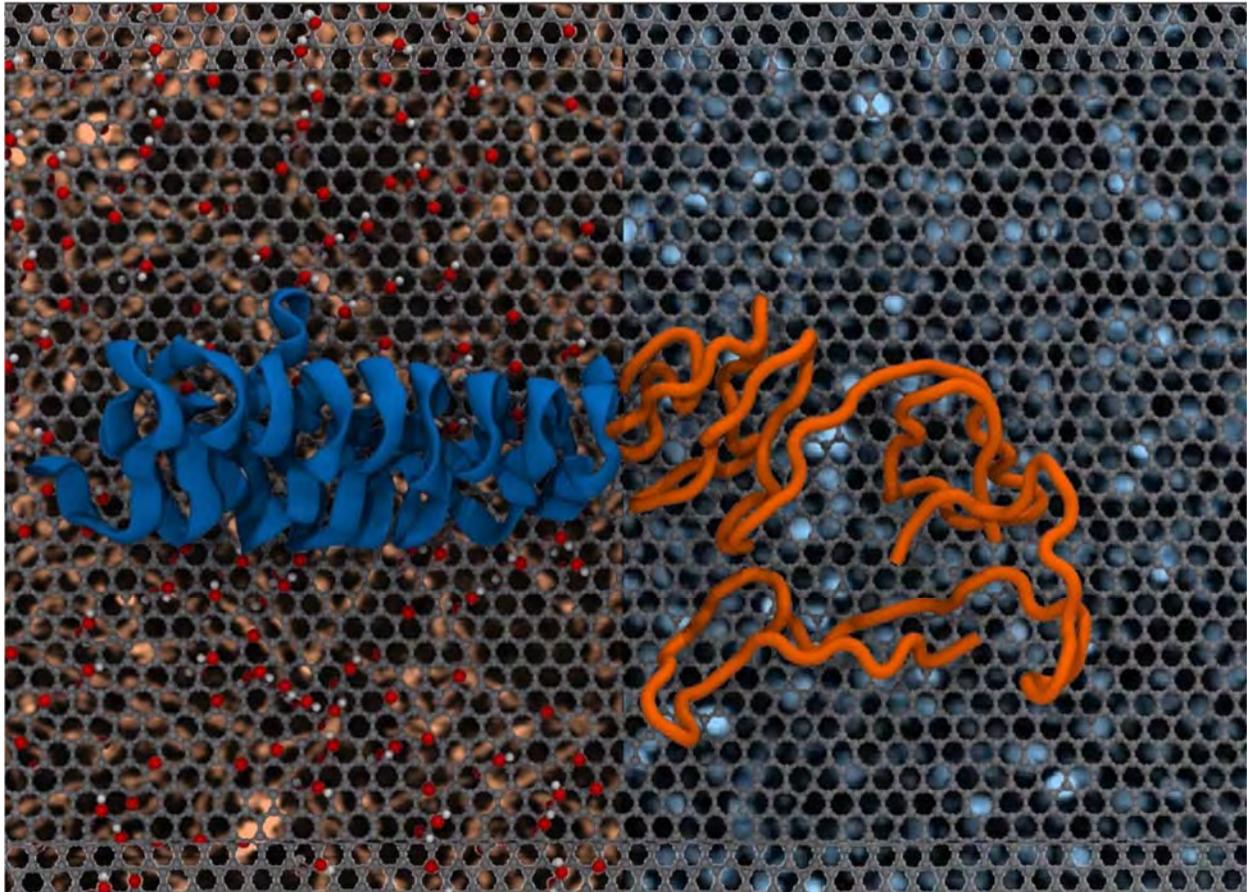
Gelatin methacrylamide (GelMA) is a photo-curable hydrogel scaffold that is used for tissue engineering- often in the engineering of cell culture microdevices. Due to native peptide sequences and favorable mechanical properties, cells proliferate readily on GelMA. Herein, we present an analysis of GelMA as a three-dimensional tissue scaffold with tunable mechanical properties. Specifically, we elucidate *the source dependent physical and covalent gelation properties of GelMA synthesized from three sources of gelatin- pig, cow, and cold water fish*, and we investigate how cell proliferation is impacted. Reaction conditions of GelMA were varied by adjusting the ratio of methacrylic anhydride to gelatin with standard one-pot synthesis. Methacrylation was quantified by measuring the available primary amine groups after synthesis. Rheological properties of GelMA were measured under dynamic strain. Rheological data is used to determine crosslink density as it is directly related to the equilibrium modulus obtained via frequency sweep. Furthermore, molecular weight between crosslinks was determined by observing the stress relaxation of the hydrogel. GelMA source directly impacted and resulted in significant differences in degree of methacrylation, viscoelastic behavior, and crosslink density. Differing cell morphology and growth was observed on GelMA from the different animal sources, as demonstrated with human endothelial cell proliferation on GelMA scaffolds. GelMA synthesized from different animal sources results in significantly different functional properties, and this information can be used to tune the behavior of resident cell populations after fabrication of 3D scaffolds. This work will contribute to defining the available materials space for the engineering of 3D tissue constructs from GelMA. Further analysis of gelatin peptide sequences will provide insight into the variation of cell adhesion phenomena to better characterize and correlate animal source with scaffold properties.



POLY 258: Assembly of protein assembly at bionanocomposite interphases

Anise M. Grant, anise.grant@gmail.com, Vladimir V. Tsukruk. *Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States*

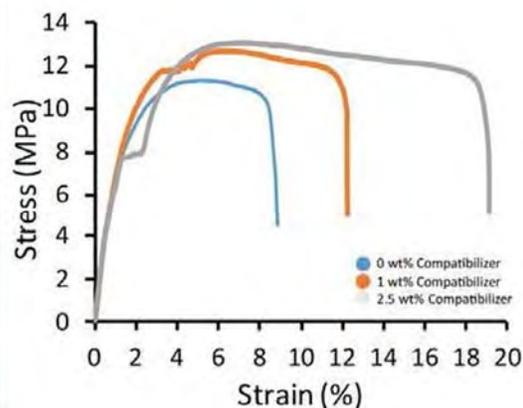
Protein biopolymer composites bring together the tunability and flexibility of protein matrices and functionality of filler components. We demonstrated this through layer-by-layer assembly of silk fibroin and graphene. To do this, we used high resolution surface and assembly analysis to identify ways to control silk assembly on graphene. Herein, we utilize a similar approach to developing bionanocomposites containing silk-like proteins and to discern what lessons from our studies with silk fibroin still apply. This talk will discuss the assembly of silk-like proteins at inorganic interphases; the implications of assembly on mechanical performance; and how this relates to previous findings with silk fibroin. Interfacial forces and protein assembly are monitored by high resolution attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and atomic force microscopy (AFM). X-ray diffraction is used to probe crystallization. All surface and interphase characterization is mapped with mechanical response data obtained via buckling tests. Molecular dynamics simulations of analogous systems are used to probe the interfacial forces contributing to the conformational behavior and corroborate FTIR and AFM observations.



POLY 259: Synthesis of polysaccharide ABA triblock copolymers by one-pot cross-metathesis ring-opening metathesis polymerization

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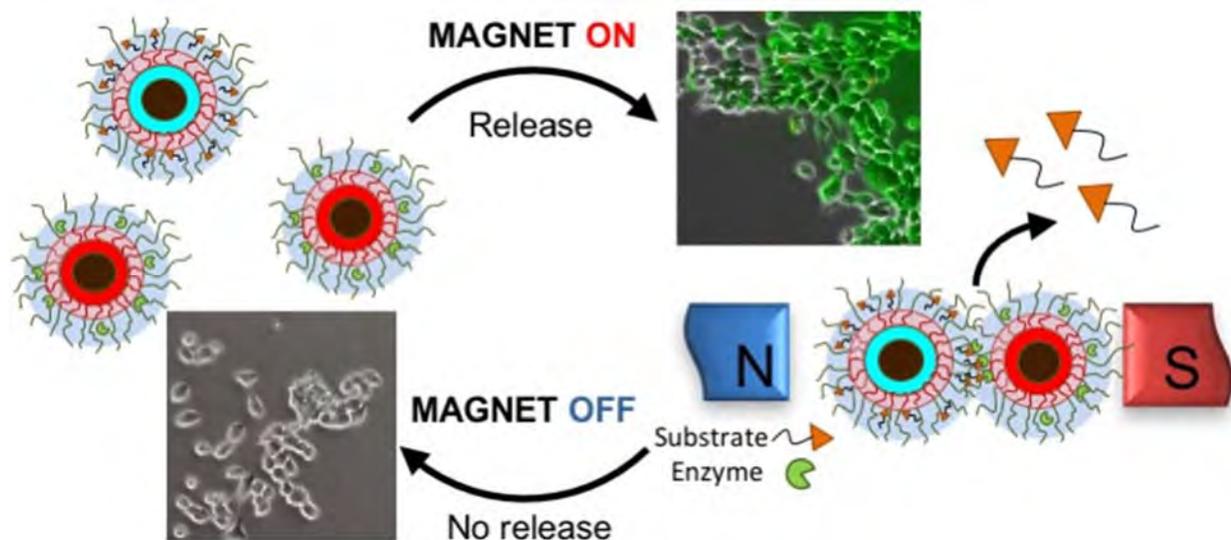
The synthesis and study of a methylcellulose (MC) and polyethylene (PE) ABA triblock compatibilizer for the development of MC and PE blends is described. The compatibilizer is made in three steps resulting in a MC-*block*-PE-*block*-MC ABA triblock copolymer. First MC is monofunctionalized on the reducing-end to contain a pendant vinyl group. The mono-functionalized MC is then used as a chain transfer agent in a one pot cross-metathesis ring-opening metathesis polymerization of cyclooctadiene(COD). The resulting triblock copolymer is then hydrogenated resulting in the final ABA triblock copolymer. MC and PE blends were then prepared by coprecipitation with varied amounts of compatibilizer. These blends were then melt pressed to form films. The mechanical properties were tested by tensile and dynamic mechanical analysis, showing improved properties with as little as 1 wt % compatibilizer. Scanning electron microscopy was performed on the tensile samples showing a change from a brittle fracture for uncompatibilized films to a ductile fracture for the compatibilized films. Oxygen barrier studies show a significant enhancement as an oxygen barrier as more MC is added to the blend. Thermal properties of the films were studied by differential scanning calorimetry showing an increase in the melting point for the PE in more compatibilized films.



POLY 260: Magnetic field remotely controlled highly-selective biocatalysis

Andrey Zakharchenko³, zakhara@uga.edu, Natali Guz¹, Amine Jardj², Sergiy Minko², Evgeny Katz¹. (1) Clarkson University, Potsdam, New York, United States (2) The University of Georgia, Bishop, Georgia, United States (3) TXMI, University of Georgia, Athens, Georgia, United States

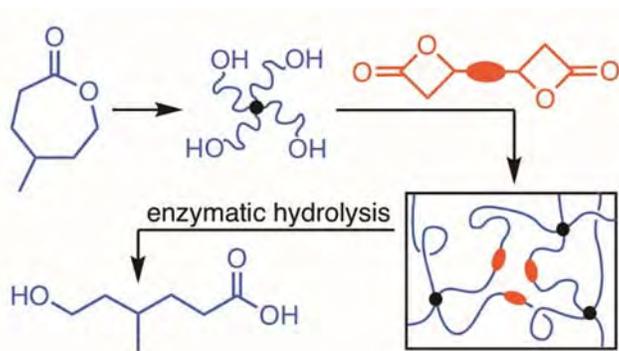
Applications of biological and chemical materials for medical therapy, biotechnology and biosensors rely on emerging methods of efficient active substance delivery and release. A well-controlled substance release on demand is critical for these applications. Numerous examples proved biocatalysis to be a perfect mechanism for controlled, selective, fast and high-conversion processes in a complex biological environment, when combined with the nature-inspired paradigm of stimuli-responsive compartmentalization of biocatalytic reactions. To this end, we developed a novel biocatalytic platform that explores magnetic field-responsive compartmentalization of biocatalytic reactions in spherical polymer brushes. The novel platform combines two different kinds of core-shell magnetic nanoparticles: one loaded with enzymes and another - with substrate-bound therapeutic (bio)chemicals. Both cargos are shielded with a polymer brush structure of the nanoparticle shell, which prevents any kind of enzyme-substrate interactions. The shield's barrier is overcome when a relatively weak (a fraction of 1 T) external magnetic field is applied and when the enzyme and the substrate are merged and forced to interact in the generated nano-compartment. We adapted the developed biocatalytic system for well-controlled-on-demand release of therapeutic drugs when the enzymes degrade the substrate and liberate the substrate-bound drug. The developed platform provides ample opportunities for a remotely-controlled release of drugs or (bio)chemicals using energy of a noninvasive weak magnetic field.



POLY 261: Biodegradable polyester elastomers from bio-based lactones

Guilhem De Hoe³, dehoe001@umn.edu, Michael Zumstein², Brandon J. Tiegs¹, Jacob Brutman³, Kristopher P. McNeill², Michael Sander², Geoffrey W. Coates¹, Marc A. Hillmyer³. (1) Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York, United States (2) Dept. of Environmental Science, ETH-Zurich, Zurich, Switzerland (3) Chemistry, University of Minnesota, Minneapolis, Minnesota, United States

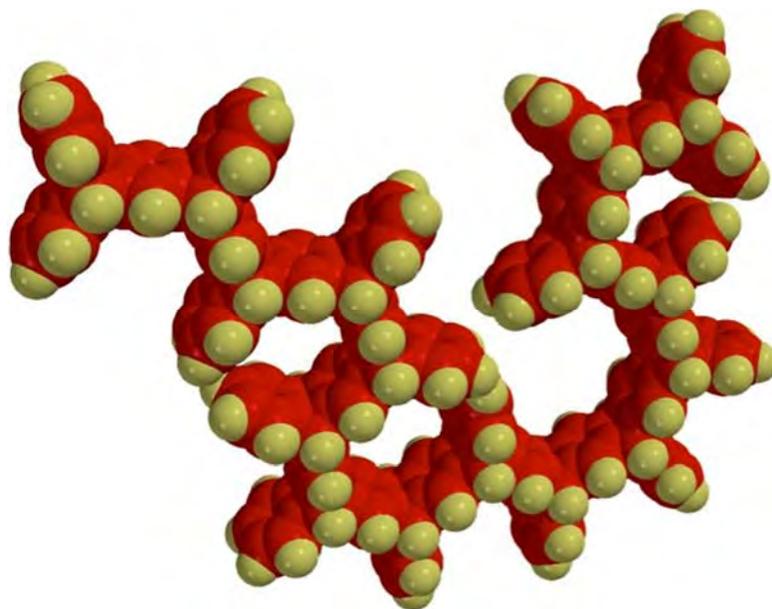
Chemically cross-linked elastomers are an important class of polymeric materials with excellent temperature and solvent resistance. However, nearly all elastomers are petroleum-derived and persist long in the environment or in landfills after they are discarded; this work strives to address these issues by demonstrating the synthesis of renewable, enzymatically degradable, and mechanically competitive polyester elastomers. The elastomers described were synthesized using a novel bis(β -lactone) cross-linker and star-shaped, hydroxyl-terminated poly(γ -methyl- ϵ -caprolactone). Using model compounds, we determined that the bis(β -lactone) cross-linker undergoes acyl bond cleavage to afford β -hydroxyesters at the junctions. The mechanical properties of the cross-linked materials were tunable and competitive with a commodity rubber band. Furthermore, the elastomers demonstrated high thermal stability and a low glass transition ($-50\text{ }^{\circ}\text{C}$), indicating a wide range of use temperatures. The polyester networks were also subjected to enzymatic hydrolysis experiments to investigate the fate of these materials in the environment. We found that they readily hydrolyzed at neutral pH and environmentally relevant temperatures ($2\text{--}40\text{ }^{\circ}\text{C}$); complete hydrolysis was achieved in all cases at temperature-dependent rates. The results presented in this work exemplify the development of high performance yet sustainable alternatives to conventional elastomers.



POLY 262: Shape persistent bicyclic [2.2.2] and [2.2.1] building blocks for porous materials

Timothy M. Swager, tswager@mit.edu. MIT, Cambridge, Massachusetts, United States

This lecture will detail our latest results in the formation of porous polymers using selected bicyclic building blocks. We originated the use of triptycene and related materials to give materials to give high degrees of free volume 20 years ago and this approach has proven to be a robust design. As a result, we continue to examine these types of materials in pursuit of advanced materials. New routes to functional triptycene containing poly(ether ether ketone)s PEEKs and poly(ether sulfone)s will be reported and their use as membrane materials. We will also report on the use of rigid macromonomers having a combination of [2.2.2] and [2.2.1] ring systems to create high surface area materials. In this case the conversion of the macromonomer to a pendant side chain polymer gives rise to a large increase in free volume and surface area as determined by BET measurements. The later methods are robust and significant fractions of comonomers can added into the polymer, while maintaining the high surface area. The utility of these materials as absorbents and as separation materials will be detailed.



Space Filling Model of a Oligotriptycene Polymer

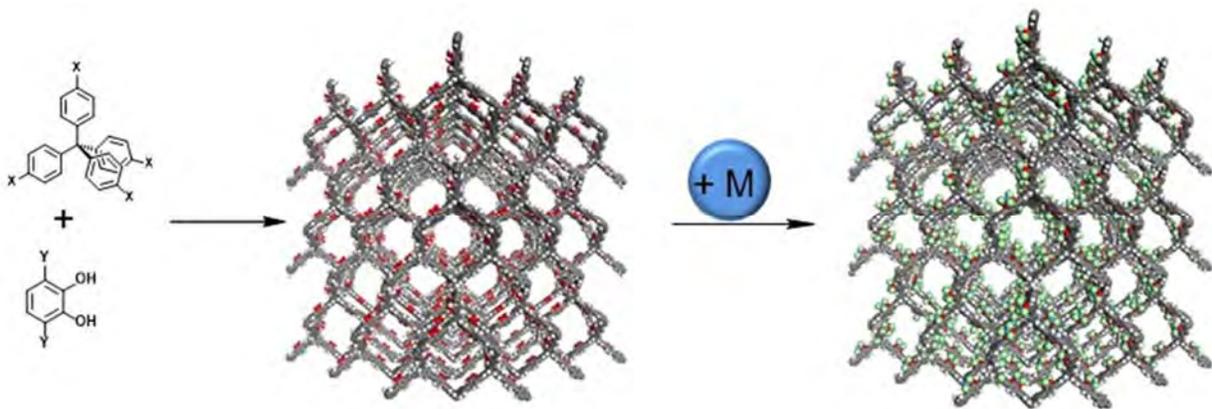
POLY 263: From single-site catalysts and supramolecular assemblies to porous organic polymer (POPs): Bridging homogeneous and heterogeneous catalysis

SonBinh T. Nguyen^{1,2}, stn@northwestern.edu. (1) Dept. of Chemistry, Northwestern University, Evanston, Illinois, United States (2) Argonne National Laboratory, Argonne, Illinois, United States

This presentation will discuss the efforts by our research groups at Northwestern University and Argonne National Laboratory in bridging homogeneous and heterogeneous catalysis through the application of single-site and supramolecular catalyst-design principles to the development of porous organic polymer (POPs) as heterogeneous catalysts.

Supramolecular assemblies are large soluble structures constructed from molecules rather than atoms as building blocks. As thermodynamically stable structures, the stability of these materials comes from marshalling multiple weak interactions in a highly reinforcing way. In this sense, supramolecular chemistry has the potential for bringing together cooperative catalytic sites, stabilizing potent reaction centers, and creating architectures that elicit reaction selectivity. Previous examples from our group include assemblies capable of catalyzing enantioselective oxidation reactions, enantioselective epoxide ring-opening, and acyl transfer reactions with applications in sensing.

As hybrid materials derived from well-defined molecular building blocks, POPs are natural solid-state 3-D versions of supramolecules. These materials have many of the desirable features of zeolites, such as high surface area and porosity, and can be similarly effective in size- and shape-selective catalysis. However, given the enormous diversity of potential structures and chemical functional groups that can be incorporated into the pores of POPs, these porous materials have the potential to extend catalysis far beyond the realm of zeolitic chemistry to include enzyme-like behaviors such as adapted flexibility during catalysis, substrate pre-concentration effects, active-site isolation and protection, and tunable hydrophobicity. Most importantly, recent developments in POP synthesis have given rise to catalytically active materials with unprecedented stability and novel activity that were not observed in solution

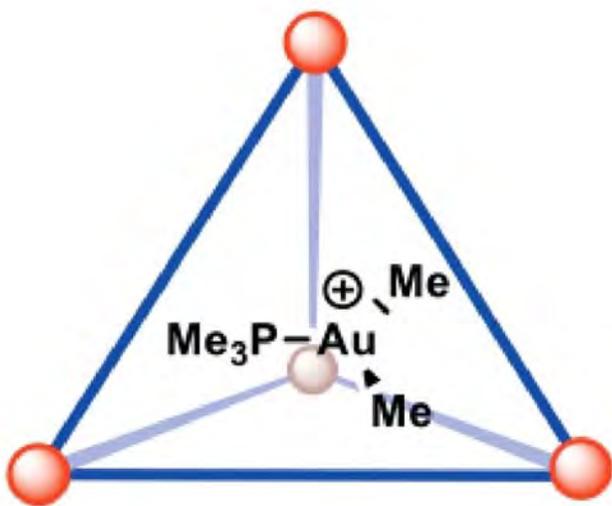


A schematic synthesis of a metallated catechol-functionalized Porous Organic Polymers (POPs).

POLY 264: Organic reactions inspired by the organometallic chemistry of gold

Dean Toste^{1,2}, fdtoste@berkeley.edu. (1) Chemistry, UC Berkeley, Berkeley, California, United States (2) Lawrence Berkeley National Laboratory, Berkeley, California, United States

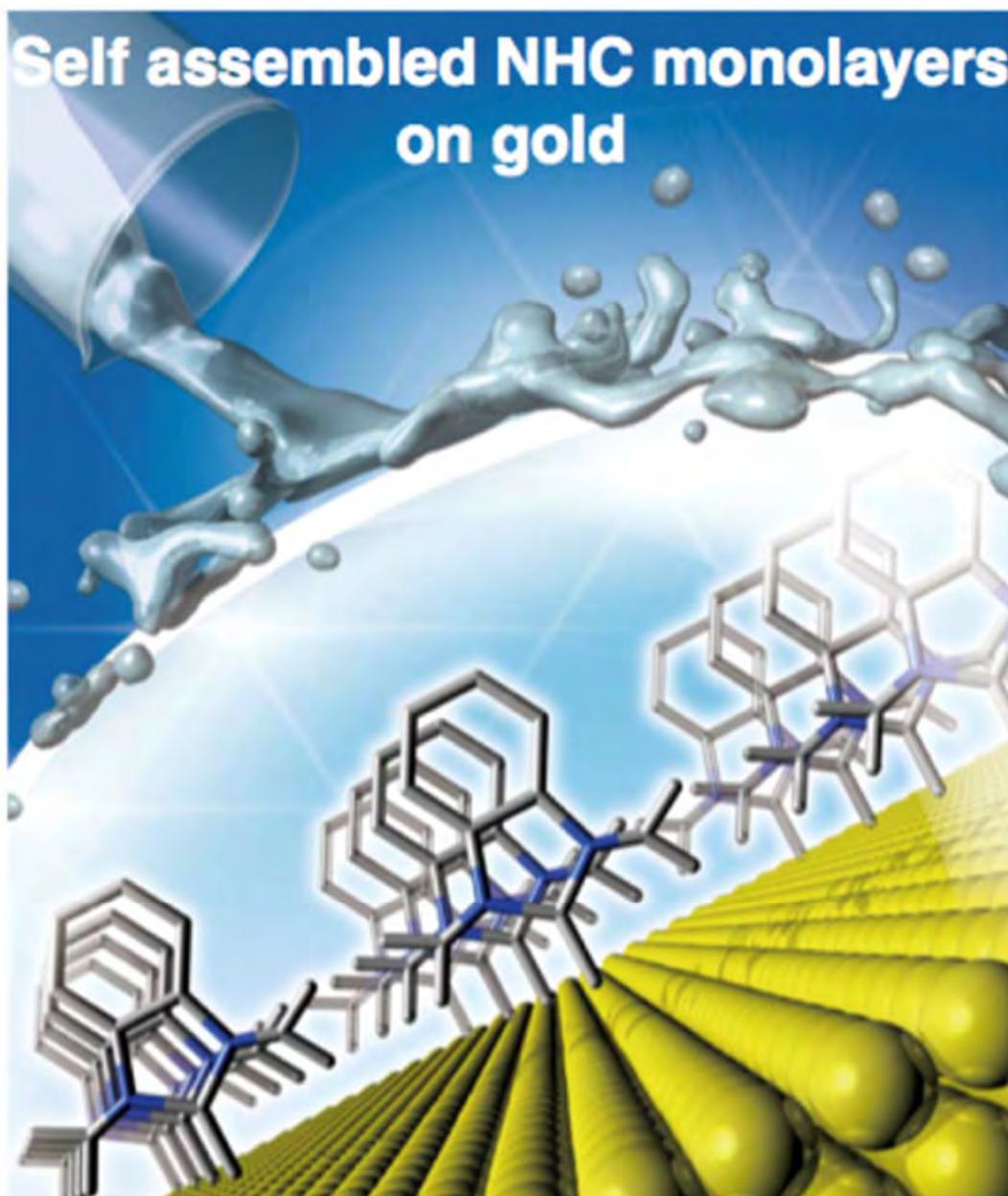
The past decade has witnessed remarkable development in the use of cationic gold(I) complexes as homogeneous catalysts for the transformation of carbon-carbon π -bonds. Several years ago, we demonstrated that the reactivity of these complexes could be controlled by modification of the counter anion to these cationic transition metal complexes. This discovery provided a general platform for inducing enantioselectivity in reactions not only using cationic transition metal complexes, but also with reactive cationic reagents and intermediates. As an extension of this concept, we have been exploring the use of supramolecular assemblies (Ga_4L_6 tetrahedral) as chiral anion for catalysis or as the anionic component in reactions catalyzed by cationic transition metal complexes. Finally, recent studies aimed at harnessing the reactivity of gold(III) will be introduced. This will include mechanistic studies on elementary processes for gold(III) and utility in carbon-carbon bond formation.



POLY 265: N-heterocyclic carbenes as ligands for metal surfaces

Cathleen M. Crudden, cruddenc@chem.queensu.ca. Dept Chemistry, Queens University, Kingston, Ontario, Canada

The use of N-heterocyclic carbenes to modify homogeneous metal catalysts is widespread, however despite the versatility of these complexes, the high metal–NHC bond strength and oxidative stability of NHC–ligated metals, and the ease of synthesis of NHCs, there have been only a handful of reports of surfaces functionalized by NHCs. In this presentation we will describe the functionalization of different types of metals, different types of surfaces and the effect of the structure of the NHC.

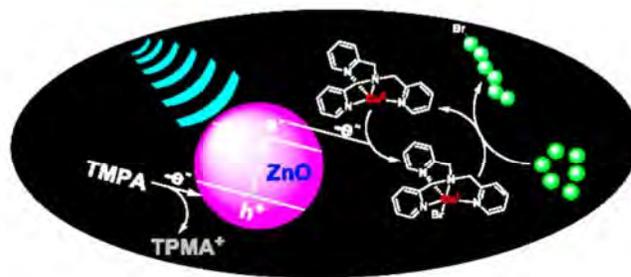


POLY 266: External control in ATRP

Krzysztof Matyjaszewski, *km3b@andrew.cmu.edu*. CMU, Pittsburgh, Pennsylvania, United States

Atom transfer radical polymerization (ATRP) is a catalytic process with Cu-based complexes.

The catalytic activity can be externally controlled by pressure, temperature, solvents, pH and also by light, electrical current and mechanical forces. Examples of such systems including dual control will be presented.



POLY 267: Award Address (Nobel Laureate Signature Award for Graduate Education in Chemistry sponsored by Avantor™ Performance Materials Inc.). Johnson group research in the post-Zhukhovitskiy era: Extremely stable NHC-functionalized gold nanorods and polyMOCs that switch between phantom and affine behavior

*Michelle Macleod², Yuwei Gu¹, **Jeremiah A. Johnson²**, jaj2109@mit.edu. (1) Massachusetts Institute of Technology, Boston, Massachusetts, United States (2) MIT, Massachusetts Institute of Technology, Boston, Massachusetts, United States*

This talk will highlight our recent efforts in two fields pioneered by Dr. Aleksandr Zhukhovitskiy. First, a new strategy for the formation of NHC-metal surface linkages will be described, which has enabled the successful synthesis of NHC-functionalized gold nanorods. These nanorods display exceptional stability under a range of biologically relevant conditions, and are outstanding candidates for use in photothermal therapy. Second, polymer metal-organic-cage (polyMOC) gels with photoswitchable ligands will be discussed. The topology of these polyMOCs can be reversibly switched, which results in transitions between phantom and affine network behavior.

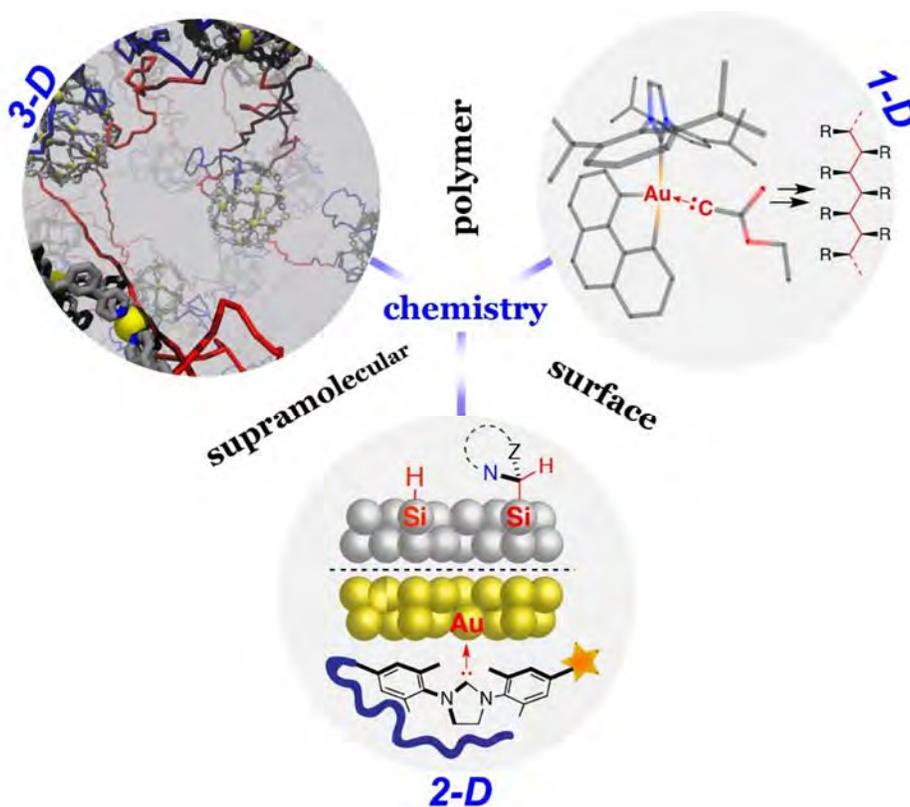


**POLY 268: Award Address (Nobel Laureate Signature Award for Graduate Education in Chemistry sponsored by Avantor™ Performance Materials, Inc).
New frontiers for carbenes and metal-organic cages in surface and polymer chemistry**

Aleksandr V. Zhukhovitskiy^{2,4}, alexzhuko@berkeley.edu, Iliia J. Kobylanskiĭ⁴, Dean Toste¹, Jeremiah A. Johnson³. (1) Department of Chemistry, Berkeley, California, United States (2) Chemistry, MIT, Cambridge, Massachusetts, United States (3) MIT, Massachusetts Institute of Technology, Boston, Massachusetts, United States (4) Chemistry, UC Berkeley, Berkeley, California, United States

The first part of this lecture will describe our efforts to harness the reactivity of carbenes in the contexts of surface and polymer chemistry. We will examine the reactivity of persistent carbenes toward representative examples of metal and metalloid surfaces and demonstrate their utility as surface anchors. Beyond persistent carbenes, reactive metallocarbene intermediates will be discussed in the context of gold chemistry and polymer synthesis.

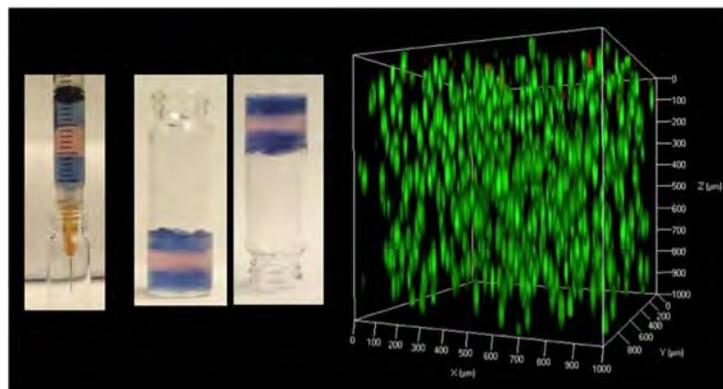
In the second part of this lecture, the application of metal-organic cages as junctions in polymer network design and synthesis will be discussed. Structure/property relationships in such materials will be delineated, and opportunities in polymer network junction engineering will be presented.



POLY 269: Biomolecules for non-biological things: Materials construction through peptide design and solution assembly

Darrin J. Pochan, pochan@udel.edu. Univ of Delaware, Newark, Delaware, United States

Self-assembly of molecules is an attractive materials construction strategy due to its simplicity in application. By considering peptidic molecules in the bottom-up materials self-assembly design process, one can take advantage of inherently biomolecular attributes; intramolecular folding events, secondary structure, and electrostatic and hydrophobic interactions to define hierarchical material structure and consequent properties. Two classes of materials will be discussed. First, the local nano- and overall network structure, and resultant viscoelastic and cell-level biological properties, of hydrogels that are formed via beta-hairpin self-assembly will be presented. Importantly, the hydrogels do not form until individual peptide molecules intramolecularly fold into a beta-hairpin conformation. Subsequently, intermolecular assembly occurs into a branched, nanofibrillar network. The resultant hydrogels are inherently cytocompatibility, have a porous morphology, and exhibit shear-thinning but instant recovery viscoelastic properties. During assembly and gelation, desired components can be encapsulated such as drug compounds and/or living cells. The system can shear thin but immediately reheel to preshear stiffness on the cessation of the shear stress. Recent adaptation of the materials to high throughput screening will be described. Second, a new solution assembled system comprised of coiled coil motifs designed theoretically to assemble into one or two-dimensional nanostructures not observed in nature will be introduced. The strategy provides the opportunity for arbitrary nanostructure creation with peptides. New results revealing the versatility of computational design of peptide building blocks for physical and covalent interaction to build new forms of network material will be discussed.

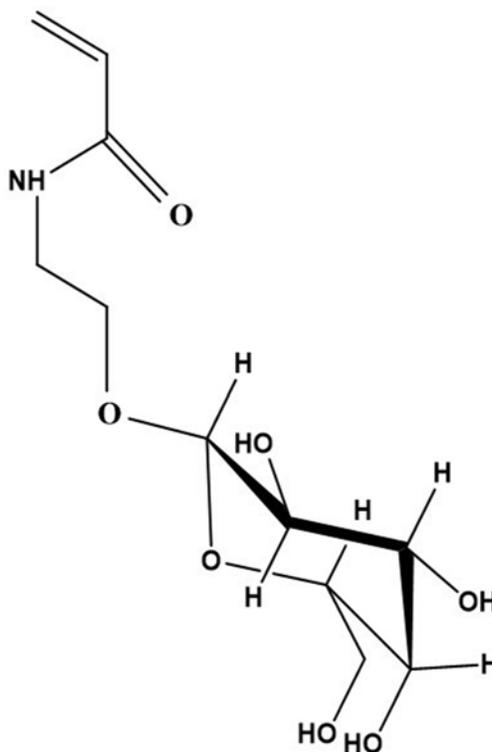


Injecatable solid beta hairpin peptide hydrogel allows simple shear-thinning syringe injection and immediate rigid hydrogel formation. Encapsulated payloads can include viable cells and desired small and large molecules.

POLY 270: Bio-inspired glycopolymer hydrogels for biomedical applications

Sarah E. Morgan, *sarah.morgan@usm.edu*, April Fogel, Bishal S. Upadhyay, Kelli A. Stockmal, Pradipta K. Das. School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, Mississippi, United States

Natural polysaccharide hydrogels, such as those formed from hyaluronic acid, provide unique rheological, lubrication, and water absorption/desorption properties for a variety of processes in the body, and have been used for a wide range of pharmaceutical and personal care applications. Glycopolymers are synthetic polymers with a stable C-C backbone and hydrophilic pendant saccharides. Acrylamide-based glycomonomers with β -D-glucose and β -D-galactose pendant groups were synthesized with structure and stereochemistry identical to those found in natural polysaccharides. Glycopolymer-silicone hydrogels were prepared via UV initiated free-radical polymerization with systematic variation of hydrophobic/hydrophilic content and cross-linking agent. Water within hydrogel networks plays a pivotal role in dictating network properties such as mechanical stability, permeability, and network architecture. Diffusion of water within the networks, nanomechanical properties, and rheological properties are determined by the hydrogel structure. Specific peptide interactions are related to the stereochemistry of the pendant saccharide groups.

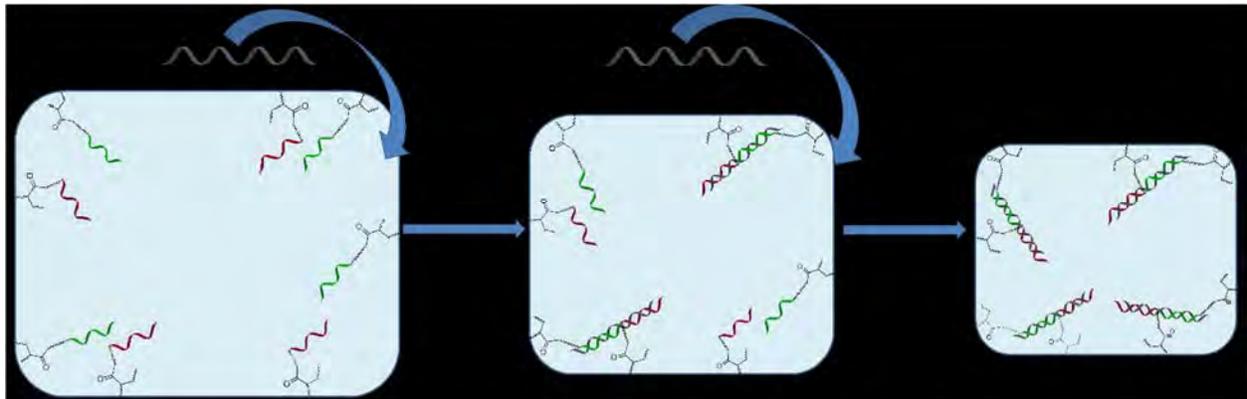


2'-acrylamidoethyl-2,3,4,6-tetra-O-acetyl- β -D-galactopyranoside

POLY 271: Molecularly imprinted super-aptamer hydrogels for RNA and DNA biosensors

David Spivak¹, dspivak@lsu.edu, **Britney Hebert**². (1) Louisiana State Univ, Baton Rouge, Louisiana, United States (2) Louisiana state university, Baton Rouge, Louisiana, United States

We have recently reported aptamer-based bioimprinted hydrogels exhibiting a visible volume shrinking response to target protein biomarkers down to the femtomolar to millimolar concentration range. Specific recognition is even maintained in biological matrices such as urine and tears; furthermore, the gels can be dried for long-term storage, and regenerated for use without loss of activity. In the case of the virus imprinted gels, the visual assessment is enhanced by micromolding the virus-imprinted hydrogel on a diffraction grating to form the first “double-imprinted” film with an optical diffraction output. In this presentation a new hydrogel sensor system was developed for a DNA mimic of the RNA biomarker mir21, a 22 base pair sequence that has been linked to colon and breast cancer. Initial investigation using a capillary imprinted hydrogel system was optimized to give 5.7 % shrinkage of the gel only when exposed to the mir21 biomarker mimic. In addition, a new approach to the hydrogel imprinting was employed using thiol-ene polymer lithographic molds. The thiol-ene composite material is more hydrophilic which allowed for the effective and reproducible transfer of the pattern versus historically used PDMS stamps. The diffraction hydrogels displayed similar results to the capillary hydrogels with a 4.2 % response to the DNA mir21 target. The limit of detection by these imprinted hydrogels is comparable to other sensor methods.



POLY 272: β -Sheet nanocrystal-reinforced supramolecular elastomers

Li Jia, ljia@uakron.edu. Inst of Polymer Science, University of Akron, Akron, Ohio, United States

Many synthetic supramolecular thermoplastic elastomers (TPEs) are analogs of natural silks in the sense that both types of materials contain β -sheet crystalline domains that serve to crosslink and reinforce the elastic network. However, one of the key differences between the synthetic and natural analogs is the aspect ratio of β -sheet crystals. The nanocrystals in silks are particulate, with the sizes in all three dimensions less than 10 nanometers (e.g., $2.1 \times 2.7 \times 6.5 \text{ nm}^3$ in spider dragline), while the crystalline domains in synthetic supramolecular TPE display fibrous morphology with the longest dimension ranging from hundreds of nanometers to micrometers (Figure 1).

In this presentation, I will first show that particulate β -sheet nanocrystals with the longest dimension well-below 100 nm can be attained without an elaborate amino acid sequence. The small size is attributed to the grafting topology. The topology renders a rapid increase of entropic loss as the degree of association increases to stop the growth of the β -sheet. Second, I will show that the particulate nanocrystals display a remarkable ability to simultaneously provide stiffness, extensibility, and strength to the synthetic elastic network and do so highly efficiently at a low volume fraction of the material. The herein studied butyl rubber-based thermoplastic elastomers containing 3.6 volume % of β -sheet nanocrystals are stiffer, stronger, and more extensible than vulcanized butyl rubber reinforced by 20 volume % of carbon black and poly(styrene-*b*-isobutylene-*b*-styrene) reinforced by >33 volume % of polystyrene domains. The latest experimental evidence suggests that a layer of polymer brush is key to the observed high modulus and high extensibility. Finally, the reinforcing characteristics of particulate and fibrous β -sheet nanocrystals will be compared and contrasted.

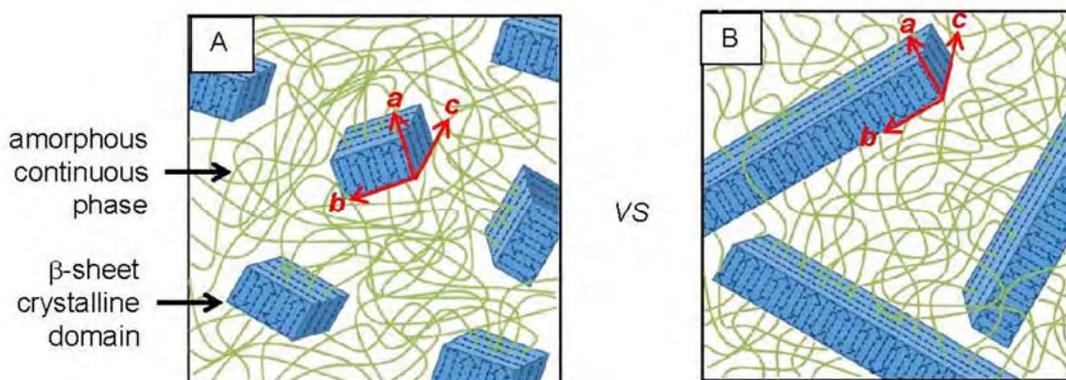
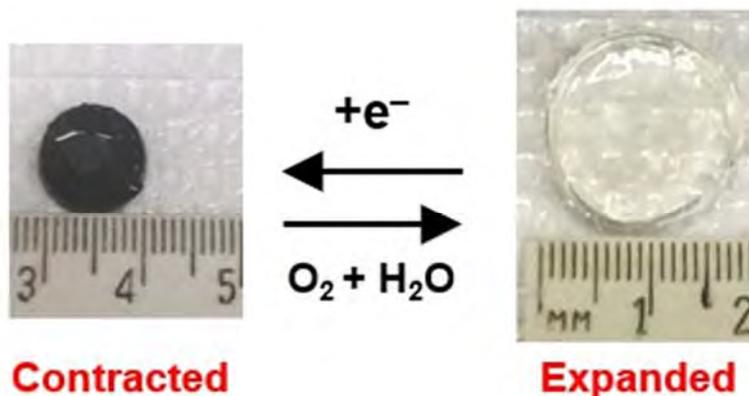


Figure 1. Schematic illustration of β -sheet nanocrystallites (A) and fibrous crystalline domains (B) dispersed in an amorphous phase. The *a*, *b*, and *c* axes correspond to the direction of covalent bonding, hydrogen-bonding, and β -sheet stacking, respectively.

POLY 273: Redox-responsive artificial molecular muscles

Jonathan Barnes, *jcbarnes@wustl.edu*, **Angelique F. Greene**, **Mary Danielson**, **Kevin P. Liles**, **Abby Delawder**. *Chemistry, Washington University, St. Louis, Missouri, United States*

The actuation of materials – i.e., changing their size, shape, and mechanical properties – in response to an external stimulus has gained considerable attention recently; largely for developing new functional sensors, self-healing materials, and soft actuators that may find applications in soft robotics. The use of redox-active polymers in stimuli-responsive materials is particularly attractive because they can be called into action either chemically or electrochemically. My research group has recently developed a new unimolecular redox-responsive macromolecular platform comprising up to ten 4,4'-bipyridinium (a.k.a. viologen) subunits that are tethered by water-soluble and flexible oligoethylene glycol spacers. Upon chemical reduction, radical-based intramolecular recognition between the viologen subunits takes place along the polymer backbone; a process which results in chain folding. Incorporation of these oligoviologens into a hydrogel network made primarily of polyethylene glycol, followed by chemical reduction resulted in reversible contraction of the hydrogel to one-tenth its original volume, where the large majority of contraction occurred in the first 25 – 45 minutes. My group is now exploring how this process can be controlled by other stimuli. In my presentation, I will discuss the activation of our viologen-based actuators using a photoredox-based mechanism, and I will highlight how these materials are capable of lifting weights over defined distances, and therefore performing work as an artificial molecular muscle.



POLY 274: From cartilages to mussel glues: Extreme properties by network design

Xuanhe Zhao, zhaox@mit.edu. MIT, Cambridge, Massachusetts, United States

Nature designs a vast library of soft materials to constitute most machineries of living bodies. Soft living materials possess a set of attributes – such as high compliance, resilience, robustness, and capabilities of sensing, responding and self-healing – unattainable in conventional engineering materials. For example, articular cartilage, a natural hydrogel that contains 70% water, can maintain impressively high fracture toughness under millions of cycles of loads. Skeletal muscles can achieve high actuation stress, strain and energy efficiency, yet operating over years. Mussel secretes soft glues to form extremely robust adhesions to rocks and metals in flowing water with high salinity. What are nature's strategies in designing various soft living materials? How to fabricate soft materials that possess properties and functions as living organisms?

These questions have fostered a nascent field that not only advances fundamental knowledge in mechanics and materials but also impacts on our society's grand challenges in health, food, water and joy of living. In this talk, I will show that unconventional polymer network architectures represent a general strategy to design soft living materials with extraordinary properties. Guided by our theory, I will demonstrate the design of synthetic cartilages, artificial muscles, and mussel-inspired glues with world-record performances. I will then introduce a general method based on our 3D bio-printing system to integrate soft materials, living cells with sensors, actuators and computer chips for systematic design of various soft living machines. The interplays between theory, experiments and design will be emphasized throughout the talk.



POLY 275: Finding value of lignin through chemical and physical cross-linking for versatile applications

Ngoc A. Nguyen¹, Mengmeng Cui¹, Kelly Meek¹, Sietske H. Barnes¹, Christopher C. Bowland¹, Jong K. Keum², **Amit K. Naskar**¹, NASKARAK@ORNL.GOV. (1) Materials Science Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States (2) Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States

Lignin is the second most abundant biomass material. However, utilization of lignin as a feedstock for value added materials remains very limited. This is because of its natural hyper-branched oxygenated structures and characteristics associated with such structures e.g., high rigidity of the macromolecules, low thermal stability and poor processability either in melt or solution. This is the main hurdle for engineering a polymeric product from lignin. In this study, we characterized different lignins and further developed different kinds of functional composite materials. We determined the chemistry of selected lignins having reactive linkages and rich hydroxyl groups for chemical and physical cross-linking. Significant improvement of the mechanical properties and processability with high lignin content in our new composite materials (up to above 40 wt%) opens a new door for automotive and building applications. Intriguingly, formation of the crosslinked networks and tunability of the glass transition temperatures of a rubber – lignin composite were employed to control the shape memory effects of the materials. We made programmable and tunable electrically conducting skins for stress/ strain sensing applications. We discovered that the stored elastic work for shape recovery and fixity of the composites can be tuned by thermal annealing the rubber – lignin composites. Thermally activated lignin linkages generated free radicals for macromolecular rearrangement and strong cross-linked structure formation. In this research, the hydroxyl groups of lignins were also cross-linked with functional chain-end capped-polyethylene oxide to make self-healing electrical conducting materials for human motion detection.

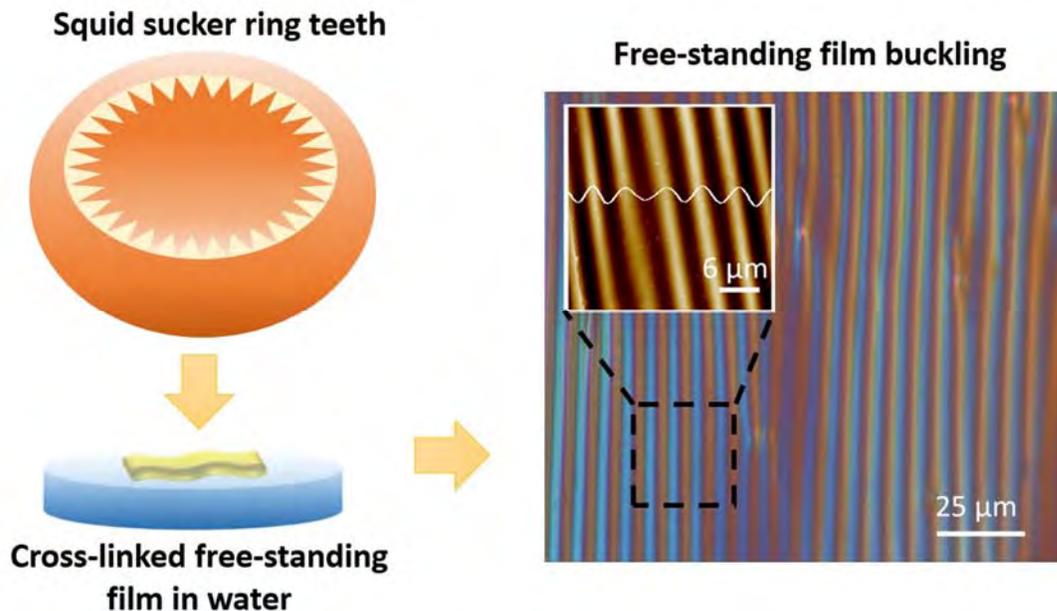


Excellent shape fixity of a lignin based composite

POLY 276: Aqueous toughening in crosslinked marine animal proteins

Anise M. Grant¹, *anise.grant@gmail.com*, Michelle Krecker¹, Sirimuvva Tadepalli³, Maneesh Gupta², Marquise Crosby², Patrick Dennis², Srikanth Singamaneni³, Rajesh R. Naik², Vladimir V. Tsukruk¹. (1) Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States (2) Air Force Research Laboratory, Wright Patterson Air Force Base, Ohio, United States (3) Mechanical Engineering and Materials Science, Washington University in St. Louis, St. Louis, Missouri, United States

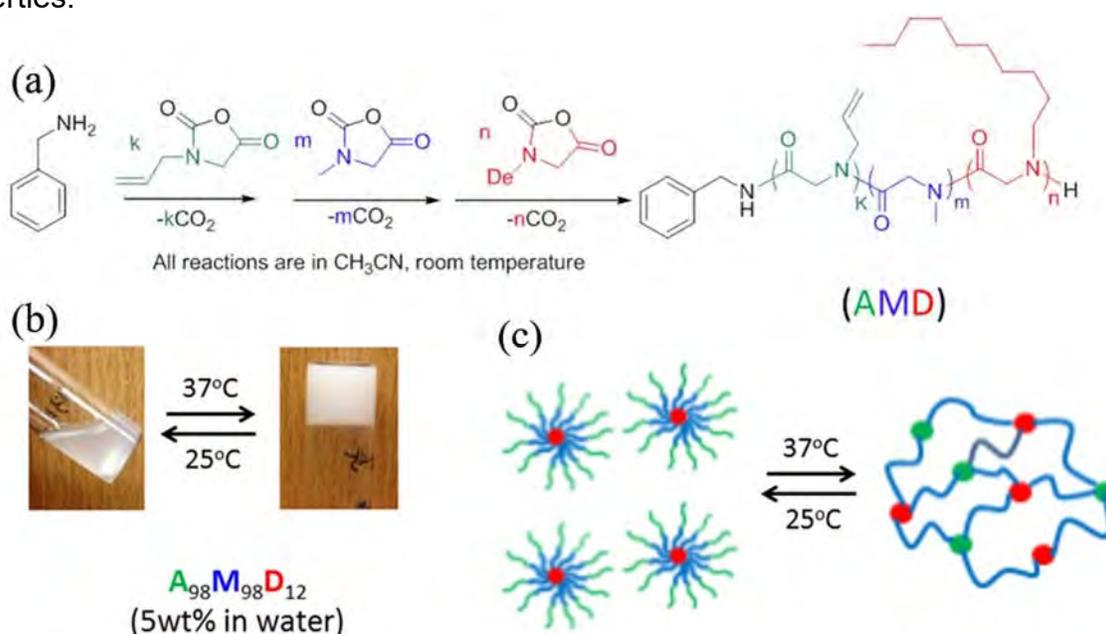
Humbolt squids are among the largest and fiercest animals in the ocean. They owe the latter distinction in part to their all protein sucker ring teeth. The sucker ring teeth protein (SRTTP) of which there are many variations that form a composite-like material with strength comparable to Bombyx mori silk. However, unlike silk, SRTTPs exhibit toughening when wet. Herein, we probe the mechanism of aqueous toughening as well as the role of salt anions on this process. Insoluble monolayers films of SRTTP were formed by spin assisted deposition then crosslinked using horseradish peroxidase for mechanistic analysis. Structural changes characteristic of the toughening process is monitored via time-resolved high resolution atomic force microscopy and Fourier transform infrared spectroscopy. The rearrangement of nanoconfined crystalline regions is probed via X-ray diffraction. Observed surface and cross-sectional assembly are mapped with changes in mechanistic response characterized via buckling test for membrane mechanical analysis.



POLY 277: Structural evolution of thermoreversible triblock terpolypeptoid hydrogels undergo sol-gel transition

Naisheng Jiang¹, naishengjiang@gmail.com, Garrett L. Sternhagen¹, Tianyi Yu¹, Sunting Xuan¹, Yueheng Zhang², Vijay T. John², Donghui Zhang¹. (1) Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana, United States (2) Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana, United States

We have prepared novel thermoreversible hydrogels from a series of ABC triblock terpolypeptoids [i.e., poly(N-allyl glycine)-b-poly(N-methyl glycine)-b-poly(N-decyl glycine) (AMD)] with well-defined structure and varying composition. A combination of small-angle neutron scattering (SANS) and microscopic techniques demonstrate that the ABC triblock terpolypeptoids form poly(N-decyl glycine)-core micelles in water at room temperature and undergo a thermoreversible sol-gel transition through the formation of two-compartment micellar networks upon heating above the lower critical solution temperature (LCST) of poly(N-allyl glycine). The effects of chemical composition and polymer concentration on the structure of hydrogel networks and the hydrogel mechanical property are revealed. It was found that the structural reorganization of the binary micellar network during the sol-gel transition strongly depends on the molar ratio between the hydrophobic and hydrophilic blocks. These results shed new lights on the gelation mechanism and structural-property relationships of ABC terpolypeptoid hydrogels, which are of great significance in the development of thermoreversible polymeric hydrogels with tunable structures and mechanical properties.



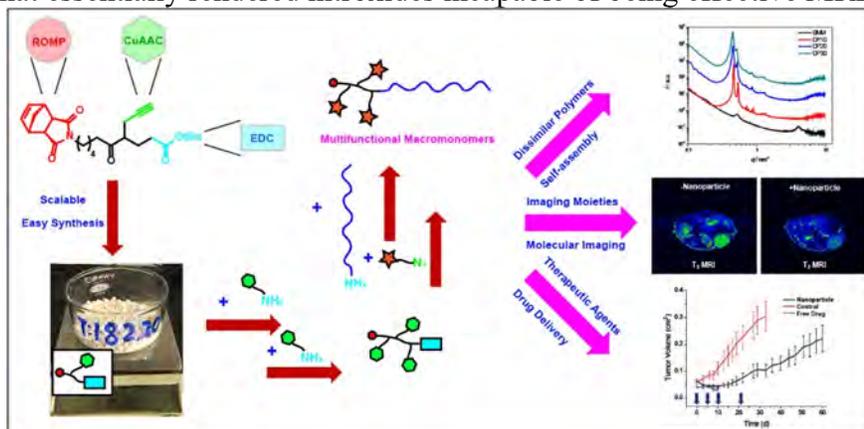
(a) Synthetic scheme for the AMD triblock terpolypeptoids. (b) Photos of the AMD hydrogel upon thermo-reversible gelation. (c) Schematic showing the proposed gelation mechanism of the AMD triblock terpolypeptoids.

POLY 278: Brush-first ring-opening metathesis polymerization as a modular and scalable strategy for combination cancer therapy and molecular imaging

Hung V. Nguyen², hvtn191@mit.edu, Nolan Gallagher², Farrukh Vohidov¹, Yivan Jiang², Ken Kawamoto², Hui Zhang⁴, Jonathan C. Barnes⁵, Andrzej Rajca⁴, Jeremiah A. Johnson³. (1) Chemistry, MIT, Arlington, Massachusetts, United States (2) Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (3) MIT, Massachusetts Institute of Technology, Boston, Massachusetts, United States (4) UNL, Lincoln, Nebraska, United States (5) Chemistry, Washington University in St. Louis, St. Louis, Missouri, United States

In recent years, bottlebrush polymers (BPs) have found widespread applications in fields ranging from drug delivery and molecular imaging to photonics and lithography. Graft-through ring-opening metathesis polymerization (ROMP) offers distinct advantages for BP synthesis including exceptionally high functional group tolerance and efficiency even for sterically-hindered multivalent macromonomers (MMs). In our group, a branched MM platform consisting of a ROMP-compatible norbornene analogue along with two orthogonally functionalizable sites is employed for the synthesis of novel bottlebrush and star polymer architectures. These sites can be furnished with either a therapeutic/imaging agent and a diluent polymer (eg. PEG) for biomedical applications, or 2 dissimilar polymers for branched block copolymer self-assembly studies. We recently developed a revised synthetic protocol that dramatically simplifies the synthesis of branched MMs, enabling hundred-gram scale preparations in overall 87% yield (compared to 43% for our previous system) and minimal purification steps. Furthermore, by repeating these steps in a manner similar to peptide synthesis, we were able to introduce additional functionalizable sites which can be subsequently loaded with the aforementioned moieties.

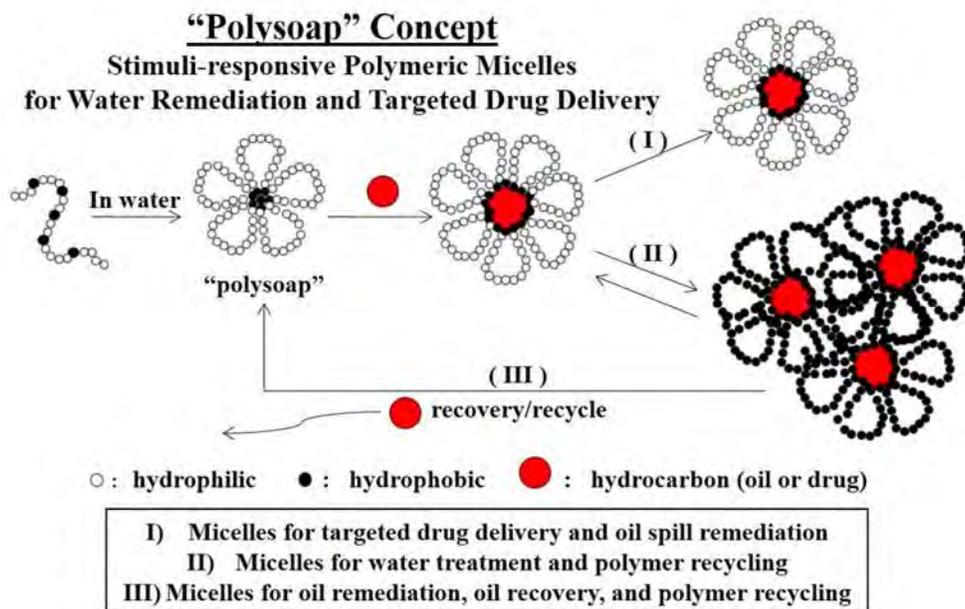
Given the previously reported excellent therapeutic efficacy of our brush-arm star polymer nanoparticles (BASP NPs) based on the ability to precisely control the drug loading onto a three-drug-conjugated NP with favourable *in vivo* circulation and biodistribution, we are currently utilizing this concept to tackle multiple myeloma via deploying clinically relevant combination therapy to our BASP platform. Moreover, we have developed nitroxide-based BASP MRI organic contrast agents capable of tumor imaging over long time periods using clinical high-field ¹H MRI techniques. As a consequence of their unique nano-architectures, nitroxide-containing-BASPs feature per nitroxide transverse relaxivities up to ~44-fold greater than common nitroxides, exceptional stability in highly reducing environments, addressing long standing weaknesses that essentially rendered nitroxides incapable of being effective MRI contrast agents.



POLY 279: “Polysoaps” via RAFT copolymerization forming well-defined, unimeric micelles for water remediation and targeted drug delivery: An old concept with contemporary relevance

Phillip D. Pickett, phillip.pickett@eagles.usm.edu, Mason A. Dearborn, Kaden Stevens, Charles L. McCormick. Polymer Science and Engineering, University of Southern Mississippi, Hattiesburg, Mississippi, United States

Research in the area of stimuli-responsive amphiphilic (co)polymers continues to grow at a remarkable rate, largely due to the plethora of synthetic methods and “tools” available to polymer chemists. The impetus for this activity arises from the behavioral characteristics in water, as well as the biological relevance of these architecturally advanced systems for biomedical, pharmaceutical, and environmental applications. Structurally-tailored, statistical amphiphilic copolymers or “polysoaps” can self-assemble into single-chain or unimeric micelles, eliminating any concentration dependence on domain formation. Such micelles offer vast potential for dispersion of hydrophobic molecules in water at high dilution, making them desirable candidates for novel water remediation and targeted drug delivery technologies. Our group has synthesized a number of these “polysoap”-type copolymers utilizing reversible addition-fragmentation chain transfer (RAFT) polymerization, which provides control over molecular weight and gives narrow molecular weight distributions. Controlling the hydrophobic monomer content along the copolymer backbone allows the study of solution properties, including those pertaining to micelle formation and hydrocarbon sequestration in aqueous media. Additionally, we can statistically incorporate stimuli-responsive co-monomers to determine the reversibility of micelle-to-unimer or micelle-to-aggregate phase transition behavior in response to external stimuli, including pH or CO₂. This presentation will highlight current research efforts in our labs to synthesize and characterize “polysoap”-type copolymers as hydrocarbon dispersants that can, conceptually, circumvent several limitations of classical water remediation and drug delivery technologies.



POLY 281: Swelling pressure and compressive behavior of cartilage polymers

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The main macromolecular components of cartilage extracellular matrix are proteoglycans (PGs) and collagens, which provide the biomechanical properties of the tissue. The PGs are negatively charged and exhibit a high osmotic swelling pressure that is essential to the compressive resistance of cartilage. The collagen network immobilizes the proteoglycan assemblies and provides resistance of cartilage to tension. The dominant PG in cartilage is the bottlebrush shaped aggrecan, which forms large aggregates with hyaluronic acid (HA) and link protein. The aggrecan bottlebrushes contain long sulfated glycosaminoglycan (GAG) chains, primarily chondroitin sulfate (CS) and keratan sulfate (KS) chains. CS and KS provide the fixed charged density to the tissue due to their sulfate and carboxyl groups. The electrostatic repulsive forces arising from the high charge density of the negatively charged GAG molecules favor chain extension and generate highly swollen gel-like structures. The microgel nature of aggrecan/HA assemblies defines important biomechanical properties of cartilage. We report a systematic experimental study aimed to determine the interactions between the main macromolecular constituents of cartilage extracellular matrix. The static properties were determined from scattering (light, neutron and X-ray) measurements and macroscopic osmotic swelling pressure observations. The dynamic behavior was investigated by dynamic light scattering, neutron spin-echo and rheological measurements. A unified framework was developed to evaluate the experimental results obtained by these complementary techniques probing the structure and dynamics over a wide range of length and time scales.

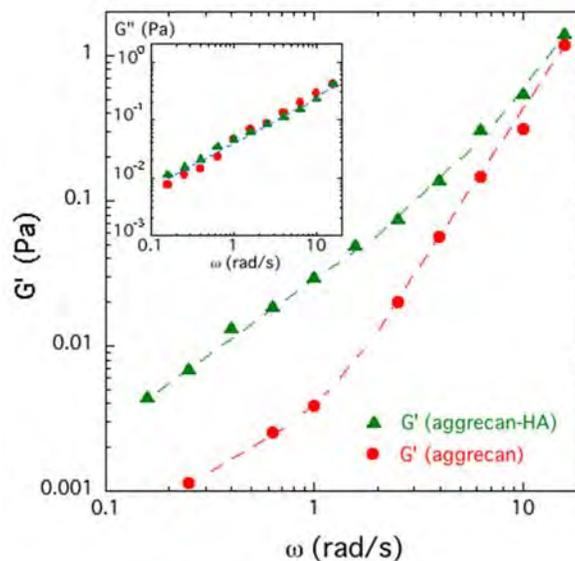


Figure 1. Frequency dependence of the storage modulus G' in aggrecan and aggrecan-HA solutions (polymer concentration: 5 mg/cm^3). Inset: loss modulus G'' as a function of the frequency, ω .

POLY 282: Synthesis of novel water soluble semiconducting polyrhodamine

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The development of organic semiconducting materials (OSC) has opened a new window in electronic industry due to their superior properties. Though they were discovered 40 years ago, conjugated polymers (CP) play a leading role in the field of developing OSC. These polymers have great electronic, thermal, and optical properties. In addition, they also have better solubility, low temperature processability, and mechanical properties when compared to conventional semiconductors. These characteristics are very important in applications such as display backpanels, sensors and active/passive matrix devices. Still the real-life applications of CP are limited due to major drawbacks, such as poor solubility in polar solvents and low reversibility of the redox reaction.

This work describes the synthesis, chemical stability, redox properties, and sensory properties of a novel electrical semiconducting water soluble polymer. The polymer was synthesized by a Buchwald cross-coupling reaction between fluorescein ditriflate and *p*-phenylenediamine. According to the UV-visible spectroscopic studies, the material showed very good chemical stability towards extremely acidic and basic conditions, even after several cycles back and forth. Furthermore, under acidic conditions, the wavelength of maximum absorbance (λ_{max}) of the diluted polymer solution was blue shifted from 510 nm to 488 nm when it was exposed to hydrogen peroxide (H_2O_2). On the contrary, the basified polymer became colorless in the presence of H_2O_2 . When doped with polyprotic acids such as polystyrene sulfonic acid, *p*-phenylene sulfonic acid and sulfuric acid, the material acted as an electrical semiconductor, and the cyclic voltammetry (CV) studies showed good redox stability with reversible redox potentials. The results obtained indicate that this polymer could be a building block for a sensory or energy storing material.

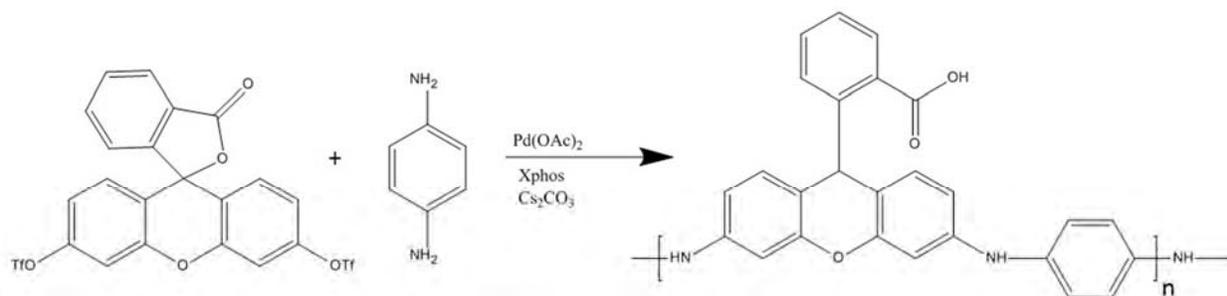
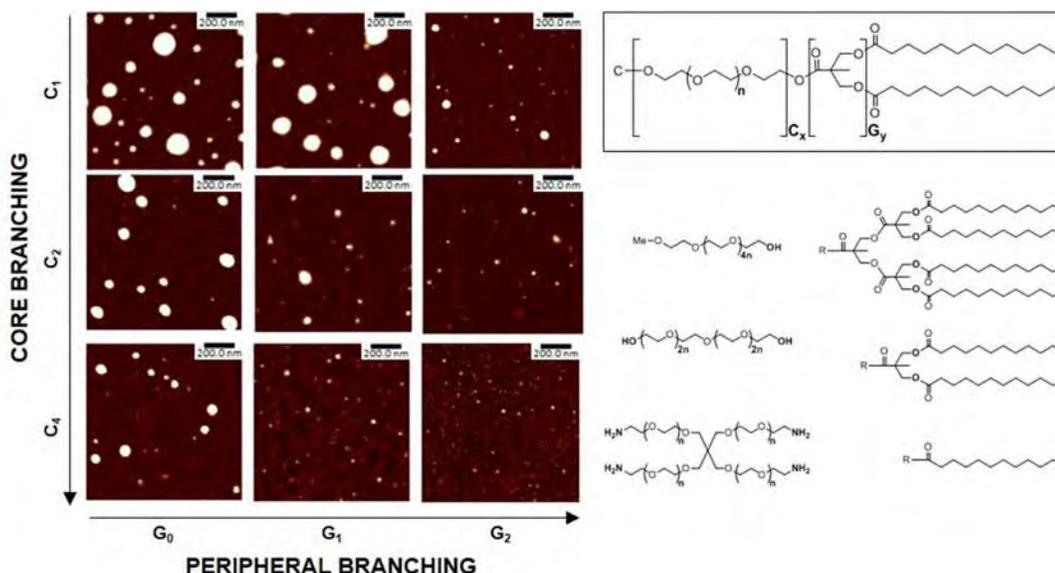


Figure 1: Synthesis of polyrhodamine by Buchwald cross-coupling

POLY 283: Directed reverse micelle self-assembly of branched amphiphiles: Effect of polymer architecture on aggregation behavior

Karolina Kosakowska¹, *kkosakow@gmail.com*, **Brittany Myers**¹, **Louise B. Lawson**³, **Julie Albert**², **Scott M. Grayson**¹. (1) Tulane University, New Orleans, Louisiana, United States (2) Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana, United States (3) Department of Microbiology, Tulane University School of Medicine, New Orleans, Louisiana, United States

Herein, the self-assembly of a series of systematically branched amphiphilic polymers into reverse micelles is investigated to determine architecture-induced aggregation behavior. While branching in polymers is known to significantly affect material properties, the relative contributions based on the placement of branching motifs within a polymer chain have been less extensively explored. Towards that end, a series of poly(ethylene glycol) (PEG)-based amphiphiles was generated, incorporating branching within either the core-forming domain and/or the hydrophilic-hydrophobic interface. Three separate one-, two- or four-armed PEG cores of equivalent molecular weight were end-group functionalized with polyester dendrons of generations 0 through 2. Subsequent peripheral functionalization with lauryl esters produced a library of amphiphilic polymers with variable degrees of branching at both the core and the periphery. Material characterization via MALDI-TOF MS, GPC and NMR, confirmed the materials were well-defined and suitable for a systematic comparison. Aggregate size, dispersity, critical micelle concentration (CMC) and encapsulation efficiency were determined through detailed DLS, AFM, and spectroscopy analysis, enabling the physical properties and reverse-micellar behavior to be directly compared across amphiphilic analogues. The observed self-assembly trends provide meaningful evidence that control of polymer behavior can be achieved by optimizing the location of branching motifs.



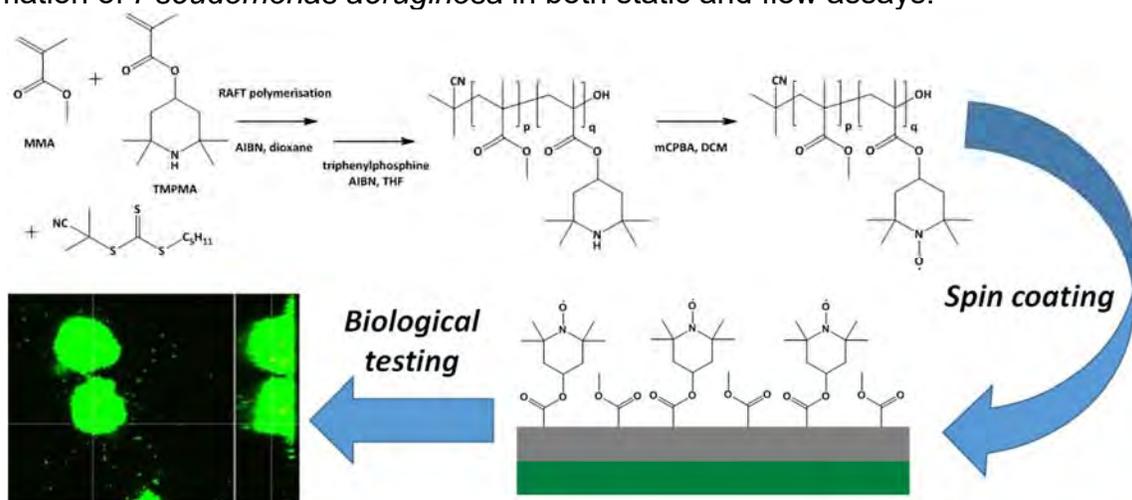
POLY 284: Polynitroxides to protect against bacterial biofilms

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Biofilms are highly organised colonies of bacteria and other microorganisms at a surface or interface. These colonies show a high level of structural complexity, which helps to protect the microorganisms from removal from a surface by both physical and chemical processes. Biofilms can cause major issues for industry, for example through the fouling of ship hulls or food processing plants. They are also implicated in the majority of nosocomial infections where they can show increased resistance against conventional antibiotic therapy.

Our research group has shown that small molecule nitroxides (persistent and stable free radical species) are able to inhibit the formation of biofilms on a surface, as well as being able to disperse existing biofilms. In this project, we look to extend these molecules further by designing polymeric materials bearing pendant nitroxide groups, which have the potential to be used as anti-biofilm surface coatings.

This presentation will detail our efforts to synthesise and characterise thin films with controlled concentration of the nitroxide radical. This has been achieved through the spin coating of methacrylate copolymers, synthesised by RAFT polymerisation. Through this process, we were able to control the concentration of nitroxide in our polymer, as measured by EPR, which in turn controls the concentration at the surface, as determined by XPS. We have investigated these films for their ability to prevent biofilm formation of *Pseudomonas aeruginosa* in both static and flow assays.

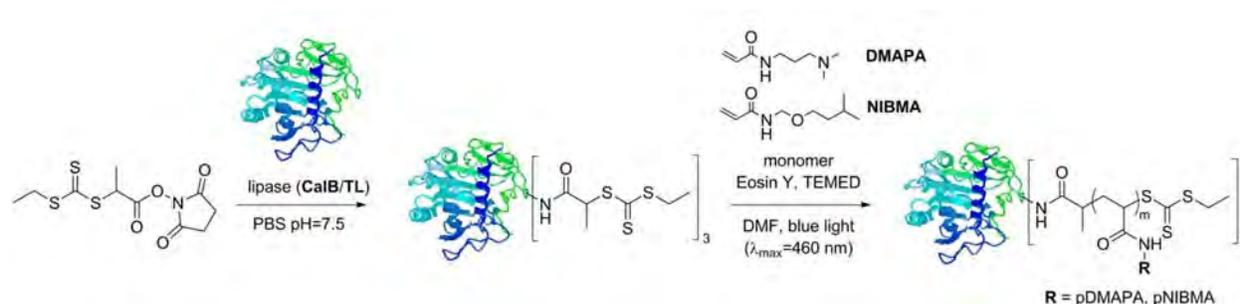


Schematic of the synthesis and fabrication of poly(TEMPO-co-MMA) thin films as anti-biofilm surface coatings.

POLY 285: Synthesis of lipase polymer hybrids via the grafting-from approach

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The use of enzymes as catalysts has become increasingly important in many industrial applications such as food processing, detergents, textiles and organic synthesis. However, a limiting factor for the industrial application of enzymes is their poor operational or long-term stability when exposed to environmental challenges, such as elevated temperatures and pH extremes. To extend the range over which proteins are useful for conducting organic transformations, polymers have been ligated onto proteins. The polymer-protein conjugation strongly affects the properties of the enzyme by potentially improving its activity and stability, and offers a means to modify functions. There are two primary means of attaching polymers to biomolecules; the 'grafting-to' strategy, which pairs reactive end-groups on a preformed polymer with amino acid residues on a protein, and the 'grafting-from' strategy, where a small molecule polymerization initiator or chain-transfer agent has been attached onto a biomolecule, with the polymer grown *in situ* off the biomolecule's surface. In this study we modified an industrially important enzyme, lipase by the 'grafting-from' method, employing photoinduced electron transfer reversible addition-fragmentation chain transfer (PET-RAFT) polymerization. Polymer-protein conjugates were synthesized using two representative lipases, *Candida antarctica* lipase B (CalB) and *Thermomyces lanuginosa* lipase (TL). To study the effects of polymer composition and molecular weight on the enzyme activity a hydrophilic and hydrophobic polymer were grafted at three different polymer lengths. We found a significant impact of polymer composition on enzyme activity with hydrophobic polymer substantially increasing enzyme activity.



POLY 286: Thermotropic one-handed spiralization of polyacetylenes based on main-chain conformation change from *Cis-transoid* to *Cis-Cisoid*

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Polyacetylene prepared by rhodium catalyst, such as $[\text{Rh}(\text{nbd})\text{Cl}]_2$, is a typical dynamic helical polymer, and its main-chain conformation can be *cis-transoid* or *cis-cisoid* depending on the monomer structure and the environment. In this study, we report that a thermotropic chiral induction system consisting of a chiral amine and a polyacetylene prepared from an achiral phenylacetylene having two hydroxyl groups shows a tunable *critical one-handed spiralization temperature (COST)* in nonpolar solvents such as toluene, hexane and CCl_4 .

The conformation of poly(**1**) in the system of poly(**1**)/chiral phenylethylamine/toluene (Figure 1) could be induced into one-handed helix along with transformation of main chain conformation from *cis-transoid* to *cis-cisoid* by heating the system to a temperature higher than the **COST**. The induced CD absorption of poly(**1**) was much stronger than the CD absorption of poly(**1**) prepared by helix-sense-selective polymerization. The **COST** can be adjusted by changing the chiral amine concentration in the system, and the higher concentration affords the higher **COST**. This unique thermotropic chiral induction phenomenon may be caused by the difference in strength of H-bonds of -OH/-NH₂ and -OH/-OH at different temperature. In addition, the induced one-handed helical clarity of the polyacetylene can be self-stabilized by intramolecular H-bonds after precipitating the polyacetylene in methanol to remove the chiral amine, i.e. the induced one-handed helical chirality of the polyacetylene can be perfectly saved in solid state.

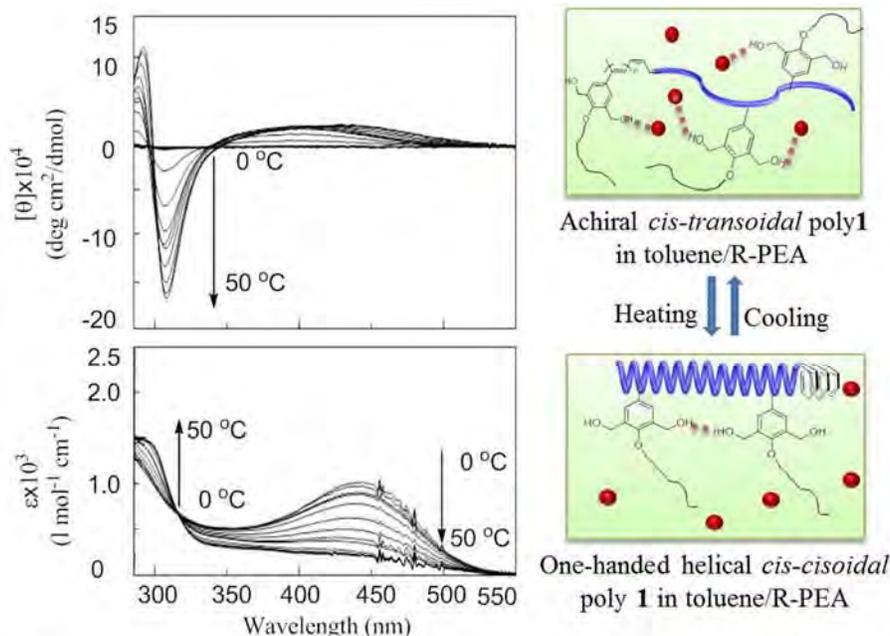
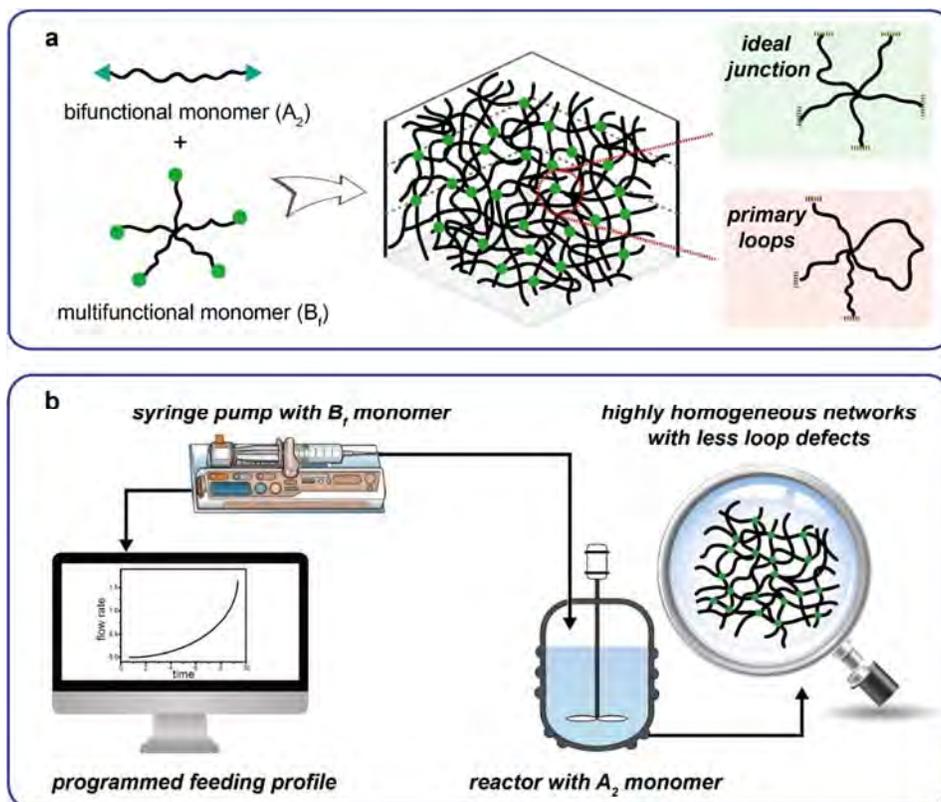


Figure 1. CD and UV spectra of poly**1** in the mixture of (*R*)-phenylethylamine/hexane (amine content =20vol.%) at the temperature from 0 °C to 50 °C.

POLY 287: Loop control of gel mechanics

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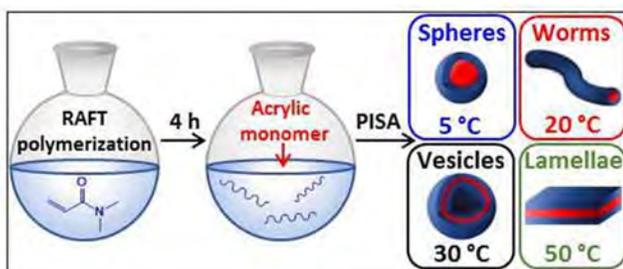
Controlling the molecular structure of amorphous cross-linked polymeric materials is a longstanding challenge. Herein, we disclose a general strategy for precise tuning of loop defects in covalent polymer gel networks. This “loop control” is achieved through a simple semibatch monomer addition protocol that can be applied to a broad range of network-forming reactions. By controlling loop defects, we demonstrate that with the same set of material precursors it is possible to tune and in several cases substantially improve network connectivity and mechanical properties (e.g., ~600% increase in shear storage modulus). We believe that the concept of loop control via continuous reagent addition could find broad application in the synthesis of academically and industrially important cross-linked polymeric materials, such as resins and gels.



POLY 288: Unique aqueous self-assembly behavior of a new thermoresponsive diblock copolymer

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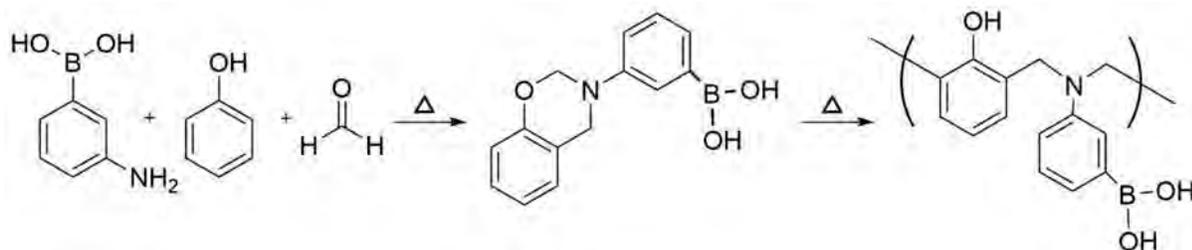
We describe the synthesis of a new amphiphilic diblock copolymer via a one-pot RAFT polymerization protocol and investigate its unique thermoresponsive behavior. More specifically, dimethyl acrylamide (DMAC) was polymerized at 80 % w/w solids in aqueous solution at 30 °C in the presence of a carboxylic acid-functionalized RAFT agent. ¹H NMR spectroscopy confirmed full monomer conversion and GPC analysis indicated good batch-to-batch reproducibility for the synthesis of this water-soluble precursor block. Subsequently, this PDMAC macro-CTA was chain-extended with a water-miscible acrylic monomer under aqueous dispersion polymerization conditions at 30 °C to produce diblock copolymer nano-objects at 20 % w/w solids. As the second block grows, it becomes insoluble at a critical DP which results in polymerization-induced self-assembly (PISA). On cooling to ambient temperature, a viscous fluid was obtained. Oscillatory rheology studies indicated that a decrease in viscosity occurs on cooling the 20 % w/w diblock copolymer dispersion from 20 °C to 5 °C. This phase transition is reversible: the viscosity increases on returning to ambient temperature. SIPLI studies performed at around 20 °C confirm the appearance of a characteristic Maltese cross motif: this indicates birefringence resulting from the in situ alignment of anisotropic particles. Heating this aqueous copolymer dispersion up to 30 °C resulted in disappearance of the Maltese cross and a concomitant significant reduction in solution viscosity. An intense Maltese cross motif was again observed at around 50 °C and was accompanied by an increase in solution viscosity. DLS and SAXS suggest that these changes in physical properties are the result of thermally-induced morphological transitions from spheres (5 °C) to worms (20 °C) to vesicles (30 °C) to lamellae (50 °C). Moreover, these thermal transitions occur rapidly and are fully reversible even at copolymer concentrations as low as 0.1 % w/w. Variable temperature ¹H NMR spectroscopy was used to probe this remarkable self-assembly behavior: this technique provided direct evidence for a continuously varying degree of hydration for the weakly hydrophobic block over the 5-50 °C temperature interval.



POLY 289: Polybenzoxazine based on phenol and *m*-amino phenyl boronic acid

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The studies on modification of polybenzoxazines as an attractive alternative to epoxides and traditional phenolic resins have been increased almost exponentially not only for defence and aerospace but also for electronic industrial and technological applications. The characteristics of these polymers such as no need for harsh catalysts, high thermal stability, good mechanical properties, excellent electrical properties and molecular design flexibility and low melt viscosity make this class of polymers a promising candidate for high performance composites. Their facile and versatile syntheses from relatively abundant materials involving phenols, amines, their functional analogues and formaldehyde offer wide range of molecular design flexibility. However, some limitations, such as high curing temperature, on their use in practical applications exist. To overcome these problems and to improve thermal and mechanical properties composites of polybenzoxazines involving graphite, carbon nanotubes, organoclays, boron compounds were prepared. Recently, decrease in curing temperature of the benzoxazine monomer was detected in the presence of aromatic monoboronic acid [1]. In this work, polybenzoxazine based on phenol and *m*-amino phenyl boronic acid and aniline mixture was prepared and characterized. Our main objective was to decrease the curing temperature of the monomer, and to improve thermal properties such as thermal stability and char yield of the polybenzoxazine produced. The effect of the type of the functional amine group was investigated by varying the amount of *m*-amino phenyl boronic acid systematically. Significant Improvement in thermal characteristics became more significant as the amount of *m*-amino phenyl boronic acid ratio was increased.

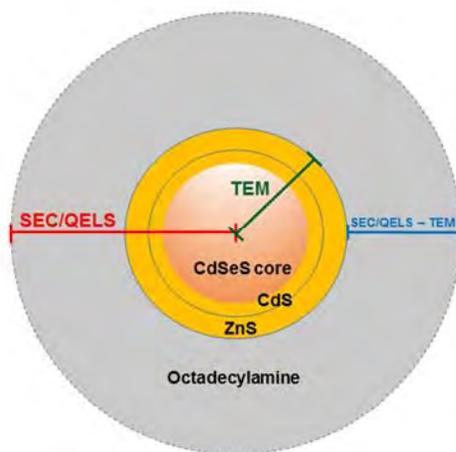


POLY 290: Determining the core, corona, and total size of CdSeS/ZnS quantum dots by SEC/QELS and TEM

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Due to their brightness and large extinction coefficients, which allow for easy detection and visualization, quantum dots (QDs) have found application in solar cells, biological imaging and labeling, lasers, light-emitting diodes, etc., advantages which have been found to be size-dependent. So-called core-shell QDs were developed to, among other things, improve the photoluminescence efficiency of the materials. For example, capping a CdSeS core with a layer of ZnS has been shown to enhance the quantum yield of the QDs. Further enhancements can be effected by adding an oligomeric or polymeric corona to the core-shell QDs. This corona can serve to e.g., passivate surface states and suppress non-radiative recombination at surface vacancies. Many of the advantages brought by the corona, such as the enhancement of photoluminescence efficiency, have been found to depend on the size (degree of polymerization) of the oligomeric/polymeric groups.

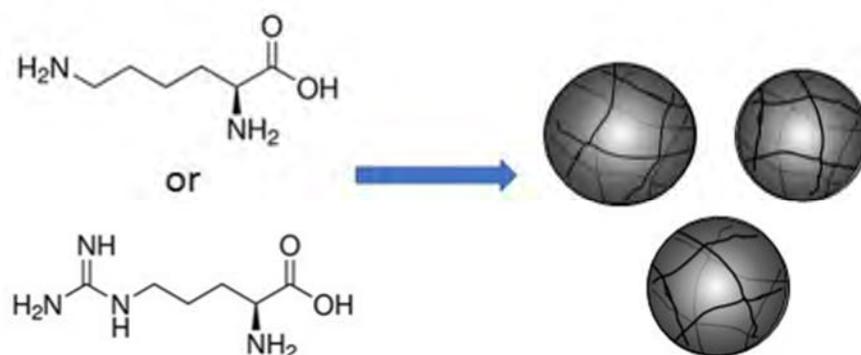
As seen from the above, being able to determine the size of QDs, as well as of their individual components, is of great importance in both fundamental research and applied science. Here, that challenge is addressed first by combining a size-based chromatographic separation with a size-sensitive detection method, in the form of size-exclusion chromatography coupled on-line to quasi-elastic light scattering detection. The SEC/QELS results are augmented by transmission electron microscopy measurements of QD core size, whereas the combination of both measurements provides insight into the size of the surrounding corona.



POLY 291: Synthesis, characterization and some of applications of colloidal microgels from amino acids

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Because of the continuing interest in multifunctional materials for biomedical applications, materials from natural sources or biological origin are on great demand. Due to the inherited biocompatibility and benefits, amino acid derived microgels possess great application potential in biomedical fields such as drug delivery, gene therapy, tissue engineering, bio-sensors, and so on. Here, a single step synthesis of amino acid based polymeric microgels based on L-lysine and arginine is reported by employing microemulsion polymerization technique. The prepared poly(amino acid) microgels are treated with HCl, and NaOH solution to demonstrate the variable zeta potential values of the prepared microgels. Moreover, these amino acids based microgels are shown to be chemically modifiable by using different modifying agents such as 1,3-propanesultone and alkyl halides of various chain lengths to induce different surface functionalities on the surface of colloidal microgels. Furthermore, the biodegradability, biocompatibility, hemolysis and antibacterial properties of the synthesized poly(amino acid) microgels are investigated. Also, the drug delivery and biomolecule separation potentials of these poly(amino acid) microgels are investigated.



Polymeric microgels from amino acids

POLY 292: LC-MS studies of serum phase chemistry and interfacial behavior of aqueous oligomers during emulsion polymerization

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In free radical emulsion polymerization, water soluble initiator radicals are generated by either a thermal or redox process. Initiator radicals in the aqueous phase react with soluble monomer molecules until they reach a composition which favors entry into a surfactant micelle, resulting in particle nucleation, or adsorption onto a pre-existing particle to carry out the intended chain propagation. Some oligomer radicals may also be terminated in the aqueous phase, forming serum oligomers which can be found in the final product.

In this study, a model emulsion polymerization system was established to generate sulfate radical initiated acrylic oligomers with various compositions and chain lengths. In-process samples were analyzed by a combination of liquid chromatography and mass spectrometry (LC-MS) to explore serum phase chemistry and the formation of aqueous species during the emulsion process. The effort to capture the living radicals in the aqueous phase will be discussed. Sulfate radical initiated acrylic oligomers have structures similar to commonly used alkyl sulfate surfactants. By correlating LC elution time to that of alkyl sulfate molecules, we have been able to quantify the amphiphilicity or surface activity of the water-soluble oligomer molecule generated in acrylic emulsion polymerization (Figure 1).

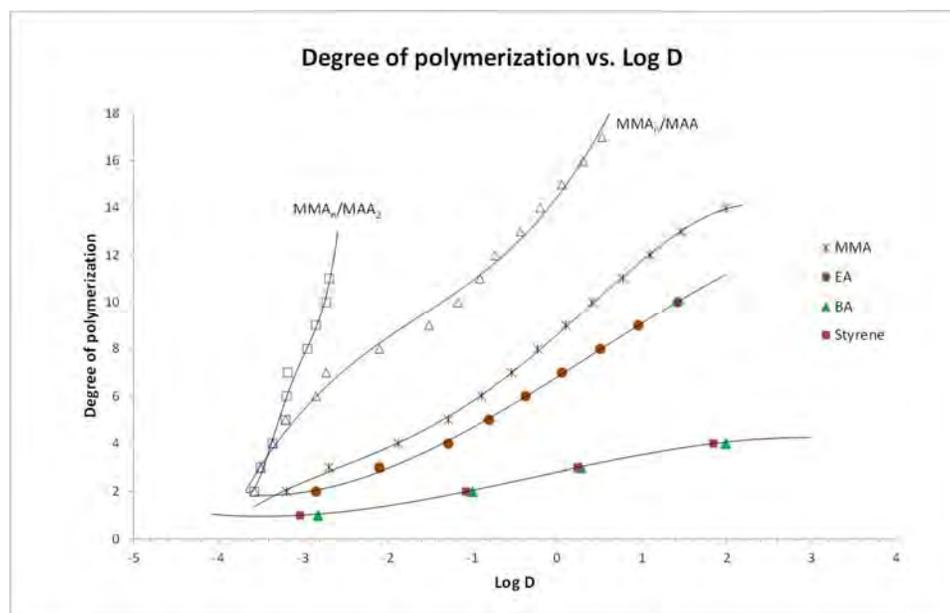


Figure 1. Distribution coefficients of aqueous phase oligomer molecules

POLY 293: Polypeptide composite particles

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Polypeptides have been attached covalently to silica templates with various shapes, either by growing them from a functionalized surface or by attaching them using "click" coupling chemistry. These hybrid polymer-colloid particles join the features of polypeptides--chirality, definable and switchable secondary structures, chemical versatility within the same basic synthetic scheme--to the ease of manipulation inherent to colloidal particles. Particular effort has been devoted to characterizing the helix-coil transition for the polypeptides bound to the curved particle surfaces. The transition, which alters the overall size of the particles and how they interact with each other and with other surfaces, can be detected by dynamic light scattering and NMR spectroscopy. The sharpness of the transition varies with surface curvature and polypeptide chain length. A special feature of polypeptides, not matched by most polymers used to cover colloidal particles, is the ability to sustain a liquid crystalline phase as mesogens. When the polypeptide composite particles are mixed with untethered polypeptide mesogens, entropic considerations cause the particles to align into superstructures. Such liquid crystal-assisted assembly is only one intriguing opportunity afforded by polypeptide composite particles mixed with polypeptides of the same type as liquid crystals. The particles also make excellent model systems for studies of diffusion in complex fluids and the jamming transition. Supported by NSF DMR Polymers Program.



POLY 294: Investigating the effect of ionic group location in the self-assemblies of sequence-defined peptoid block copolymers

Garrett L. Sternhagen², *gstern1@lsu.edu*, **Sudipta Gupta**⁵, **Gerald Schneider**⁶, **Yueheng Zhang**⁴, **Vijay T. John**³, **Donghui Zhang**¹. (1) 437 Chemistry Materials Building, Louisiana State University, Baton Rouge, Louisiana, United States (2) Chemistry, Louisiana State University, Baton Rouge, Louisiana, United States (3) Tulane Dept of Chem Bio Engr, New Orleans, Louisiana, United States (4) Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana, United States

A series of amphiphilic poly-N-substituted glycine (polypeptoid) block copolymers were synthesized by solid-phase methods with ionic functional groups located precisely along the chain. The peptoid amphiphiles self-assemble into spherical micelles upon dissolution in aqueous media. Micellar structures were confirmed by dynamic light scattering and cryoTEM techniques, and further investigated using small-angle neutron scattering (SANS) techniques. SANS measurements revealed that decreasing the distance of an ionic group from the micelle core-shell interface decreased both the micellar radius (R_m) and the aggregation number (N_{agg}). R_m and N_{agg} were found to scale with ionic monomer position (n) as $n^{0.04-0.1}$ and $n^{0.3}$, respectively. It is interesting to note that the chain density of the singly charged system remains constant with respect to monomer position, while the triply charged system scales as $n^{0.18}$, indicating an enhanced electrostatic effect. This study highlights the possibility of controlling micellar structures via the adjustment of monomer sequence of the amphiphilic block copolymer.

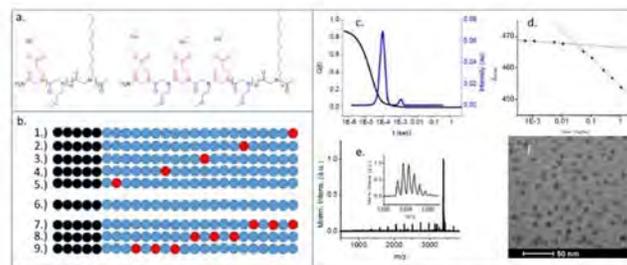


Figure 1: Representative depictions and characterizations. a, Structures for one (sequence #1) and three (sequence #7) charged peptoid amphiphiles (left and right, respectively). b, Cartoon representations of synthesized peptoid amphiphile sequences with colors denoting hydrophobic (black), hydrophilic neutral (blue) and hydrophilic charged (red) monomers. c, Dynamic light scattering size distribution. d, Critical micelle concentration determination by fluorescence spectroscopy. e, MALDI-TOF mass spectrum. f, CryoTEM image.

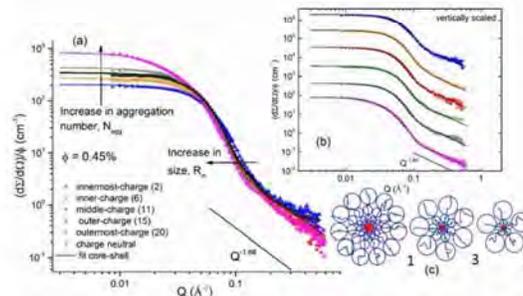
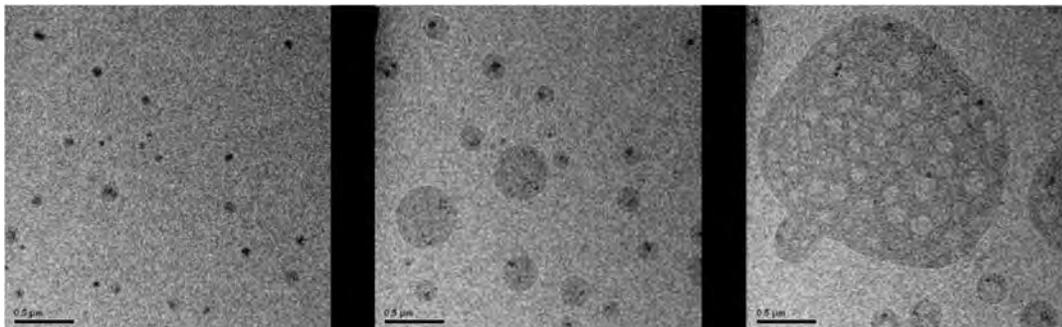


Figure 2 SANS measurements and model fits of micellar solutions. a, an overlay of curves from samples 1-5, showing an increase in micellar radius, R_m , evidenced by a shift of the curves to lower Q values. b, SANS data from plot (a) vertically scaled by arbitrary constants. c, cartoon depictions of the structural differences in micelles as a result of charge placement.

POLY 295: Watching block copolymer self-assembly with liquid phase transmission electron microscopy

*Hanglong Wu², Alessandro Ianaro², Mark van Rijt², Catarina C. Esteves², Heiner Friedrich², Remco Tuinier², Nico A. Sommerdijk¹, **Joseph P. Patterson²**, j.p.patterson@tue.nl. (1) Eindhoven Univ of Tech, Eindhoven, Netherlands (2) Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, Netherlands*

Amphiphilic block copolymers in solution can assemble into a wide range of colloidal materials, which have been widely investigated as drug delivery vehicles and catalytic nanoreactors. Due to their kinetically trapped nature, self-assembly is often performed using the solvent switch protocol. While numerous experimental and theoretical investigations into the mechanism of self-assembly have been conducted in an effort to gain more control over this process, there has never been a real-time, real space investigation of the assembly process on the nanoscale. Here we present the first observation of block copolymer assembly via the solvent switch process using liquid phase transmission electron microscopy. We show the formation of polymer vesicles, cylindrical micelles and multicompartmental structures and discuss the different mechanisms of self-assembly with supporting data from ex-situ cryoTEM measurements and self-consistent field (SCF) lattice computations.

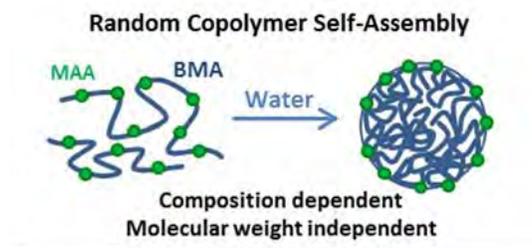


Snapshots from LP-TEM movie showing the formation of a dense liquid precursor phase in the formation of PCL-b-PEO assemblies by acetone:water solvent switch

POLY 296: Control of self-assembly of amphiphilic statistical copolymers by their composition

Thomas NEal¹, *tjneal1@sheffield.ac.uk*, **Martin W. Murray**², **Steven P. Armes**¹, **Seb Spain**¹, **Oleksandr Mykhaylyk**¹. (1) *Chemistry, University of Sheffield, Sheffield, United Kingdom* (2) *AkzoNobel, Slough, United Kingdom*

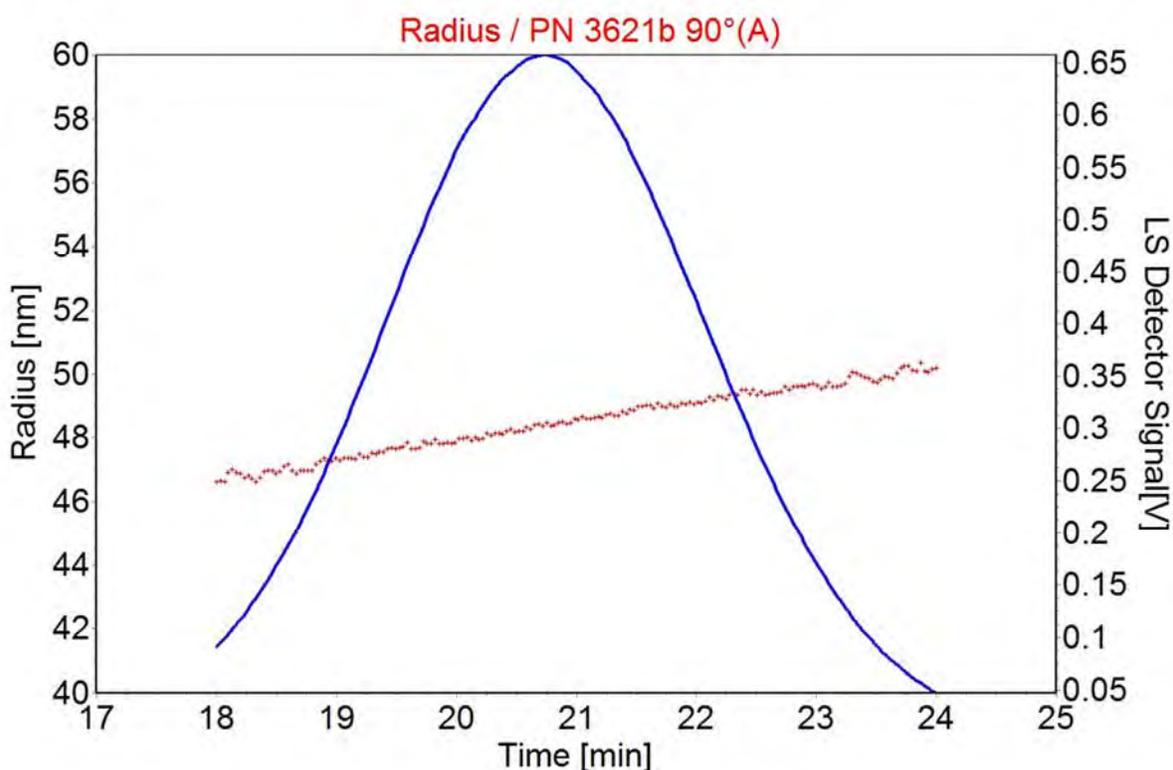
A range of poly(butyl methacrylate-*stat*-methacrylic acid) [P(BMA-*st*-MAA)] copolymers of various compositions and molecular weights from 5-30 kDa has been synthesised in order to establish a relationship between self-assembled morphologies, molecular architecture and composition of statistical copolymers. Small-angle X-ray scattering (SAXS) analysis together with transmission electron microscopy (TEM) have demonstrated that the copolymers form spherical micelles in aqueous media. More importantly, it was found that the resulting micelle radii are copolymer composition-dependent, but independent of molecular weight. These results, along with aqueous electrophoretic measurements, have demonstrated that all the stabilizing (MAA) units are located on the micelle surface. A proposed structural model describes the experimental data well and enables the micelle radii to be predicted from the content of stabilizing units which could make this model universal and applicable for other statistical copolymer systems. Additionally, the effect of solvent composition and copolymer concentration on the self-assembled morphology was monitored using SAXS and rheology. SAXS models of different levels of complexity, including inhomogeneous structure of the micelle core and the formation of mass fractals, have been developed. These studies revealed that the copolymers are present in solution as molecularly-dissolved Gaussian chains when the solvent composition is IPA-rich. However, the copolymer chains self-assemble into spherical micelles when the solvent composition is water-rich. At intermediate solvent compositions, SAXS analysis confirmed the formation of an interconnected micelle network. A good correlation between the structure, detected by SAXS, and the rheological properties of the materials has been observed.



POLY 297: Polymer, particle, vesicle? The new challenge for analytical separation technologies in polymer characterization

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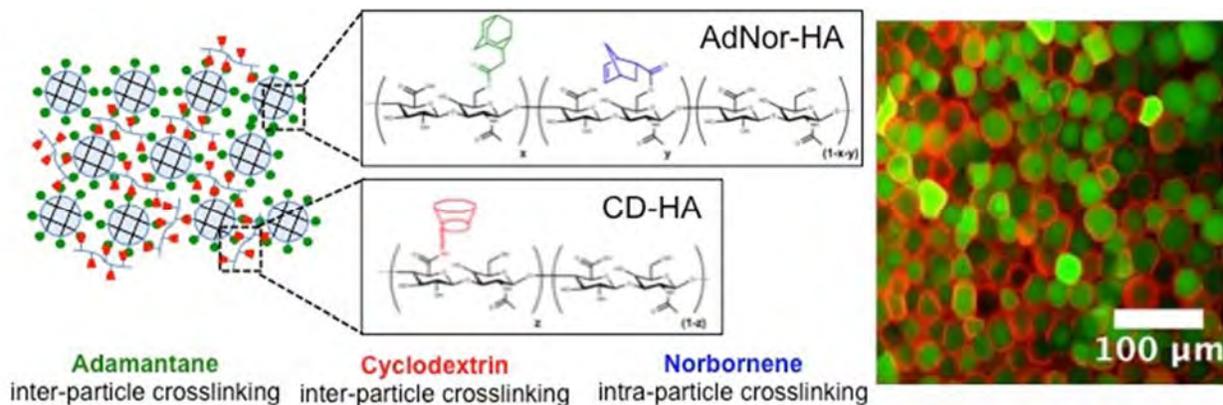
The characterization of polymers in solution for molecular weight and size/structural information by size exclusion chromatography (SEC) is somewhat restricted by the requirement that the polymer must be dissolved in the mobile phase and have no interaction with the column packing material. More importantly, SEC cannot be used after the formation of polymer latex, polymer particles, or other supramolecular structures such as vesicles (polymersomes) and we must resort to batch techniques such as static multi-angle light scattering (MALS) or dynamic light scattering (DLS). Of course, these batch techniques yield very limited information about the distribution of molecular weight or size, and furthermore may give misleading information due to the weighting of the data by larger species. Field flow fractionation (FFF) is a technique which can separate polymers and polymer structures in solution or suspension and can be coupled on-line to DLS or MALS to get accurate size and molecular weight distribution information. We will show several examples of how unique analytical data can be obtained from FFF analysis of polymers, polymer latex, polymer particles and vesicles.



POLY 298: Shear-thinning and self-healing hydrogels for therapeutic delivery

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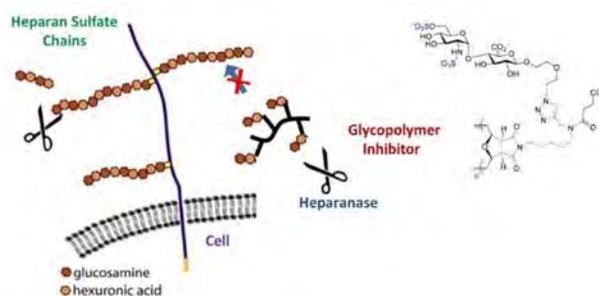
Hydrogels represent a class of biomaterials that have great promise for the repair of tissues, particularly due to our ability to engineer their biophysical and biochemical properties. Hydrogels can provide instructive signals through material properties alone (e.g., mechanics, degradation, structure) or through the delivery of therapeutics that can influence tissue morphogenesis and repair. Here, I will give examples of the design of hydrogels based on hyaluronic acid (HA) for use as injectable therapeutics, where local and sustained delivery overcomes many of the challenges (e.g., off-target complications) of systemic delivery. Towards cardiac repair, my laboratory is interested in designing materials that can influence the left ventricular remodeling process that occurs after myocardial infarction. To permit percutaneous delivery of hydrogels (e.g., via catheters), we are developing classes of shear-thinning and self-healing hydrogels that can be used for the delivery of therapeutics. These hydrogels assemble based on either dynamic covalent crosslinks (e.g., hydrazone bonds) or via guest-host (e.g., adamantane/cyclodextrin) interactions, where shear during injection permits the material to flow and rapid healing occurs upon reaching the injection site. There are numerous therapeutic molecules that are useful for delivery to the heart, including protease inhibitors that limit matrix remodeling and microRNA that can stimulate cardiomyocyte proliferation. Hydrogels are being designed to degrade in response to matrix metalloproteinases (MMPs) to release therapeutics “on-demand” or to bind directly to drugs to sustain their release. Recently, and to increase the complexity of possible therapeutic release profiles, we are designing granular hydrogel systems where multiple microgels with independent degradation and release behavior can be combined to deliver multiple therapeutic molecules. Microfluidic devices are used to fabricate the microgels using photoinitiated thiol-ene reactions for intraparticle crosslinking where crosslinkers can be stable or responsive to local proteases and microgel assembly occurs through interparticle crosslinking. These efforts in engineered hydrogels will advance our abilities to treat tissue after myocardial infarction.



POLY 299: Glycosidase inhibition by "sweet" bottlebrush polymers

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Multivalent scaffolds with attached saccharide units are a useful and effective way to mimic the glycocalyx and its interaction with carbohydrate-binding proteins. Of these multivalent scaffolds, synthetic glycopolymers are the most widely studied and are capable of replicating the properties of natural polysaccharides. Although synthetic glycopolymers have shown wide utility, their use as glycosidase inhibitors remained unanswered. To resolve these questions we report the design, synthesis, and utilization of glycopolymers endowed with pendant heparan sulfate (HS) disaccharides for inhibition of the glycosidase, heparanase, a regulator in aggressive tumor behavior. To achieve inhibition the well-established glycotope of heparanase was manipulated *in silico* into an inhitope leading to an inhibition value in the picomolar to low nanomolar range by a "recognition and blockage" mechanism. For optimal inhibition, several different studies were conducted including: hydrolytic stability, monomer architecture and saccharide presentation, and polymer length. Overall, the results of these studies show that the multivalent presentation of saccharides on bottlebrush polymers can serve as potent glycosidase inhibitors.

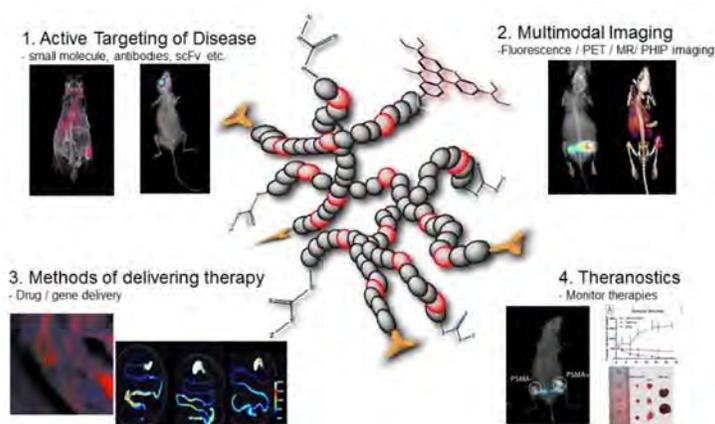


POLY 300: Development of polymer theranostics to probe the behaviour of nanomaterials in biology

Kristofer Thurecht^{1,2}, k.thurecht@uq.edu.au, Yongmei Zhou¹, Nicholas Fletcher¹, Zachary Houston¹. (1) The University of Queensland, Brisbane, Queensland, Australia (2) ARC Centre of Excellence in Convergent BioNano Science and Technology, The University of Queensland, Brisbane, Queensland, Australia

Polymer and nanoparticle-based devices have evolved to significantly enhance therapeutic efficacy. However, in order to be truly effective, these polymeric devices must maintain their physical and chemical integrity under physiological conditions – this can only be achieved by developing a strong understanding of the fundamental properties of the nanomaterial-delivery system, in addition to identifying and successfully *delivering* new therapies. Central to the development of these future therapeutic platforms, is the field of theranostics. This is the premise that future medical devices need to be capable of delivering a therapeutic dose to the correct site within the body, but must also possess mechanisms for online diagnosis, monitoring of disease progression and visualisation of drug delivery, release and efficacy of treatment. Such materials require significant advancements in chemistry, materials science and engineering such that the nanomedicine is complementary with the biological milieu.

While there are countless examples of polymer or nanoparticle systems that show efficacy in animal models, the ability to rationally-optimize the materials is hindered by the inability to directly assess the behaviour of the materials *in vivo*. For example, improvements in administration for most biologically-targeted polymeric nanomaterial systems are achieved by monitoring efficacy in animals rather than monitoring the fundamental behaviour of the nanomaterial itself (e.g. measuring efficacy, rather than quantifying how a change in material properties results in a biological response). In this presentation, we describe recent efforts to develop self-reporting nanomedicines for a truly closed-loop approach to medicine, where nanomaterial behaviour is monitored in real-time using molecular imaging as a function of therapy. These materials are based on architectural polymers that form a scaffold allowing combination of imaging and therapeutic modalities. Molecular imaging provides a route to validate how structure and property affects function in animals.



POLY 301: Detection of tumor biomarkers based on MIP-antibody proximity ligation assays

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Alterations in glycosylation impact a wide spectrum of key biological processes needed for the development and progression of the neoplastic disease. Tumor cells tend to produce increased levels of glycoconjugates containing sialic acid or specific sulfated motifs that impart a negative charge to the glycan chain. Increased sialylation is often associated with the increased invasive potential of tumor cells in clinical tumors as well as cultured cell lines, and this feature correlates with poor prognosis. There is therefore a need for diagnostic tools for analyzing and determining these glycosylation motifs but reagents with discriminative power and sufficient affinities for specific and sensitive detection are generally missing.

In the work presented herein we develop novel glycan specific probes in the form of DNA-modified molecularly imprinted polymer (MIP) nanoparticles in combination with DNA modified antibodies in proximity ligation assay (PLA) of glycosylated proteins (Figure 1). This approach profits from the robustness and reproducibility of MIPs and the ability to engineer the MIP nanoparticles with respect to size, and binding of elusive modifications where antibodies are scarce. The proof-of-concept will be demonstrated with single model proteins in solution (e.g. Transferrin) followed by Western blot tests in gels and finally cells or tissue samples.

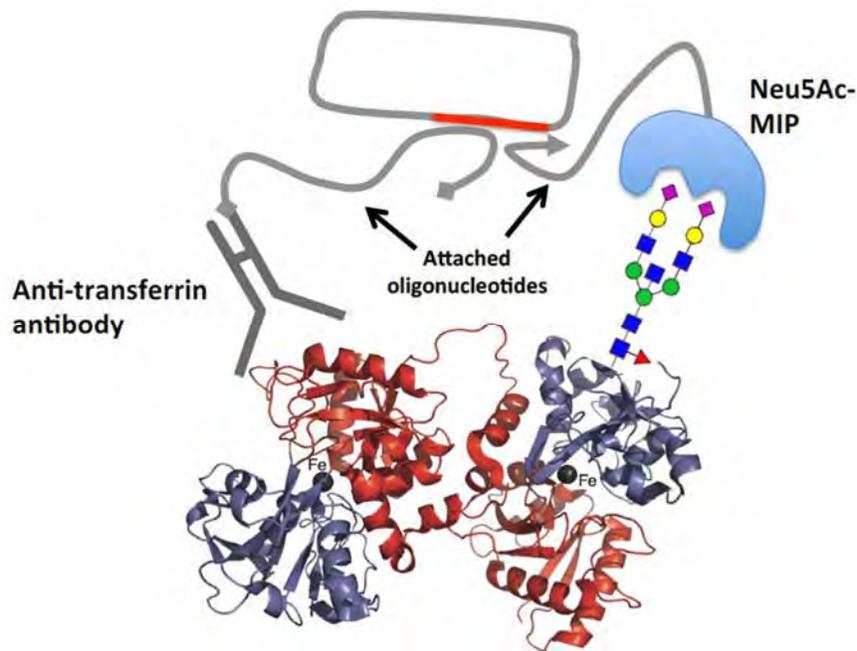


Figure 1. Principle of proximity ligation assay (PLA) employing a transferrin specific antibody (Ab) and PTM-specific MIP both containing attached DNA oligomers compatible with the PLA assay protocol.

POLY 302: Phase-separating biopolymer conjugates to manipulate cell signaling and healing in cardiovascular tissues

Kristi L. Kiick, *kiick@udel.edu*. *Dept of Materials Sci Eng, University of Delaware, Newark, Delaware, United States*

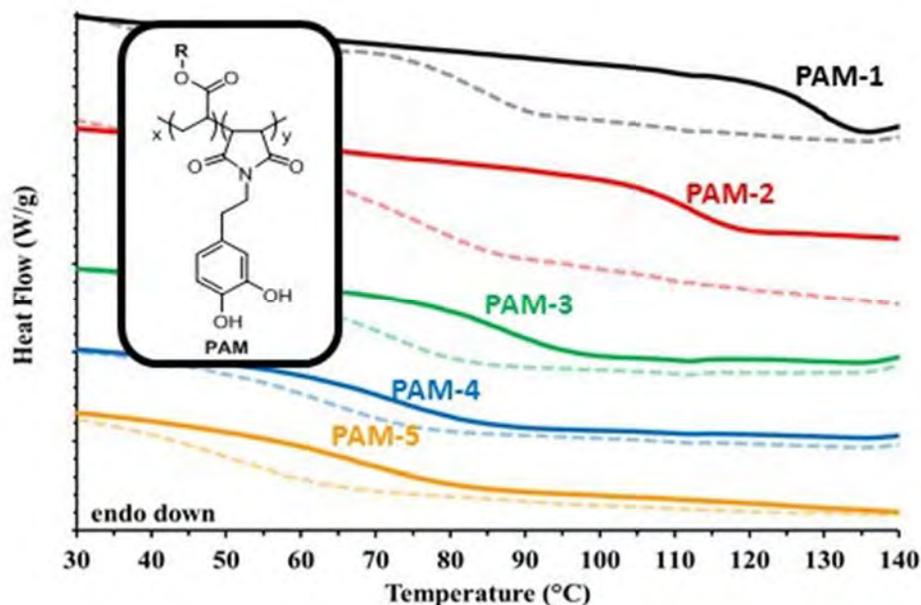
The incorporation of motifs from natural proteins, such as collagen and resilin, into bioconjugates offers important opportunities in designing biomaterials with useful stimuli-responsive behavior. Their conjugation to polymers affords biomaterials with diverse properties responsive to multiple biologically relevant triggers. Conjugates are able to form a range of structures that modulate cell behavior and influence the retention and release of cargo, offering substantial improvement in cargo activity. These materials can be designed with microstructural heterogeneity as well as into particles that are useful in a variety of drug delivery approaches. The materials exhibit high cytocompatibility, can be used to modulate signaling by vascular cells, and to restore radial compliance in skeletonized vessels.



POLY 303: Catechol-functionalized bioinspired synthetic adhesives: Effect of comonomer on mechanical properties

Scott Radzinski², *scr014@bucknell.edu*, **Matthew Bartucci**², **David Flanagan**², **Joseph Lenhart**², **Joshua A. Orlicki**¹. (1) Army Research Laboratory, Aber Provs Grd, Maryland, United States (2) U.S. Army Research Laboratory, Bel Air, Maryland, United States

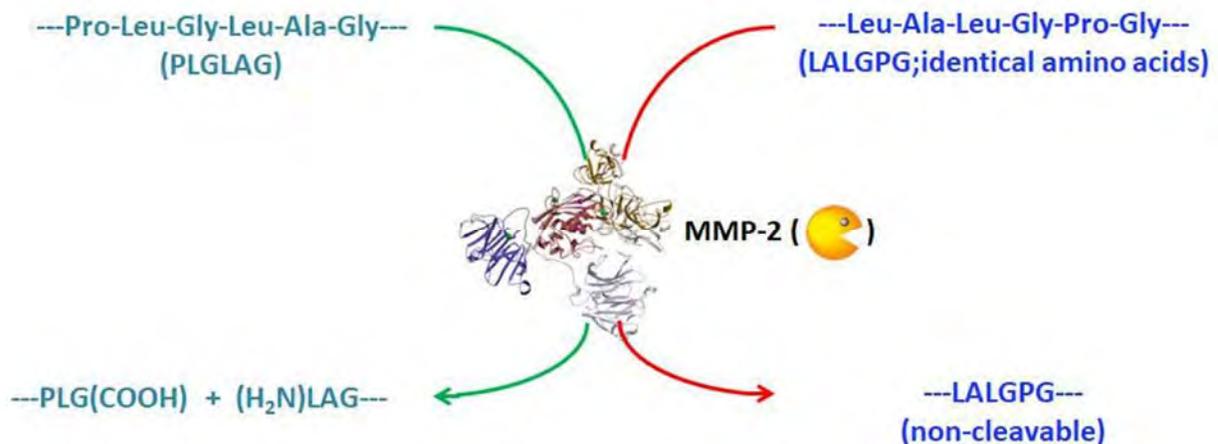
Most commercial adhesive performance degrades under wet and dirty environments, while mussel foot proteins have been optimized for these conditions. Sequencing of the interfacial protein residues has revealed that nearly a third of the repeat units consist of 3,4-dihydroxyphenylalanine (DOPA) which have pendent catechols. The versatile chemistry exhibited by catechols (e.g. covalent cross-linking, metal chelating) has led to a number of groups exploring the incorporation of catechol functionality into synthetic backbones. We have synthesized a library of poly(meth)acrylate-co-1-[2-(3,4-dihydroxyphenyl)ethyl]-maleimides (**PAMs**) that vary in their aliphatic side-chain length on a common polymer backbone, allowing for control over T_g and backbone polarity. It is expected that the modest adhesive performance garnered by the library will provide fundamental insight for the coupling of established adhesive chemistries with novel bioinspired approaches, allowing for the rational design of improved interfacial adhesion in adverse environments. Structure-property relationships have been developed as a function of variable monomer composition, and their impacts on adhesion to alumina substrates will be reported.



POLY 304: Biodegradable blockcopolymers as drug carriers in cancer therapy

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Blockcopolymers for medical applications should be based on biodegradable polymers. In the ideal case they allow for a controlled drug release and fulfill a targeting function. Herein, we present amphiphilic blockcopolymers based on polypeptides and polyethylene glycol as polar block and polylactides as unpolar structure. The polymers are obtained by using polypeptides with serine moieties as initiators for the lactide polymerization or as unit to link via esterification PEG or a homopeptides like polylysine. We are able to form nanoparticles with the amphiphilic block copolymers and to load them with drugs. The particles show an excellent cell uptake. The linker peptide in the block copolymer contains a special sequence which is sensitive to MMP-2 a special enzyme overexpressed in cancer cells. It could be demonstrated that these nanocarriers release their payload in a very controlled way just in the presence of the cancer cells due to the degradation of the block copolymers by cleaving of the linker. This destroys the cancer cells, healthy cells survive however.

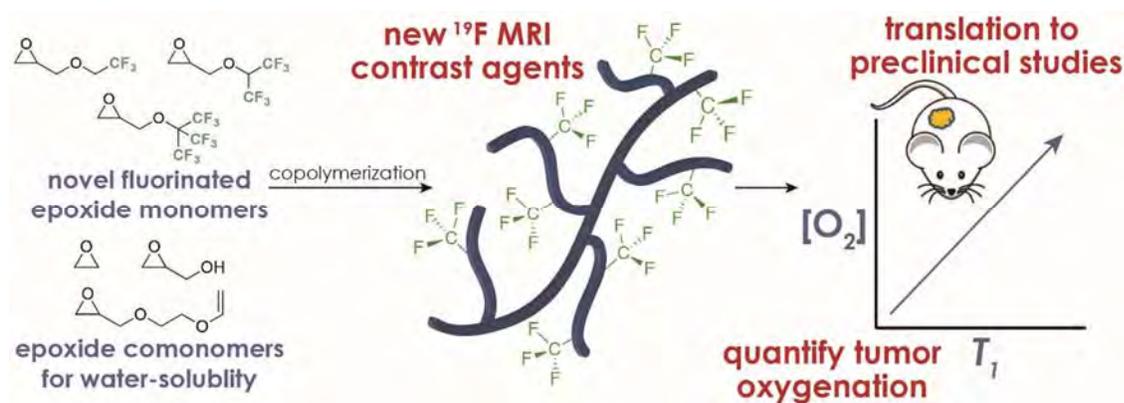


POLY 305: Partially fluorinated polymers for spatiotemporal mapping of tissue oxygenation

Frank A. Leibfarth, FrankL@email.unc.edu. Chemistry, University of North Carolina, Chapel Hill, North Carolina, United States

Molecular oxygen (O_2) is a vital component of aerobic respiration, and thus its partial pressure (pO_2) in various tissues can be considered a key physiological biomarker for pathologies known to alter the normal metabolic process. In particular, inadequate levels of tissue oxygenation have been linked to a variety of afflictions, including myocardial infarction, ischemic stroke, cancer, peripheral artery disease, deep vein thrombosis, and metabolic syndrome. Furthermore, tumor oxygenation has been identified as a significant factor affecting the efficacy of cancer therapy. Spatiotemporal mapping of tissue pO_2 , therefore, holds the potential to guide decision-making in the crucial early stages of treatment for various disease states. Oxygen quantification *in vivo*, however, remains a significant challenge for which there is an opportunity for more sensitive, universal, and versatile contrast agents.

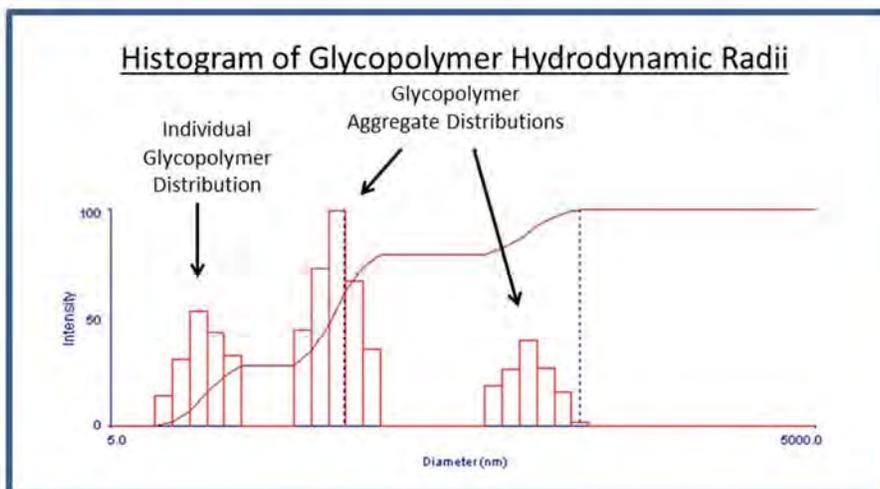
Magnetic resonance imaging (MRI) methods for interrogating tissue oxygenation are attractive due to the wide availability of MRI equipment and avoidance of expensive and short-lived radiopharmaceuticals. Specifically, ^{19}F MRI has transformative potential to dynamically map oxygenation in tissue. The spin lattice relaxation rate (T_1) of ^{19}F is exquisitely sensitive to O_2 concentration and it offers high spatial and temporal resolution and arbitrary tissue depth penetration. We report the synthesis of partially fluorinated epoxide monomers and their polymerization into partially fluorinated polyethers for use as ^{19}F MR imaging agents. These novel polyether (co)polymers have a high density of chemically equivalent fluorine nuclei to ensure MRI sensitivity and have a low chemical shift dispersion for high resolution spatiotemporal mapping of tissue oxygenation. With this synthetic platform established, we will discuss current efforts in understanding the critical structure–property relationships for eventual translation to medical imaging.



POLY 306: Elucidation of glycopolymer aggregation mechanism for determination of structure/binding interactions with amyloid β peptides

Ashleigh N. Bristol¹, *ashleigh.bristol@eagles.usm.edu*, **Pradipta K. Das²**, **Dexter N. Dean¹**, **Vijay Rangachari¹**, **Sarah E. Morgan²**. (1) Dept of Chemistry Biochemistry, University of Southern Mississippi, Hattiesburg, Mississippi, United States (2) School of Polymer Science and Engineering, University of Southern Mississippi, Hattiesburg, Mississippi, United States

GM1 ganglioside is known to exacerbate A β aggregation, which is implicated in Alzheimer's disease. GM1 ganglioside consists of a hydrophilic head group comprised of specific saccharide moieties and a hydrophobic tail. Acrylamide-based glycopolymers with pendant saccharide groups of the same stereochemistry as those found in GM1 were synthesized via aqueous RAFT polymerization to obtain polymers of desired architectures and molecular weights. The glycopolymers were used as bio-inspired models to evaluate the effect of saccharide clusters on the A β assembly process in solution. It was found that the rate of peptide association and the aggregate type were dependent on the polymer molecular weight and the nature of the saccharide pendant group. It was also determined that the glycopolymers formed intermolecular associations in solution. In order to gain a better understanding of the mechanism of A β aggregation in the presence of saccharide clusters, the conformation and assembly states of the neat glycopolymers were evaluated as a function of solution conditions (i.e. concentration, buffer, and pH) and polymer architecture via dynamic light scattering and fluorescence analysis.

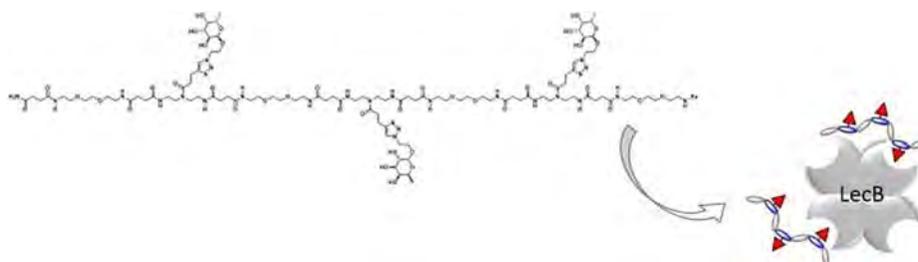


POLY 307: Monodisperse fucosylated glycooligomers to investigate multivalent binding to LecB

Katharina Buecher, *Katharina.buecher@web.de*, Laura Hartmann. Institute of organic and macromolecular chemistry, Heinrich Heine Universität, Duesseldorf, Germany

Multivalent presentation and recognition of complex carbohydrate structures are important in the adhesion processes of pathogens like viruses and bacteria. In spite of the fast evolution of many pathogens, the attachment to specific glycans on cell membranes seems to occur often by multiple conserved binding sites. It has been shown that terminal α -L-fucose is an important attachment factor. Nevertheless, the underlying multivalent binding mechanisms of carbohydrate-mediated adhesion processes are still not well understood and novel model compounds are required to gain new insights.

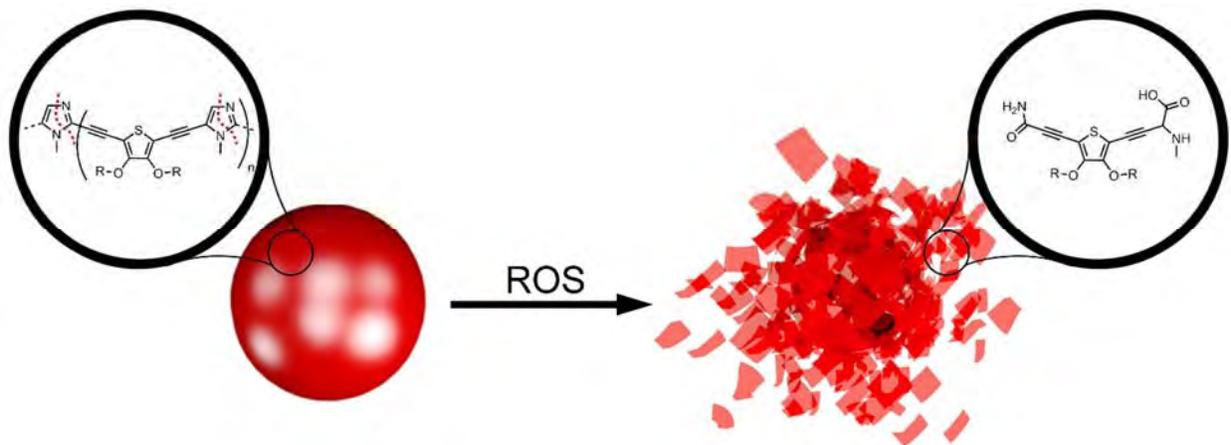
Monodisperse glyco(oligoamidoamine)s have been shown to be a suitable tool to study multivalent interactions between glycans and lectins of plants and bacteria. Here we show the adaption of the previously presented solid phase polymer synthesis to give a series of monodisperse glycooligomers presenting α -L-fucose units. By the step wise assembly of tailor made building blocks according to previously reported protocols and conjugation of fucose side chains on solid support, the sequence-controlled and multivalent presentation of fucose was realized. Furthermore, variation of number and spacing of fucose units on the oligomeric backbone was achieved. The obtained glycooligomers were then tested for their binding to the capsid protein LecB from *Pseudomonas aeruginosa*, suspected of being responsible for bacterial antibiotic multiresistance. The binding behavior was analyzed using surface plasmon resonance and showed the influence of the different structural parameters onto the binding affinity.



POLY 308: Bio-degradable conjugated polymer particles as biomedical imaging probes

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Conjugated polymer particles represent high potential imaging probes for biomedical analysis and diagnosis due to their high contrast in fluorescence and photoacoustic tomography and their low cytotoxicity. Furthermore, conjugated polymer particles are practically non-bleaching, they can be tuned in their resonance frequency depending on the respective imaging modality and they can be functionalized with biological recognition motifs for specific targeting towards pathological tissue. However, conjugated particles are not biodegradable, which prevents their clinical application as the particles would accumulate in the body and cause undesired side effects. I will present the synthesis of highly fluorescent particles, which consist of fully π -conjugated imidazole copolymers. The imidazole can be oxidized, which leads to degradation of the conjugated polymer particles into small water soluble molecules. I will show that this oxidative degradation can be performed by activated macrophages, immune cells which collect foreign particles in the body. The particles can be surface functionalized using simple click chemistry allowing targeting of cells specifically. The small degradation products are small enough to be excreted renally, making this approach a first step towards clinical applications of conjugated polymer particles as theranostic probes. Furthermore, biodegradable conjugated polymer are interesting for other applications in transient organic electronics and optoelectronics at the biointerface.

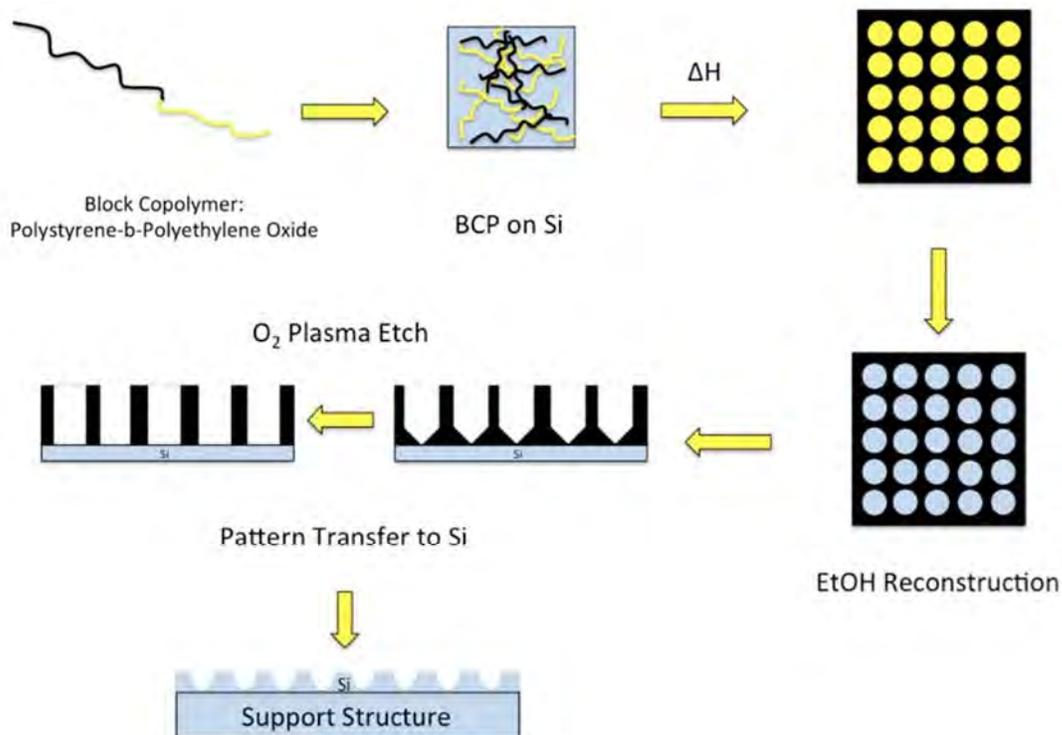


Fully π -conjugated polymer particles with incorporated imidazole co-monomer can be degraded oxidatively. This oxidation can be performed by activated macrophages and the particles are degraded into small molecular and water soluble building blocks.

POLY 309: Self-assembly of uniform nano pores for membrane transfer to silicon

Dakota F. Ehlenberg¹, Dakota.ehlenberg@eagles.usm.edu, Xiaodan Gu^{2,1}, Daniel Weller³. (1) Polymer Science and Engineering, The University of Southern Mississippi, HATTIESBURG, Mississippi, United States (2) Polymer Science and Engineering, Univ. of Southern Mississippi, Hattiesburg, Mississippi, United States (3) Polymer Science and Engineering, University of Southern Mississippi, Hattiesburg, Mississippi, United States

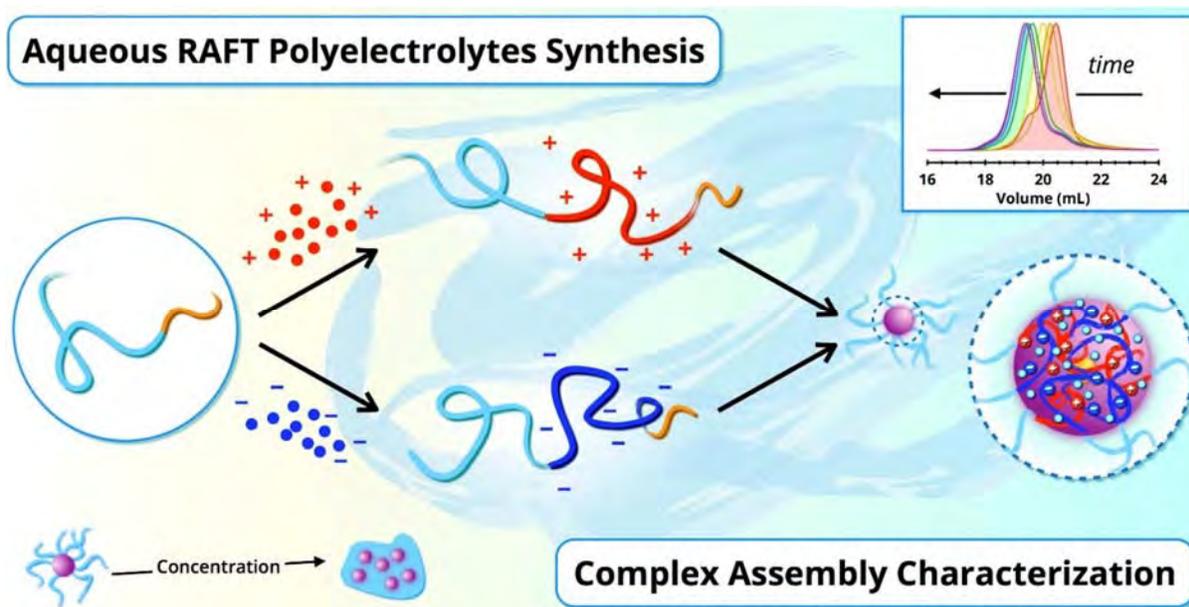
This project focuses on the creation of Nano pores using a block copolymer network. The network self assembles into the pores because they are thermodynamically favored to be in this position. This comes about while being thermally annealed in a nitrogen-purged environment. Once a network is created ethanol reconstruction will cause the minority block to become a hole on the Nano scale. Once the pores have been made Oxygen plasma etching removes the polymer in the bottom of the holes all the way to the silicon substrate that the BCP is initially coated on. The Nano pores shapes are then transferred onto the silicon substrate using silicon cryogenic etching.



POLY 310: Synthesis and structural investigation of customizable polyelectrolyte complexes

Abraham Herzog-Arbeitman^{2,3}, abeherzarb@uchicago.edu, Jeffrey M. Ting³, Hao Wu³, Olivia Werba³, Samanvaya Srivastava¹, Matthew V. Tirrell³. (1) Institute for Molecular Engineering, The University of Chicago, Chicago, Illinois, United States (2) Chemistry, University of Chicago, Chicago, Illinois, United States (3) IME, University of Chicago, Chicago, Illinois, United States

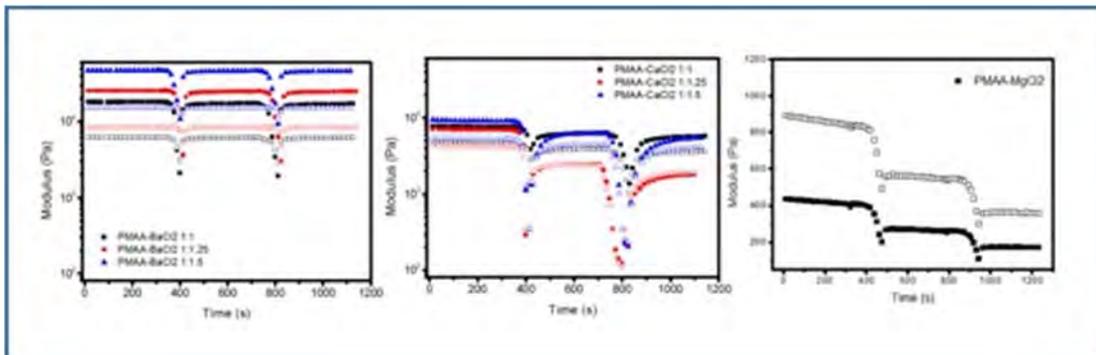
Hydrogels, in particular polyelectrolyte complexes (PECs), represent a class of biomaterials that have received increasingly significant attention due to their capacity for self-assembly, stimuli-responsivity, self-healing abilities, and high tunability to achieve desirable chemical and physical properties. As such, PECs have shown promise in tissue engineering, controlled drug delivery, and biosensors. However, the effects of block polymer variables like charged/neutral block lengths, salt content, and charge density on the (1) kinetics of the complexation process from charge moieties in aqueous solution, and (2) the properties of the resulting PEC hydrogel are still poorly understood, and this deficiency remains a longstanding obstacle in the design of intelligent hydrogel technologies. Using aqueous Reversible-Addition Fragmentation chain-Transfer (RAFT) polymerization techniques, we prepared a series of designer charged block polymers with a parallel synthesizer, varying molecular parameters such as molar mass and chemical composition. The PECs produced by their combination were then used to examine the relationships between the constituent block polymer electrolytes and the kinetics/dynamics of complex formation. To determine the size and stability of these complexes, characterizations were undertaken using dynamic light scattering, cryo transmission electron microscopy, and small-angle X-ray scattering. These studies provide a foundation for the extrapolation of structure-function relationships in PEC hydrogels, and therefore facilitate the engineering of advanced multifunctional materials for a spectrum of bioapplications on the molecular scale.



POLY 311: Self-healing polyelectrolyte/metal ion materials

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Dept. of Polymer Engineering, University of Akron, Akron, Ohio, United States (2)
Chemical Engineering, Rose Hulman, Terre Haute, Indiana, United States

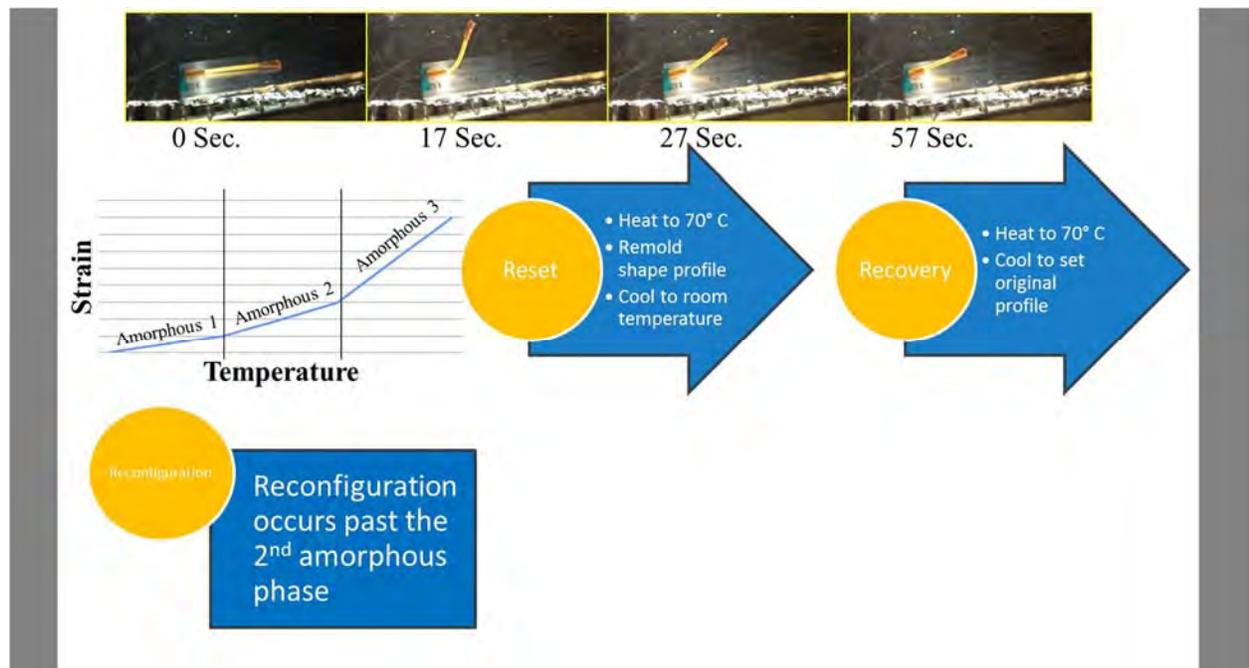
Dynamic interactions such as electrostatic or coordination bonds can be used as the basis of self-healing in polymeric materials. Self-healing of materials might be used to extend the life time of products, or as an adaptation to some mechanical damage. For example, a network made from mixing polyacrylic acid and calcium salts in solution and collecting the precipitate is a material that can be stretched, torn apart, and made to self-heal within a few seconds. This is in contrast to a network made from mixing oppositely charged polyelectrolytes, which can also self-heal but on the length scale of tens of minutes due to the limited mobility of the high molecular weight materials. For the case of networks of polyacrylic acid and metal ions, the nature of the metal ion influences the ability to self-heal. Divalent ions or ions with higher valency are required to create the self-healing property. Certain metal ions are able to create a visco-elastic self-healing network while other metal ions are not. In order to compare to polyacrylic acid, the more hydrophobic polymethacrylic acid was also studied. These materials were characterized by rheology.



POLY 312: MoS₂ dispersed epoxy vitrimer composite: Role of solvent and surface chemistry of MoS₂ on network formation, mechanics, and stimuli response

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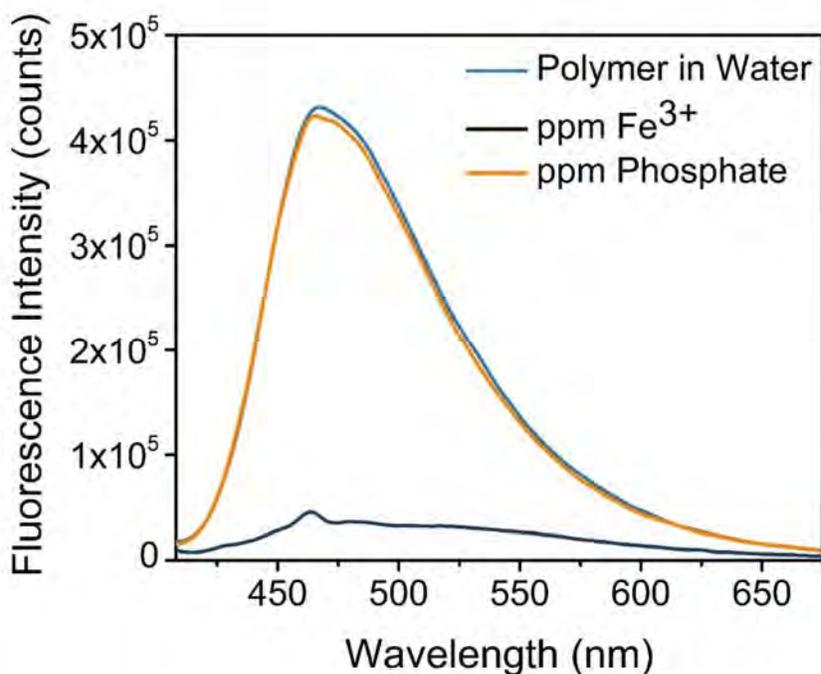
Vitrimers are a new class of stimuli-responsive polymers which undergo dynamic covalent reaction while keeping a constant cross-link density. Some of the significant attributes of these materials include shape memory and self healing, which has opened up avenues for a wide range of applications. Some of the key challenges of these materials are the lack of control of the exchange kinetics, poor mechanical integrity (brittleness), and slow response time. This study incorporates MoS₂ nanoparticles as reinforcement materials in a vitrimer composite to a) improve the toughness through efficient load transfer, and b) advance the stimuli response through harnessing electro-optical properties. A systematic processing technique was developed to ensure excellent dispersion of the nanocomposites of high weight percentage of MoS₂ in a DGEBA/Sebacic/TBD system. The detailed characterization using in-situ FT-IR, DSC, DMA, AFM-IR enabled insights into the local polymer network and interphase formation with various solvents and surface functionality of MoS₂. High-resolution TEM, SEM, AFM, and nano-X-ray computed tomography provided an understanding of 3D dispersion status of these nanosheets. The incorporation of MoS₂ into the vitrimer significantly improves mechanical properties, and produces an excellent shape memory effect with near IR sensitivity.



POLY 313: Rational design of sensitive and selective conjugated polymer based fluorescent sensors for the detection of phosphate

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Conjugated polymers (CPs) are ideal signal transduction elements in sensing platforms due to signal amplification upon binding of a specific analyte. While CPs are commonly used in fluorescent assays for the sensitive detection of small molecule analytes, little work has been done to improve sensitivity and selectivity through precise control of polymer architecture. In this work, a series of fluorene copolymers with pendant recognition elements and varying copolymer compositions were synthesized. Upon subsequent addition of Fe^{3+} and pyrophosphate turn off/on assays were realized with quenching and dequenching sensitivity that are highly dependent on molecular structure. Careful manipulation of the CP structure afforded the capability to fine-tune assay performance in organic and aqueous solutions and achieve parts-per-million sensitivity to Fe^{3+} and pyrophosphate. Our results demonstrate new molecular design paradigms toward increased sensing sensitivity of CP sensors in both organic and aqueous environments.



POLY 314: Novel binder development in binder jet additive manufacturing to improve green part strength

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Additive Manufacturing (AM) of metals is a potentially disruptive technology that could significantly change the value chain in industries such as aerospace, automotive, tool-manufacturing, and medical industry. A few AM methods can create metal parts, mainly utilizing powder bed fusion such as (Selective Laser Sintering, SLS, Selective laser Melting, SLM, and Electron Beam Melting, EBM). Many challenges though exist in the powder bed fusion processes, due to thermal stresses within the printed parts, operator burden in completing the build process, and overall cost of the equipment. Binder Jet 3D printing utilizes inkjet technology to selectively deposit binder into a powder bed and it exhibits significant potential for metal AM. One challenge that limits binder jetting technology is its green part strength, which limits application of the process due to broken parts and geometric inflexibility. The research presented here introduces a new binder system utilizing a difunctional monomer binder. This monomer when heated polymerizes and holds the structure of the printed green part before sintering. The novel binder successfully increases the strength of the green part and allows more flexibility in geometric design. This presentation summarizes efforts on optimizing various parameters including viscosity, surface tension, solution composition, drop size, curing temperature and time with respect to the new binder system.



POLY 315: Scavenging ruthenium in ring-opening metathesis polymerization-based branched polymers

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The development of drug-conjugated, pH-responsive polymeric nanoparticles for drug delivery applications promises more effective forms of cancer therapy based on the target-specific, triggered release of therapeutic agents at the tumor site. Previous studies have shown the potential of multidrug-conjugated polymeric nanoparticles synthesized via the brush-first ring-opening metathesis polymerization (ROMP) method in treating tumor cells while reducing the off-target toxicity compared to traditional chemotherapy. We present a method that improves the ruthenium levels per drug-loading in ROMP-based branched polymers by adding a scavenging resin, e.g., silica dimercaptotriazine. These branched polymers with various ratios of poly(ethylene glycol)-norbornene-terminated macromonomer (MM) added were synthesized and characterized via gel permeation chromatography (GPC) and dynamic light scattering (DLS). Ruthenium concentrations obtained by inductively coupled plasma mass spectrometry (ICP-MS) indicated that resin scavenging lowered the amount of ruthenium per theoretical drug-loading. Differences in ruthenium levels between resin-treated and non-treated branched polymers become less significant as more MM is added, suggesting decreased accessibility of ruthenium. For example, it was found that the Ru concentration decreased from 270 (± 20) ppm in dialyzed 7-20 (ratio of MM to crosslinker) branched polymers to 100 (± 10) ppm in resin-treated 7-20 branched polymer. Adding resin to branched polymers reduced ruthenium levels with a statistically significant difference, indicating promise to this technique.

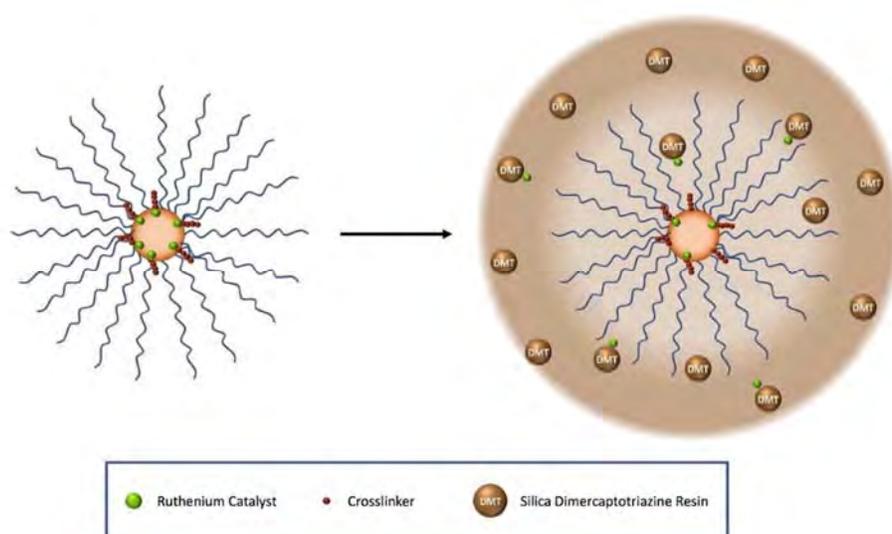
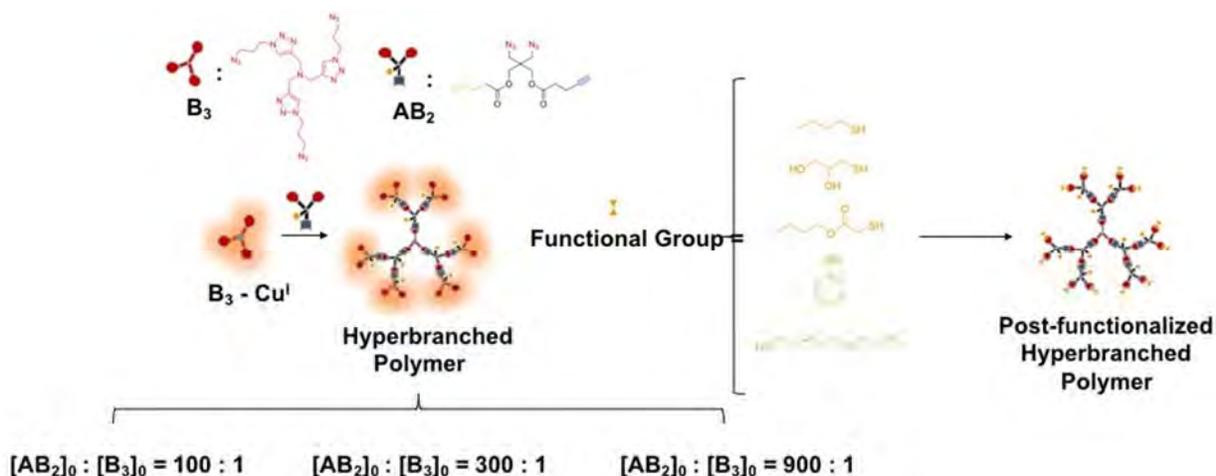


Figure 1. Schematic illustration of resin method used to reduce ruthenium levels in branched polymers.

POLY 316: Synthesis of hyperbranched polymers with post-functionalization specificity

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The ease and convenience involved in the one-pot syntheses of hyperbranched polymers using the CuAAC mechanism makes these polymers ideal starting points for the construction of a variety of polymeric macromolecules. However, due to the irregularity of their final structures inherently resulting from their step-growth mechanism, improving the uniformity of the molecular weights of hyperbranched polymers becomes a parameter desirable to regulate. The copolymerization of a trifunctional B₃ core with an AB₂ monomer using copper catalyzed azide-alkyne cycloaddition (CuAAC) polymerization techniques produces a hyperbranched polymer with a molecular weight in the hundreds of thousands as well as a sophisticated, layered architecture, and thousands of dangling reactive groups. Such dangling groups, in addition to peripheral azide groups from the AB₂ monomer, are then available for post-functionalization modifications. When consecutively integrated, copolymerizations and post-functionalizations provide greater accessibility to a broad range of desired hyperbranched polymers both in molecular weight and surface functionalities. It is known that thiolene reactions exhibit high conversions, and thus, such reactions highlight the versatility and applicability of post-functionalizations of copolymers. Due to the diversity of thiols readily available, a variety of functional groups are able to be appended to the surface of hyperbranched polymers via this thiolene mechanism. The development of multi-layered hyperbranched polymers introduces the ability to change the properties of the polymer, especially concerning solubility, which has promising applications in topics such as drug delivery methods and light harvesting techniques.



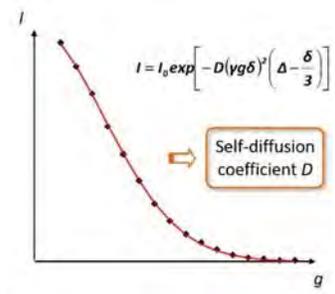
POLY 317: Liquid and solid state NMR investigations of low MW Polyether and non-polyether polymer electrolytes for supercapacitor and battery applications

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Future electrochemical power sources require new electrolytes to adapt to disruptive changes in the basic working chemistry, such as moving from Li ion to Na ion, or to Li metal electrodes. We highlight several recent collaborative activities on electrolytes in our group (i) Na ion; (ii) Li metal polymer.

Low molecular mass polyethers (i.e. glymes), serve as useful models for investigating ion/polymer and ion/ion interactions in higher molecular mass polyethers, i.e. PEO. Glymes have also garnered recent attention as attractive solvents for use in lithium metal and lithium sulfur batteries. We have undertaken a comprehensive study of variable chain length glymes, containing lithium salts or sodium salts.. NMR methods employed include (i) natural abundance ¹⁷O, (ii) pulsed field gradient diffusion of solvent (through ¹H), cation (⁷Li or ²³Na), and anion (¹⁹F). In lithium salt glyme complexes, correlations between both solvent and anion ¹⁷O chemical shifts and chain length yield insight into solvation structures and ion pairing tendencies which are supported by the diffusion measurements. Similar behavior is observed in the corresponding sodium solutions, with some differences attributed to the larger ionic radius of Na⁺. This work has most recently been extended to NaPF₆ – glyme solutions being developed for supercapacitor applications.

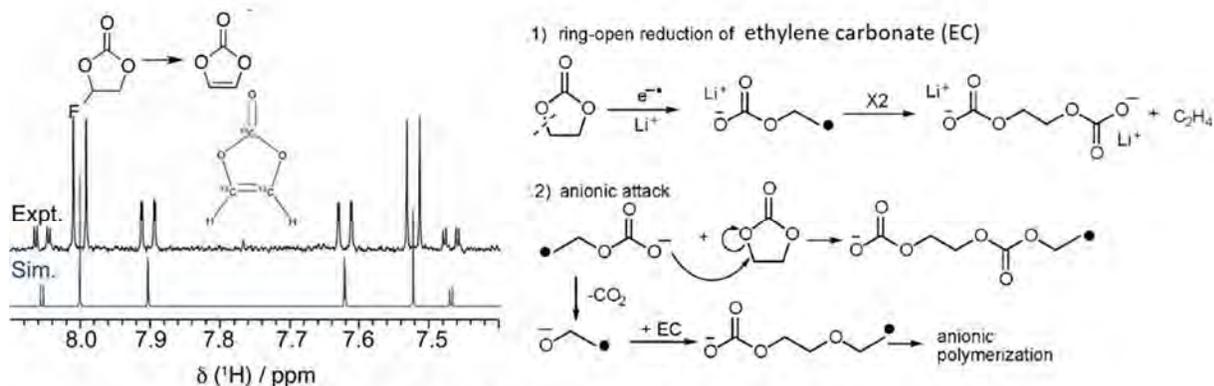
We next discuss a novel solvent-free solid polymer with room temperature ionic conductivity exceeding 1 mS/cm, is non-flammable, has attractive mechanical properties for lithium dendrite suppression, and is compatible with Li metal as well as a wide variety of cathodes. It is based on semicrystalline polyphenylene sulfide and Li salts familiar to the battery community. The ionic transport mechanism is decoupled from polymer host motion, and NMR measurements reveal Li self-diffusion coefficients at room temperature that are the highest reported in any known solid, with a Li⁺ transport number greater than 0.6.



POLY 318: Solid-state NMR investigation of the solid electrolyte interphase on silicon electrodes for lithium ion batteries

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In my talk I will demonstrate how multinuclear NMR spectroscopy is being used in the Grey group for the characterisation of silicon anode materials for lithium ion batteries, and the solid electrolyte interface (SEI) formed on these anodes. Both *ex situ* and *in situ* NMR methods are employed, and it is the conjunction of these two approaches which yields the most useful and relevant information. The subsequent formation of various Li_xSi_y phases during charging and discharging is monitored *ex situ* by use of magic-angle spinning (MAS) ^7Li NMR of materials collected from coin cells, and *in situ* by use of static ^7Li NMR of radio-frequency permeable pouch cells inside the NMR detector. The quality of the pristine silicon nanoparticles is checked with ^{29}Si MAS NMR, which shows a generally very high degree of oxidation. Fast magic angle spinning (MAS) ^7Li , ^{31}P and ^{19}F NMR gives insight into the inorganic part of the SEI formed from the decomposition of the electrolyte, such as lithium fluoride. Advanced one- and two-dimensional ^1H and ^{13}C MAS NMR experiments of selectively ^{13}C -labelled systems yield information on the organic SEI part. We employ rinsing with dimethylcarbonate (DMC) to remove non-decomposed ethylene carbonate (EC). MAS NMR of the remaining solid SEI part shows a variety of organic species, such as lithium formate, lithium carbonates, poly-ethylene oxide and molecules with alkyl moieties. Solution ^{13}C NMR of the rinsing liquid shows that it contains ethylene-oxide oligomers.



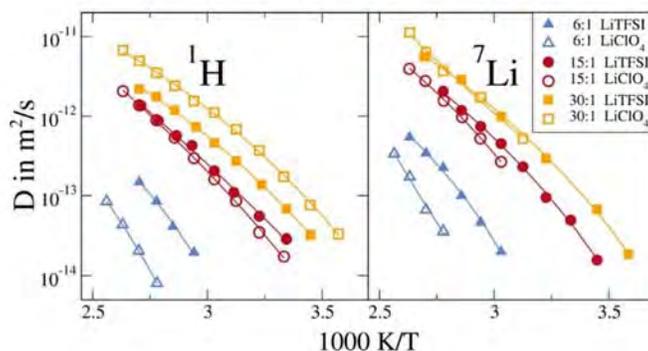
NMR studies of electrolyte decomposition in batteries

POLY 319: NMR studies of dynamical couplings in ionic liquids and polymer electrolytes

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The properties of liquid mixtures crucially depend on dynamical couplings of the components. We exploit the capabilities of multi-nuclear and multi-method NMR approaches to investigate this interplay for two classes of materials with high technological relevance: ionic liquids and polymer electrolytes. Specifically, we use the isotope selectivity of the method to separately study the dynamics of the individual components. Moreover, we take advantage of the possibility to ascertain motions on various time and length scales. Field-cycling relaxometry, line-shape analysis, and stimulated-echo experiments are combined to elucidate motions on microscopic length scales over a dynamic range of more than 10 orders of magnitude. Moreover, field-gradient techniques are utilized to study diffusion on mesoscopic length scales. Thus, our combined NMR approaches allow us to follow the evolution from the elementary steps of the motion to the eventual transport.

Applying this multitude of NMR techniques, we investigate anion and cation dynamics in ionic liquids composed of bis(trifluoromethylsulfonyl)imide (^{19}F NMR) and 1-alkyl-3-methylimidazolium (^1H NMR). In particular, we analyze the change of the ion mobilities and the degree of the dynamical couplings when using the same anion, but varying the length of the alkyl tail of the cation. Likewise, we analyze couplings of ion dynamics (^7Li NMR) and polymer dynamics (^1H and ^2H NMR), which determine the electric conductivity in polymer electrolytes. For materials comprising lithium bis-trifluoromethanesulfonimide or lithium perchlorate and poly(propylene oxide), we observe very prominent structural and dynamical heterogeneities at intermediate salt concentrations, which manifest themselves in complex transport mechanisms.



Temperature-dependent self diffusion coefficients D of (left) polymer molecules and (right) lithium ions for several compositions of the studied polymer electrolytes, as given by the ether oxygen:lithium ion ratios .

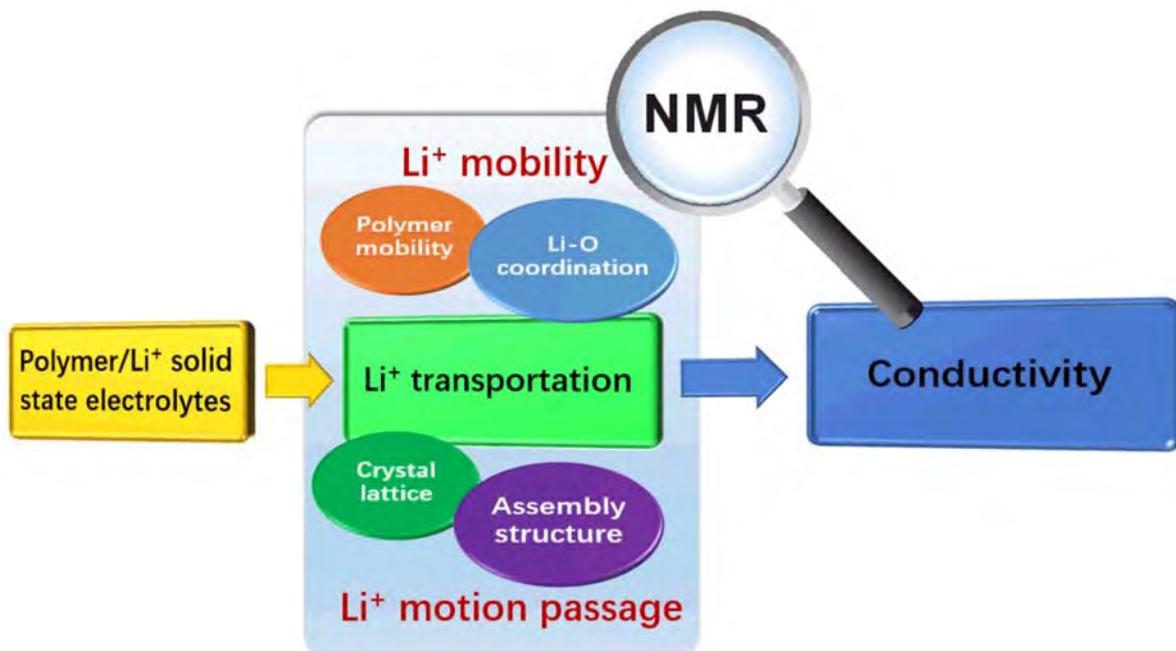
POLY 320: Towards understanding the ionic conduction in solid state polymer electrolytes - a solid-state NMR study of PEO/Li⁺ complex

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In this talk, we will present several examples showing the potential of modern solid-state NMR to elucidate the complicated structures and dynamics in the solid state polymer electrolytes, and subsequently help to understand the ionic conductivity in molecular level. The factors that can influence the Li⁺ transportation are the focus of the study. These factors include the segmental mobility in the Li-O coordination structure, the strength of Li-O coordination and the passage of Li⁺ motion/transportation. We will demonstrate that:

1. The segmental motions in the PEO/Li⁺ crystal lattice may initiate the long-range transportation of the Li⁺ ions.
2. Weakening the Li-O coordination (by adjusting the conformation of PEO chain in the PEO-Li⁺ coordination structures) can facilitate the enhancement of the Li⁺ mobility.
3. Constructing the Li⁺ motion passages may facilitate the long-range transportation of the Li⁺ ions.

Based on the knowledge of the ionic conductivity in molecular level, we anticipate the development of the design strategy of the highly conductive solid state polymer electrolytes.



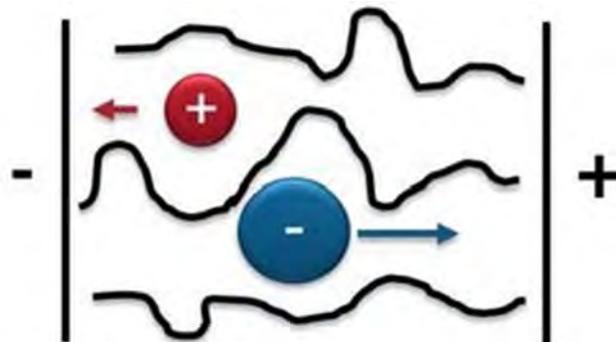
POLY 321: Studying ion transport in polymer electrolytes by NMR methods

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For application of electrolyte materials in energy storage devices their transport properties are essential. Commonly determined transport coefficients are conductivity, viscosity and diffusion coefficients, where the latter are ion-specific quantities, available by multinuclear Pulsed-Field-Gradient (PFG)-NMR diffusion.

This lecture presents ion transport studies in advanced electrolytes for Li ion batteries, i.e. (i) ionic liquid (IL)- based liquid electrolytes and (ii) ternary polymer gel electrolytes consisting of ionic liquid, polymer and Li salt, which are suitable materials to yield a compromise between sufficient conductivity and mechanical stability. Here, multinuclear PFG-NMR of ^7Li , ^{19}F (anions) and ^1H (cations) serves to analyze the transport processes as influenced by complex mutual interactions of the constituents. For example, in systems based on the poly(ionic liquid) PDADMATFSI a detailed comparison of relative diffusivities of anions and Li showed that charged chains are superior polymeric constituents in ternary gels in terms of their ability to enhance Li^+ conduction. Transport numbers calculated from PFG-NMR diffusion coefficients thus serve to optimize materials for transport of specific ion species.

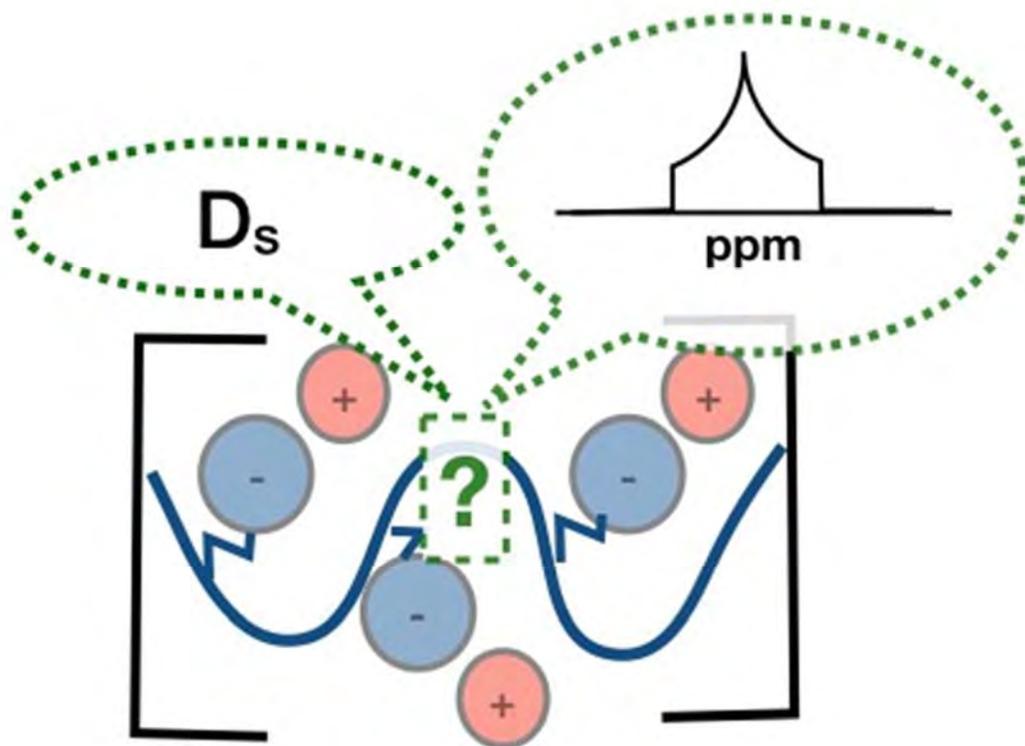
Furthermore, to identify the conductivity contribution of a specific ion species remains a challenge, since from diffusion coefficients transference numbers can only be obtained under the assumption of completely uncorrelated ion motion. In order to determine true transference numbers, the electrophoretic mobility μ has to be known. Here, electrophoretic NMR (eNMR) allows to directly measure the electrophoretic mobility μ of NMR-active ions. Again, multinuclear studies (e.g. ^1H , ^7Li , ^{19}F) yield a full characterization of all ionic species of typical liquid electrolytes. Various examples such as pure ionic liquid, IL/Li salt mixtures, and glyme-based solvate ionic liquids are demonstrated, providing unique information on the mobility of any single ion species and thus allowing conclusions on correlated motion of different ion species.



POLY 322: Understanding ion dynamics in conducting polyelectrolytes from angstroms to millimeters

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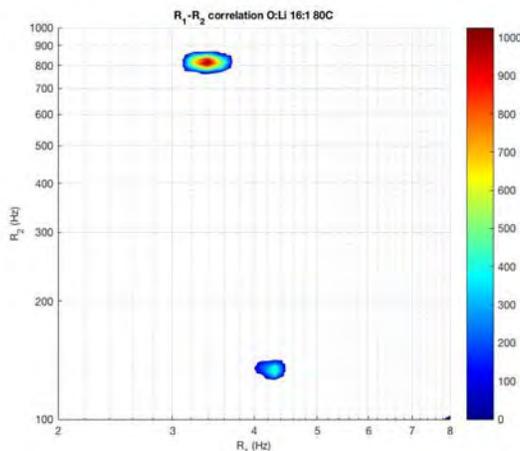
The selective transport of ion across a separation layer is an important thermodynamic driven phenomenon that enables a variety of processes including the crucial signaling of biological cells, the proper functioning of many batteries, and the optimization of desalination membranes for clean water. Nuclear Magnetic resonance is uniquely suited to give insight to the dynamic behavior of ions adsorbed in these complex media systems as it's sensitivity to local fluctuations and ion mobility is reflected in the observed spectral patterns, relaxation rates, and apparent self-diffusivities. Ion imbedded complex media were studied in order to assist in the description local ion behavior and mobility.



POLY 323: Ion dynamics in solid polymer blend electrolytes via inversion of the laplace transform

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NMR spectroscopy can provide element specific information on ion motion in solid polymer electrolytes via pulsed field gradient diffusion measurements and relaxation rate studies. While PFG measurements can determine the diffusivity of the ions, such as Li^+ , the relative population of the ions can be difficult to infer as the spin-spin relaxation times for slow or immobile cations can be too short to be captured in stimulated echo PFG measurements. Local motions can be inferred from measurements of longitudinal, T_1 , and spin-spin, T_2 , relaxation rates, however extraction of relevant correlation times can be challenging due to the distributions of dynamics present in these polymer systems. The inversion of the Laplace transform can extract distributions of relaxation rates. When used in conjunction with T_1 - T_2 correlation NMR experiments, the different dynamic environments for the ions can be observed based on T_1 - T_2 pairings and thus aspects of the distributions can be dissected in terms of correlation times, electric field gradients, and dipolar couplings to the hydrogen in the polymer environment. This approach has been applied to the study of a highly conductive solid polymer electrolyte made from polymer blends of linear poly(ethyleneimine)-graft-poly(ethylene glycol) with linear poly(ethyleneimine) bearing lithium N-propylsulfonate groups. While conductivities on the order of 10^{-3} S/cm at 80°C have been observed for this polymer blend, the amount of free lithium ion participating in conductivity is not obvious. In order to further optimize these materials, information on how well the lithium ion dissociates from the N-propylsulfonate group is needed. Using T_1 - T_2 correlation spectroscopy, the varying lithium populations as a function of temperature and Li:O ratio in these blends will be presented and the utility of this method described.

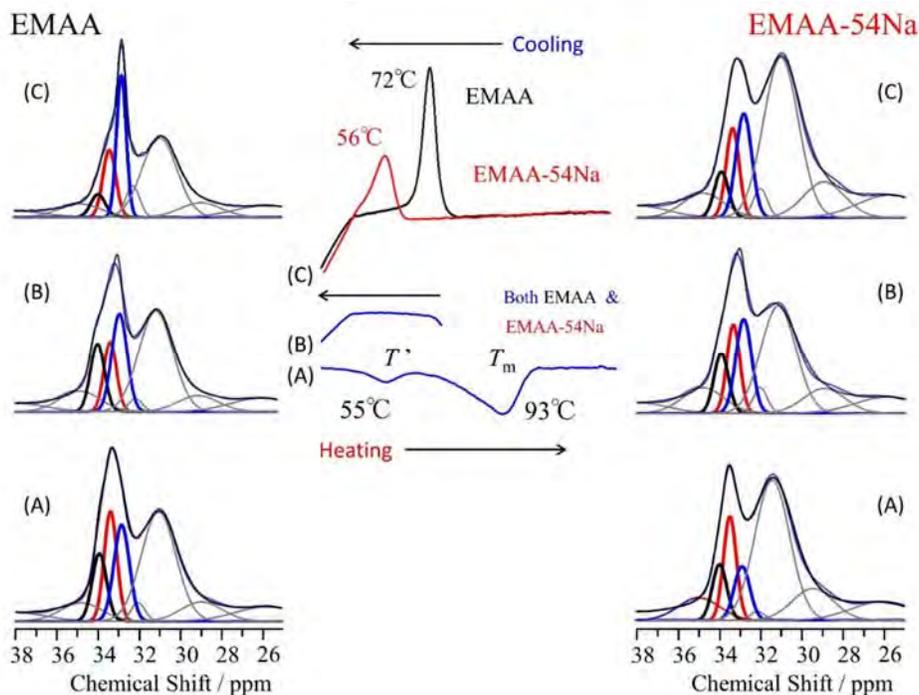


^7Li R_1 - R_2 ($1/T_1$ - $1/T_2$) Correlation Spectra

POLY 324: Solid state ^{13}C NMR study of ethylene ionomers: Crystalline phase after heat treatment

Atsushi Asano, *asanoa@nda.ac.jp*, Takayuki Matsukawa, Chikako T. Nakazawa.
Applied Chemistry, National Defense Academy, Yokosuka, Japan

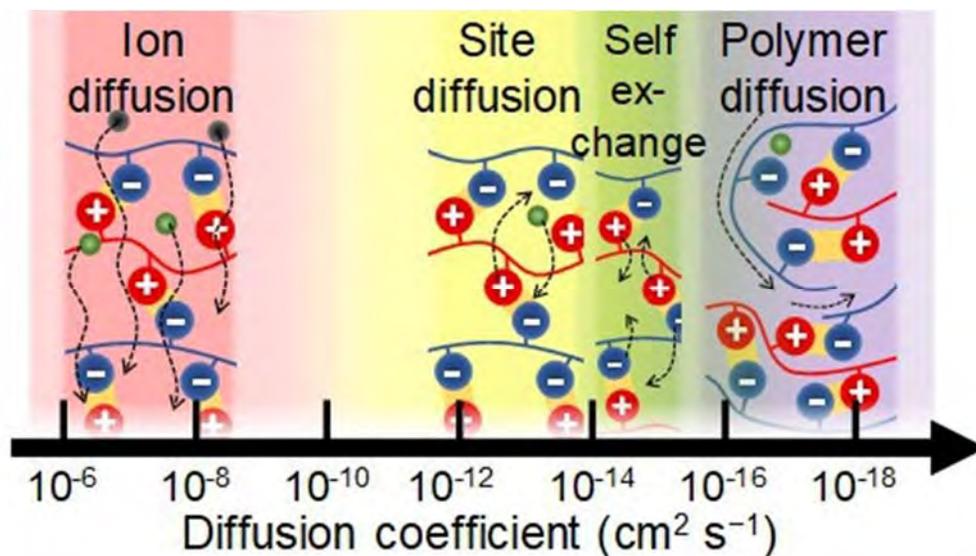
The high-resolution solid-state ^{13}C CP and DPMAS NMR results on morphological and molecular motion changes for poly(ethylene-methacrylic acid) (EMAA) and EMAA- Na^+ ionomer (EMAA-54Na: 54% of carboxyl group was neutralized by Na^+) depending on temperature history were presented. The singlet carboxyl peak of EMMA divided three peaks, which were ascribed to the dissociated carboxyl group, un-dissociated carboxyl group, and interacted dissociated carboxyl group with Na^+ cations from the lower field. The peak of polyethylene (CH_2) region apparently divided to two peaks that are ascribed to the crystalline and non-crystalline phases. From a ^{13}C - T_1 (T_1^{C}) measurement, the apparently singlet crystalline peak was cleared to be divided to three peaks at least. The peak consists of monoclinic and orthorhombic crystals at 34 and 33 ppm, and CH_2 chains neighborhood of carboxyl group (referred to ion-cluster) at 33.5 ppm. Estimated crystallinity of the CH_2 region in the EMAA-54Na was 32%, while that of EMAA was 40%. The DSC results show two endothermic transitions for both EMAA and EMAA- Na : unknown T' at 55-56°C and the melting temperature (T_m) at 93°C of the crystalline phase for polyethylene chains. The crystallinity of recrystallized samples, after raising temperature beyond T_m , was not changed for both EMAA and EMAA-54Na. However, the ratio of the orthorhombic crystal increased by 14-19%. After raising temperature beyond T' , the crystallinity and the ratio of the orthorhombic crystal of EMAA-54Na increased by 7% and 15%, respectively, while those were not changed for EMAA.



POLY 325: Insights into the assembly of polyelectrolyte multilayers and complexes

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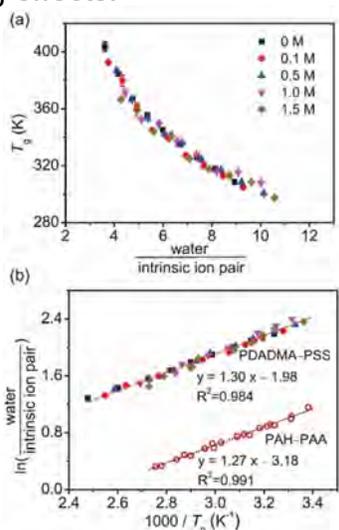
Since they were made popular more than two decades ago, thin films termed polyelectrolyte multilayers (PEMUs) have gained widespread attention for their potential uses as membranes, reservoirs and drug carriers, among others. Here, two core concepts, overcompensation and polymer kinetics, affecting the layer-by-layer buildup of PEMUs were elucidated in a series of radiolabeling and isotopic exchange experiments. Both polymers used in this study, poly(diallyldimethylammonium) and poly(styrenesulfonate), were found to reach approximately the same limit when added in excess to stoichiometric thin films. Their equilibrium overcompensation did not depend on salt concentration and polymer molecular weight. The diffusion of polymer chains and sites – the hopping of counterions between one monomeric site and another – was also examined, showing that the latter is orders of magnitude faster than the former. Buildup of multilayers was found to be mainly dominated by site diffusion, which explains their internal layered structure. A universal plot connecting salt concentration with the site diffusion coefficients of the polycation and the polyanion was established. It served as a starting point to inspect different multilayer buildup mechanisms using the same polyelectrolyte pair, and, in a broader sense, as a guide to the formation of these films and other forms of polyelectrolyte complexes.



POLY 326: Thermal transitions in hydrated PDADMA–PSS complexes

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Polyelectrolyte complexes (PECs) have been attracting great interest due to their promising applications as stimuli responsive materials, but their thermal properties still stay unclear. Here, modulated differential scanning calorimetry (DSC) and all-atom molecular dynamic (MD) simulation are cooperatively exploited to investigate the thermal properties of PECs, paired from poly(diallyldimethylammonium chloride) (PDADMAC) and poly(sodium 4-styrenesulfonate) (PSS). Due to the strong attractions in ion pairing, dried PECs were brittle and exhibited no transitions. Hydrated PECs, on the other hand, underwent a glass-transition. It is found that the temperature of this glass transition, T_g , declined in value with increasing salt doping level and water content. We further show that one unifying parameter, the molar ratio of water to intrinsic ion pair, controls T_g as exhibited in a master curve. The activation energy obtained from a van't Hoff plot is close to the value of restructuring one hydrogen bond. In addition, MD simulations reveal a strong dependence of the number of the hydrogen bond between water and intrinsically compensated PSS with temperature. These findings strongly suggest that the water acts as a nontraditional plasticizer inasmuch as it facilitates polymer relaxation by weakening ion pairing. The influence of salt and water on the thermal properties of PECs is interpreted in terms of increased screening and weakening of intrinsic ion pairing effects.

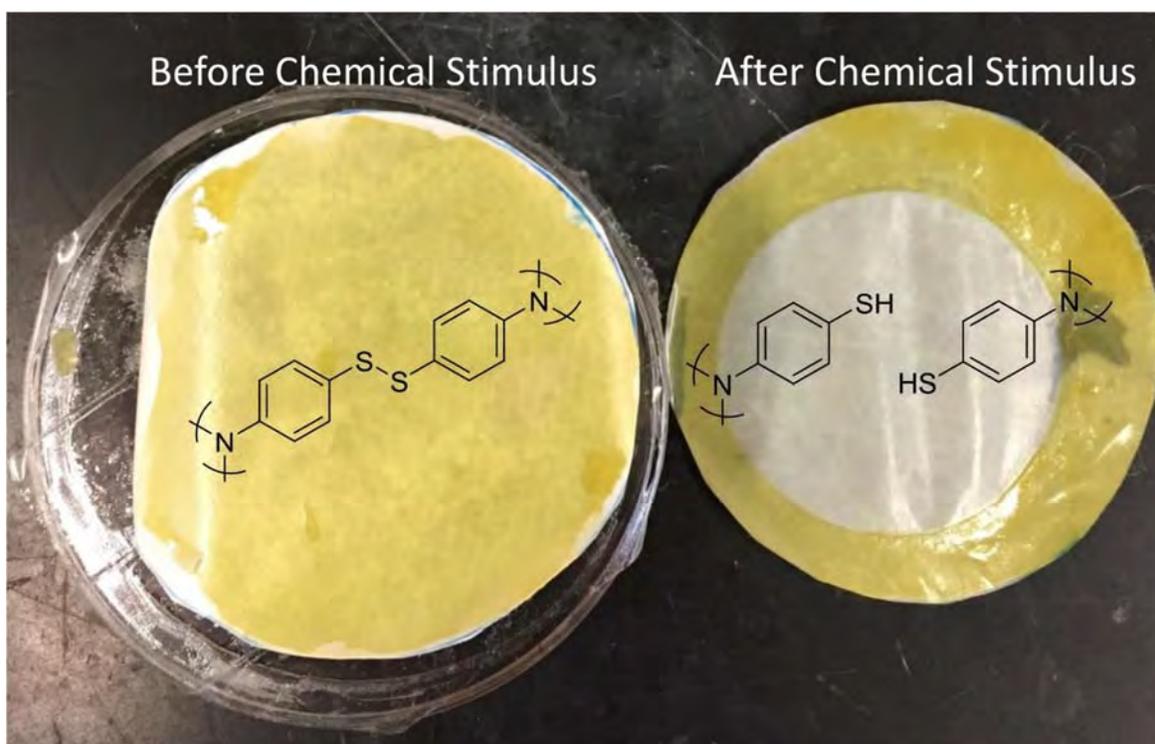


(a) T_g as a function of the ratio of water molecules per intrinsic ion pair in hydrated PDADMA–PSS complexes prepared from solutions of different NaCl concentrations. (b) Linear fitting of $\ln(\text{water}/\text{intrinsic ion pair})$ vs $1000/T_g$. The red and black dotted lines indicate the fitted lines. The legend in (a) also applies to (b). PAH–PAA data are from the authors' previous work.

POLY 327: Smart epoxy nanofiltration membranes for multicomponent separations

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Membranes are excellent at isolating one component in high purity, but multicomponent separations with membranes remains a significant challenge. We report the fabrication of stimulus-responsive epoxy nanofiltration membranes containing a labile disulfide bond that can be broken with a chemical stimulus. The selectivity and flux of chemicals through the membranes was controlled by the concentration of disulfide bonds in the membrane. When the disulfide bond was cleaved, the pores in the membrane became larger and yield different separation properties. Using this method, membrane selectivity changed by up to 70% and flux was increased by 5x. The rapid change in selectivity of the membrane allows for the separation of three-component mixtures. A three-component mixture of 33.3% *m*-dinitrobenzene, 33.3% triphenylmethane, and 33.3% 1,3,5-tris(diphenylamino)benzene was separated into three different fractions that were significantly enriched in one of the three molecules. The first fraction contained *m*-dinitrobenzene with 82% purity in 84% yield, the second fraction contained triphenylmethane with 67% purity at 49% yield, and the third fraction contained 1,3,5-tris(diphenylamino)benzene at 71% purity in 88% yield.

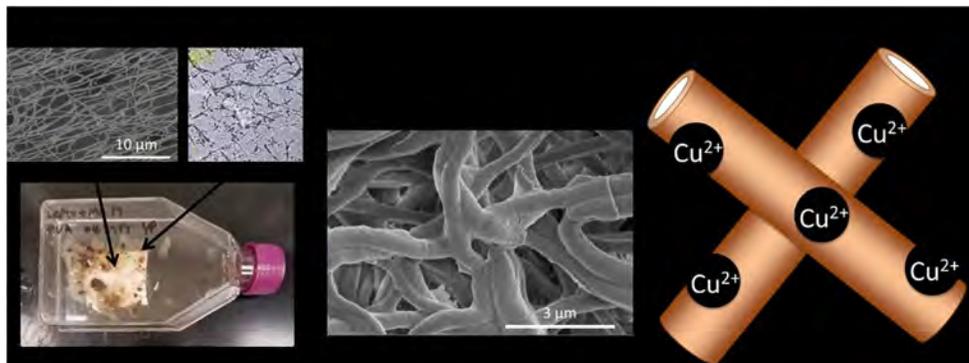


Smart epoxy nanofiltration membranes contain a labile disulfide bond that responds to a chemical stimulus. Cleavage of the disulfide bonds changes the membrane's separation properties to perform separations of three chemicals in a single mixture.

POLY 328: Biomineralization-inspired mineral coating for nanofiber adsorbents development

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Biomineralization- the growth of mineral forms such as shells and bones among living organisms- is a naturally important process that results in protective mineral layers. For instance, human bone consists of collagen fibrils that are covered with hydroxyapatite nanocrystals. Proteins absorbed into the voids of collagen fibrils nucleate and grow nanocrystals. Inspired by bone growth, we emulated protein behavior with polymerized micelles. CaCO_3 particles were deposited onto nanofibers by alternating dips into aqueous CaCl_2 and Na_2CO_3 solutions. Polymerized micelles, below the nanofiber surface, attracted more Ca^{2+} and CO_3^{2-} ions, thus forming denser CaCO_3 coatings that also promoted greater dye removal from water. Nanofibers were mineralized in the presence of metal ion oxidizing fungi that have shown efficacy towards bioremediation and the safe decontamination of heavy metals from soil and water. Oxidative enzymes, found among soil fungi, convert Mn^{2+} into manganese oxide particles. This biogenic form of manganese oxide supports the natural removal of harmful Mn^{2+} heavy metal ions from the environment, as well as other heavy metals and phosphates. Because biogenic manganese oxides are superior adsorbents to synthetic forms, we proposed the combined use of those particles with fibers that could filter contaminated water. Nanofibers are high surface area materials for filtration. Once treated with the biogenic manganese oxide coating, treated nanofibers removed copper (Cu^{2+}) contaminants from water more effectively. For instance, manganese oxide nanofibers adsorbed 57 mg/mg of Cu^{2+} from water after 24 hours, which is almost 4 times greater than untreated nanofibers of poly(vinyl alcohol). Copper adsorption by these manganese oxide nanofibers were tested against contaminants in laboratory charged water and NC groundwater. This work is supported in part by the NC Sea Grant (NCSG) – Water Resources Research Institute (WRRI).

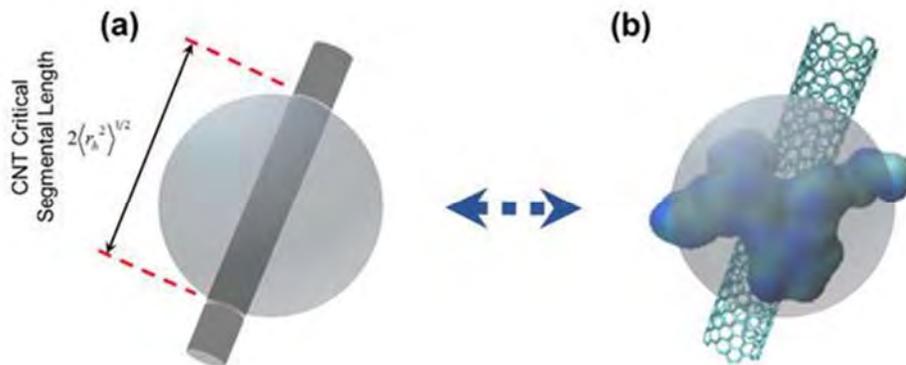


Coniothyrium sp., soil fungus, coated nanofibers with manganese oxide deposits that were then capable of copper removal from water.

POLY 329: CNT ‘trapping’ via non-solvent induced phase separation

Heng Li, *li.heng@husky.neu.edu*, Marilyn Minus. *Mechanical and Industrial Engineering, Northeastern University, Boston, Massachusetts, United States*

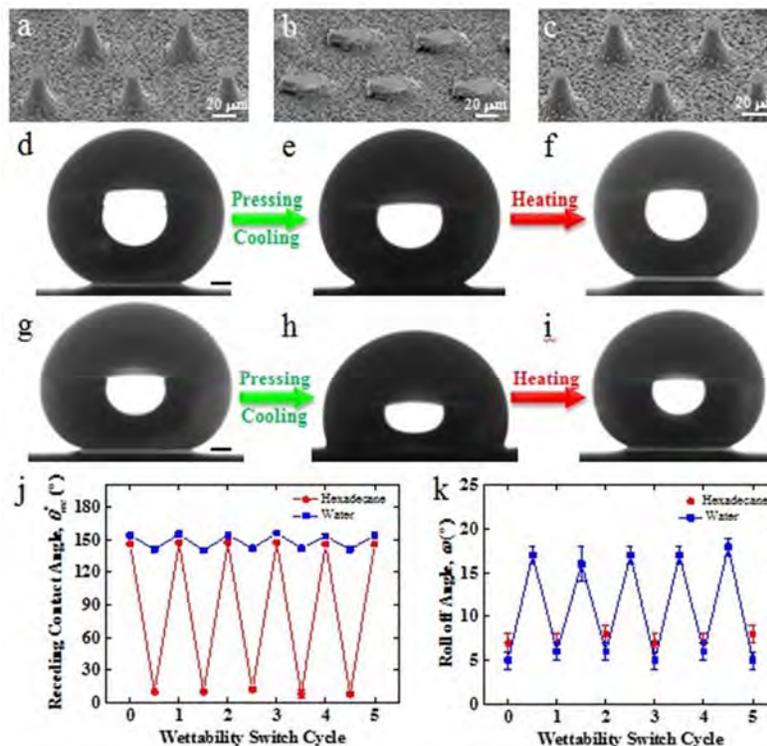
In this work, a CNT ‘trapping’ mechanism is presented to fundamentally address dispersion of carbon nanotubes (CNTs) within a polymer matrix. The ‘trapping’ process is accomplished via a non-solvent induced liquid-solid phase separation in CNT/polyacrylonitrile (PAN) composite systems. The effect of phase separation and CNT ‘trapping’ was visualized experimentally by formation of hybrid CNT/PAN buckypapers through filtration of CNT-polymer dispersions. The resultant composite material exhibits a multi-phase morphology, which gradually changes from a CNT-rich to polymer-rich layer. Examination of the layered structures reveals CNTs with specific bundle size are uniformly dispersed within the polymer-rich layer due to preferred polymer-CNT interaction during phase separation. Experimental, theoretical, and molecular dynamics studies further support the CNT ‘trapping’ mechanism responsible for phase formation as well as the specificity and preference of the polymer-CNT interactions. A geometric dependence described by a ‘cylinder-in-sphere’ model is established links a critical CNT bundle size to the polymer coil. This model is able to provide understanding regarding the preferential polymer-CNT interactions, which may also suggest that the polymer is able to solvate the CNT. This CNT ‘trapping’ process represents the interactive relationship required to potentially form a blended polymer-CNT phase in the system. Understanding the use of CNT ‘trapping’ as well as this geometrical dependence between filler and polymer is important to pinpoint nano-filler dispersion limits. Identifying these dispersion limits is critical toward the processing of superior polymer-based composites, which fully utilizes the nano-filler reinforcement.



POLY 330: Wetting transition on metamorphic superomniphobic surfaces

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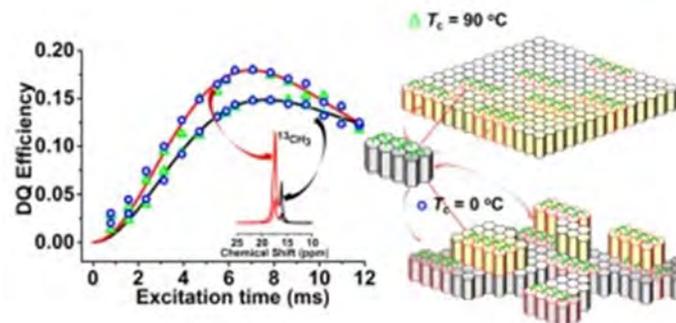
Superomniphobic surfaces are extremely repellent to virtually all liquids. Prior work have emphasized the importance of low solid surface energy and re-entrant texture (i.e., multi-valued or convex or overhang texture) in the design of superomniphobic surfaces. While superomniphobic surfaces with a wide variety of textures have been reported in literature, to the best of our knowledge, there are no reports of superomniphobic surfaces with metamorphic textures (i.e., textures that transform their morphology in response to an external stimulus). In this work, we present the first-ever metamorphic superomniphobic (MorphS) surfaces fabricated with a thermo-responsive shape memory polymer. Unlike prior work, utilizing our MorphS surfaces, we demonstrate the distinctly different wetting transitions of liquids with different surface tensions and elucidate the underlying physics. The wetting transitions on our MorphS surfaces are solely due to transformations in morphology of the texture. We envision that the rapid and reversible wetting transitions on our MorphS surfaces will have a wide range of applications including controlled drug release systems, liquid-liquid separation membranes, lab-on-a-chip devices, and biosensors.



POLY 331: Understanding of polymer crystallization at the molecular scale: Topology, kinetics, and molecular weight effects

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Over the last half century, chain-folding structure of semicrystalline polymers has been debated in polymer science. Thereby, it is not well understood that how topological constraints via entanglement, solvent-polymer interactions, molecular weight, and kinetics influence chain trajectory of semicrystalline polymers. Recently, ^{13}C - ^{13}C double quantum (DQ) NMR spectroscopy combined with ^{13}C selective isotope labeling has been developed to investigate re-entrance sites of the folded chains, mean values of adjacent re-entry number $\langle n \rangle$ and fraction $\langle F \rangle$ of semicrystalline polymer. This talk highlights the versatile approaches of using solid-state (ss) NMR and isotope labeling for revealing i) chain trajectory in melt- and solution-grown crystals, ii) kinetics and molecular weight effects on chain trajectory in polymer crystals, iii) solvent-polymer interactions in good or poor solvents, and iv) topological constraints on chain-folding process and structure.



Kinetics effect on the chain folding structure of PLLA solution grown crystals.

POLY 333: Peptide-loaded microgels as carriers of antimicrobial peptides

Lina Nyström², Randi Nordstrom², Jane Bramhill¹, Brian Saunders¹, Rubén Álvarez-Asencio^{3,4}, Mark W. Rutland^{3,5}, **Martin Malmsten**^{2,6}, Martin.Malmsten@farmaci.uu.se.
(1) University of Manchester, Manchester, United Kingdom (2) Department of Pharmacy, Uppsala University, Uppsala, Sweden (3) Department of Surface and Corrosion Science, School of Chemical Science and Engineering, KTH Royal Institute of Technology, Stockholm, Sweden (4) Institute for Advanced Studies, IMDEA Nanoscience, Madrid, Spain (5) SP Technical Research Institute of Sweden, SP Chemistry, Materials and Surfaces, Stockholm, Sweden (6) Department of Pharmacy, University of Copenhagen, Copenhagen, Denmark

Microgels are weakly cross-linked polymer colloids, which can be designed to display responsive volume transitions triggered by a range of parameters. In the context of drug delivery, microgels are of particular interest as carriers for biomacromolecular drugs, such as peptides and proteins, including protection against enzymatic degradation and controlled or triggered release. In order to elucidate these effects, we here investigate effects of microgel charge density and conformationally induced peptide amphiphilicity on AMP loading and release, using detailed nuclear magnetic resonance (NMR) structural studies combined with a battery of other physicochemical methods. In parallel, consequences of peptide loading and release for membrane interactions and antimicrobial effects were investigated, as was protection of microgel-incorporated peptides by infection-related proteases. Furthermore, we elucidate factors determining volume transitions of electrostatically triggered surface bound microgels, as well as their use as delivery systems for peptides. In doing so, we investigate effects of microgel charge density, pH, and ionic strength on microgel volume transitions at surfaces, surface-induced microgel deformation and nanomechanical properties, as well as consequences thereof for peptide loading and release, using a battery of experimental techniques, including AFM PeakForce QNM, QCM-D, ellipsometry, and confocal and cryoTEM microscopy.

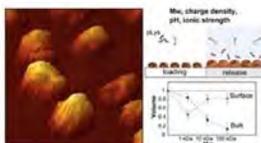


Figure 1. Factors affecting peptide loading into, and release from, microgels was investigated with regards to microgel and peptide properties, as well as to ambient conditions. The consequences of such effects for the function of antimicrobial peptides are addressed as well.

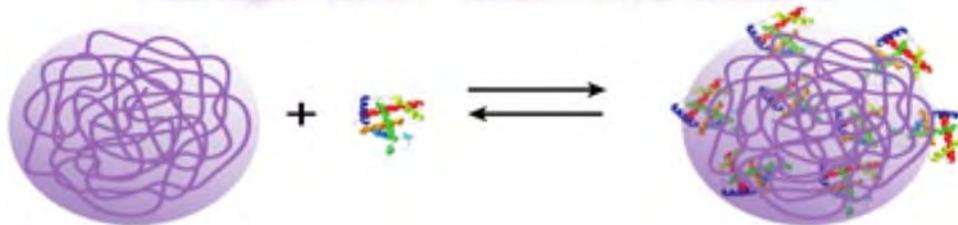
POLY 334: Adaptable synthetic polymers as protein and peptide affinity ligands. An alternative to the lock and key paradigm

Kenneth J. Shea, kjshea@uci.edu. Univ of California, Irvine, California, United States

Just as medicinal chemists routinely design and synthesize small molecules to target the active site of a single protein in the proteome, we suggest that advances in polymer synthesis, structural biology and nanotechnology have progressed to the point where we can design synthetic polymer nanoparticles (NPs) with antibody-like affinity and selectivity for targeted biomacromolecules.

The talk will describe abiotic protein/peptide and carbohydrate affinity agents (“plastic antibodies”). These agents, synthetic polymer NP hydrogels, are formulated with functional groups complementary to the biomacromolecule target. Unique to these materials is that their affinity can be switched on/off by external stimuli including temperature, pH and ionic strength, a strategy exploited in “catch and release” of target proteins. The talk will be concerned with exploring the applications of these materials for protein detection, separation and as potential therapeutic agents to replace antibody drugs.

Nanoparticle-Protein Interactions

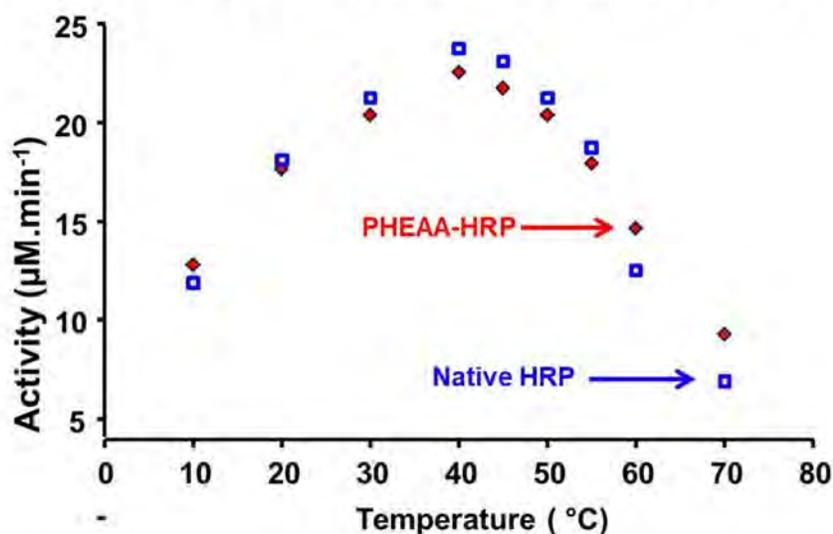


POLY 335: Aqueous microgels as reference beads for mass cytometry and supports for enzyme reactions at elevated temperatures

Mitchell Winnik, *mwinnik@chem.utoronto.ca*. Univ of Toronto Dept of Chem, Toronto, Ontario, Canada

Over the past 30 years many groups have been interested in microgels and nanogels, particularly colloidal aqueous hydrogels that respond to their environment (temperature, pH, etc). We have two very specific interests in these types of materials. The first is as reference beads for mass cytometry, a high throughput bioanalytical technique based on atomic mass spectrometry for determining biomarker expression on cells. Microbeads containing known amounts of lanthanide (Ln) ions allow the instrument to be calibrated in situ. Initially we prepared poly(N-isopropyl acrylamide-co-vinyl caprolactam-co-methacrylic acid) microgels loaded with precipitated LnF_3 . Unfortunately, the Ln ions slowly leached from the microgels at mildly acid pH. Using these microgels as reactors to generate the less soluble LnPO_4 nanocrystals was a challenge that makes a very interesting story. The second area of interest to us is the use of colloidal hydrogels as covalent hosts for enzymes for reactions to be carried out at elevated temperatures. The thermally induced collapse transition of common aqueous microgels normally interferes with enzyme activity. We designed and synthesized a functional poly(hydroxyethyl acrylamide) microgel, a thermally unresponsive microgel (no cloud point for $T \leq 140^\circ\text{C}$). We attached the enzyme horseradish peroxidase (HRP) to the microgel, and, for comparison, also attached HRP to PEGMA microgels, which have a collapse transition in water at about 55°C . We studied the activity of HRP on both microgels at temperatures up to 70°C .

Enzyme activity of native and microgel-supported HRP



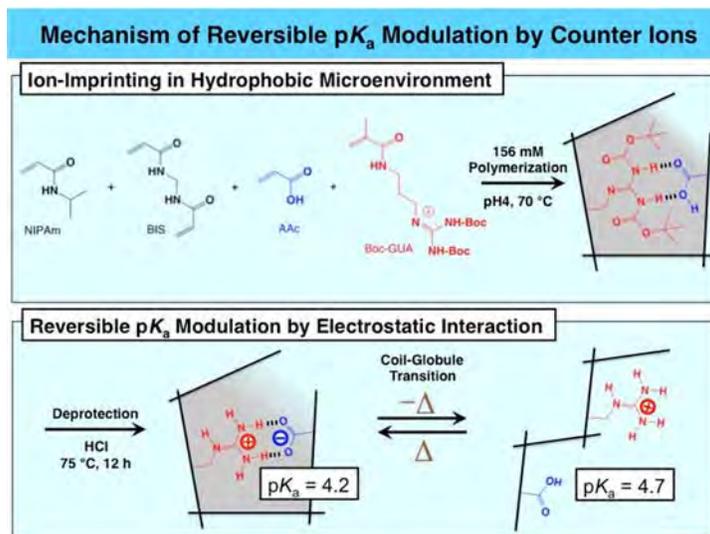
POLY 336: Tuning pK_a of Brønsted acids in temperature-responsive hydrogel particles by proton- and ion-imprinting strategy

Yu Hoshino, *yhoshino@chem-eng.kyushu-u.ac.jp*. Chemical Engineering, Kyushu University, Fukuoka, Japan

Reversible pK_a shifts of Brønsted acids such as carboxylic acids, alcohols, ammonium ions, and imidazolium ions in proteins play crucial roles in enzymatic reactions and efficient molecular/ion transport. To vary the pK_a values of acids, the proteins change the dielectric constants around the acids and/or reversibly stabilize/destabilize protons on the acids by hydrogen bonding and/or coulombic interaction through conformational changes induced by external stimuli.

Synthetic materials that alter their binding affinity to protons in response to external stimuli have gained considerable attention as substitutes for proteins. We revealed that pNIPAm-based NPs that show large and reversible pK_a shifts can be prepared by the “proton imprinting” and “microenvironment imprinting” strategy: When acidic monomers such as acrylic acids were protonated in the polymerization process, the protonated acids were easily incorporated into the less polar domains of growing collapsed-pNIPAm NPs, and were subsequently stabilized by a cross-linker. As a result, high pK_a acids (pK_a ~8) were imprinted in the NPs. When the degree of cross-linking was low, the structure of the high pK_a acidic sites was reversibly denatured by temperature-induced conformational changes of the polymer chains, resulting in a large reversible pK_a shift as proteins. The range of pK_a shift was in the neutral pH around 6-8.

The pK_a variation range of carboxylic acids in the NPs can be tuned by designing structure of monomers containing carboxylic acids and imprinting cationic group in the NPs. The pK_a variation range can be lowered/raised to be 4.3/8.7 by stabilizing/destabilizing carboxylate anions by modifying the acids with electron withdrawing/donating group. The pK_a of acids can also be lowered dramatically by imprinting cationic functional group such as guanidium group around the carboxylate anions.



POLY 337: Microgels as building blocks for tissue regenerative materials

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We apply microgels as building blocks for tissue regenerative materials. The different types of microgels are spherical or anisometric, responsive or hollow, and are produced using different methods, such as microfluidics and in mold polymerization. Due to their size, the microgels can be injected, with or without a surrounding hydrogel in a minimal invasive manner.

Hollow microgels are produced to enable direct loading of drugs or cells with a virtually 100% encapsulation efficiency. The release can be controlled by the dimensions of the microgels and the thickness, crosslinking density, and degradation rate of the shell.

Anisometric microgels can be applied for multiple functions. The larger ones (diameter ~ 100-200 μm) can embed cells to protect the cells after transplantation, reducing cell migration and death. Their internal structure, biomodification, and degradation properties control tissue formation. To obtain anisotropic matrices after injection, smaller rod-shaped elements (diameter ~ 1 to 10 μm) are rendered magneto-responsive by the incorporation of superparamagnetic iron oxide nanoparticles (SPIONs). Due to their anisometric shape, the guiding elements align parallel to a low external mTesla magnetic field, after which a surrounding hydrogel can crosslink to fix their unidirectional orientation. Fibroblasts and nerve cells sense this structural and mechanical anisotropy, resulting in directed cell growth inside 3D hydrogels. Neurons inside the Anisogel show spontaneous electrical activity with signals that propagate along the anisotropy axis of the material. The developed hybrid hydrogel can be applied as a low invasive, injectable material to repair complex, sensitive tissues, such as the spinal cord.

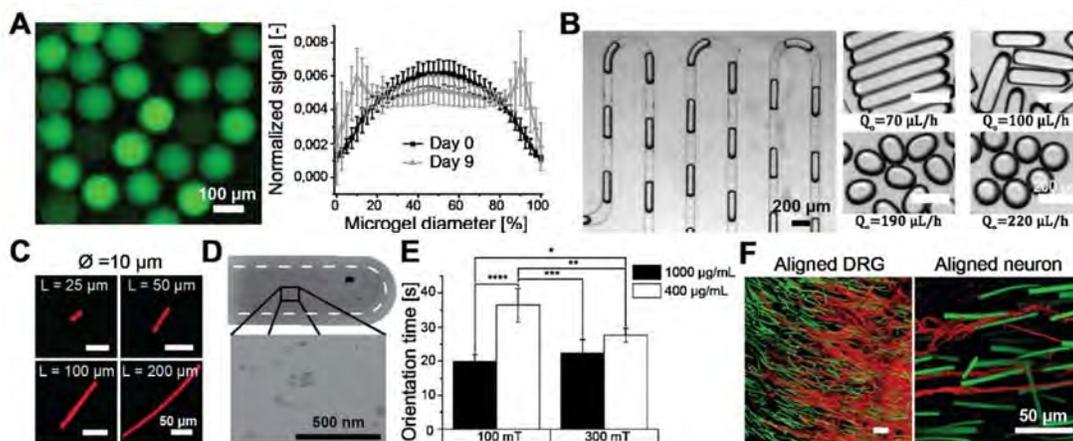


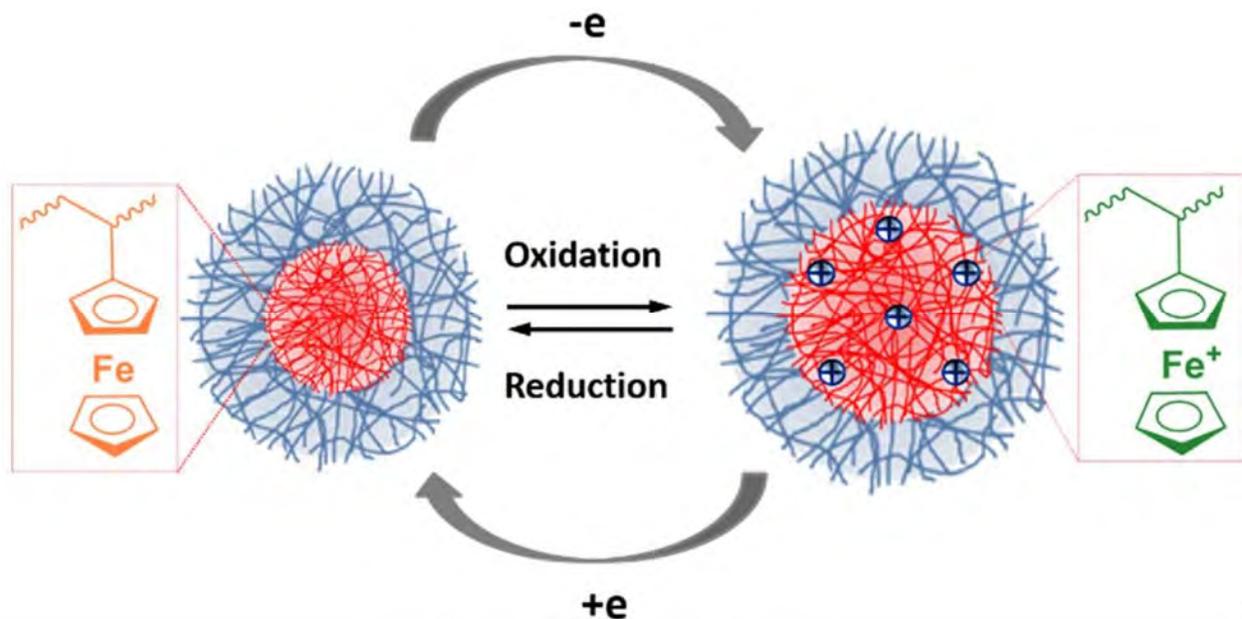
Figure 1. A) Hollow microgels containing FITC-dextran with normalized fluorescence spectra across the diameter of the microgels over time. B) Microfluidic production of anisometric microgels with varying aspect ratios depending on the oil flow rate. C) Printed microgels with different aspect ratios and SPION incorporation (D). E) Microgel orientation rate depending on the SPION concentration and magnetic field strength. F) Unidirectionally nerve growth inside the Anisogel. DRG: Dorsal root ganglion.

POLY 338: Electrochemically-active iron-containing microgels

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Microgels are crosslinked polymeric particles consisting of a porous network, able to be swollen by a solvent. They have often the ability to undergo a volume phase transition with respect to environmental changes, allowing an adjustment of segmental proximity and network dynamics. In case of redox-active units, either as network-bound moieties or complexing entities, the properties of the microgels can be changed by electrochemical means.

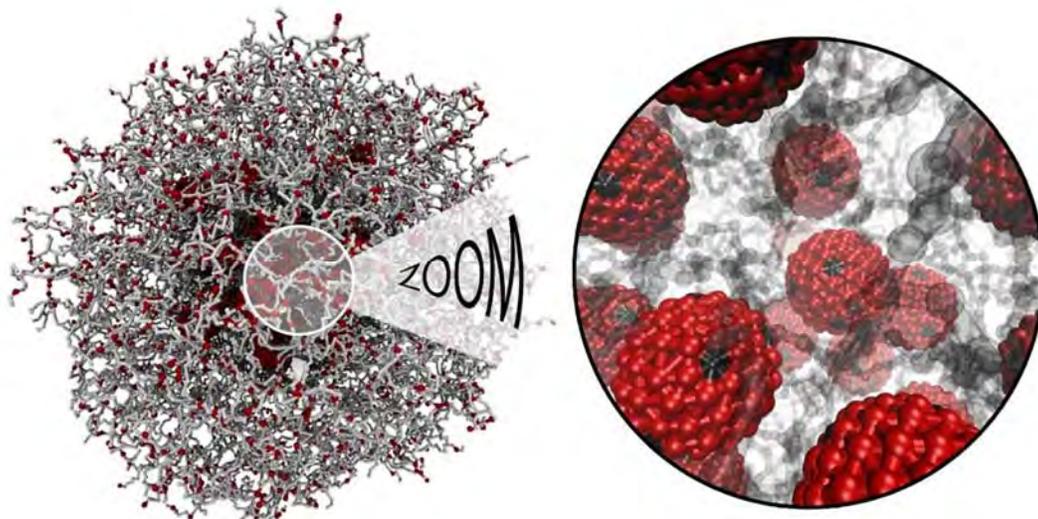
Uniting double-stimuli-responsive features, we address thermoresponsive and electrochemically active microgel systems. One attempt is based on the electrochemical switching of guest ions, leading to a reversible swelling/deswelling of the microgel hosts. Another attempt addresses electroactive microgel colloids with permanently linked redox-active units. For this reason, a simple one-shot polymerization toward core-shell microgels is presented, leading to a core with high amounts of redox-active units and a thermoresponsive shell. Despite the shell, the system is electrochemically addressable: substantial changes in the microgel size can be induced. Furthermore, it can be used to release and capture active molecules in a reversible way by purely electrochemical means. As these microgels are non-cytotoxic, their use in biomedical applications is envisioned.



POLY 339: Polyelectrolyte and polyampholyte nanogels: Effect of electrostatics on internal structure, uptake and release of guest-molecules

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In the present paper, we report about new effects characteristic for the nanogels, which (at the first glance) can be classified as counterintuitive. In particular, we demonstrate inhomogeneous swelling of structurally homogeneous polyelectrolyte nanogels revealing quasi-hollow central part and dense periphery. The physical reason for such structure is a tendency of the charged groups of the nanogel to be concentrated at the periphery which is caused by the decrease of the electrostatic energy. Swelling of pH-switchable polyampholyte nanogels is studied. Both random and core-shell distribution of ionizable cationic and anionic groups is considered. The size of the nanogels as a function of pH reveals V-like shape. The nanogels are highly swollen at low and high pH due to the dominance either cationic or anionic groups. They collapse in the isoelectric point due to the attraction of oppositely charged groups. If the polyampholyte nanogels with random distribution of the charges are nearly homogeneous, the core-shell nanogels can have quasi-hollow structure in very wide range of pH. Uptake and release of charged macromolecules (cytochrome C) at different pH is studied. We demonstrate that the polyampholyte core-shell nanogels can serve as Coulomb trap, when charged shell of the microgel creates a potential barrier enforcing similarly charged nanoparticles (proteins) to “levitate” inside the core prohibiting their escape, Figure. Release of the blocked macromolecules can be induced via salt adding or adsorption of the nanogels on a solid surface.

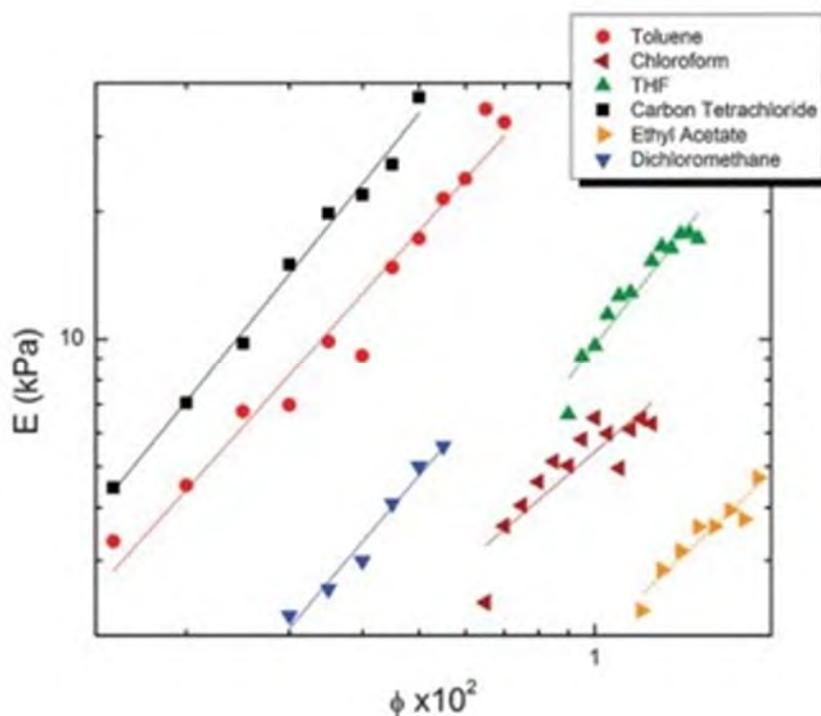


Snapshot of the polyampholyte nanogel with entrapped protein (neutral core and similarly charged shell). Zoom demonstrates “levitation” of the protein molecules inside the core of the nanogel.

POLY 340: Shear and cavitation rheology of polymer organogels

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Chemistry, University of Florida, Gainesville, Florida, United States

We present two classes of polymeric organogels here. First, peptide block copolymer organogels were produced consisting of poly(Z-lysine) through a polymerization-induced gelation process in THF. In these systems, the protecting group on the P(Lys) side-chains remains intact. As such, the secondary structure of the polypeptide chains retains beta-sheet character over a wide range of solution conditions. Gel formation in these systems results from the assembly of the solventphobic P(Lys(Z)) chains, which pack densely in an anti-parallel fashion, minimizing interfacial curvature. In the second system, we describe a new method for the facile, one-pot synthesis of polymeric organogels through modification of Jeffamine polymers with diisocyanate. This precursor can then be dissolved in the desired liquid phase and, upon addition of an amine, gelled. This study will present the mechanism by which gelation takes place in Jeffamine-based materials and determine how factors such as polymer backbone (R_1), diisocyanate spacer (R_2), amine capping agent (R_3) and solvent polarity affect mechanical properties. Throughout these studies, a quantitative comparison between shear and cavitation rheology will be developed.



POLY 341: Rate dependent mechanics of crosslinked polymers

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This presentation will cover a comprehensive program in crosslinked polymer networks at the Army Research Laboratory, where we investigate the rate dependent mechanical response over a broad range of crosslink density. For soft networks we have investigated the role of chain entanglement on the mechanical response, and are developing these materials as testing media for the assessment of military protective equipment. For rigid materials we have focused on highly crosslinked epoxies and Ring Opening Metathesis Polymerized (ROMP) resins based on polymeric dicyclopentadiene (pDCPD). For the ROMP resins, the molecular weight between crosslinks (M_c) was systematically varied by co-polymerizing (DCPD) with either a chain extender that increases M_c , or a di-functional crosslinker, which decreases M_c . A critical M_c of 500 ± 100 g/mol was identified that dictated the failure process. Resins with M_c above this value were ductile, deep in the glassy regime, over a broad range of strain rates. Resins with M_c below this value were brittle, exhibiting low fracture toughness, poor elongation to break, and substantial radial fracture during high velocity impact. We were able to formulate crosslinked resins with a glass transition temperature (T_g) of 150 C that maintained ductility deep in the glassy regime at quasi-static to ballistic strain rates, which is in stark contrast with crosslinked epoxy resins. Molecular dynamics simulations showed that resins with lower M_c were more prone to forming molecular scale nanovoids. We postulate that the higher chain stiffness in low M_c resins inhibits relaxation and plastic deformation in the vicinity of these nanovoids, causing embrittlement. The experimental and computational results suggests that when M_c approaches the persistence length of the crosslinking chains, that the glassy network becomes brittle. These ROMP copolymers offer the potential for new adhesives, resins, and fiber reinforced composites that circumvent the traditional trade-off between structural performance and energy dissipation.

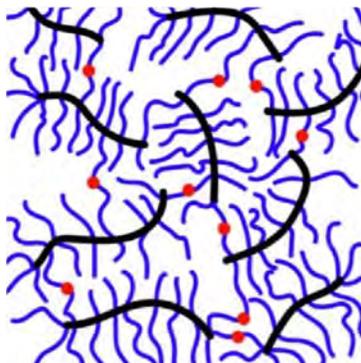


Ballistic failure for a range of crosslinked polymer networks

POLY 342: Fracture of soft but solvent-free polymer networks

Joel Sarapas¹, Emma Rettner², Kathryn Beers¹, **Edwin Chan¹**, edwin.chan@nist.gov.
(1) NIST, Gaithersburg, Maryland, United States (2) University of Minnesota,
Minneapolis, Minnesota, United States

Polymer gels formed from crosslinked polymers swollen with solvent are unique soft materials. They display highly tailorable and nonlinear mechanical behavior yet the presence of solvent also leads to dilution of the polymer chain density thus leading to low fracture toughness. In this contribution, we address this limitation by synthesizing soft but solvent-free bottlebrush polymer networks, and then studying their elasticity and fracture behavior. As a robust and versatile synthetic platform, we polymerized mono- and di-norbornene poly(n-butyl acrylate) macromonomer and crosslinker with Grubbs 3rd generation catalyst to achieve bottlebrush networks, and demonstrate control over network properties via systematic variation in the macromonomer to crosslinker ratio. We characterize the elasticity of these materials using compression testing to show the systematic tunability in their shear modulus as well as their entanglement-free nature. Finally, we use a wire cutting fracture test method to quantify their fracture energy and show how this synthetic platform enables the design of soft but tough materials.

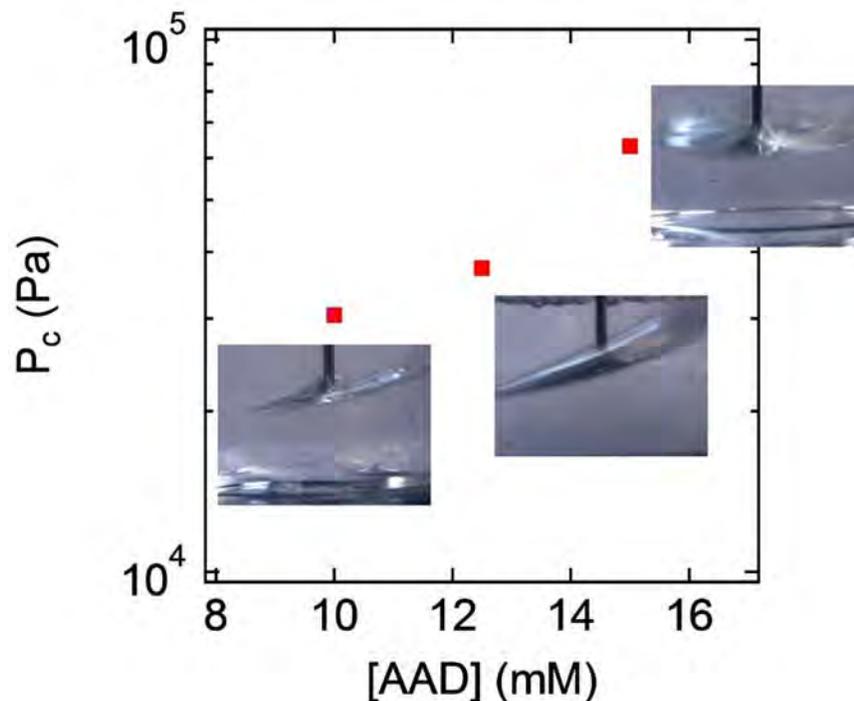


Schematic of a bottlebrush network illustrating the entanglement-free characteristic.

POLY 343: Mechanical properties and failure behavior of alginate hydrogels

Santanu Kundu, *santanukundu@gmail.com*, Seyed Meysam Hashemnejad, Rangana Wijayapala, Rosa Maria Badani Prado, Satish Mishra. Dave C Swalm School of Chemical Engineering, Mississippi State University, Starkville, Mississippi, United States

Alginate hydrogels are commonly used in biomedical applications and these hydrogels are usually prepared by ionic or covalent crosslinking. Calcium salts have been used to obtain ionically crosslinked gels. To obtain covalently crosslinked gels, diamines and amine functionalized carbon nanodots (CNDs) have been used. CNDs with amine functional groups have been synthesized from ortho, para and meta phenylenediamine by using solvothermal method. The CNDs display yellow, red, and blue color when excited with a UV light with 365 nm wavelength and similar photoluminescence has also been observed for the CNDs crosslinked hydrogels. Small angle x-ray scattering results capture the presence of junction zones in ionic alginate gels, whereas, a random network has been observed in the covalently crosslinked gels. Shear rheology data capture strain stiffening and negative normal stress for these gels. These behaviors also depend on the nature of crosslinking. Cavitation rheology technique and custom built fracture set-up have been used to capture the failure behavior of these gels. In cavitation rheology experiments, fracture like behavior was observed at a critical pressure. The critical pressure changes with the type of crosslinking and as a function of crosslinker concentration. The results presented here provide new understanding of the mechanical properties of alginate hydrogels as a function of their structure.

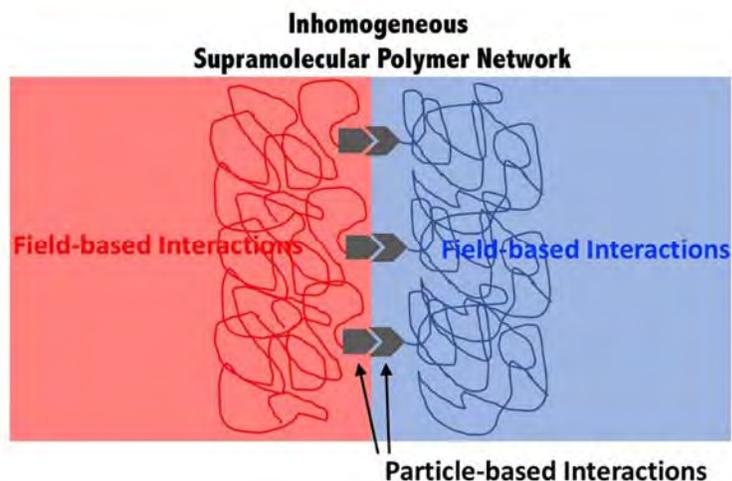


Critical pressure for fracture as a function of crosslinker concentration. The crack propagation at the critical pressure is also shown.

POLY 344: Hybrid particle-field approach for simulating inhomogeneous supramolecular polymer networks

Dong Meng, dm2596@msstate.edu, **Jing Zong**. *Chemical Engineering, Mississippi State University, Starkville, Mississippi, United States*

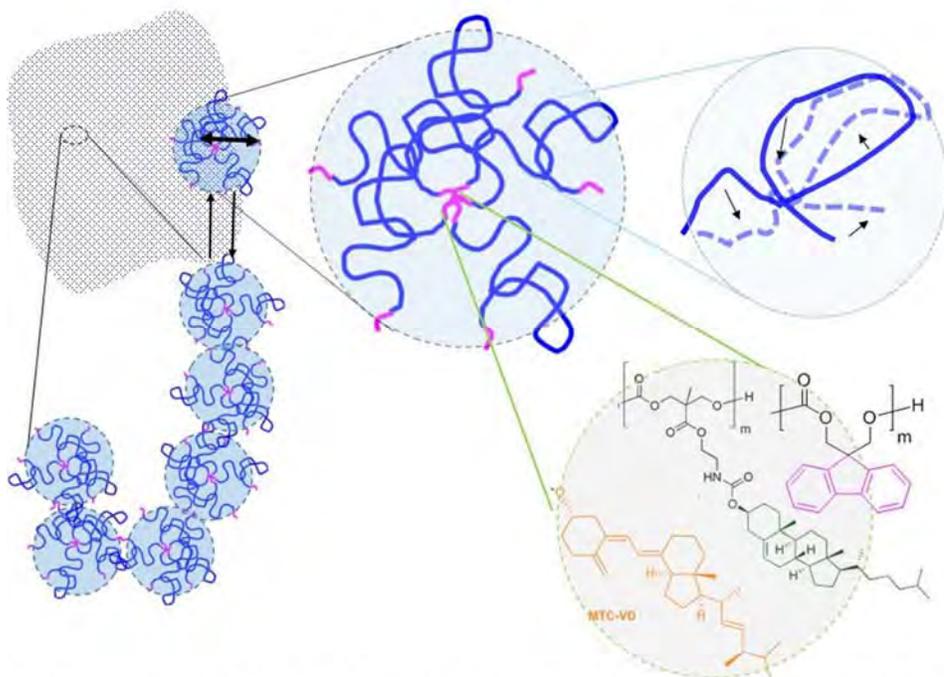
Through hierarchical assembly at multi-scales, inhomogeneous supramolecular polymers (ISP) serve as a promising self-assembly foundry for creating high-performance materials that can perform multiple functions through combinations of structural properties and functional capability. Understanding the mechanisms governing hierarchical assembly of ISP plays a key role in unlocking such potential. From a computational perspective, the major challenge in simulating IPS is to efficiently resolve the interplay of chemical and thermodynamic equilibrium, as well as reaction kinetics and polymer dynamics. Previous methods either rely on a full particle-based approach that imposes prohibitive computational cost when applied to system with mesoscale structure features, or a full field-based approach that lacks a microscopic description of reversible supramolecular interactions. In this work, we develop a hybrid particle-field simulation approach that accounts for the weak van der Waals type interactions using *effective* fluctuating fields experienced by polymer segments, while retaining particle-based microscopic treatment for the strong supramolecular interactions. By doing so, the new hybrid paradigm wields the strengths of both worlds – with fully resolved specific supramolecular bonding and variable chemical kinetics, and computational efficiency in capturing mesoscale structure features. To validate the approach and to illustrate its applications, we examine three supramolecular systems: homogeneous simple associating fluids, end-functionalized homopolymers, and end-functionalized polymer blends in ordered micro-phases. By varying association strength, reaction kinetics and extent of immiscibility, we investigate the effects of coupled chemical-thermodynamic equilibrium, reaction-diffusion kinetics on equilibrium composition, micro-phase morphology, associative bonding/ rebonding lifetime, and polymer diffusion. Future applications of the method to more complicated IPS systems will also be discussed, with an aim of providing predictive knowledge for guiding experimental investigations.



POLY 345: Characterization of the transient networks formed by oligocarbonate-functionalized PEG block polymers

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Amphiphilic block copolymer gels are an important class of materials for drug encapsulation and delivery. The sol-gel transition temperature and concentration are key variables when designing or tailoring rheological properties towards injectable gels. Recent advancements in the synthesis of aliphatic polycarbonates have shown nontraditional micellar and hierarchical structures driven by the supramolecular assembly of the carbonate block functionality that includes cholesterol, vitamin D, and fluorene. In order to understand the gel structure and dynamics of model ABA polymers with end-groups that interact via strong interactions, we studied the effect of end-group molecular mass of model oligocarbonate-fluorene end-functionalized poly(ethylene glycol) ABA triblock copolymers. These materials form micelles in aqueous solution and depending upon the end-group molecular mass form irreversible or reversible clusters. This presentation will highlight the supramolecular assembly structure and dynamics observed by static and dynamic light scattering, small-angle neutron scattering and neutron spin-echo spectroscopy. We show by supporting rheology how the sol-gel thermal transition is coupled to the transient network micellar structure.

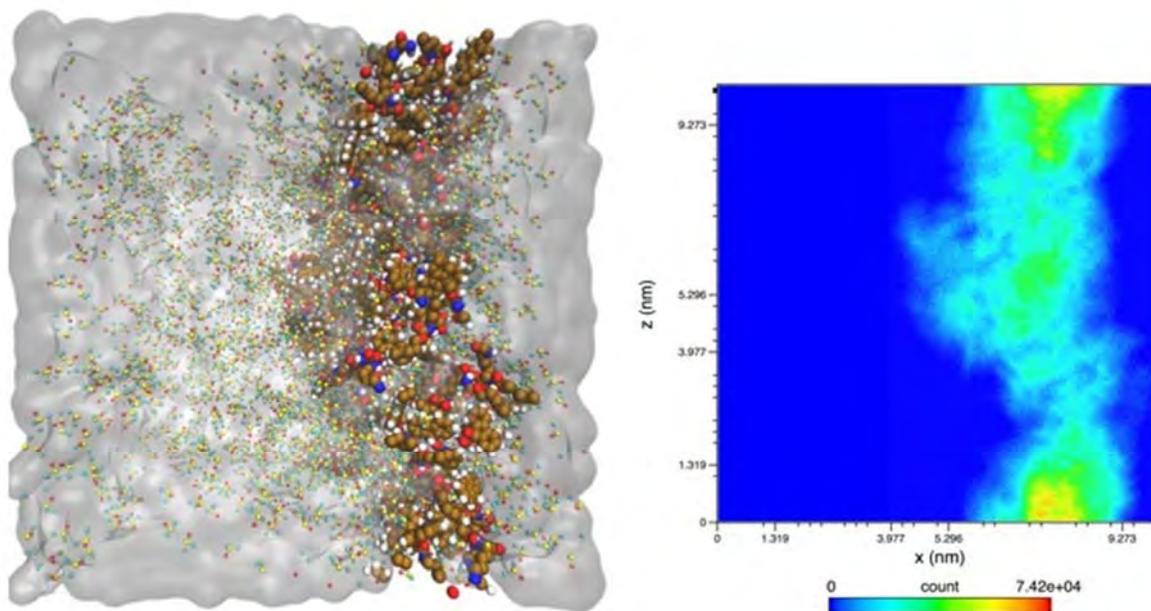


Hierarchy: Gel > Cluster > micelle > chain > junction

POLY 346: Molecular insights into early stage aggregation of molecular mass organic gelators

Neeraj Rai, neerajrai@gmail.com, Masrul Huda. *Chemical Engineering and Center for Advanced Vehicular Systems, Mississippi State University, Starkville, Mississippi, United States*

Molecular gels are formed by the supramolecular assembly of low molecular weight gelators (LMWGs) in organic solvents and/or water. Hierarchical self-assembly of small gelator molecules lead to three-dimensional complex fibrillar networks, which immobilizes solvent molecules and results in viscous solid-like materials or gels. These gels have drawn significant attention for their potential applications for drug delivery, tissue engineering, materials for sensors etc. However, self-assembly of gelator molecules into one-dimensional fibers is not well understood. Here, we present molecular dynamics study that provides molecular level insight into early stage aggregation of selected gelators in organic solvents and/or water. We will also present the effect of concentration of gelator and solvent on the self-assembly. These large scale molecular dynamics simulations provide useful glimpse of early stage aggregation.



POLY 347: Can percolation theory account for the aqueous gelation behavior of diblock copolymer worms?

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It is well-known that polymerisation-induced self-assembly (PISA) offers a versatile and efficient synthetic route for the production of highly anisotropic methacrylic diblock copolymer worms directly in aqueous solution. Such worms form thermoresponsive free-standing hydrogels that can (i) act as a 3D matrix for the culture of normal mammalian cells and (ii) induce stasis in human stem cell colonies. Herein we critically examine the aqueous gelation behavior of such copolymer worms in terms of recent advances in percolation theory for rigid rods, which explicitly account for the effect of rod length polydispersity. More specifically, we use small-angle X-ray scattering (SAXS) to determine the weight-average worm length L_w and the mean worm cross-sectional radius R : this enables a direct comparison to be made between the theoretical critical worm volume fraction required for gelation and the experimental worm volume fraction indicated by rheological measurements and tube inversion experiments. Bearing in mind that the copolymer worms are relatively flexible rather than rod-like, reasonably good agreement between these two parameters is observed. These findings are expected to have implications for the aqueous gelation behaviour exhibited by various other anisotropic particles, such as cellulose nanocrystals, small molecule (e.g. dipeptide) gelators and semicrystalline block copolymer rods.

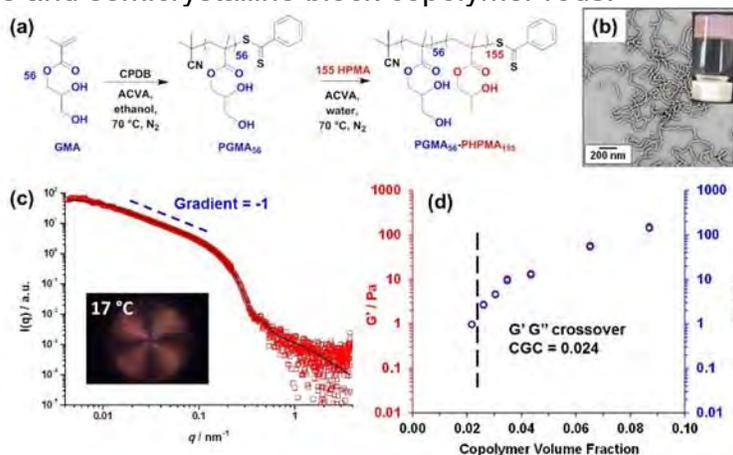
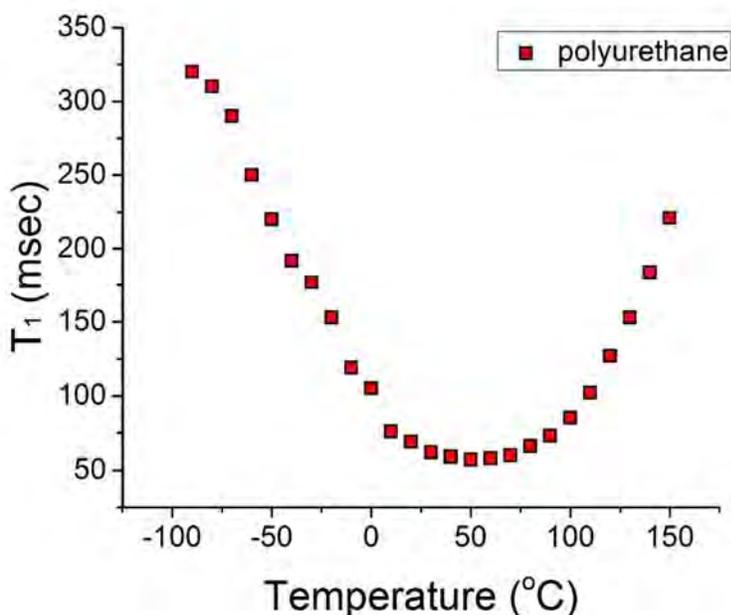


Figure 1. (a) PISA synthesis of PGMA₅₆-PPHMA₁₅₅ diblock copolymer via RAFT aqueous dispersion polymerization; (b) TEM image of PGMA₅₆-PPHMA₁₅₅ worms (inset: tube inversion test confirms formation of a free-standing gel by such worms); (c) SAXS pattern recorded for PGMA₅₆-PPHMA₁₅₅ worms at 17 °C fitted to a worm model (black line) [inset shows the characteristic Maltese cross motif observed via shear-induced polarized light imaging, which indicates birefringence owing to worm alignment]; (d) concentration dependence of G' and G'' obtained for aqueous dispersions of PGMA₅₆-PPHMA₁₅₅ worms as judged by oscillatory rheology.

POLY 348: The role of chain extender in controlling the kinetics of morphology development of polyurethane elastomers

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Polyurethanes have a broad range application such as foams, fibers, coatings, sealants, elastomers and others. This versatility is attributed to the ease with which their chemistry is tuned by changing stoichiometry or monomer type resulting in various interesting morphological features. Because of the different structures present, Polyurethanes generally exhibit a phase-separated structure. This originates from their multi-blocked chain structure composed of the relatively flexible soft segment and relatively rigid hard segment with short chain extenders. In this study, we seek to understand how changing the symmetry of the chain extender can influence the morphological development kinetics. 1,2-propanediol based chain extender was compared to other more traditional chain extenders on the kinetics of morphological evolution. The presence of the pendant group (methyl or phenyl) in the asymmetric chain extender structure altered the local segmental mobility of the hard segment structure. The different categories of chain extended polyurethanes have been characterized using thermal analysis, infrared and low field NMR. There are a large number of studies dealing with the formation of phase-separated morphology in polyurethanes. However, we found the low field NMR technique provided new information dealing with phase separation kinetics that complement with the well-established DSC and infrared analysis.

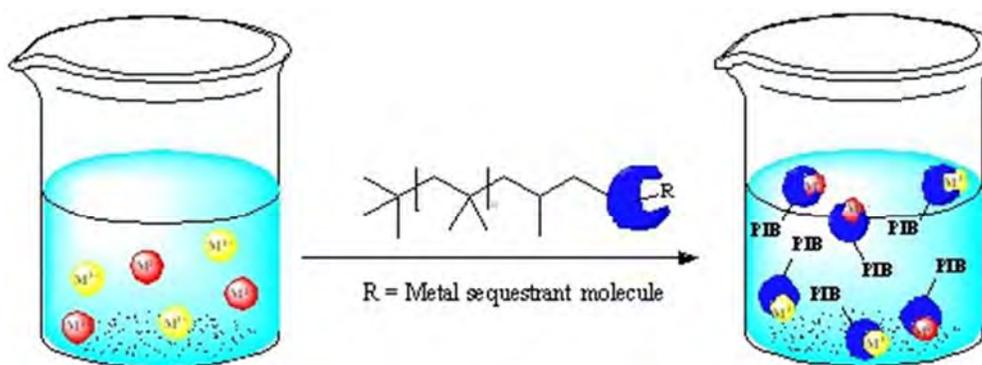


NMR relaxation of polyurethane as a function of temperature

POLY 349: Soluble polymer-supported bidentate sulfur ligand for metal sequestering

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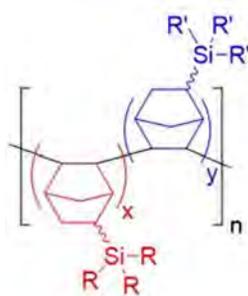
Whether it is industry, agriculture, research experiments, or just ordinary activities, modern societies in the 21st century produce unwanted waste. In some cases, this waste is concentrated and can be easily dealt with. In other cases, such waste can be minimized, this has been demonstrated in the development of environmentally benign syntheses that have used polymer-bound metal catalysts to minimize chemical waste in homogeneous catalysis. However, waste most often cannot be completely eliminated. Even if it is minimized, unwanted by-products from industrial or agricultural endeavor or from a modern city often end up in organic or aqueous waste streams in a highly diluted form. Herein, we report the use of Polyisobutylene (PIB) as a polymeric support for metal sequestration in organic solutions. PIB is functionalized to convert its terminal C=C into metal sequestering groups (carboxylic acid, thiol or amine group). The use of a cleavable linker to regenerate the PIB-sequesterant is also studied.



POLY 350: Enhancing the selectivity of addition-type polynorbornenes for post-combustion carbon dioxide sequestration

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Due to the rising levels of atmospheric CO₂, the development of energy efficient methods to separate CO₂ from power plant emissions has become increasingly important. Toward this goal, the use of passive membrane systems has emerged as a particularly intriguing method due to multiple advantages such as their inexpensive and easily processable nature. Recently, reports by our group and others have discovered that siloxane-substituted, addition-type polynorbornenes show tremendous promise for the separation of CO₂ from N₂, as well as the separation of light hydrocarbons. In an effort to elucidate the origins of their notable gas separation performance, we have conducted a detailed structure-activity relationship to better understand the interplay between their siloxane-based structure and their CO₂/N₂ permeation performance. These materials were synthesized using the catalyst *trans*-[Ni(C₆F₅)₂(SbPh₃)₂] and were successfully solution-cast into thin-film, defect-free polymer membranes. We observed that by increasing the concentration of certain comonomers that the membranes overall CO₂/N₂ selectivity could be increased substantially while CO₂ permeability only decreased by a very small amount. Our data will demonstrate that this drastic increase in CO₂ selectivity arises due to solubility selectivity, which is abnormal for most glassy polymer films, and defies the traditional “permeability/selectivity tradeoff.”



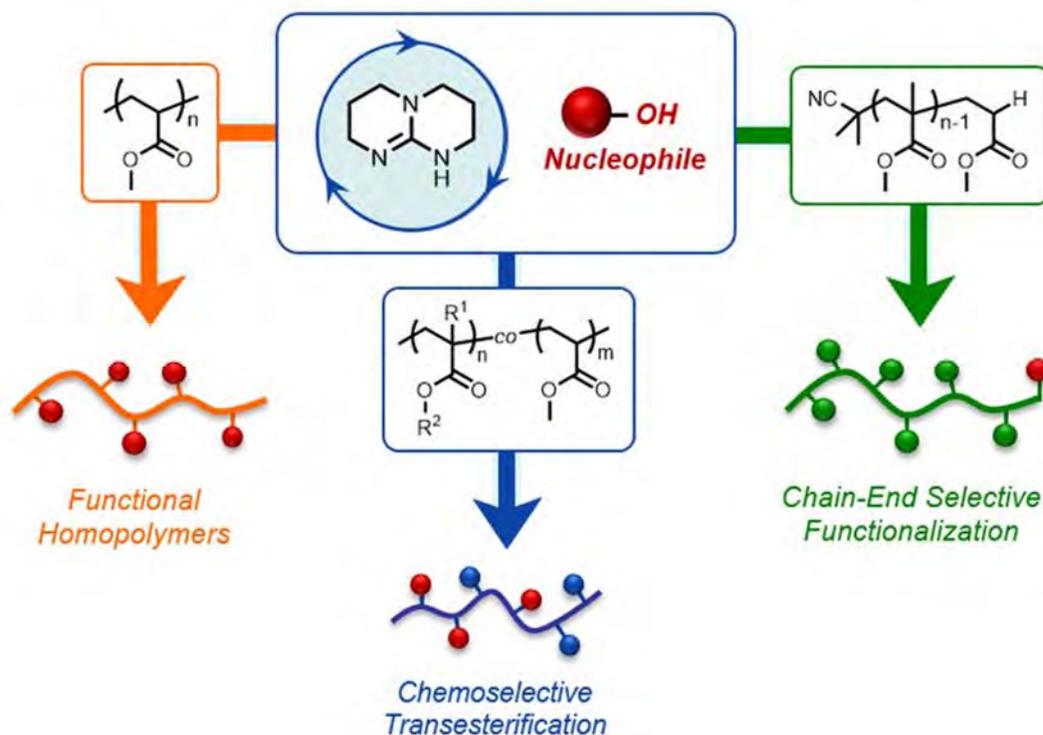
as [y] increases, polymer membranes:

- disregard traditional permeability/selectivity "trade-offs"
- dramatically increase CO₂/N₂ selectivity
- exhibit very small decreases in CO₂ permeability
- maintain excellent thermal stability and processability

POLY 351: Accessing functional materials through organocatalyzed post-polymerization modification

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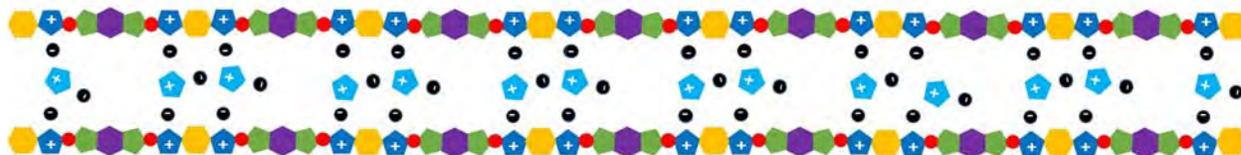
The direct modification of commercial polymers remains a strong challenge due to their benign chemical nature. Such synthetic methodologies would widen the range of foreseeable applications of chemically recycled waste by allowing access to functionalized products possessing properties different from the parent polymer material. We developed a strategy for achieving efficient functionalization of commercial polyacrylates such as poly(methyl acrylate) through the use of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) serving as a nucleophilic catalyst for acyl substitution. Furthermore, this strategy exhibits high chemoselectivity during ester activation and provides a convenient pathway towards site-selective polymer functionalization.



POLY 352: Ionenenes inspired by high-performance and ultra-high performance polymers

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We are exploring the synthesis of complex monomers and their subsequent polymerization to produce ionenenes with structural elements typically associated with high-performance and ultra high-performance polymers. Our methods take advantage of established chemistries that impart great control over repeat unit structure and regiochemistry. The resultant materials possess precisely alternating functionalities that can include multiple types/series of linkages (e.g. imide-amide). This presentation will focus on the design and synthesis of these highly tailorable materials, including discussion of their synthesis, thermal properties, interactions with ionic liquids, and potential application as advanced gas separation membranes.

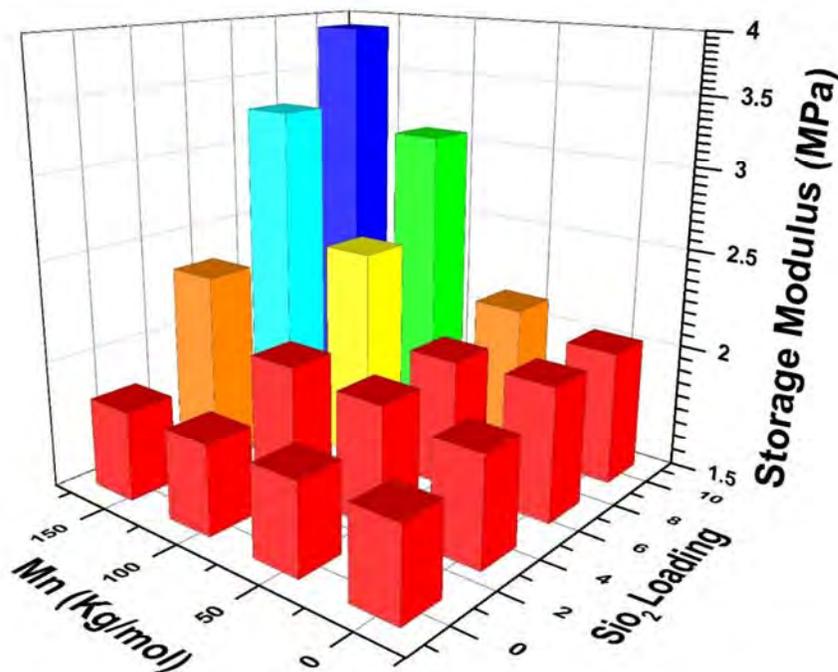


POLY 353: Reinforcement of industrial chloroprene rubber by polychloroprene grafted silica nanoparticles

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Improving rubbery materials has been done for many years by adding inorganic fillers to the base rubber. Carbon black and metal oxides are the most common types of fillers that have been used with rubbery materials. These fillers, combined with curing agents have remained the fundamental technique for achieving the unbelievable range of mechanical properties required for a wide variety of rubbery products in industry. The reinforcements of the rubbery materials have aimed on improving the rubber properties such as stiffness, modulus, rupture energy, tear strength, tensile strength, cracking resistance, fatigue resistance, and abrasion resistance.

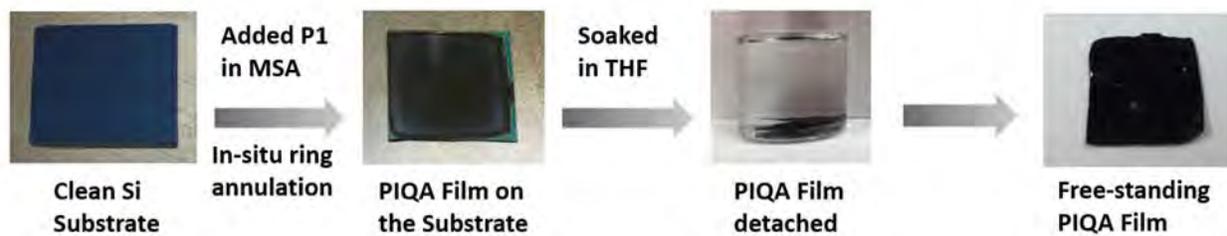
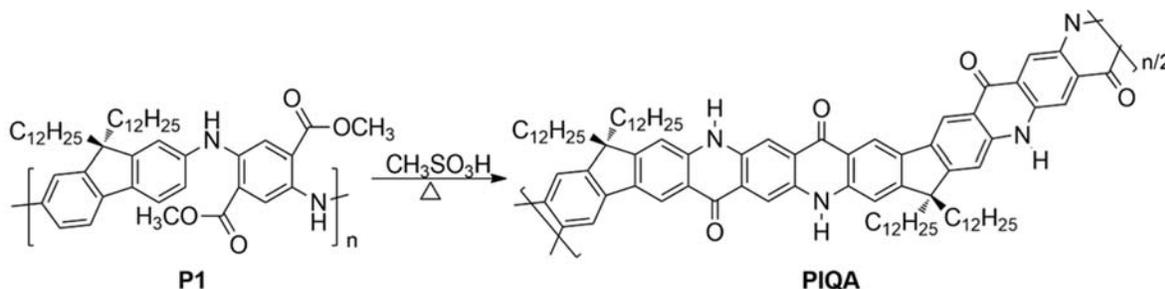
Two major factors that control the reinforcing mechanism of inorganic fillers with the rubber matrix is the dispersion into the matrix and the interaction between the rubber and fillers. In this work, polychloroprene grafted silica nanoparticles were used to prepare silica filled rubber nanocomposites. The effects of silica nanoparticles on the reinforcement of the composites was studied as a function of particle loading, dispersion of nanoparticles, and molecular weight of the grafted brushes.



POLY 354: Facile preparation of a free-standing hydrogen-bonded ladder polymer film

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Ladder polymers are an intriguing subset of macromolecules which possess excellent thermal, chemical, and mechanical stability. However, efficient synthesis and processing of such materials remained a challenge due to their low solubility in most solvents. Herein, we report a facile preparation method of free-standing films of a quinacridone-derived ladder polymer with intermolecular hydrogen bond. Highly soluble polymer precursor was dissolved in methanesulfonic acid and solution-casted onto a silicon substrate. After a one step ring annulation reaction, a ladder polymer free-standing film was formed and released from the substrate. Different solid-state characterization techniques were used to confirm the formation of desired product. The intermolecular hydrogen bond rendered this material excellent solvent resistance and mechanical property. This procedure avoided the separation and purification of the intermediate polymers, thus greatly reduced the use of solvents and working time.



Top: Synthetic route of preparing PIQA free-standing film through in-situ ring annulation. Bottom: Photographs of the procedures to prepare PIQA free-standing film.

POLY 355: Air-friendly synthesis of well-defined polypeptides by ring-opening polymerization of amino-acid derived N-thiocarboxyanhydrides

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α -Amino-Acid derived N-thiocarboxyanhydrides (NTAs) have notably enhanced thermal and moisture stability relative to the analogous N-carboxyanhydrides (NCAs), making the former attractive substrates for polypeptide synthesis. However, controlled polymerizations of NTAs have proven to be challenging, often resulting in limited conversions. Our recent studies have revealed that α -Amino-Acid derived NTAs can be polymerized with nearly quantitative conversions using simple primary amine initiators by suspending the monomer in non-polar solvents such as hexanes or heptane, producing a variety of polypeptides with controlled molecular weight ($M_n = 2.4 - 50.3$ kg/mol) and low-to-moderate molecular weight distribution (PDI = 1.2-1.3). Mechanistic investigation revealed that the high conversion in non-polar solvent is resulted from the suppression of isocyanate formation which terminates the chain growth in conventional solvents (e.g., dioxane or DMF). It was recently found that addition of acids can significantly improve the polymerization conversions of NTAs in dioxane and DCM and that the pKa of the acid has notable impact on the resulting polymer molecular weight and molecular weight distribution.

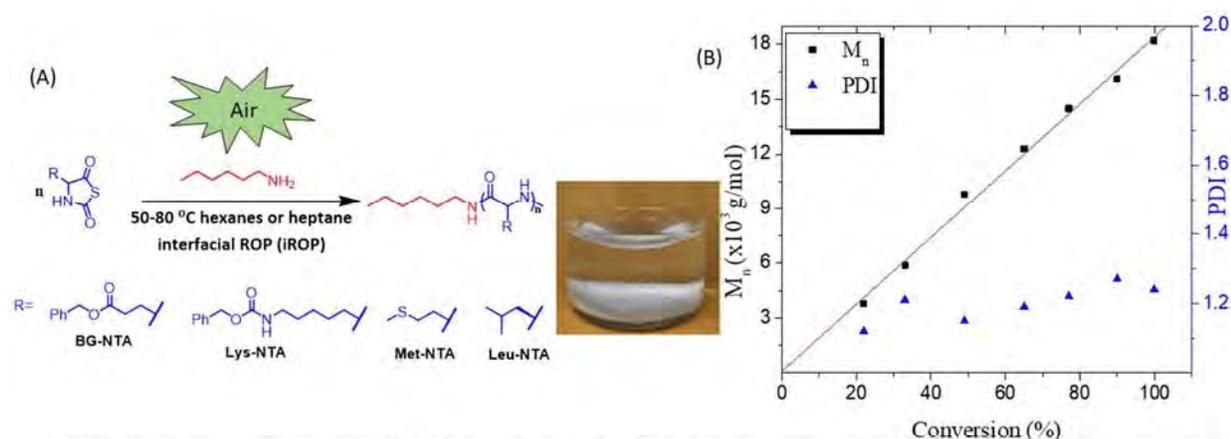
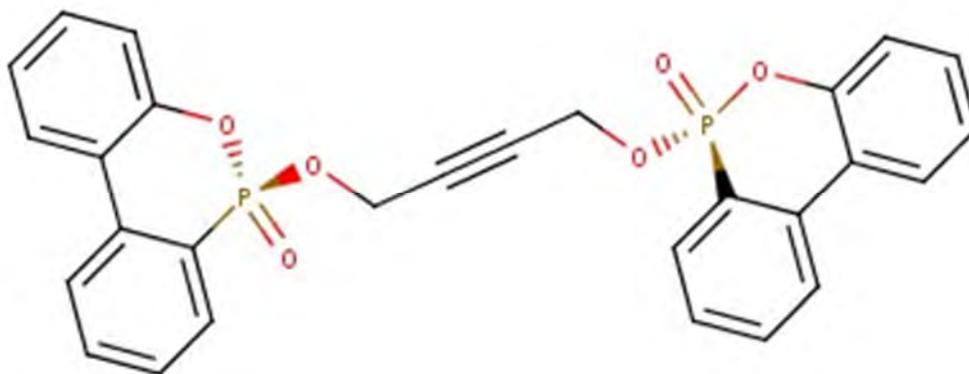


Figure 1: (A) Reaction scheme of ROP of amino acid derived NTAs using soluble primary amine initiators in hexane or heptane. (B) Plot of M_n (■) and PDI (▲) versus conversion for the iROP of BG-NTA with the linear fit (—) of the M_n versus conversion plot.

POLY 356: Impact of alkyne unsaturation on the flame retardant behavior of simple phosphorus diesters

Eric Ostrander, *Ostra2ea@cmich.edu*. Chemistry and Biochemistry, Central Michigan University, Mount Pleasant, Michigan, United States

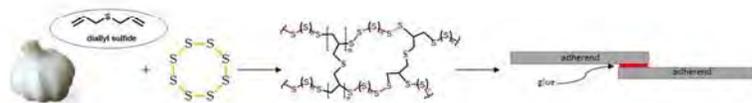
It has been suggested that the formation of alkyne unsaturation during the decomposition of flame retardants in a polymer matrix enhances the effectiveness of the additive. To test this potential directly a series of phosphorus esters derived from 2-butyn-1,4-diol have been prepared, characterized using spectroscopic and thermal methods, and evaluated as flame retardants in DGEBA epoxy. The effectiveness of these compounds could be compared to that of similar compounds from 1,4-butanediol, the full saturated analog. Results from laboratory scale flame tests [limiting oxygen index (LOI), UL-94 vertical burn test (UL-94), microscale combustion calorimetry (MCC)] suggest that both sets of compounds are effective flame retardants with the unsaturation compounds promoting some what more char formation during combustion.



POLY 357: Solvent-free formation of functional polymers by repurposing sulfur

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cljenkins@bsu.edu. Chemistry, Ball State University, Muncie, Indiana, United States

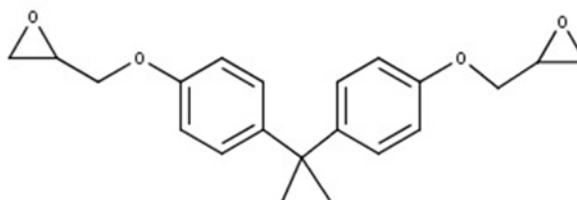
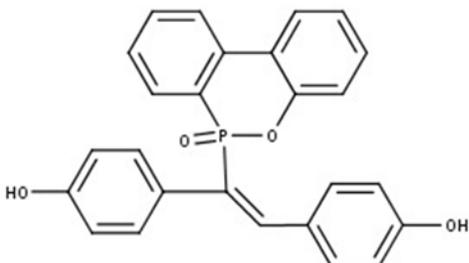
During petroleum refinement, organosulfur compounds in crude oil are converted to elemental sulfur for storage. Despite millions of tons being produced annually, elemental sulfur has very few uses. Inverse vulcanization, developed by the Pyun group, repurposes this waste into polymers. Heating sulfur above 159 °C generates free radicals that bind to monomers, creating high sulfur content polysulfides. Only a subset of monomers has been explored utilizing inverse vulcanization. Here, compounds found in garlic such as diallyl sulfide (DAS) were used. They are challenging to polymerize using standard methods but react readily in the presence of elemental sulfur at 180 °C forming poly(S-DAS). Polymer formation was confirmed by ¹H-NMR. Initially, these polysulfides were viscous liquids. Once cured, the copolymer hardened allowing repurposed industrial waste and natural monomers to function as an adhesive. Characterization by gel permeation chromatography (GPC) and differential scanning calorimetry (DSC) revealed higher molecular weights and higher glass transition temperatures upon curing. Viscous polysulfides were applied to aluminum adherends, cured at 160 °C, and tested in shear. Despite the many benefits of inverse vulcanization, high reaction temperatures preclude the use of many monomers. Once in a linear arrangement, however, sulfur radicals can form at much lower temperatures (80-100 °C) allowing polymers formed by inverse vulcanization, such as poly(S-divinylbenzene), to act as initiators. This work uses poly(S-DVB) to polymerize, solvent free, a broader range of monomers with much lower boiling points using relatively mild temperatures. Additional monomers with vinyl and allyl functional groups were incorporated with boiling points as low as 94 °C. Copolymers were examined by NMR, GPC, and DSC. Utilizing different monomers led to changes in reaction times, and material properties. Modifications enabled tailoring of their metal binding capabilities. Inverse vulcanization offers a solvent free method to create functional materials from the repurposed petroleum waste product, sulfur.



POLY 358: 1-Dopyl-1,2-(4-hydroxyphenyl)ethene as a flame retardant curing agent for epoxy

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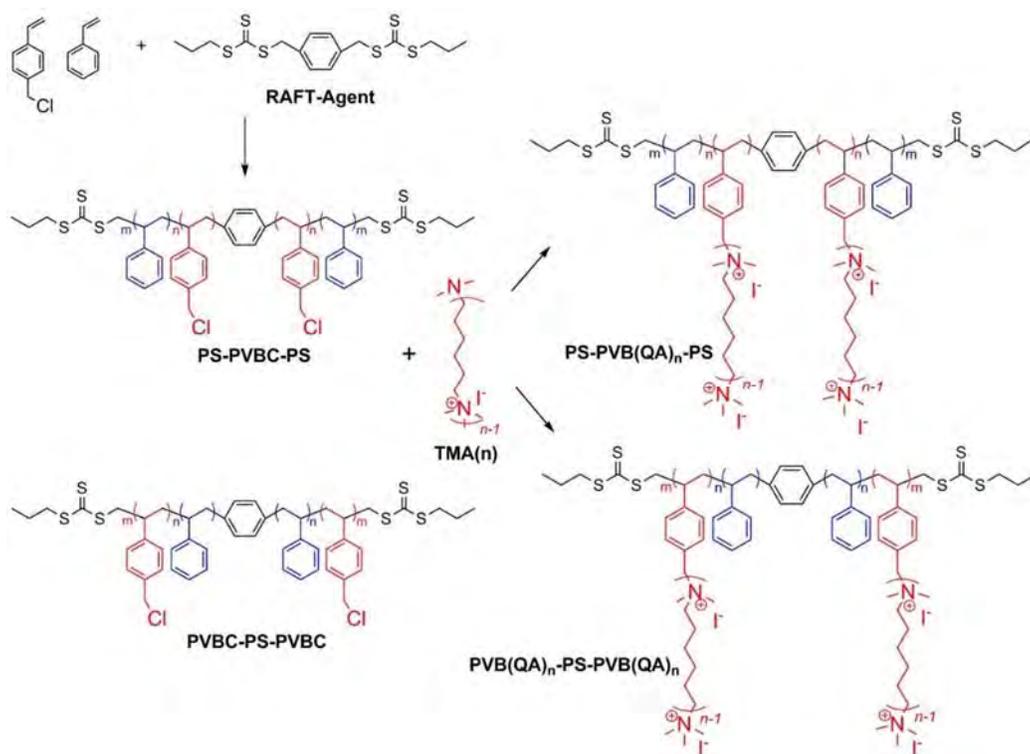
Epoxy resins represent a very important class of polymers. They find use in a wide variety of applications, notably as adhesives in the construction of electronics and other consumer goods. As with other organic polymers, epoxy resins are intrinsically flammable and must be flame retarded to ensure safety through the lifespan of the product. Traditionally this was accomplished using organohalogen compounds such as tetrabromobisphenol A and polybrominated diphenyl ethers. In recent years, health concerns associated with halogenated flame retardants have become apparent, creating an urgent need for replacement. Organophosphorus compounds have emerged as potential alternatives. Incorporating organophosphorus functionality into the backbone of an epoxy is an attractive option to prevent migration over time. To accomplish this, the diol 1-dopyl-1,2-(4-hydroxyphenyl)ethene was synthesized from desoxyanisoin and used as a curing agent for the diglycidyl ether of bisphenol A (DGEBA) epoxy resin.



POLY 359: Design and synthesis of highly stable triblock copolymers for anion exchange membrane fuel cells

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Anionic exchange membranes (AEMs) have recently been demonstrated to function in fuel cells with non-precious electrocatalysts, offering a viable path to commercialize fuel cells; however alkaline stability remains a major issue. AEMs contain fixed cationic charges that electrostatically interact with mobile anions, providing anions pathways to transport across the material. We are developing highly stable, symmetric poly(styrene)-*b*-poly(vinyl benzyl chloride) (PS-PVBC) triblock copolymers with densely packed, flexible multi-cation side-chains to address the conductivity – stability challenge facing AEMs. Our difunctional R-type RAFT agent allows the trithiocarbonate groups to remain at chain ends during polymerization, preventing degradation of triblocks to diblocks. The symmetric triblock design allows us to independently control architecture (ABA vs BAB) and block lengths. Substitution of multi-cation side-group is easily accomplished to boost conductivity and take advantage of the high alkaline stability provided by the styrenic backbone. The effect of cationic side-group content on phase segregation and the interrelationship between conductivity, alkaline stability and water management properties of the membranes will be discussed. To our knowledge, this is the first systematic study of how triblock architecture affects AEM properties. Additionally, flexible multi-cation chains employed in a block copolymer for the first time, that effectiveness of the cations improved due to dense packing of the multi-cation chains.



Synthesis route for ABA and BAB type triblock anion exchange membranes

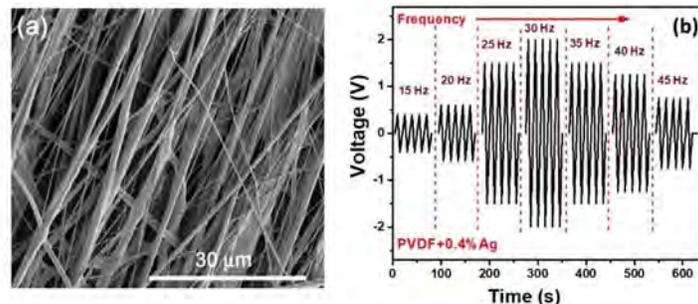
POLY 360: Poly(vinylidene fluoride) based nanocomposites: Dielectric, piezoelectric, and pressure sensing characteristics

Mohamed K. Hassan¹, mohammadhassan72@gmail.com, Ahmed A. Issa¹, Aisha Al-Saygh¹, Deepalekshmi Ponnamma¹, Mariam A. Al-Maadeed², Adriaan S. Luyt¹. (1) Center for Advanced Materials, Qatar University, Doha, Qatar (2) Material Sciences and Technology Program, Qatar University, Doha, Qatar

Poly(vinylidene fluoride) (PVDF) is a material with outstanding electro-activity and mechanical properties which mainly depend on the β -phase content and degree of crystallinity. To further improve these characteristics, a broad range of nanoadditives including cellulose nanofibers, titania nanolayers (TNL), silver nanoparticles (Ag-NPs), and reduced graphene oxide (rGO) were utilized. The nanocomposites presented herein were prepared using electrospinning and the simple solvent casting techniques. This presentation will discuss the preparation of different types of PVDF nanocomposites, using the above nanofillers, and the characterization of their piezoelectric, dielectric, and pressure sensing properties.

For the electrospun fibrous PVDF/Ag-NPs mats, the β -content in PVDF was found to increase by $\approx 8\%$ for Ag-NPs content of 0.4–0.6%. Dielectric analysis revealed weak interfacial adhesion between the PVDF and the Ag-NPs, however, good piezoelectric response was observed in the electrospun fibers containing 0.4% AgNPs, as indicated in the enclosed Figure. In case of the PVDF/cellulose nanofiber films, improvements in the extent of crystallinity and the β -phase content were thought to be related to the chain- and β -crystals orientation not to the presence and amount of cellulose in the nanocomposites. In addition, the dielectric storage permittivity increased with increasing cellulose content, but the presence of cellulose had no influence on the dynamics of the γ - and β -relaxations of the PVDF.

The PVDF/rGO-TNL composites, prepared by solvent casting, showed excellent flexibility, improved tensile strength and wettability, less roughness, when compared to the neat polymer. The composites exhibit good interactions and dispersion of the rGO and TNL additives in the matrix which increased the pressure sensitivity by 333.46% at 5 kPa, 200.7% at 10.7 kPa, and 246.7% at 17.6 kPa. The results confirmed the great potential of the PVDF/rGO-TNL composites in fabricating low cost and light weight pressure sensing devices and electronic devices with reduced quantity of metal oxides.

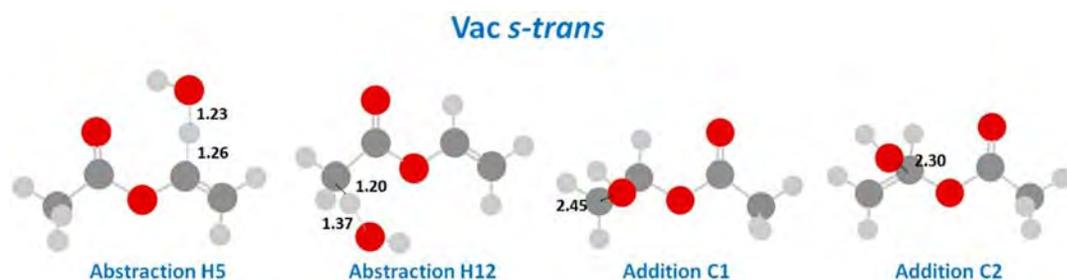


SEM micrograph of the PVDF/AgNPs electrospun fiber mat (a) and the piezoelectric response of the sample depicted in the voltage vs. time plot at different vibrating frequencies (b).

POLY 362: Calculation of oxygen-centered radical reaction rates in emulsion polymerization processes

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Scientists and engineers understand most of what happens during an emulsion polymerization process. However, secondary reactions with reactive radicals, particularly in the aqueous phase, still occur and are somewhat uncontrolled. Secondary reactions sometimes form branched monomers that may cause branching or crosslinking within the resulting polymer material. Fundamental research on the rates of secondary reactions will help control the formation of material that is detrimental to performance properties. Electronic structure methods are used to determine overall reaction rates of oxygen-centered radicals with acrylate monomer and vinyl acetate in the aqueous phase. Density-functional theory methods are screened to find the most accurate method. Extra consideration is used to compute rates of reaction involving sulfate radical due to the anionic nature of the species. Symbolic regression is applied to determine whether costly transition-state computations can be replaced by an empirical formula with descriptors found from electronic structure computations of isolated monomers.

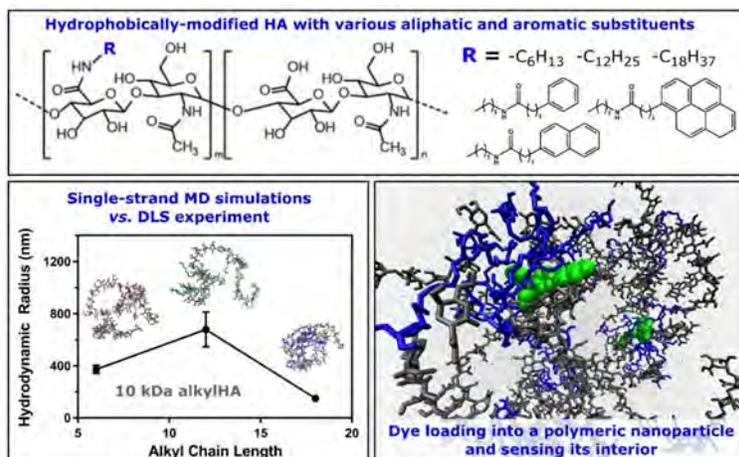


POLY 363: Self-assembly dynamics and inner morphology of hydrophobically modified hyaluronic acid nanoparticles: Towards design of optimized drug nanocarriers

Denis Svechkarev¹, denis.svechkarev@unmc.edu, **Alexander Kyrychenko**², **William Payne**¹, **Aaron Mohs**¹. (1) *Pharmaceutical Sciences, University of Nebraska Medical Center, Omaha, Nebraska, United States* (2) *Institute for Chemistry, V. N. Karazin Kharkiv National University, Kharkiv, Ukraine*

Development of new cancer chemotherapeutics and combination therapies using well-known front-line drugs stipulates a growing need for rational approach to design nanocarriers optimized for specific formulations. Computational methods, largely used in drug discovery, can play an important role in developing such materials. We hereby describe the dynamics of a series of hydrophobically modified derivatives of hyaluronic acid (HA) – a natural polysaccharide used for nanoformulations due to its biocompatibility. A combination of dynamic light scattering, fluorescent spectroscopy and molecular dynamics simulations are used to study their inner structure, hydration state, polarity and morphology of the hydrophobic domains formed inside the modified HA nanoparticles. The role of aliphatic and aromatic hydrophobic side moieties in the polymer self-assembly is discussed from the standpoint of intra- and intermolecular polymer-polymer and polymer-solvent interactions.

Simulation results show that longer alkyl side chains lead to formation of better defined hydrophobic domains within the polymer, as well as allow producing smaller nanoparticles with better monodispersity. Aromatic substituents, in contrast, do not show significant dependence of the nanoparticle characteristics upon the size of the hydrophobic ligand. Such derivatives do not form extensive hydrophobic domains – their self-assembly is rather driven by the pi-pi interactions, leading to stable aggregates similar to those produced using longer aliphatic side chains. The differences in nanoparticles morphology were confirmed by fluorescence spectroscopy experiments, where environment-sensitive ratiometric fluorescent dyes indicated higher hydrophobicity of their microenvironment inside the nanoparticles derived from alkyl-modified HA polymers. Results are discussed in context of design of optimal nanocarriers for drug formulations.



POLY 364: Real-time control and optimization: Demonstration in semi-batch emulsion polymerization

Wolfgang Gerlinger, wolfgang.gerlinger@basf.com, Omar Naeem, Ekkehard Jahns.
BASF SE, Ludwigshafen, Germany

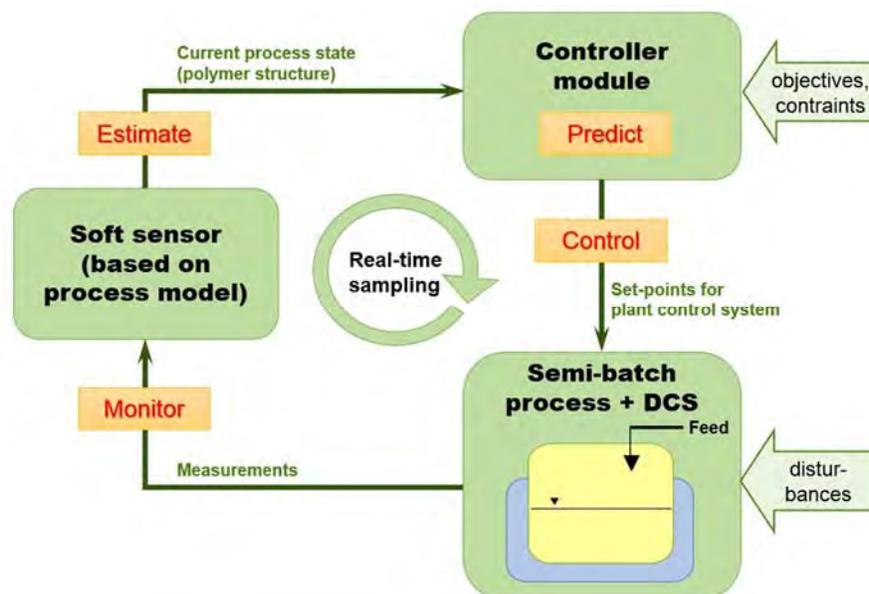
Nonlinear model-predictive advanced process control solutions are already existing for continuous processes, for instance in petrochemical industry. However, an implementation in a semi-batch polymerization process is still not standard yet. The few implementations for semi-batch polymerization processes deal mostly with in-silico case studies for simpler polymerization systems, but not much is described for more complex systems at pilot-plant or even at production scale.

Besides the intensification of semi-batch emulsion copolymerization processes advanced process control creates new opportunities for full-asset and resource utilization, model based optimization and control in real time and production of tailored products with desired properties.

The current presentation is focused on the development of advanced industrial optimization and control systems. By this, the semi-batch production can be shifted from a recipe-based to a state-based approach, by which batch-to-batch variations in production output and product quality can be minimized, and the reaction time can be reduced while keeping the safety constraints.

In an industrial implementation, the process model must be fast and robust enough to provide estimation of the process trajectory reliably and quickly. We focus on the practical aspects of on-line control and optimization for industrial semi-batch emulsion polymerization including the complexity of uncertainty in the model due to changes in monomer quality, fouling on heat transfer surfaces etc.

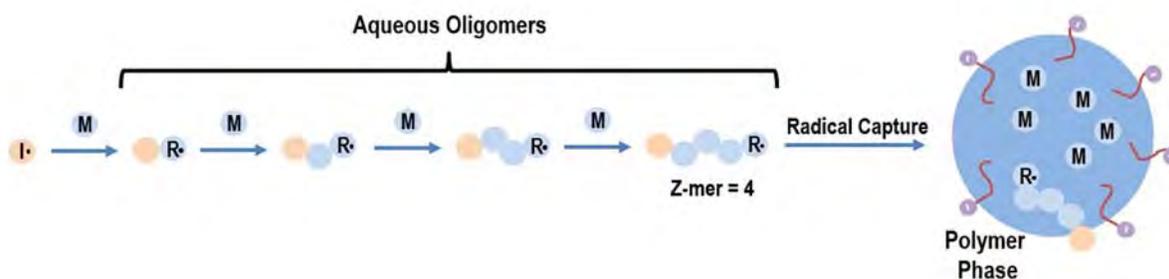
Pilot-scale demonstration of on-line control and optimization of semi-batch emulsion copolymerization involved testing of a simple temperature control, batch time optimization, and modification of product quality in the optimum batch time.



POLY 365: Z-mer lengths revisited with a modern phase behavior model

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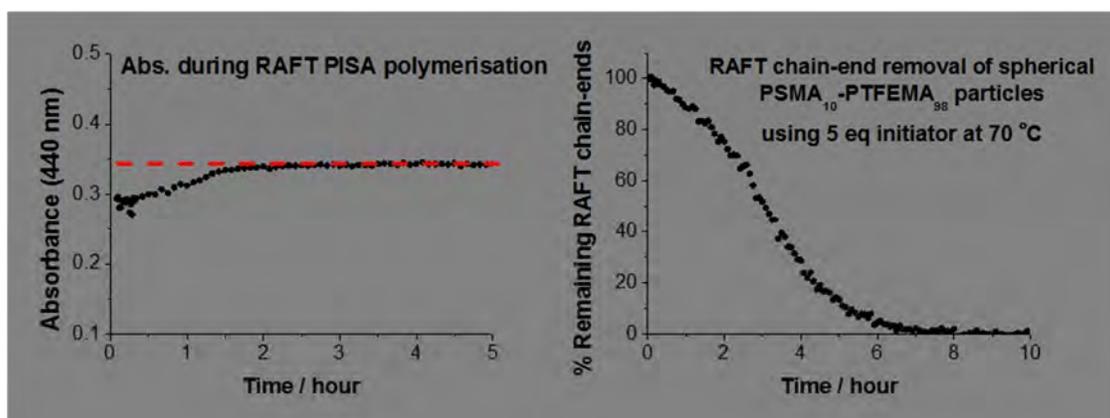
The phase behavior emerging from the mixture of monomer, polymer, water and initiator forms the environment in which high molecular weight polymer can be made economically. The particles resulting from polymerization are stabilized by both surfactants and the composition of polymer chains at the surface of the particle. Engineering the latex particles surface could reduce surfactant need for particle stabilization and help improve film formation. The composition of polymer chains at the surface of the particle is related to the aqueous phase polymerization and, in particular, to radical oligomers that reach critical length (z-mer) when they partition to the surface of the latex particle. More efficient z-mer partitioning to the surface translates to better control of the particle surface and increased radical flux for bulk polymerization. The partitioning behavior of z-mers is studied in this work. Z-mer lengths for homopolymer and copolymers of acrylate monomers are revisited with a modern phase behavior model.



POLY 366: In situ spectroscopic studies of highly transparent PSMA-PTFEMA diblock copolymer dispersions in non-polar media

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Over the past decade, polymerisation-induced self-assembly (PISA) has become a powerful technique for the synthesis of a wide range of block copolymer nano-objects, including spheres, worms, vesicles and lamellae. Herein we report the synthesis of highly transparent poly(stearyl methacrylate)-poly(2,2,2-trifluoroethyl methacrylate) (PSMA-PTFEMA) diblock copolymer nanoparticles via PISA in non-polar media. This was achieved by chain-extending a PSMA macro-CTA via reversible addition-fragmentation chain transfer (RAFT) dispersion polymerisation of TFEMA in *n*-tetradecane. This *n*-alkane solvent was selected because it has the same refractive index as the PTFEMA core-forming block, which allows highly transparent dispersions. This enables visible absorption spectra to be recorded with minimal light scattering. Moreover, focusing on a very weak forbidden band at 440 nm, assigned to the trithiocarbonate-based RAFT end-group, and a suitable optical probe allows a series of spectra to be recorded *in situ* during PISA. Thus, the living character of this RAFT dispersion polymerization can be assessed throughout the TFEMA polymerization. More specifically, the significant contraction in the reaction solution volume that occurs when converting TFEMA (1.18 g cm^{-3}) into PTFEMA (1.47 g cm^{-3}) leads to an *increase* in absorbance at 440 nm that can be used to monitor the progress of the polymerization. Once high TFEMA conversions ($> 95\%$) are attained, this absorption band becomes constant for at least 3 h at $90 \text{ }^\circ\text{C}$, indicating remarkably high RAFT chain-end fidelity even under monomer-starved conditions. At the end of such PISA syntheses, the kinetics of RAFT chain-end removal can be monitored by visible absorption spectroscopy after addition of excess initiator at $70 \text{ }^\circ\text{C}$. This eventually resulted in complete discoloration of the dispersion, with small-angle X-ray scattering (SAXS) studies confirming no change in morphology under these conditions. Finally, using the TFEMA monomer also enabled *in situ* ^{19}F NMR spectroscopy studies to be conducted during this RAFT dispersion polymerization: these experiments provided (i) direct evidence for the onset of micellar nucleation and (ii) subsequent solvation of the growing PTFEMA core-forming chains by the unreacted TFEMA monomer.



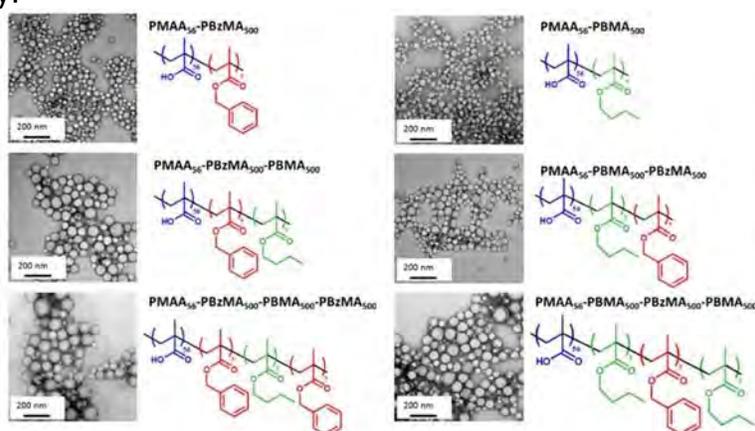
POLY 367: Multiblock copolymer nanoparticles synthesized via RAFT aqueous emulsion polymerization using a high-throughput robot

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High-throughput experimentation is well established in pharmaceutical research. More recently, it has been applied to polymer science, not least because a large number of parameters can be screened during synthesis. One rapidly growing area of polymer science is the synthesis of a wide range of diblock copolymer nanoparticles via polymerization-induced self-assembly (PISA). In the present work, reversible addition-fragmentation chain transfer (RAFT) aqueous emulsion polymerization formulations were optimized for use in conjunction with a high-throughput Chemspeed A100 robot. More specifically, a poly(methacrylic acid)-based macro-CTA (PMAA₅₆) was chain-extended in turn using benzyl methacrylate (BzMA), *n*-butyl methacrylate (BMA), methyl methacrylate (MMA) or (4-hydroxybutyl methacrylate (HBMA)); this series of four methacrylic monomers was deliberately selected to cover a range of monomer solubilities and densities. Optimized reaction conditions utilized a propeller stirrer at 550 rpm targeting a core-forming block DP of 500 in mildly acidic aqueous solution (pH 5) at 70 °C.

In a second series of experiments, a small library of various triblock and tetrablock copolymer nanoparticles were prepared via a one-pot PISA protocol using sequential monomer addition. In this case, the same PMAA₅₆ macro-CTA was chain-extended with BzMA, followed by BMA and then (in the case of the tetrablocks) BzMA, with each insoluble block having a target DP of 500. The order of the core-forming blocks was also reversed; the PMAA₅₆ macro-CTA was chain-extended first with BMA, followed by BzMA and then BMA. Such PISA syntheses were completed within 3 h for the triblocks (40 w/w % solids; final conversions = > 99 %) and 5 h for the tetrablocks (45 w/w % solids; final conversions ranging from 88 to 97 %). TEM and DLS studies confirmed that colloiddally stable spherical nanoparticles were obtained in all cases.

These preliminary studies provide the basis for further high-throughput screening of RAFT-mediated PISA formulations, which is likely to be required for commercialization of this technology.



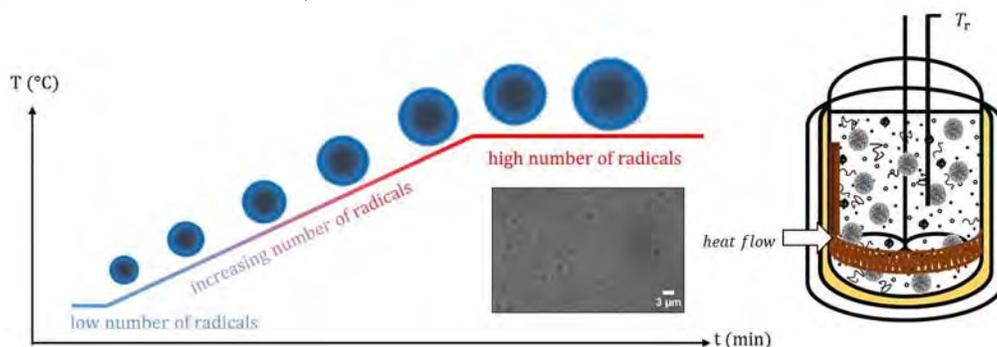
POLY 368: Synthesis of micron-sized poly(*N*-Vinylcaprolactam) microgels by temperature-ramp polymerization

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Microgels are cross-linked polymer networks that can respond to environmental change like temperature or pH. When triggered, they collapse or swell in a solvent, preserving their 3D structure. Micron-sized microgels can have plenty of interesting applications in crystallization studies, microlensing or mimicking cells. Microgels with size above 10 μm can be synthesized using microfluidics. However, very low yields and specific equipment requirements lead to high demand on synthesis of microgels via dispersion polymerization approaches. Moreover, the typical size of micro/nanogels synthesized using standard batch polymerization reactions is in nanometer scale. Thus particles ranging from 1 to 10 μm are not easily reachable and means to obtain them need further investigation.

For the first time, we have synthesized temperature-responsive poly(*N*-Vinylcaprolactam) (pVCL) microgels with large diameter (1 -10 μm) via aqueous, surfactant-free precipitation polymerization. The size control was achieved by employing programmed temperature ramp during the nucleation stage of polymerization. Micron-sized poly(*N*-Isopropylacrylamide) (pNIPAm) microgels have been obtained previously, however known toxicity and suspected cancerogenicity of pNIPAm disqualifies the usage of these gels in medical applications. In contrast to pNIPAm, pVCL is non-toxic and biocompatible, making it a great candidate in medical and biomaterial fields.

In this work, the influence of various parameters such as monomer, cross-linker and initiator concentration, rate of temperature ramp, start and end temperature as well as dosing of the reagents was investigated. We were able to obtain microgels in different size ranges, depending on parameters altered. To best characterize such big but soft particles, laser diffraction particle sizing technique as well as confocal microscopy were utilized. Consequently this study hopes to give more insight and understanding about the formation mechanism of larger pVCL microgels. For this purpose, in-situ dynamic light scattering measurements as well as in-line reaction calorimetry, where heat flow of the reaction can be monitored, were carried out.



POLY 369: Microfluidically produced microgels with biomedical applications

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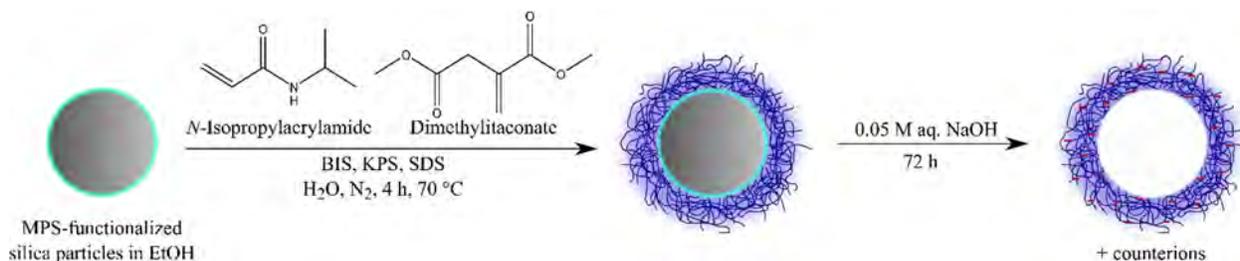
Microgels present interesting materials for uptake and release of biomedically relevant molecules. Microfluidic liquid handling allows for precise allocation of compounds and functional groups during microgel synthesis. We present microgel precursor systems based on polyethylene glycol, which enable fast crosslinking dynamics and can be used to produce capsules and microgels. Microfluidic synthesis allows the creation of monodisperse microgels in the range of tens to hundreds of micrometers in diameter. We investigate the retention potential of microgel capsules and the uptake kinetics for full microgels toward biomolecules. We can equip these microgels during their microfluidic synthesis with glycan recognition motifs to which lectins bind selectively. We find cooperative binding modes, where at least two glycans bind one lectin, accounting for binding affinity as good as: $K_d = 1.06 \mu\text{M}$. The microgels present interesting materials for the uptake and binding of bacterial toxins in the body, for example, as alternative cures for *C. difficile* induced colitis.

POLY 370: Hollow charged microgels: Structural investigations by SANS

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Hollow microgels have the potential to meet one of the key challenges in biomedical research: The design of nano-carriers allowing for triggered uptake, storage and release of drugs. Temperature-sensitivity of the polymer enables a temperature-controlled permeability of the shell. Introduction of charges into the polymeric network leads to additional responsiveness to pH or osmotic stress.

In this work, we address the synthesis of hollow charged microgels and the investigation of their applicability for uptake and release of charged guest molecules. *N*-isopropylacrylamide (NIPAM) is copolymerized with dimethylitaconate (DMI) onto sacrificial silica cores in a seed and feed precipitation polymerization. Sodium hydroxide is used to etch the silica cores and to saponify the DMI to itaconic acid introducing negative charges into the shell. We analyze the pH-dependent behavior of charge density and hydrodynamic radius. Additionally, small-angle neutron scattering is used to study the internal structure of these microgels, proving that the void remains for the charged and the uncharged state of the microgel. Furthermore, the suppression of the temperature-sensitive collapse of the shell due to the presence of charges is demonstrated.



General scheme of the synthesis procedure for hollow charged microgels: Silica particles as sacrificial cores used as seeds in a precipitation polymerization of *N*-isopropylacrylamide with dimethylitaconate. Addition of sodium hydroxide leads to the dissolution of the silica and to saponification of the ester.

POLY 371: Design and synthesis of rotaxane crosslinked polymeric microspheres

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In this study, we focused on the crosslink structure in the soft microsphere, and we made microsphere crosslinked with rotaxane structure.

In the soft and deformable elastomer microspheres case, it can be used to generate colorless transparent films by upon evaporating the solvent from dispersions of colloidal microspheres. We discovered that tough elastomer microspheres that are crosslinked with rotaxanes can form tough and stretch bulk films upon evaporating of water from microsphere dispersions, without post-polymerization reactions (Figure).

In the soft gel microspheres (microgels) case, it dual-responsive smart microgels, where thermo-responsive polymers are cross-linked by rotaxane networks, were developed. Although charged monomers, which usually afforded the pH-responsiveness for such material, were not used, the rotaxane cross-linked microgels respond to change in pH value and temperature.

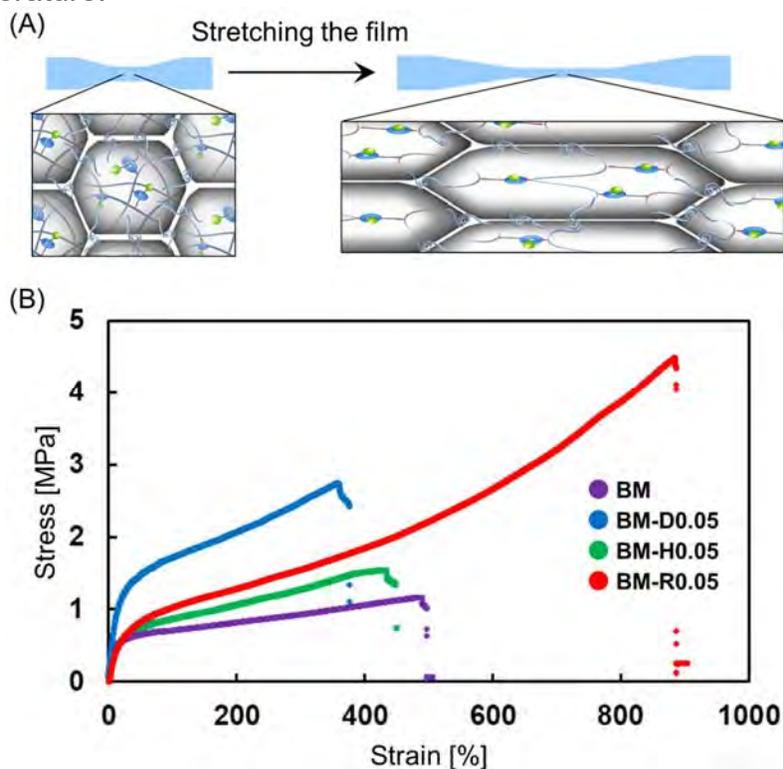


Figure (A) Schematic illustration the film of rotaxane-crosslinked elastomer microsphere (B) Stress-strain curves for films prepared from microspheres without a crosslinker (purple), for films using 0.05 mol% divinylbenzene (DVB, blue), for films using 0.05 mol% 1,6-hexanediol dimethacrylate (HDD, green), or for films using 0.05 mol% Rotaxane crosslinker (RC, red).

POLY 372: Interplay of spatially separated polymeric shells in doubly thermoresponsive microgels in presence and absence of an incompressible core

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Hollow microgels reveal promising properties for applications as novel carrier systems. The combination of two spatially separated polymeric shells with distinct volume phase transition temperatures (VPTTs) in water lead to an advanced responsiveness which enables the separate control of the interactions between both the microgel and its surrounding and the microgel and possible guest species inside the cavity. This makes these microgels highly interesting as potential thermoresponsive nanocapsules.

Here, doubly thermoresponsive microgels with an inner poly(N-isopropylmethacrylamide) shell and an outer poly(N-isopropylacrylamide) shell are studied in presence and absence of a stiff silica core. Above, below and between the distinct VPTTs of the two polymers, small-angle neutron scattering with contrast variation reveals different responses of the core-double-shell and the corresponding hollow microgels. The former show a strong interpenetration of the polymeric shells when the outer network is collapsed while the inner shell is already swollen. We observe an increase of the polymeric volume fraction above the volume fraction of the microgel in the complete deswollen state. As predicted by our computer simulations, an appropriate choice of cross-linking density, leads to the generation of pitted double-shell nanocapsules which maintain an inner cavity independently on the swelling state of the shells (see figure).

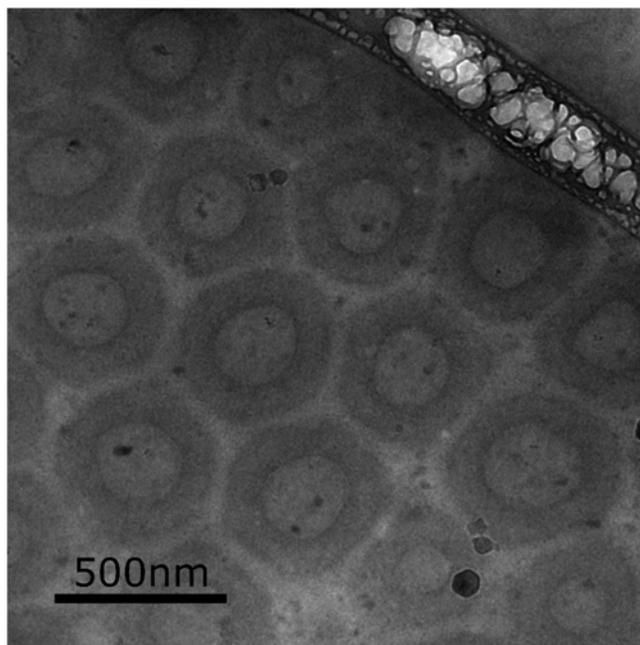


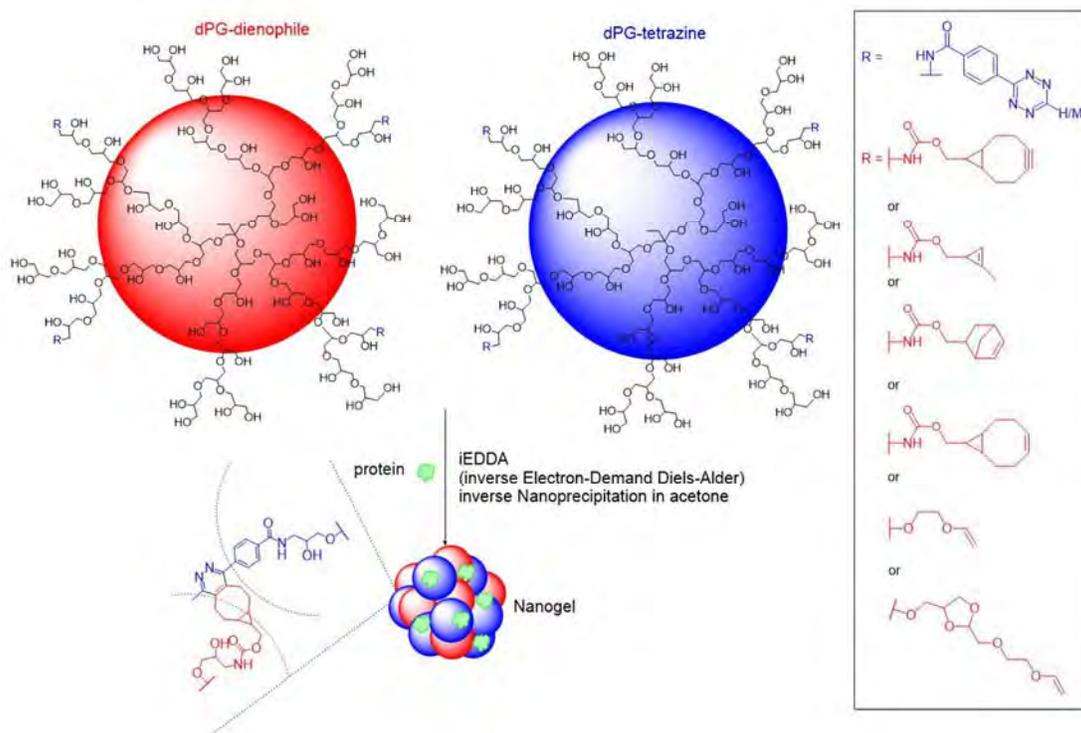
Figure: Cryogenic transmission electron micrograph of hollow double-shell microgels.

POLY 373: Bioorthogonal preparation of dPG-based nanogels using iEDDA inverse nanoprecipitation

Alexander Oehrl, alexandero@zedat.fu-berlin.de, Rainer Haag. Department of Chemistry, Biology and Pharmacy, Freie Universität Berlin, Berlin, Germany

The development of nanocarrier systems for targeted therapeutics and improvement of plasma half-lives and immune evasion of proteins includes the necessity of a suitable linker strategy for the synthesis of the carrier and for conjugation of targeting ligands. Click chemistry is playing a major role in this field due to reaction rates, selectivity and orthogonality to biological systems. Especially strain-promoted azide-alkyne cycloaddition (SPAAC), introduced by Bertozzi *et al.*, was and still is one of the most important coupling strategies within biological systems, e.g. cell staining or antibody conjugates. However, this strategy suffers from specific drawbacks, as the strained alkynes are obtained through tedious synthesis and show some reactivity towards free thiols of proteins, rendering SPAAC not completely bioorthogonal.

Recently, another click approach utilizing inverse electron-demand Diels Alder (iEDDA) has emerged. Based on electron-deficient tetrazine derivatives and electron-rich olefins, it is used in this work as a linker strategy for the formation of nanogels from functionalized dendritic polyglycerol (dPG) scaffolds by inverse nanoprecipitation. Therefore, some novel dPG-olefin derivatives as well as literature known derivatives are synthesized and compared regarding their ability to allow fast and stable nanogel formation. The strategy is also currently employed to evaluate the bioorthogonal encapsulation of therapeutic proteins.



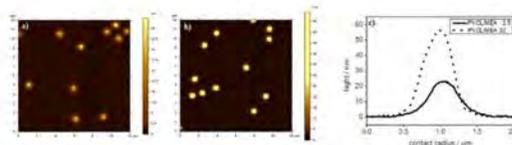
POLY 374: Microgels decorated with 2-methoxyethyl acrylate as new building block for biomaterials

Andrea Melle^{1,2}, melle@pc.rwth-aachen.de, **Sheila Moli**¹, **Laura De Laporte**¹, **Walter Richtering**², **Andrij Pich**¹. (1) DWI-Leibniz Institute for Interactive Materials, Aachen, Germany (2) Physical Chemistry, RWTH Aachen University, Aachen, Germany

Novel, biocompatible, thermo-responsive microgels are synthesized by surfactant-free precipitation copolymerization of *N*-Vinylcaprolactam (VCL) with 2-methoxyethyl acrylate (MEA). MEA is chosen because PMEA is known for his excellent blood compatibility and low protein adsorption and therefore already in use as coating for artificial organs.

Using optimized precipitation polymerization procedure, up to 32 mol% of MEA can be incorporated into PVCL-based microgels without loss of colloidal stability. Via Raman-Spectroscopy the microgel composition is quantified. Both, calorimetric measurements and a high resolution transverse relaxation NMR study deliver that MEA is located mainly in the microgel shell due to its lower polymerization rate in comparison to VCL. The swelling degree of the microgels decrease with increasing comonomer content. This behavior can be explained by the temperature-responsivity of both monomers: While pure PVCL microgels exhibit a VPTT = 32 °C, linear PMEA has a very low LCST = 0-5 °C. It follows that the microgel shell is already collapsed at room temperature which prevents the swelling of the PVCL-rich core. Consequently, the PVCL/MEA microgels become more rigid and less temperature-sensitive with increasing MEA-content. While the particles with low MEA-content exhibit a core-shell like structure which indicates that the core is denser than the shell, the particles with high MEA-content are rigid and compact that could be approved by AFM measurements (see Figure).

Furthermore, the protein repellent properties of microgel films are investigated. High protein repellence can be obtained for PVCL/MEA microgels, as expected. Cytotoxicity tests with L929 mice fibroblasts show good cell proliferation on PVCL/MEA microgel films that indicates the high biocompatibility of these microgel films. Due to the switchability of PVCL/MEA microgel films from a hydrophobic (collapsed state, cell attachment) to a hydrophilic surface (swollen state, cell repellance) by temperature change, these microgel films can be used for non-invasive cell recovery.



AFM micrographs of PVCL/MEA 3.5 (a) and PVCL/MEA 32 (b) with the appropriate height profiles (c).

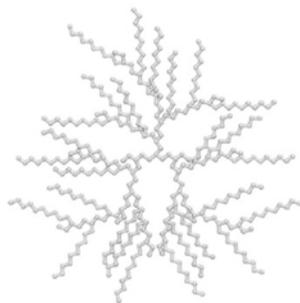
POLY 375: Arborescent polymers via living radical polymerization

Robin R. Höhner, *robin.hoehner@rwth-aachen.de*, Jens Köhler, Helmut Keul, Martin Moller. RWTH Aachen University, DWI – Leibniz Institute for Interactive Materials and Institute of Technical and Macromolecular Chemistry, Aachen, Germany

Arborescent, or Comb-Burst® polymers are different words for the same polymer architecture from the dendrigraft family which can be described as treelike. The use of living or controlled polymerization techniques enables the production of linear core polymers. Post functionalization of the core polymer leads to a linear core polymer with either coupling or initiating sites. Grafting onto or grafting from these sites results in a graft copolymer. This graft copolymer is named the 0. generation of an arborescent polymer. Followed by another functionalization and grafting step, an arborescent polymer of 1. generation is built up. Repeating the functionalization and grafting step iteratively, arborescent polymers of higher generations are manufactured.

Since a high reaction control is necessary, synthesis of arborescent polymers is mainly limited to ionic polymerization techniques. Most commonly ionic polymerization followed by functionalization with coupling sites is performed. Subsequently, branches are introduced by grafting onto the coupling sites.

Here, we present the synthesis of arborescent polymers using controlled radical polymerization. Radical polymerization enables the use of acrylates and methacrylates. Furthermore, the reaction conditions are mild and water can be used as solvent. Based on computersimulations these (meth)acrylate based arborescent polymers promise, interesting behavior at interfaces. Post crosslinking of arborescent polymers leads to microgel like structures. Knowledge of the crosslink density and sequence length, enables to study the influence of flexibility in the transition from arborescent polymers to microgels.



Computersimulated arborescent polymer of 1. generation.

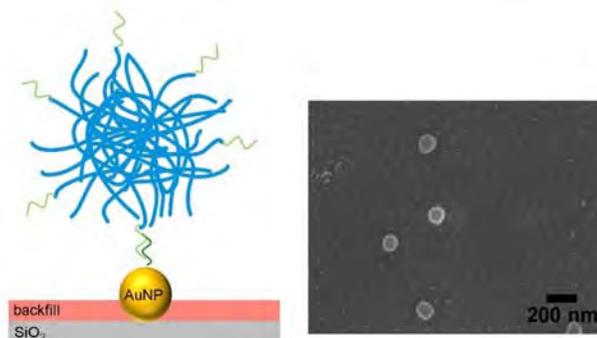
POLY 376: Directed immobilization of thermo-responsive functionalized microgels via DNA

Sabine Eisold¹, *sabine.eisold@ac.rwth-aachen.de*, Catalina Molano Lopez², Ahn Quang Tran⁴, Alex Oppermann³, Dominik Wöll³, Dirk Mayer⁴, Andrij Pich², Ulrich Simon¹. (1) Inorganic Chemistry, RWTH Aachen University, Aachen, Germany (2) DWI-Leibniz Institute for Interactive Materials and Institute for Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany (3) Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany (4) Institute of Complex Systems (ICS-8), Forschungszentrum Jülich GmbH, Jülich, Germany

Water-swollen microgels (MGs) with complex architectures, being soft, deformable and with smooth interfaces are emerging polymer colloids for advanced materials. In order to characterize the structure and dynamics of individual MG structures, their directed immobilization is necessary. We report the synthesis of DNA functionalized poly(N-vinylcaprolactam-co-N-(methacryloxy)succinimide) MGs. The MGs were synthesized by a precipitation polymerization process and single stranded, amine-terminated DNA (ssDNA) was coupled to succinimide groups of the MGs. Thereby the thermal-responsiveness of the DNA-MGs is retained.

To achieve the directed immobilization of individual MGs onto a solid support, gold nanoparticles (AuNPs) were deposited with well-defined inter-particle distances. Prior to functionalizing the AuNPs with ssDNA having a base sequence complementary to the DNA-MGs, a highly fluorinated backfill covering the inter-particulate surface of the wafer was introduced. This backfill reduces unspecific binding of the hydrophilic MGs and minimizes the interaction of immobilized MGs with the substrate. The immobilization of the MGs onto the substrates was realized by sequence specific DNA hybridization. Thus, immobilization is highly controllable and reversible. We characterized the immobilized MGs by scanning electron microscopy (SEM) as well as atomic force microscopy (AFM) and revealed that the immobilized MGs retain in their spherical shape.

In an analogous procedure the DNA-MG were immobilized on glass substrates and functionalized with fluorescently labeled DNA. This allows imaging individual MGs by means of superresolution fluorescence microscopy, whereby the MG remain in the close-to-solution state.



Left: Scheme of DNA-MG on AuNP-decorated SiO₂ support with highly fluorinated backfill.

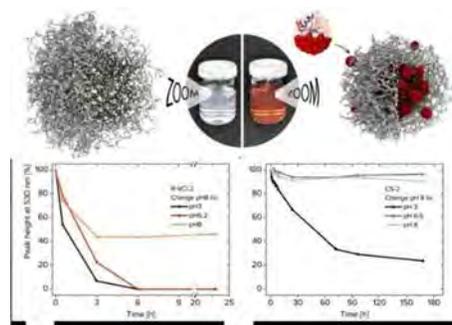
Right: SEM image of immobilized DNA-MGs .

POLY 377: Distribution of ionizable groups in polyampholyte microgels controls interactions with captured proteins: From blockade and "levitation" to accelerated release

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Polyampholyte microgels as container systems to entrap guest molecules like proteins, dyes or nanoparticles has been intensively studied in the past years and has also drew great attention in the field of bio-medical application. This kind of smart materials are extremely interesting due to their facile functionalization and their high bio-compatibility. Additionally, the functionality of such microgels can be controlled by the applied monomers and crosslinker density during the synthesis. In this way the properties of the particles and the response to outer stimuli can be tuned. Proteins tend to attach into microgel systems through chemical- (covalent) or physical- (electrostatic) binding. The latter one has attracted more attention since it offers the opportunity to achieve an efficient binding and triggered release in the surrounding medium via electrostatic interactions.

In this content we aimed to synthesize polyampholyte microgels with different structures (random or core-shell distribution of ionizable groups and Janus-like microgels). Furthermore the influence of outer stimuli (pH, temperature, salt concentration and different medium) to the interaction between the model protein cytochrome c and the synthesized microgels was studied. Also, we demonstrate for the first time that the distribution of the ionizable groups in the microgels (random vs. core-shell) also has a strong influence to the release procedure of the proteins. Once the proteins were entrapped inside the microgel containers at pH 8 by electrostatic attraction forces (protein and microgels are oppositely charged at pH 8), they remain strongly bound and show no leaching effects for months. An effective triggered release can be achieved by variation of the pH value (from pH 8 to pH 3, at pH 3, protein and microgels are equally charged) of the surrounding medium. Computer simulations were carried out to support the experimental results of the electrostatic nature of uptake and release of the proteins and their trapping by core-shell microgels.



POLY 378: Synthesis of hydrogel/solid composite microgels by seeded emulsion polymerization in the presence of polyelectrolytes microgels

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Hydrogel particles, or microgels, are composed of cross-linked hydrophilic (or amphiphilic) polymer chains and they were used for a variety of applications because of their specific properties such as high colloidal stability, softness and stimuli-responsivity. Since Pelton and Chibante first prepared a uniform poly(*N*-isopropylacrylamide), pNIPAm microgels, variety types of composite microgels were reported such as core-shell microgels and hollow microgels. In general, the core-shell (or hollow) types of microgels were synthesized by seeded precipitation polymerization with water-soluble monomer. Under such back ground, we have reported that a series of microgel/solid composite microgels were synthesized by seeded emulsion polymerization (SEP) with hydrophobic (water insoluble) monomer such styrene (**Figure**).¹⁻³ Different from the conventional microgels, our composite microgels are non-spherical. Moreover, the characterization of morphology of composite microgels lead to understanding the relationships between the properties of the local micro-hydrogel environment, such as polarity and hydrophobicity, and the capability to serve as a nucleation site for hydrophobic polystyrene particles. These finding will help to design novel shape-anisotropic composite micro-hydrogels for potential applications in the variety fields, and to understanding the interaction between microgels and hydrophobic materials. In this study, we demonstrated the seeded emulsion polymerization in the presence of polyelectrolytes microgels with styrene and polystyrene nanoparticles could not form the polyelectrolytes within core microgels. The results indicated that the charge distribution within the core microgels is key factor for designing morphology of composite microgels.⁴



Figure. Scheme of our polymerization system.

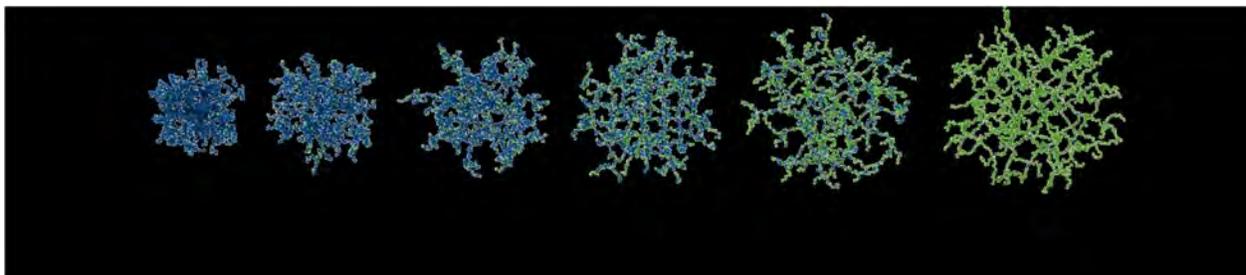
POLY 379: Monte Carlo simulations of weak polyelectrolyte nanogels: pH-dependence of conformation and ionization

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Weak polyelectrolyte nanogels are three-dimensionally cross-linked polymer networks of colloidal dimension exhibiting acidic or alkaline groups. In dependence of the pH of a surrounding medium, their degree of ionization changes. This change in degree of ionization is accompanied by a swelling/collapse of the gel network, which can be attributed to additional electrostatic and osmotic pressure contributions. The mutual interconnection of likewise-ionizable groups into one macromolecule leads to a suppression of the degree of ionization as compared to the single ionizable monomer at high dilution. The shift of the effective pK_A -value is an effect commonly known for weak polyelectrolytes and can be explained by the increasing additional free energy cost for ionization due to the spatial proximity of the titratable groups in the polymer chain.

In this contribution, we investigated the conformation and ionization behavior of a weak polyelectrolyte nanogel with acidic functionalization. The polymer network was modeled as a bead-spring network within the framework of the primitive model for polyelectrolytes. The model system was examined by means of Monte Carlo simulations on a coarse-grained level and the protonation/deprotonation was included in the simulations using a titration Monte Carlo move.

Upon variation of the pH, a transition between a neutral, collapsed network and a highly charged and swollen network can be found. The suppression of the degree of ionization as compared to a dilute system of low-molecular acidic or basic compounds is found to be particularly pronounced. We find an inhomogeneous distribution of charges within the network with an enhanced degree of ionization at the surface of the gel particle. In addition to the investigation of a reference network, the influence of the cross-linking density, the relative content of titratable monomers and the polymer volume fraction was investigated.

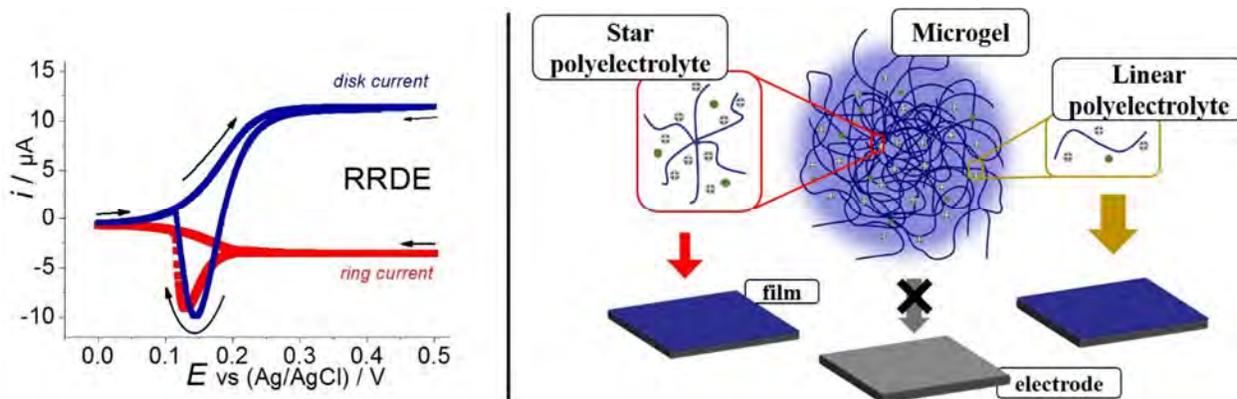


Simulation snapshots showing the pH-dependent swelling behavior of an acidic nanogel particle. While blue groups carry no charge, green groups indicate the negative charge of an ionized acidic function. For reasons of clarity the mobile counterions are omitted.

POLY 380: Polyelectrolyte microgels oppose electrodeposition

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The possibility of polyelectrolytes to interact with oppositely charged counterions (host-guest interplay) can be exploited for an electrochemically-induced film formation when using redox-active counterions. The charge of these guest molecules can be altered electrochemically changing concomitantly the solubility of the polyelectrolyte-counterion complexes at the electrode. Under certain circumstances film formation on the electrode can be observed. Previous work has shown that polyelectrolyte microgels show an insufficient deposition behavior compared to other polyelectrolyte systems. Hence, we address various architectures of cationic polymers made of quaternized poly(dimethylaminoethyl methacrylate) to mimic the architectural features present in the crosslinked porous and swollen microgel network. Thereby linear polymers are chosen to imitate the bridges between the crosslinks while the polymer stars resemble the situation around these crosslinking points. Electrodeposition of the different systems is studied with hydrodynamic voltammetry exploiting a rotating ring disk electrode (RRDE) allowing for quantification of the deposition efficiency DE . Results demonstrate linear polymers of moderate molar mass to be most efficient in the deposition due to pronounced intermolecular physical crosslinking (by help of the hexacyanoferrates). Branching and higher molar mass favor more intramolecular physical crosslinking. The combination of both aspects, branching and high molar masses, aggravates deposition for the polyelectrolyte microgel.



Schematic description of hydrodynamic voltammetry data and different investigated polyelectrolyte architectures and their performance in electrodeposition.

POLY 381: Fluorescence microscopy investigation of microgels at interfaces

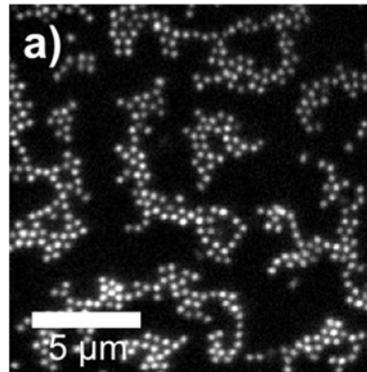
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Unlike most ordinary colloids, microgels have a soft cross-linked polymer structure, which allows them to deform significantly. Particularly at interfaces, this is an advantage, since e.g. emulsions can be efficiently stabilized. Due to the incorporation of stimuli-responsive comonomers, these emulsions can be destabilized on demand, leading to a controlled coalescence of the droplets.

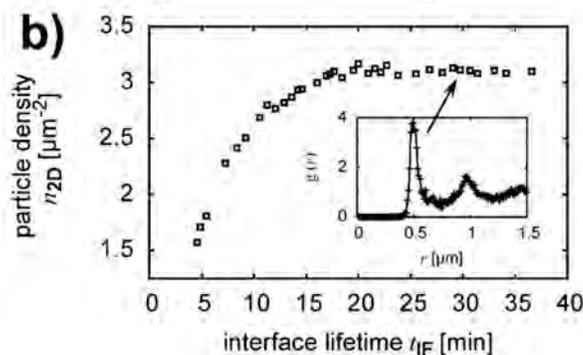
The observation of microgel arrangement at the interface and the elucidation of their structure is currently predominantly performed with indirect methods such as AFM, Langmuir trough or Freeze-fracture shadow-casting (FreeSCA) cryo-SEM.

We present modern high-resolution Fluorescence Microscopy techniques which allow us to position and track the microgels in situ at liquid/liquid interfaces and additionally to investigate their structure by superresolution.

Our current results allow us to dynamically measure the saturation of an interface over time, and further to obtain information on the diffusion behavior of individual microgels. Moreover the temporal change in radial distribution function reveals information about the evolution of structural order of microgels at a liquid-liquid interface.



Diffraction limited fluorescence microscopy image of NIPAM-based microgels at decane/water-interface, revealing a cluster-like arrangement of microgels.



Increasing particle density at 23 °C at the decane/water-interface as a function of interface lifetime. Inset: Radial distribution function revealing an ordered structure.

POLY 382: Real-time adsorption behavior of hydrogel microspheres onto solid/liquid interface

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Understanding contact and adsorption phenomena of colloidal microspheres onto a solid/liquid interface is important in an industrial or biological context. In general, whether rigid colloidal microspheres adsorb or not onto a solid surface is theoretically determined by electrostatic and van der Waals interactions. On the other hand, in natural systems, colloidal microspheres usually exhibit at least some degree of deformability, thus, they can deform during contact with the interface. However, how such deformability affects the dynamic adsorption behavior of the microspheres onto the interface has not yet been addressed, because of the difficulties of direct observation of the dynamic adsorption and deformation behavior of individual microspheres at the nanoscale in real-time. Against this background, we revealed that deformability of individual polymeric microspheres strongly impacts their adsorption kinetics, by visualizing individual microspheres during the adsorption and subsequent deformation [Matsui et al., *Angew. Chem. Int. Ed.* **2017**, *56*, 12146].

Soft hydrogel microspheres i.e. microgels (pNA) were synthesized from *N*-isopropylacrylamide, acrylic acid, and cross-linker *N,N*-methylenebis(acrylamide) by precipitation polymerization. Elastomeric poly(ethyl acrylate) (pEA) microspheres were synthesized by soap-free emulsion polymerization. The real time adsorption behavior of the microspheres onto mica substrate treated with aminosilane (AP mica) was monitored using high-speed atomic force microscopy (HS-AFM). After the injection of the microsphere dispersions into the sample holder, the number of adsorbed microspheres increased with time up to saturation (**Fig. 1(A)**). **Fig. 1(B)** shows that the normalized number of adsorbed microspheres as a function of time, indicating the softness, i.e., deformability of the microspheres plays a crucial role on the adsorption kinetics.

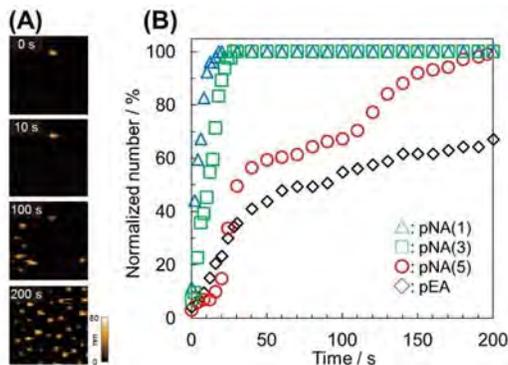


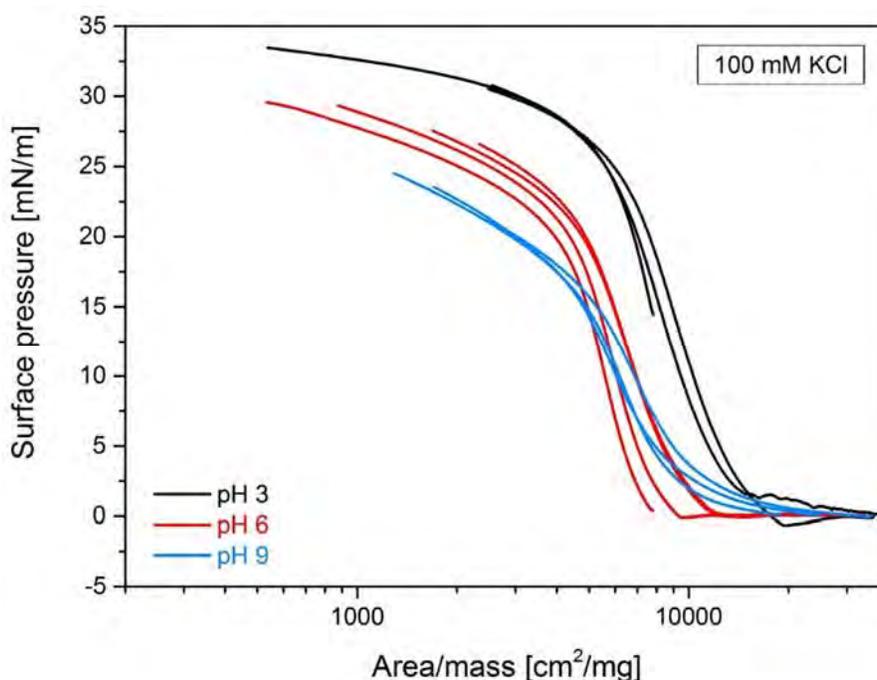
Fig. 1(A) Time-dependent adsorption behavior of microgels onto AP mica substrates monitored by HS-AFM. **(B)** Normalized number of adsorbed microspheres as a function of time.

POLY 383: Investigation of highly charged microgels at flat liquid-liquid interfaces

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Stimuli-sensitive microgels are highly interfacial active and, therefore, suitable for application as responsive emulsifiers leading to emulsions that can be broken on demand. The stability of microgel-stabilized emulsions seems to be dominated by the viscoelastic properties of the microgel-laden interface. However, the interfacial properties of microgels are far from being completely understood. Langmuir trough experiments of pH-responsive microgels revealed that the compressibility of microgels at flat liquid interfaces is not determined by direct Coulomb repulsion as microgels in the charged state could be compressed more easily than in the uncharged state. Instead, it is proposed that the different swelling of the microgel in the two states is the decisive parameter.

In order to further elucidate how electrostatics affect the interfacial properties of polyelectrolyte microgels we focus on synthesizing *N*-isopropylacrylamide (NIPAM)-based microgels with high content of itaconic acid as ionic co-monomer. Each itaconic acid monomeric unit can carry up to two negative charges depending on the solution pH. The influence of pH and ionic strength of the aqueous subphase on the microgel monolayer properties is investigated at decane-water interfaces utilizing a Langmuir trough. Different types of salt are employed to control the ionic strength. Furthermore, microgel monolayers are transferred onto solid substrates and imaged via atomic force microscopy.

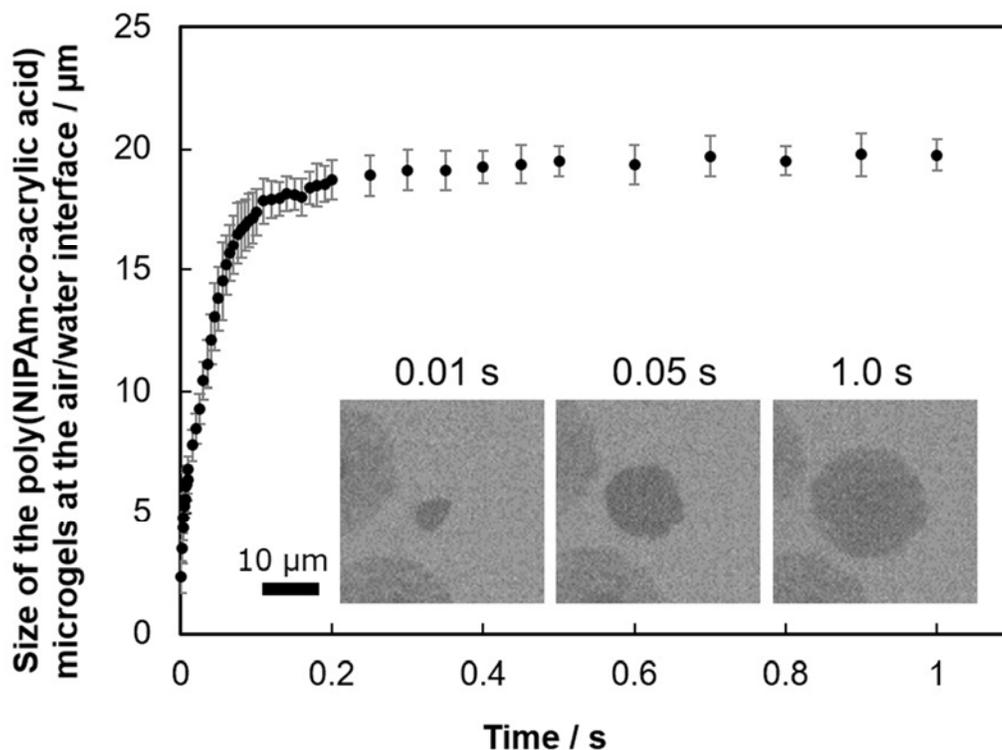


Normalized compression isotherms of poly(NIPAM-co-itaconic acid) microgels at decane-water interfaces at different pH with 100 mM KCl in the aqueous subphase.

POLY 384: Dynamics of large poly(*N*-isopropyl acrylamide)-based hydrogel microspheres at the air/water interface

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The “softness” of hydrogel microspheres (microgels) which are colloidal particles of cross-linked polymeric networks plays a crucial role in many applications. In order to further develop and create new applications for soft microgels, understanding the interfacial behaviors of microgels is especially important. However, the detailed mechanism of microgels upon adsorption and deformation at the air/water or oil/water interfaces is still unclear. In the present study, the dynamics of large poly(*N*-isopropyl acrylamide)-based microgels (>6 μm) synthesized by a modified aqueous precipitation polymerization method were evaluated at the air/water interface for the first time. It was clearly visualized and quantified that the pNIPAm-based microgels were adsorbed and deformed very quickly at the air/water interface irrespective of their softness and finally engaged in contact with each other before gradually deforming during drying.

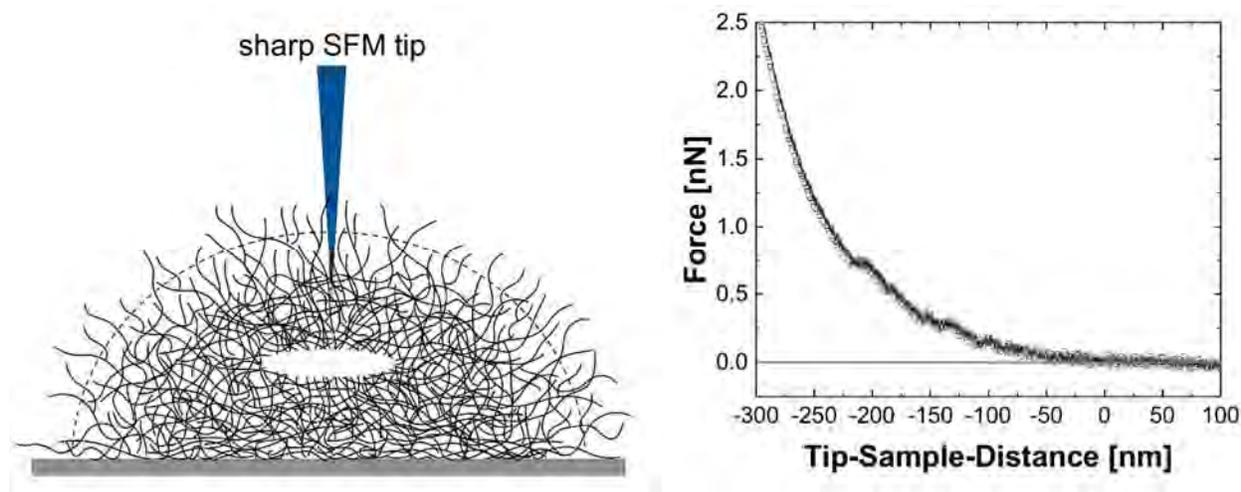


Poly(NIPAm-co-acrylic acid) microgels upon adsorption at the air/water interface were visualized by fluorescence microscopy equipped with a high-speed camera. Time evolution of their size was evaluated.

POLY 385: Probing the internal heterogeneity of responsive microgels adsorbed to an interface by sharp tip SFM

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Microgels prepared from temperature responsive poly(*N*-isopropylacrylamide) (PNIPAM) and featuring a complex three dimensional radial polymer density distribution adsorb and deform easily at interfaces causing conformational changes that substantially affect their interactions. The morphology of the interfaces is a property that affects the macroscopic responses of such coatings, and it is therefore desirable to relate interface morphology to the microscopic structure of the polymer network. Here, we use sharp tip scanning force microscopy (SFM) to probe the internal structure of microgels physically adsorbed on a solid / water interface. In particular, we investigate two types of unique microgels, (i) one with a hard silica core and a PNIPAM shell and (ii) second a hollow microgel obtained by dissolving the silica core. Thus, both systems have the same polymer network as peripheral structure but a distinctly different internal structure i.e. a rigid core vs. a void. We find that the cavity of the swollen hollow microgels is still present when adsorbed to the solid substrate. This information is important for applications of hollow microgels in coatings. Furthermore, we demonstrate that the bulk structure, previously evaluated by SANS, can be correlated to the force profile required to insert a sharp tip into the microgel. This allows extracting structural information beyond probing the periphery of the microgels. Information on the *internal* structure can be obtained by SFM.



Left: Scheme of a sharp tip approaching the water/hollow microgel interface, such that the density variation in the vicinity of the tip is probed. Right: Force-distance curve for the vertical approach of an sharp SFM tip towards the solid substrate at the apex of a hollow microgel in swollen state.

POLY 386: Thermo-responsive microgels at interfaces: Correlation between microgel softness and monolayer properties

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Responsive microgels allow the realization of smart emulsions, which can be broken on demand. However, their interfacial properties and demulsification mechanism are not fully understood. In our study we aim to elucidate the connection between their temperature-dependent swelling (i.e. softness) and properties at liquid-liquid interfaces.

We synthesised thermo-responsive poly(*N*-isopropylacrylamide) p(NIPAM) microgels and measured their interfacial properties in swollen (10 °C) and collapsed (40 °C) state. At these temperatures microgels lower the interfacial tension of water-decane interfaces to values below 20 mN/m. A Langmuir trough was used to investigate the mechanical properties of the microgel monolayer, with subsequent deposition to a substrate. With respect to the swollen microgels, the compression isotherms of collapsed microgels show an unusual one-staged course, albeit similar surface pressures (Figure 1). Furthermore, the collapsed microgel monolayers possess a lower compression modulus. The deposited microgels were recorded *ex situ* with atomic force microscopy (AFM). By image analysis we found structurally identical phases for both states, yet the transitions take place at different compressions. The results of cryo-SEM and ellipsometry at liquid interfaces demonstrate that their interfacial radius and height of protrusion into the non-polar phase are temperature independent, but the microgel parts situated in the aqueous phase are still thermo-responsive. As a consequence, at elevated temperatures the microgels are collapsed and the monolayer becomes more brittle. Our findings emphasize the fundamental differences between rigid and soft colloids at liquid-liquid interfaces.

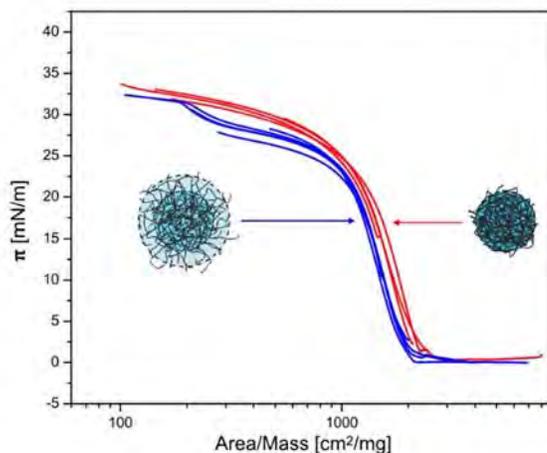


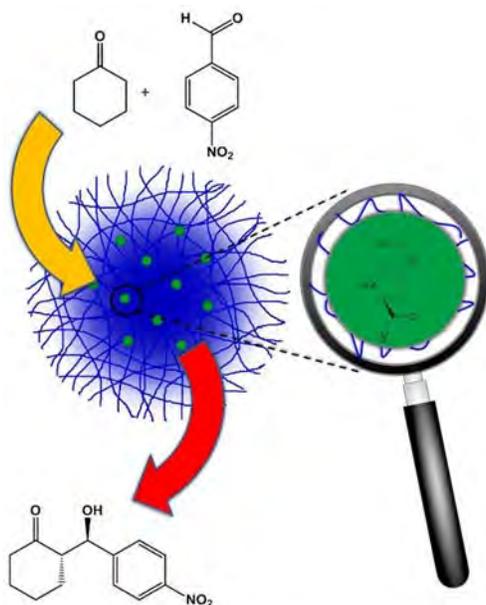
Figure 1: Compression isotherms of swollen (blue lines, $T = 10\text{ °C}$) and collapsed (red lines, $T = 40\text{ °C}$) p(NIPAM) microgels. To obtain master curves the area is normalized by the added amount of microgels.

POLY 387: Versatile nanoreactors based on temperature-responsive microgels

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Catalysis has become an essential tool for the development of sustainable industrial processes. Especially the field of homogenous catalysis has caught attention in recent chemical research due to its advantages like solubility, high reactivity and selectivity. Synthesizing such catalytic compounds is well known from literature, merely recycling and reuse of the catalysts still remains challenging. In order to solve this issue catalysts are often immobilized on a suitable substrate. However, because of phase boundaries conventional immobilization can lead to substantial reduction of efficiency and selectivity of the catalyst.

Lately, microgels have been used as substrate for catalytically active materials. In general, microgels are cross-linked, porous and mostly spherical polymer-particles which can form stable dispersions in continuous medium (e. g. in water) as these particles are permeated by the solvent (single phase system). To changes of their environment stimuli-responsive microgels respond with a collapse of the polymer-network. Consequently, microgel dispersions turn into a two-phase system. These features make stimuli-responsive microgels ideal candidates as substrate materials for homogenous catalysts. In this context we aim to combine chosen organo-catalysts with temperature-responsive microgels based on Poly-*N*-isopropylacrylamide forming a covalently bound microgel-catalyst. This microgel-catalyst can be used as nanoreactor for various types of reactions. Furthermore, due its temperature-sensitivity the microgel-catalyst can be recovered after the catalyzed process and be reused for further cycles of reactions.

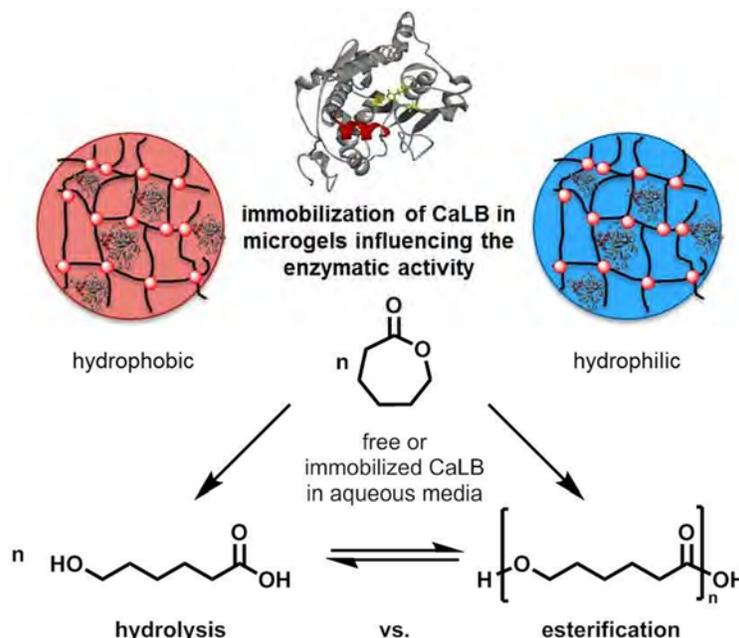


POLY 388: Polyglycidol based microgels as promising supporting materials: Entrapment of (bio)catalyst guests

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The immobilization of guest molecules to a supporting material is a field of high interest in the current research. Due to the wide variety of guest molecules like e.g. drugs, proteins, peptides and (bio)catalysts and just as many different hard or soft supporting materials these hybrids find application in various fields like drug delivery in medicine and catalysis.

Immobilization of catalysts in particular has the advantage of efficient recovery and improving process economy. In addition, also the catalytic performance itself can be improved and/or directed by protecting the catalyst in the supporting material against the microenvironment. Furthermore, the activity of enzymes changes due to the interaction with the supporting material, which induces conformational changes and thus resulting in a changed accessibility for the substrate to the catalytic center. A class of promising host particles are microgels which are distinguished by their open and soft structure. Based on polyglycidols we have investigated a route to entrap guest molecules like *Candida antarctica* Lipase B (CaLB) in functional microgels. These microgels have been tailored in their polarity to direct the reactivity of the entrapped catalyst. The influence of surfactants and engineered hydrophobic CaLB variants on the polymerization activity in aqueous medium was investigated. By further introducing hydrolysable groups in the polyglycidol we developed a degradable microgel which releases its guest molecule / drug in basic medium. This further opens the possibility for application of the microgel as a drug delivery system.



POLY 389: Molecular separation by stimuli-responsive hydrogel microspheres

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Hydrogel particles (microgels) are colloidal particles with average diameters ranging from several tens of nanometers to single micrometers. In appropriate solvents, these particles become highly swollen with water and demonstrate stimuli-responsiveness. The swelling/deswelling behavior of these microgels is suitable for various applications, such as drug delivery systems, separation carriers, and sensors, as the interactions between target molecules and the microgels can be controlled quickly. Under such background, we have investigated the molecular separation behavior of the microgels (**Figure**). In particular, the relationship between the microscopic structural changes in the microgels and the molecular uptake behavior was clarified, and the obtained kinetics of deswelling due to the adsorption of target molecules allowed us to understand the fast response and the effect of the distribution of functional group, which interact with the target molecules, in the microgels on the uptake behavior. Thus, we will provide the detailed results to discuss the molecular separation functions of the microgels at the session.

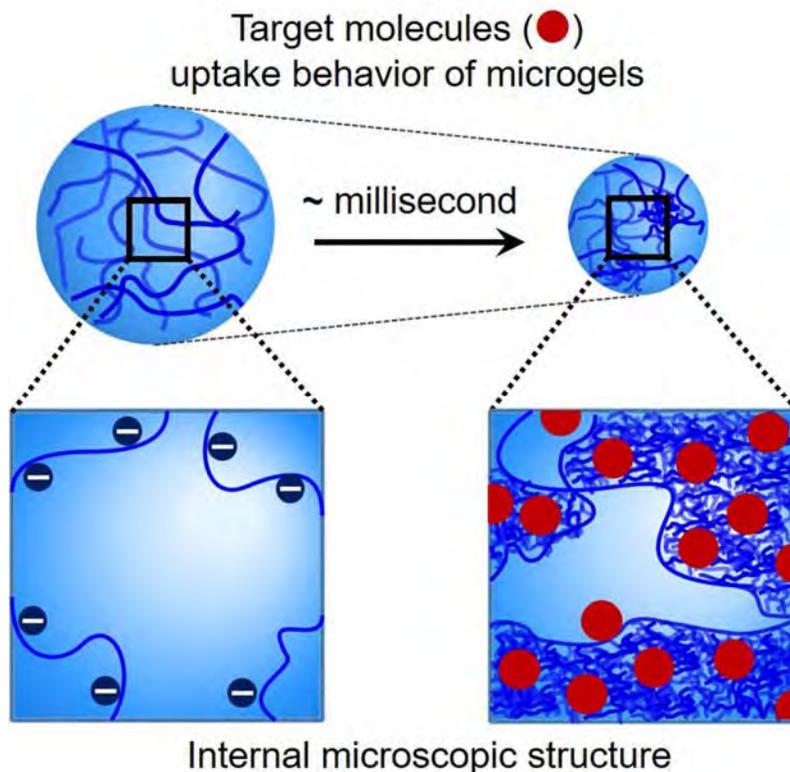
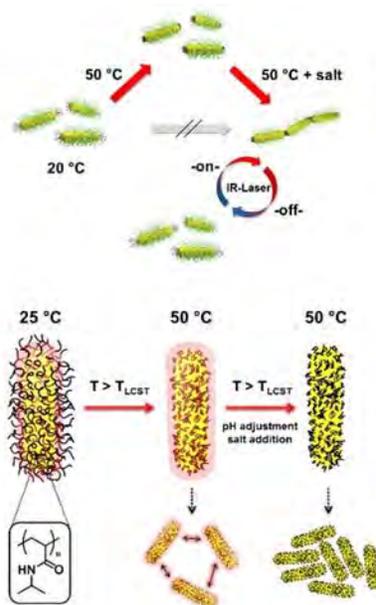


Figure. Schematic illustration of the molecular uptake behavior of microgels.

POLY 390: Thermo-reversible, directed association of polymer decorated gold nanorods in aqueous solution

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As it is well-known, the plasmonic resonance of gold nanorods (AuNR) does not only depend on their size, aspect ratio and orientation relative to polarized light, but is also substantially affected by small interparticle distances within aligned AuNR assemblies. Here particularly the number of AuNR and their relative orientation determines the formation of new plasmon modes. We exploit this behavior to develop nanoscopic systems where the absorption band can be strongly and reproducibly shifted by light or heat. In particular, the surface modification of AuNR with distinct polymers is described, that enables them to undergo a thermo-reversible self-assembly into defined aggregates for tunable optical properties. The assembly mode in aqueous solution is programmed by the thermally-induced and solubility-driven interaction of poly(N-isopropylacrylamide), which is selectively grafted to the AuNR surface. For end-to-end assembly, it is demonstrated that the aggregation of the grafted polymers into clusters, whose size is limited by the small chain number and correspondingly by the small volume between the ends of the associated AuNR, cannot be achieved by mere temperature changes, but must be supported by addition of salt or free PNIPAm. Hence, the experimental data shows that the solubility-driven association of end-tethered PNIPAm requires a complex interplay of hydrophobic interaction, salt effects and electrostatic repulsion. Furthermore, investigations on the thermo-reversible non-specific aggregation are presented, where the pivotal role of salt and inevitability as trigger for the association is demonstrated in more detail.



POLY 391: Dynamic investigations of the cononsolvency of poly-N-isopropylacrylamide microgels

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Crosslinked poly-N-isopropylacrylamide (pNIPAM) is a prominent example of a stimuli-responsive microgel. pNIPAM is swollen in both water and methanol (MeOH). However, the polymer network collapses at intermediate MeOH/water ratios, referred to as cononsolvency. Cononsolvency couples the volume phase transition to the transport of the cosolvent into the polymeric network. Hence, the mechanism is fundamentally different from the temperature-dependent collapse. So far, the mechanisms underlying cononsolvency have not been fully elucidated.

In this work, we focus on the dynamics of the cononsolvency of pNIPAM microgels. To this end, pNIPAM microgels were synthesized by microfluidics. The dynamic behavior during a solvent jump from water to a 20 mol% MeOH/water mixture was investigated in a microfluidic observation channel by Confocal Raman Spectroscopy (Figure 1b). Here, the composition of the continuously changing solvent mixture was quantified within the polymer network and in the channel next to the gel by spectral analysis using indirect hard modeling. The results were compared to the size evolution of fluorescent microgels observed in identical experiments using Confocal Fluorescence Microscopy (Figure 1a-c). The experimental data provide unique detailed insight into the volume phase transition due to cononsolvency.

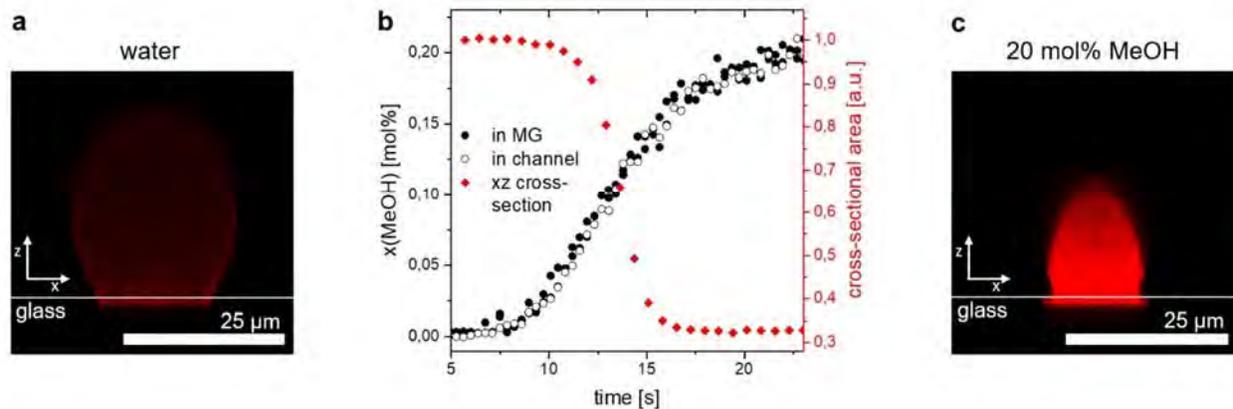
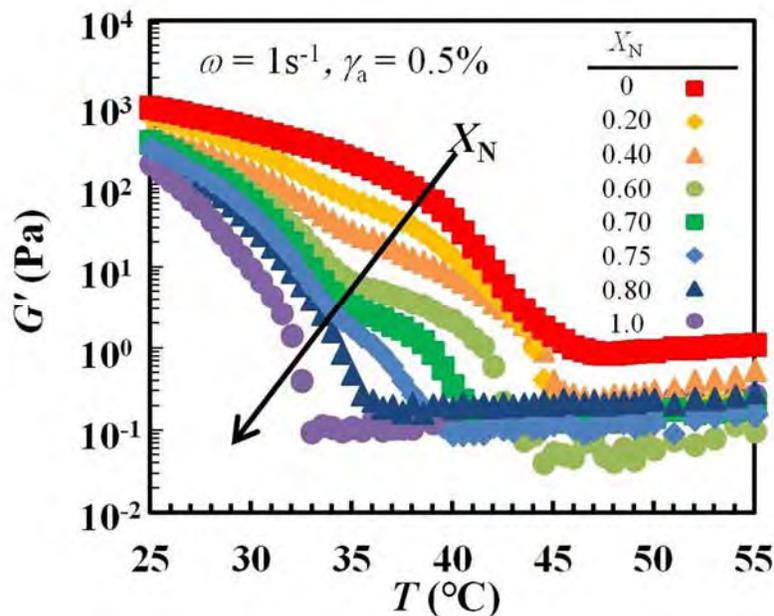


Figure 1: Micrographs of xz cross-section of a fluorescent microgel in (a) water and (c) a 20 mol% MeOH/water mixture. b) Time-dependent evolution of the MeOH mole fraction in a microgel (MG), in the channel next to it and evolution of the cross-sectional area.

POLY 392: Rheology of dense suspensions of temperature-responsive microgel mixtures

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The dense suspensions of the mixtures of poly(*N*-isopropylacrylamide) (N) and poly(*N*-isopropylmethacrylamide) (NM) microgels with different volume transition temperatures ($T_c^N = 31\text{ }^\circ\text{C}$ and $T_c^{NM} = 39\text{ }^\circ\text{C}$) exhibit the characteristic temperature (T)-dependent viscoelasticity according to the changes in the type of interparticle interaction as well as the volume fraction (Φ) for each gel (Figure). In the range of $T < T_c^N$ where the swollen microgels with repulsive interparticle interactions are densely packed, the equilibrium modulus (G) decreases upon heating entirely due to a reduction in the total volume fraction of the microgels. At $T > T_c^N$ where finite hydrophobicity of the microgels emerges, the suspensions still show the solid-like elastic feature due to the network-like flocculation formed by the shrunken attractive microgels, even when Φ of microgels becomes considerably lower than the threshold for randomly close packing. The T dependence of G shows a minimum at characteristic temperature (T_B) as a result of the competition between the packing-degree effect and the attractive interparticle interaction. The temperature T_B shifts to higher T region with a decrease in N content (X_N) in the mixtures. We will discuss the contributions of packing degree effect and interparticle interaction effect to viscoelasticity.

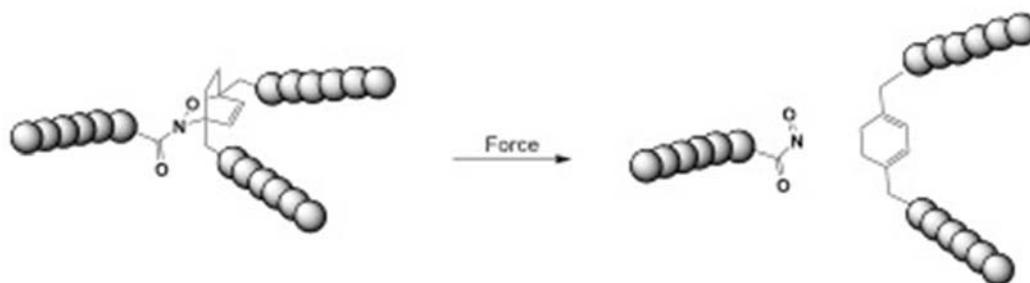


T dependence of storage modulus (G') for the suspensions of various X_N

POLY 393: Investigation of mechanochemical reactivity of 1,2-oxazines

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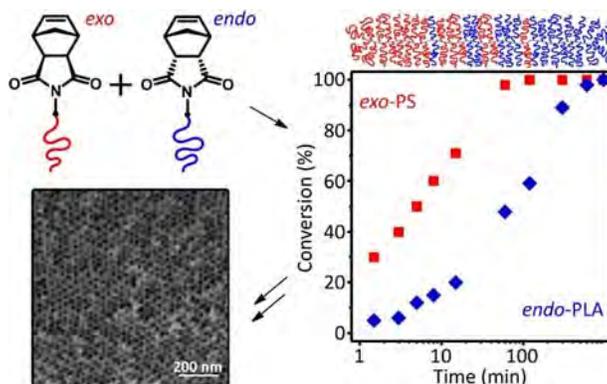
Inspired by the thermally reversible hetero-Diels–Alder reaction of the 1,2-oxazine, we are exploring an oxazine derived from a nitrosocarbonyl dienophile and cyclohexadiene as a candidate for a new mechanophore. Specifically we are interested in how polymer chain scission rates are affected by the regio-chemistry and substitution pattern of the diene. Constrained geometries simulate external force (CoGEF) computational technique predicts large disparities in activation energy of different polymer architectures including linear and star polymer variants.



POLY 394: Synthesis and melt self-assembly of tapered bottlebrush copolymers

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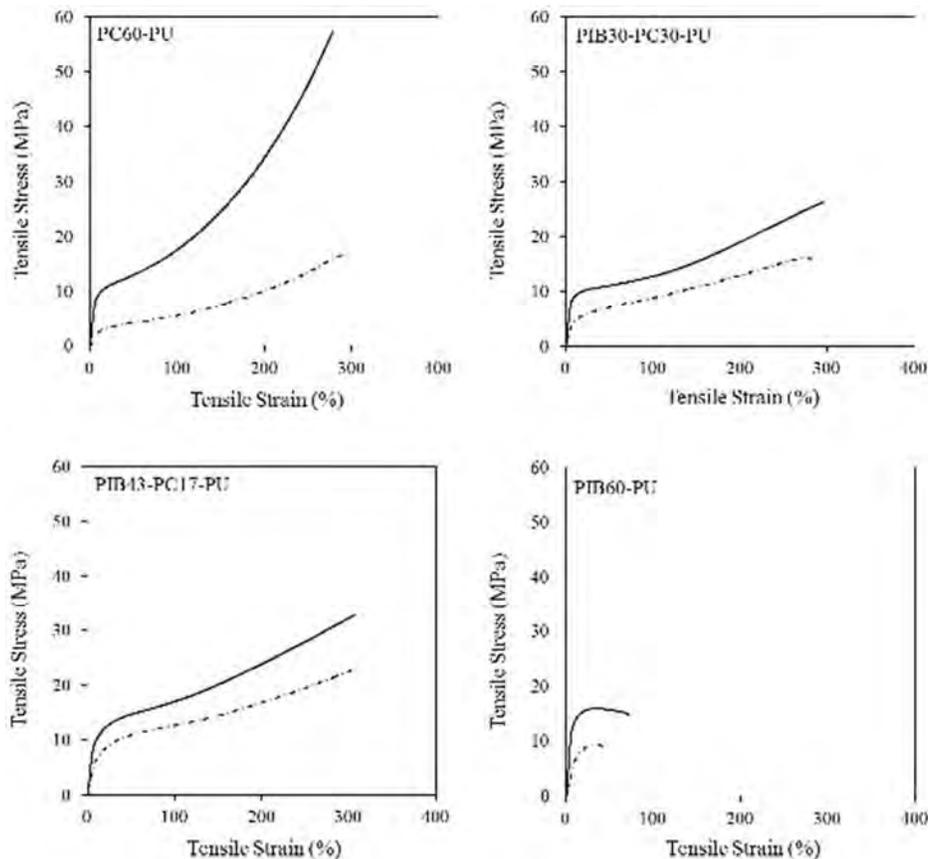
We developed a synthetic protocol for tapered bottlebrush copolymers using ring-opening metathesis polymerization (ROMP). This new bottlebrush copolymer architecture is prepared by copolymerizing *exo*- and *endo*-norbornene functionalized macromonomers. The vastly different ROMP reactivities of the two norbornene configurations lead to a unique compositional profile, where homopolymer domains at both ends of the molecule are separated by a gradient compositional transition. A model system comprised of polystyrene (PS) and polylactide (PLA) side chains was designed to gain insight into the effect of gradient interface on melt state polymer self-assembly. A series of near symmetrical PS-*taper*-PLA bottlebrush copolymers was synthesized. Self-assembled samples were analyzed by small-angle X-ray scattering (SAXS) and revealed a morphology with a hexagonal symmetry. Inspection by transmission electron microscopy evidenced the formation of a rare perforated lamellae morphology. Shear aligned samples, on the other hand, exhibited a well-ordered cylindrical morphology, confirmed by 2D SAXS and scanning electron microscopy after selective etching of the PLA domain. Such molecular packing is drastically different from the self-assembly of bottlebrush block and random copolymer analogs with similar composition and dimensions. Domain spacings of PS-*taper*-PLA bottlebrush copolymers increased linearly with the backbone length and were consistently smaller than pitch sizes obtained for their PS-*block*-PLA bottlebrush copolymers analogs, which suggested a non-perpendicular molecular orientation at the domain interface. SAXS studies also revealed an unusual and large d-spacing changes with temperature, which was observed only for tapered bottlebrush systems. Thus, gradient interface in bottlebrush copolymers has a strong influence on molecular packing and orientation unlike their linear copolymer counterparts. In summary, the newly developed tapered bottlebrush copolymer system exhibits morphological behavior that is different from previously established copolymer architectures and provides a new avenue to direct molecular assembly.



POLY 395: Synthesis of hydrolysis-resistant polyisobutylene-based polyurethanes

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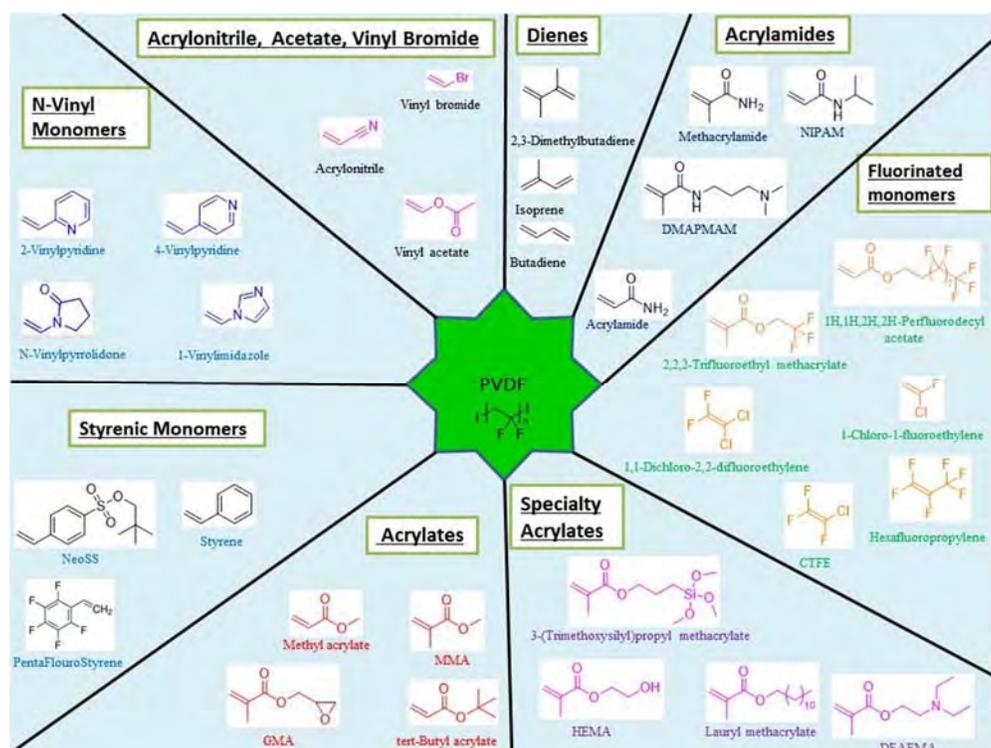
Polyurethanes (PUs) with polyisobutylene (PIB)-diol of $M_n = 1900$ g/mol, $M_w/M_n = 1.8$ and chain end functionality $F_n = 2$ were synthesized using tin-octoate as catalyst. The soft segments (SS) contained PIB-diols or a mixture of PIB-diols and an aliphatic polycarbonate (PC)-diol, and the hard segment (HS) comprised of 4,4'-methylene dicyclohexyl diisocyanate (HMDI) and 1,4-butanediol (BDO). The PU with pure PC-diols made without the use of solvent had 58 MPa tensile strength, but it lost 78.5% strength after ASTM hydrolytic stability testing. The PU with 100% PIB-diols needed solvent during synthesis because of the high viscosity of the mixture. This sample had 15.8 MPa tensile strength and lost 47.7% after hydrolytic stability testing. Optimum performance was found with 30wt% PIB-diols that could be made without the use of solvents and lost only 38% of its ~30 MPa tensile strength after hydrolytic stability testing.



POLY 396: Investigation of PVDF block copolymer architecture and their interface properties

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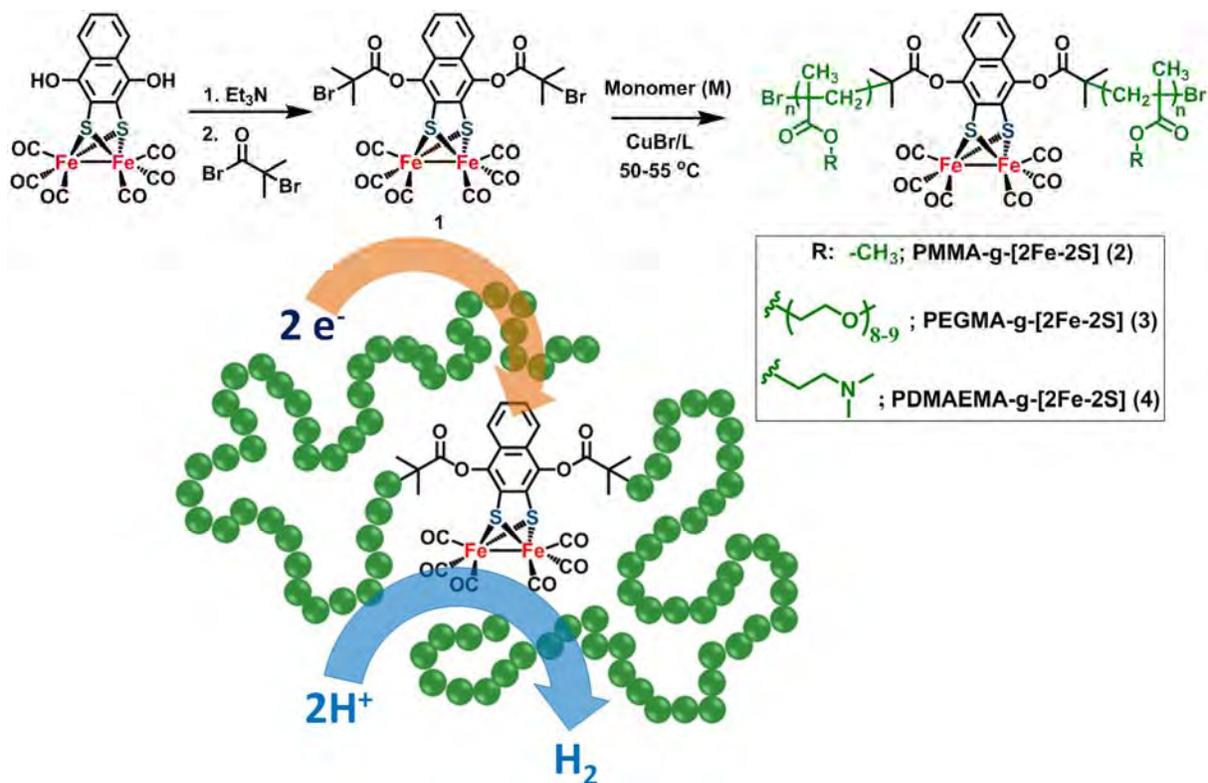
Vinylidene fluoride (VDF) monomers are gaseous in nature with low boiling point (-84°C), high k_p which require highly pressurized and elevated temperature autoclaves for their corresponding polymer synthesis. VDF propagates with two different modes of propagation leading to head to tail (HT) ($\sim\text{CF}_2\text{CH}_2\text{-X}$) or tail to head (TH) ($\sim\text{CH}_2\text{CF}_2\text{-X}$) additions, with varying bond dissociation energies. In order to overcome the difficulties in VDF polymerizations, a series of metal carbonyl catalyst, $\text{L}_z\text{Mt}_x\text{CO}_y$ (Re, Mn, Fe, Cr, Mo) were used as photo-catalyst to mediate iodine degenerative transfer at room temperature under visible light irradiation to synthesize PVDF homopolymers with high chain end fidelity ($\sim 95\%$). Stoichiometric amount of metal carbonyl catalyst was used to simultaneously activate the dual chain ends of PVDF macroinitiator to synthesize homogenous PVDF block copolymer (BCP). A range of di, tri- BCP were synthesized with varying chain lengths. The BCP architecture was characterized by ^1H , ^{19}F , $^{2\text{D}}$ $\{^1\text{H}\text{-}^{19}\text{F}$ HETCOR $\}$ Nuclear magnetic resonance, gel-permeation chromatography and differential scanning calorimetry studies. The nature of the BCP interface was tuned from highly hydrophilic to hydrophobic by using different type of monomers classes such as acrylates, dienes, main chain fluoro monomers, side chain fluorinated monomers and acrylamides. The effect of the composition, nature of the secondary monomer on the interface of PVDF-BCP were studied by small angle x-ray scattering, atomic force microscopy, sessile pendant drop contact angles.



POLY 397: Synthesis of [FeFe]-hydrogenase mimetic metallopolymers via ATRP for robust and O₂ resistant H₂-evolution catalysts

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Metal-containing polymers can combine the useful properties of polymers with the key functions of metal complexes. These metallopolymers are applicable to a wide range of areas such as photovoltaics, stimuli responsive materials and catalysis. Catalysis, for example, includes designing artificial metalloenzymes which can mimic the biological functionalities by engineering the environment of a metal complex using polymeric materials. FeFe-hydrogenase enzyme found in bacteria is an efficient H₂ generation catalyst and there has been extensive research on making FeFe-H₂ase mimics to produce H₂ as a carbon-free energy carrier. The mimics have shown high catalytic activities in organic media, however, limited lifetime, low oxygen stability and low solubility preclude the applicability of the mimics. We, for the first time, made a metalloinitiator from a FeFe-H₂ase mimic to grow polymers via atom transfer radical polymerization (ATRP). The polymers not only provide water solubility and oxygen stability in neutral water but also enhance the activity of the complex by tuning the secondary coordination sphere of the mimic. We will discuss our most recent efforts to synthesize a difunctional metalloinitiator and metallopolymers grafted via ATRP. [Figure 1]

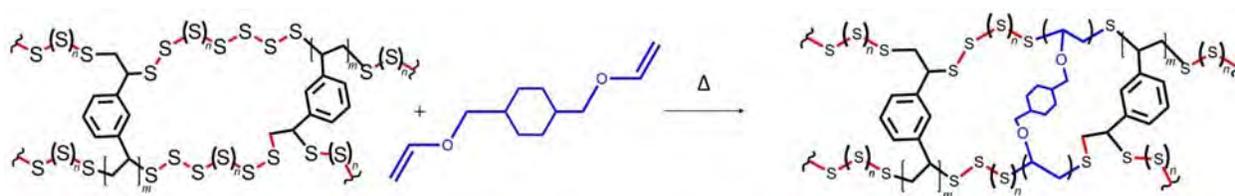


Synthesis of a difunctional ATRP metalloinitiator and metallopolymers

POLY 398: Solvent free addition of allyl and vinyl monomers into polysulfides formed by inverse vulcanization

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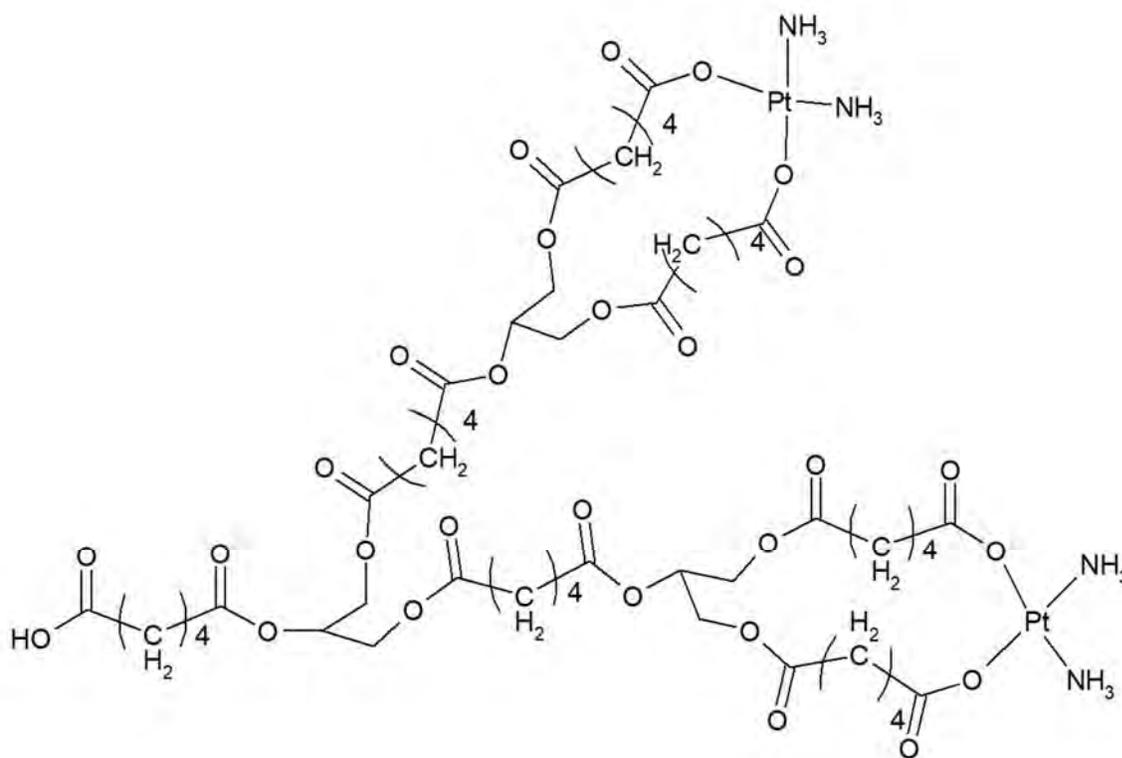
Elemental sulfur is a byproduct of the refining process, removed during hydrodesulfurization. Its abundance offers an inexpensive source of reagent. Inverse vulcanization, developed in 2013, by Jeffrey Pyun, uses large amounts of sulfur with very little monomer. The sulfur ring opens above 159°C, forming free radicals to bind monomers. Combining sulfur and divinylbenzene (DVB) forms poly(S-DVB) after 30 minutes at 185°C, a very high polymerization temperature. Most monomers do not have boiling points above 185°C. As a result, few monomers can be added. At lower temperatures, 80-100°C, linear sulfur chains in poly(S-DVB) will cleave forming radicals allowing additional monomers to be incorporated. Diallyl, allyl, divinyl, and vinyl monomers with similar structures were included into poly(S-DVB), solvent free at 90°C. Polymerization times were examined for each monomer. The use of poly(S-DVB) as a cost-effective initiator was studied using ratios up to 1:100 [poly(S-DVB):monomer]. The incorporation of the additional monomer was confirmed by ¹H-NMR showing the appearance of peaks from the additional monomer between 1-2 ppm, and disappearance of the double bonds in the 4-6 ppm range. Characterization was conducted using gel permeation chromatography, and differential scanning calorimetry. The molecular weights showed a gradual increase with increasing sulfur content in poly(S-DVB), and increasing the ratio of [poly(S-DVB):monomer]. Glass transition temperatures increased with increasing sulfur content in poly(S-DVB) and decreased when increasing monomer in [poly(S-DVB):monomer]. Metal binding studies were conducted using different polysulfides by altering the monomers added to poly(S-DVB), changing the sulfur content in poly(S-DVB), and varying the ratio of [poly(S-DVB):additional monomer]. The binding efficiency differs between the various monomers and [poly(S-DVB):monomer] ratios. Poly(S-DVB) initiated polymer formation from allyl and vinyl monomers, under mild reaction temperatures, and without additional solvent. Altering functionality and sulfur content enabled tailoring of material properties and affected metal binding efficiency.



POLY 399: Platinum(II) end-capped glycerol/adipic acid poly(ester)s as antitumor prodrugs

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Organoplatinum antitumor agents have had tremendous effectiveness against various forms of cancer. The discovery of *cis*-dichlorodiamineplatinum(II) (Cisplatin), the first of the organoplatinum antitumor drugs represented a major advance in the treatment of this disease. The early drugs were platinum(II) compounds containing two *cis* inert ligands and two labile ligands (necessary for hydrolysis and subsequent binding to adjacent guanine units of DNA). Three of these compounds (Cisplatin, Oxaloplatin and Carboplatin) are currently commercial successes widely used in cancer treatment. However, administration of these drugs is accompanied by rather severe side effects such as kidney damage and nausea due to low water solubility and dose-limiting side-effects. A way to address this problem is to deliver the drug at low concentration such that the antitumor activity is maintained while the threshold for toxicity is not reached. To provide a release vehicles, platinum(II) end-capped glycerol adipic acid hyperbranched polyesters were prepared. The materials not only contain releasable platinum moieties as an integral part of the structure but also provide a water-soluble carrier.

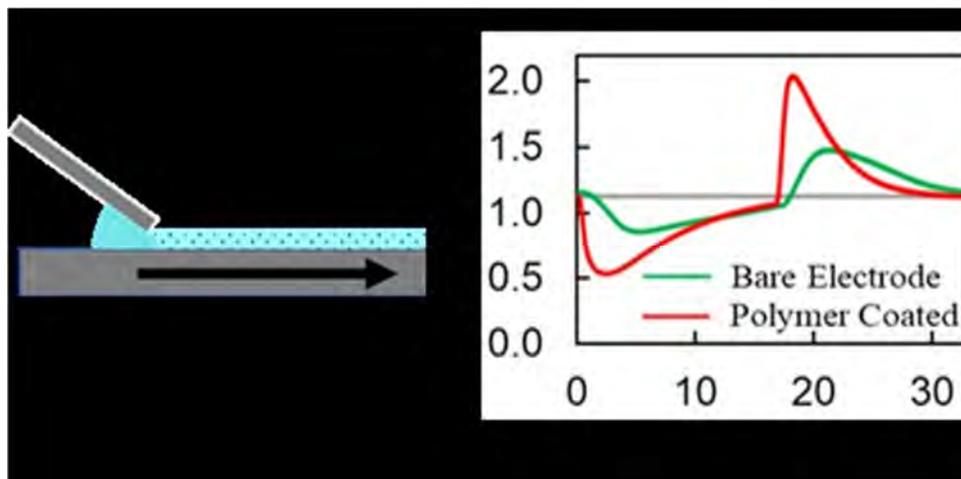


Diamino platinum(II) end-capped glycerol/ adipic acid hyperbranched polyester

POLY 400: Aqueous-processed, high-capacity electrodes for membrane capacitive deionization (MCDI)

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Membrane Capacitive Deionization (MCDI) is a low-cost desalination technology that utilizes ion-exchange polymer coated electrodes to reversibly adsorb and desorb ions. MCDI electrodes are typically prepared using hydrophobic polymer binder and organic solvents. Use of hydrophobic binder negatively affects the wettability of the electrode and use of organic solvent leads to potential health and environmental hazards. Thus, an approach using hydrophilic polymer binder and fully aqueous processing and fabrication route would be desirable. Here, we report a scalable, aqueous processing approach to prepare high capacity ion-exchange polymer coated electrodes for MCDI. Electrodes are first prepared by flow coating an aqueous slurry of activated carbon and a water-soluble polymer binder. After annealing, electrodes are subsequently flow-coated with a thin layer of cation- or anion-exchange polymer. These electrodes exhibit salt adsorption capacities up to 16.7 mg/g and overall charge efficiencies up to 98.6 %, much higher than typically achieved for activated carbon electrodes with hydrophobic polymer binder (5 - 10 mg/g). We attribute the increased capacity and charge efficiency to the use of a hydrophilic polymer binder and ion exchange polymer coating, and our overall approach demonstrates a simple, environmentally friendly, cost-effective and scalable method for the fabrication of high capacity MCDI electrodes.



POLY 401: Sulfonated terpolymers as proton exchange membranes for fuel cells: effect of aliphatic groups

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Sulfonated aromatic polymers have been investigated as possible alternatives to perfluorosulfonic acid polymers (e.g., Nafion) for proton exchange membrane fuel cell (PEMFC). Although Nafion membrane has been most used due to its high proton conductivity and high chemical stability, it is expensive because of complex manufacturing process and it has limited operation temperature. While a number of sulfonated aromatic polymer membranes have been suggested, insufficient proton conductivity especially under low humidity conditions (< 40% relative humidity) and chemical and mechanical instability still remain issues.

In this research, we report a novel series of terpolymer (SPA) membranes based on partially fluorinated sulfonated poly(phenylene)s and the effect of aliphatic groups on the membrane properties. Two types of SPA terpolymers were obtained by controlling feed comonomer ratio of aliphatic and perfluoroalkyl groups. Polymers A contained higher composition of aliphatic groups than Polymers B. Both polymers provided membranes with flexibility and mechanical stability. We found that the introducing aliphatic groups contributed to the formation of the polymers with high molecular weight and high IEC and that lower composition of the aliphatic groups contributed to higher proton conductivity with similar water uptake as shown in Figure 1. Other membrane properties including mechanical strength and fuel cell performance will be presented.

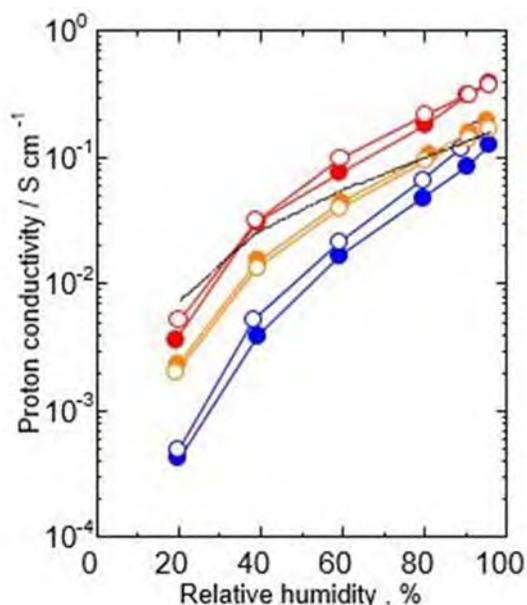
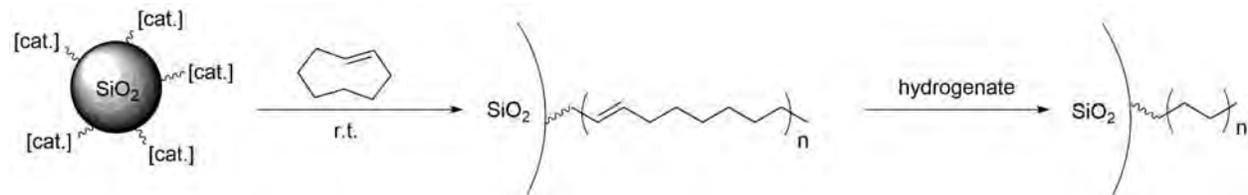


Figure 1. Proton conductivity of terpolymers A and B as a function of relative humidity

POLY 402: Recent advances in achieving nanofiller miscibility with polyolefin matrices

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In recent years, the ability to enhance polymer properties through homogenous dispersion of nanofillers in polymer matrices has gained growing attention from the synthetic community. Recent pioneering work has shown that nanofillers which are dispersed homogeneously throughout a semi-crystalline polymer above the melting point can be organized in the interlamellar domain when the system is slowly cooled to the crystallization temperature. The hierarchical ordering of the nanoparticles templated by the polymer crystallization was shown to increase the modulus of the material by an order of magnitude compared to the homogeneously dispersed filler at the same loading. This work has important implications for improving the properties of semi-crystalline polyolefin materials, already renowned for their toughness, low conductivity, and chemical inertness. However, achieving nanofiller miscibility with polyolefin matrices, specifically with linear polyethylene, is the bottleneck in mapping this crystallization driven assembly of nanoparticles onto polyolefin materials. We have recently devised a synthetic strategy which allows for covalent attachment of polyolefin analogs to the surface of silica nanoparticles with the goal of achieving filler miscibility with a polyolefin matrix. This approach, along with recent results regarding the filler dispersion will be discussed.



General synthetic scheme to functionalize silica particles with polyolefin analogs

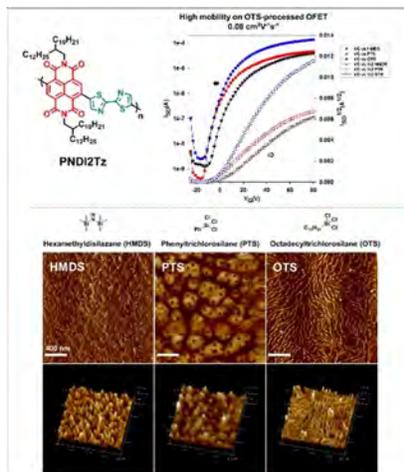
POLY 403: Enhanced conjugated polymer nanofiber network formation by synergistic effect of solution shearing and dielectric layer modification

Zhibo Yuan², zhiboyuan@gatech.edu, Simil Thomas², Carolyn Buckley², Guoyan Zhang¹, Jean-Luc E. Bredas², Elsa Reichmanis^{1,2}. (1) School of Chemical and Biological Engineering (ChBE), Georgia Institute of Technology, Atlanta, Georgia, United States (2) School of Chemistry Biochemistry, Georgia Institute of Technology, Atlanta, Georgia, United States

Since organic semiconducting polymers are sensitive to charge traps (CT), in recent years, an additional research focus has been related to identifying methods to reduce CT, particularly in organic field-effect transistor (OFET) devices. One approach to reduce CT is through surface passivation prior to semiconductor deposition. Previous studies have shown that passivated surfaces with different surface energies would greatly affect grain sizes and thin film surface morphologies. Nevertheless, the reasons why certain processing conditions and surface passivation can enhance OFET performance remain unclear.

To further elucidate the origins of the effects, a series of experiments have been conducted to understand the mechanism. Herein, we have fabricated OFETs with a series of polymers including **PDPP4Tz** and **PNDI2Tz**, and the benchmark “**N2200**” as our model polymers. Common surface treatment chemicals (OTS, HMDS and PTS) were used. Structure-process-property links between surface treatment chemical structure and treatment methods have been studied.

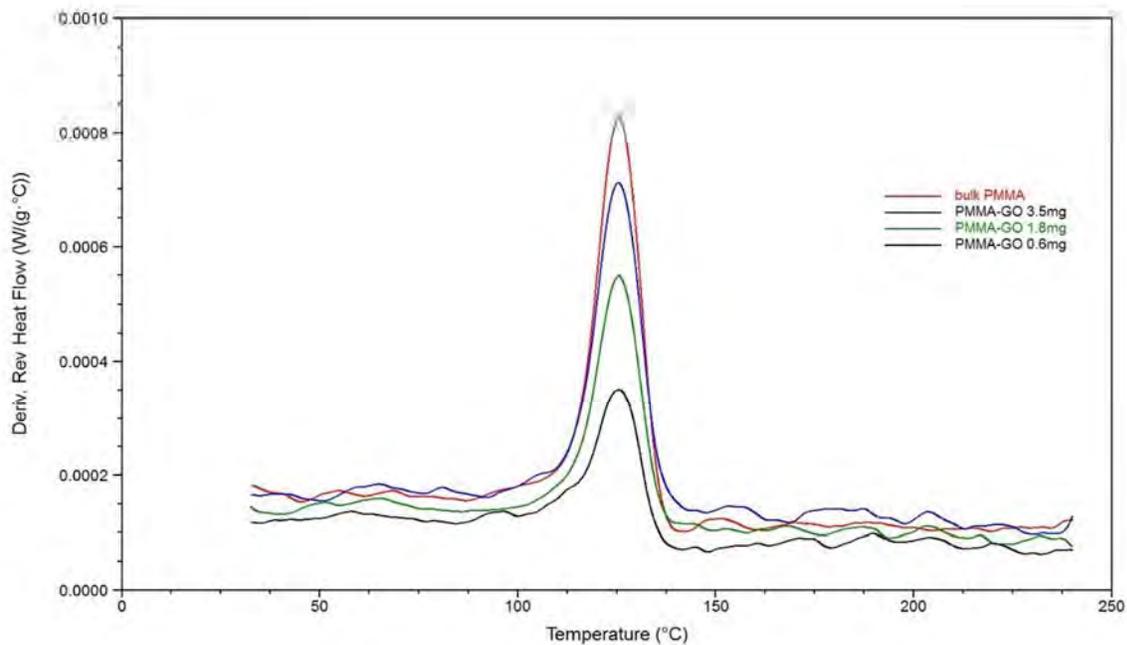
Herein, we report enhanced conjugated polymer nanofiber formation on modified dielectric layers, which positively affects OFET device performance. Polymer nanofiber (PN) networks were observed within thin films processed via solution shearing on OTS coated surfaces. With **PNDI2Tz**, OFETs with mobilities as high as $0.08 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ were fabricated. We discovered that the formation of PN on low energy surfaces is due to the synergistic effects of solution shearing and surface energy optimization. By systematically analyzing polymer thin film morphologies, we are able to provide a mechanistic explanation of previously reported results of performance enhancements in OFETs. The mechanistic insight derived from this study can play an important role in the design of materials and processes for the large scale fabrication of soft electronics on various surfaces.



POLY 404: Thermal analysis of poly(methylmethacrylate) (PMMA)-graphene oxide(GO) composites

Ishan Niranga J.A Don, ijayala@okstate.edu, Frank D. Blum. Chemistry, Oklahoma State University, Stillwater, Oklahoma, United States

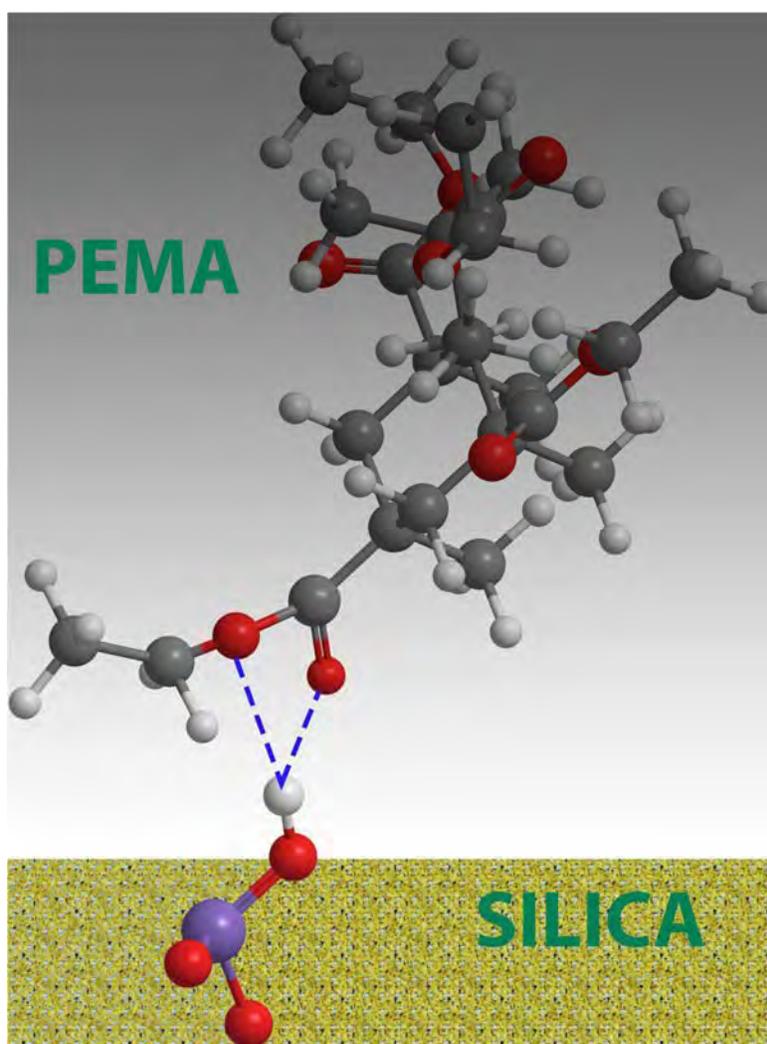
GO is a promising material as a filler that had been paired with polymers to enhance the physical and mechanical properties of their composites. We are interested in the interphase of PMMA and graphene oxide, we based our understanding of a two state model with tightly and loosely bound polymer and compare the glass transition of the composites with bulk polymer. Different amounts of PMMA were adsorbed on graphene oxide. Glass transition behavior and heat capacities of polymer composites were examined by temperature modulated differential scanning calorimetric analysis (TMDSC). We find that the interactions among the GO sheets and PMMA are weaker compared to the interactions between silica and PMMA. Using the TMDSC thermograms recorded from GO-PMMA composites we will make an attempt to study the behavior of glass transition of PMMA on GO surface.



POLY 405: Thermal analysis of poly(ethyl methacrylate) adsorbed on silica

Reza Azarfam, azarfam@okstate.edu, Ugo N. Arua, Frank D. Blum. Chemistry, Oklahoma State University, Stillwater, Oklahoma, United States

Different amounts of poly(ethyl methacrylate), PEMA, adsorbed on a silica substrate were studied. PEMA-silica samples with approximately 0.5 to 4 mg of polymer per m² silica were prepared. Thermal gravimetric analysis was used to determine the amount of polymer adsorbed on silica. Temperature-modulated differential scanning calorimetry was performed to follow the changes in glass transition temperatures of the polymer. FTIR spectroscopy was used to determine the bound fraction of carbonyl oxygens interacting with silanol groups of silica. Similar to previous studies on poly(methyl methacrylate) adsorbed on silica, a broadened and shifted glass transition of adsorbed polymer to higher temperatures was found. A comparison of the results with those for PMMA-silica systems will be made.

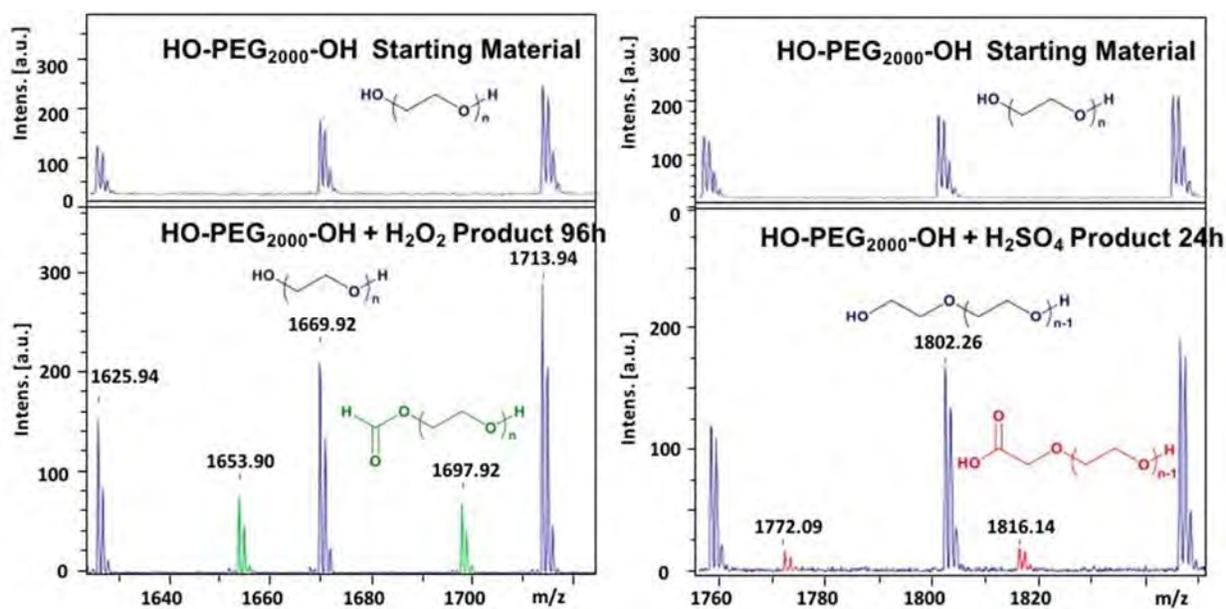


Schematic illustration of hydrogen bonding between oxygen atoms of poly(ethyl methacrylate) and silica.

POLY 406: Elucidating end group effects on the degradation of linear polyethylene glycol using matrix assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry

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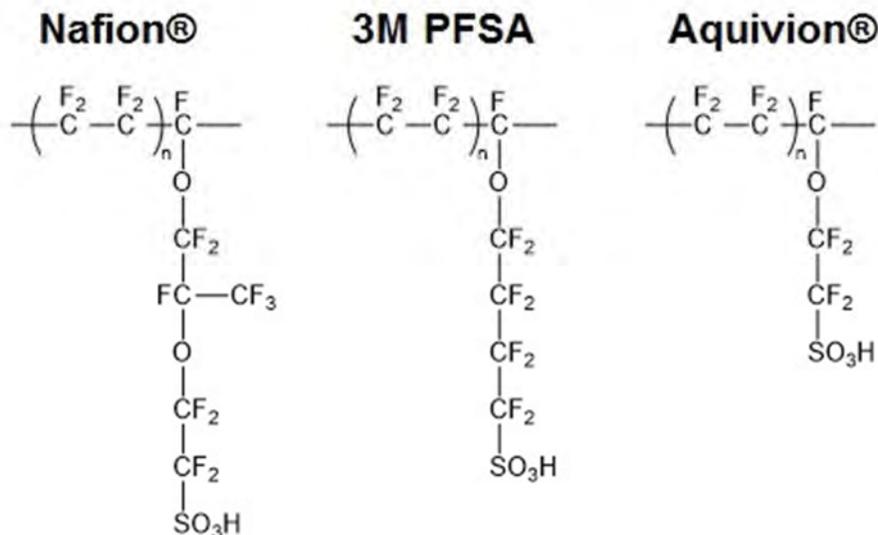
Polyethylene glycol (PEG) is an inexpensive, commercially available polymer that has many biomedical and material applications. Due to its water-solubility and biocompatibility, it has also been used widely to conjugate to drugs and proteins for improve their solubility and blood circulation times. Although ether links are generally considered robust, PEG is still susceptible to oxidation and acidic degradation. MALDI-TOF mass spectrometry has been employed to study the mechanism of degradation of PEG as well as elucidate any difference in degradation with regard to end group modification. In addition to confirming proposed mechanisms of degradation, this study clarifies the role that end groups might play in accelerating, or retarding, degradation.



POLY 407: Effect of equivalent weight on the dynamic mechanical relaxations of perfluorosulfonic acid membranes

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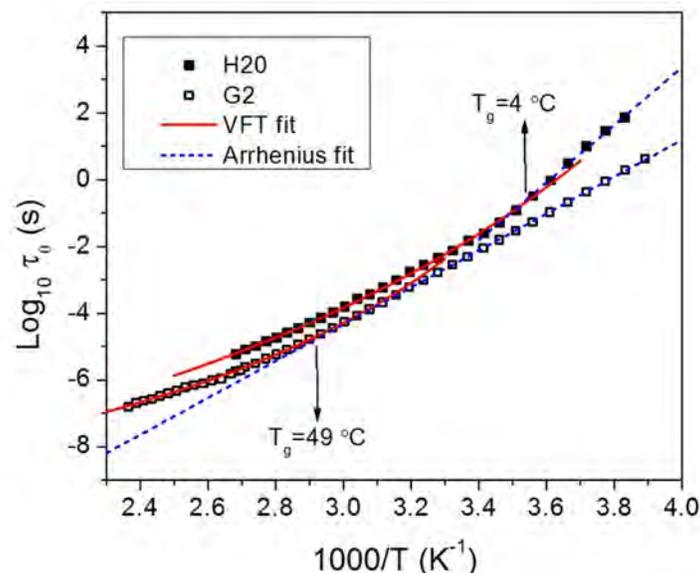
Evaluating the transport and mechanical properties of perfluorosulfonic acid (PFSA) membranes is crucial for applications in polymer electrolyte membrane (PEM) fuel cells. Increasing the ionic content of PFSA improves proton conductivity, but also decreases crystallizability and water swelling sensitivity. Previous studies using dynamic mechanical analysis (DMA) found that the α -relaxation was due to the onset of long-range mobility of the ionomer main chains and side chains via a thermally activated destabilization of the electrostatic interactions, yielding a dynamic network involving significant ion-hopping processes. Segmental motions of backbone chains within the static network is thought to be the molecular origin of the β -transition. Understanding changes in the α - and β -relaxations with membrane ionic content is needed to develop tailored processing conditions to produce high-performing membranes for PEM fuel cells. This study used DMA to examine the α - and β -relaxations of PFSA membranes of different equivalent weights. Ion-exchanged membranes were subjected to the same analysis to elucidate the relationship between relaxation temperature and strength of electrostatic interactions in the ionic domains. Membrane morphology was investigated with small- and wide-angle X-ray scattering.



POLY 408: Comparative study of dielectric relaxation and electrical conductivity behavior correlated to hydrogen bonding organization between Bis-MPA based hyperbranched polymer and dendrimer

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Dynamic relaxation studies performed on 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) based hyperbranched polymers (HBPs) have not yet been extended to their dendrimer analogues which require considerable synthetic efforts. The aim of the study is to compare dielectric behaviors of a bis-MPA based second-generation HBP, Boltorn H20, with its dendrimer analogue and study their correlation with hydrogen bonding organization which is affected by structure dispersity and irregularity. In this study, a monodispersed, ideally structured second-generation dendrimer G2 was prepared via anhydride coupling method. FTIR and NMR analysis were performed to study hydrogen bonding organization in H20 and G2. Stronger hydrogen bonding association was found in G2. Dielectric spectroscopy was employed to study the dielectric relaxation and electrical conductivity behavior of both two polyesters. The γ -relaxation of both H20 and G2, which is originated from rotation of terminal hydroxyl groups, followed Arrhenius dependence. The effect of stronger hydrogen bonds on hydroxyl motion was reflected by the higher activation energy of G2. The conductivity relaxation, contributed by proton hopping along hydrogen bonds, showed non-Arrhenius dependence above T_g and Arrhenius dependence below T_g . This indicates that the translational motions of charges become increasingly faster than structural motion and eventually decouple from it as temperature is approaching to T_g . Larger decoupling of G2 suggests higher mobility of protons in the system which can be facilitated by stronger hydrogen bonding.



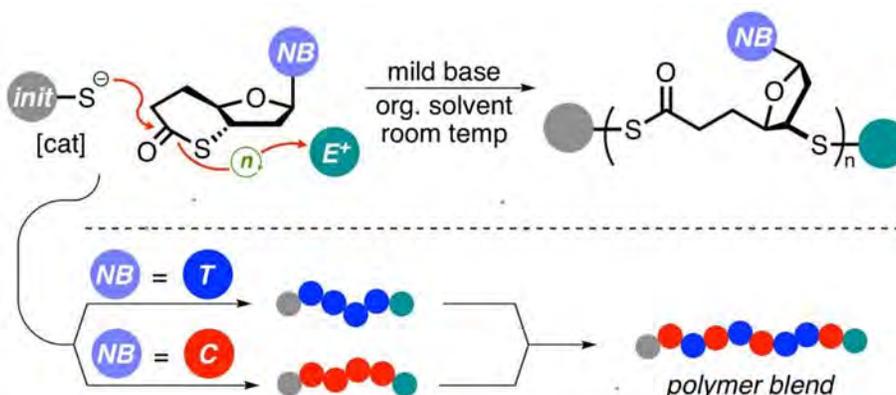
Temperature dependence of the conductivity relaxation time

POLY 409: Responsive DNA-like polymers via the ring opening polymerization of nucleobase appended thiolactones

Sudheendran Mavila, *msudheendran@gmail.com*, Brady Worrell, Trevor Goldman, Chen Wang, Benjamin D. Fairbanks, Dylan W. Domaille, Sankha Pattanayak, Matthew K. McBride, Christopher Bowman. Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado, United States

Thioester exchange is one of the most explored transformations in the literature particularly employed with biomolecules in aqueous solutions. Particularly for peptide synthesis, thioesters are the key factor of the reaction regioselectivity in native chemical ligation because of the freely reversible thiol-thioester exchange steps and exceptionally fast reaction kinetics. However, few investigations have been reported utilizing thioesters in non-aqueous systems. Recently, we demonstrated the exceptionally low activation energies for thiol-thioester exchange reactions in various organic systems. Here we present the straightforward, scalable synthesis of thiolactone appended thymidine and deoxycytidine monomers derived from their natural counterparts and their polymerization to form responsive DNA-like polythioesters in high conversions, good yields of the polymer with low polydispersities. The thiol-end group was found to be quantitatively functionalized via the thiol-Michael reaction to add water solubilizing groups or fluorescent tags.

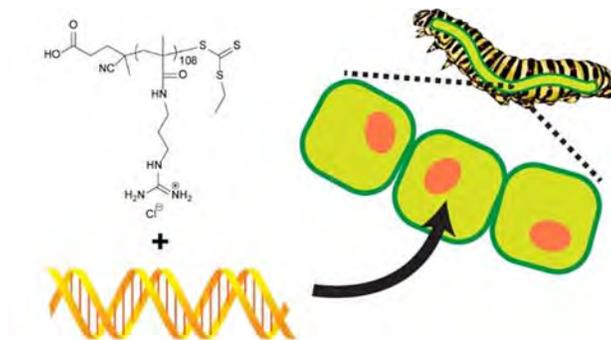
Finally, as each repeat unit is separated by a thioester functional group, dynamic behavior of the polymer is feasible via the thiol/thioester exchange, which is demonstrated here two-fold by the blending of two polymers of different chemical composition (those derived from thymidine and cytidine) and the complete depolymerization of the polymers under extremely mild conditions. As our polymeric material shares many structural, spatial, and stereochemical similarities with DNA we anticipate strong binding to native strands of DNA. This work constitutes the first step towards a platform which we hope will culminate in the routine synthesis of functional sequence controlled polymers via dynamic template directed synthesis. Synthesis, polymerizations and the dynamic behavior of the resulting polymers will be presented.



POLY 410: Guanidinium-functionalized polymer carriers enable RNAi in resistant insect pests

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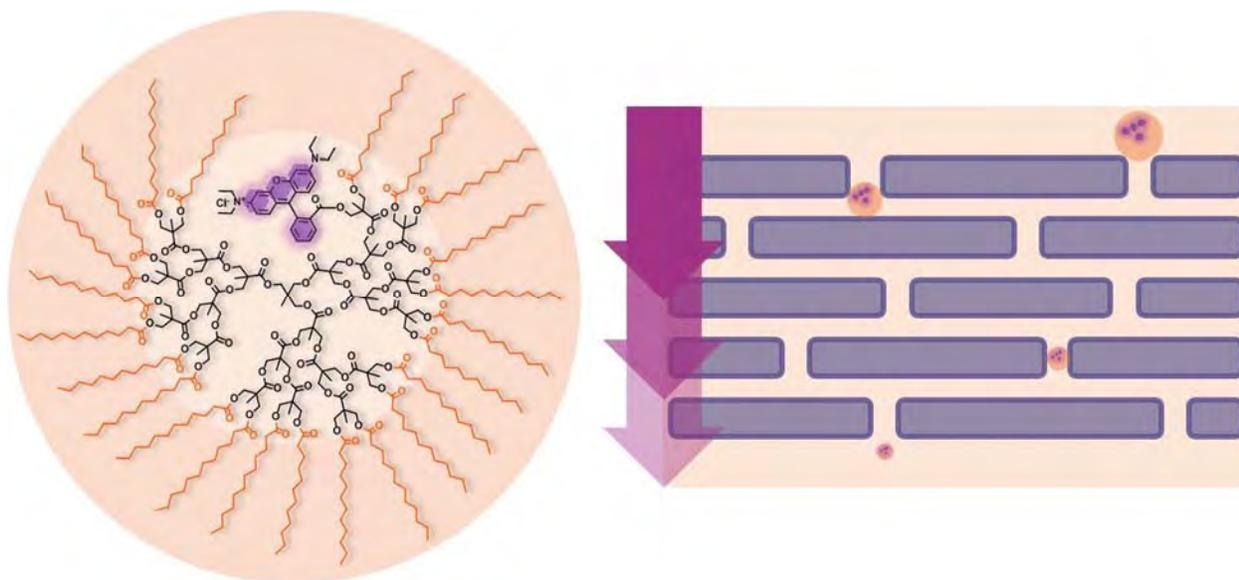
An increasingly exciting option for control of plant pests is the use of RNA interference (RNAi)-based technologies to trigger the downregulation of target genes. The improvement offered by RNAi over conventional pesticides is species specificity. Unfortunately, differences in RNAi activity between orders of pests results in major barriers to delivering the required molecules, many of which seem to exist primarily in the digestive tract. While RNAi-based pesticides have been successful in controlling some pest species, these barriers have prevented control in many others. Herein, we report interpolyelectrolyte complexes (IPECs) consisting of poly[*N*-(3-guanidinopropyl)methacrylamide] (pGPMA) and dsRNA that are capable of inducing highly efficient gene knockdown in lepidopteran pests that are typically refractory to ingested RNAi. Because the cationic polymers exhibit no toxicity towards the live animals while efficiently delivering dsRNA to lepidopteran cells both *in vitro* and *in vivo*, these IPECs offer great promise toward enabling RNAi-based pesticides across many arthropod species.



POLY 411: Dendrimer-based probes for investigating size restrictions of transdermal permeability

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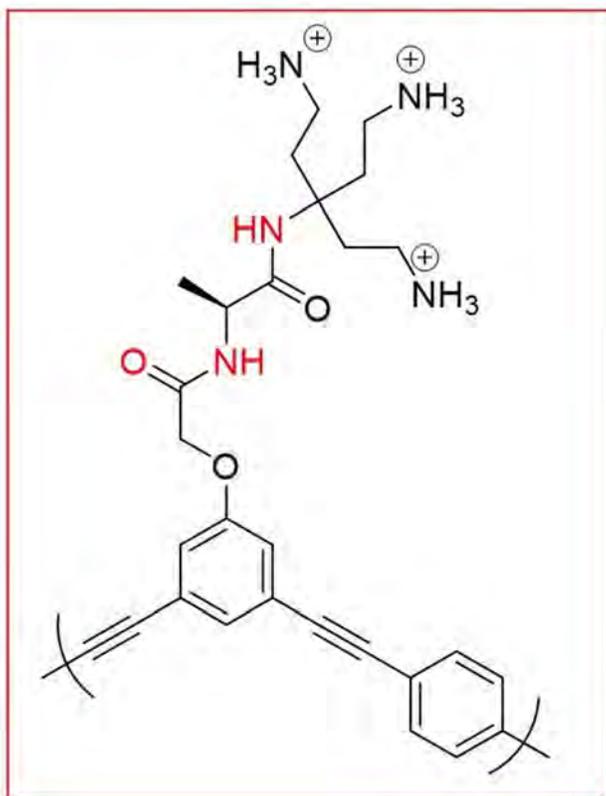
Despite the multiplicity of factors that regulate transdermal permeability, transport investigations to date have focused predominantly on solute molecular weight and extracellular matrix compatibility, rather than membrane properties of the skin itself. The present study aims to establish the size-dependent restrictions of dermal flux using dendrimer-based probes of discrete sizes and corresponding lipophilicity to assess the permeability of the “brick-and-mortar assembly” of the *stratum corneum*. The unique material properties of dendrimer particles—namely, monodisperse, compact structures with tunable size and high surface functionality allowing tailored design—afford modular access to a comprehensive range of well-defined probe sizes. 2,2-Bis(hydroxymethyl)propionic acid (bisMPA)-based polyester scaffolds were synthesized from tris- and tetra-functional cores over dendritic generations (layers of branched monomers) G0 through G3 and conjugated to a single Rhodamine B fluorophore. Comprehensive surface esterification of remaining surface alcohols was carried out using lauric (C12) acid to impart the requisite lipid solubility for transdermal transport. Thus, a library of monodisperse, hydrophobic probes was readily generated, featuring covalently-bound tags to allow for spectroscopic monitoring independent of aggregation or encapsulation phenomena. Material characterization by MALDI-TOF MS, NMR and GPC as well as physical characterization by emission spectroscopy and DLS confirm the well-defined nature of derived constructs. By this means, transdermal permeability as a function of size was assessed *in vitro* with a juvenile porcine dermis model using Franz diffusion cell apparatus.



POLY 412: Meta-linked cationic poly(phenylene ethynylene) conjugated polyelectrolyte featuring a chiral side group: Helical folding and phosphates binding

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Water soluble, meta-linked poly(phenylene ethynylene) **m-P-O-2**, featuring branched ammonium side chains in which chiral and optically active L-alanine unit is induced, has been studied by absorption, fluorescence, and circular dichroism spectroscopy. The studies of **m-P-O-2** in different ratios of methanol/water mixtures show that the polymer folds into a helical conformation, and the extent of helical folding increases with the volume % of water in the solvent. The presence of the helical conformation is signaled by the appearance of a broad, excimer-like visible fluorescence band and CD spectra signal. The interactions between the cationic **m-P-O-2** with anions like pyrophosphates or nucleotide phosphates were studied as well by absorption, fluorescence emission and circular dichroism spectroscopy in both water and methanol. Absorption, fluorescence emission spectra indicate that the addition of phosphates causes the formation of helical structure in methanol in which the polymer alone prefers a random coil conformation which results from the cooperation of opposite charge interaction and self-folding.



POLY 413: Template-directed synthesis of well-defined polysaccharides

Abby Delawder, *adelawder@wustl.edu*, *Angelique F. Greene*, *Xuesong Li*, *Jonathan Barnes*. *Chemistry, Washington University in St. Louis, St. Louis, Missouri, United States*

Polysaccharides are among the most abundant biomacromolecules available from natural resources. They are present in all types of plants, animals, and microorganisms. Whether it be for structural purposes, as an energy source, or the main components in molecular recognition at cell surfaces, Nature relies on complex carbohydrates for a wide range of biological processes. Gaining a molecular mechanistic understanding of these carbohydrate-mediated biological processes remains a major challenge largely because of the structural heterogeneity commonly associated with natural polysaccharides. Efficient and large-scale synthetic approaches is therefore needed to prepare polysaccharides – of high molecular weight and well-defined structure in terms of monomer sequence and stereochemistry that match that of natural polysaccharides. Here, we present a templation strategy for the synthesis of well-defined polysaccharides. Synthesis of functional monomers, their subsequent polymerization into “double polymers”, and characterization of the resultant isolated carbohydrates is discussed. The mechanism by which the resultant products are separated from the templating scaffold through chemical means and the isolation of the pure biomacromolecule is also highlighted. The issues associated with scalability, dispersity, and purity of oligo- and poly-saccharides are addressed using the intramolecular self-assembly templation strategy designed by the Barnes group.



Homo-Polysaccharide

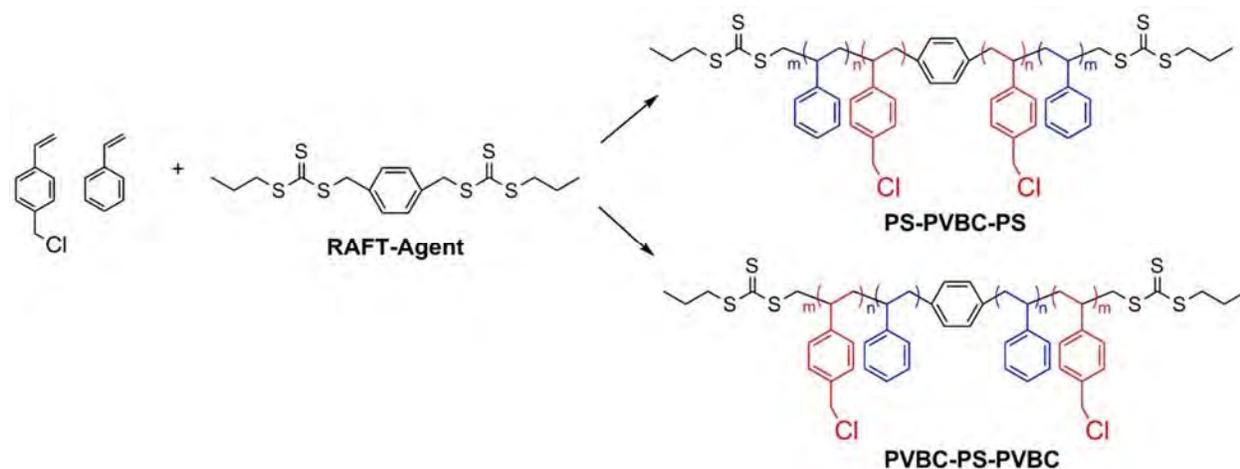


Hetero-Polysaccharide

POLY 414: RAFT synthesis of ABA-BAB type PS-PVBC triblock copolymers for polyelectrolyte materials

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Novel styrenic symmetric triblock copolymers of poly(styrene)-*b*-poly(vinyl benzyl chloride) (PS-PVBC) with chloride moieties for post-polymerization functionalization were synthesized by RAFT polymerization. Synthesis of ABA and BAB type triblocks was performed, and RAFT kinetics were investigated. A difunctional R-type trithiocarbonate RAFT agent ensured that, during chain growth, the RAFT agent grows polymers inside-out, keeping the trithiocarbonate functionalities on chain ends. This architecture guarantees the triblocks remain intact even if the trithiocarbonate degrades. RAFT synthesis of PS and PVBC is confirmed to be a controlled polymerization. The effects of several solvents were investigated. DMF as a solvent allowed narrower MW distributions, and unexpectedly improved kinetics, and allowed higher polymerization rates. ABA and BAB type triblock polymers of PS-PVBC were also studied for a wide range of total MWs. Chain extension of the macro-polymers was performed to demonstrate livingness in the triblock synthesis reactions. Reaction conditions were optimized to obtain good control over MW and MW distributions of the blocks. The novel symmetric triblock polymers studied here represent versatile a backbone that can benefit electrochemical applications. The triblock copolymers developed here can potentially serve anion exchange membranes for fuel cells that require high alkaline stability.

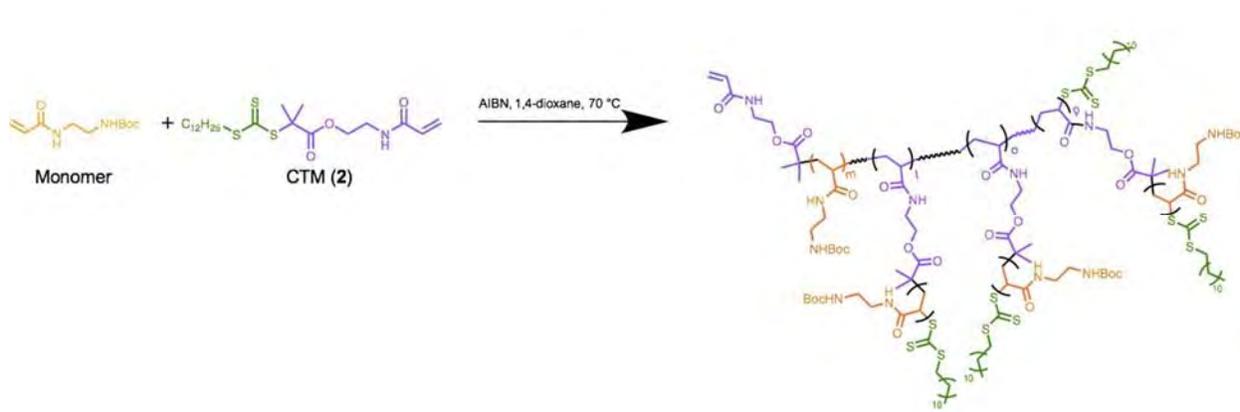


Synthesis route for ABA and BAB type PS-PVBC triblock copolymers

POLY 415: Hyperbranched bisphosphonate-functional polymers via RAFT self-condensing vinyl polymerization and post-polymerization functionalization

Patricia R. Calvo^{3,2}, pcalvo0220@gmail.com, **Kenneth B. Wagener**², **Brent S. Sumerlin**¹. (1) Department of Chemistry, University of Florida, Gainesville, Florida, United States (2) Dept. of Chemistry, University of Florida, Gainesville, Florida, United States (3) Science & Mathematics, Texas A&M University San Antonio, San Antonio, Texas, United States

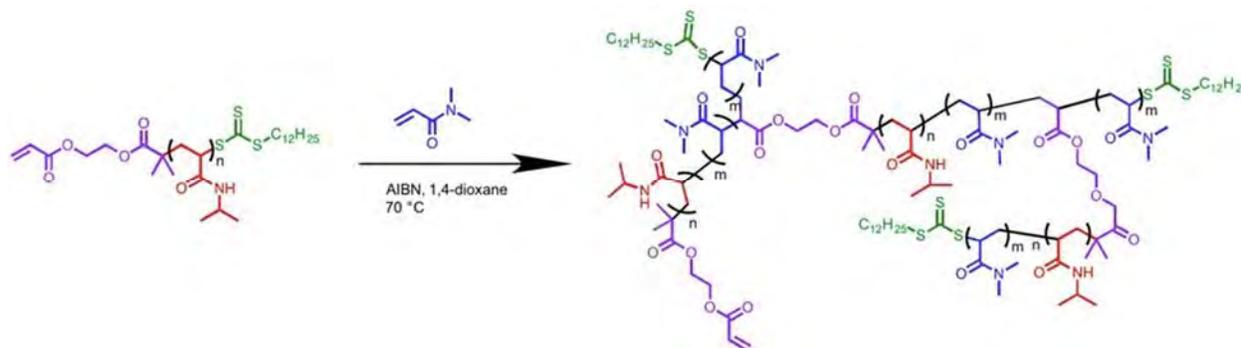
We report the synthesis of hyperbranched aminobisphosphonic acid polymers via RAFT self-condensing vinyl polymerization. A novel acrylamide functional chain transfer monomer was synthesized and characterized by ¹H and ¹³C NMR spectroscopy, elemental analysis and mass spectrometry. The monomer was subsequently copolymerized with an acrylamide monomer bearing a pendant amine group to create hyperbranched amine functional polymers. The degree of branching was controlled by changing the reaction stoichiometry and the polymerizations resulted in well-defined materials with moderate molecular weights. The aminobisphosphonate functional group was introduced via a 3-component Kabachnik-Fields reaction. The functionalized polymers were characterized using elemental analysis, IR spectroscopy, ³¹P NMR spectroscopy and dynamic light scattering. DLS revealed interesting solution behavior related to the degree of branching of the polymers. Additionally, we demonstrated an alternate functionalization of the amine polymers to create acid degradable imine hydrogels. This work demonstrated the application of multicomponent reactions to RAFT-derived hyperbranched polymers and results in materials with interesting properties and potential applications in the biomedical field.



POLY 416: Thermoresponsive hyperbranched block copolymers via RAFT self-condensing vinyl polymerization

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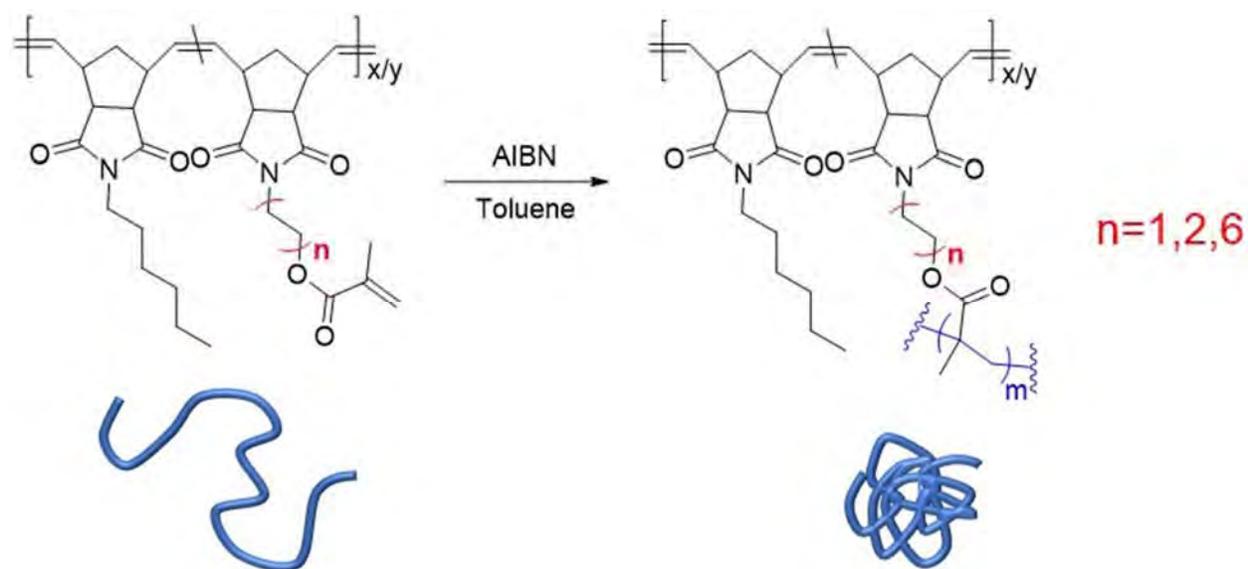
The first examples of amphiphilic, thermoresponsive hyperbranched block copolymers, consisting of blocks of temperature responsive poly(N-isopropylacrylamide) (PNIPAM) and hydrophilic poly(N,N-dimethylacrylamide) (PDMA), were synthesized using RAFT-mediated self-condensing vinyl polymerization (SCVP). The polymers are created from PNIPAM or PDMA macro chain transfer monomers (CTM), which are chain extended with DMA or NIPAM, respectively, to afford the hyperbranched block copolymers via SCVP. Polymer composition as well as degrees of branching were controlled through the reaction stoichiometry and the length of the macro CTM. The final polymers show cloudpoints that are influenced by polymer composition and DB, serving as a tunable system to design polymers with a desired cloudpoint. Temperature induced self-assembly above the cloudpoint was demonstrated by dynamic light scattering (DLS).



POLY 417: Effect of pendant groups on fabrication of poly(norbornene imide) single-chain nanoparticles

Ruiwen Chen, rc1033@wildcats.unh.edu, Sarah Benware, Jacob J. Lessard, Justin Cole, Erik B. Berda. Department of Chemistry, University of New Hampshire, Durham, New Hampshire, United States

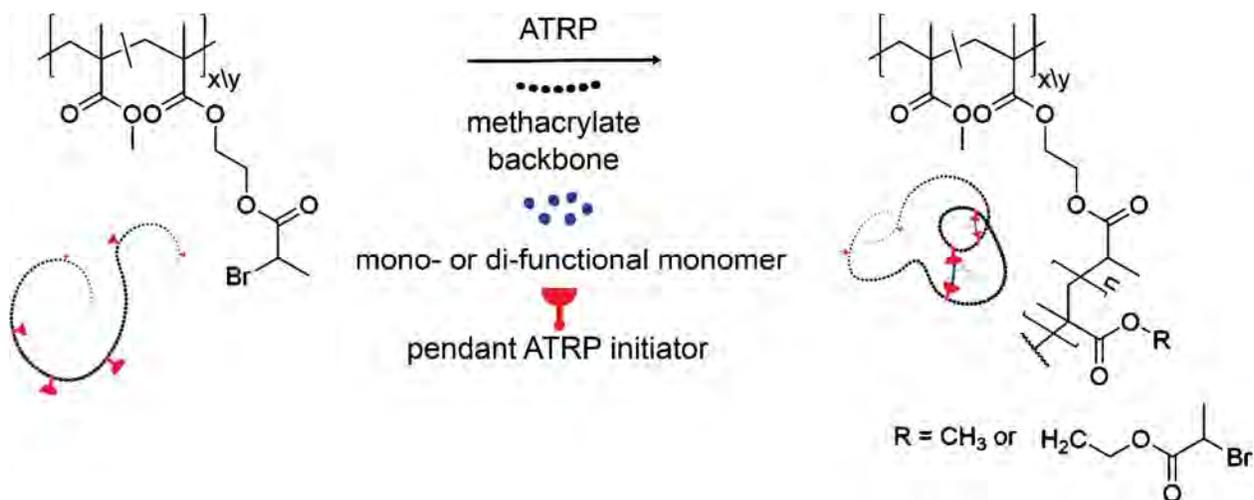
Function of biomacromolecules in nature depends largely on their precisely sequenced primary structure and highly tuned tertiary structure. Polymer chemists strive to replicate nature's remarkable ability to fabricate nanomaterials of defined three-dimensional structure. Among these effort, the intramolecular cross-linking of single linear polymer chains into well-defined globular nanoparticles, referred to as single-chain nanoparticles (SCNP) represent a reliable way to synthetically mimic the folding process seen in proteins. A variety of crosslinking chemistries with different pendant groups have been reported over the years. However, detailed research on the length and flexibility of pendent groups in relation to folding efficiency has not been thoroughly explored. Herein, a series of poly(norbornene imide) with pendant methacryloyl groups were synthesized through ring opening metathesis polymerization (ROMP). The designed polymers have various spacing between the polymerizable methacryloyl pendant groups and the polymer backbone. Upon radical initiation, intra-chain radical polymerization occurs, resulting in chain folding of the linear poly(norbornene imide) to form nanoparticles. The effect of length and flexibility of pendant groups on folding efficiency was monitored by GPC and NMR.



POLY 418: Handles for controlled architecture and functionality in single-chain nanoparticles: Cross-linking by intrachain ATRP

Elizabeth R. Bright, *erb1002@wildcats.unh.edu*, Claudia Willis, Courtney Leo, Nathan Shipley, Christopher J. LaSalle, Ashley Hanlon, Erik B. Berda. Department of Chemistry, University of New Hampshire, Durham, New Hampshire, United States

Just as single amino-acid chains fold into dimensionally defined structures, so too may synthetic polymer chains with pendant cross-linkable functionalities collapse into dimensionally defined shapes. Protocols have been developed for accessing this so-called single-chain nanoparticle (SCNP) motif using a wide range of cross-linking chemistries. In this diversity lies a great potential to impart additional morphological and functional designs within the soft nanomaterial framework. In this work, SCNP were prepared from parent polymers capable of initiating intra-chain polymerization by ATRP under conditions favoring termination by coupling. Because of the wide variety of compatible monomers, the design imparts handles with which to control both architecture and functionality. To demonstrate this potential, model simple and hyperbranched examples were prepared.



POLY 419: Hydrogenated polyisoprene-g-silica nanoparticles in polyolefin nanocomposites

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We have been conducting polymerizations of isoprene onto the surface of 15 nm silica nanoparticles (NPs) using surface-initiated RAFT polymerization with controlled molecular weights and chain densities. These polymerizations resulted in 90% of 1,4 polyisoprene isomer which could be hydrogenated to poly(ethylene-co-propylene). Hydrogenation of polyisoprene-g-silica NPs via p-toluenesulfonyl hydrazide was explored and resulted in poly(ethylene-co-propylene)-g-silica NPs [Figure 1]. We then investigated the dispersion of these “polyolefin-like”-grafted-particles in different polyolefins for their applications in reinforced nanocomposites. Preliminary results have shown promising results for the dispersion of these particles in a polypropylene matrix [Figure 2].

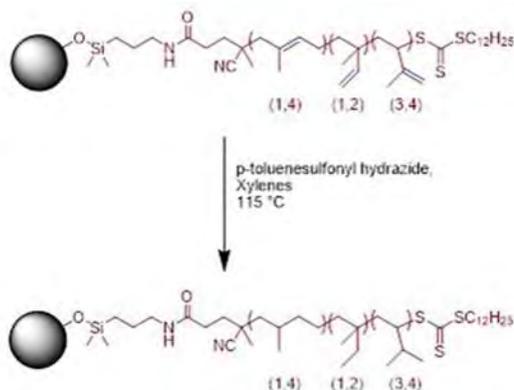


Figure 1. Hydrogenation of PI-g-silica NPs

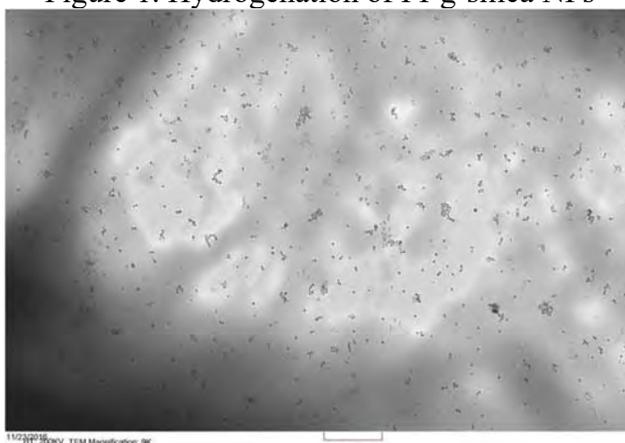
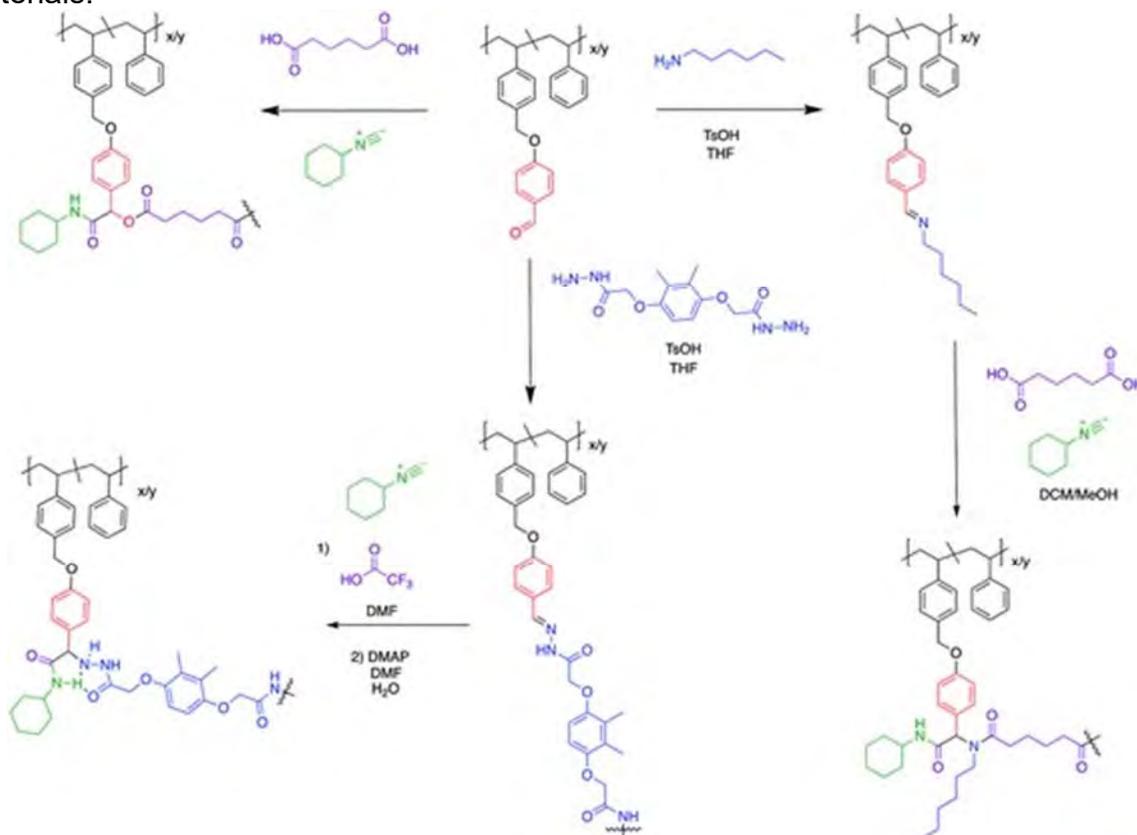


Figure 2. TEM image of HPI-g-silica NPs in isotactic polypropylene matrix.

POLY 420: Synthesizing single-chain nanoparticles: Bio-inspired functionality via isocyanide-based multicomponent reaction chemistry

Erinn Reville¹, ekb24@wildcats.unh.edu, Justin Cole¹, Jacob J. Lessard¹, Kyle Rodriguez¹, Ashley Hanlon¹, Joseph P. Mancinelli¹, Erik B. Berda². (1) Chemistry, University of New Hampshire, Durham, New Hampshire, United States (2) Department of Chemistry, University of New Hampshire, Durham, New Hampshire, United States

Multicomponent reactions have the ability to generate products of high complexity and diversity that can be further functionalized as bio-inspired polymeric scaffolds. Such synthetic scaffolds have been explored for their potential to mimic natural macromolecules as a gateway to sophisticated medical remedies. By using intra-chain isocyanide-based multicomponent reactions (ICMR), we were able to synthesize single-chain nanoparticles (SCNP) containing peptide and depsipeptide cross-links attached to a polystyrene backbone. These segments created a pathway to producing materials of multiple protein-inspired elements. Nanoparticle formation occurs via intramolecular cross-linking, providing well-defined structural elements incorporated within a highly disordered tertiary structure. The resulting nanostructures were characterized using ¹H NMR, DOSY NMR, and size-exclusion chromatography. Initially, the intended mode of SCNP formation was through covalent cross-linking, but secondary noncovalent interactions contributed more significantly to nanoparticle folding in relation to natural materials.

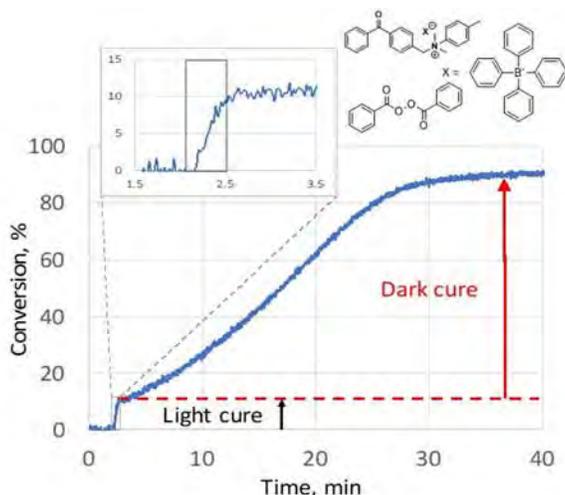


Scheme 1. Synthetic scheme for cross-linking SCNP using isocyanide-based multicomponent reaction chemistry

POLY 421: Designing free-radical redox photoinitiators for practical dark curing

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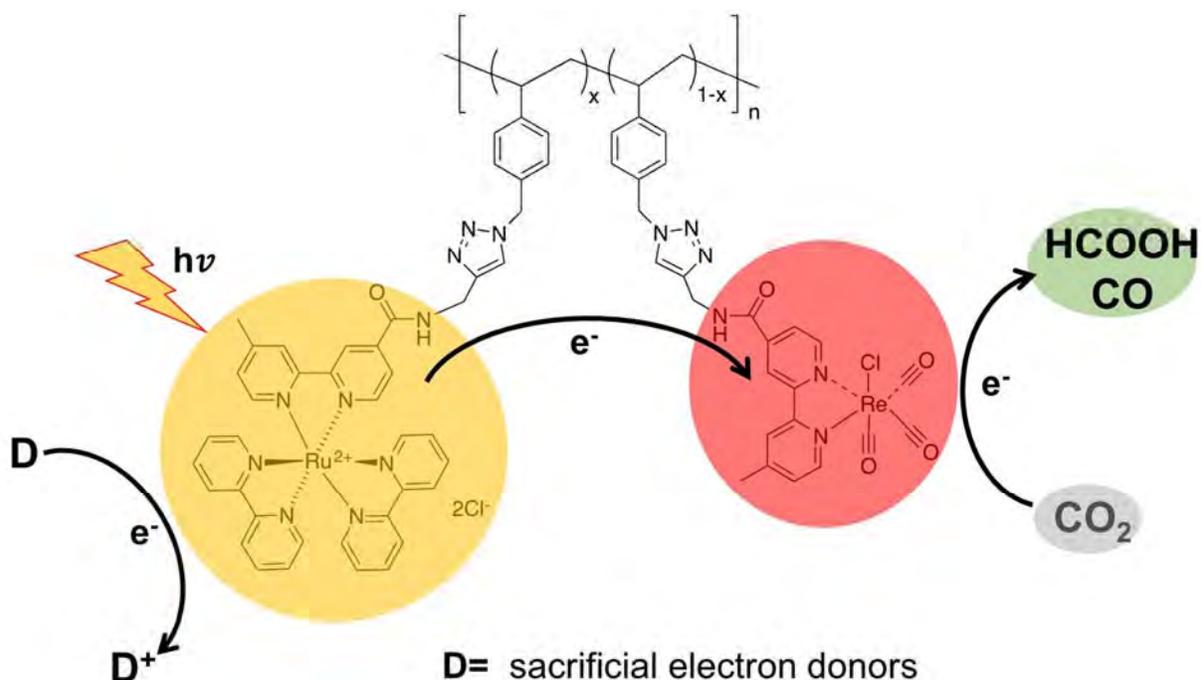
The ability to achieve maximum conversion throughout an optically thick photopolymer material requires extended irradiation of the exposed surface to obtain near-comparable levels of conversion at the light-attenuated, opposite surface. Due to the high efficiency of bi-radical termination processes in radical-based polymerizations, only limited post-cure occurs if access to the curing light and continued production of initiating radicals is interrupted. A strategy to uniformly maximize final conversion within photopolymers by extending radical initiation well beyond the temporal exposure of the curing light is advanced here through a photoinduced redox initiation. Redox photoinitiators (redox PI) release various reductants (amines) upon 365nm irradiation, which react over extended intervals with oxidants (peroxides) to provide initiating radicals. For a real-time FTIR study of dark curing, the redox PI system achieved an initial conversion of 15% during a brief irradiation period. However, the continuous generation of radicals from dark redox reactions achieved a final conversion of 80% over 30 min without reliance on thermal assistance in conventional comonomers. The initial photopolymerization was rapid due to a synergistic effect of direct radical production from photodegradation of the PIs while the released amines reacted with peroxides to provide latent initiating radicals via the redox mechanism. This dark cure result is juxtaposed against the analogous condition with a conventional photoinitiator such as 2,2-dimethoxy-2-phenylacetophenone, which when interrupted at 12% conversion plateaued with a final conversion of 14%. We further demonstrated that dark curing rates can be well-controlled based on the reduction potential difference between the redox pairs. The capacity to reach full conversion under non-ideal photocuring conditions or throughout light-attenuated and thick films, such as bulk fill dental composites, can be accomplished with the redox photoinitiation.



POLY 422: Polymeric chromophore-catalyst assembly for the photocatalytic CO₂ reduction

Yan Zhao, zhaoyan0629@gmail.com, Soojin Kim, Yu Kyung Eom, Gyu Leem, Kirk S. Schanze. Department of Chemistry, University of Texas at San Antonio, San Antonio, Texas, United States

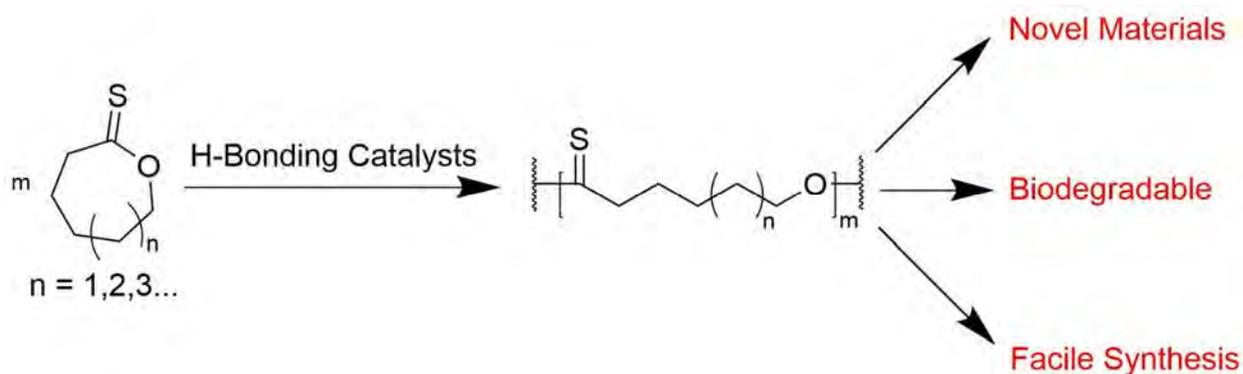
The conversion of solar energy to the chemical energy by using the CO₂ reduction catalysts has been of great interest in solving global warming and shortage of energy. A polystyrene-based chromophore-catalyst assembly, used for photocatalytic CO₂ reduction, has been synthesized and characterized. The polystyrene backbone, synthesized by nitroxide mediated radical polymerization, was used as the scaffold to construct the chromophore-catalyst assembly. The CO₂ reduction catalyst centers based on Re(bpy)(CO)₃Cl and [Ru(bpy)₃]²⁺ derivatives as the chromophores were connected to the polystyrene backbone by the click reaction (bpy = 2,2'-bipyridine). The resulting polystyrene-based assembly was characterized by NMR and IR spectroscopy, confirming the high efficiency of the click grafting. The photophysical and electrochemical properties of the polychromophore-CO₂ reduction catalyst assembly were investigated in both aqueous solution and DMF/TEOA mixed solution. Further photocatalytic reactions will be separately carried out in the aqueous solution and DMF/TEOA mixed solution with sacrificial electron donors. The possible photocatalytic products, CO and HCOOH, will be tested by GC and NMR.



POLY 423: Organocatalytic synthesis of poly(thionolactone)s: New materials abilities from sulfur-containing polylactones

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The field of organocatalytic ring-opening polymerization (ROP) has exploded in depth the breadth since the first report by Hedrick et al in 2001¹. Despite sporadic efforts to increase the monomer scope of organocatalytic ROP, the field has largely been limited to esters and carbonate monomers. This has been the case despite the fact that the mild organocatalyst systems are the perfect platform for the ROP to traditionally-inaccessible polymers. For example, a sulfur analogues of lactones – thionolactones – have been largely unexplored by traditional methods. Indeed, ϵ -thionocaprolactone is the only thionolactone² whose ROP has been explored and, even then, only in a handful of reports. The ROP of the larger and small thionolactones have been entirely unexplored. With our recently-developed class of urea cocatalysts, we can facilitate the ROP of thionolactones to predictable weights with narrow dispersities. Along with incredible control and living behavior in the ring-opening polymerization of these monomers, the resulting polymer demonstrate remarkable physical characteristics versus the corresponding lactones: lower melting points, flexibility and altered hydrolysis rates. The unusual characteristics of this newly available class of polymers promises new applications.



POLY 424: Anion conductive polymers consisting of perfluoroalkylene, fluorenyl, and pendant ammonium groups

Naoki Yokota¹, *n.yokota@takahata.biz*, **Hideaki Ono**², **Junpei Miyake**^{3,4}, **Kenji Miyatake**^{3,4}. (1) Takahata Precision Japan Co., Ltd., Yamanashi, Japan (2) Integrated Graduate School of Medicine, Engineering, and Agricultural Sciences, University of Yamanashi, Yamanashi, Japan (3) Clean Energy Research Center, University of Yamanashi, Yamanashi, Japan (4) Fuel Cell Nanomaterials Center, University of Yamanashi, Yamanashi, Japan

Alkaline fuel cells using anion conductive polymers offer several advantages, such as possible use of abundant metal electrocatalysts (Ni, Co, Ag, etc.) and better kinetics of the oxygen reduction reaction. The issues associated with alkaline fuel cells are lack of anion conductive polymers with high conductivity and durability.

In this research, we report synthesis and properties of novel copolymers consisting of perfluoroalkylene and fluorenyl groups in the polymer backbones with pendant ammonium groups (QPAF-4). Lack of heteroatom linkages in the polymer backbones, and the ammonium groups tethered at the pendant alkyl groups contributed to the excellent alkaline stability of the membranes (Figure 1). Synthesis, structural analyses, anion conductivity, water uptake, and mechanical and chemical stabilities of the copolymer membranes will be discussed.

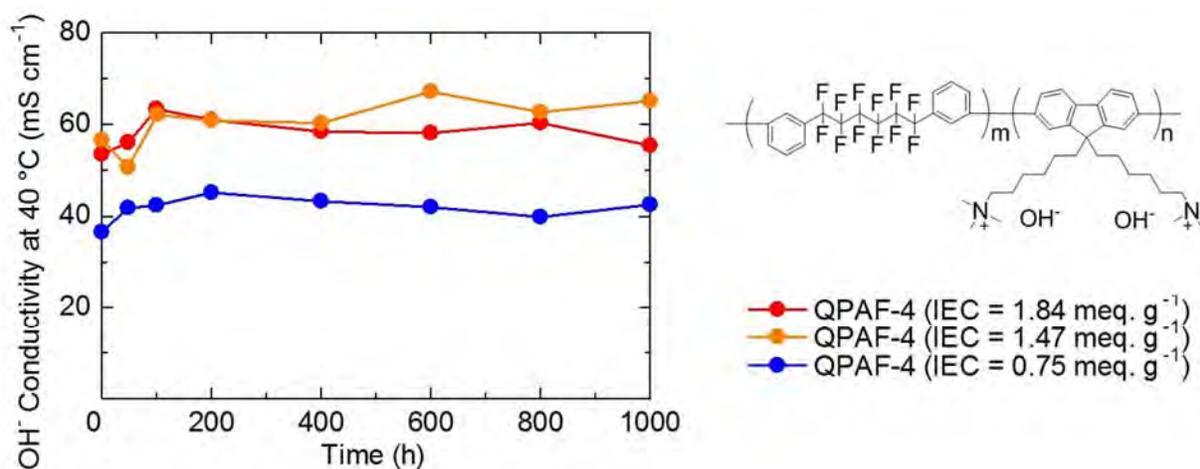


Figure 1. Time course of hydroxide ion conductivity of QPAF-4 membranes in 1 M KOH aqueous solution at 80 °C. IEC stands for ion exchange capacity.

POLY 425: Photo controlled two-stage reactive polymer construction and application

Xinpeng Zhang, xizh5879@colorado.edu, Sijia Huang, Weixian Xi, Katelyn Long, Christopher Bowman. University of Colorado Boulder, Boulder, Colorado, United States

Dual cure systems attract significant attention as they afford great advantages: an intermediate polymer that enables optimal handling characteristics, while maintaining the ability to tune the final polymer properties nearly independently. Despite these benefits, there is relatively little effort on fully photo controlled (with different wavelengths) 2-stage polymer systems. By applying a photobase generator (NPPOC-TMG) and a UV radical initiator, it is possible to develop a fully photoactivatable dual cure polymer: 1st stage stoichiometric thiol-Michael reaction controlled with light around 400nm and 2nd stage radical homopolymerization triggered by 365nm.

By designing a series of non-stoichiometric thiol-acrylate systems, a polymer network is initially formed via anion-mediated thiol-Michael addition photopolymerization. Afterwards, through radical initiation, a highly crosslinked network is formed as triggered by UV irradiation. The reaction kinetics of the non-stoichiometric systems confirm the two distinct light controlled stages. (**Figure 1**) The mechanical performance of these two stage resins was characterized with DMA as were its potential applications in shape memory polymers and impression materials.

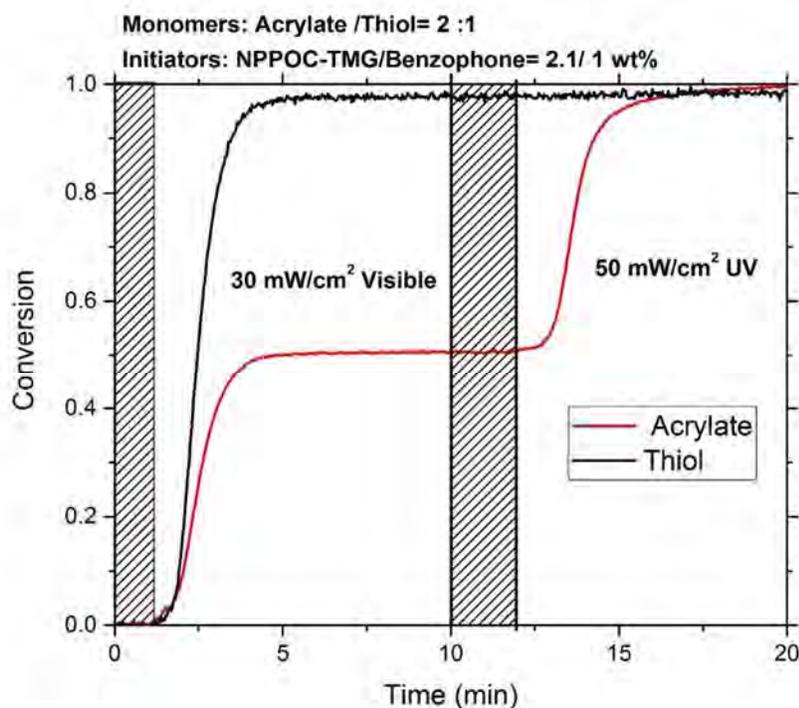
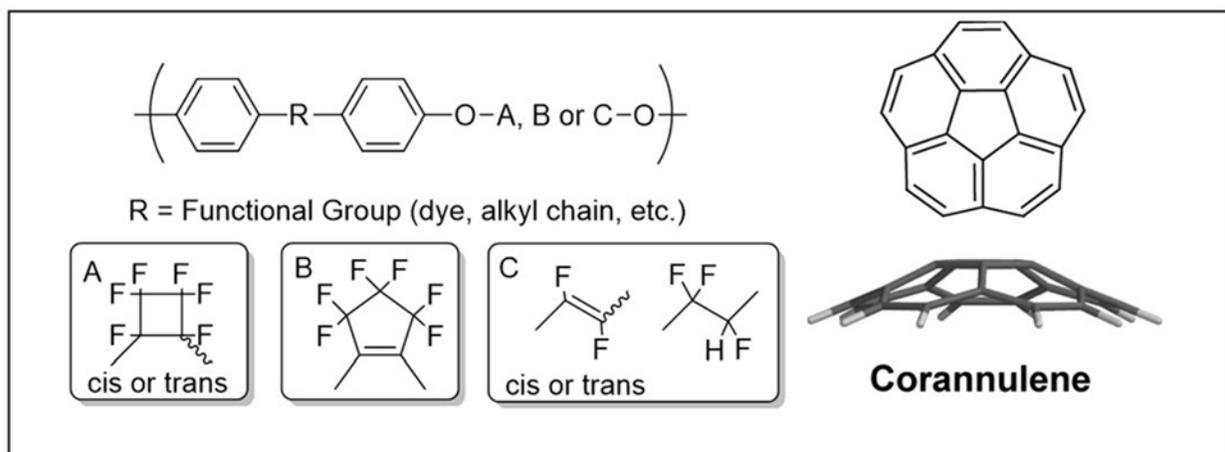


Figure 1. FT-IR result of dual cure system, TCDDA: PETMP= 2: 1, initiation system: NPPOC-TMG and Benzophenone.

POLY 426: A modular approach to semi-fluorinated aromatic ether polymers via step-growth polymerization of fluoroalkenes

Ketki Shelar², kes748@msstate.edu, **Karl Mukeba**², **Andrzej Sygula**¹, **Dennis W. Smith**². (1) Chem Dept, Mississippi State University, Mississippi State, Mississippi, United States (2) Chemistry, Mississippi State University, Mississippi State, Mississippi, United States

Our research laboratories have successfully demonstrated the synthesis of semi-fluorinated aryl ether polymers which include perfluorocyclobutyl (PFCB) aryl ether polymers prepared via [2+2] radical mediated thermal cyclodimerization of trifluorovinyl ethers (TFVE). PFCBs have been widely used in high performance passive optics, electro-optics, polymer light-emitting diodes (PLEDs), space survivability, and polymeric fuel cell membranes (PEMs), high use temperature fluorosilicones, POSS composites, liquid crystalline polymers, and exhibit similar advantages as their fully fluorinated analogs. We have also demonstrated the nucleophilic addition of bisphenols to TFVEs to form fluoro-arylene vinylene ether (FAVE) polymers. Moreover, we have successfully synthesized poly(perfluorocycloalkenyl aryl ether) homopolymers and copolymers in one step *via* nucleophilic addition/elimination with bisphenols and perfluorocycloalkenes (PFCAs). We are currently working on a project to attach TFVEs to corannulene or other buckybowls (curved-surface polycyclic aromatic hydrocarbons) and introduce a novel functional group aspect to these materials. This presentation will overview the projects currently ongoing in our laboratory including three fluoropolymer platforms and new strategies to fluoro-functional corannulenes.



POLY 427: Xerogel-sequestered transition metal catalysts: A new generation of marine antifouling materials

Corey A. Damon, coreydam@buffalo.edu, Michael R. Detty. Chemistry, University at Buffalo, Amherst, New York, United States

Marine biofouling is the accumulation of biological organisms on any submerged surface. Biofouling on ship hulls leads to added roughness and drag, increasing fuel consumption and greenhouse gas emission in order to meet range and speed demands. In addition, biofouling may lead to the introduction of invasive species, a major concern for New York's Great Lakes. Antifouling hull coatings that discourage settlement, and fouling-release coatings to minimize adhesion of fouling organisms, represent two approaches to combat biofouling.

Sol-gel-derived xerogel coatings incorporating organically modified silanes (ORMOSILs) have shown promise as fouling-release coatings and have previously been modified to incorporate organochalcogenide catalysts for the oxidation of bromide with hydrogen peroxide (H_2O_2). The catalytic oxidation of oceanic halides with H_2O_2 found in aquatic environments can produce hypohalous acids *in situ*, which have known biocidal effects and discourage settlement of aquatic species. Grafting of transition metals to mesoporous silica has also provided catalysts for the oxidation of halide salts with H_2O_2 ; albeit only under acidic conditions.

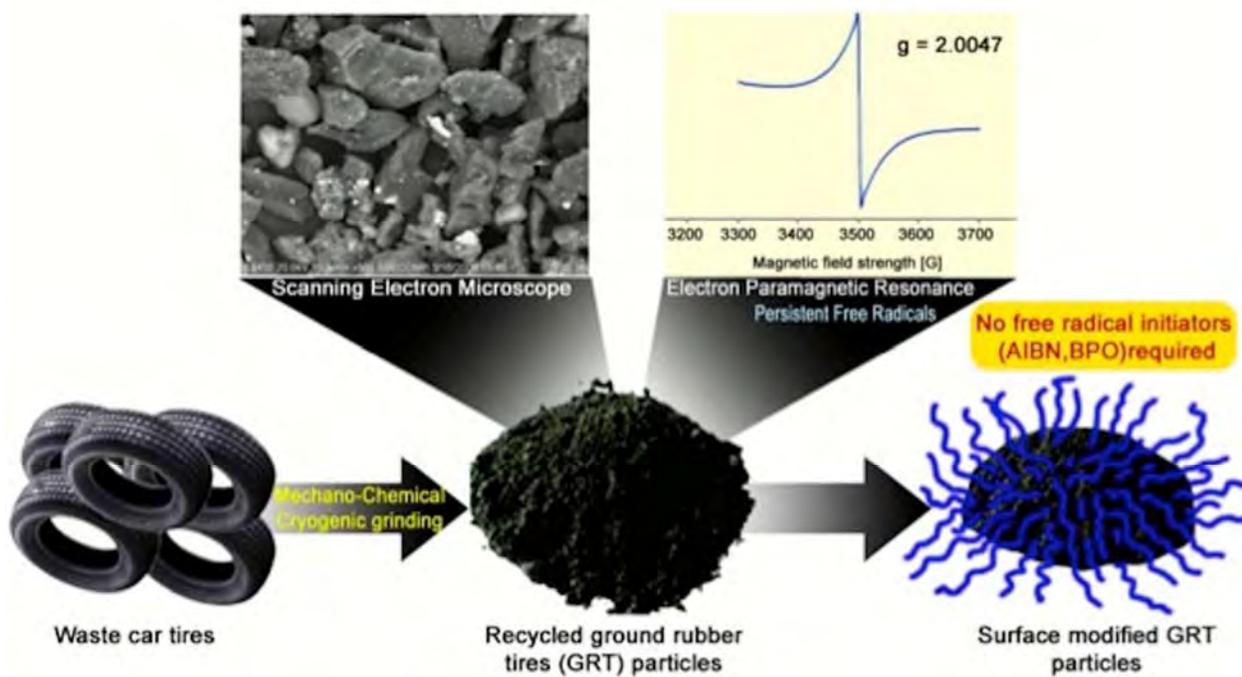
Active xerogels incorporating transition metals have been prepared to catalyze the oxidation of both bromide and chloride with H_2O_2 at the pH of seawater, the first evidence of chloride oxidation under oceanic conditions. Biological assays performed with the green alga *Ulva linza* yielded a significant reduction in zoospore settlement and increase in sporeling removal in the presence of H_2O_2 , indicating antifouling properties have been introduced to a fouling-release surface. Select ORMOSILs have been introduced to coatings to increase hydrophobicity, resulting in reduced drag and faster sail times in Lake Ontario. The impact of transition metals and ORMOSILs on xerogel surface characteristics has been evaluated by contact angle analysis, scanning electron microscopy, and inductively coupled plasma mass spectrometry. A new generation of antifouling/fouling-release hybrid coatings have been deployed to be tested against bacteria and macrofoulers worldwide.



POLY 428: Self-initiated functionalization of waste tire rubber networks and new composite applications

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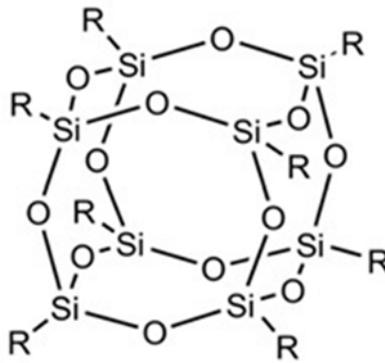
Due to their low-cost, chemical resistance, and thermal stability, ground rubber tires (GRT) prepared via cryogenic grinding, have found application as functional fillers in composites, asphalt formulations, and as a chemical / fuel source. Self-initiated functionalization via free radical polymerization provides enhanced compatibility with matrix resins for new applications such as functional coatings, feedstocks for biomass and biochar products, and possibly new proppant materials and related components in fracturing technologies for oil and gas recovery. Self-initiated surface grafting of GRT via acrylic acid bulk polymerization without the use of initiator affords composites with improved bonding and variable rheological properties. For instance, asphalt/GRT composites display reduced reflective cracking in overlays, improved cracking, skid, and rutting resistance, longer pavement life, and decreased noise level. Surface functionalization with polyacrylic acid gave epoxy composites with enhanced mechanical properties. This presentation will give an overview of the rubber projects in our laboratory, which includes GRT surface modification, hydrosilylation of used tire rubber, fluorination of GRT particles, and other recycled rubber materials and rubber/polymer blends and composites.



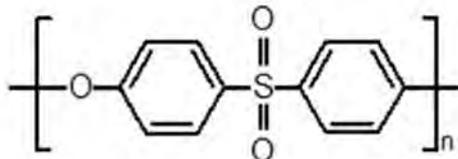
POLY 429: Structure/property/processing relationships in POSS-modified high temperature thermoplastic composites

Mitchell B. Woellner¹, *mitchell.woellner@usm.edu*, **Rahul Shankar**¹, *rahul.shankar@usm.edu*, **Aundrea F. Stewart**¹, **Kenneth T. Posey**², **Joseph D. Lichtenhan**³, **Sarah E. Morgan**¹. (1) School of Polymer Science and Engineering, University of Southern Mississippi, Hattiesburg, Mississippi, United States (2) Mississippi Polymer Institute, Hattiesburg, Mississippi, United States (3) Hybrid Plastics Inc., Hattiesburg, Mississippi, United States

Polyhedral oligomeric silsesquioxane (POSS) nano-structured additives can significantly improve the processability of high-viscosity thermoplastics at low percent loadings while also preserving, if not slightly improving, the thermal and mechanical properties of the neat polymer. Maintaining molecular dispersion of the POSS molecules throughout the polymer matrix is crucial to achieving the desired results and has been a challenge. Thus, a series of functionalized POSS additives were melt-compounded with commercial polyether sulfone (PESU) to evaluate how the organically-modified corona of the POSS molecules affects its compatibility and dispersion within the PESU matrix. Surface properties of the final melt blends were characterized via AFM, SEM-EDX and contact angle analysis. In addition, the mechanical properties were determined via tensile and impact testing; melt viscosity via low-strain dynamic frequency sweeps; and bulk morphology via TEM.



Polyhedral Oligomeric Silsesquioxane (POSS)
(R = i-butyl, i-octyl, phenyl etc.)

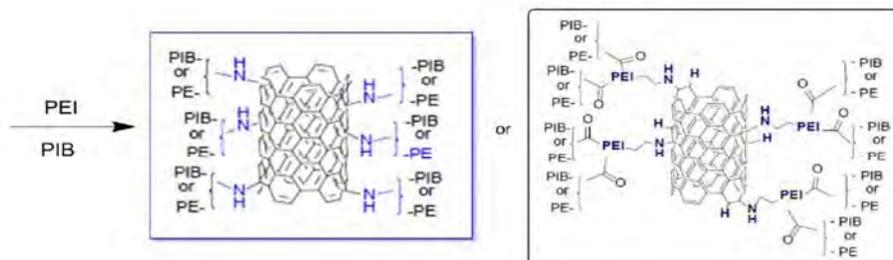


Polyether sulfone (PESU)

POLY 430: Polyolefins as tools for multiwalled carbon nanotubes solubilization

Praveen K. Manyam, *praveen.manyam@qatar.tamu.edu*. Science, Texas A&M university at Qatar, Doha, Qatar

Multiwalled carbon nanotubes (MWNTs) are of great interest as nanofillers in polymers. Nanocomposites of MWNTs with Polyisobutylene (PIB) and Polyethylene (PE) or Polypropylene (PP) have been used widely in various applications, such nanocomposites are typically formed using chemically modified MWNTs where the chemical modification step is designed to increase the compatibility of these materials with the host polyolefin. Radical grafting, oxidation of the nanotubes followed by a covalent functionalization, or physical entrainment of nanotubes by another polymer are some of the strategies used to increase MWNT/polyolefin compatibility. However, these strategies require a number of synthetic steps that alter the MWNTs' properties, reducing the desired impact of the MWNTs in the resulting nanocomposites and decomposition of the final nanocomposites. Here, in our laboratory, we used the reactions of polyolefin oligomers containing carboxylic group or a polyethyleneimine (PEI) graft to add polyolefin oligomers to MWNTs to generate in a single step thermally stable functionalized-MWNTs that are soluble in PE or PP melt phases. We followed the first strategy to build and will functionalize MWNTs with PEI and then with a -CO₂H terminated PIB or PE oligomer with an activated carboxylic acid group. A second approach used a PIB or PE oligomer terminated with acid chloride with MWNTs. Above two strategies will go to provide a direct and practical route to polyolefin compatible MWNTs avoiding others' strategies of shear mixing or the more common approach of oxidation of a MWNT and subsequent covalent derivatization of the -CO₂H groups formed in the oxidation reaction which inexorably degrades the MWNT. The loading of MWNTs in the oligomer-bound MWNT/polyolefin nanocomposites will be studying at TAMUCS or TAMUQ or industry collaborators by thermogravimetric analysis and moreover solubilization chemistry in various organic solvents. The distribution of the MWNTs in the polyolefin solid nanocomposites formed on melt mixing will be studied by using TEM at TAMUCS where they can be compression molded or injection molded into test bars for mechanical testing.



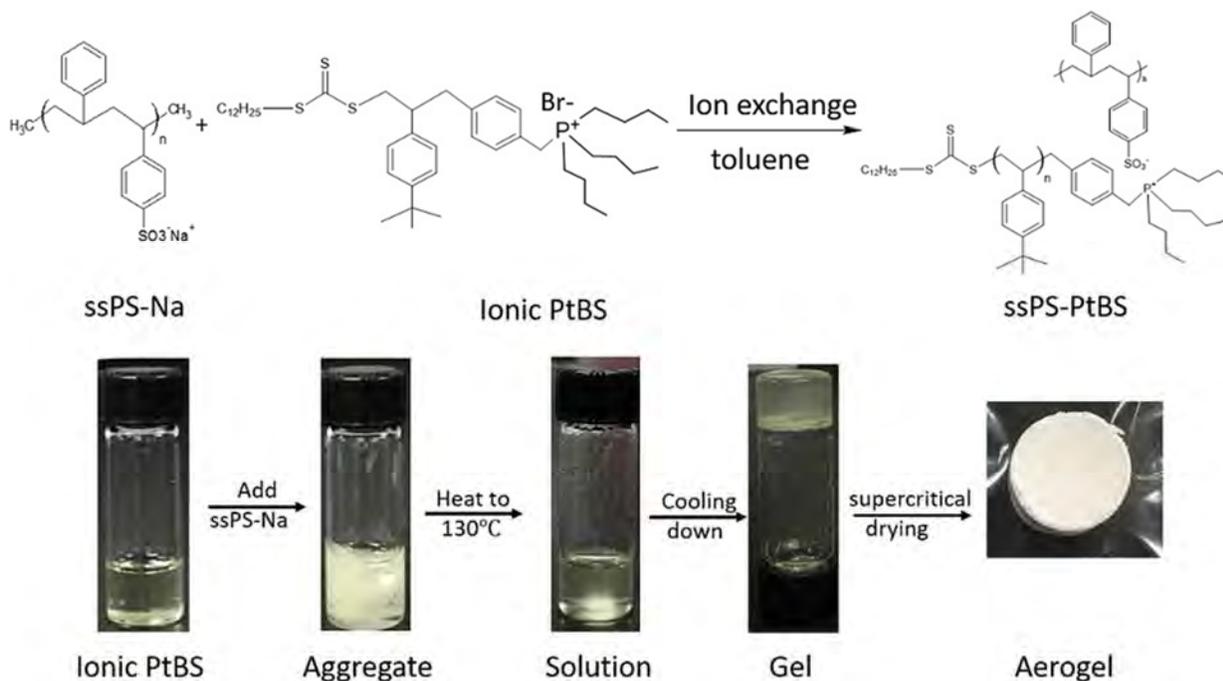
POLY 431: Modification of sulfonated syndiotactic polystyrene aerogels through ionic interactions

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This research focused on the modification of syndiotactic polystyrene first by sulfonation and then ion-exchange with cationic, end-functionalized-poly (tert-butyl styrene) which prepared by reversible addition fragmentation chain transfer (RAFT) polymerization; and the fabrication of aerogels by gelation and supercritical drying of the resultant graft copolymer.

Syndiotactic polystyrene (sPS) was sulfonated with acetyl sulfate reagent in chloroform. The sulfonation degree was measured by titration of solution of sodium hydroxide in methanol. The sulfonated syndiotactic polystyrene (ssPS) was further neutralized with sodium hydroxide to neutralize sulfonic acid group to a sodium sulfonic group.

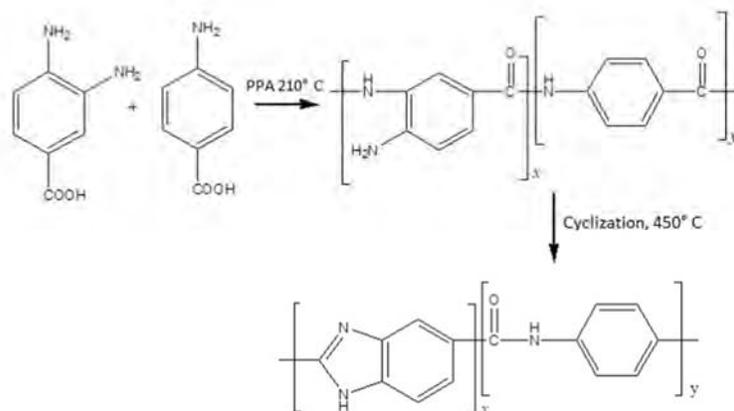
The cationic, end-functional poly (tert-butyl styrene) (PtBS) polymers was synthesized using a quaternary phosphonium-containing RAFT agent and further purified by column chromatography. The ssPS-PtBS was synthesized by blending two ionomers, sodium ssPS and the cationic PtBS. The effectiveness of the ion exchange reaction between ssPS and cationic PtBS was investigated. The toluene solution of ssPS-PtBS formed a gel, which was further processed into an aerogel by supercritical drying. A series of characterization methods were applied to investigate the properties of graft copolymer aerogel. A large fraction of mesopores appeared in ssPS-PtBS aerogel, which contribute large surface areas and may be beneficial for absorption of polar molecules.



POLY 432: Ultrahigh heat-resistance polybenzimidazole/polyamide from *Streptomyces*-derived biomonomers

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Renewable resources can provide a sustainable platform to substitute petroleum-based polymers through the design of bio-based polymers with a positive environmental impact. Aromatic polybenzimidazoles (PBI) are considered as high-performance plastics due to their outstanding thermal and mechanical stabilities owing to strong π - π stacking interaction among aromatics and imidazole rings, and H-bonding between N-H and N of imidazole ring. High-performance bio-PBIs were obtained using renewable starting material 3-amino-4-hydroxybenzoic acid (3,4-AHBA) derived from *Streptomyces* sp. Copolymer polybenzimidazole/polyamide (PBI/PA) was prepared using 4-aminobenzoic acid (PABA) which has high environmental occurrence, and they were characterized and compared with respect to bio-PBIs. Polybenzimidazoles with polyamide unit incorporated inside shows better solubility and processability as compared with the homopolymer ABPBI. Thermal degradation stability of all PBI/PA compositions was measured in inert and air atmosphere; unexpectedly all of them show very high thermal stability. One of these compositions (PBI/PA 85/15) shows ultrahigh values of 10% weight loss temperature (T_{d10}), 743 °C at max in N₂ and 689 °C at max in air. The PBI/PA films were casted over trifluoroacetic acid (TFA) solution on a glass plate. Mechanical properties for all those compositions were measured as tensile strength of 90 MPa and Young's modulus of 7.7 GPa at max. All the PBI/PAs consisted of high crystallinity 41% at max. These values are as high as some of the metal oxides and being organic material with high thermal stability. Thus, the PBI/PA would be hopefully applied as organic-inorganic hybrid materials because of its ultrahigh heat resistance and chemical resistance properties.

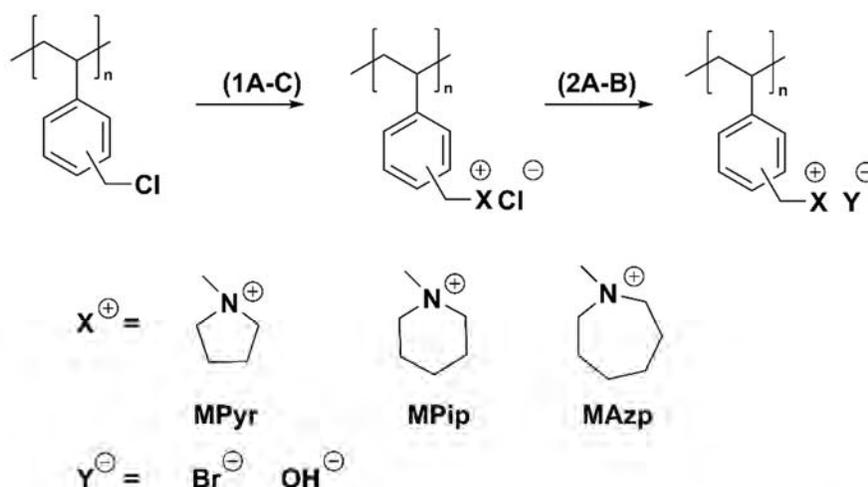


Scheme 1. Schematic route of the copolymer preparation polybenzimidazole/polyamide (PBI/PA) using 3, 4-DABA and PABA

POLY 433: Saturated *N*-heterocyclic cationic polymers: Synthesis and stability

Rui Sun, *vickiesr@tamu.edu*, Yossef A. Elabd. Department of Chemical Engineering, Texas A&M University, College Station, Texas, United States

Polymers containing unsaturated *N*-heterocyclic cations (*i.e.*, imidazolium) have been synthesized and investigated for various applications, including alkaline fuel cells and batteries. Recently, results have shown higher alkaline chemical stability for polymers bearing a saturated *N*-heterocyclic cation (pyrrolidinium) versus an unsaturated imidazolium cation. Additionally, several studies on small molecules have reported increasing stability with increasing saturated *N*-heterocyclic cation size and this was attributed to decreasing ring strain with increasing cation size. However, to date, few studies have systematically investigated polymers containing saturated *N*-heterocyclic cations, specifically *N*-heterocyclic cations with larger ring sizes (*i.e.*, azepanium, azocanium, azonanium). In this study, styrene-based saturated *N*-heterocyclic cationic (SNHC) polymers with various covalent attached cations (methylpyrrolidinium, methylpiperidinium, methylazepanium) were successfully synthesized to investigate the influence of ring size/strain on the properties of SNHC polymers. Functionalization of poly(vinylbenzyl chloride) was employed to covalently attach cations onto polymer backbone, followed by anion exchange metathesis, resulting in polymers with bromide counter anions. Alkaline chemical stability, temperature and humidity dependent water uptake, and ion conductivity of these SNHC polymers were measured and will be reported in regards to the relationship with ring size/strain. This work provides a fundamental understanding of the ring size/strain effect in SNHC polymers and further introduces a promising chemistry for producing highly stable and ion conductive solid-state separators for alkaline fuel cells and batteries.

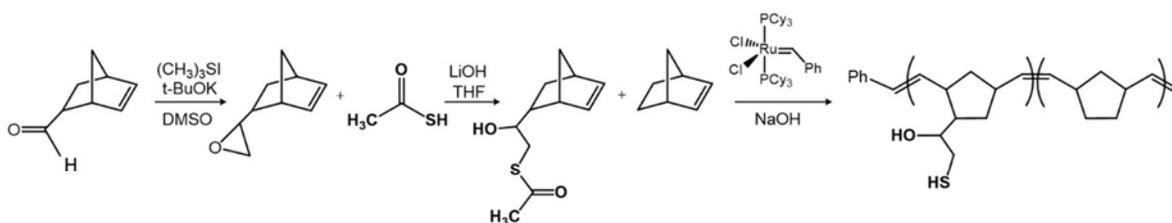


(1A) methylpyrrolidine, DMF, 65 °C, 48h; (1B) methylpiperidine, DMF, 80 °C, 48h;
(1C) methylazepane, DMF, 80 °C, 48h; (2A) LiBr, acetone, room temperature, 48h;
(2B) KOH aqueous solution, 80 °C

POLY 434: Formation of poly(norbornene) thioacetate and deprotection into polythiols

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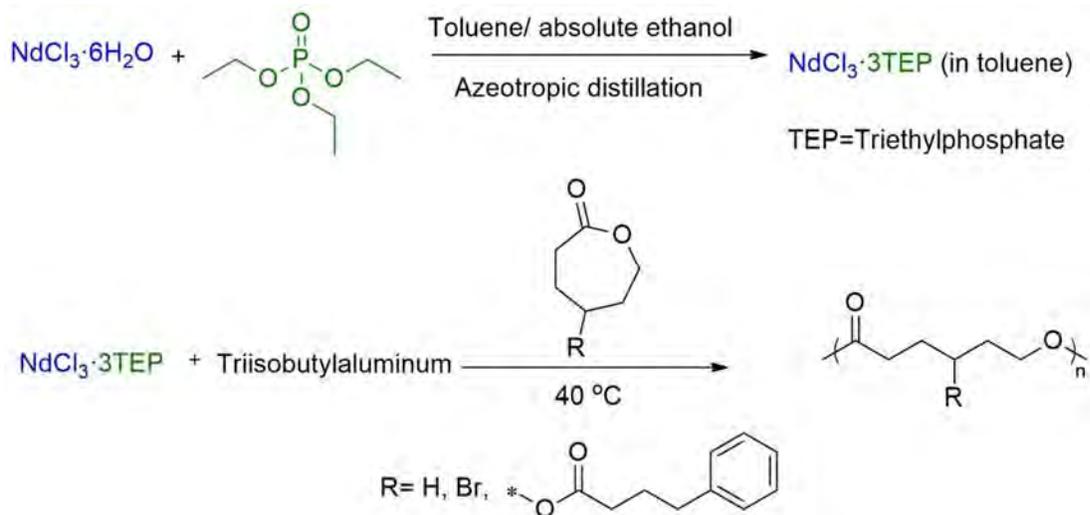
Polythiols are versatile polymers that are known to be synthesized using a range of methods with various backbones. Thiols are very unstable due to their high reactivity. To prevent side reactions and unwanted cross-linking, protecting groups are required. Dithiocarbonate has been used to protect the thiol groups on poly(norbornenes); however, it does not allow enough stability to be stored for long periods of time. The purpose of this project is to form a stable protecting group to increase the longevity and usefulness of polythiols. In this project, norbornene was used due to its easily controllable architecture. Aldehyde groups on 5-norbornene-2-carboxaldehyde were converted into an epoxide via the Corey-Chaykovsky reaction and purified by vacuum distillation. The epoxy was then reacted with thioacetate or thiophenol to form the stable thioether protecting group. Characterization of the monomer included ATR-IR, gas chromatography-mass spectrometry, and NMR analysis. The protected monomer was polymerized using Grubbs' first-generation catalyst. Characterization of the polymer included differential scanning calorimetry, gel permeation chromatography, and NMR. Conditions to deprotect the polythioether were examined. The thioacetate can be easily modified using click chemistry. These modified polymers can be obtained in high yields that are easily purifiable. With new stable protecting groups, polythiols can be used more widely and efficiently.



POLY 435: Ring opening polymerization of lactones by a neodymium coordination catalyst

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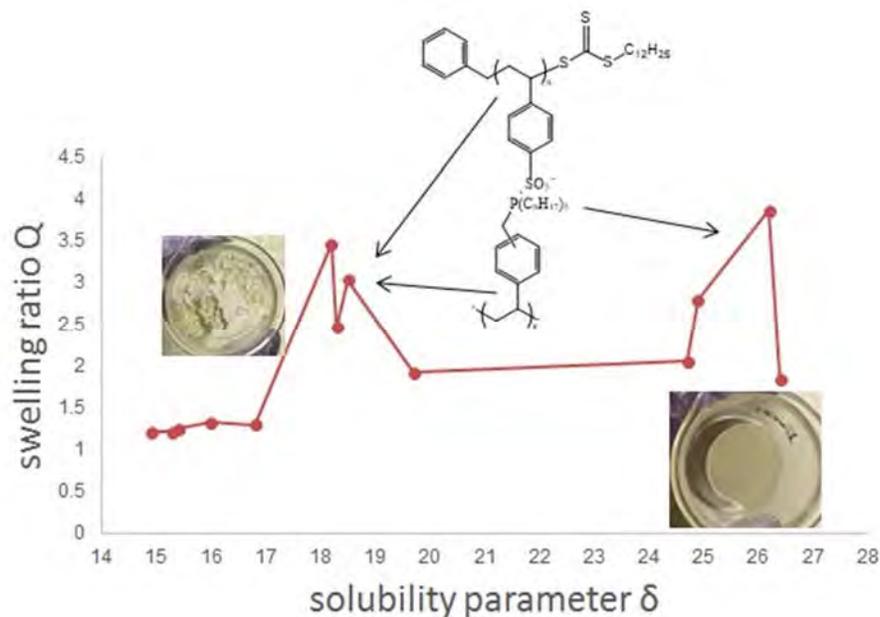
γ -Substituted and unsubstituted poly(ϵ -caprolactone)s (PCLs) are used in the field of drug delivery due to their biocompatibility and biodegradability. PCLs are mainly synthesized by the ring opening polymerization of ϵ -caprolactone using $\text{Sn}(\text{Oct})_2$. Although the Sn catalyst polymerizes unsubstituted ϵ -caprolactone, it fails to polymerize some of the γ -substituted ϵ -caprolactone monomers which connects to the lactone ring via an ester linkage. We have observed that such monomers gives predominantly a transesterified product rather than the desired polymer with the Sn catalyst. Herein, we demonstrate the catalytic activity of $\text{NdCl}_3 \cdot 3\text{TEP}/\text{TIBA}$ (TEP= triethylphosphate, TIBA= triisobutylaluminum) catalytic system for the ring opening polymerization of unsubstituted and γ -substituted ϵ -caprolactones. γ -Substituted ϵ -caprolactone monomers, which were unable to polymerize with $\text{Sn}(\text{Oct})_2$ and organic bases such as DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), were successfully polymerized with high molecular weights by using the $\text{NdCl}_3 \cdot 3\text{TEP}/\text{TIBA}$ catalytic system. Copolymerization and kinetic studies for the lactones were also carried out.



POLY 436: Synthesis of ionically crosslinked polyelectrolytes by homopolymerization of an ion-pair comonomer

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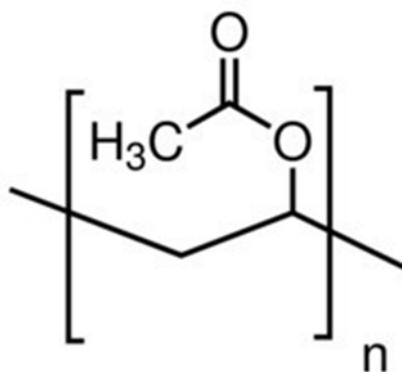
In this work, an ion-pair comonomer was synthesized via the ion-exchange of a cationic vinyl monomer and an anionic vinyl monomer. The ionically-crosslinked copolymer was then synthesized by RAFT polymerization. This study focuses on the resultant sol/gel fraction and swelling properties of the copolymers as a function of polymerization time. This polymer exhibited a two peaks in the plot of swelling vs. solubility parameter of the swelling solvents. Due to the ion-pair structure in the polymer, the polymer exhibits high swelling ratios in solvents that are good for the polymer backbone and that solvate the ion pairs.



POLY 437: Integrating polymer chemistry in the Undergraduate Chemistry Department at Hofstra University

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Integrating polymer science in the undergraduate chemistry department at Hofstra University has been a two-level approach. Level one is a special topics honor course for both Chemistry, Forensic and non-STEM majors. The second level is developing undergraduate research projects designed for the synthesis and physical characterization of Polyvinyl alkyl esters (PVAE) such as polyvinyl acetate (PVAc), copolymers and derivative thereof as well as Modified polysiloxanes

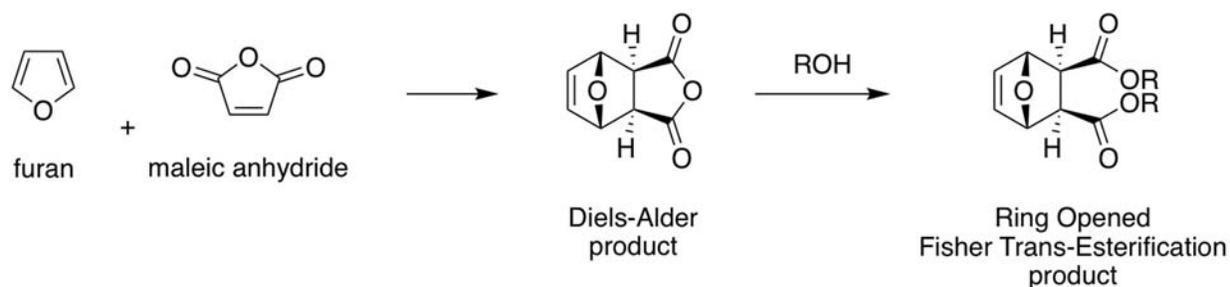


Polyvinyl Acetate (PVAc)

POLY 438: Microwave and neat synthesis of 7-oxanorbornene derivatives for organic chemistry teaching lab: A comparison study

James Bazemore, Michael Kelly, Long Phan, **Brandon P. Quillian**, *brandon.quillian@armstrong.edu*, **Sarah Zingales**, *burrosk@gmail.com*. Department of Chemistry and Physics, Armstrong State University, Savannah, Georgia, United States

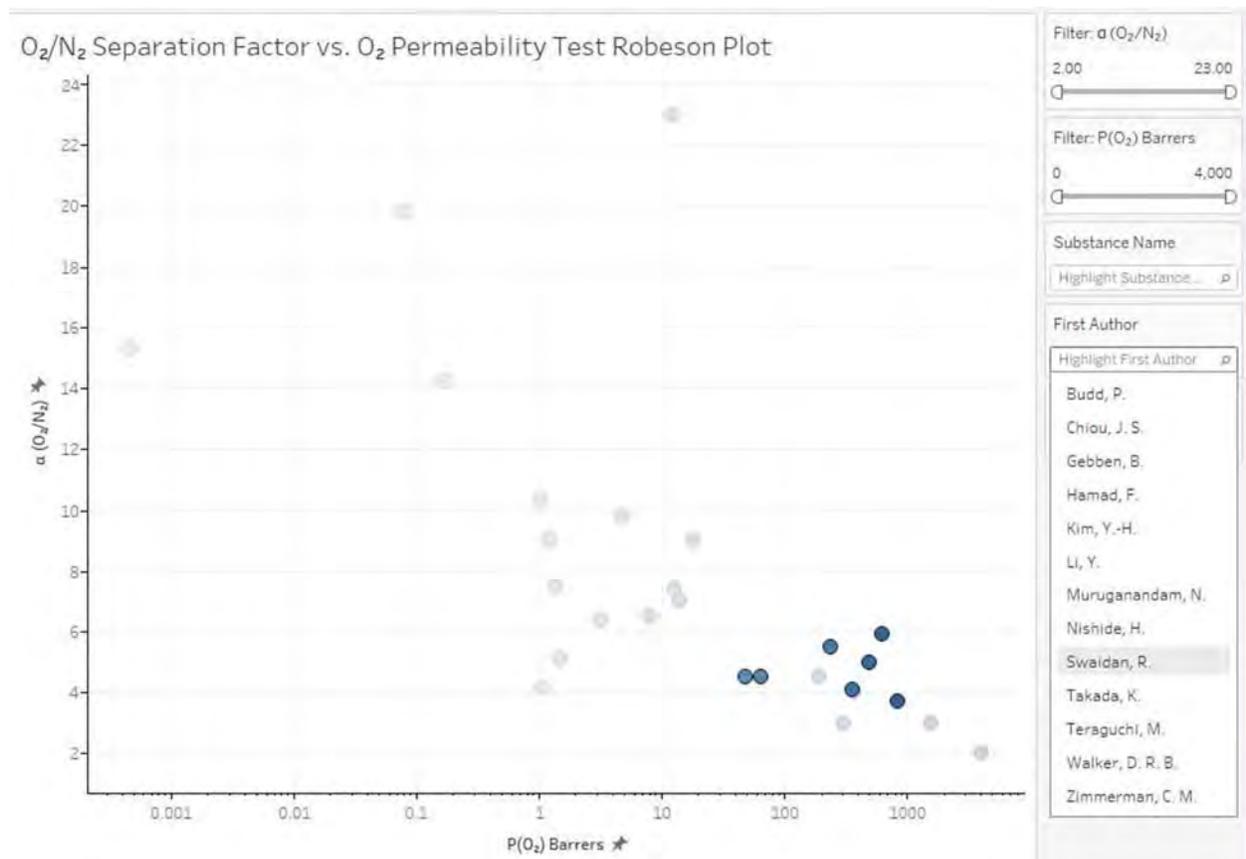
In response to a review of our degree programs by the American Chemical Society Committee on Professional Training (ACS CPT) and the newly revised guidelines for ACS-certified degrees that mandate inclusion of polymer concepts, the chemistry and biochemistry faculty at Armstrong State University (ASU) in Savannah, GA developed a new model to weave themes of synthetic polymers, biological macromolecules, and supramolecular aggregates throughout our curriculum. For example, we have developed two methods to synthesize 7-oxanorbornene derivatives for the Organic Chemistry teaching laboratory to be used as monomers for ROMP (ring-opening metathesis polymerization) reactions in the Inorganic Chemistry teaching laboratory. The general reaction scheme involves a Diels-Alder reaction of furan and maleic anhydride, followed by ring opening of the cyclic anhydride via Fischer Trans-Esterification. Unfortunately, the reported procedure requires long reaction times and/or high temperatures. The first method uses microwave synthesis, while the other is a neat, "green", one-pot synthesis. In addition, we began examining various alcohols in the trans-esterification step to gauge the applicability of this reaction to provide a collection of sterically-diverse monomers for the ROMP reaction. These experiments have already been conducted by students in organic chemistry and the monomers have been polymerized by students in the inorganic chemistry laboratory reactions using ROMP techniques. We provide here a comparison of the two reaction methods including their benefits and detriments. The two methods can provide interested stakeholders a means to incorporate the experiment into their curriculum regardless of their resources.



POLY 439: Towards open and interactive sharing of polymer membrane gas separation data

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Gas separation data for polymer membranes has traditionally been shared in the form of Robeson Plots within journal articles. Robeson Plots depict the relationship between gas selectivity and permeability for a given gas pair of interest (e.g., CO₂/N₂). For the past two decades, the membrane community has relied on Robeson Plots to benchmark and compare membrane selectivity/permeability data. Unfortunately, the current format of publishing Robeson Plots within journal articles as static figures makes it difficult to compare and share data. We are seeking to overcome these challenges by compiling and creating online repositories for Robeson Plots where researchers can interact with membrane data in new ways including enhanced visualizations, downloading machine-readable datasets, and contributing their own data via crowdsourcing. This poster will explain our initial efforts and how we have incorporated this project into our undergraduate curriculum at The University of Alabama.

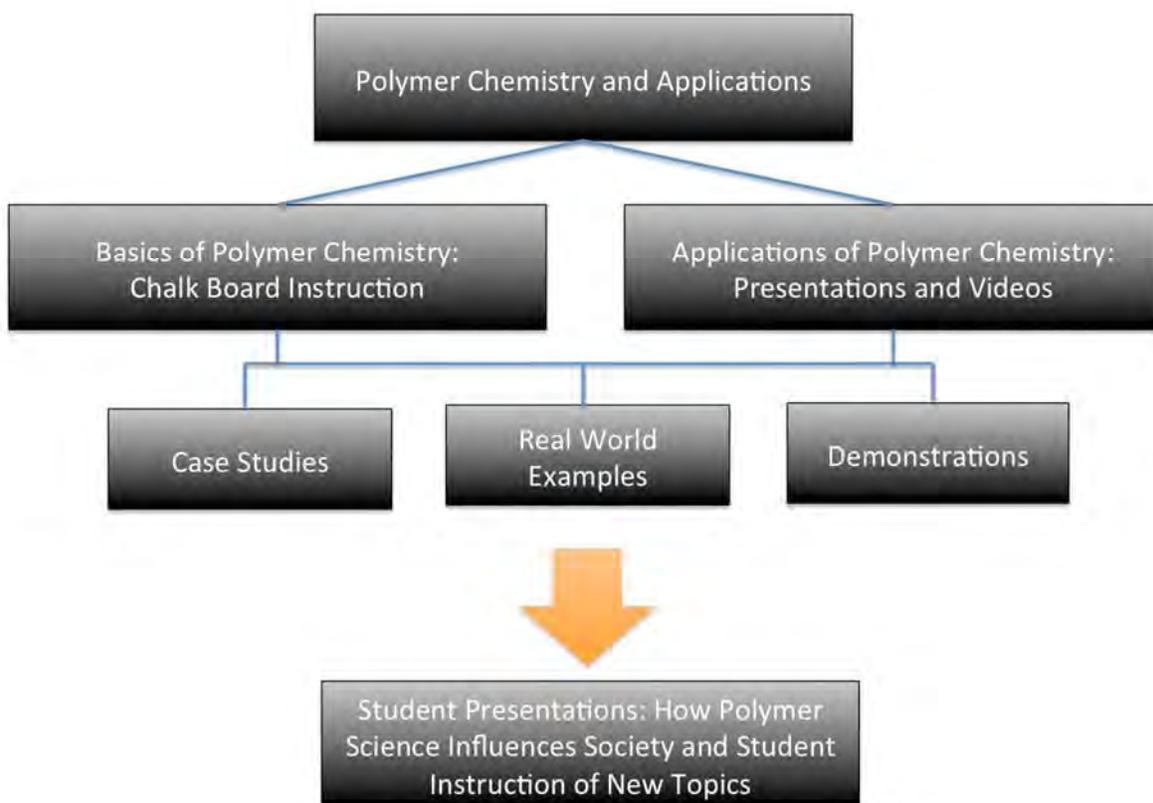


Visualization of gas permeability data using a cloud-based repository.

POLY 440: Teaching a polymer chemistry course at a primarily undergraduate institution

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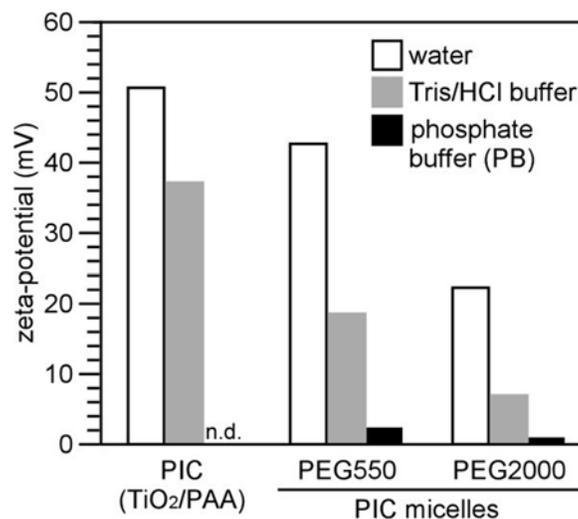
This presentation describes the course design and teaching methodology for a polymer chemistry and applications lecture course specifically aimed at small college and university instruction. This intermediate course for advanced undergraduates and masters level graduate students focuses on teaching the basics of polymer history, synthesis and characterization with connections to the core chemistry curriculum in a small class size environment and without a required textbook.



POLY 441: Polyion complex micelle incorporating TiO₂ nanoparticles for effective sonodynamic therapy

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We have investigated polyion complex (PIC) micelles incorporating TiO₂ nanoparticles (NPs) in the core for sonodynamic therapy (SDT). TiO₂ NPs-incorporated PIC micelles were prepared by mixing TiO₂ NPs and polyallylamine (PAA) bearing poly(ethylene glycol) grafts through electrostatic interaction in aqueous medium. TiO₂ NPs can generate reactive oxygen species (ROS) including singlet oxygen by sonication even after the entrapping into the micelles. PIC micelles could exhibit the cell killing effect by sonication after taken up into the cells, indicating the availability of TiO₂ NPs-incorporated PIC micelles in SDT. However, since ROS have quite low life time, the generated ROS can show instantaneous cell killing effect. Therefore, the combination of transient SDT and persistent drugs should be an attractive strategy for more effective treatment. In this study, we demonstrated that TiO₂ NPs-incorporated PIC micelles could also be used as drug carrier. It was recently found that TiO₂ NPs-incorporated PIC micelles exhibit the effective multivalent anion condensation of PAA main chain. Zeta-potentials of PIC micelles in phosphate buffer and Tris/HCl buffer were quite different in spite of same pH and ion concentration, and phosphate ions effectively neutralized positive charges of PAA in the micelles due to counter ion condensation effect. On the basis of this effect, multivalent anionic molecules were effectively entrapped into the micelles. Furthermore, PIC micelles can deliver these multivalent anionic molecules into the cells. These results suggest that TiO₂ NPs-incorporated PIC micelles have utilities as a carrier for multivalent anionic molecules. Also, the micelles can solubilize hydrophobic drugs, and the combination of cell killing effect by sonication to PIC micelles and various drug delivery might be applicable to a noninvasive and effective therapeutic approach.



Zeta-potentials of PIC micelles and PIC in various solvents.

POLY 442: Mannose residue-introduced pH-sensitive curdlan-modified liposome for antigen presenting cell-specific antigen delivery system

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Cancer immunotherapy has been gained much attention as an alternative treatment for conventional cancer treatments because of its selectivity and less adverse effect. For induction of cancer-specific immune responses, delivery of cancer antigen into antigen presenting cells (APC) such as macrophages or dendritic cells is crucial. Furthermore, the control of intracellular fate of antigen inside of APC is important for induction of cell-based immunity (cellular immunity) or antibody-based immunity (humoral immunity). To eliminate cancer burden, cellular immunity plays a crucial role, which directly kill antigen-expressing tumor cells. For induction of cellular immunity, antigen should be introduced to cytosol of APC by escaping from endo/lysosomal degradation. We previously developed pH-sensitive polymer-modified liposomes for cytoplasmic delivery of antigen. These liposomes delivered model antigenic proteins into APC and induced antigen-specific cellular immunity in vivo. To improve the immunity-inducing effect of these liposomes, in this study, mannose residue was introduced to pH-sensitive polymer. APC has a mannose receptor on their surface to recognize mannose residue selectively. Therefore, introduction of mannose to pH-sensitive polymer is expected to increase cellular association of liposomes by APC after subcutaneous administration. Furthermore, curdlan, one of beta-glucans derived from cell wall of bacteria, was used as a backbone of pH-responsive polymer having immunity-activating function. Here, synthesis of mannose-introduced pH-sensitive curdlan derivatives, characterization of polymer-modified liposomes and interaction of these liposomes with APC were examined.

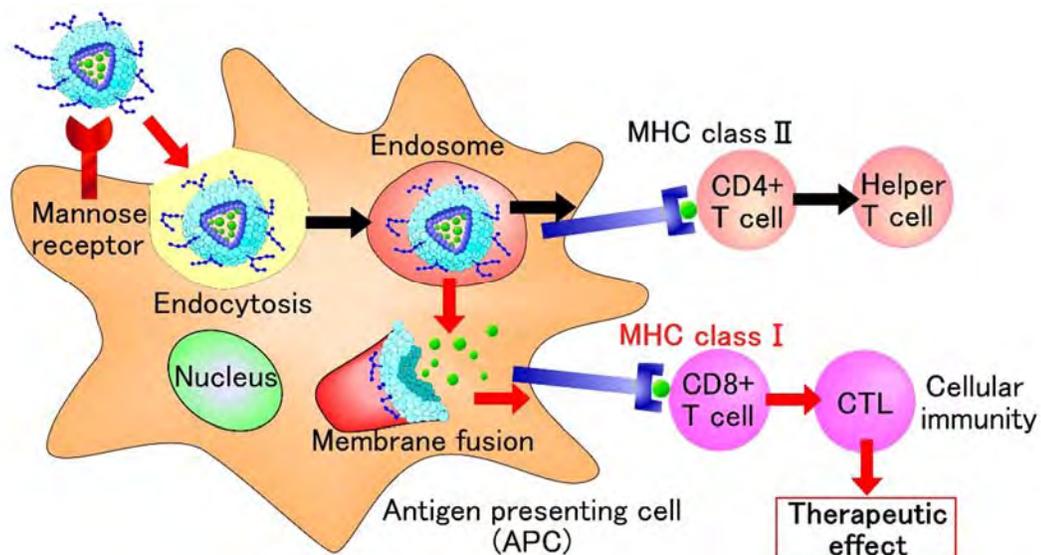
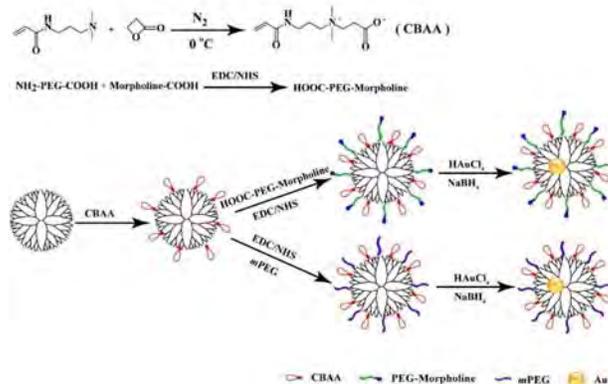


Figure 1. Intracellular delivery of antigen to antigen presenting cells using mannose residue-introduced pH-sensitive polymer-modified liposomes.

POLY 443: A gene delivery approach using zwitterion-modified dendrimer-entrapped gold nanoparticles for inhibition of cancer cell metastasis

Zhijuan Xiong¹, *xiongzj711@sina.com*, **Carla S. Alves**², **Aijun Li**¹, **Feng Chen**¹, **Jinyuan Liu**¹, **Mingwu Shen**¹, **Helena Tomas**², **Xiangyang Shi**^{1,2}. (1) College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai, China (2) CQM-Centro de Quimica da Madeira, Universidade da Madeira, Funchal, Portugal

Delivering hypermethylated in cancer 1 (HIC1) gene to cancer cells has been demonstrated to be an effective approach to inhibiting the migration and metastasis of cancer cells. Here, we synthesized a zwitterion-functionalized generation 5 (G5) poly(amidoamine) dendrimer vector for effective HIC1 gene delivery. In our study, G5 dendrimers were modified with zwitterion carboxybetaine acrylamide (CBAA) and lysosome-targeting agent morpholine (Mor) through a polyethylene glycol (PEG) spacer and used as templates to entrap gold nanoparticles. The formed $\{(Au^0)_{25}\text{-G5.NH}_2\text{-CBAA-PEG-Mor}\}$ and non-targeted $\{(Au^0)_{25}\text{-G5.NH}_2\text{-CBAA-}m\text{PEG}\}$ NPs were systematically characterized and their gene delivery efficacy was evaluated. We show that both dendrimer-entrapped Au nanoparticles (Au DENPs) having an Au core size of 1.5-1.6 nm are cytocompatible in a given concentration range and are able to effectively deliver plasmid DNA (pDNA) carrying enhanced green fluorescent protein and luciferase reporter genes (pEGFPLuc) or HIC1 gene to cancer cells in medium with or without serum. Most strikingly, due to the antifouling property exerted by the attached zwitterion CBAA, the gene delivery efficiency of Mor-modified Au DENPs and the nontargeted Au DENPs in the serum-containing medium are even 1.4 and 1.7 times higher than the corresponding vector in serum-free medium, respectively. In addition, although the Mor modification enables the polyplexes to enter more easily into cancer cells and lysosomes than the vector without Mor modification, in all cases the non-targeted vector has a better gene expression efficiency than the Mor-modified one. Wound healing assay data reveal that the expression of HIC1 gene in cancer cells enables effective inhibition of cell migration. Our results suggest that the designed zwitterion-modified dendrimers may be used as a promising vector for gene delivery to inhibit tumor metastasis in a serum-containing environment.



Schematic design of the synthesis of zwitterion-modified dendrimer-entrapped gold nanoparticles for effective inhibition of cancer cell metastasis in a serum-containing environment.

POLY 444: Liver-specific DDS using liposomes modified with sugar moiety-introduced dendron lipids and pH-responsive polymer-lipids

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Osaka prefecture university, Osaka, Japan

Liver fibrosis is induced by chronic liver inflammation and leads to liver cancer. Recently, delivery of matrix metalloprotease (MMP) or its transcription factor to hepatocytes has been developed as a new treatment approach for liver fibrosis. MMP can degrade collagen in fibrotic tissues and is expected to improve liver fibrosis. To realize this novel treatment for liver fibrosis, the development of delivery carriers that can specifically deliver MMP or its transcription factors to hepatocytes is required. Hepatocytes have asialoglycoprotein receptors (ASGR) on their surface, which selectively recognize sugar-moieties such as galactose. In addition, transcription factor should be introduced to cytosol of hepatocytes by escaping from endo/lysosomal degradation. In this study, we designed polyamidoamine dendron-bearing lipids with galactose moieties (Gal-DL) as a targeting ligand to hepatocytes. Furthermore, pH-sensitive polymer-lipid, 2-carboxycyclohexane-1-carboxylated poly(glycidol)-modified distearoyl phosphatidylethanolamine (CHexPG-PE) was used to promote endosomal escape of carrier. Liposomes modified with both Gal-DL and CHexPG-PE are expected to be recognized by ASGR and accumulate to the liver tissue. After internalization to hepatocytes, CHexPG-PE becomes hydrophobic in response to low pH of endosome and destabilizes endosomal membrane, which might lead to cytosol release of MMP transcription factors. Here, the synthesis of Gal-DL, characterization of Gal-DL/CHexPG-PE-modified liposomes and interaction of these liposomes with hepatocytes were examined.

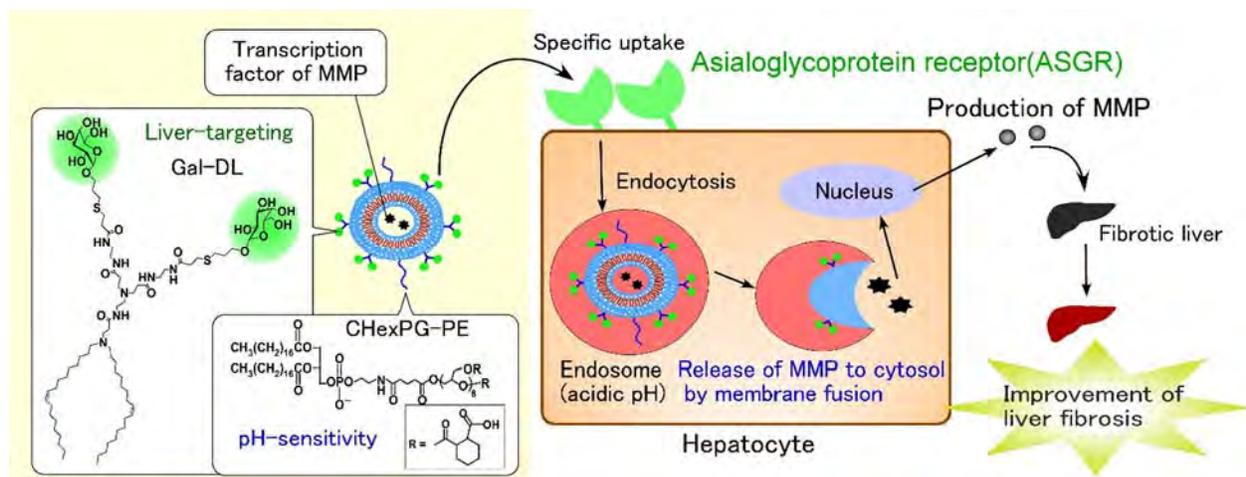
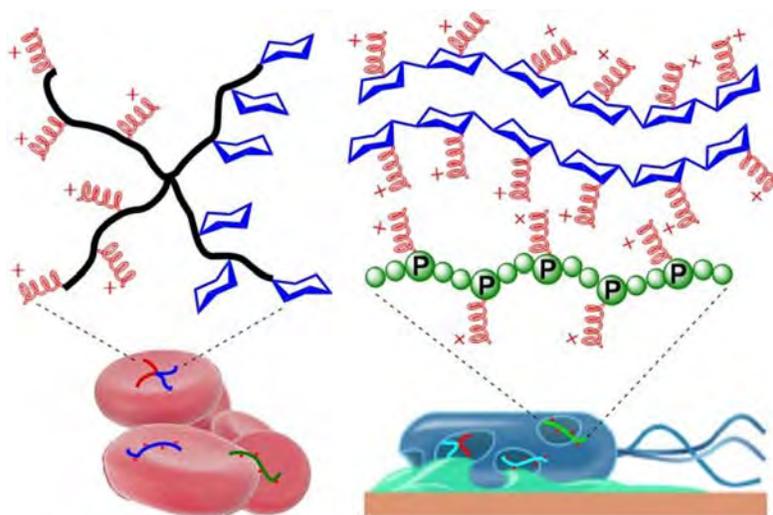


Fig.1. Liver-specific delivery system of MMP transcription factor using liposomes containing galactose-conjugated dendron lipids and pH-responsive lipids.

POLY 445: Cationic poly(peptidophosphoesters) and poly(peptidosaccharides) for antimicrobial therapy

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Cationic antimicrobial peptides (AMPs) possess direct bactericidal mechanism with minimal risk of inducing drug resistance and detrimental toxicity towards blood and mammalian cells. The cationic AMP HHC10 with cysteine terminal (CysHHC10) was conjugated via thiol-yne 'click' reaction onto the polyphosphoesters with alkynyl moieties, prepared by ring-opening polymerization (ROP) of cyclic dioxaphospholanes. On peptide mass-fraction basis, the polyphosphoester-peptide conjugates showed enhanced bactericidal efficacy with reduced hemolytic activity and cytotoxicity in comparison to the free peptide. Propargyl-terminated α -polylysine, prepared by N-carboxyanhydride ROP, was conjugated via 'click' cycloaddition onto the azido-terminated mannose, glucose, and galactose-based glycopolymers prepared by atom-transfer radical polymerization (ATRP). The resulting four-arm star glycopolymers-polypeptide conjugates were non-hemolytic and enhanced the cytocompatibility of linear α -polylysine without losing the bactericidal properties. In particular, the pendant mannose moieties of the star copolymers facilitated microbial targeting through molecular recognition and specific affinity with bacterial surfaces. CysHHC10 was also conjugated via thiol-maleimide 'click' reaction to maleimido-functionalized chitosan on the amino-C2 position or hydroxyl-C6 position. On peptide mass-fraction basis, the resulting peptido-polysaccharides inhibited bacteria growth and reduced cytotoxicity of the free peptide. Antibacterial coatings were readily constructed via layer-by-layer assembly of these peptido-polysaccharides with tannic acid through Michael addition or Schiff base reactions. The peptido-polysaccharide coatings immediately eliminated the adhered bacteria while still facilitated adhesion and proliferation of fibroblasts.

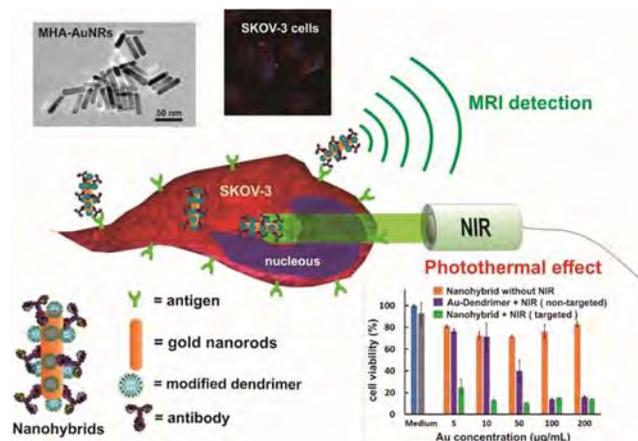


Cationic antimicrobial poly(peptidophosphoesters) and poly(peptidosaccharides) with minimal risk of inducing drug resistance and toxicity towards blood and mammalian cells.

POLY 446: Development of multifunctional nanohybrid: antibody-conjugated gold nanorods stabilized by functional dendrimer for targeted photothermal therapy and imaging

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Multifunctional theranostic agents having targeting function, therapeutic function and imaging function are promising for cancer treatment and diagnosis. Herein, gold nanorods (AuNRs) covered with mercaptohexadecanoic acid (MHA) for functionalizing the surface to bind amino group from both, antibody and functional dendrimer using condensing reagents. Trastuzumab was conjugated to improve cellular uptake by HER2-overexpressing cancer cells. Beforehand, AuNRs was stabilized by polyamidoamine (PAMAM) dendrimer which was modified with Gd-DOTA molecule for MRI detection and poly(ethylene glycol) (PEG) chain to provide the colloidal stability and enhanced permeability and retention effect in the bloodstream after intravenous injection. The fabricated nanohybrid (Trastuzumab-AuNRs-functional dendrimer) had homogeneous hydrodynamic size about 75 nm and showed typical surface plasmon absorption peaks at 520 nm and 820 nm, which corresponds to the transverse and longitudinal electronic oscillation of AuNRs, respectively. Trastuzumab-modified nanohybrids were efficiently internalized by SKOV-3 cells, HER2-overexpressing ovarian cancer cells, even at low concentration (5 $\mu\text{g}/\text{mL}$ of AuNRs). Furthermore, nanohybrid exhibits low toxicity to SKOV-3 cells even at high concentration (200 $\mu\text{g}/\text{mL}$ of AuNRs). In addition, the photothermal effect induced by near-infrared (NIR) laser irradiation to nanohybrid was sufficient to induce 80-90% of cancer cell killing. Therefore, fabricated nanohybrids are promising for targeted photothermal therapy and imaging.



Design of AuNR-functional dendrimer nanohybrids modified with antibody for targeted photothermal therapy and imaging

POLY 447: Development of hyaluronic acid derivative-modified liposomes as dendritic cell-specific antigen delivery carriers

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For achievement of cancer immunotherapy, the induction of cytotoxic T lymphocyte (CTL)-based cellular immunity is required because CTL can kill tumor cells directly. Antigen presenting cell (APC)-specific antigen delivery and control of intracellular fate of antigen are important for induction of antigen-specific immune responses. Especially, antigen delivery to early endosomes or cytosol leads the induction of cellular immunity, which is called as “cross-presentation”. We previously reported intracellular delivery using liposomes modified with carboxylated polyglycidols or carboxylated dextrans to transfer antigen to inside of cells by pH-responsive fusion or destabilization of endosome (*Biomaterials* 2014, **35**, 3091). The use of polysaccharide as backbone of pH-sensitive polymer has beneficial because of its biodegradability and biofunctions. In this study, hyaluronic acid (HA) derivative was designed as a multifunctional polymer having both pH-sensitivity and specificity to cells expressing CD44, which is known as a surface marker for various kinds of cells. Dendritic cell, the professional APC, also expresses CD44 on its surface and reportedly CD44-HA interaction induces activation of dendritic cell (*Int J Cell Bio*, 2015, **563818**). Here, synthesis of HA derivatives, activation of dendritic cells by HA derivatives, preparation of HA derivative-modified liposomes and their antigen delivery performance to dendritic cells were examined. Results show the importance of HA backbone and side chain structures on their intracellular delivery performance and activation of dendritic cells.

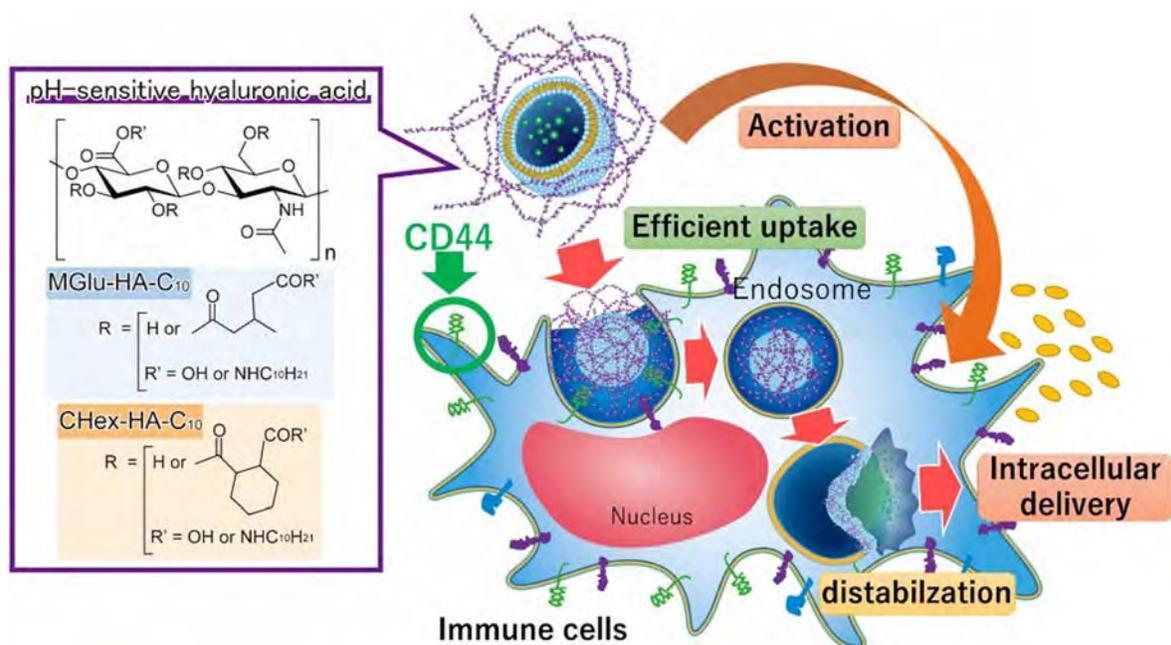


Figure 1. Structures of pH-sensitive HA derivatives and intracellular antigen delivery to immune cells using HA derivative-modified liposomes.

POLY 448: Multifunctional nanohybrids composed of functional dendrimer and gold nanorod for photothermal-chemotherapy

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Toward establishment of novel methodology for cancer treatments, we designed multifunctional nanohybrids, which thoroughly attack cancer cells through the synergy of photothermal effect and anticancer drug, by conjugation of PAMAM dendrimers to gold nanorods (AuNRs). PAMAM G4 dendrimers modified with poly(ethylene glycol) (PEG) and oleoyl chains were combined to mercaptohexadecanoic acid-modified AuNRs (40 nm × 10 nm) using a condensing reagent. Parent AuNRs without dendrimers formed aggregation in saline, whereas nanohybrids showed excellent colloidal stability because highly hydrated PEG chains might cover the nanohybrids surface. We also found that introduction of oleoyl groups to nanohybrids increased the loading of doxorubicin (DOX) through hydrophobic interaction and obtained nanohybrids released DOX gradually in physiological environments. DOX-loaded nanohybrids were taken up by HeLa cells through endocytosis and released DOX in endo/lysosomes. Nanohybrids without DOX showed the negligible cytotoxicity to HeLa cells, whereas DOX-loaded nanohybrids showed the cytotoxicity. In addition, near infrared (NIR) light irradiation further increased the cytotoxicity of nanohybrids. These results suggest that the DOX-loaded nanohybrids exhibited strong cell killing capability through the synergy of DOX-induced chemo-effect and AuNR-induced photothermal effect. Furthermore, intravenously or intratumorally injected nanohybrids showed efficient therapeutic effect on colon 26 tumor-bearing mice in combination with NIR light irradiation to tumor site. This work demonstrated the utility of multifunctional nanohybrids for application to minimally invasive cancer treatment.

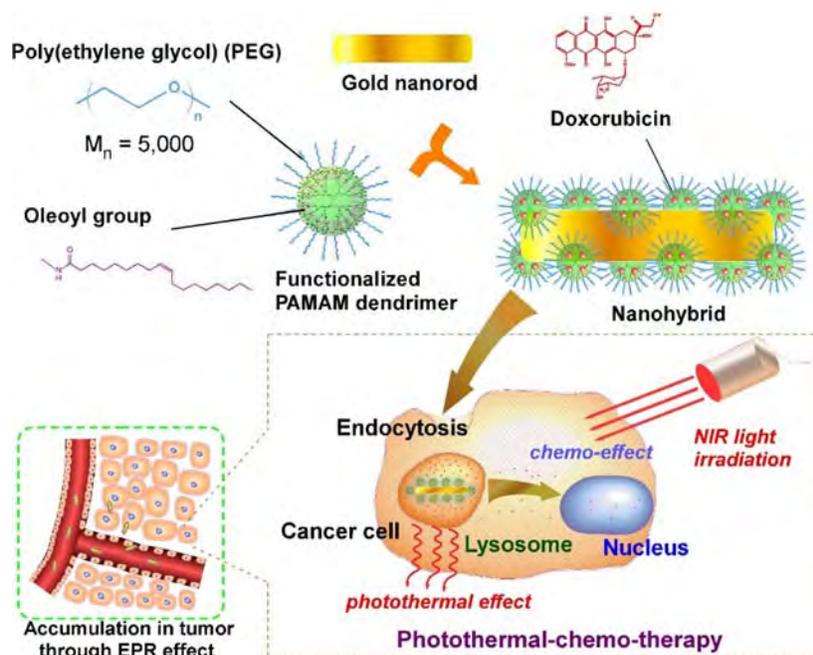


Figure. Design of nanohybrids composed of gold nanorod complexed with PEG/oleoyl group-modified PAMAM dendrimers containing anticancer drugs for photothermal chemotherapy.

POLY 449: Hydrogels based on peg and chitosan-reduced graphene oxide for volumetric muscle loss treatment

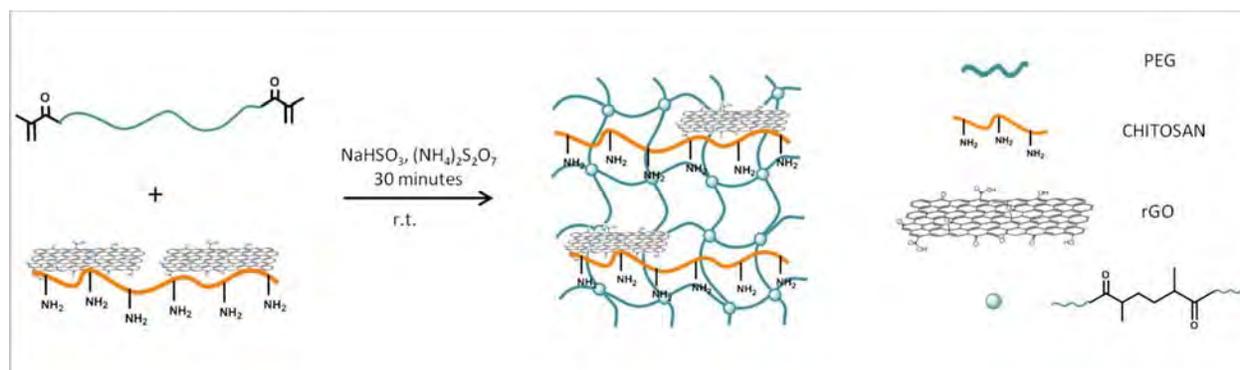
Jéssica F. Petry, *jessica.ftcp@gmail.com*, Douglas Gamba. Institute of Chemistry, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil

Volumetric muscle loss (VML) treatments are limited and associated to morbidity. The muscular tissue corresponds to more than 40% of body mass and plays an important role in human body, including breathing, locomotion and postural support. Muscular diseases affect about 561 milion people in the world and represent a serious social and economic problem.

Unlike other tissues, muskular skeleton has the ability to regenerate itself after injury. Nevertheless, this regeneration can be unefficient when large amounts of tissue are lost, leading to an incomplete recovery and resulting in scars or muscle damage. Tissue engineering has been studied as a possibility to find new materials capable of replacing damaged tissues. The main goal of this field is to create biocompatible materials with characteristics of extracellular matrix (ECM), integrating cells, tissues and organs.

Hydrogels are materials with attractive charcacteristics for tissue engineering application, such as tridimensional porous structure, biodegradability, capability of absorbing large amounts of fluids and elastic properties similar to tissues. Besides that, they show physical-chemical properties similar to ECM. This behavior makes them an ideal medium for tissue and cells development.

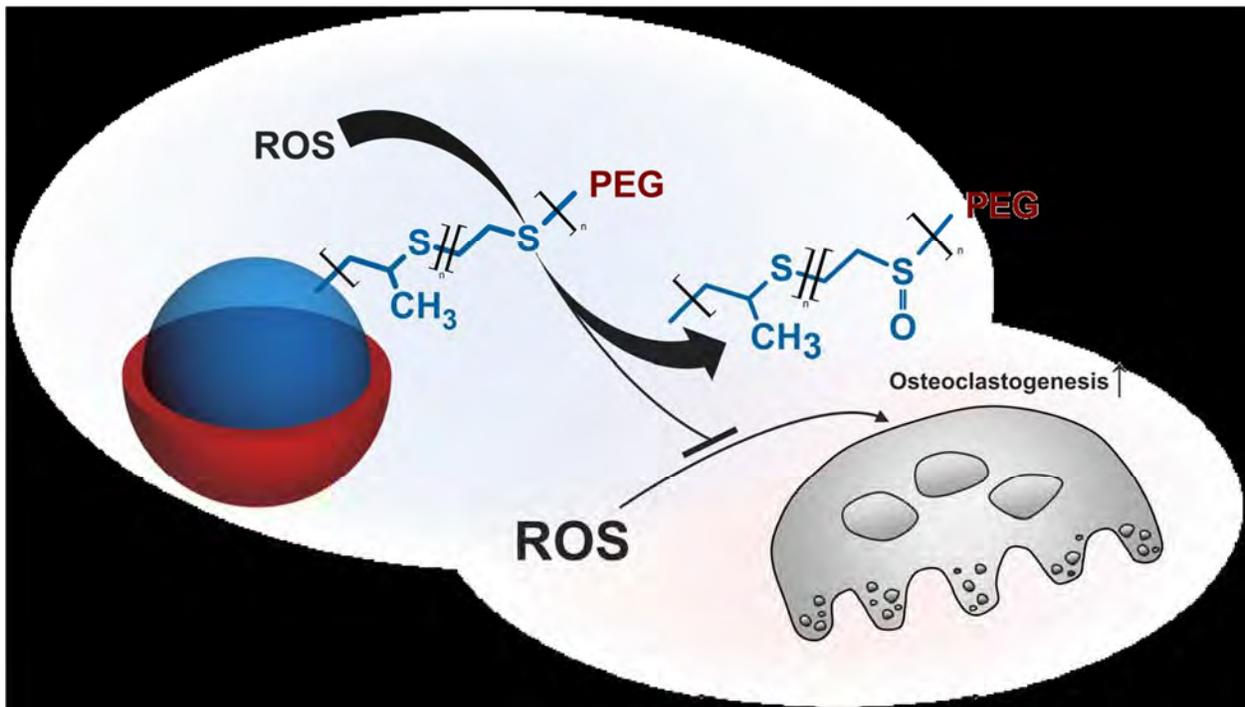
In this work, hydrogels based on poly(ethyleneglycol) (PEG) and chitosan-reduced graphene oxide (CS-rGO) were prepared for further application as muscle tissue. Firstly, PEG was functionalized with crosslinking groups using methacrylic anhydride. Graphene oxide (GO) was then prepared by graphite oxidation using potassium permanganate (KMnO_4) and phosphoric and sulfuric acid (H_3PO_4 and H_2SO_4). This GO was reduced by reacting with chitosan in an acid medium, leading to a black product (CS-rGO). GO and CS-rGO were characterized by X-ray diffraction. The diffractogram showed specific peaks for graphene oxide and a large band which corresponds to chitosan. The hydrogels were prepared using methacrylated PEG and CS-rGO with different ratios of GO. The materials were characterized by compression analysis and swelling degree.



POLY 450: Polysulfides... a 'break-through' for osteoporosis?

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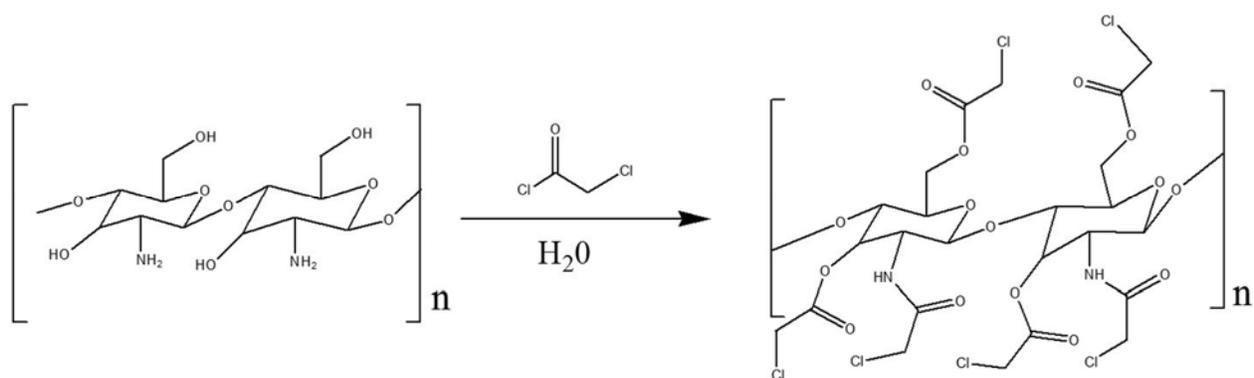
The word osteoporosis is derived from Greek meaning "porous bones". As the name suggests osteoporosis is a bone degeneration disease typified by brittle, easy to fracture bones. It is commonly considered a disease of aging as it usually only manifests after middle age such as after menopause in women (due to a reduction in estrogen). In fact, 80% of those affected are women and for those aged over 45, osteoporosis contributes to more days in hospital than diabetes, breast cancer or heart attacks. Bone as an organ is under a constant state of remodeling with osteoblasts being the 'bone producing' and the osteoclasts being the 'bone resorbing' cells. In healthy conditions there is a homeostatic balance between the two conditions, however, in osteoporosis the homeostasis becomes skewed towards bone resorption due to an increase in RANKL production and a decrease in osteoprotegerin leading to increased osteoclast formation and survival. Through downstream signaling, RANKL exploits reactive oxygen species (ROS) as a chemical messenger intermediate in order to stimulate the differentiation of pre-osteoclasts/macrophage-like cells into osteoclasts resulting in their increased survival through activation of the NF- κ b pathway. Here, we exploit an oxidation-responsive PEGylated-polysulfide in the form of star-micelles for 1) the delivery of rapamycin (an osteoclast inhibitor through the mTOR pathway) and 2) complementary inhibition of the osteoclastogenic pathway via inhibition of NF- κ b pathway (inherent properties of the polysulfide micelles as ROS scavengers).



POLY 451: Synthesis and characterization of chitosan derivatives for high performance gene delivery

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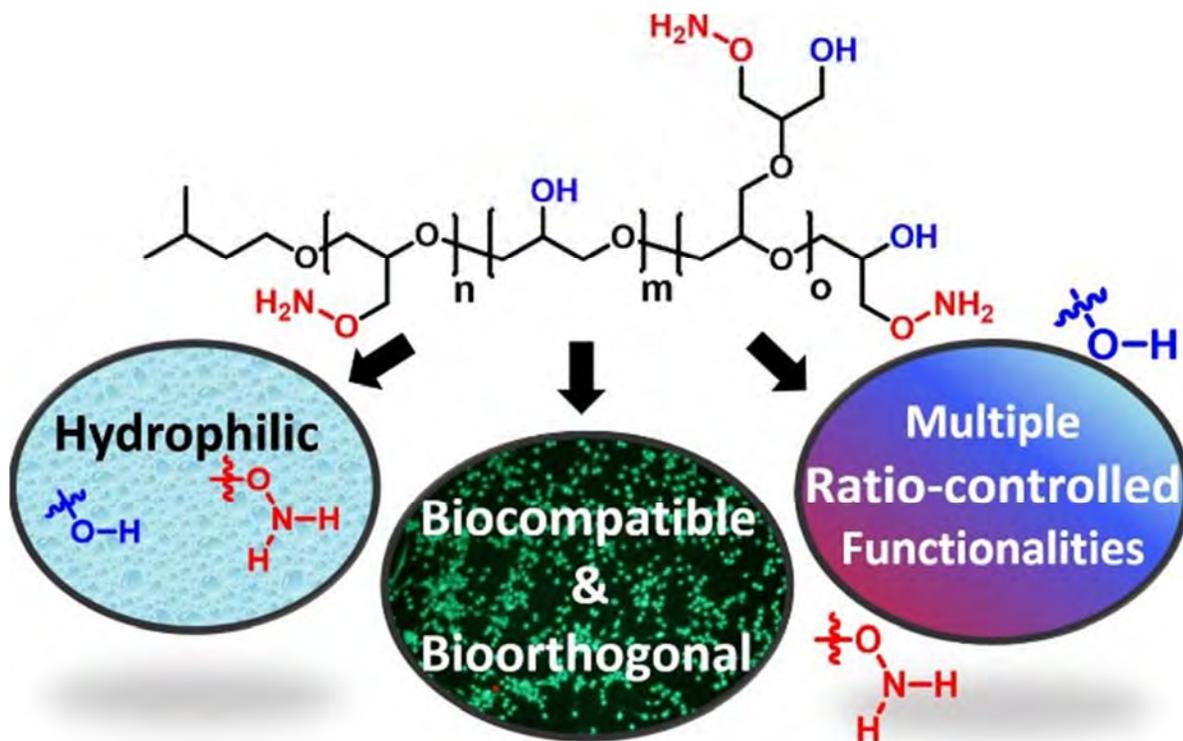
Chitin and chitosan are naturally abundant and renewable polymers that have excellent properties such as biodegradability, biocompatibility, non-toxicity, and adsorption. Due to its favorable physical and chemical properties, chitosan is being used in a vast array of widely different products and applications, ranging from biomedical and cosmetic products to water treatment and plant protection. However, chitosan is only soluble in acidic aqueous solutions. The aim of this work was to modify chitosan to improve its water solubility and to make it an effective vector for the purpose of gene delivery. More specifically, in this work we have synthesized chitosan derivatives containing ammonium groups for effective condensation of biomolecules as well as chitosan derivatives containing both ammonium groups and poly(ethylene glycol) to improve its cellular uptake and its cytotoxicity. Moreover, the effect of the nature of the alkyl substituents attached to ammonium groups on the toxicity and complexation ability of the derivatives have been studied. The chitosan derivatives made in this work have been characterized by IR and H NMR spectroscopies. The derivatives have also been characterized in terms of their particle size, critical micelle concentration and their abilities for complex formation with DNA. Synthesis and characterization of these polymers and their interactions with nucleic acids will be presented and discussed.



POLY 452: Polyglycidol-based hydrogels for applications in regenerative medicine

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Regenerative medicine strategies for articular cartilage involves the development of constructs to support regeneration of damage and diseased tissues. Hydrogels are hydrophilic 3D polymer networks with high water content. Their water absorption and retention ability, biocompatibility, and tunable chemical and physical properties make these materials attractive for applications as scaffolds for articular cartilage. Herein, we present tunable polyglycidol oxime hydrogels that are a result of the combination of aminoxy and ketoester functionalized polyglycidol derivatives. The aminoxy and ketoester derivatives undergo a biorthogonal click reaction that results in a hydrogel exhibiting high strength and elasticity.



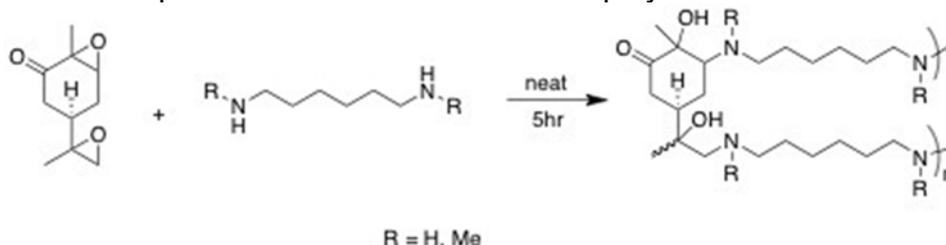
POLY 453: Terpene-based polymers by step-growth polymerization: Renewable monomers and polymers for biomedical applications

Dara O'Brien¹, *pcxdo2@nottingham.ac.uk*, **Steven M. Howdle**¹, **Cameron Alexander**², **Robert A. Stockman**¹. (1) Chemistry, University of Nottingham, Nottingham, United Kingdom (2) School of Pharmacy, University of Nottingham, Nottingham, United Kingdom

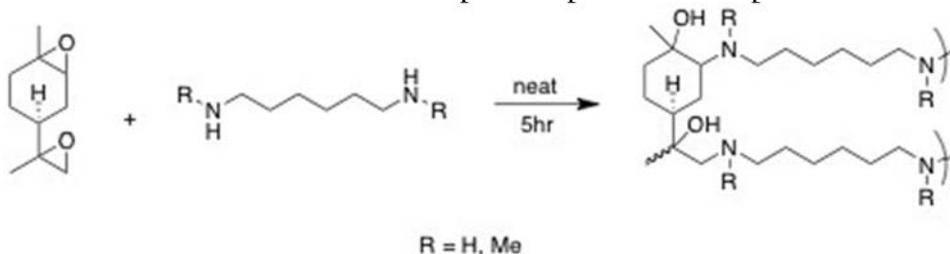
In looking to replace crude oil as a feedstock for the synthesis of polymers, only biomass can provide the renewable carbon required, in sufficient quantities, to meet the ever-growing global demand for these materials. Terpenes are a diverse family of hydrocarbon-rich molecular biomass, potentially making them an attractive source of novel, sustainable monomers. This work investigates the use of the terpenes (*R*-carvone and (*R*)-limonene as precursors for the synthesis of renewable monomers and polymers.

A number of carvone-derived small-molecules were synthesized, including two epoxides and one bis-epoxide species. The latter is of particular interest, as bis-epoxides are known to polymerize with diamine co-monomers. These kinds of materials have a long history of use in resins for coatings and adhesives, but also have been shown to have potential applications in dental and orthopedic fields. While much of this work has focused on the use of aromatic bis-epoxide and diamine co-monomers, it is hypothesized that the use of aliphatic alternatives may lead to the formation of more supple materials of lower molecular weights, with potential applications as biomedical materials.

To investigate this, the carvone-derived bis-epoxide monomer was co-polymerized with commercially-available, aliphatic, primary and secondary diamines. These polymerizations were conducted at a range of temperatures and in the absence of solvents or catalysts. Analogous bis-epoxide monomers derived from (*R*)-limonene were also synthesized and polymerizations were conducted with these species. Initial investigations have yielded short-chain oligomers; future work will require optimization of the reactions to expand these structures to useful polymeric materials.



The polymerization of the carvone-based bis-epoxide species with aliphatic diamines.

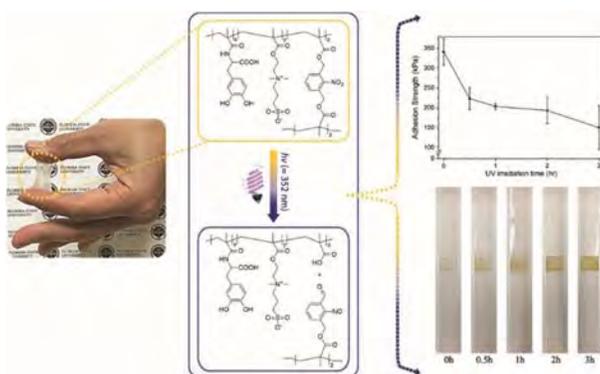


The polymerization of the limonene-based bis-epoxide species with aliphatic diamines.

POLY 454: Photo-responsive bio-inspired adhesives for facile control of adhesion strength

Minkyu Kim, *unique11324@gmail.com*, Hoyong Chung. *Chemical and Biomedical Engineering, Florida state university, Tallahassee, Florida, United States*

A new photo-responsive bioinspired adhesive that includes zwitterionic polymer, poly(sulfobetaine methacrylate) (pSBMA), catechol group, and photocleavable nitrobenzyloxycarbonyl containing crosslinker was prepared by facile thermally-initiated free radical polymerization. The main component pSBMA is highly hydrophilic and biocompatible polymer which has gained substantial attractions as the biomedical material. The mussel's adhesive protein inspired catechol group is recently studied bioinspired functionality that enhances adhesion property on universal surfaces even in the presence of water. The third component dimethacrylate crosslinker containing nitrobenzyloxycarbonyl functionality effectively cleaves upon UV irradiation. UV/vis analysis of the adhesive revealed that chemical bonding cleavage rapidly occurs within 30 minutes and then slowly continued until 3 hours. The photocleavage results weakened adhesion strength according to lap shear strength measurement. After 30 minutes of exposure to UV radiation, the adhesion strength was reduced by 35% (from 341 kPa to 223 kPa). Adhesion strength was gradually reduced to as low as 56% of the original value (150 kPa) until 3 hours of UV irradiation. The decreasing tendency in adhesion strength was similar with loss tendency of crosslinking in the polymer. By conducting ^1H NMR analysis, we could confirm pure crosslinker shows fast chemical bonding cleavage within 30 min and then slowly proceeds until 3hr in the same way as was discovered in adhesion property tests. We anticipate that the developed photo-responsive adhesive can be effectively utilized in biomedical applications requiring biomedical adhesive with tunable adhesive strength. Additionally, this strategy will be significantly helpful in the development of new biomedical adhesive technologies.

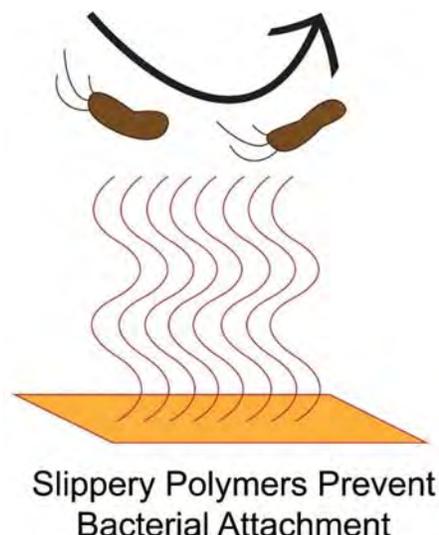


A new photo-responsive bio-inspired terpolymer adhesives consisting of a zwitterionic polymer, catechol-containing moiety, and photocleavable nitrobenzyl moiety were prepared for facile control of adhesion strength under UV irradiation.

POLY 455: Bioinspired polymer composites for antifouling surface coatings

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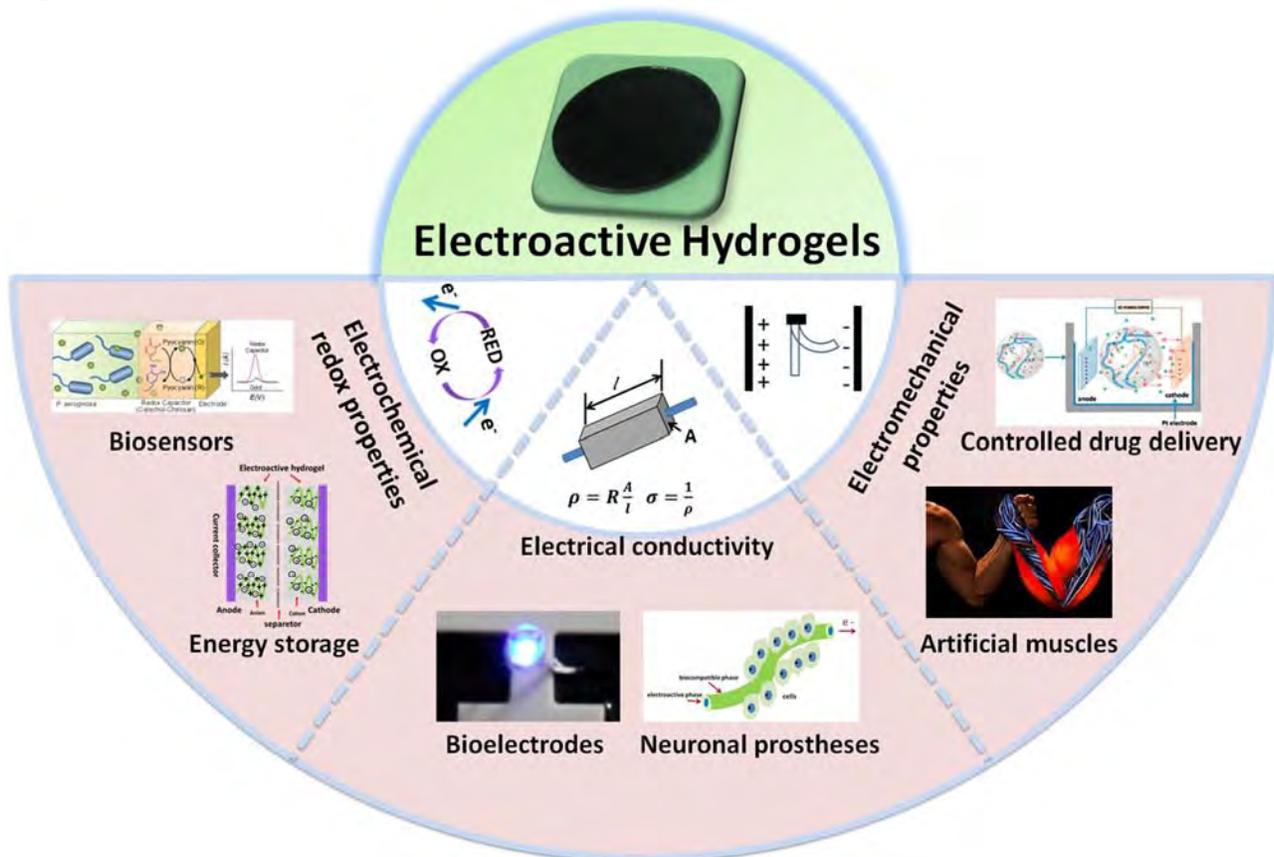
Bacterial adhesion, a common problem for a wide range of applications including water purification and medical implants, is a complex and ongoing challenge. Traditional means of addressing biofouling, namely antibacterial agents, prevent bacterial adhesion by killing microbes. Unfortunately, this approach encourages bacteria to become resistant to commercial antibiotics, diminishing their efficacy and exacerbating the problem of bacterial contamination. Alternatively, antifouling surfaces address biofouling without contributing to antibiotic-resistant bacteria by preventing bacterial attachment to surfaces without killing any microbes. In this work, we focused on synthesizing and evaluating antifouling surface coatings that avoid complex surface reactions or pretreatment. A strongly adhesive molecule attached the surface coating to a variety of surfaces without complex surface chemistry, while a slippery molecule prevented microbial attachment. By using in-house synthesized bifunctional copolymers, we quantified the role of sticky and slippery groups by systematically varying the amounts of “sticky” and zwitterion groups. By codepositing polydopamine, a biological glue with functional copolymers, the effects of chemical composition on the efficacy of the antifouling surface coating were further explored. The material characteristics of the antifouling surface coatings were evaluated using x-ray photoelectron spectroscopy and atomic force microscopy, while their efficacy was quantified using the model microbe *Escherichia coli*. For the first time, we have demonstrated that a stable antifouling surface coating has been produced using a bioinspired glue and a polymer zwitterion without reliance on complex chemistry. This work provides insight into the next generation of antifouling surfaces with broad implications for a wide range of applications including medical implants and chemical separations.



POLY 456: Electroactive hydrogels for biomedical applications

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Hydrogels prepared from polymers have received immense considerations over the past decade due to their safe nature, biocompatibility, hydrophilic properties, and biodegradable nature. More recently, when treated with electroactive materials, these hydrogels were endowed with high electrical conductivity, electrochemical redox properties, and electromechanical properties; consequently, forming a smart hydrogel. The biological properties of these smart hydrogels, classified as electroactive hydrogels, can be combined with electronics. Here, we have developed various types of electroactive hydrogels. These hydrogels are good candidate materials for use in biomedical devices, such as biosensors, electro-stimulated drug release devices, bioactuators, nanogenerators, and implanted electrodes. More than that, they are can be electrically conductive pathways to facilitate the electrical communication among cells. Electroactive hydrogel combined with electrical stimulation, which can influence cell performances such as cell attachment, viability, migration and differentiation, and further to help tissue regeneration, especially in neuron, muscular, bone and skin tissue regeneration.

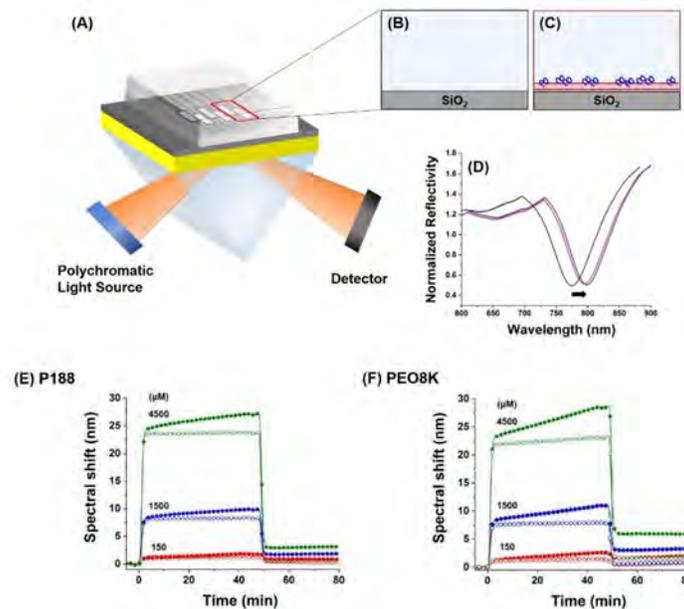


Electroactive hydrogels offering various potential applications

POLY 457: Surface plasmon resonance study of interaction between membrane protective block copolymers and supported lipid bilayer

Mihee Kim, *kimx4807@umn.edu*, Milan Vala, Sang-Hyun Oh, Frank Bates, Benjamin J. Hackel. University of Minnesota, Minneapolis, Minnesota, United States

Poly(ethylene oxide)-poly(propylene oxide) (PEO-PPO) block copolymers have shown protection against membrane-related injuries such as Duchenne muscular dystrophy, ischemia/hypoxia reperfusion injury, and traumatic brain injury. However, the mechanism of block copolymer-based membrane protection is largely unknown. As part of a comprehensive effort to reveal the protection mechanism, we used surface plasmon resonance (SPR) to probe the binding behavior of the block copolymers onto lipid bilayers supported on a SPR chip surface. The dynamics and extent of binding of two polymers were examined and compared: Poloxamer P188, a well-known membrane protective amphiphilic triblock copolymer, and hydrophilic PEO homopolymer that does not show any membrane protection efficacy. Most notably, the PEO exhibited comparable membrane association to P188 (SPR signal of 2.0 ± 1.6 nm vs. 1.5 ± 1.1 nm at 4.5 mM concentration, respectively), which highlights the need for other mechanisms beyond membrane association to explain their differential efficacy.



(A) Schematic of surface plasmon resonance (SPR) spectroscopy

(B) Schematic of bare SiO₂ surface

(C) Schematic of supported lipid bilayer and polymer adhesion

(D) SPR wavelength shift upon lipid bilayer (red) or polymer (blue) adhesion on SiO₂ surface (black)

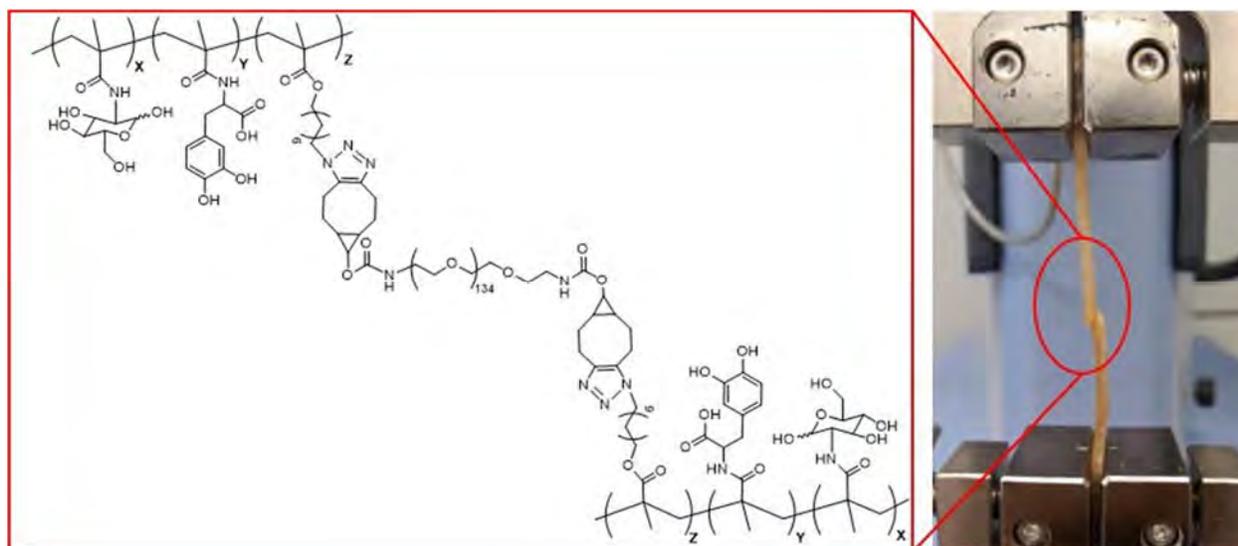
(E) Representative SPR binding curve for Poloxamer 188 (P188) on bare SiO₂ surface (○) and lipid bilayer surface (●)

(F) Representative SPR binding curve for poly(ethylene oxide) 8581 g/mol (PEO8K) on bare SiO₂ surface (○) and lipid bilayer surface (●)

POLY 458: Controllable glucose-based bioadhesive through strain-promoted azide-alkyne cycloaddition (SPAAC)

*Irawan Pramudya*², *ip15c@my.fsu.edu*, *Hoyong Chung*¹. (1) Florida State University, Tallahassee, Florida, United States (2) Chemical Engineering, Florida State University, Tallahassee, Florida, United States

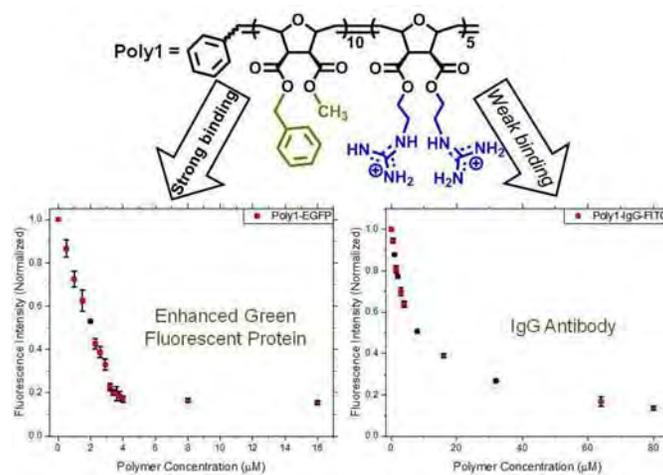
A new glucose-based bioadhesive, poly(glucosamine methacrylate-co-N-methacryloyl-3,4-dihydroxyl-L-phenylalanine-co-3-azidopropyl methacrylate) is synthesized by thermally initiated free radical polymerization. Adhesion strength of the synthesized terpolymer is finely controllable via crosslinking. The used crosslinking chemistry is strain-promoted azide-alkyne cycloaddition (SPAAC)) which has advantages of no releasing byproducts and no requiring chemical reagents and/or special stimulus. The SPAAC mediated crosslinking enhanced overall adhesion properties and the fine-tuning of adhesion enhancement was possible by employing various lengths of crosslinkers, concentrations of crosslinkers, and temperatures. The chemistry of covalent bond formation of SPAAC was clearly confirmed by ¹H-NMR and FTIR. The glycopolymer segment in the new bioadhesive is highly hydrophilic polymer, which resembles chemical structure of natural saccharides. Due to high water solubility of the glycopolymer, the entire bioadhesive was able to be used as a form of water swollen bioadhesive presenting strong adhesion property on biological surfaces (porcine skins). The adhesion property of synthesized adhesive is examined by lap shear test on porcine skins after moistening the adhesive and crosslinker (PEG-Di BCN) with water. Poly(GM-co-MDOPA-co-AOM) adhesive has 25 times higher adhesion strength (120kPa) compared to rubber cement (4.5 kPa). Furthermore, addition of 20% mole of crosslinker in the poly(GM-co-MDOPA-co-AOM) increases the adhesion strength up to 1.5 times (180 kPa). Those revealed features, which include strong adhesion on biological surface, water compatibility, biocompatibility of each polymeric segment, non-toxic adhesion enhancement principle via SPAAC crosslinking, and potentials capability of glycopolymer segment in biological recognition, indicate that the new terpolymer bioadhesive can be successfully applied in biomedical fields.



POLY 459: Role of transporter-cargo binding in polymer mediated intracellular protein delivery

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Delivering biologically active macromolecules into the cellular environment is a promising approach for both the development of novel therapeutics and the discovery of new cellular processes. However, progress towards these goals is hindered because the cellular membrane generally acts as a restrictive barrier to exogenous biomacromolecules. Finding ways to surmount the barrier is crucial because it has far reaching implications in the fields of nanomedicine and fundamental cell biology. Historically, cell penetrating peptides (CPPs) have provided one way to cross the cellular membrane and deliver other biomacromolecules. More recently, CPPs have been mimicked with synthetic block copolymer scaffolds to create CPPMs resulting in more effective membrane penetrators. One advantage in using polymer mimics is that, unlike their CPP counterparts, they do not require covalent attachment to the desired cargo for delivery. Simultaneously, the non-covalent nature of the polymer-cargo association also introduces a rich area of exploration concerning polymer-cargo binding interactions, including binding strength, and their impact on intracellular delivery downstream. Herein, ring-opening metathesis polymerization (ROMP)-based CPPMs were examined for their ability to bind to a variety of protein cargoes with various isoelectric points and sizes. Binding curves were obtained using fluorescence quenching titrations whereby the dissociation constants for each polymer-protein pair were calculated by fitting the data using a non-interacting, multi-site binding model. The calculated dissociation constants varied by orders of magnitude, from very strong to weak binding, depending on the charge and size of the protein cargo. These results suggest that ROMP-based CPPMs have binding preferences for some protein cargoes over others. Currently, intracellular delivery of CPPM-protein cargo complexes into T cells is underway to understand how changes in transporter-cargo binding equilibrium affect subsequent intracellular delivery.



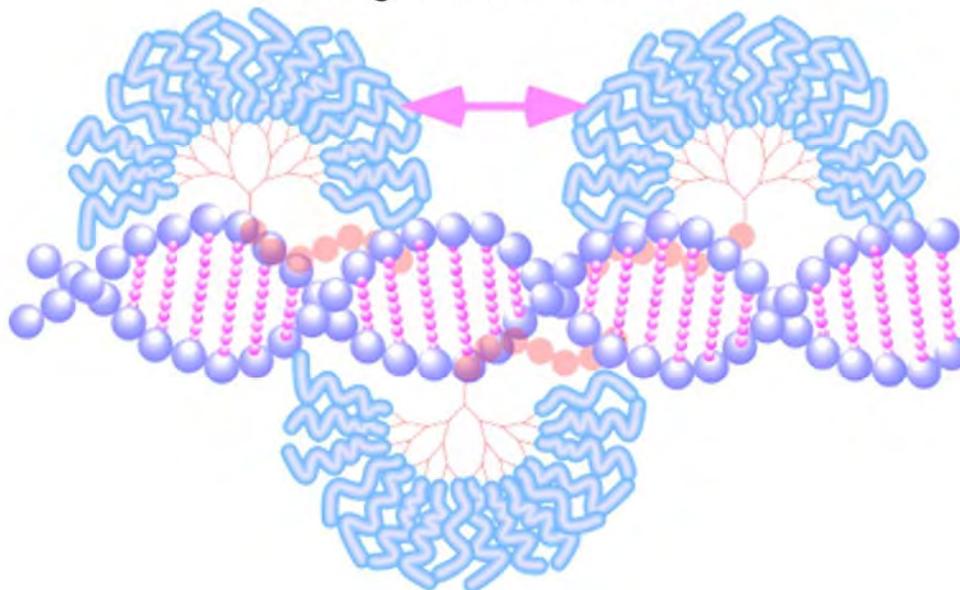
CPPMs and protein cargo binding

POLY 460: Aspect ratio-controllable polyplexes prepared from poly(L-lysine) terminally bearing multi-arm PEG

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Various types of polycations have been design for the purpose of the application as non-viral gene vector. We have investigated the non-viral gene vector based on the molecular design of polycations. We studied for the head-tail type polycations composed of polyamidoamine (PAMAM) dendron head and poly(L-lysine) tail (PAMAM dendron-PLL), in which tertiary amines in the interior of PAMAM dendron head showed buffering effect for endosomal escape and PLL tails formed stable complexes with DNA. To improve the stability of the polyplexes in the presence of serum proteins, PEG chains introduced to the periphery of PAMAM dendron head. The introduction of PEG chains provided not only improvement of stability but also polyplex morphology. Multi-arm PEG structure was constructed through the introduction of PEG chains to PAMAM dendron head, and multi-arm PEG could have effective exclusion volume. Due to large exclusion volume of multi-arm PEG, the polyplex surface was effectively surrounded and the elongated polyplexes, i.e. nanorod and nanofiber, were formed. In this study, the effect of multi-arm PEG density at the polyplex surface was evaluated by the polyplexes prepared using the polycation mixture of PLL homopolymer and nanofiber-forming polymer. The aspect ratio of polyplexes, which determined by AFM observation, could be controlled by changing the mixture ratio of PLL and nanofiber-forming polymer. Importantly the polyplex morphology influenced to cellular uptake and transfection efficiency.

Crowding of multi-arm PEG



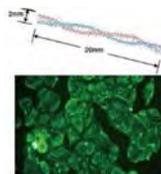
POLY 461: Rigid, fibrous-structured protein showed superior cell-penetrating activity

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Because of the nature of plasma membranes, it prevents most of therapeutic macromolecules from intracellular penetration. Therefore, the development of suitable DDS carrier for the efficient delivery of macromolecules to cells is a critical issue. Cell-penetrating peptides (CPPs) have been studied as cellular delivery vehicles of macromolecules. A typical CPP, R8, has been shown to be an efficient intracellular delivery system, but it is required for effective cellular delivery to a concentrations of several micromolar. On the other hand, materials with rigid and anisotropic structures such as asbestos and carbon nanotubes are known to penetrate cells. However, these materials also show high pathogenesis caused by both high cell-penetrating activity and nonbiodegradability.

In a previous study, we have designed an artificial protein for cellular delivery with a high aspect ratio, rigid structure, surface cationic properties and biodegradable. The designed cellular delivery carrier protein, named CCPC 140, showed significant fluorescence detection in all cells at a concentration as low as 3.1 nM. We also exploited CCPC 140 for the intracellular delivery of GFP. The activity of CCPC 140 for intracellular delivery of GFP was compared with R8. The cellular delivery of proteins by CCPC 140 was at least 20-fold greater than that of R8.

To evaluate the effect of molecular length on cell-penetrating activity, we produced deletion and mutation variants of CCPC 140. A variant with an aspect ratio 4.5:1 showed similar cell-penetrating activities when compared with CCPC 140. The incorporation of further deletions, i.e., decreased their aspect ratio, reduced the cellular uptake. That is, the anisotropic structure, aspect ratio of protein molecule is a determining factor of the superior cell-penetrating activity of CCPCs.

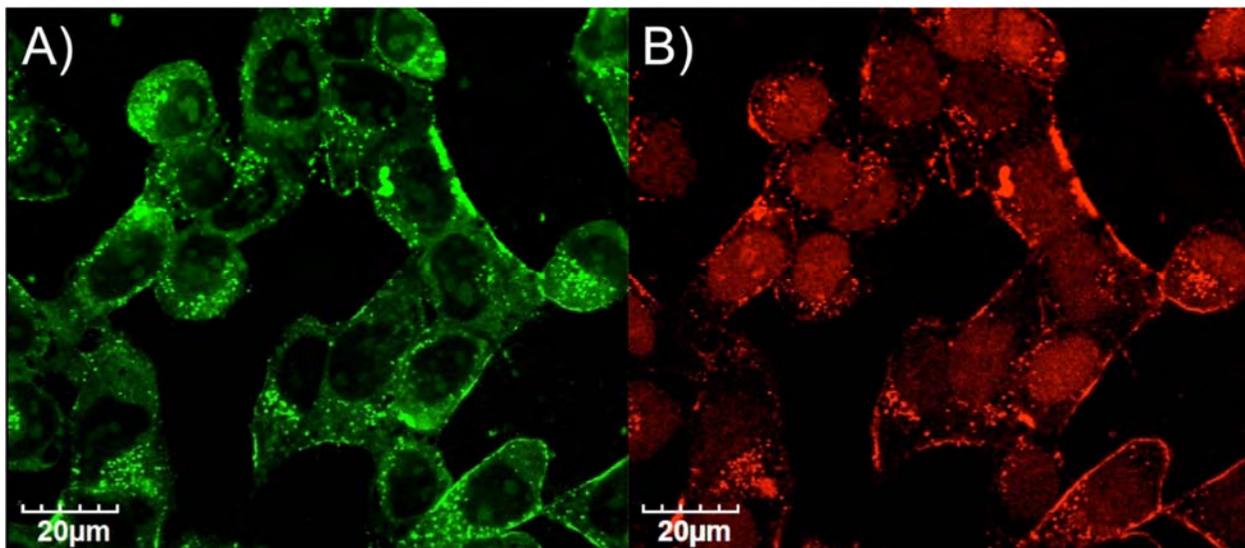


Structure of CCPC 140 and intracellular delivery

POLY 462: Conjugated polymers for RNA interference in human primary bronchial cells

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Chemistry Biochemistry Cp338a, Florida International University, Miami, Florida, United States

Small RNA molecules have extraordinary ability to regulate gene expression known as RNA interference (RNAi) upon successful delivery to target cells. Although various synthetic materials have been developed and demonstrated RNAi in various cell lines, transfection efficiency in primary cells is quite low due to low cellular entry efficiency and toxicity. We have demonstrated successful down regulation of a target gene in primary normal human bronchial cell (NHBC) using modulated guanidine containing conjugated polymers (CPs). In this presentation, we will discuss dramatic effects of the chemical modulation at guanidine group of CPs on cellular entry, intracellular localization, and target gene down regulation. The amphiphilicity of CPs from the hydrophobic p-electron conjugated backbone and the charged hydrophilic side chain contributes to non-toxicity and efficient cellular entry. This new CP-based technology can open a new window for future therapeutic delivery to target tissues.

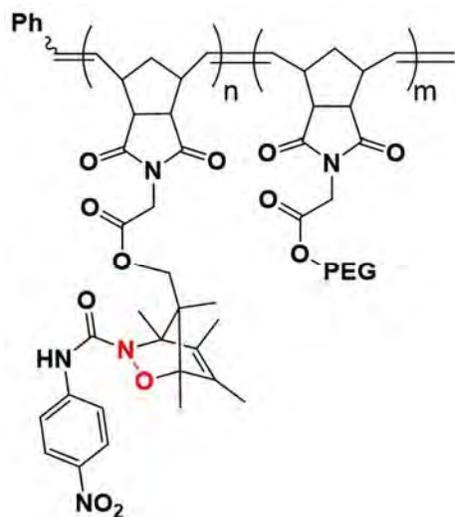


Fluorescent microscopic images of HeLa cells incubated with modulated guanidine CP/siGLO complex for 1 h. The green channel shows CP and the red channel shows siGLO.

POLY 463: Amphiphilic block copolymers, hydrogels, and micelles for the controlled release of HNO

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Chemistry, University of Washington, Seattle, Washington, United States

We have developed a series of polymers that contain 1,2-oxazines within the polymer side chains. The oxazine units have been found to release HNO upon thermal activation, with concomitant release of an organic dye molecule that can be used as an indirect indicator for quantifying activation. The modular nature of the polymeric materials enabled access to random (statistical) and block copolymers via ring-opening metathesis polymerization. The resulting amphiphilic copolymers were found to yield robust hydrogels, shear thinning hydrogels, and micelles depending upon the copolymer structure and processing conditions. We will report on our efforts toward using these materials as a modular platform for the controlled release of HNO.



tough hydrogels

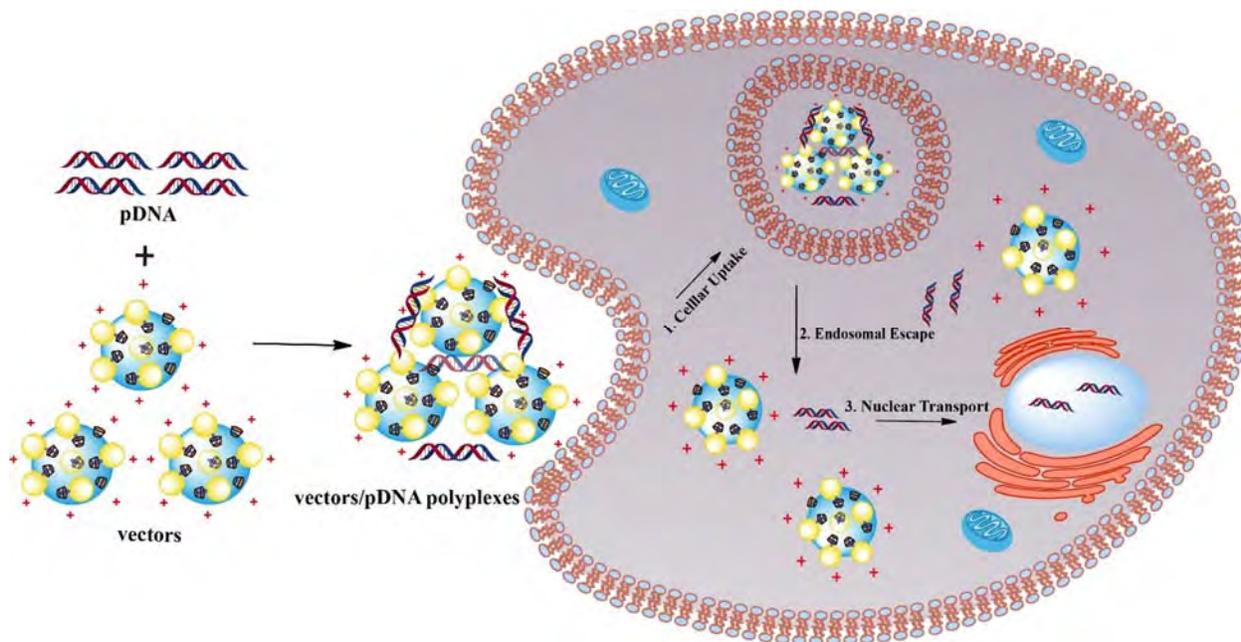


shear thinning hydrogels

POLY 464: Construction of core-shell tecto dendrimers based on supramolecular host-guest assembly for enhanced gene delivery

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Design of dendrimer-based nanoarchitecture for enhanced gene delivery still remains a great challenge. Here, we report the design of core-shell tecto dendrimers using a supramolecular assembly approach for enhanced gene delivery applications. Firstly, β -cyclodextrin (CD)-modified generation 5 (G5) poly(amidoamine) (PAMAM) dendrimers (G5-CD) and adamantane (Ad)-modified generation 3 (G3) PAMAM dendrimers (G3-Ad) both having amine termini were synthesized. Through the supramolecular recognition of CD and Ad, G5-CD/Ad-G3 core-shell tecto dendrimers with G5 core and G3 shell were formed. The formed G5-CD/Ad-G3 core-shell tecto dendrimers with a size of 8.4 nm possess good monodispersity, well-defined three-dimensional structure, and quite low cytotoxicity. Importantly, with the abundant amines on the surface, the core-shell tecto dendrimers are able to transfect luciferase (Luc) gene with an efficiency 20 times and 170 times higher than G5-CD and G3-Ad dendrimers, respectively. The higher gene transfection efficiency can also be qualitatively confirmed by transfection of plasmid DNA encoding enhanced green fluorescence protein. Our results suggest that the developed G5-CD/Ad-G3 core-shell tecto dendrimers may be used as a promising vehicle for enhanced gene transfection applications.

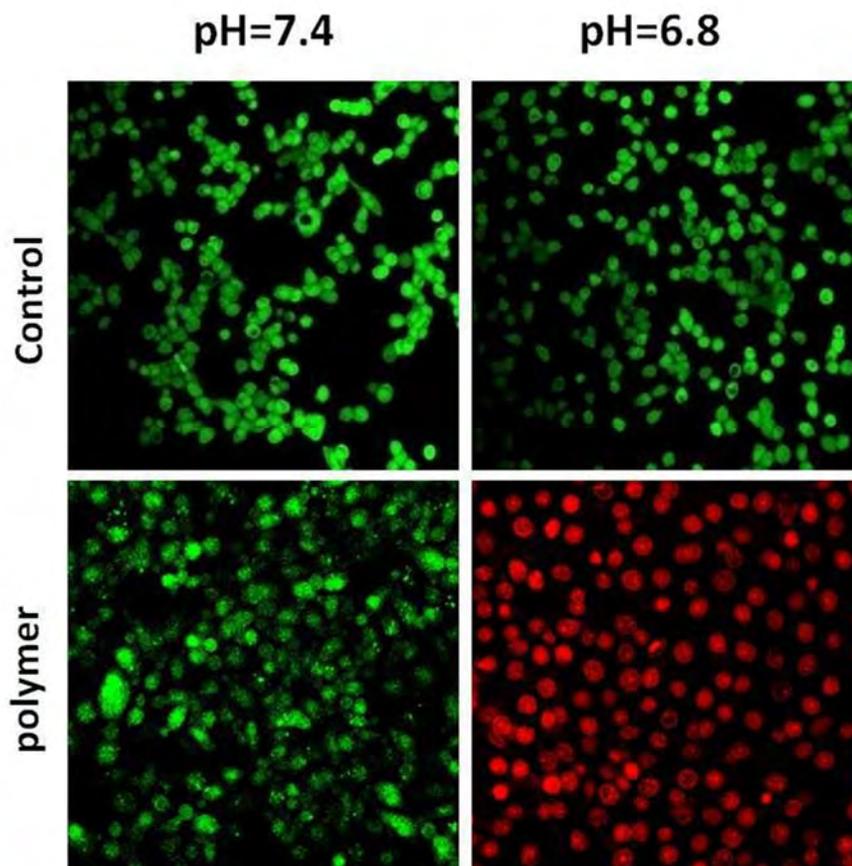


Schematic design of core-shell tecto dendrimers based on supramolecular host-guest assembly for enhanced gene delivery applications.

POLY 465: Polymeric mimetics of antimicrobial peptides as anticancer agents

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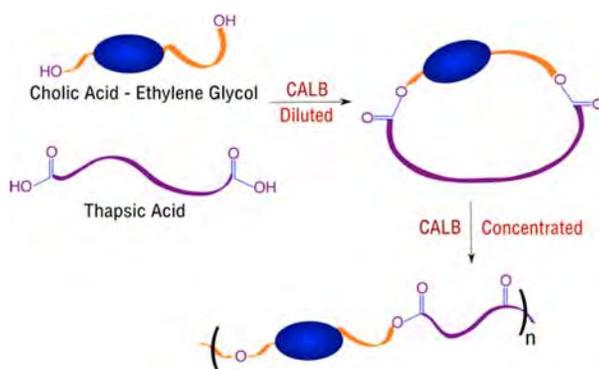
Multi-drug resistance of cancer cells is a major factor in the failure of many forms of chemotherapy (*Nat. Biotechnol.*, 1999, 17, 94). Mechanisms of cancer cells' multi-drug resistance are, in fact, similar to those of bacterial antibiotic-resistance. Therefore, antimicrobial peptides and their synthetic mimetics, a widely-recognized promising source of novel anti-infective agents especially against antibiotic-resistant bacteria, may be an effective source for overcoming cancer drug-resistance. Inefficiency of these agents in differentiating cancer cells from normal ones, however, greatly hinders their anti-cancer applications. Having this concern in mind, we develop ways to make antimicrobial peptides and their synthetic mimetics capable of ablating cancer cells including the drug-resistant ones without hurting the normal cells. Preliminary results on how we design the systems and how they perform will be presented.



POLY 466: Degradable Polyesters Made by Enzymatic Polymerization

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julian.zhu@umontreal.ca. Chimie, Université de Montréal, Montreal, Quebec, Canada

Degradable polyesters can be made through entropy-driven ring-opening metathesis polymerization (ROMP) of macrocycles. Grubbs' catalysts based on ruthenium are often used for both ring-closure reactions for the formation of macrocycles and also for the ROMP reactions. For polymers to be used for biomedical applications, the trace amounts of the transition metal catalysts left in the resulting polymers may become a problem for their uses. We have explored the use of an enzyme, particularly the solid-supported *Candida antarctica* lipase B (CALB) in the preparation of macrocyclic monomers containing ester bonds, followed by an entropy-drive ring-opening polymerization using the same enzymatic catalyst. Both the ring-closure and ring-opening reactions are highly successful, yielding a collection of new polyesters. The lipase-catalyzed reactions were carried out on the ring closure of simple diacid-diol coupling as well as on bile acid-based macrocycles in organic solvents and at relatively high temperatures (70-80°C). Cholic acid, a major bile acid in the body, contains one carboxylic acid group and three hydroxyl groups. CALB demonstrated a good selectivity towards one of the hydroxyl groups (3 α -OH) of cholic acid, indicating the versatility of the enzymatic catalyst. We have obtained bile acid-based degradable polymers of high molar masses, rubber-like elasticity, and glass transitions close to ambient temperatures. Such polymers also manifested interesting shape memory properties.



Preparation of a macrocyclic monomer via enzymatic ring-closure reaction and the preparation of a polyester via enzymatic ring-opening polymerization.

POLY 467: Radical copolymerization of vinyl ethers and cyclic ketene acetals as a versatile platform to design functional polyesters

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The ring-opening polymerization of cyclic ketene acetals (CKA) by free radical mechanism attracts considerable research interest since it presents an alternative route for the synthesis of aliphatic polyesters. These monomers can indeed undergo radical addition on their C=C double bond that subsequently leads to propagation by ring opening. By a theoretical approach based on DFT calculations combined with PREDICI modelings, the radical copolymerization of CKA and common vinyl monomers was studied to find optimized CKA/vinyl monomer couples to obtain functionalized polyesters.

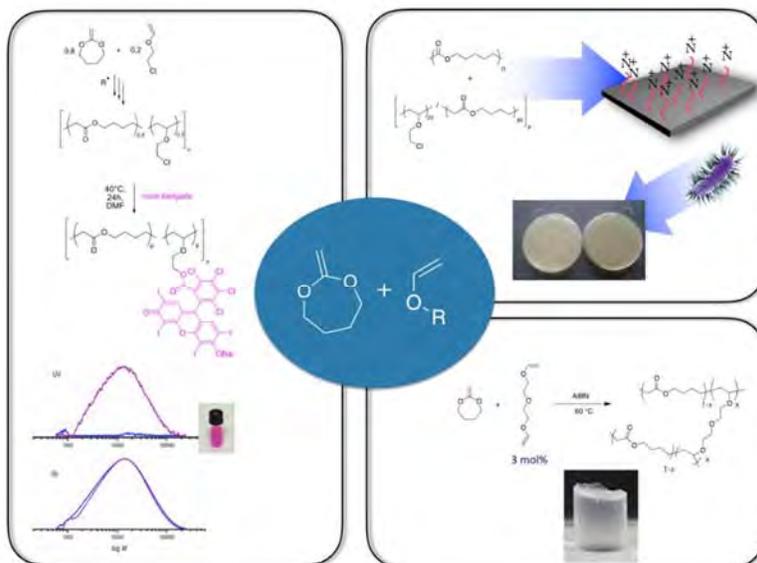
Indeed, whereas polyesters based on lactones are widely used, such materials nevertheless exhibit severe limitations due to the absence of functionality on the polymer backbone, which could otherwise be used either for tuning their physical properties or for coupling various molecules of interest.

Recently a few authors

developed an elegant approach to prepare functionalized polyester-like structures based on the radical ring-opening copolymerization of CKA with traditional vinyl monomers.

Whereas this approach is promising, severe limitations still remain: the unfavorable reactivity ratios of CKA compared to those of traditional vinyl monomers lead to a considerable difference between the fraction of 2-methylene-1,3-dioxepane (MDO) incorporated and the initial fraction in the co-monomer feed.

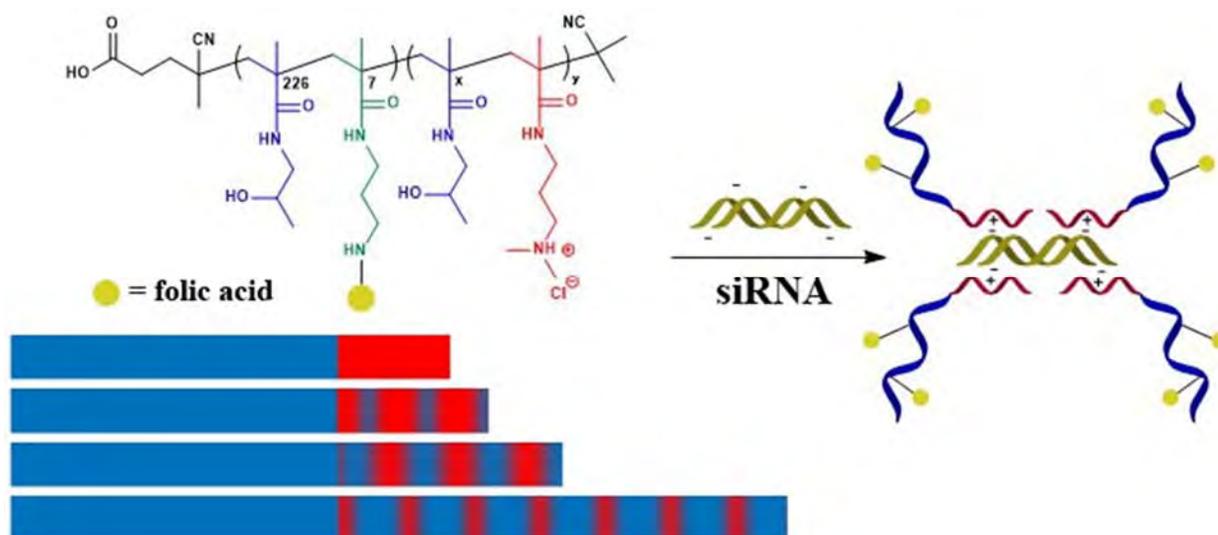
Optimized vinyl monomer/CKA couples are highly desired. Once this vinyl monomer/CKA couple has been selected, this system was further used to prepare interesting materials for biomedical applications such as antibacterial surfaces and bioelastomers.



POLY 468: Variable charge density in siRNA-containing block ionomer complexes: Optimizing complex binding strength, stability, and gene suppression

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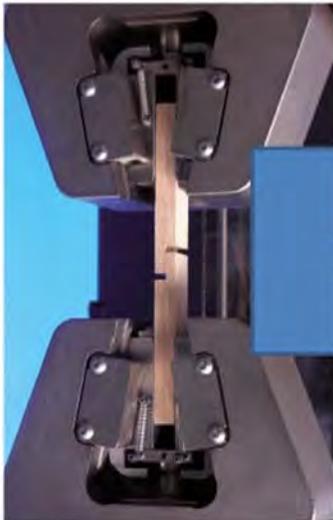
Block ionomer complexes (BICs) formed from electrostatic association between hydrophilic-*block*-cationic copolymers and small interfering RNA (siRNA) are known to serve as superior vehicles for gene delivery. Such BICs stabilize and protect the siRNA while conferring hydrophilicity and reduced cytotoxicity, and incorporation of a cellular targeting moiety deters nonspecific cellular uptake. Our group has previously demonstrated that BIC stability and siRNA delivery efficacy strongly depend upon cationic block length: increased block length greatly stabilizes the complexes and also increases the time required to achieve maximum gene knockdown. To explore this phenomenon further, aqueous RAFT (aRAFT) polymerization was utilized to synthesize hydrophilic-*block*-cationic copolymers in which the cationic block contains a statistical incorporation of a neutral, hydrophilic monomer such that the number of cationic groups remains unchanged but varies in distribution along the polymer backbone. These copolymers with varying charge density were then complexed with siRNA and siRNA analogues. Calorimetric and potentiometric investigations of these BICs revealed trends of increasing complex stabilities and polymer-oligonucleotide binding strengths with greater cationic block charge density. Finally, *in vitro* gene suppression studies revealed improved gene knockdown with increased charge density. Quantification of siRNA delivery and cell fractionation revealed higher cellular siRNA content as well as increased activation of the RNA interference pathway with greater charge density.



POLY 469: Washed cottonseed meal-based products as bio-based wood adhesives for non-structural interior applications

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Proteins are renewable biopolymers, and can be used as green bio-based wood adhesives. We have tested the bonding performance of cottonseed meal (CSM), water-washed cottonseed meal (WCSM), and cottonseed protein isolate (CSPI). Our data showed that WCSM and CSPI possessed comparable adhesive performance. Both products demonstrated much better water resistance than CSM. As WCSM is more cost-efficient and environment-friendly than CSPI which production involves alkaline extraction and acidic precipitation, WCSM is more promising as a cheap industrial wood adhesives. Used pilot-scale produced WCSM, we further optimized the bonding parameters for non-structural interior applications. Under tested conditions, addition of Cao or MgO did not improve any of the three strength measurements we tested (i. e., dry, wet, and soaked strength). However, WCSM can mix with denaturant agents to improve its bonding capability and operational flowability. Per the experimental data, several WCSM-based adhesive formulations were proposed and could be used as low-temperature glues for the domestic small utensils bonding or high-temperature adhesives for plywood and composite making.

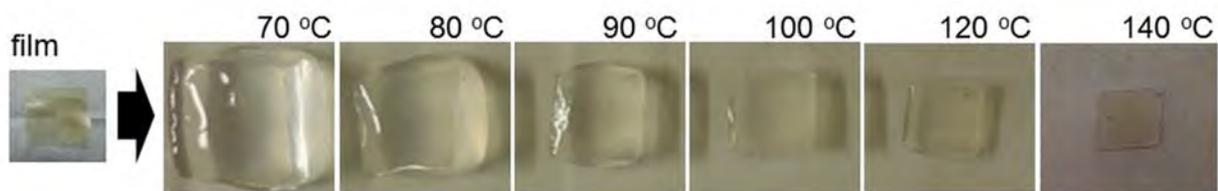


Testing type	Method applied	Adhesive strength	
		WCSM 1	WCSM 2
Durability class D1	EN 204/205	10.7 MPa	9.3 MPa
Durability class D2	EN204/205	1.2 MPa	No Test
Durability class D3	EN204/205	0.5 MPa	0.3 MPa
Heat resistance	EN14257	8.9 MPa	9.1 MPa

POLY 470: Preparation of anisotropic physical hydrogels of cyanobacterial super-polysaccharides

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Hydrogels are three-dimensional network structures obtained from a class of synthetic and/or natural polymers which can absorb and retain significant amount of water. The hydrogels have been used extensively in various biomedical applications such as drug delivery, cell carriers and/or entrapment, wound management and tissue engineering. Sacran is cyanobacterial-polysaccharide extracted from *Aphanothece sacrum* which contain 11 % of sulfate group, 22 % of carboxyl group and about 250 % of hydroxyl group to sugar residues. Moreover sacran has a very high molecular weight of 29 Mg/mol and then a super-absorbent property to induce an anti-inflammatory activity. We found that it can be prepared the physical hydrogel of sacran from the film which is made by cast-drying method. Concretely, the 0.5 % sacran solution was dried in oven at 60 °C for 12 h to create the thin film (about 50 mm), and the film was immersed into pure water to anisotropic hydrogels (this phenomenon was observed only in sacran not in another polysaccharide). It was additionally found that the swollen degree of the gels was controlled by the heating temperature treating precursor film ranging 60-140 °C. As a result, we controlled the swollen degree of the gels from 20 to 800 times to the dry weight depending on the heating temperature of the films. The following properties of the hydrogels were evaluated: water content, swelling ratio in water, gel strength, and then their structure was analyzed by FT-IR spectroscopy and X-ray analysis.



Cyanobacteria-derived gels prepared from in-situ gelation of super-polysaccharide films annealed at various temperatures, swelling anisotropically to thickness direction

POLY 471: Developing sustainable acrylates for 3D printing

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3D printable photopolymers have seen expanding applications in prototyping, medical devices, and particularly, in the advancing field of digital dentistry. Stereolithographic 3D printers are used to print orthodontic devices such as dentures, retainers, and bridges. Dental resins with high precision, good strength and toughness, fast photo-curing, biocompatibility, and antiseptic properties, are growing in demand for greater strides in this direction of additive manufacturing. Our effort aims at developing acrylate monomers and formulations based on sustainable feedstocks to replace bisphenol A (BPA)-based monomers, which have significant health concerns. Eugenol, guaiacol, and vanillin, bearing natural aromaticity are synthesized to (meth)acrylates to impart structural rigidity into free-radical photo-crosslinked network. With the photoinitiator (0.5 wt% TPO), the sustainable monomers were formulated with flexible polyethylene glycol (meth)acrylates. The photo-curing kinetics and dynamic mechanical properties of the formulations were investigated. Photo rheology demonstrated that the gel time is affected by the viscosity and molecular structure of the monomer (meth)acrylates in the formulations. The storage modulus, glass transition and cross-link density measured by dynamic mechanical analysis (DMA) indicate the improved manipulation of those properties by the novel thiol-ene clicked eugenol acrylate monomer. Continuing work on mechanical tests, antibacterial test and further enhancement on curing rate and 3D printability will be performed.

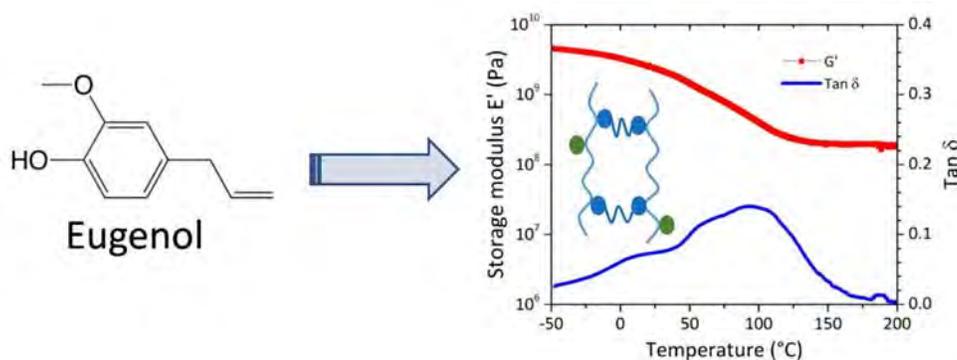
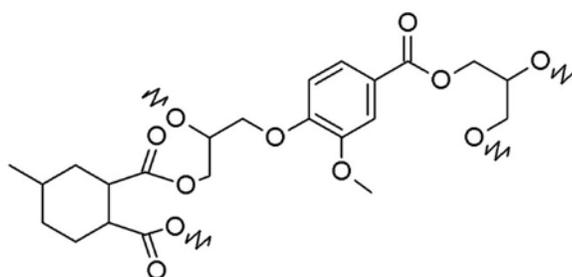


Figure 1. Storage modulus of formulation made with thiol-ene clicked eugenol acrylate monomer. (Inset image) Schematic drawing of the cross-linked network.

POLY 472: Sustainable and degradable epoxy resins containing multifunctional biobased components

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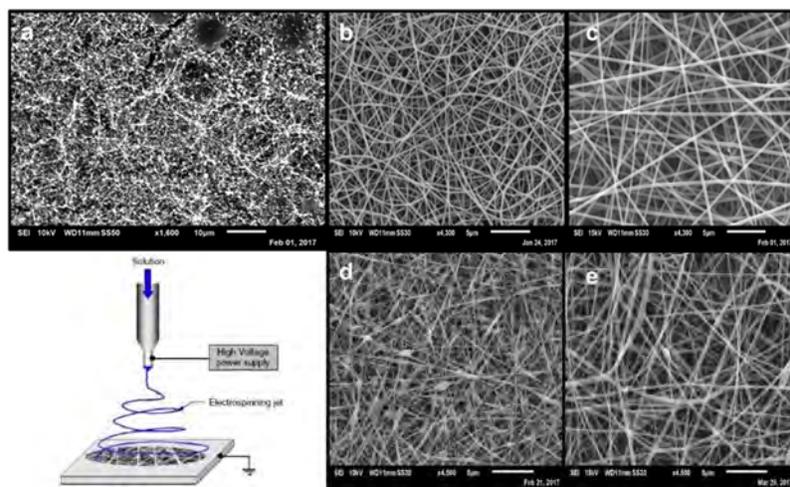
Vegetable oils, phenolic acids, and lignin were investigated as sustainable sources to produce degradable epoxy resins with a reduced environmental impact. Epoxy resins are thermoset polymers widely used in composites, coatings and adhesives, with applications spanning automotive and aerospace industries, structural components, and wind turbine blades, among others. The standard precursor to epoxy resins, the diglycidyl ether of bisphenol A (DGEBA), is derived from petroleum and also has potential harmful health impacts. Lignin, an abundant bioresource, was explored as a source for replacing DGEBA in epoxy resins. Vanillic acid, a byproduct of the chemical degradation of lignin was investigated as a replacement for DGEBA in anhydride-cured epoxy resins. Functionalization of vanillic acid with epoxide groups was carried out through allylation, followed by epoxidation. Epoxidized vanillic acid was subsequently cured with an anhydride curing agent. The resulting vanillic acid-based epoxy resins exhibited high glass transition temperatures, comparable to conventional DGEBA-based epoxy resins. The accelerated hydrolytic degradation of epoxy resins containing degradable ester groups, such as in epoxy resins derived from vanillic acid, plant-sourced phenolic acids, and epoxidized soybean oil (ESO), was explored, to provide additional end-of-life options such as composting. The polymer mass loss was monitored after exposure to a base solution at elevated temperature. The biobased epoxy resins exhibited rapid degradation in the base solution, in contrast to the slow degradation rate of the traditional DGEBA-based epoxy resin.



POLY 473: Therapeutic electrospun natural polymer based fiber scaffolds for biomedical applications

*Kathryn Penton, William Weeks, Amber Wilson, Zachary Kinler, Virginia F. Baker, Tia Brown, Scarlett Salter, **Sharon K. Hamilton**, sharon.k.hamilton@gmail.com. Chemistry and Physics, Delta State University, Leland, Mississippi, United States*

Recent evolutions in the field of biomaterials have focused on developing materials that can facilely interface with biological systems to treat or replace tissues or functions of the body. Natural polymers, including polysaccharides, have been investigated as suitable biomaterials to mimic the environment of body tissues and facilitate tissue regeneration. Electrospinning natural polymers, like alginate and chitosan, yields nanofibers that have shown promise as tissue scaffolds and drug delivery vehicles. However, little research has been published on the controlled delivery of drugs from natural polymer fibrous dressings. The lack of studies in this area is due in part to the difficulty of electrospinning charged polymers, like alginate and chitosan, and the slow degradation of these polymers under physiological conditions. The long term goal of this project is to generate a better understanding of natural polymer based wound healing materials and their small molecule release profiles towards their implementation in wound healing treatments. This research has taken a three-pronged approach regarding the investigation of natural polymer based fibers. One facet focuses on the development of novel alginate based, degradable nanofibers. Another facet focuses on the preparation of drug loaded, alginate and chitosan based fibers via electrospinning and the exploration of the release profiles of these scaffolds. A third facet investigates covalently modified alginate and chitosan drug conjugate nanofibers and the hydrolytic release profile of these novel innately therapeutic scaffolds. Studies from all approaches will lead to improved understanding of alginate and chitosan based materials for biomedical applications, especially in the field of modern drug laden, wound dressings.



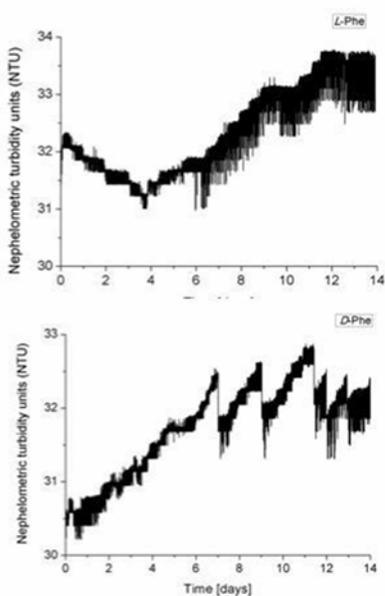
SEM images of fibers: a) Oxidized alginate and PVA fibers; b) Alginate and PVA fibers; c) Chitosan and PVA fibers; d) Drug loaded alginate and PVA fibers; e) Drug loaded chitosan and PVA fibers. Inset is electrospinning set up.

POLY 474: Comparison of the dynamics of spontaneous peptidization of selected α -amino acids in the abiotic aqueous organic solutions and heavy water (D₂O)

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In a series of papers, we have demonstrated an oscillatory nature of the spontaneous peptidization of a vast number of the proteinogenic α -amino acids, using for this purpose a selection of different analytical techniques (e.g., high-performance liquid chromatography, polarimetry, or turbidimetry). Although these experiments were carried out in the abiotic liquid systems, we had a feeling that the molecular mechanisms responsible for these processes might be of a biological and even evolutionary importance. One mechanistic feature which might suggest such a conclusion was that with certain proteinogenic *L*- α -amino acids, the circadian rhythm of the oscillatory peptidization was observed.

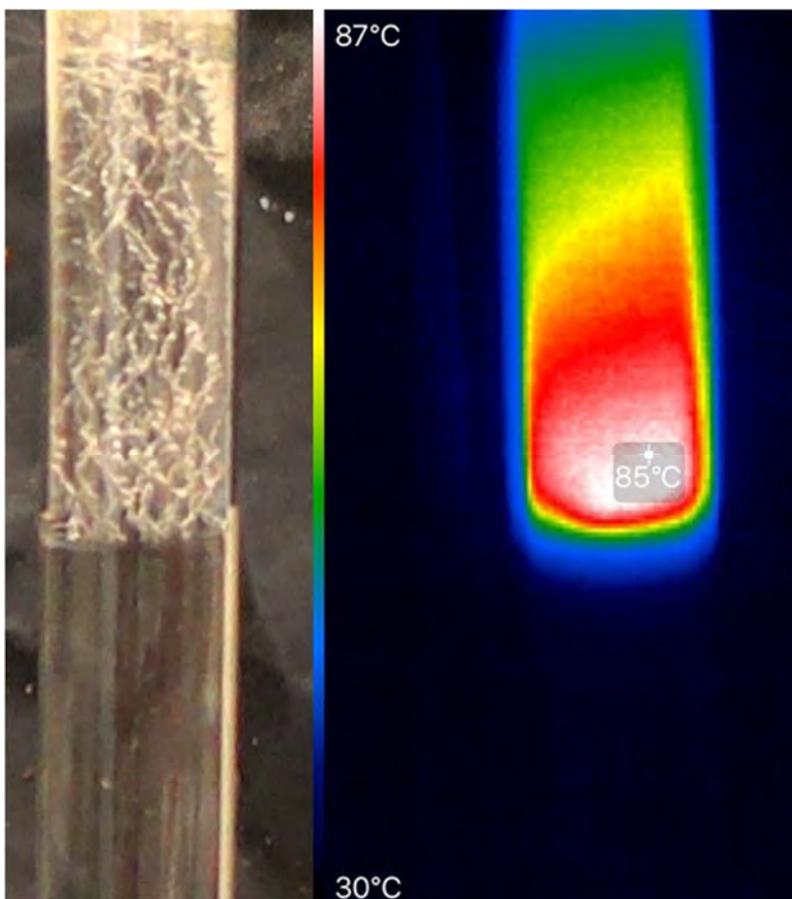
In a search for additional analogies between the spontaneous oscillatory peptidization of the proteinogenic α -amino acids running in abiotic aqueous-organic systems on the one hand and the biochemical processes carried out in living organisms on the other, we assumed an evidence '*a rebours*', by selecting heavy water (D₂O) as a liquid medium well recognized from numerous biological studies for hampering biochemical processes of such living organisms as, e.g., bacteria. As a result, spontaneous oscillatory peptidization of α -amino acids was to a large extent suppressed by heavy water, which might serve as an additional justification of our hypothesis that the biological processes running in living organisms and involving α -amino acids are oscillatory in nature.



POLY 475: Low-temperature frontal polymerization of acrylate-based composites for use in bone repair

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Thermal frontal polymerization is a process in which a localized reaction zone propagates through an unstirred system by the coupling of thermal conduction and the Arrhenius kinetics of an exothermic polymerization. Frontal polymerization allows “cure-on demand” of a system with a long pot life once a localized reaction is initiated. One area where the cure-on-demand nature of frontally polymerizable systems could prove very useful is orthopedic repairs. One potential drawback typically associated with thermal frontal polymerization is a large exotherm leading to high front temperatures, often above 200 °C. By modulating the concentration of functional groups using mixtures of commercially-available high and low molecular weight multifunctional acrylate and thiol-containing monomers, front temperatures in the range of 80-100 °C have been achieved. The addition of relatively inexpensive ceramic and silica-based fillers yields a mechanically robust biocompatible material that has a putty-like consistency with a long pot life.



POLY 476: Time-lapse materials: Using the enzymatic hydrolysis of urea in polymerization

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Urea undergoes enzymatic hydrolysis in the presence of urease and water to produce ammonia and carbon dioxide, a well-documented process that occurs in bacteria, plants, and soil. This process follows Michaelis-Menten kinetics, forming a bell-shaped pH-rate curve with maximum enzymatic hydrolysis at pH 7. These kinetics result in an induction period at low pH before the enzyme's maximum rate hydrolyzes large amounts of urea to ammonia and causes the switch to high pH, also called the reaction clock time. Using the induction period before the clock reaction, it is possible to "program" the time of polymerization of a pH-sensitive polymer. Instead of using expensive, purified urease crystals that are highly sensitive to environmental conditions, these experiments are performed with an alternative raw-source of urease: watermelon seeds. Using ground watermelon seeds, we will examine timing base-catalyzed polymerizations, effects of raw-source urease on clock time such as particle size, and possible applications of resulting polymers.

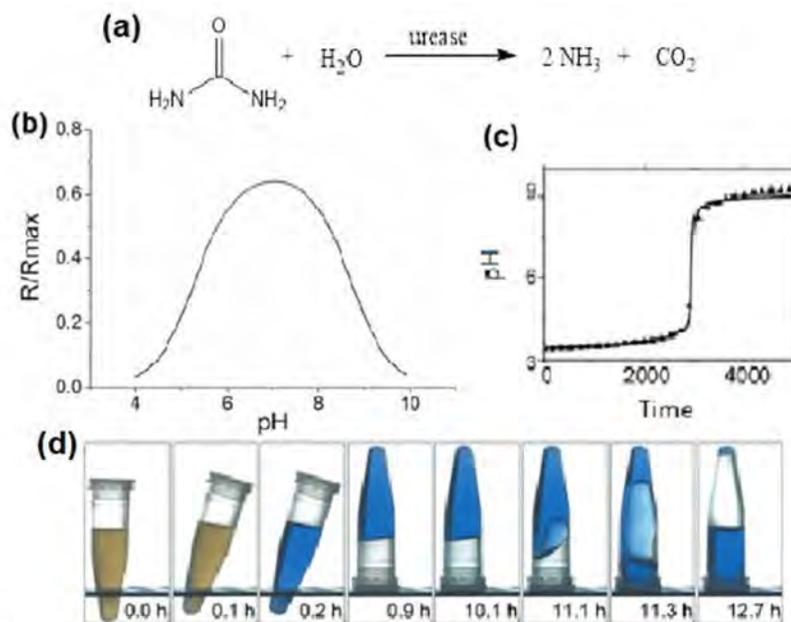
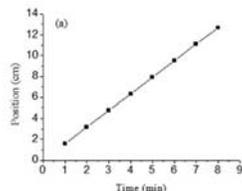


Figure 1. (a) Reaction scheme for the enzymatic hydrolysis of urea into ammonia and carbon dioxide, (b) Michaelis-Menten enzyme rate kinetics as a function of pH, (c) pH-time curve of the clock reaction caused by (b), and (d) time-lapse of pH-sensitive polymerization using urea-urease clock with pH indicator.

POLY 478: Preparation of acrylic acid-*graft*-carboxymethyl cellulose superabsorbent hydrogels by frontal polymerization

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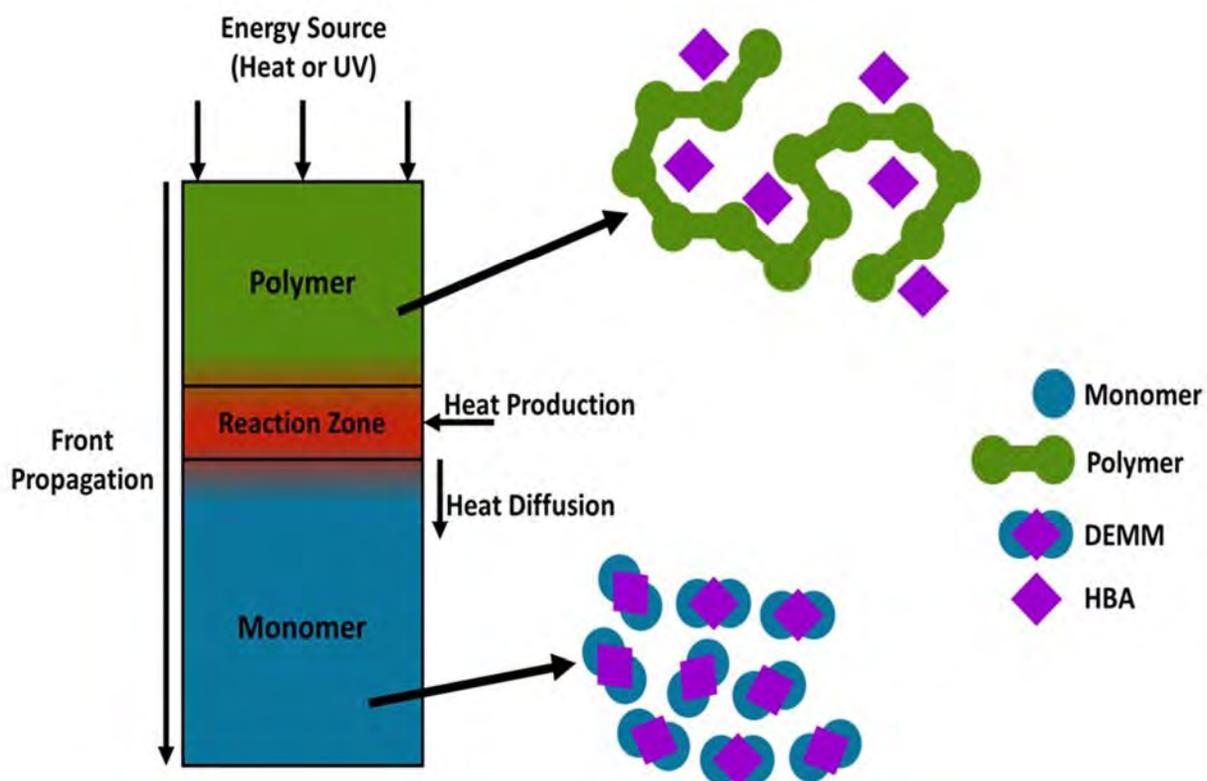
Acrylic acid-*graft*-carboxymethyl cellulose superabsorbent hydrogels were prepared by frontal polymerization using carboxymethyl cellulose and acrylic acid as raw materials and water as solvents. The as-synthesized hydrogels were characterized by IR and scanning electron microscopy. The effects of initiator, cross-linking agents and the ratio of CMC and AA on frontal polymerization and swelling ratio were studied in this paper. It was found that the reaction condition had important effects on the velocity of the frontal polymerization and swelling properties of hydrogels. The acrylic acid-*graft*-carboxymethyl cellulose hydrogels prepared by frontal polymerization have excellent superabsorbent properties.



POLY 479: Frontal polymerization of deep eutectic solvents composed of acrylic and methacrylic acids

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Frontal polymerization of deep eutectic solvents (DESs) made with acrylic or methacrylic acid as the monomer and hydrogen bond donor was studied. Fronts with acrylic acid and choline chloride propagated more uniformly than with pure acrylic acid, so an exploration into how the DES affected frontal polymerization was performed. The hydrogen bond acceptor of the DES was replaced by several analogs to determine the effect on the DES front behavior. None of the methacrylic acid-analog systems were able to sustain a front. While the acrylic acid-analog systems did sustain a front (with the exception of stearic acid), none of the fronts replicated the acrylic acid DES behavior. We propose that the reactivity of the acrylic acid and methacrylic acid is enhanced in the DES, and this was further explored by infrared spectroscopy.



POLY 480: Radical-induced cationic frontal polymerization using divinyl ethers

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Frontal polymerization is a polymerization process in which the reaction occurs directionally in a localized zone. The system developed involves the use of tandem radical and cationic initiators; diaryliodonium photoacid generators are reduced in the presence of thermally-generated radicals in order to facilitate rapid formation of cationogenic species capable of initiating cationic polymerization. Neat divinyl ether monomers and mixtures with epoxidized soybean oil were polymerized frontally using this technique. Front velocity versus epoxy concentration was analyzed, along with the physical properties of the resulting polymers. Materials created were elastomeric thermosets, a first in the field of frontal polymerization.

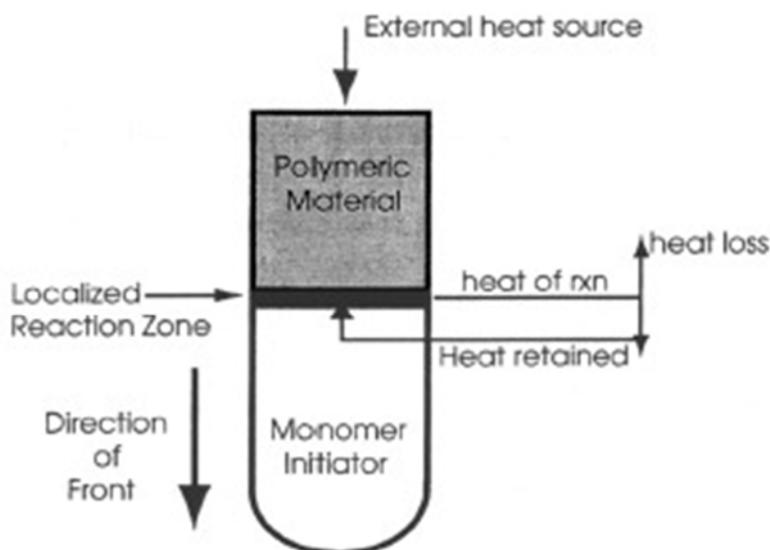


Figure 1. Schematic of frontal polymerization illustrating positive feedback for a sustained traveling wave.

POLY 481: Chemical oscillating particles through encapsulation of the urea-urease reaction

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Oscillatory behavior in nature usually involves a complex set of regulatory mechanisms. Recreation of these phenomena is of interest to engineers and chemists either in the fields of biological analogues or drug delivery. In this work we seek to utilize the enzyme reaction of urea-urease and the addition of an acid to study their performance when encapsulated. Each component can be encapsulated with different media to control each release profile. Mathematical modeling of this system compartmentalizes the reactants giving numerical studies to the constraints and stability of the model. The particles potentially mimic biological aspects of cellular regulation and has potential applications in controlled drug delivery.



Agar particles with bromothymol blue indicator at varying pH levels.

POLY 482: Cyclic versus acyclic acetal-based monomers: Using monomer design and thiol-ene photopolymerization to tailor network architecture and degradation profiles

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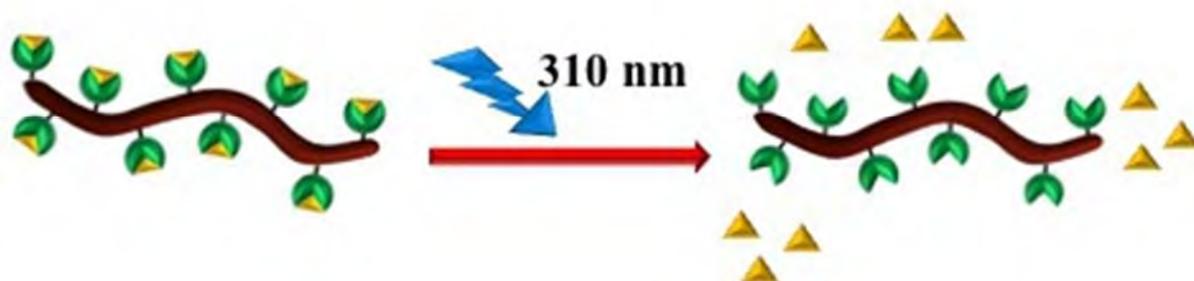
Pro-active networks from degradable acetals (PANDAs) obtained via thiol-ene photopolymerization offer control over network architecture, crosslink chemistry and density, and network structure for tunable degradation profiles. These networks are comprised of degradable acetal linkages, which release aldehyde byproducts upon hydrolysis. These acetals can be incorporated directly into the polymer backbone, resulting into total degradation of the network upon hydrolysis, or as pendant groups to the backbone, leaving an intact network with potentially useful mechanical properties upon degradation. Pendant group and main chain acetal incorporation is achieved either through cyclic and acyclic acetals, respectively. A library of acetals was synthesized for incorporation into networks with pendant and main chain acetal architectures. These networks were characterized for mechanical properties and degradation profiles to elucidate structure-property relationships to explore further network tunability.



POLY 483: Utility of photolabile protecting groups in amine functionalized polymers

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Primary amines play a significant role in both synthetic and polymer chemistry by involving various reactions such as amide, imine formation, Michael addition and ring opening reactions. The nucleophilicity of amine functional groups make them more susceptible towards numerous reactions enabling further chemical modifications. However, the reactivity of amine groups can also generate challenges by introducing unwanted side reactions. In particular, primary and secondary amine groups react with thiocarbonylthio groups common to all RAFT groups, making them incompatible with RAFT. To elude side reactions, it is essential to protect amine functional groups when performing a series of chemical reactions. Protection enables maintaining functional groups dormant in an occasion to prevent side reactions where two functional groups competing for the same reaction. Thus far, many amine protection groups have been employed in various synthetic pathways. All these protection methods employed with exacting chemical deprotection methods such as acid base treatments, and heat applications. In this project we synthesized an amine protected monomer with photo labile protecting group which could be deprotected using UV radiation. The main advantage of this strategy is, it does not need any extra treatments or special workups. We synthesized amine protected 2-methylprop-2-enoate (ONBAMA) with the reaction between 2-isocyanatoethylmethacrylate and 2-nitrobenzyl alcohol. Polymerization of this monomer was carried out using RAFT polymerization method with cyanoisopropyl dithiobenzoate (CPDB) as the chain transfer agent. Three consecutive polymer chains were synthesized with low, medium and high molecular weight with the corresponded monomer units of 25,50 and 100 respectively. Polymer chains were irradiated with 310nm, 390nm, 440 nm, 520 nm and 630nm lights and explored their deprotection efficiencies. Photo labile protection group shows no deprotection under visible light but efficiently deprotected with 310nm light by yielding an amine functionalized polymer chains. Deprotected polymer chains were characterized using DLS and zeta potential measurements.

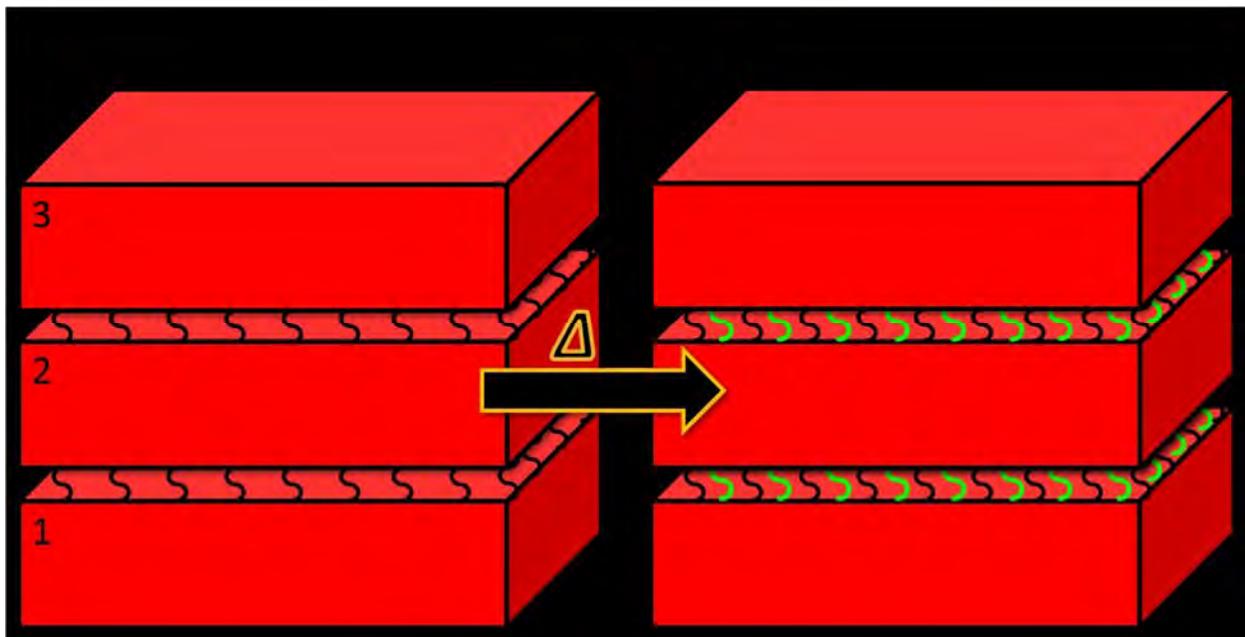


Photochemical liberation of the amines from RAFT polymerized ONB-protected amine functionalized polymer (poly-ONBAMA)

POLY 484: Layered polymer networks with dual-cure mechanisms based on multi-functional benzoxazines

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Mississippi, United States

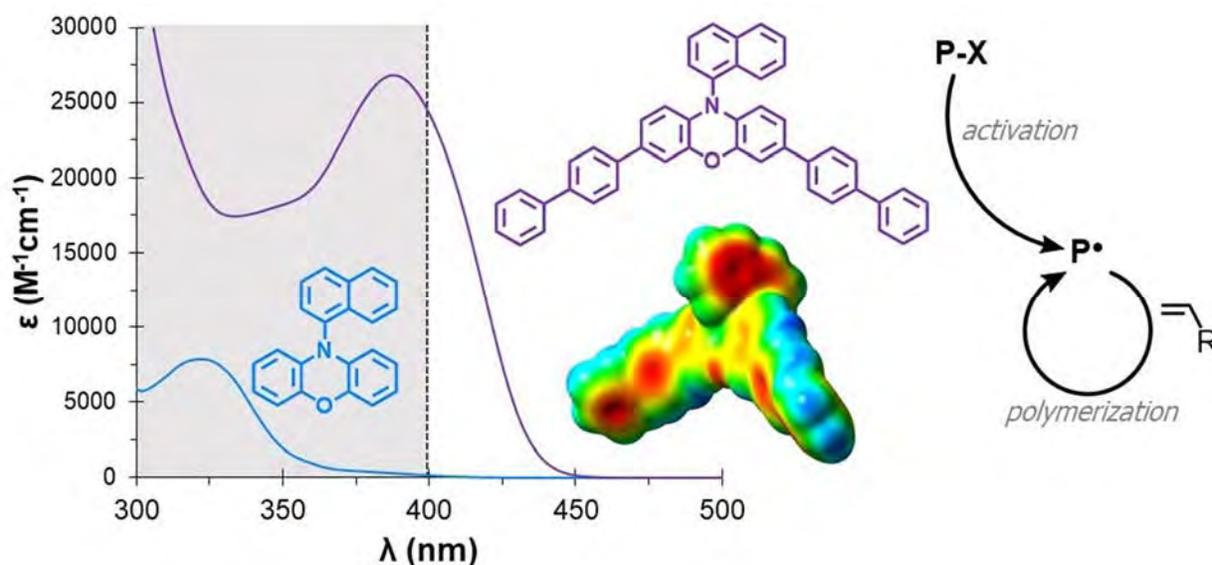
The advantages of dual-cure interpenetrating polymer networks (IPNs) regarding their utility in additive manufacturing (AM) techniques have been well established. These advantages include mitigation of cure induced shrinkage, reduced sensitivity toward oxygen inhibition, and tunable viscoelastic properties. While IPNs offer unique advantages for AM, the materials studied have mainly focused on acrylates blended with epoxides or similar systems. This research combines thermal, and UV initiated polymerization techniques to prepare dual-cure IPNs by incorporation of benzoxazine (BOX) monomers with multi-functional acrylate monomers. Multi-functional BOX monomers offer distinct advantages for AM due to their high UV resistance, near-zero shrinkage during polymerization, and molecular design flexibility. The UV cure kinetics and viscosity of this dual-cure formulation is studied as a function of BOX monomer loading level. Formulations studied are then used to prepare layered IPNs via stereolithography 3-D printing. The thermomechanical properties of these layered networks are studied using dynamic mechanical analysis. This is done as a function of BOX monomer loading level and thermal post-processing time and temperature.



POLY 485: Application of core modified phenoxazine photoredox catalysts in organocatalyzed atom-transfer radical polymerization

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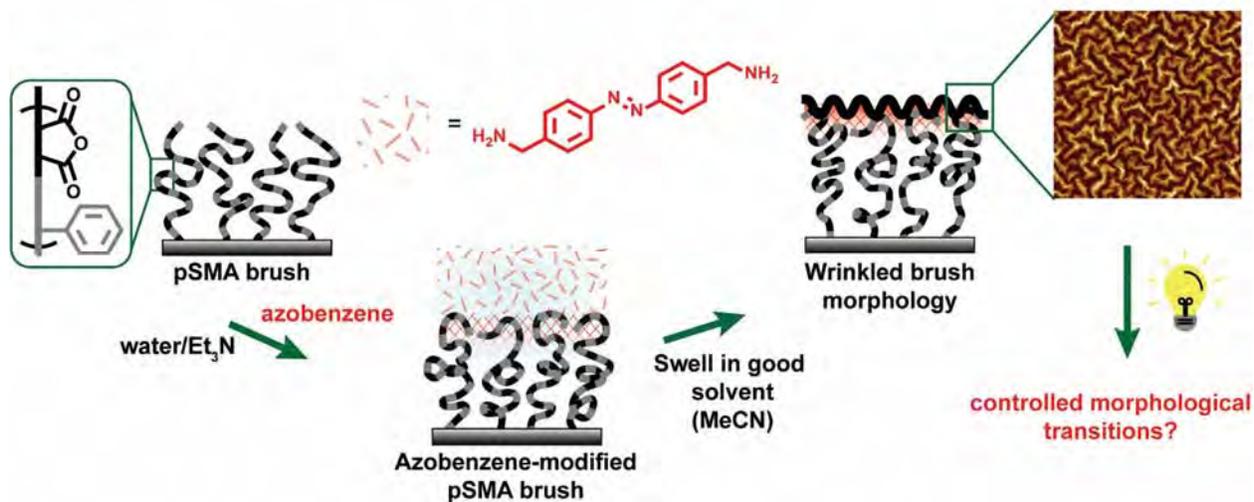
Organocatalyzed atom transfer radical polymerization (O-ATRP) employs organic photoredox catalysts and alkyl halide initiators to synthesize well-defined polymers of target molecular weights and low dispersity. In this work, a new class of core modified phenoxazines are used as photoredox for O-ATRP. These molecules were found to exhibit superior catalytic performance in O-ATRP compared to their parent compounds which were previously studied.



POLY 486: Photoresponsive surface wrinkling in polymer brush thin films

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Buckling instabilities in polymer films have received significant attention due to their well-defined and complex topological features. Wrinkled interfaces represent one class of buckling instabilities in thin films, with multiple examples apparent in nature (i.e. wrinkling in skin, grooves on cerebral cortex) and engineered polymer thin-film applications (i.e. flexible electronics, controlled adhesion, microfluidic devices). Surface wrinkles frequently occur from an in-plane compression (i.e. mechanical, thermal, or osmotic) of a bilayer film comprised of a thin, rigid skin layer attached to a semi-infinite, low modulus elastic substrate. Recent efforts have focused on stimuli-responsive wrinkle formation. Specifically, light-induced wrinkle formation represents an attractive stimulus because it enables morphological changes with high spatial resolution. Herein, we report a simple route to engineer wrinkled ultrathin poly(styrene-*alt*-maleic anhydride) (pSMA) brush surfaces using a simple post-polymerization modification (PPM) approach with an azobenzene crosslinker. The azobenzene moieties undergo a UV-induced photoisomerization transition from a *trans* to a *cis*-state enabling the design of ultra-thin pSMA surfaces with tunable and controlled morphological transitions.

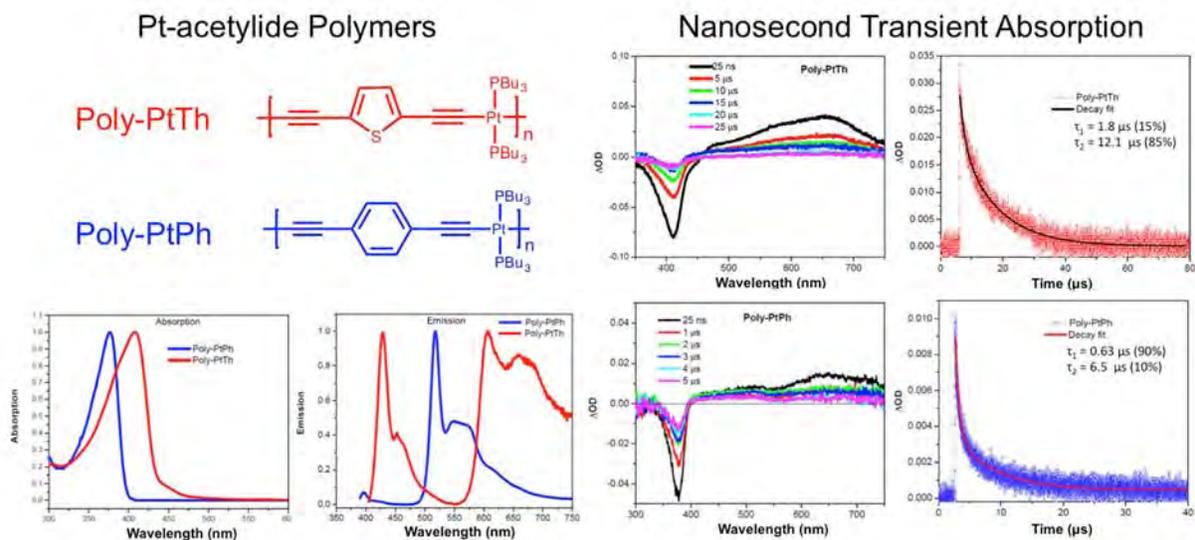


POLY 487

Excited state dynamics and exciton diffusion in platinum-acetylide polymers

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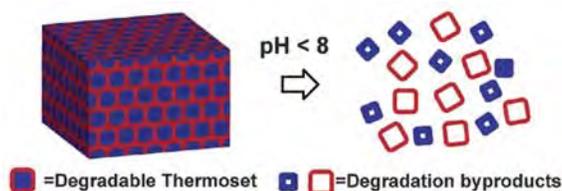
Platinum-acetylide polymers upon photoexcitation undergo fast intersystem crossing resulting in triplet excited state. Relatively high triplet energy level, large triplet yields and significant amount of phosphorescent emission make them attractive materials for organic light emitting diodes, photovoltaic cells and non-linear optical process. We are interested in exploring the singlet and triplet excited state dynamics as well as triplet exciton diffusion in Pt-acetylide polymers containing different spacer units. In this work, we have synthesized Pt-acetylide oligomers and polymers (poly-PtPh and poly-PtTh) having phenyl and thienyl spacer groups, respectively. Steady state and time resolved photophysics of Pt-polymers have been explored in the solution as well as in thin films. Both of the polymers yield high amount of triplet excited state and are phosphorescent at room temperature. Femtosecond and nanosecond transient absorption spectroscopy revealed short-lived singlet excited state and very fast intersystem crossing in both of the polymers. However, triplet lifetime of Poly-PtTh is much longer than the triplet lifetime of Poly-PtPh. Power-dependent study of triplet transient absorption in both polymers showed that the triplet-triplet annihilation is more evident in poly-PtPh even at very low excitation energy. We are investigating the triplet exciton diffusion and energy transfer between the Pt-polymers and fullerene in thin films.



POLY 488: Synthesis of acetal-based multifunctional thiols as building blocks for degradable poly(thioether acetal) thermosets via thiol-ene photopolymerization

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In the last decade many efforts towards understanding, designing, and synthesizing fully degradable thermosets have been made for applications in drug delivery and green materials. Thiol-ene photopolymerization is a well-established tool for the polymer synthetic chemist and is especially appealing for the synthesis of crosslinked thermoset networks. The salient features of thiol-ene include rapid kinetics, near quantitative yields, and homogeneous network structures. In thiol-ene photopolymerization, a standard series of multifunctional thiols are typically employed based on either a tris(hydroxymethyl)propane or pentaerythritol core; however, these thiols are not readily degradable except under harsh conditions which makes these materials unsuitable for many biological applications. This presentation will describe the synthesis of a library of thiol-functionalized acetal-based monomers via orthogonal protecting and deprotecting chemistries. These novel thiols enable the design of fully degradable poly(thioether acetal) thermosets and will provide a platform to explore tailorable release profiles of bioactive aldehydes for antimicrobial applications.



POLY 489: Synthesis of photo-responsive optically active conjugated polymers and photo-reaction field

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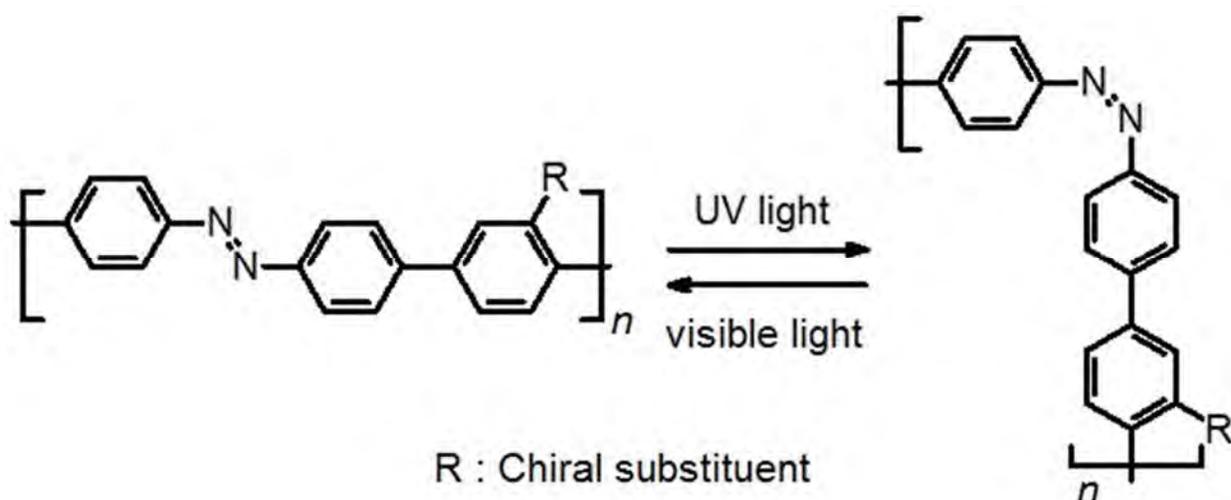
In this study, we synthesized a novel optically active polymer containing azobenzene in the main chain. We attempted to induce a helical structure in the main chain by introducing a chiral substituent. Introduction of an azobenzene moiety in the polymer backbone allows to control helical direction with light irradiation.

Azobenzenes show rapid and reversible isomerization between rod-like *trans*-isomer and *cis*-isomer by irradiation of UV or visible light.

In the previous studies, conjugated polymers having azobenzene units and various conjugated moieties in the main chain has been synthesized. Molecular design for obtaining polymers having solubility and high molecular weight has been carried out. Introduction of chiral substituents into conjugate polymer can induce main chain helical structure. Therefore, combination of light isomerization function and chirality of conjugated polymer produces light-driven change in chiroptical activity accompanied by structural change of azobenzenes.

In this research, we successfully synthesized an optically active polymer containing azobenzene in the main chain. Optical properties of the polymer were evaluated by in-situ UV-vis absorption spectra, in-situ circular dichroism (CD) spectra, and fluorescence spectra. Repeatable photo-isomerization behavior of the polymer by repeating irradiation of UV and Vis light was confirmed. From the CD spectra, photo-isomerization of azobenzene moiety can tune the 3-D structure of the main chain. Polymerization in azobenzene-based liquid crystal solvent is also carried out.

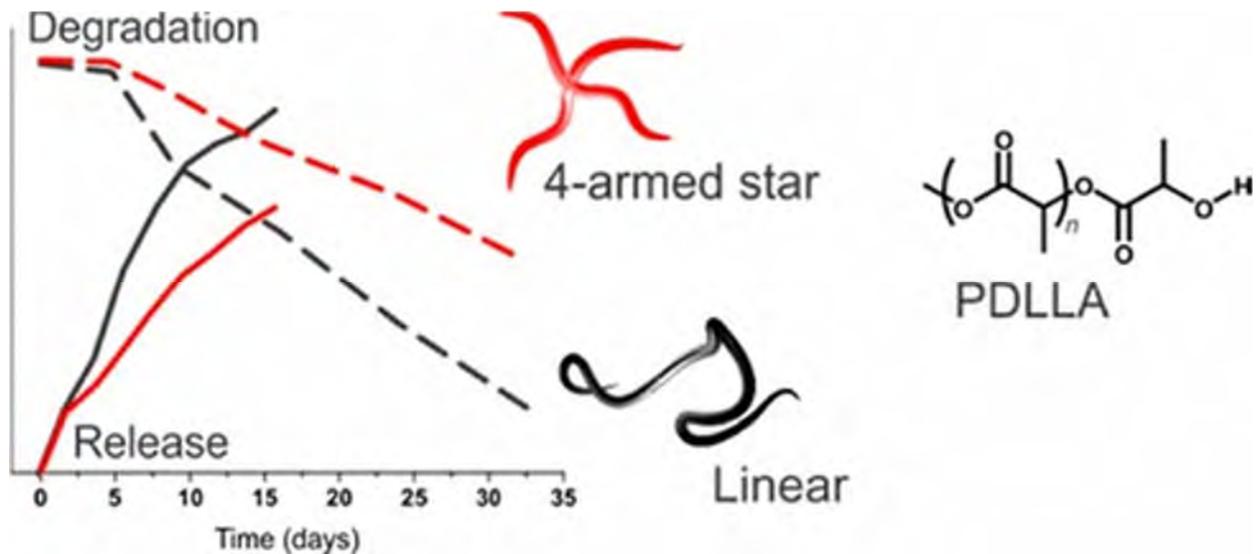
In this communication, we report synthesis and "chiral-photo-responsive" function of the azobenzene based polymer.



POLY 490: Effect of branching (star architecture) on poly(d,l-lactide) (PDLLA) degradation and drug delivery

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This study focuses on the comparative evaluation of star (branched) and linear poly(l,d-lactic acid) (PDLLA) as degradable materials employed in controlled release. The polymers were prepared via ring-opening polymerization initiated by decanol (linear), pentaerythritol (4-armed star) and dipentaerythritol (6-armed star), and processed both in the form of films and nanoparticles. Independent of the length or number of their arms, star polymers degrade slower than linear polymers, possibly through a surface (vs bulk) mechanism. Further, the release of a model drug (atorvastatin) followed zero-order-like kinetics for the branched polymers, and first-order kinetics for linear PDLLA. Using NHOst osteoblastic cells, both linear and star polymers were devoid of any significant toxicity and released atorvastatin in a bioavailable form; cell adhesion was considerably lower on star polymer films, and the slower release from their nanoparticles appeared to be beneficial to avoid atorvastatin overdosing.



POLY 491: Development of antimicrobial-loaded polyurethane films for drug-eluting catheters

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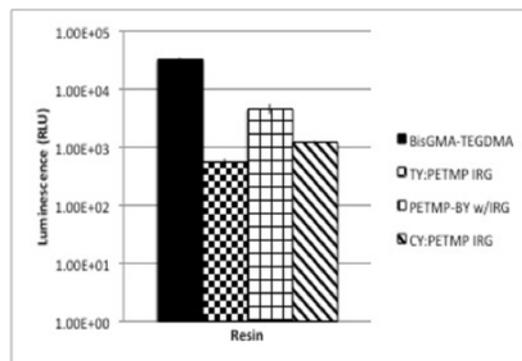
The purpose of the present research is to develop a polymeric material for catheter, that contains an antimicrobial. A thermoplastic polyurethane was solubilized in a solution of dimethylformamide and tetrahydrofuran. Different amounts of drug (sulfathiazole and metronidazole, separately) were added to polyurethane solution. The resultant solution was constantly stirred for 24 hours. Neat and drug-loaded polyurethane films were prepared by solvent casting. The dried films were stored in a desiccator. Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) were performed to analyze drug-loaded and neat films. In order to confirm that a drug can diffuse out of the polyurethane, a precisely weighed portion of the drug-loaded polymer film was immersed in distilled water constantly stirred at 37°C for 8 hours. Every hour, 5 mL aliquot was taken out and tested with a Shimadzu UV-2450 spectrophotometer to measure the absorbance at 270 nm for sulfathiazole and 319.5 nm for metronidazole. The concentrations of aliquots were calculated from their absorbance values and a pre-calibrated plot of absorbance against drug concentration. Varying concentrations of sulfathiazole and metronidazole showed similar release mechanisms which followed the Korsmeyer-Peppas kinetic model of diffusion. From the similarity in release rates and kinetic modeling, it can be concluded that the diffusion behavior of the medication is independent of its concentration in polyurethane. The drug-incorporated films also inhibited bacterial growth as compared to neat films, rendering them to be potential material for catheters.



POLY 492: Novel bacterial anti-adhesion films with polymers derived from natural products

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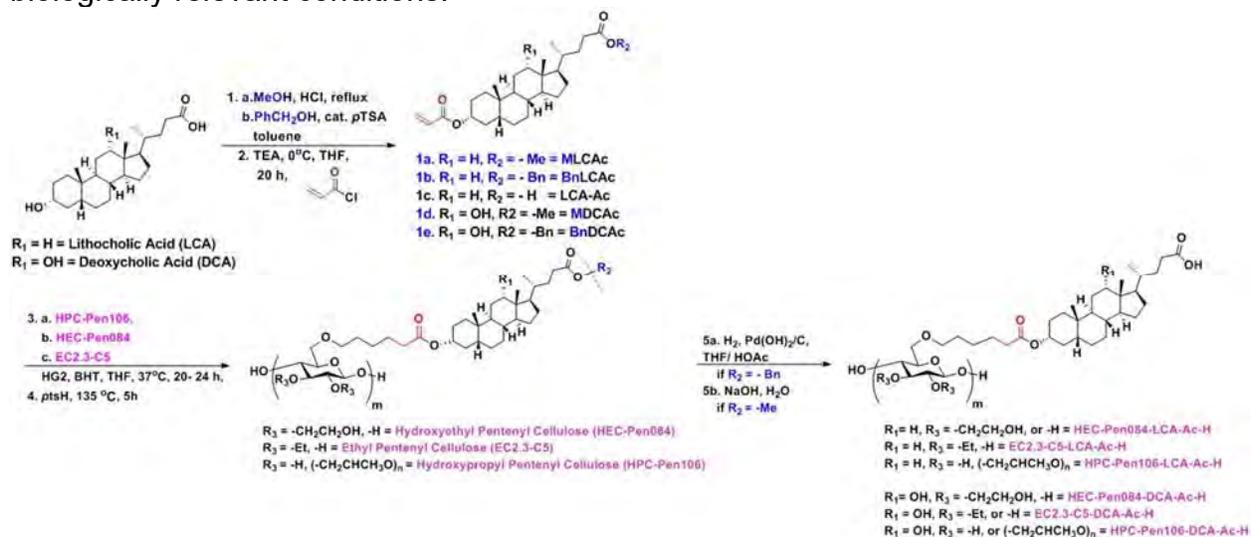
The major cause of dental filling failure stems from bacteria entering crevices in the filling or the cavity not being cleaned sufficiently before adding the filling. Novel films were made to counteract this issue based off natural plant oils that have already been shown to have high antibacterial activity. Monomers were made by adding appropriate functional groups for a thiol-ene polymerization. Initial results from a luminescence evaluation of *S. mutans* biofilm grown on novel resin showed that the novel films had a significant reduction when compared to the BisGMA:TEGDMA standard.



POLY 493: Design of synergistic drug crystallization inhibitors via olefin cross-metathesis of hydrophilic cellulose ethers and bile acid derivatives

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Poor aqueous solubility is a major hurdle in the pipeline of developing new drugs. This lowers drug effectiveness and results in limited drug bioavailability. Crystallization inhibitors have been employed as excipients in amorphous solid dispersions in order to form metastable, supersaturated drug formulations with enhanced solubility. Olefin cross-metathesis has successfully provided an array of new and multifunctional cellulose-based derivatives for amorphous solid dispersion polymer matrices. Several of these derivatives, as well as endogenous bile salts, effectively extend nucleation induction times of hydrophobic therapeutics in physiologically similar settings. In this study, cellulose ether derivatives are appended to bile salt mimics to yield conjugates that may act synergistically as drug-crystallization inhibitors while also increasing drug solubility. Conjugate hydrophilicity is enhanced via selective modification of bile salt mimics and by choice of cellulosic backbones (hydroxypropyl and hydroxyethyl cellulose). Increased hydrophilicity enhances the ability of these conjugates to achieve supersaturation. Here we report, the synthesis of these novel conjugates and characterization by NMR spectroscopy, DSC, SEC and FTIR. Amorphous solid dispersion candidacy is evaluated via aqueous stability, solubility, and retention of amorphous properties of these novel candidates, as well as induction time studies in biologically relevant conditions.



Synthetic Strategy for Olefin Cross-Metathesis of Hydrophilic Bile Salt-Cellulose Ether Derivatives

POLY 494: Characterization of acrylic alkali soluble polymer dispersions by asymmetrical flow field-flow fractionation

Graham P. Abramo¹, *gp_abramo@yahoo.com*, **Wei Gao**¹, **Lisa Rhodes**², **Jonathan Park**¹. (1) Core R&D, The Dow Chemical Company, Collegetown, Pennsylvania, United States (2) Dow Coating Materials, The Dow Chemical Company, Collegetown, Pennsylvania, United States

Asymmetrical flow field-flow fractionation (AF4) is rapidly becoming a technique of choice for the separation and characterization of complex materials. It is capable of fractionating samples over a wide size (from a few nanometers to micrometers in diameter) and molecular weight range (10^3 – 10^{10} g/mol). It offers gentle, low shear, low pressure separation conditions. These conditions are essential to ultra large polymer characterization because the size fractionation upper limit is extended, and the polymer chain deformation and degradation can be minimized compared to the most commonly practiced size exclusion chromatography technique. Alkali soluble acrylic polymer dispersions are an industrially important class of polymers used as thickeners in multiple applications. A set of these dispersions with systematic molecular weight changes was made using the Large Volume Semi-Continuous Parallel Pressure Reactor (LV-ScPPR) which is an automated system designed for running emulsion polymerizations. These polymers were analyzed via AF4 with on-line multi-angle light scattering, and the results will be discussed. Complementary characterization techniques including Gel Permeation Chromatography of the polymer backbone after hydrolysis of the acrylic ester groups, solubilized viscosity, and gel fraction were also used to characterize the polymers, and these results will be presented for comparison.



POLY 495

High-performance polymers for industrial applications

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Dow Chemical Company, New Castle, Delaware, United States

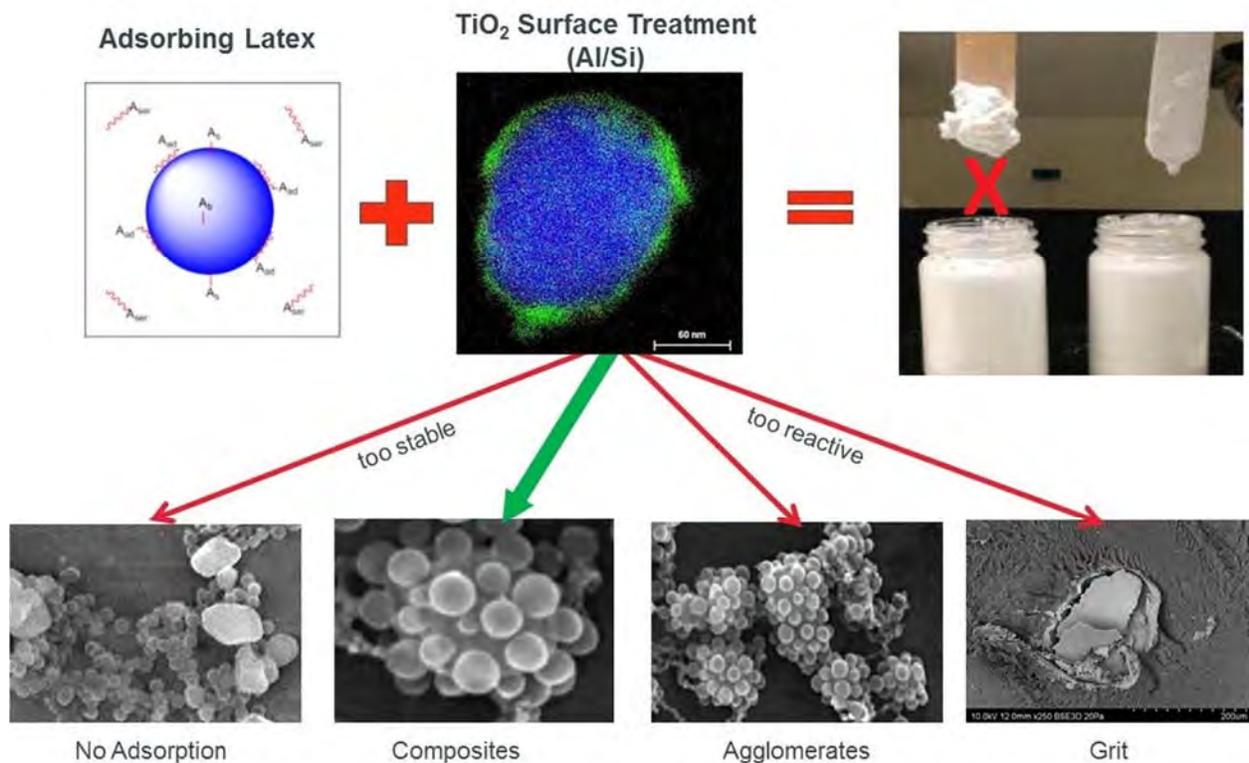
High performance waterborne, industrial coatings are designed to resist harsh conditions and must display good hardness and scratch resistance, flexibility and toughness, chemical resistance and block resistance. Additionally, excellent durability and UV resistance, as well as moisture resistance are important properties for high performance coatings. Resins and by extension coatings that possess these attributes provide the longest possible lifespan for substrates, for example, wood and metal (Figure 1). The literature describes several approaches for the preparation of films with good barrier properties. Now described are the recent efforts aimed at preparing high performance coatings with enhanced water resistance and improved anti-corrosion properties.



POLY 496: Chemistry which enabled coatings with polymer pigment self-assembly to become a commercial reality

James Bohling, jbohling@dow.com, **Kebede Beshah**, **Michael Clark**, **Alvin M. Maurice**, **Wei Gao**, **Stan Brownell**, **John R. Reffner**. *The Dow Chemical Company, Collegetown, Pennsylvania, United States*

Dow scientists were recently awarded 2017 Heroes of Chemistry from the American Chemical Society for the development of self-assembled polymer pigment composite technology. This technology is based on 100-200 nm polymeric particles which are designed to controllably adsorb onto the opacifying TiO₂ pigment in the wet paint. Composite formation in the wet state better disperses the TiO₂ particles such that they are more evenly distributed in the dried paint film yielding higher hiding efficiency and a novel binder rich protective top layer that enhances coating durability. The polymer, analytical and formulation chemistry required to successfully enable/control assembly under a wide range of commercially relevant conditions will be presented. This technology has also earned a Presidential Green Chemistry Award and more than 1 billion pounds of these products have now been sold, saving millions of pounds of natural resources while yielding coatings with longer service life.



POLY 497: Fundamental understanding of acidic monomer incorporation in acrylates emulsion polymerization

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The stability of the latex particles made with an emulsion polymerization process is dependent upon the balance between interparticle attractive van der Waals forces and repulsive electrostatic and steric forces. The electrostatic forces between particles arise from surface charged groups, which can be physically adsorbed or covalently bonded to the particle surface. One way to manipulate the electrostatic force on a particle surface is through the incorporation of chargeable monomers, i.e. acid monomers. In this study, a series of butyl acrylate/methyl methacrylate based latex samples with different levels of acrylic acid were made using thermal or redox processes. The goal of the study was to develop a fundamental understanding of the incorporation of the acidic monomers. For the first time the new analytical technique of electrical flow-Asymmetrical Field Flow Fractionation (EIAFFFF) was applied to determine the variation in electrophoretic mobility across the particle size distribution. The results are compared to information obtained from alternative analytical techniques, such as Zeta-potential measurements using Phase analysis light scattering (PALS) and acoustic methods, serum phase polymer characterization by Liquid Chromatography with on-line Mass Spectrometry (LC-MS), bulk polymer characterization by (Gel Permeation Chromatography with online Multi-Angle Light Scattering detection (GPC-MALS), and acid distribution by titration. The study probed aspects of acid incorporation including: 1) how much acidic monomer is incorporated onto and into latex particles during emulsion polymerization; 2) how the incorporation of acidic functional group affects the aqueous phase and bulk polymers formed during emulsion polymerization process; and 3) how the particle surface charge being affected by the incorporation of acidic monomers.

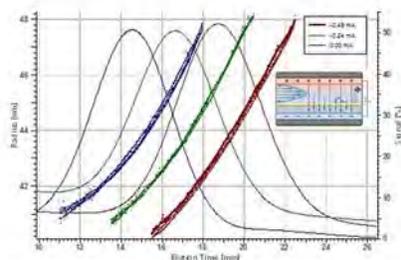
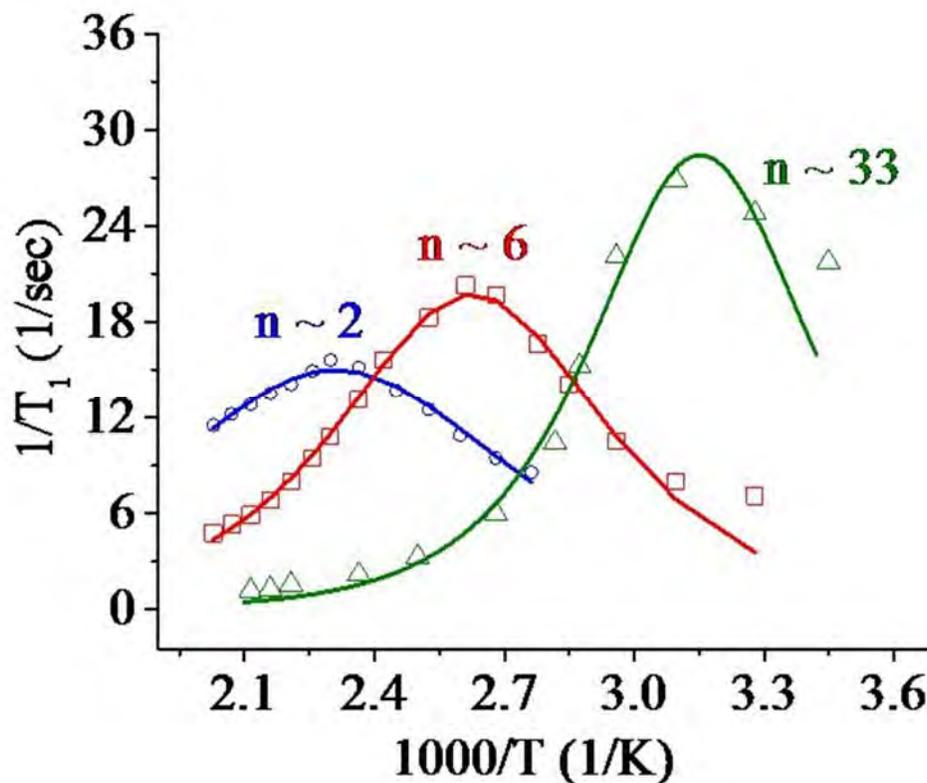


Figure 1. Overlaid EIAFFFF fractograms of an acrylic acid containing latex and the determined radius at each elution moment. The inset is a schematic graphic of EIAFFFF process. The EIAFFFF fractograms are the UV absorbance at 260 nm (right Y axis, solid lines) as a function of the elution time without applied electric field (blue), with 0.24 mA (green) and 0.49 mA (red) applied electric current. The radius (left Y-axis, dotted data points from triplicated injections and the fitted line) were determined with on-line-MALS based on spherical model.

POLY 498: Analysis of segmental dynamics for rigid crosslinked system using low field NMR

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Our low field NMR study established the correlation between the degree of crosslinking in the rigid epoxy model system to the proton spin lattice relaxation time (T_1) measured. Our data have shown that as the number of crosslinks increases the T_1 minima shift toward higher temperatures. In addition, the magnitude of the T_1 minimum is also observed to shift to higher values or slower decay. These trends are consistent with the predictions of the Bloembergen, Purcell and Pound analysis. In these highly crosslinked systems, it was necessary to incorporate the Fuoss Kirkwood distribution function for describing the coupled dynamics of the individual monomer units of each crosslink. By fitting the spin lattice relaxation data at different temperatures to the Fuoss Kirkwood modified BPP theory, the average activation energy for the molecular motion and the breadth of the relaxation spectrum were obtained. For these model crosslinked epoxy systems, the increase in the activation energy to achieve mobility and the broadening of relaxation distribution has been determined quantitatively. The results of this study provide the foundation for using T_1 to analyze the crosslinking process of various polymeric systems with a broad range of “stiffness” achieved.

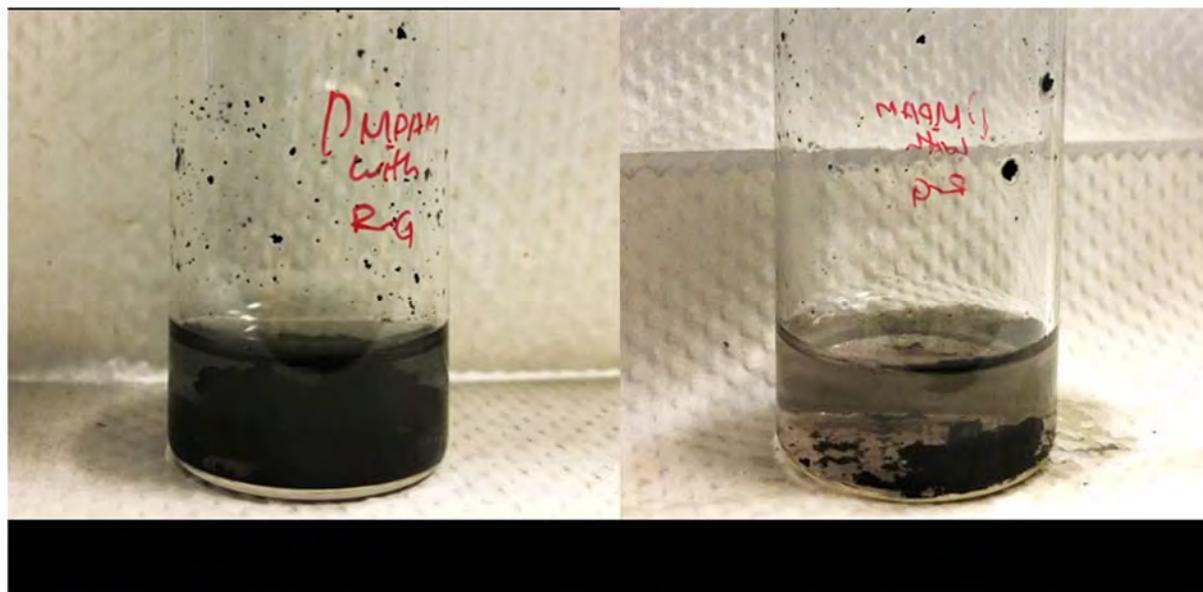


Relaxations of various crosslinked epoxy samples

POLY 499: Thermally responsive and conductive PNIPAM hydrogel spheres

Deepthi Varghese¹, deepthi.varghese05@gmail.com, Douglas H. Adamson^{1,2}. (1) Chemistry, University of Connecticut, Storrs, Connecticut, United States (2) Polymer Program, University of Connecticut, Storrs, Connecticut, United States

Electrically conductive and thermally responsive hydrogels are a new class of conductive polymeric material with a potential range of applications including electrical, electrochemical and biomedical devices. However, the synthesis of stimuli responsive hydrogels with electrical conductivity has been challenging. The addition of graphene to polymer hydrogels is one approach to increase their electrical conductivity, and graphene oxide is often used as a nanofiller to make conductive polymer composites. However, graphene oxide has limitations, and its electrical and mechanical properties are inferior to pristine graphene. Graphene has its own challenges, including the difficulty exfoliating the graphene sheets from graphite. Here we present a simple and inexpensive one-pot method to spontaneously exfoliate pristine graphene and synthesize stimuli responsive and conductive PNIPAM hydrogel spheres using self-assembled graphene spheres as a template.

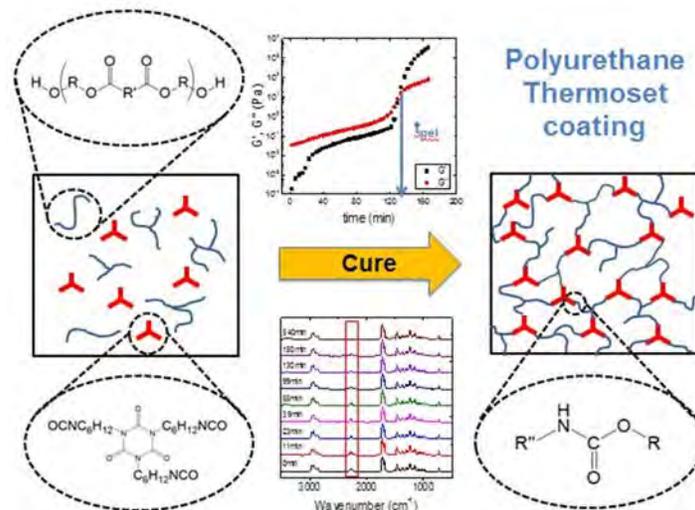


PNIPAM/graphene hydrogel spheres before and after heating

POLY 500: How do cross-linking kinetics relate to rheological property evolution in thermoset coatings?

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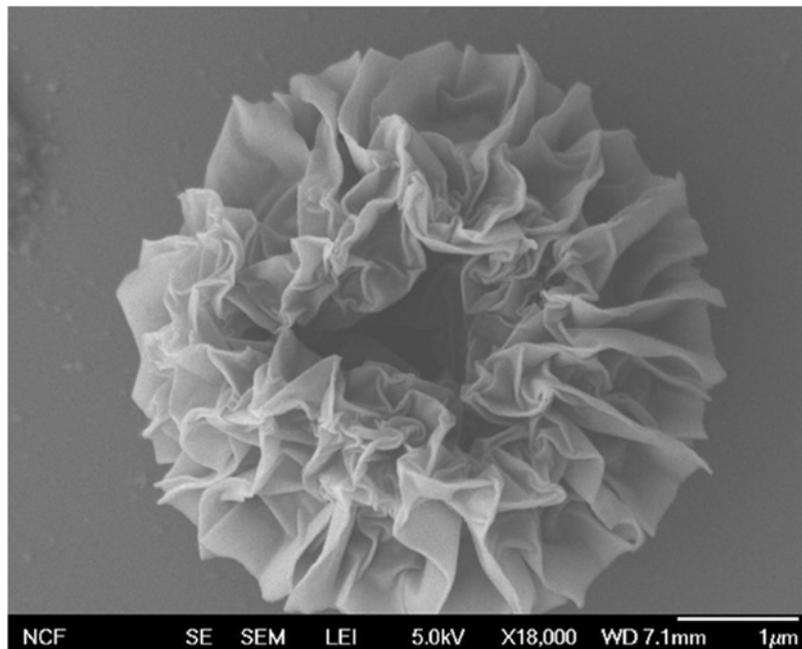
Polyester-urethane thermoset coatings are used in a wide array of applications, with their properties largely dictated by the choice of monomer units incorporated along the polyester backbone. While independent studies have previously interrogated either rheological property evolution or cure kinetics in similar systems, studies concurrently using both rheological and spectroscopic techniques to investigate a specific system are less common. To discern the effect of glycol selection on cure behavior, we have examined a series of polyester polyols with differing ratios of secondary/primary hydroxyl content. The primary objective here is to bridge the gap between chemical information acquired from variable-temperature Fourier-transform infrared spectroscopy (FTIR) and rheological behavior obtained by dynamic rheology up to the gel point time, t_g . In this work, t_g is not a true gel point identified by the Winter-Chambon criterion, but is instead defined as the time required for the moduli to cross and begin to exhibit more solid- than liquid-like behavior from rheological analysis. If t_g and chemical cross-linking reflect related thermally-activated processes, dynamic rheology and FTIR can be employed in concert to extract coupled activation energies. Little prior work has endeavored to relate these two types of activation energies. Activation energies vary as the 2,2,4,4,-tetramethyl 1,3-cyclobutanediol content is varied, and a strong correlation between the activation energy for gelation and the chemical cross-linking activation energy is observed. In addition, Carothers' theory for gelation can be used to ascertain the conversion required for network formation in this type of cross-linking system. Gel time data obtained from dynamic rheology are related to spectroscopic data collected from FTIR spectroscopy to pinpoint the conversion in these systems at the time when they become solid-like.



POLY 501: Controlled storage and release of elastic energy in crosslinked polymer microparticles

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Polymer microparticles are widely used in applications ranging from photonics to drug delivery. For most of these applications, the geometric parameters such as size and shape as well as surface chemistry are the primary design parameters, while thermo-mechanical properties of the particles are normally not relevant. In this presentation, we show that controlled storage and release of elastic energy in the polymer particles can be reliably achieved based on the shape-memory effect. Using model crosslinked PS particles, we show that mechanical energy can be stored in the non-spherical temporary shapes, achieved using nanoimprint lithography (NIL). When exposed to heat and solvent vapors, these particles can recover to the permanent spherical shapes, during which the elastic energy is released. We show that the degree of this shape memory effect (storage and release) can be controlled by NIL parameters, recovering conditions, particle properties, which can be used for applications such as smart dry adhesives.

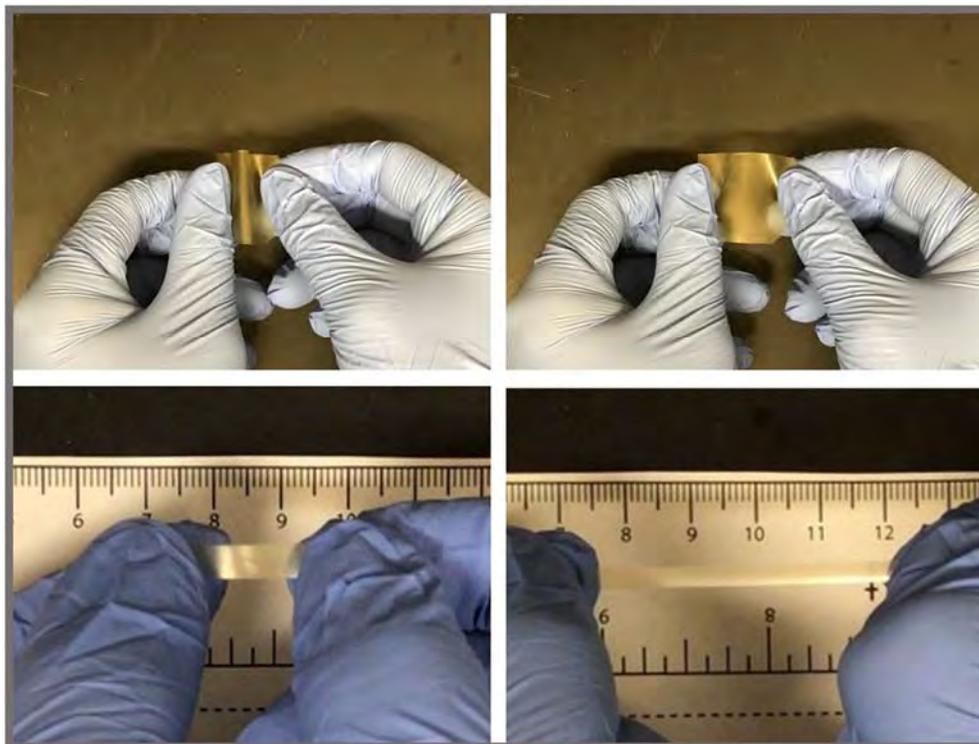


POLY 502: Elastic multi-functional poly (ionic liquids) membrane

Bingrui Li², ciacleebing@gmail.com, Pengfei Cao¹, Sheng Zhao⁴, Kunyue Xing⁵, Janmejay Hingu⁶, Alexei P. Sokolov³, Tomonori Saito². (1) Chemical Science Division, Oak Ridge National Lab, Knoxville, Tennessee, United States (2) Chemical Sciences Division, Oak Ridge National Laboratory, Knoxville, Tennessee, United States (3) Chemistry, University of Tennessee, Knoxville, Tennessee, United States (4) Department of Chemistry, University of Tennessee, Knoxville, Tennessee, United States (6) The College of New Jersey, Ewing, New Jersey, United States

Poly (ionic liquids) (PILs), known as a new class of polyelectrolytes, has attracted increasing interest during the past decade. Continuous efforts on developing novel PILs via different synthetic strategies has resulted in the application of PILs across a multitude of fields, such as responsive materials, electrochemical energy materials and absorption/separation materials. Although there're many successful efforts to attain high conductivity in PILs reported, PIL materials are still suffering low elasticity and flexibility which obstructs PILs' potential for application such as flexible electronics. Herein, we report elastic solid-state PILs with high elasticity and conductivity. Utilizing chemical cross-linking to tailor the molecular structure of brush PILs, we abate the brittleness of raw PILs. The mechanical, thermal and dielectrical properties of PILs were investigated, we achieved well-controlled mechanical property (Young's modulus 2.5-4.0 MPa, elongation 180-250%) as well as dielectric performance. We've also demonstrated the PILs' application capability as CO₂/N₂ separation membrane.

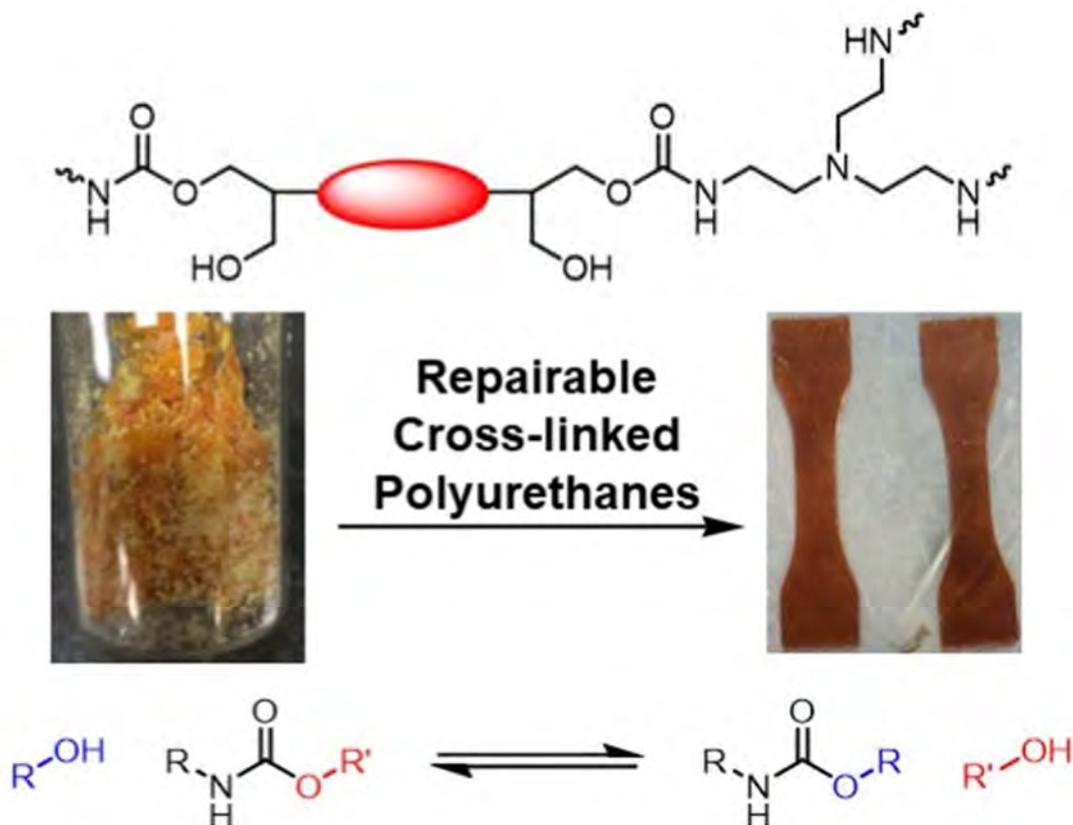
Cross-link PDMS-G-Br



POLY 503: Reprocessable cross-linked polyurethanes

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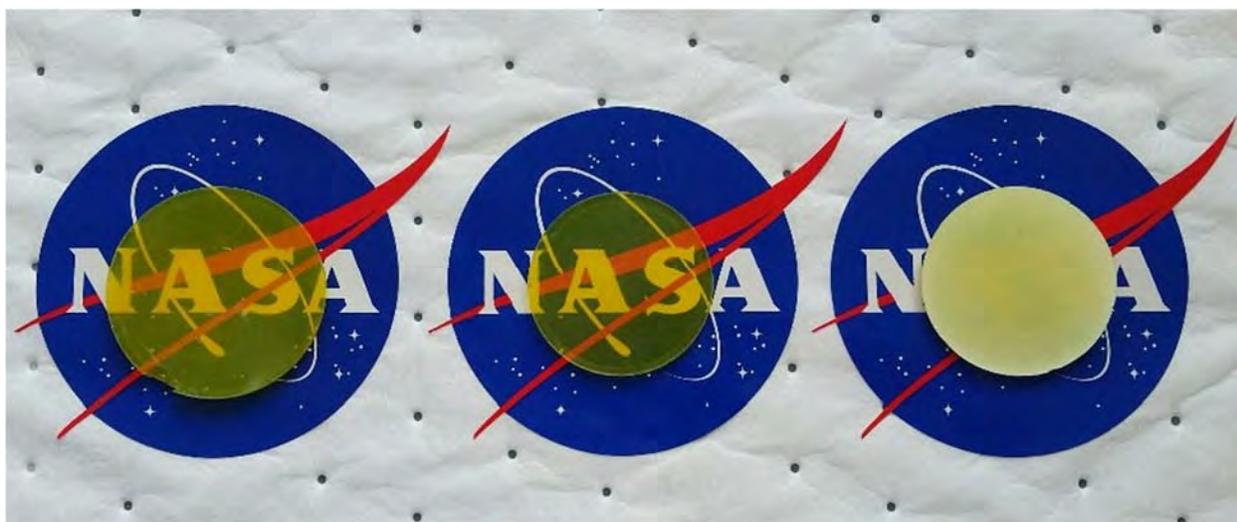
Vitrimers are an emerging class of cross-linked polymers that display thermoset-like mechanical properties at service temperatures, but can be reprocessed at elevated temperatures due to the incorporation of chemical bonds that undergo thermally-activated dynamic exchange reactions. We have developed several non-isocyanate polyhydroxyurethane vitrimers derived from bis(6-membered cyclic carbonates) and polyamines. These networks exhibit tensile properties competitive with traditional thermosets at room temperature, and undergo associative transcarbamoylation reactions at elevated temperatures enabling recovery of as much as 75% of their tensile strength after reprocessing. We will present our investigation into the stress relaxation behavior and reprocessability of polyhydroxyurethane networks. Furthermore, we will discuss how these studies have informed our design of reprocessable cross-linked polyurethanes that can potentially be reprocessed more quickly and efficiently.



POLY 504: Influence of trifluoromethyl substituents on optical properties of polyimide aerogels

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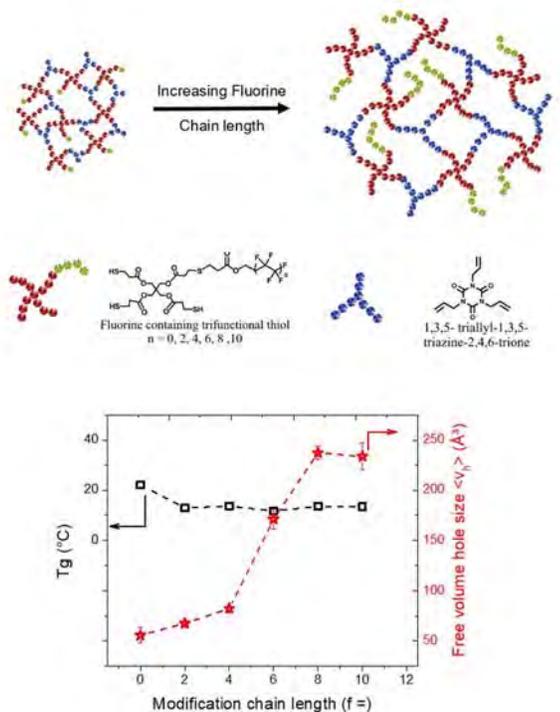
Incorporating fluorine moieties into polymers can lead to dramatic improvements to many of the characteristics of the material properties such as increased solubility in organic solvents, lower dielectric constant and water uptake, higher thermal and thermo-oxidative stability, better optical transparencies along with higher gas-permeability and flame resistance as compared to their non-fluorinated counterparts. Polymers such as polyimides are desirable materials for aeronautics and space applications due to their ability to retain their physical and mechanical properties over a wide range of temperatures. Cross-linked polyimide aerogels are three dimensional structures with added attributes such as high porosity, low density, extremely high surface areas, low dielectric constants and low thermal conductivity. A highly translucent polyimide aerogel was prepared by combining stoichiometric amounts of pyromellitic dianhydride (PMDA) and 4, 4'-hexafluoroisopropylidene dipthalic anhydride (6FDA)), and (2,2'-dimethylbenzidine (DMBZ) producing polyimide aerogels with optical properties that include high transmission, high clarity, and low haze. Herein we examine the optical property effect of incorporating fluorinated monomers into the backbone of polyimide aerogels as well as the effect on dielectric constant, surface areas, and thermal stabilities. The formulations used for fabrication consisted of combinations of dianhydride and diamine fractions with and without trifluoromethyl (-CF₃) substituents. Three variables were used for fabrication: the length of the repeat unit (n), dianhydride and diamine fraction, and the weight percent of polymer. Structure property relationships of the resulting aerogels will be discussed.



POLY 505: Thiol-ene networks containing perfluorinated n-alkanes: Effect of n-alkane length on free-volume and gas permeation

Vivek Vasagar², *vivek.vasagar@usm.edu*, **Ramesh Ramakrishnar**², **James Goetz**³, **Bruno M. Ameduri**¹, **Sergei I. Nazarenko**². (1) Ecole Nat Sup Chim Montpellier, Montpellier, France (2) School of Polymer Science and Engineering, University of Southern Mississippi, Hattiesburg, Mississippi, United States (3) Eastman chemical company, Kingsport, Tennessee, United States

Perfluorinated amorphous polymers exhibit an unusual combination of properties, i.e. excellent chemical resistance, low surface energy, low water adsorption, optical clarity, high gas permeability, and their applications range from transparent water repellent coatings to gas separation membranes. The aim of this study was to incorporate perfluorinated n-alkanes of different length into UV-curable thiol-ene networks thus forming amorphous films with high fluorine content. A tetra-functional thiol was modified with monofunctional fluorinated acrylates of varying chain length via thiol-Michael addition reaction and subsequently crosslinked with a trifunctional alkene. Analysis of the glass-transition temperature, and rubber elasticity plateau modulus confirmed that incorporation of perfluoroalkyl chains did not affect the network topology (the extent of cross-linking). Free volume analysis carried out using pressure-volume-temperature (PVT) and positron annihilation lifetime spectroscopy (PALS) showed a noticeable increase in fractional free volume and average hole size as well as an increase in gas permeability with the increase of n-alkane chain length.



Unaltered crosslink density(no change in Tg) and increase in free volume with increasing n-alkane chain length modification

POLY 506: Development of thermally reversible polyimide gels for coating carbon nanotube wires

Rocco P. Viggiano¹, rocco.p.viggiano@nasa.gov, Jose J. Maldonado⁴, Baochau N. Nguyen⁵, Haiquan N. Guo⁵, Linda S. McCorkle⁵, Tiffany Williams³, Mary Ann Meador².
(1) Materials Chemistry and Physics, National Aeronautics and Space Administration, Cleveland, Ohio, United States (2) NASA Glenn Research Center, Cleveland, Ohio, United States (3) 49-3, NASA Glenn Research Center, Cleveland, Ohio, United States (4) Universidad de Puerto Rico, Río Piedras, Puerto Rico, United States (5) Materials Chemistry and Physics, Ohio Aerospace Institute, Cleveland, Ohio, United States

To reduce the fuel consumption of aircraft launch vehicles, potential weight savings can be achieved through the replacement of the electrical wiring with alternative materials. A large commercial aircraft uses up to 140 miles of copper wiring encased in PVC, weighing a total of 3,500 pounds. Replacement of the copper wiring with a conductive carbon nanotube wire could result in weight savings of up to 50%. Further weight savings as well as reductions in electrical interference in the wiring could be achieved by developing a low density polyimide aerogel coating in place of PVC. Advantages of polyimide aerogel over traditional PVC wire coatings include improved thermal stability, lower density as well as a lower dielectric constant which improves the signal-to-noise ratio of the wiring. The production of a polyimide aerogel wire coating requires the production of a stable pot-life polyimide with sufficient viscosity to ensure uniform coating of the wire followed by a cross-linking step to enhance the strength of the resultant aerogel. The goal of this study is to examine how the addition of various chemical moieties in the polyimide backbone produce gels which demonstrate thermal reversibility from a gel to a viscous liquid and back to a gel once coated on the carbon nanotube wire. Thirty-five separate formulations of polyimide gels were synthesized through combinations of five different diamines and 4 different dianhydrides. Of the thirty-five formulations, 5 showed thermal reversibility, with thermal transitions occurring between 97 °C and 140 °C. The polyimide formulation consisting of 4,4'-oxydianiline-3,3',4,4'-biphenyltetracarboxylic dianhydride-9,9'-bis(4-aminophenyl)fluorene was selected to coat the carbon nanotube yarns due to its low melting temperature, 113 °C, and its sufficiently high viscosity, 2000 cP.



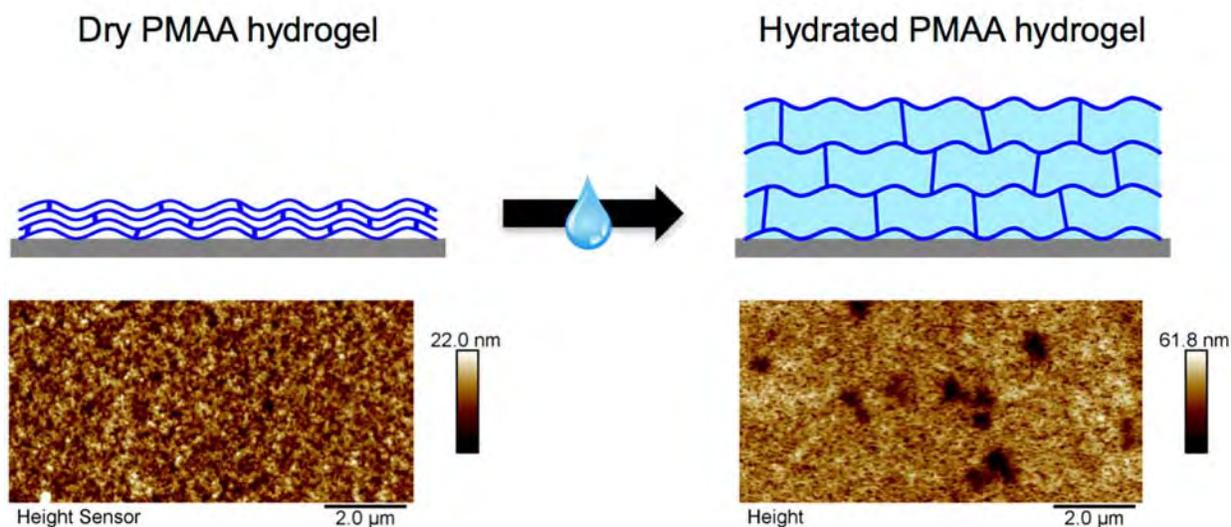
The top three images show the thermally reversible transition cycle of the polyimide from a gel to a liquid and back to a gel. The bottom two images are SEM micrographs. The left image is a neat, uncoated carbon nanotube yarn and the right is an aerogel coated carbon nanotube yarn.

The scale given is 200 μm .

POLY 507: Nanomechanics of thin poly(methacrylic acid) multilayer hydrogels probed by AFM

Kelli A. Stockmal², kelli.stockmal@usm.edu, Veronika A. Kozlovskaya¹, Eugenia P. Kharlampieva¹, Sarah E. Morgan². (1) Department of Chemistry, University of Alabama at Birmingham, Birmingham, Alabama, United States (2) Polymer Science and Engineering, University of Southern Mississippi, Hattiesburg, Mississippi, United States

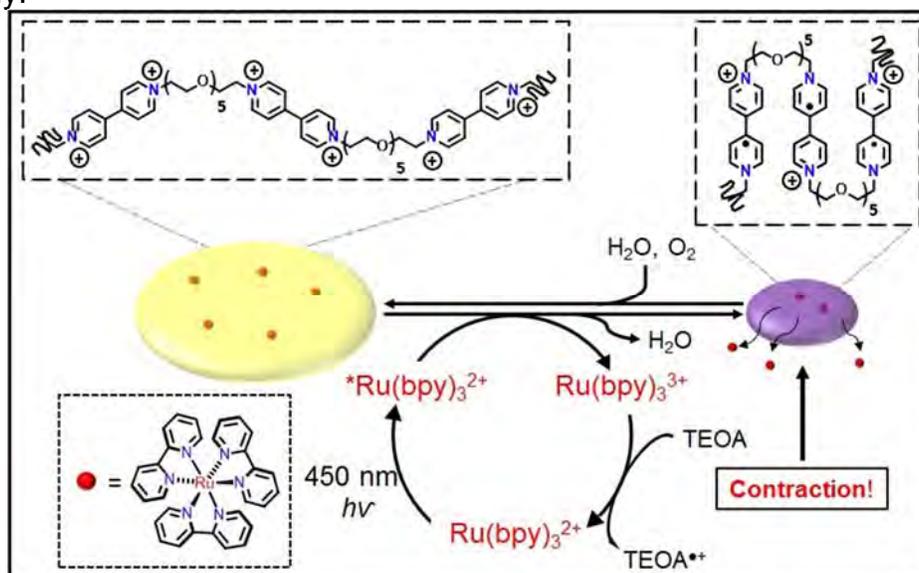
Thin surface-attached multilayer hydrogels of stimuli-responsive polymers have great potential for applications in sensing, actuation, and advanced delivery of functional molecules. Spin-assisted layer-by-layer (LbL) assembly of polymers at surfaces allows for fabrication of ultrathin multilayer films with highly stratified internal architectures. Previously, pH-triggered swelling of poly(methacrylic acid) (PMAA) multilayer hydrogel films has been shown to be modulated by the mode of the LbL construction where spin-assisted PMAA multilayer hydrogels retained internal organization upon crosslinking and exhibited increased swelling thickness when compared to less organized hydrogels obtained via conventional dipped LbL assembly. The molecular weight of poly(N-vinylpyrrolidone) (PVPON) sacrificial layers in PMAA/PVPON hydrogen-bonded precursor films significantly affected thickness, morphology, and architecture of hydrogen-bonded (PMAA/PVPON) precursors and the corresponding PMAA hydrogels as studied by ellipsometry and neutron reflectometry. In this study, nanomechanical properties of PMAA multilayer hydrogels and hydrogen-bonded PMAA/PVPON precursor films were probed using atomic force microscopy (AFM) in quantitative nanomechanical mapping (QNM) mode. Nanomechanical behavior of the surface-attached multilayers was studied in both dry and hydrated states to elucidate the effects of PVPON molecular weight on pH-dependent rigidity of the hydrogels.



POLY 508: Actuation of viologen-based soft materials using a photoredox mechanism

Kevin Liles, *k.liles@live.com*, Angelique F. Greene, Mary Danielson, Andrew Wellen, Nathan D. Colley, Jeremy Fisher, Jonathan C. Barnes. *Chemistry, Washington University in St. Louis, St. Louis, Missouri, United States*

Light is a universal energy source that can be controlled both temporally and spatially. Recently, the use of light as a cheap and abundant energy source has been investigated in the context of photoredox chemistry, whereby a photosensitizer can, upon irradiation, reduce or oxidize another molecule. These photoredox mechanisms have seen a recent surge in applications such as in small-molecule transformations or in metal-free polymerizations such as atom transfer radical polymerization and reversible addition fragmentation chain transfer polymerization. Light has also been used to actuate soft materials in the past, such as in the isomerization of azobenzene, however, photoredox-based actuation is less explored. This poster will show how light can be used to actuate a large-scale soft material using a ruthenium trisbipyridine dichloride photocatalyst to reduce polyviologen moieties in a hydrogel. Viologens are alkylated 4,4'-bipyridinium units that are capable of molecular self-recognition when reduced from the dication state to the radical-cation. This radical-cation molecular self-recognition causes a decrease in electrostatic charge, loss of counter anions, and folding of the polyviologen chain, decreasing the hydrogel mesh size and shrinking the material. This mechanism of reduction, and hydrogel contraction, capitalizes on the photoredox potential of the ruthenium photocatalyst to reduce these polyviologens moieties when exposed to 450 nm blue light. The actuation kinetics of polyethylene glycol-based hydrogels with varying molar amounts of polyviologen chains are presented after irradiation for several hours with blue light, along with rheological data of the contracted and expanded hydrogels in both the reduced and oxidized states, respectively.

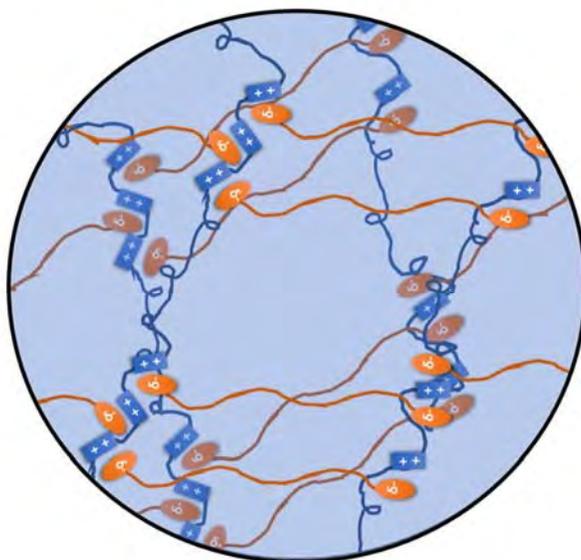


Cartoon of a ruthenium photocatalyst doped gel contracting and expanding. Includes viologen structure and ruthenium photocatalyst cycle.

POLY 509: Redox-to-donor-acceptor interconversion of supramolecular hydrogels

Angelique F. Greene¹, *afgreene@wustl.edu*, **Mary K. Danielson**², **Andrew Weller**², **Anushree Natraaj**², **Nathan D. Colley**², **Jonathan C. Barnes**². (1) Chemistry, Washington University in St. Louis, St. Louis, Missouri, United States (2) Chemistry, Washington University in St. Louis, St. Louis, Missouri, United States

There has been great interest in designing water-soluble polymeric networks that rely on dynamic non-covalent (supramolecular) processes, with a strong emphasis in the current literature focusing on utilizing host-guest or donor-acceptor interactions as the cross links. Supramolecular cross-linked networks are of particular interest due to the unique physical properties that they possess over traditional covalently linked networks, as the cross links that connect the network can be reversibly broken and reformed, i.e., self-healing. Here we present the synthesis and full characterization of water-soluble unimolecular main-chain viologen copolymers incorporated into a stimuli-responsive non-covalently cross-linked hydrogel network comprising of donor-acceptor interactions between viologens and electron-rich donor moieties. The aforementioned supramolecular cross-linked hydrogels exhibit a dual nature in that they can capitalize on the facile redox chemistry of viologens to undergo substantial physical transformations as a result of generating viologen radical cations, which can undergo radical-based self-assembly to form a different connectivity in the network. This redox-based transition results in the dissolution of the original donor-acceptor cross-linked hydrogel network to form a second distinct hydrogel network based on viologen radical-radical interactions between each viologen subunit in the network. The unique rheological and self-healing properties of each hydrogel are investigated, as well as their electrochemical properties.

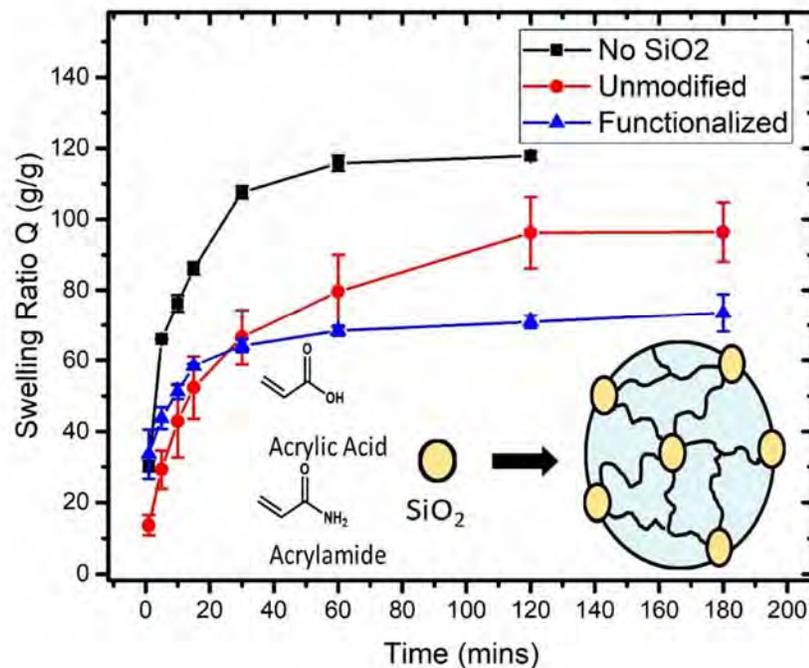


Supramolecular viologen-based donor-acceptor hydrogel

POLY 510: Synthesis and characterization of composite hydrogel networks for use in high performance concrete

Travis L. Thornell, tthornel@purdue.edu, Matthew J. Krafcik, Kendra A. Erk. School of Materials Engineering, Purdue University, West Lafayette, Indiana, United States

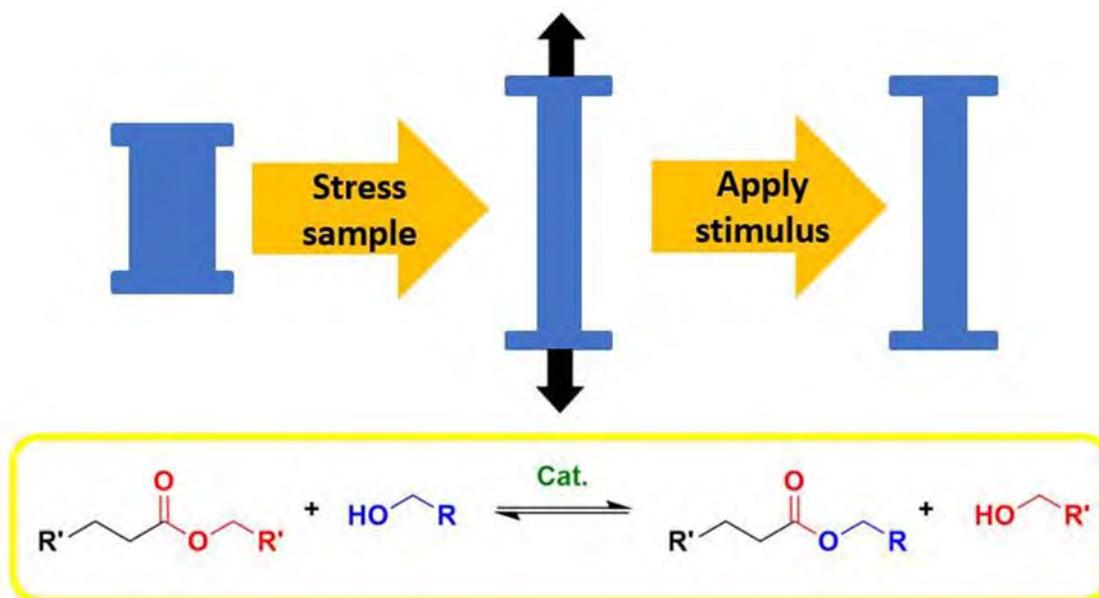
Composite hydrogels composed of polymer networks with silica (SiO_2) nanoparticles were studied as model systems for use in high performance concrete. These highly swellable networks in aqueous environments allow for more water to be available internally as the curing reaction of concrete proceeds. The hydrogels are synthesized from inverse suspension polymerization to create chemically crosslinked poly(acrylic acid) (PAA) and poly(acrylamide) (PAM) spherical particles. SiO_2 nanoparticles are introduced in the reaction as either an unmodified colloidal dispersion or functionalized to react into the polymer network. Hydrogel copolymer composition was varied from majority PAA to majority PAM and SiO_2 loading levels ranged from 0-10 wt. % of monomer feed. Particle size analysis from optical microscopy indicated the gel particle diameters ranged from 50-100 microns in the dry particle state. Gravimetric swelling of the gels in pure water showed that incorporation of SiO_2 into the networks decreased the swelling and that the SiO_2 could be acting as additional crosslinking sites. Swelling performance at various pH and salt concentrations was further investigated. Thermogravimetric analysis was used to quantify the level of SiO_2 inclusion into the gel networks. Interactions among PAA, PAM, surfactant, and SiO_2 were studied using zeta potential experiments to understand the effects of possible molecular adsorption onto nanoparticles.



POLY 511: Advances in polyester vitrimer design

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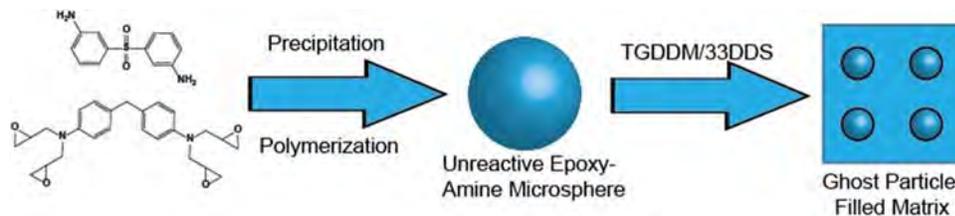
Vitrimers are permanently cross-linked polymeric networks comprising dynamic bonds that undergo associative bond exchange. This work describes new strategies to access polyester vitrimers with a wide, tunable range of mechanical properties and relaxation kinetics. Our approach exploits facile synthetic chemistry involving ring-opening polymerization coupled with strategic catalyst design. These advances are anticipated to be of value for a variety of applications including reconfigurable thermosets and composites that leverage vitrimers to promote (re)processibility and recyclability.



POLY 512: Ghost particles: Effect of constrained space on glassy polymer network formation and mechanics

Travis Palmer¹, t.palmer@usm.edu, Jordan Winetrout¹, Jeffrey S. Wiggins². (1) Polymer Science and Engineering, The University of Southern Mississippi, Hattiesburg, Mississippi, United States (2) School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, Mississippi, United States

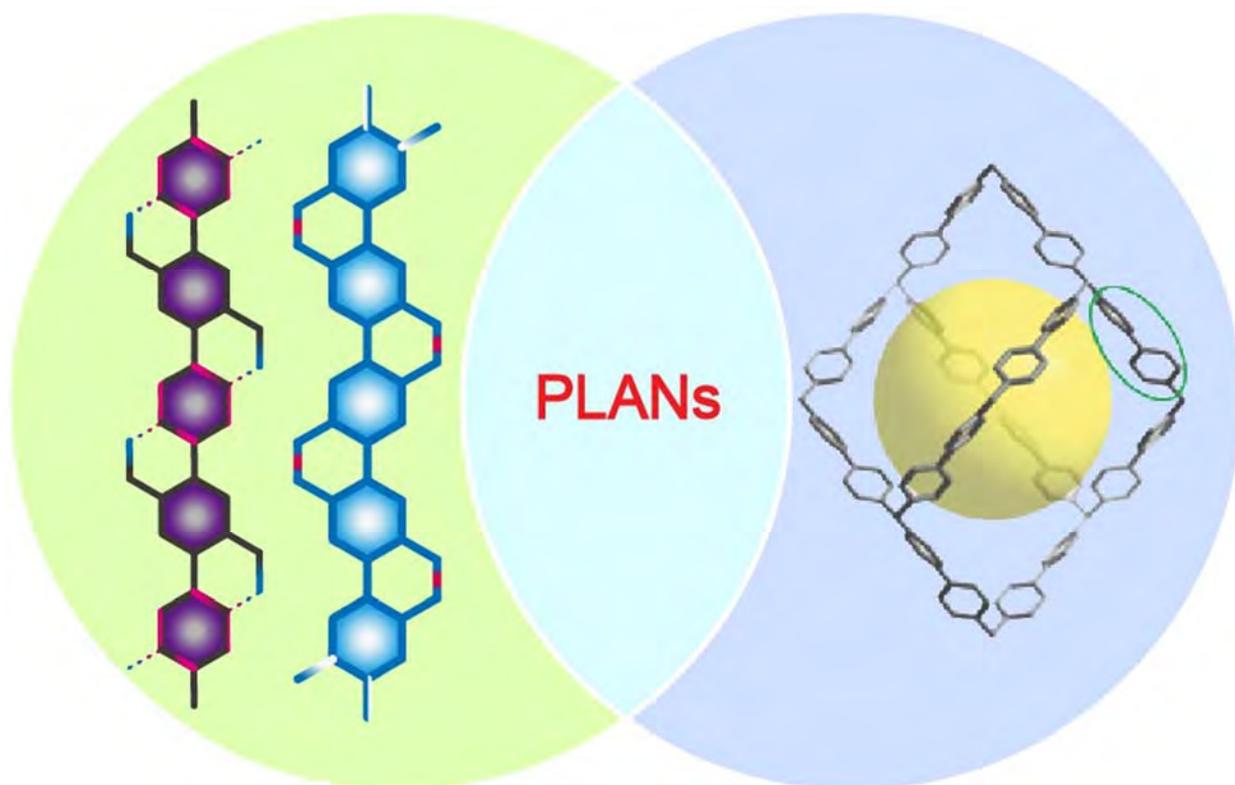
Carbon fiber composite materials, while known for high T_g and modulus, are brittle. Many different methods have been proposed to toughen these materials, generally utilizing particles or separated phases in the matrix. In particle-filled systems there exist both interfacial tension and an interphase between particle and matrix, which have direct implications for the final network properties of composite materials. While the energetic driving forces for the formation of the interphase are well studied, the steric effect of additives has yet to be established. To establish the effect of constrained space, rather than enthalpic forces, on the formation of the interphase unreactive TGDDM/33DDS epoxy-amine "Ghost Particles" have been synthesized by precipitation polymerization. The resulting microspheres have been observed to be spherical and of low size dispersity. Thermal properties of the particles were tested and were comparable to those of the bulk TGDDM/33DDS matrix. Utilizing continuous high-shear reactor technology, multiple loading levels of Ghost Particles have been dispersed in the selfsame TGDDM/33DDS matrix while simultaneously targeting industrially relevant prepolymer conversions. Effect of Ghost Particles on cure was elucidated for all loading levels. Formulations were then cured and their thermal, thermomechanical, and mechanical properties were tested. Fracture surfaces were studied by SEM and AFM to investigate fracture mechanics, particle dispersion and interphase properties.



POLY 513: Porous LAdder-polymer networks (PLANs)

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Porous Polymer Networks (PPNs) have drawn much attention to the researchers due to their superior chemical/thermal stabilities, high porosities and various functionalities. They have been used in plenty of applications, such as gas adsorption, catalysis, and sensors. However, most of them contain more or less carbon-carbon single bonds, which have certain degree of freedom to rotate within the framework and hinder their further applications in certain fields, like thermal and electrical conduction. By locking the the adjacent aromatic rings with second strand of bonds, we can get a new kind of porous material, Porous LAdder-Polymer Networks (PLANs). The ladder type polymer backbone not only further increases the thermal and chemical stabilities, but also enable them interesting π - π interactions with inner guest molecules. This new type of material may have potential applications in electronic devices and host materials.



POLY 514: Bringing furan/maleimide Diels-Alder HA hydrogel chemistry to physiological conditions, for biomedical applications

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Chemical Engineering & Applied Chemistry, University of Toronto, Toronto, Ontario, Canada

Microenvironment mimicry is crucial for the success of many biomedical applications. 3D organoid culture, local cell delivery and explant time-lapse imaging are as many examples of applications that depend heavily on properly designed scaffolds. Chemically crosslinked hydrogels are ideal materials in that matter as they allow tunable composition and stiffness. However, most of the crosslinking reactions are either toxic to the cells and tissues, or incompatible with physiological conditions (e.g., pH, medium).

In the past, using the furan/maleimide Diels-Alder reaction, we developed and used hyaluronan (HA)-based hydrogels to investigate cell survival and migration, with much success. However, in the initial system, the slow crosslinking reaction and the maleimide degradation required an overnight pre-gelation step at acidic pH, and extensive washes with medium; limiting these hydrogels to 2D culture. To expand their potential, we systematically studied three key factors of the physicochemistry of Diels-Alder HA hydrogels, at physiological pH: polymer entanglement, diene substituents and degrees of substitution.

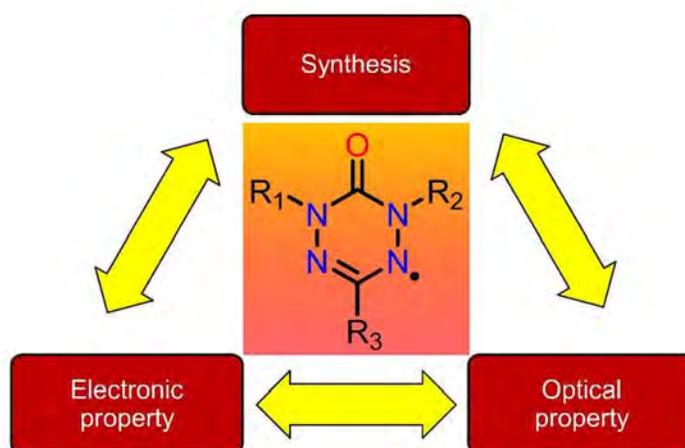
Using HA with different molecular weights (240 kDa vs 1.5 MDa), we showed that an increase in polymer chain entanglement considerably decreases the gelation time, the initial swelling and the overall swelling rate of the HA gels, while minimally increasing the stiffness of the material and not affecting its injectability. The comparison of methylfuran and furan groups confirmed that electron-donating substituents on dienes can dramatically decrease the gelation time (down to minutes), at the cost, however, of the hydrogel stability. Finally, to investigate the effect of the degree of substitution of the crosslinker, we synthesized various HA-maleimide crosslinkers (10, 20, 40, 60 kDa), and showed that increasing the number of maleimide per chain can lead to much faster gelation and more stable gels.

Overall, these newly designed furan/maleimide Diels-Alder HA hydrogels can gel within minutes at physiological pH, and are stable for months; paving the way towards successful cell encapsulation and transplantation.

POLY 515: Correlating molecular structure with the optoelectronic properties of tailored oxoverdazyl radical species

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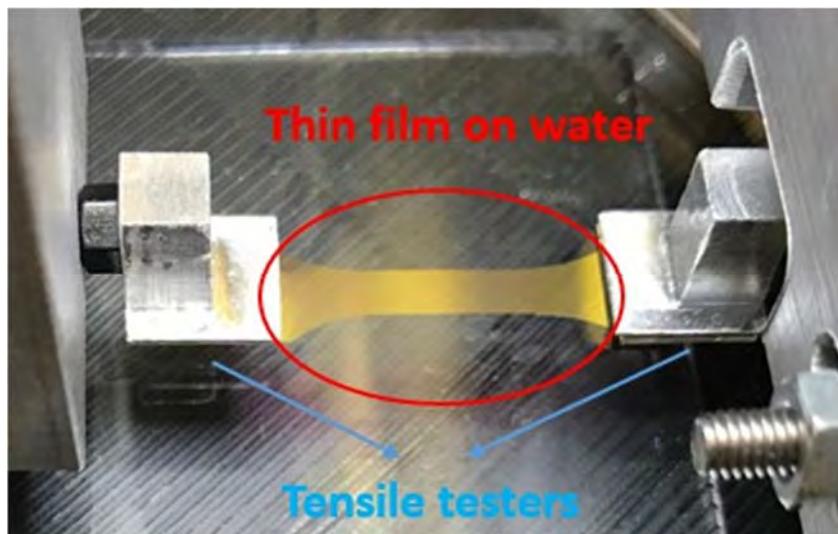
The oxoverdazyl moiety is an intriguing open-shell species whose chemical structure is based on a tetrazinanone parent architectural motif. In particular, the unpaired electron resides on the two equivalent nitrogen atoms that are removed from the carbonyl group in the planar tetrazinanone ring. Recently, this molecule has been of intense interest in a number of seminal studies as appropriate placement of key substituents along the tetrazinanone base allow for oxoverdazyl systems to display liquid crystalline behavior. Moreover, the promising optical properties of the oxoverdazyl radical have been studied in some detail as well. Thus, there is a solid foothold from which to work in this emerging materials class; however, the electronic properties of the oxoverdazyl radical have been largely unexamined, outside of common electrochemical characterization in solution. In contrast, here we have synthesized and evaluated a series of oxoverdazyl-based materials with tailored substituent groups in order to intentionally alter the solution and solid-state optoelectronic properties of the material. In doing so, we are able to quantify the impact of the myriad substituent groups through ultraviolet-visible (UV-Vis) light absorption spectroscopy and solid-state electrical characterization. In this way, we have been able to tie the molecular properties of this open-shell species to its final end-use performance. As such, these results will be able to aid in guiding the design of next-generation radical materials for organic electronics applications.



POLY 516: Structure-mechanical property of stretchable organic ultra-thin film for electronic applications

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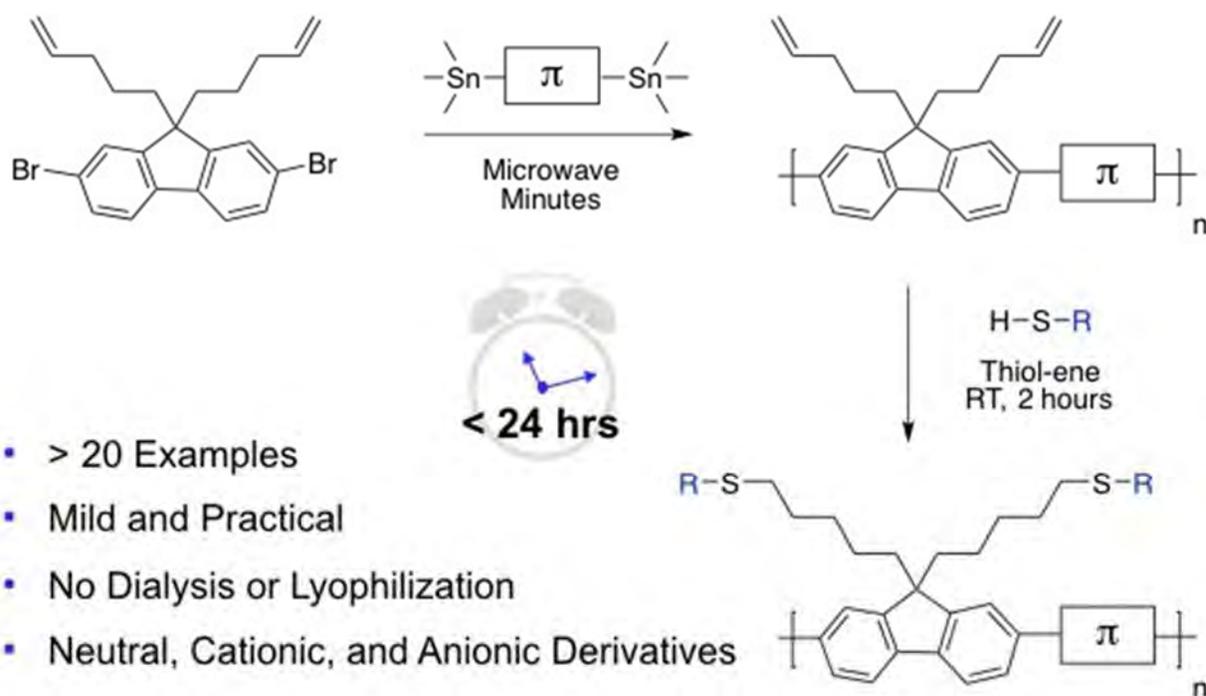
Flexible electronics have gained significant attention due to its potential of achieving large area fabrication and a wide range of application in wearable and implantable devices. A blended system consists of conjugated polymer/elastomer serving as flexible, lightweight, solution-processable, cost-effective, structure tailorable active layer plays a pivotal role in the modern flexible electronics development. To systematically investigate the morphology of the blend system, the different blend ratio of conjugated polymer/elastomer systems were studied by resonant soft x-ray scattering (RSoXs) and correlated to the temperature controlled mechanical tester. We used a pseudo-free standing tensile tester to measure the mechanic property of the ultra-thin films with a thickness of 50 ~ 200nm, which otherwise cannot be obtained using the traditional tensile tester. The full stress-strain curve and the related mechanical property was measured and discussed for the film being floated on water. In the meantime, microstructure morphology, as one of the key variables of electronics performance, was investigated by RSoXs technique to establish the relationship between different blend ratio and phase separation, domain size, and domain spacing in each composite. This study is aiming to provide a unique insight into the structure-property relationship and bridge the currently obvious gap between conjugated polymer design and flexible electronics performance.



POLY 517: Simple and rapid functionalization of conjugated polymers via thiol-ene “click” chemistry

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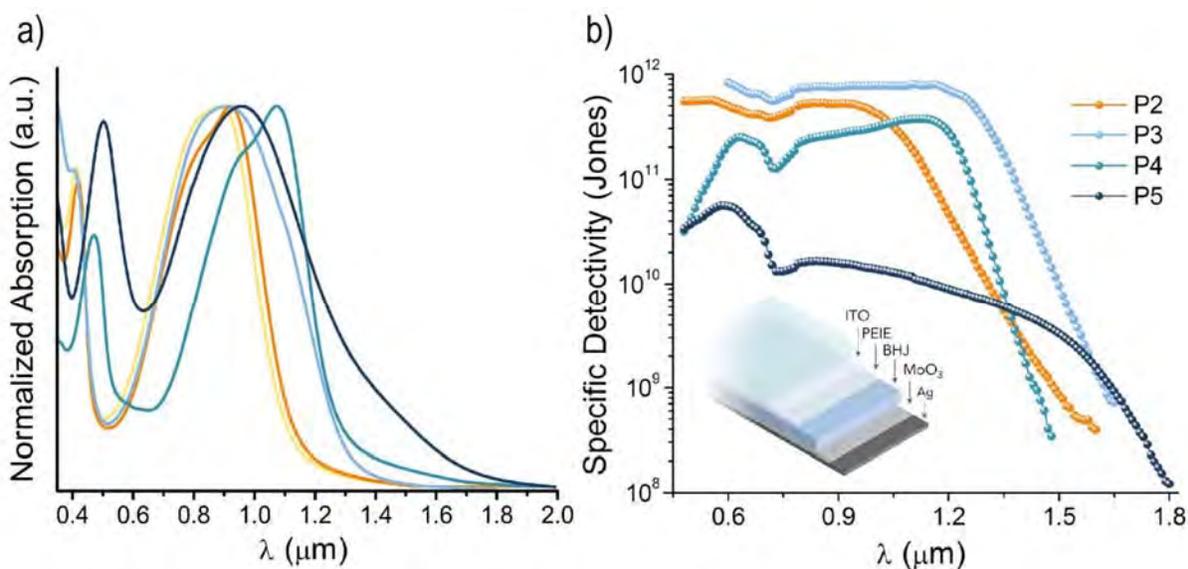
Conjugated polymers demonstrate complex properties that are difficult to predict *a priori* from simple molecular structure considerations. Pendant substituents are critical for solution processing, strongly influence ensemble optoelectronic properties, and dictate the ultimate performance of conjugated polymer-based systems. Arduous bottom-up synthetic approaches have limited available functionalities, forced difficult purification, and results in significant batch-to-batch variability, which also confounds fundamental studies. Recently, we demonstrated that thiol-ene “click” chemistry can be applied toward the rapid and practical synthesis of highly functionalized conjugated polymers. Using a microwave mediated polymerization reaction, we rapidly generated a prototypical (fluorene-co-thiophene) copolymer with pendant alkene functional groups on a multigram scale. This base polymer was subsequently functionalized using thiol-ene chemistry with a library of commercially available thiols including neutral, bulky, cationic, and anionic variants. This top-down approach, carried out under mild reaction conditions, demonstrated complete conversion within hours without the need for laborious purification procedures. We expect this methodology to find widespread utility as it allows for the direct comparison of different functionality with the same polymer backbone for structure-function-property analysis.



POLY 518: Donor–acceptor polymers with tunable infrared photoresponse

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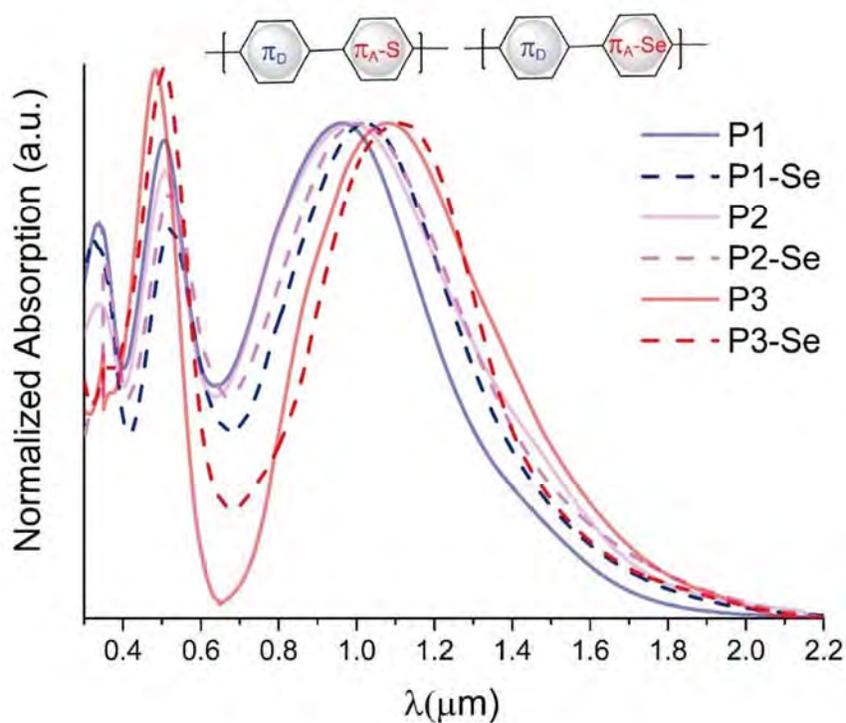
Lowering the optical bandgap of conjugated polymers while maintaining a high efficiency for photoinduced charge transfer to suitable electron acceptors continues to remain a formidable challenge in the area of organic electronics. For donor–acceptor (DA) copolymers, conformational disorder in the solid state has complicated the identification of design guidelines to control the band gap at low energies limiting the design of new optoelectronic and device functionalities. Recently, we demonstrated that DA copolymers comprised of an exo-cyclic olefin substituted cyclopenta[2,1-b:3,4-b']dithiophene donor in combination with conventional electron acceptors displayed very narrow band gaps (1.2 to 0.6 eV) and primary photoexcitations spanning the near- and short wavelength infrared (NIR-SWIR: $0.9 \mu\text{m} < \lambda < 2 \mu\text{m}$). The exo-cyclic olefin functionality lead to extended conjugation, reduced frontier orbital energetics, strong intermolecular interactions, and strategic placement of solubilizing substituents necessary for solution processing. Modular synthetic approaches permitted installation of functionality that affords careful control of energetic alignments and molecular indices such as bond-length alternation. Bulk heterojunction photodiodes fabricated using these new materials demonstrate a detectivity (D^*) of $> 10^{11}$ Jones within a spectral range of 0.6–1.43 μm and measurable D^* to 1.8 μm , the longest reported to date for conjugated polymer based systems.



POLY 519: Structure-function property relationships of narrow bandgap donor-acceptor polymers containing selenium

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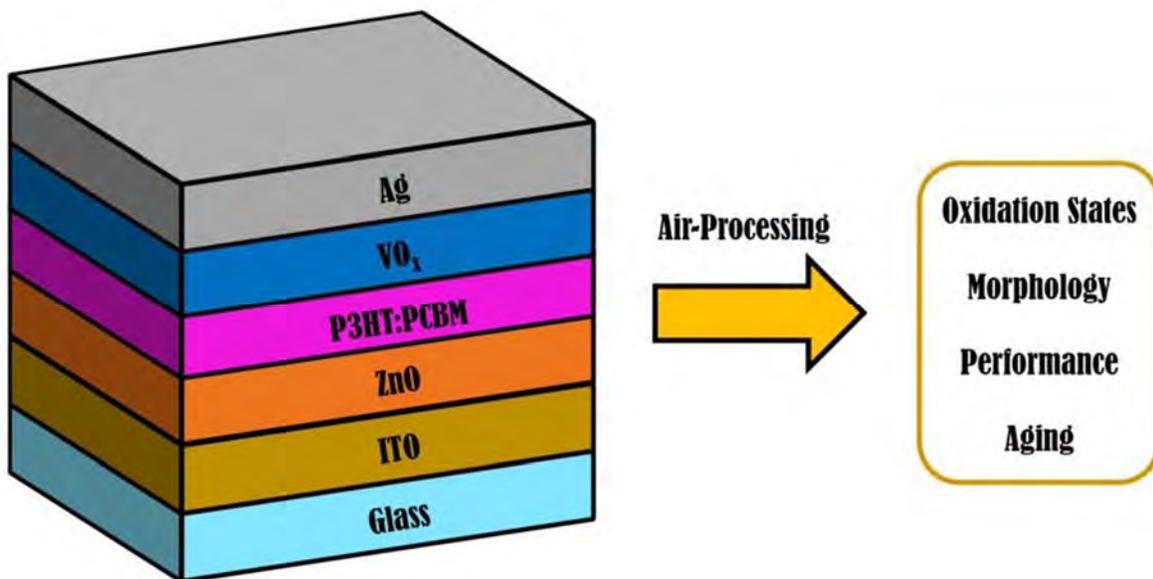
Donor-acceptor conjugated polymers with narrow bandgaps and infrared absorption are technologically relevant for a wide range of applications, including harvesting low-energy photons, infrared photodetectors, ambipolar field-effect transistors, non-linear optics, and other emerging technologies. The complex interrelation between electronic properties and conformational disorder has traditionally limited the availability of narrow bandgap materials with IR absorption. Here, we demonstrate that substitution of sulfur (S) for selenium (Se) is an effective method to modify the optical and electronic properties of narrow bandgap polymers. In general, replacing a thiophene with selenophene heterocycles along the conjugated backbone results in a red-shifted absorption, reduction in the lowest unoccupied molecular orbital, strong intermolecular interactions, and enhanced interchain electronic couplings. The use of Se in place of S in narrow bandgap materials also lends new properties. The structure-function-property relationships and applications of these Se-containing conjugated polymers will be discussed in detail.



POLY 520: Interface engineering of air-processed inverted OPV devices via sol-gel processed vanadium oxide hole-extraction layer

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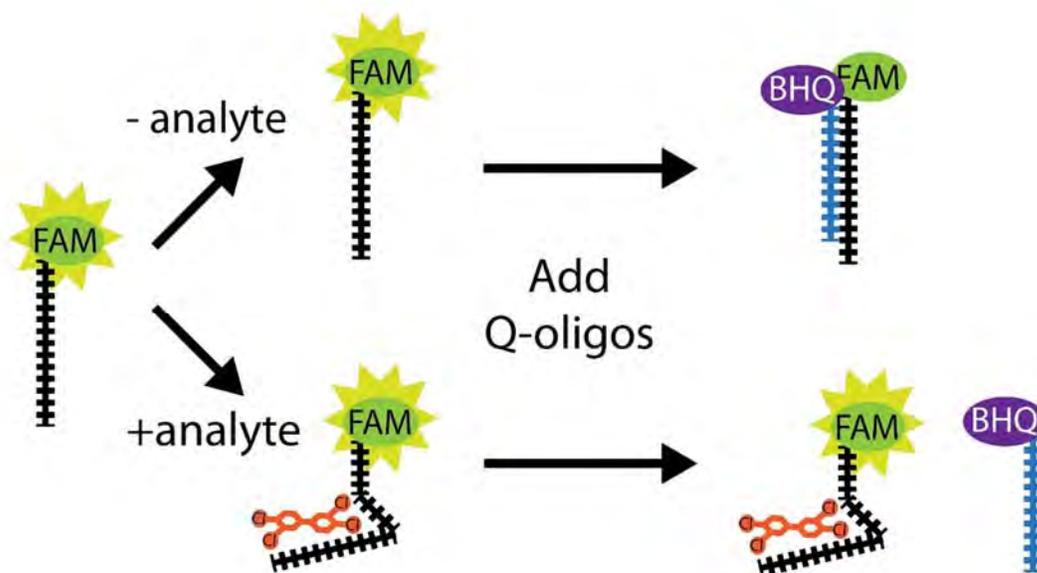
Within bulk heterojunction (BHJ) organic photovoltaic (OPV) devices, photogenerated excitons are extinguished prematurely due to the inherent, simplistic device architectures lacking charge carrier (hole and electron) selectivity at the electrode interface. Moreover, energy is lost due to the high contact resistance between the active semiconducting layer and metal electrode due to their chemical nature. These inherent limitations in OPV systems lead to a decrease in device performance and long-term stability. Recent OPV devices well-exceeded previous performance by incorporating compatible layers of material between the photoactive organic layer and metal electrode. The types of materials used for the interfacial layer includes metals, metal salts, transition metal oxides, doped polymers, fullerene derivatives, conjugated polyelectrolytes, and small molecules. This study primarily focused on air-processed poly(3-hexylthiophene):phenyl-C61-butyric acid methyl ester (P3HT:PCBM) inverted OPV devices with a sol-gel processed vanadium oxide (VO_x) hole-extraction layer. Vanadium oxide is one of the several well-established transition metal oxide materials utilized in organic electronic applications and has shown promising attributes for future commercialization of OPVs. Through morphological analysis techniques, the underlying interfacial domains responsible for long-term stability and consistency in output performance were studied.



POLY 521: Incorporation of DNA aptamers into conjugated polymer-based optical sensors

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Nucleic acid-based aptamers are biomolecule-derived receptors that provide an alternative to antibodies for specific binding. Nucleic acids offer facile, wholly synthetic fabrication and a means to quickly develop competitive inhibitors through use of complementarily base-pairing oligonucleotides (oligo). In this study, we are developing an aptamer based sensing platform through attaching aptamers to highly fluorescent, water soluble conjugated polymers (CP) through the Copper (I) Azide Alkyne cycloaddition (CuAAC) reaction. Detection of analyte binding will be transduced by modulating CP fluorescence through differential binding of a complementary oligo bearing a black hole quencher moiety. Presence of analyte in the aptamer binding site will compete with the quencher bearing oligo, providing a differential response. The sensitivity and specificity of this method was validated using two aptamer systems for binding of Adenosine Triphosphate (ATP) and Polychlorobiphenyl (PCB). This study provides a method for incorporating aptamers into CP optical sensing technologies, providing a means to greatly expand options for analyte sensing.



POLY 522: Enzyme-catalyzed “click” Michael addition between fluorescein monoacrylate and thiol-functionalized polyethers

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This paper investigates Michael addition reactions between fluorescein monoacrylate and thiol-functionalized poly(ethylene glycol) (PEG, PDI = 1.139, M_n = 1160 g/mol) and tetraethylene glycol (TEG, FW = 370.48 g/mol) catalyzed by *Candida antarctica* lipase B (CALB). Thiol functionalized PEG and TEG were synthesized by CALB catalyzed transesterification reactions. The progress of the Michael additions was monitored by ¹H-NMR, which showed the disappearance of the proton signals at 6.52 and 6.17 ppm (=CH₂) and 6.40 ppm (-CH=) which were present due to the acrylate group. The reactions were complete in less than five minutes, the time necessary to record a spectrum. The structure of the products was also confirmed using ¹³C-NMR. Mass spectrometry demonstrated the formation of very pure products without any post-reaction treatment. Enzyme catalysis is found to be a powerful tool to synthesize fluorescein-based imaging agents for a wide variety of applications.

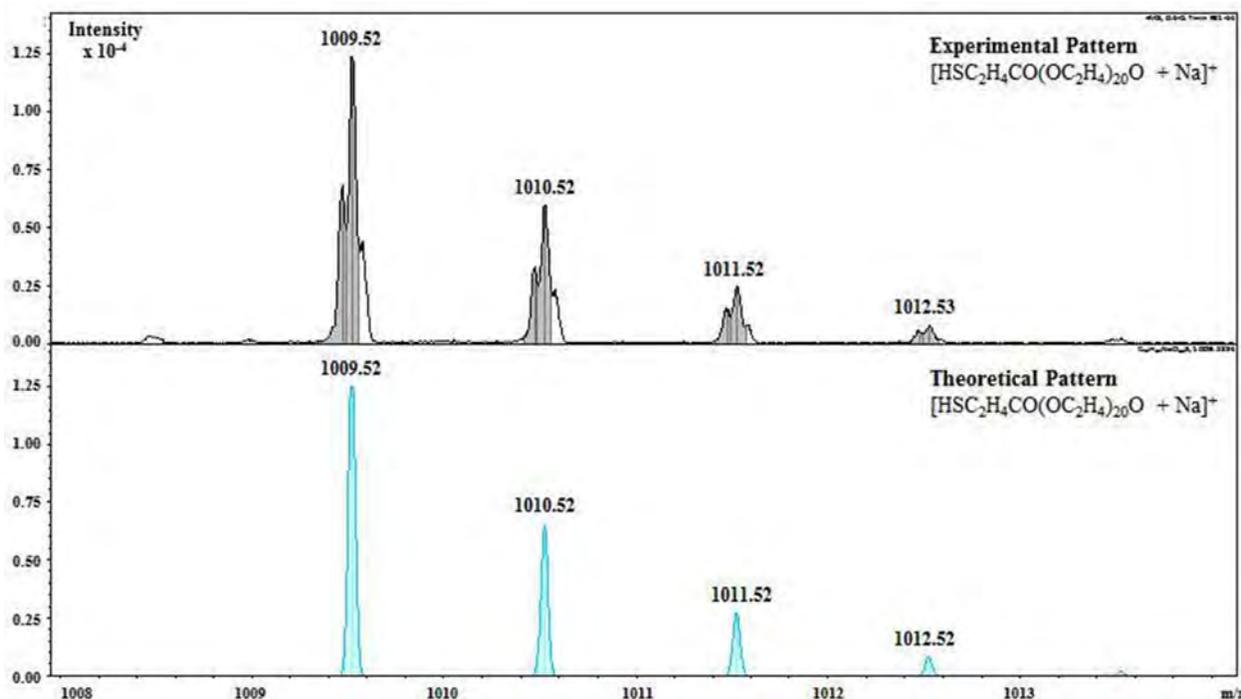


Scheme 1: CALB catalyzed Michael addition reaction

POLY 523: Synthesis of thiol-functionalized tetraethylene glycol and poly(ethylene glycol)s via enzyme-catalyzed transesterification

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In this research, thiol-functionalized compounds were successfully prepared by the transesterification of methyl 3-mercaptopropionate with tetraethylene glycol, and poly(ethylene glycol)s (PEGs) having $M_n = 987.16$ and 2044.41 g/mol and PDI = 1.14 and 1.09, respectively. These reactions were performed without using solvents (in bulk) and using *Candida antartica* Lipase B (CALB) as an enzyme catalyst. $^1\text{H-NMR}$ spectroscopy was used to monitor the progress of the reactions. Longer chains required longer reaction times. Monothiols were obtained by precise timing of the reactions. The synthesis of dithiols required additional CALB and methyl 3-mercaptopropionate. $^{13}\text{C-NMR}$ spectroscopy and mass spectrometry confirmed the structure of the products. Enzyme catalyzed transesterification is a convenient and green method to effectively synthesize thiol-functionalized compounds, to be used for the synthesis of cancer diagnostic and therapeutic agents.

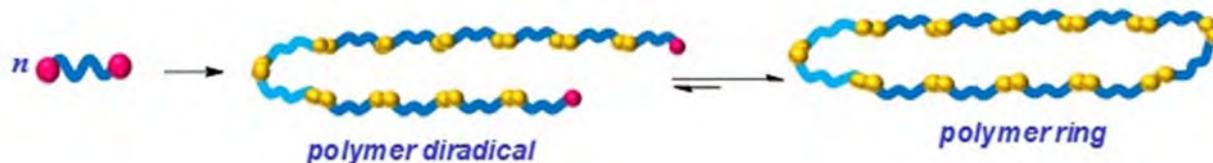


Electrospray Ionization (ESI) spectrum of sodium complex of 20-mer fraction of HS-PEG-OH ($M_n = 987.16$ g/mol, PDI = 1.14)

POLY 524: Structural studies of polydisulfide macrocycles by 2D gHMBC NMR

Sanghamitra Sen², ssen@uakron.edu, Venkat Dudipala³, Judit E. Puskas¹. (2) Department of Chemical & Biomolecular Engineering, The University of Akron, Akron, Ohio, United States (3) Department of Chemistry, The University of Akron, Akron, Ohio, United States

This paper reports structural studies of two polydisulfide polymers synthesized from 2-[2-(2-sulfanylethoxy)ethoxy]ethanethiol (DODT) and telechelic polyisobutylene (HS-PIB-SH) dithiol using a “green” oxidative polymerization system (R3P, Radical Redox Ring-opening Polymerization) developed in the Puskas group. Initial characterizations of both poly (DODT) and PIB-SS by ¹H, ¹³C NMR and Raman spectroscopy indicated the absence of thiol end groups. In order to gain more insight into the structure of these polymers, 2D gradient Heteronuclear Single Quantum Coherence (gHSQC), and 2D gradient Heteronuclear Multiple Bond Correlation (gHMBC, ¹H-¹³C correlation spectroscopy) experiments were conducted on both DODT and HS-PIB-SH along with their respective polymers exploiting a Varian 750 MHz NMR instrument using a triple resonance ¹H(¹³C/¹⁵N) pulsed field gradient 5mm probe. Both DODT and HS-PIB-SH showed correlation peaks corresponding to the thiol end groups and neighboring methylene carbons. However, these correlation peaks were absent in the corresponding poly (DODT) and PIB-SS indicating the absence of thiol end groups in the polymers. The 2D NMR spectroscopic studies provide evidence that under carefully selected conditions R3P of dithiols produces exclusively macrocycles.



Radical Reversible Recombination Polymerization

POLY 525: Chemical degradation of model sulfonated polyphenylene proton exchange membranes

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Proton-exchange membrane or polymer-electrolyte membrane (PEM) fuel cells are becoming increasingly popular due to their versatility, high efficiencies and low pollutant output. One of the main failure modes of PEM fuel cells is the degradation of the polymer membranes, and therefore considerable research and resources are being committed to understand the important aspects of the process. One key degradation pathway is initiated by peroxide radical attacks at the membrane electrode interface; peroxides that are generated as the result of the associative oxygen reduction reactions when in contact with low concentrations of transition metal ion impurities. Previous work on the degradation of the Sandia developed sulfonated poly(phenylene) (SDAPP) membranes used solution ¹H and ¹³C NMR to characterize the decomposition products. However, the complicated chemistry of the full polymer led to inconclusive identification of all the resulting chemical species. The work described in this poster focuses on the intentional degradation of simpler constitutive model compounds that will ultimately lead to a better understanding of the degradation chemistry that occurs in SDAPP PEMs. These model compounds underwent testing with Fenton's reagent, in which the compounds are directly exposed to varying concentrations of both H₂O₂ and trace ferrous iron contaminants. Solution ¹³C NMR is used to observe the decomposition as a function of time and identify the degradation products of each reaction at various temperatures. These results are then used to evaluate the degradation of the complete SDAPP membrane.



POLY 526: Miscibility analysis of polymer based ultrafiltration membranes through two dimensional Wideline SEparation solid state NMR spectroscopy

Kevin Dizon^{1,2}, *K.Dizon@westernsydney.edu.au*, **James D. Oliver**^{1,2}, **Geoffrey Johnston-Hall**³, **Richard Wuhrer**⁴, **Patrice Castignolles**¹, **Marianne Gaborieau**^{1,2}. (1) Australian Centre for Research on Separation Science, Western Sydney University, Parramatta, New South Wales, Australia (2) Medical Sciences Research Group, Western Sydney University, Parramatta, New South Wales, Australia (3) Memcor, Evoqua Water Technologies, South Windsor, New South Wales, Australia (4) Advanced Materials Characterisation Facility, Western Sydney University, Parramatta, New South Wales, Australia

The increasing trend of urbanisation has shifted reliance away from natural production of freshwater to man-made processes. Alternative methods of freshwater production are marred by costly processes specific to the type of feedwater (salt water, ground water). Importance is placed on ultrafiltration membranes to reduce the number of chemical engineering processes required in a setting with various types of feedwater. Ultrafiltration membranes consist of nanopores that selectively screen particulates like bacteria and viruses while producing drinkable water. Formulations of ultrafiltration membranes primarily stem from the mixing of synthetic polymers to obtain optimal pore size dimensions and durability. Structural incompatibilities between polymers causes resistance in complete mixing thereby creating a partially miscible mixture. Determinations meaningful to optimize functionality require tools able to determine structural features and miscibility. Current tools commonly found within industrial facilities are limited, FTIR and Raman spectroscopy are considered ill-suited as a low depth penetration only allows for surface composition determinations. This project aims to develop solid state NMR spectroscopy as a bulk analysis tool for meaningful determinations of miscibility of polymers used in membranes. Miscibility determinations are conducted through 2 Dimensional Wideline SEparation (2D WISE) which correlates a ¹H spectrum with a ¹³C Cross polarisation spectrum. Optimal miscibility (refer to figure 1) is inferred through similar molecular mobility along all molecular structures. Membrane characterisation through XRD, and DSC can be coupled with solid-state NMR as a basis for the optimisation of ultrafiltration membrane synthesis.

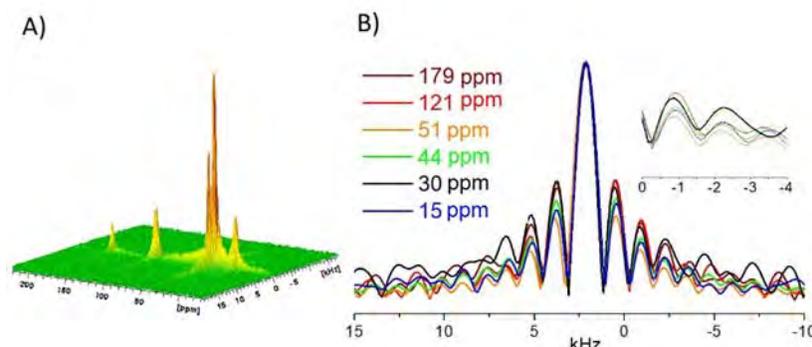
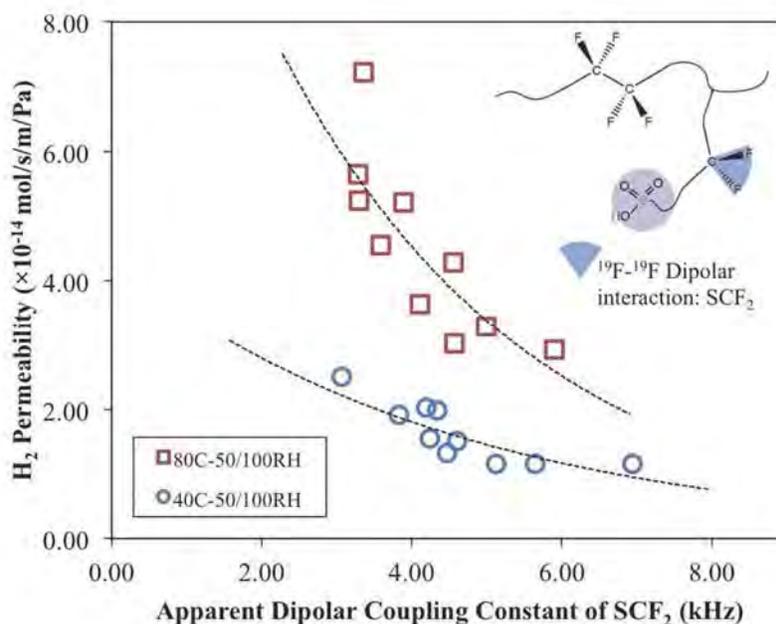


Fig 1A) 2D WISE spectrum of an ultrafiltration membrane B) ¹H spectra extracted at different carbon sites of the 2D WISE spectrum. Molecular mobility is empirically determined through the signal broadness at each carbon site.

POLY 527: Understanding polymer dynamics in perfluorosulfonic acid membranes *via* solid-state NMR

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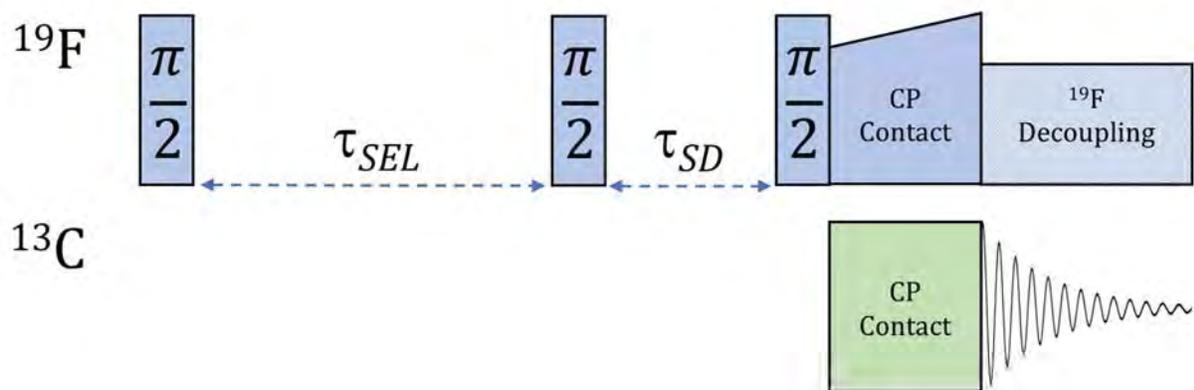
Perfluorosulfonic acid (PFSA) materials have been used in polymer electrolyte membrane fuel cells (PEMFCs) as electrolyte materials due to their mechanical durability and high proton conductivity. To understand the molecular physicochemical properties, local dynamics studies using double quantum filtered ssNMR spectroscopy have been recently developed and validated.^[1] The local dynamics information has been separated and analyzed in terms of fluorine interactions with respect to different temperatures and hydration levels. The polymer side chain is proven to be more locally mobile which is reflected by the lower apparent dipolar coupling constant (D_{app}) compared to the backbone. This observation agrees with the micro-phase separation morphology development. In the current study, the dynamics investigation of different PFSA materials has been conducted at various conditions. *In operando* membrane performance analyses have been obtained in parallel at Ballard Power Systems. PFSA membranes are prepared into membrane electrode assembly (MEA) form, with catalyst layers and gas diffusion layers. From the cyclic voltammetry measurements of the MEAs, the H₂ crossover values have been extracted. There is a strong correlation between the H₂ permeability and the PFSA side chain local dynamics from the NMR analysis. As the side chain mobility increases (lower D_{app}), an increase in the H₂ permeability is observed. The link between the fundamental dynamics study and the PFSA performance analysis provides insight into gas transport mechanisms in this type of material.^[2]



POLY 528: ^{19}F spin diffusion and X-ray scattering analysis of fluoropolymers

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The determination of domain sizes in polymers is tremendously useful in the assessment of spatial relations between different phases and polymer aging and degradation. Spin diffusion NMR in the solid state is a viable means to determine domain size, via magnetization transfer processes mediated by homonuclear dipolar coupling between neighboring nuclei. Spin diffusion techniques have been successfully applied to protonated polymers, wherein the homonuclear dipolar coupling between protons is probed. The application of spin diffusion techniques to fluoropolymers via ^{19}F however has been very limited. The ^{19}F nucleus is comparable to ^1H in sensitivity and abundance, thus the homonuclear dipolar couplings between neighboring ^{19}F nuclei dominate their spectra, and can be used in spin diffusion experiments. In the present work we seek to apply ^{19}F spin diffusion techniques to model fluoropolymers such as polytetrafluoroethylene (PTFE), polychlorotrifluoroethylene (PCTFE), and polyvinylidene fluoride (PVDF). These materials are ideal for determining the effect of varied chain substituents on rates of spin diffusion in partially crystalline polymers. X-Ray scattering results provide useful information regarding domain size and shape. We hope these results provide the foundation for analysis of fluoropolymers of more complex structure and composition.



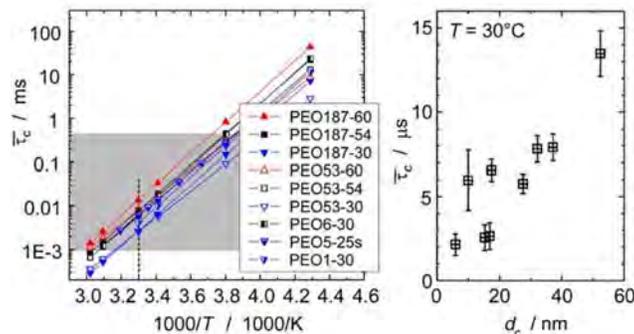
POLY 529: NMR investigations of dynamics in the different phases of semicrystalline polymers

Mareen Schaefer¹, mareen.schaefer@physik.uni-halle.de, Ricardo Kurz¹, Anne Seidlitz², Martha Schulz², Thomas Thurn-Albrecht², Kay Saalwaechter¹. (1) Institute of Physics - NMR, MLU Halle-Wittenberg, Halle (Saale), Germany (2) Institute of Physics - Polymerphysics, MLU Halle-Wittenberg, Halle (Saale), Germany

The structure formation of melt-crystallized semicrystalline polymers strongly depends on the interplay of the different dynamics in the crystalline and amorphous phases and the kinetics during the growth of the crystallites. Here, the decisive role of intracrystalline chain mobility, the so-called α_c -relaxation, and the effect of entanglements on the morphology is addressed.

The connections between structure formation and dynamics of polymer chains are presented on the example of two model polymers with and without α_c -relaxation: Poly(ethylene oxide) (PEO) [1] and poly(ϵ -caprolactone) (PCL) [2] which are investigated with small-angle X-ray scattering (SAXS) and NMR spectroscopy, respectively. The morphology of PCL has, in agreement with classical crystallization theories, a well-defined crystalline thickness. In PEO the intra-crystalline mobility causes a thickening of the crystalline lamella which leads subsequently to a minimization and formation of a well-defined amorphous thickness. NMR analysis reveals that the crystal reorganization occurs on the same time scale as the crystal growth itself. The analysis of poly(oxymethylene) (POM), which exhibits a comparably slow α_c -relaxation, enables the separate investigation of crystal reorganization and crystal growth on the morphology.

Further investigations address the relationship between morphology and entangled dynamics in the amorphous phase and the melt. The addition of short chains from the same species prior to crystallization reduces the entanglement density in the melt and allows us to study the topological restrictions of entanglements and the influence on the structure formation, while all other parameters are kept constant.

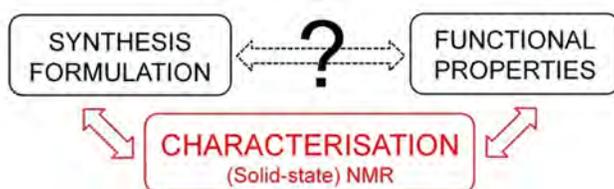


POLY 530: Characterisation of industrial adhesives with (solid-state) NMR spectroscopy

Kash Bhullar^{1,2}, Joel J. Thevarajah³, Aaron Rebmann^{1,2}, Scott Cheevers³, Richard Wuhrer⁴, Patrice Castignolles², **Marianne Gaborieau**^{1,2}, m.gaborieau@uws.edu.au. (1) Medical Sciences Research Group, School of Science and Health, Western Sydney University, Parramatta, New South Wales, Australia (2) Australian Centre for Research in Separation Sciences (ACROSS), School of Science and Health, Western Sydney University, Parramatta, New South Wales, Australia (3) Imatech, International Materials & Technology Pty Ltd, Castle Hill, New South Wales, Australia (4) Advanced Material Characterisation Facility, Western Sydney University, Parramatta, New South Wales, Australia

Adhesives are an important class of industrial polymers with applications ranging from adhesive tape and sticky notes through to resins used in mines. This poster will showcase the development of a new hot-melt adhesive to repair conveyor belts in mines. Any downtime in the production process is very costly. A repair tool of choice is in this case a hot-melt adhesive: it can be applied quickly, and once applied it does not require a long curing time until it has the desired properties that the process demands. Since there are many possible sources of physical and chemical stress in a mining process, the adhesive needs not only to be strong in its adhesive properties and its flexibility, but also very stable against mechanical stress, heat, UV radiation, acids, bases and other aggressive chemicals, mostly hydrocarbons.

The base resin thus needs to be strengthened by the right combination of additives. ATR FT-IR, solid-state NMR and Raman spectroscopies were assessed for their potential to reveal the composition and homogeneity of the final product. The results were used to evaluate the extrusion process used to form the final product, RubbaFIX® (www.rubbafix.com.au).

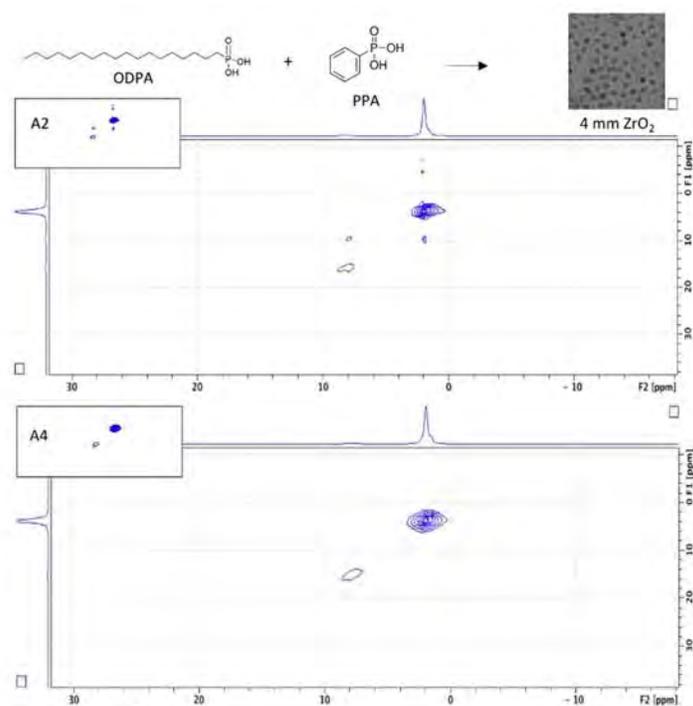


Importance of reliable characterisation methods for the elucidation of the relationship between the synthesis (or formulation) and the functional properties of industrial adhesives.

POLY 531: Detection of nanoscale phase separation in nanoparticles with mixed ligand shells

Brenda I. Guzman Juarez², *brenka13@me.com*, **Kuenhee Kim**², **Ahmed Abdelaa**², **Safiya Allie**², **Violeta Toader**², **Linda G. Reven**¹. (1) Dept of Chem McGill Univ, Montréal, Quebec, Canada (2) Chemistry, McGill University, MONTRÉAL, Quebec, Canada

Spontaneous phase separation has been detected in mixed ligand shells of nanoparticles for both low molecular weight and polymeric ligands. Although there is growing interest in such “patchy nanoparticles”, the majority of the studies have been theoretical rather than experimental due to difficulties in preparing significant quantities of nanoparticles with controlled ligand compositions. [1] Experimental validation has also lagged to due to the lack of appropriate tools to detect nanoscale phase separation. Here we apply NMR methods developed for characterizing heterogeneities in complex materials on different length scales to nanoparticles with polymer and low molecular weight mixed ligand shells. The mixed ligand shells consisted of different ratios of aromatic (polystyrene or phenyl) and aliphatic (polyethylene oxide or dodecyl) phosphonic acids on 4 nm ZrO₂ nanoparticles. The results for ¹H NOESY, ¹H double quantum MAS, ¹H spin diffusion and ¹H-¹³C HETCOR NMR experiments on the nanoparticles with polymer versus small molecule ligand shells were compared. In the case of the low molecular weight mixed ligand shells, model systems consisting of Janus particles or physical mixtures of nanoparticles functionalized with only one ligand were studied to calibrate the ¹H spin diffusion experiments originally developed for polymeric materials.

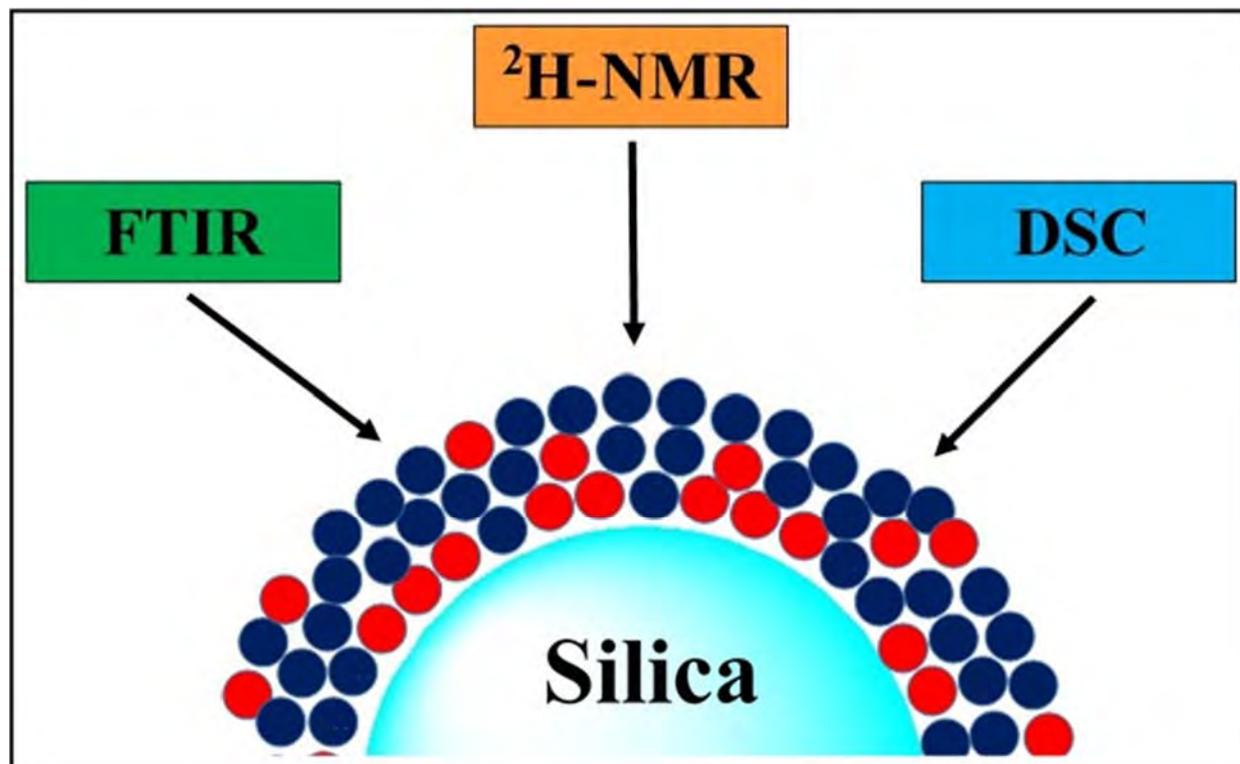


2D ¹H DQ NMR spectrum of the 50 ODPA:50 PPA physical mixture. In A2, the appearance of cross-peaks verifies the proximity of ODPA and PPA protons. In A4, the absence of cross peaks indicates the successful synthesis of the physical mixture.

POLY 532: ^2H -NMR, FTIR, and DSC: The structure and dynamics of poly(styrene-*r*-methyl methacrylate- d_3) on silica

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Temperature modulated differential scanning calorimetry (TMDSC), FTIR, and solid-state deuterium NMR spectroscopy were used to observe the dynamics of bulk and adsorbed poly(styrene-*r*-methyl methacrylate- d_3). These characterization techniques have different sensitivities associated with them. FTIR showed the binding of MMA- d_3 carbonyl groups to the silica surface for all polymer compositions. As the fraction of MMA- d_3 in the polymer increased, the fraction of bound carbonyls decreased. ^2H -NMR spectra of adsorbed samples showed significant differences from those of the bulk; decreased segmental mobility of the MMA- d_3 units was clear in all the small-amount adsorbed samples at all the polymer compositions. TMDSC, which characterizes the entire polymer, showed that the proportion of tightly-bound polymer in the adsorbed samples increased with the increase in MMA- d_3 content. Using the information obtained from these different techniques, we will attempt to determine the surface structure of adsorbed poly(styrene-*r*-methyl methacrylate- d_3).



POLY 533: Effect of water on the structure and dynamics of [3-¹³C] Ser, [3-¹³C] Tyr and [3-¹³C] Ala-*Bombyx mori* silk fibroin studied with ¹³C solid-state NMR

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The key to the further development of silk as a preferred material for medical applications is to understand the structure and dynamics of *Bombyx mori* silk fibroin (SF) in the hydrated state and the characteristics of associated water. In this work, the effect of water on the structure and dynamics of ¹³C labeled SF fiber was revealed through the use of several ¹³C solid-state NMR techniques. The mobile and immobile components of SF in the hydrated state could be analyzed selectively by ¹³C refocused-INEPT NMR and ¹³C CP/MAS NMR, respectively. The fractions of several different structures in the hydrated state were also determined by ¹³C DD/MAS NMR spectra. In addition, the dynamics of water molecules interacting with SF was studied by ²H solution NMR relaxation and exchange measurements. Using an inverse Laplace transform algorithm, we were able to identify four distinct components in the ²H relaxation times for water in SF fiber-water system (Figure). Our measurements provide new insights relating to the hydration structure of silk and the characteristics of water, which are relevant in light of current interest in the design of novel silk-based biomaterials.

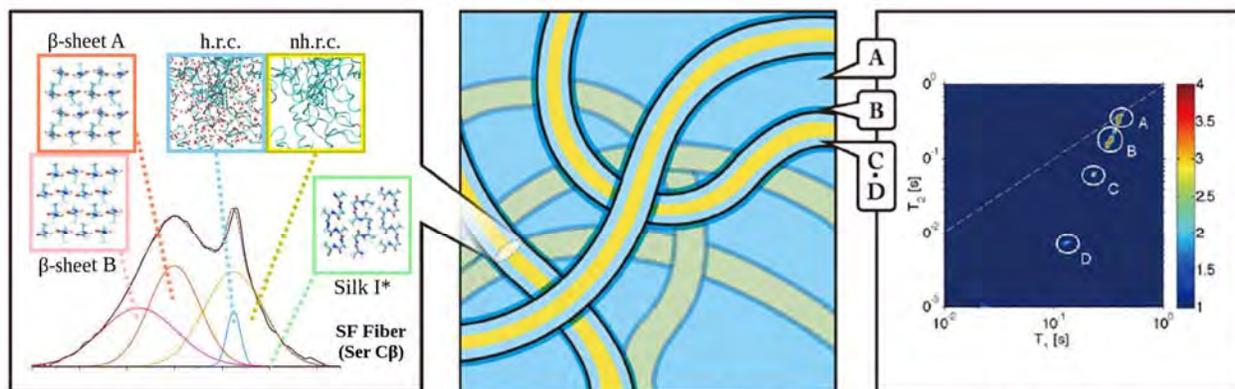
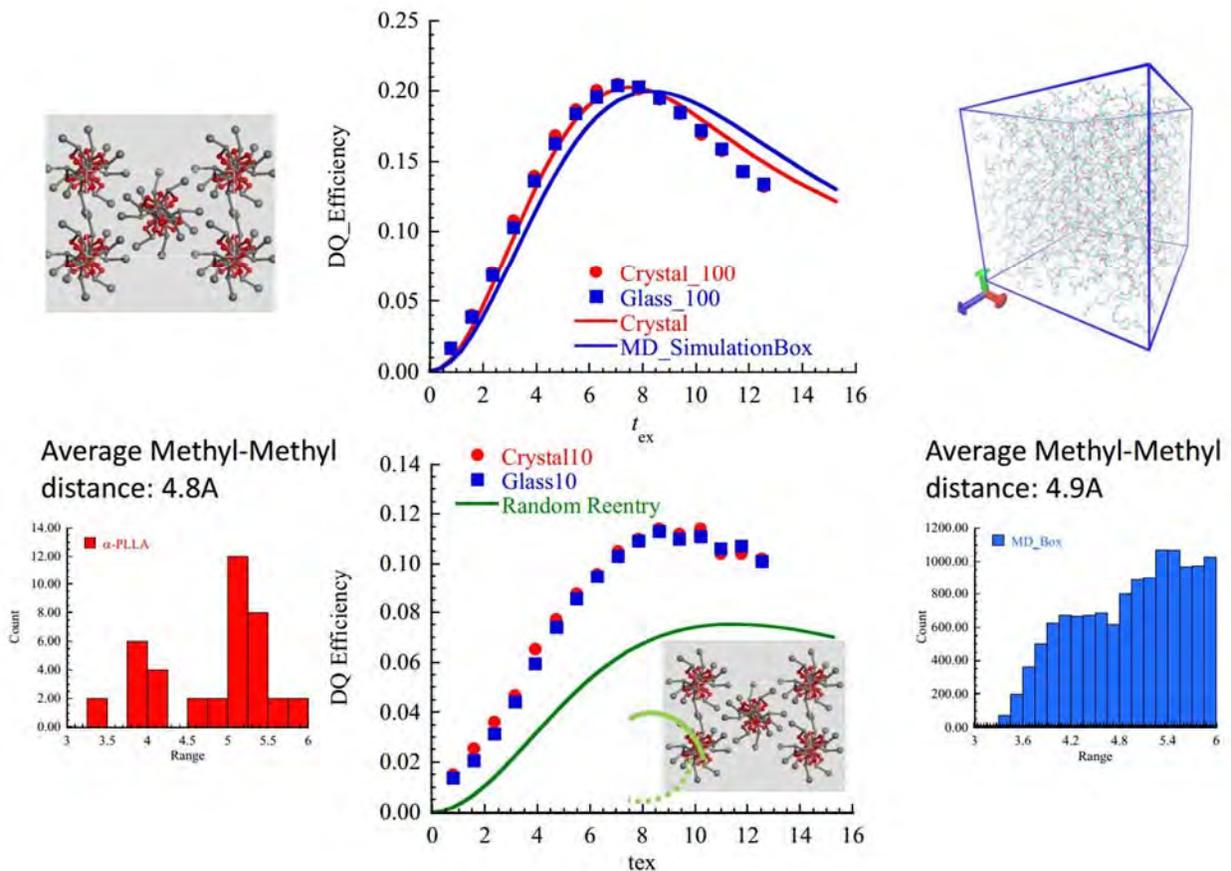


Figure: An image of SF fibers in water (center), several different structures of hydrated SF fiber (left) and four distinct components in the ²H relaxation times for water in SF fiber-water system (right).

POLY 534: Chain conformation, packing, and folding structures of poly(L-lactic acid) in glassy state as studied by ^{13}C solid-state NMR and selective isotope labeling

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Deep quenching of semi-crystalline polymer from the melt state down to below glass transition temperature results in the glassy state. Comparing with the melt grown process, the cold-crystallization of glass samples usually exhibit a much higher overall crystallization rate, which triggers numerous investigation of the glassy state. The short-range-ordered nature of polymer in the glassy state poses difficulty in analyzing the chain conformation, packing and folding structure by conventional characterization techniques. Here, we synthesized ^{13}C single and double sites labeled PLLA and investigated the structures of the glassy sample in detail. It was demonstrated that the conformational/packing/folding structures are quite similar between glassy and crystalline states. This result suggests that even rapidly quenched glassy sample possess the same local structure as the crystalline form.

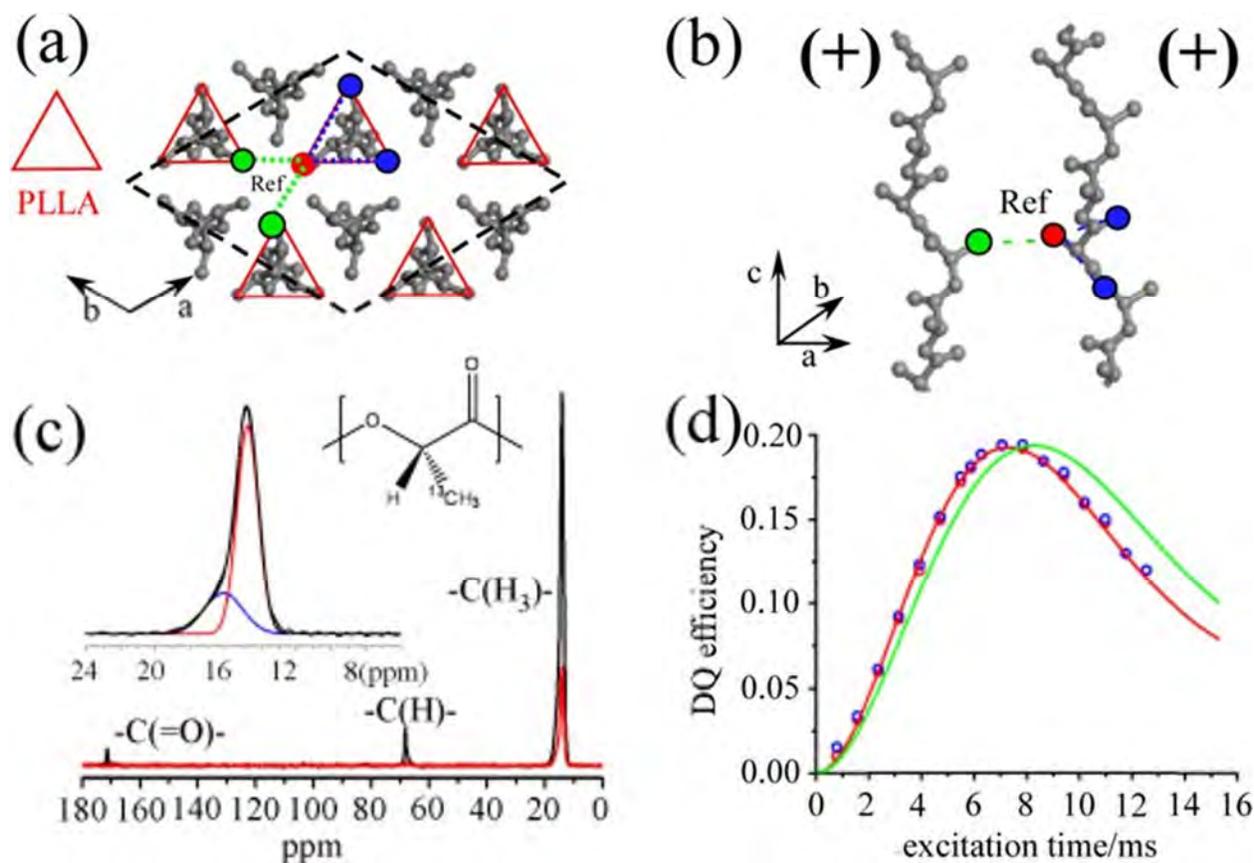


PLLA Chain Packing and chain folding analysis characterized by Double Quantum NMR.

POLY 535: Crystal structure of poly(lactic acid) stereocomplex as studied by ^{13}C - ^{13}C double quantum NMR

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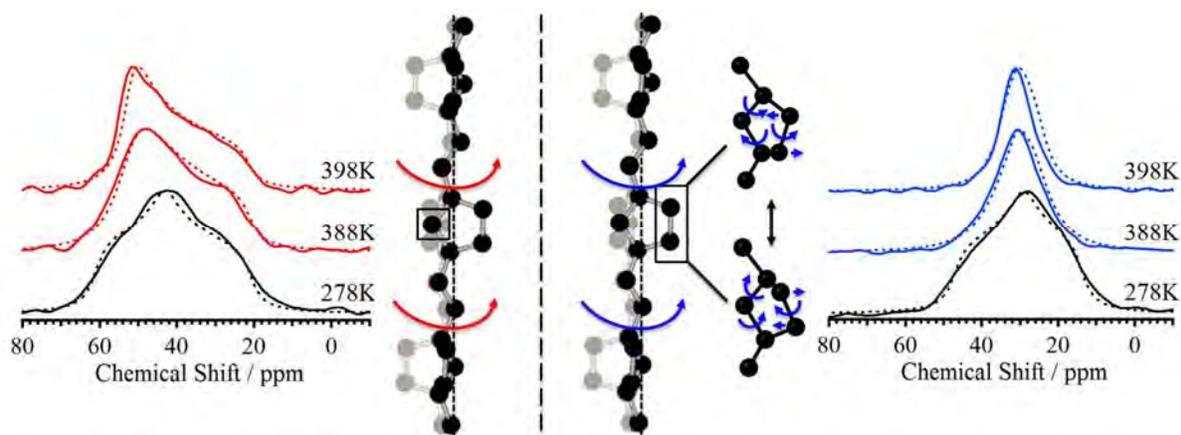
PLA has caught widely attention because of its biocompatibility and similar mechanical properties with that of poly(styrene). The chiral carbon of PLA gives it a potential to form different crystal structure. Among them, PLA stereocomplex (SC) crystal, is the most attractive system, because of its high melting point ($\sim 230^\circ\text{C}$). To understand origins of excellent thermal property of SC, fundamental crystalline structural analysis is necessary. So far, X-ray and electron diffraction analysis has provided packing structure of SC is either $R3c$ or $R3c-1$, which represent PLLA regularly and alternatively pack with PDLA. Very recently, XRD fiber diffraction analysis supported a different packing model, P3, where PLLA stems randomly pack with either PLLA or PDLA. In this presentation, we investigate packing structure of PLA SC crystals by applying ^{13}C - ^{13}C double quantum (DQ) NMR spectroscopy. Local dipolar interaction can provide local packing structure in PLA SC.



POLY 536: Effect of stereoregularity on local dynamics of hydrogenated polynorbornenes as studied by solid-state NMR

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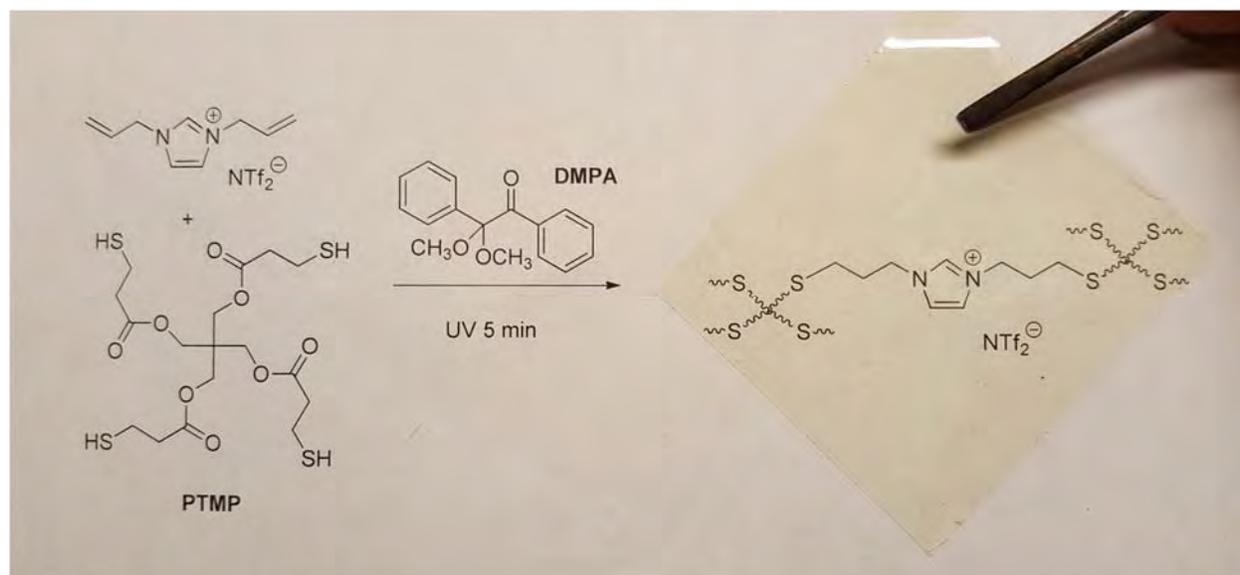
Solid-state NMR spectroscopy can be used to study both the structure and dynamics of macromolecular systems that exhibit different degrees of order to understand the fundamental properties of materials. One such point of interest is to determine the difference of a polymer's structure, local dynamics and phase transition between various isomers of semicrystalline polymers. Recently, a thorough study on stereospecific ring-opening metathesis polymerization has been conducted on norbornenes making the synthesis and the study of hydrogenated polynorbornene (hPNB) stereoisomers possible. The unique local dynamics of atactic- syndiotactic- and isotactic-hPNBs under various temperatures below melting temperatures will be shown and the relationship between tacticity and molecular dynamics will be discussed.



POLY 537: Imidazolium-containing thiol-ene poly(ionic liquid) membrane networks: Conductive and gas separation properties

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Department Of Chemistry, Murray State University, Murray, Kentucky, United States

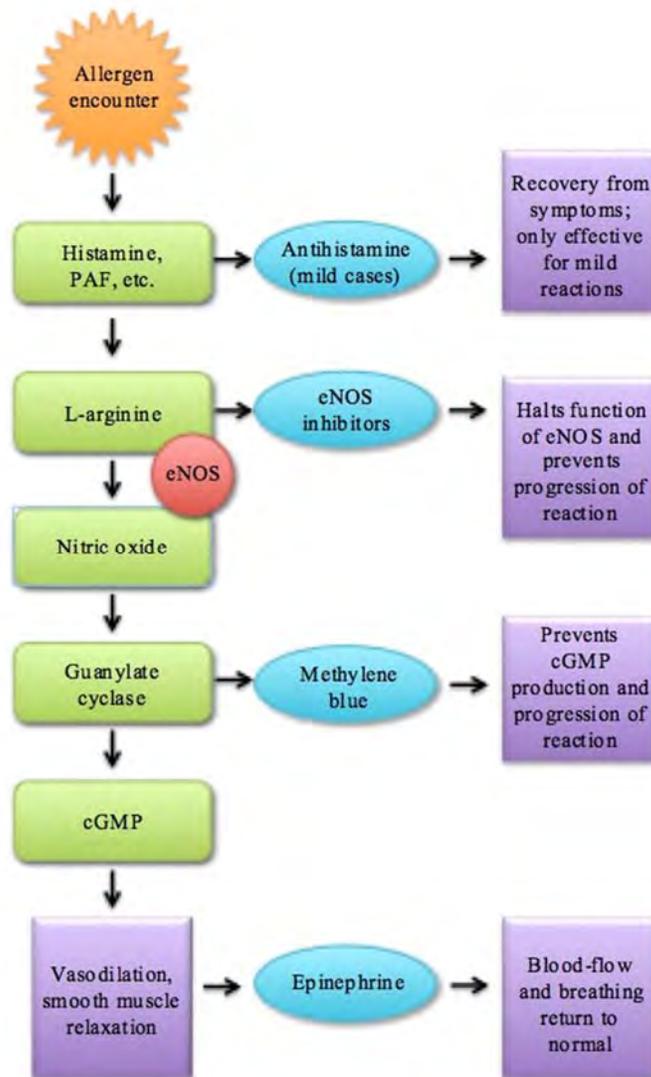
Imidazolium-containing poly(ionic liquid) (PIL) networks were prepared using thiol-ene 'click' photopolymerization for the purposes of investigating their conductive and gas separation properties. Commercially available multifunctional thiols were photopolymerized with synthesized imidazolium-containing 'ene' monomers. Variations in 'ene' functionality and thiol:ene ratio resulted in PILs with a wide range of thermal, mechanical and conductive properties. Overall, PILs employing the [NTf₂]⁻ counteranion were found to exhibit promising conductivities with the values in the range of 10⁻⁶ to 10⁻⁵ S/cm at 30 °C at 30% RH. PIL films which contained a small amount of imidazolium-containing, monofunctional 'ene' exhibited slightly higher ionic conductivities and lower *T_g* values. The ability of these PILs to separate carbon dioxide from nitrogen and methane was explored using a time-lag measurement apparatus. PIL membranes for gas separation studies were prepared on a PVDF support and the resulting composites exhibited relatively low CO₂ permeability, however the CO₂/N₂ and CO₂/CH₄ selectivities were found to be very encouraging. The results from these studies will be discussed.



POLY 539: Methylene blue doped polymer films for anaphylaxis treatment: Film morphology and drug dispersal

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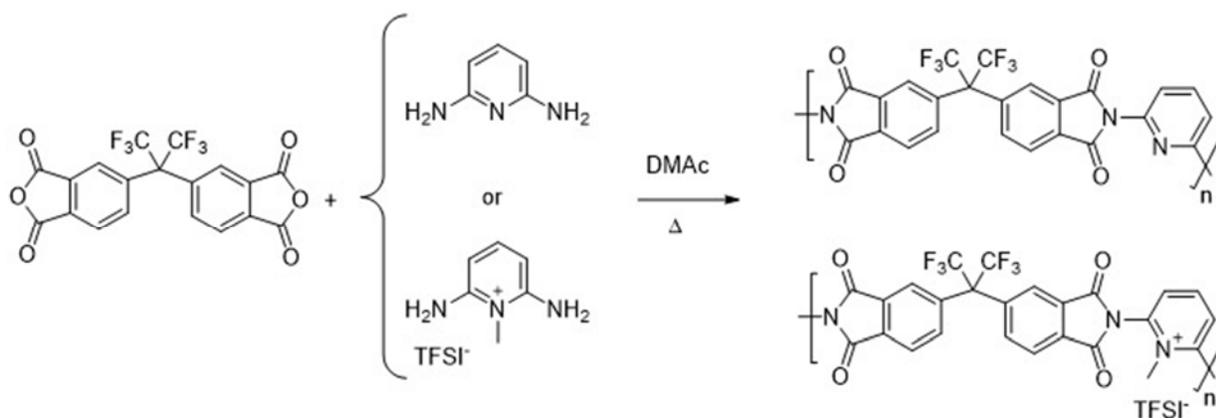
PEO-*b*-PCL diblock copolymer films of varying molecular weights and PLGA 50:50 films were integrated with methylene blue (MB) dye and prepared under various conditions to determine their respective MB release rates. Prepared films were placed in DI H₂O, and UV-Vis spectroscopy was used to measure the solution's absorbance to determine MB concentration after diffusion into the water. Data was taken over time to determine the amount and rate of MB released. Release rates were influenced by the molecular weight ratio of the PEO-*b*-PCL films, casting solvent, and film thickness, and showed various release profiles based on these factors.



POLY 540: Design, synthesis and characterization of polyimides containing pyridine/pyridinium linkages in their backbones

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This work examines the synthesis, properties and gas separation performance of polyimides synthesized from 6-FDA with 2,6-diaminopyridine. Alternatively, the analogous 2,6-diaminopyridinium monomer can be used to form an "ionic polyimide". The ionic polyimide is also capable of interacting with, and stabilizing ionic liquids within its structure. Both the neutral and ionic forms were characterized and cast into membranes. Permeabilities of CO₂, N₂, CH₄, H₂ and O₂ were measured and gas pair selectivities calculated. Membrane performances for CO₂/N₂, CO₂/CH₄, CO₂/H₂ and O₂/N₂ separations are presented in context of "Robeson Plots".

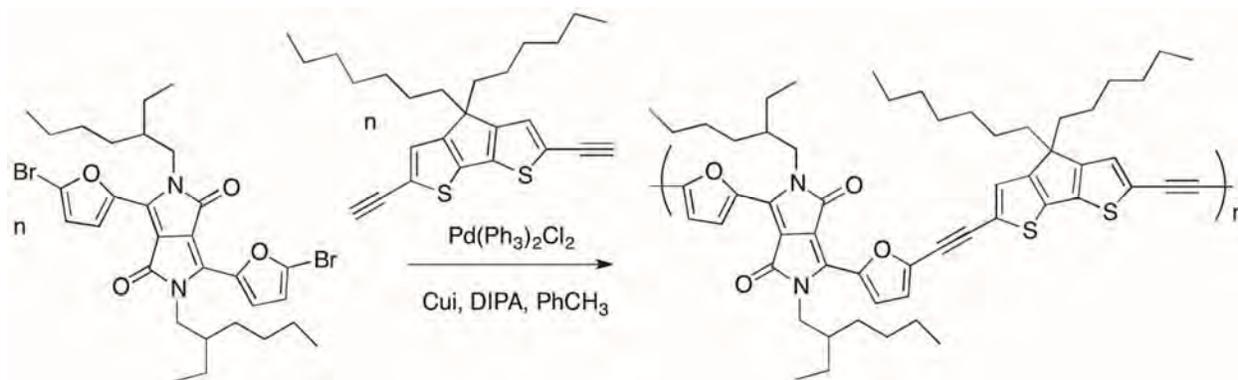


Synthesis of polyimide and "ionic" polyimide using pyridine- or pyridinium-based monomers.

POLY 541: Synthesis and characterization of a DFDPP-CPDT polymer with ethynyl spacers by means of a Sonogashira coupling

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This research explores the synthesis of a polymer based on cyclopentadithiophene (CPDT) and difurodiketopyrrolopyrrole (DFDPP) comonomers. This work differs from previously published compounds due to an ethynyl spacer between the comonomers, which will provide less steric interactions between the alkyl chains. The DPP comonomer will be synthesized via published methods and then brominated with NBS. The dibromodihexylcyclopentadithiophene comonomer will be treated with trimethylsilylacetylene under Sonogashira conditions to yield the ethynyl comonomer. The final polymer will be produced via another Sonogashira reaction of the deprotected CPDT ethynyl and dibromoDPP comonomers. This polymer will be characterized via FTIR, ¹HNMR, and GPC. The optical band gap will be determined from solid UV-Vis absorbance. This organic polymer will be employed in the construction of bulk heterojunction hybrid solar cells with a colleague at South Dakota State University.

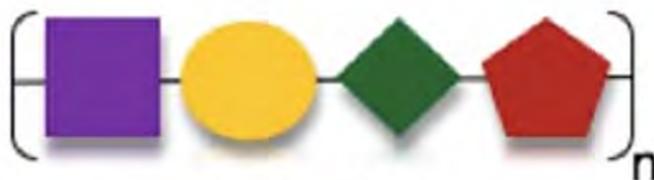


Synthetic scheme for polymer

POLY 542: Synthesis towards sequence-controlled polypeptides

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Sequence-controlled polymerizations, such as DNA replication and transcription, are essential in biological systems. However, replicating these mechanisms in laboratories remains a challenge. From biological systems, much has been learned and applied in biological contexts, such as for the autocatalytic self-replication of peptides. Beyond the scope of biology, sequence-controlled polymers have yielded advanced materials for digital data storage, among other applications. Given the importance of biological and biomimetic polymers in both biological and non-biological arenas, this work makes progress towards the synthesis of sequence-controlled polypeptides with repeating units comprised of multiple amino acids. Glycine- and proline-containing tetrapeptides, identified by theory-based calculations, were prepared using solid phase peptide synthesis and then ring closed to generate the corresponding *N*-carboxyanhydride monomers. The tetrapeptides, Gly-Gly-Gly-Gly, Gly-Gly-Pro-Gly, and Gly-Pro-Pro-Gly, were obtained in 20-55% yields and the structures were confirmed by electrospray ionization mass spectrometry (ESI MS) and nuclear magnetic resonance (NMR) spectroscopy. High-performance liquid chromatography (HPLC) experiments demonstrated the high purity of the tetrapeptides. Following reaction of the tetrapeptides with triphosgene to form the corresponding *N*-carboxyanhydride monomers, solubilization of the resulting products in organic solvents is suggestive of successful ring-closing reactions, though further syntheses on a larger scale are needed for detailed characterization studies to confirm the chemical structures. These experiments provide a foundation for future scale-up and optimization of the synthesis of multi-amino acid-containing *N*-carboxyanhydrides and for the synthesis of sequence-controlled polymers to enable technologies in a variety of fields, including medicine and engineering, among others.

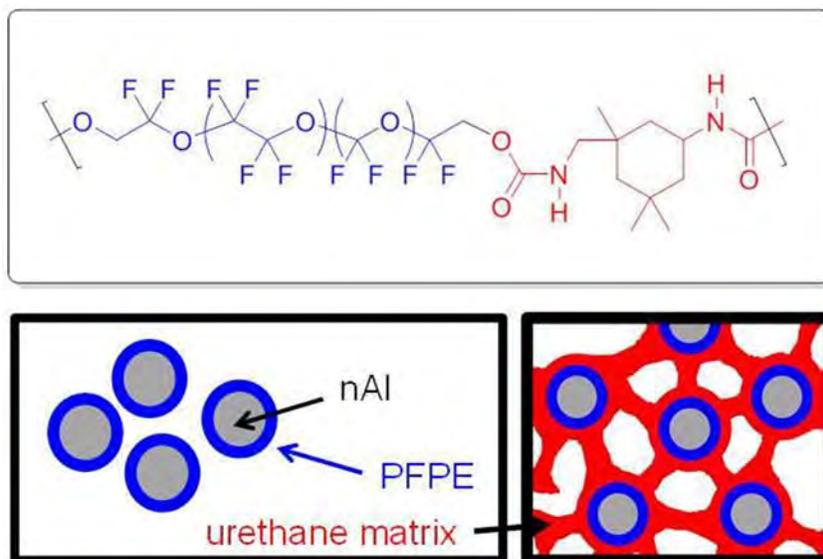


Synthesis Towards
Biomimetic Poly(tetrapeptides)

POLY 543: Interface optimization of nanoaluminum urethane composite energetic foams

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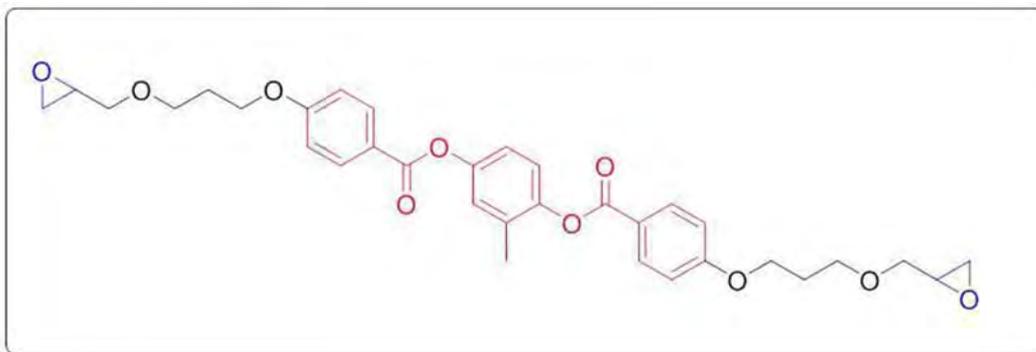
The thermite reaction between aluminum and a fluoropolymer has been well-studied as a pyrolant for a multitude of energetic applications. However, most formulations lack structural integrity to be used for a practical application. We have been investigating the utility of preparing metastable matrix composites utilizing a core/shell formulation comprising of nanometer-sized aluminum (nAl) as the fuel (the core) and a fluoropolymer coating, specifically perfluoropolyethers (PFPEs) as the oxidizer (the shell). Composites have included post-machineable thermoset molds, elastomer coatings, electrospun microfibers, and melt-processed thermoplastics. This study expands the scope of this metastable matrix composite formulation by investigating the core/shell thermite reaction in fluoropolymer-segmented, high surface area urethane foams. This work will present the preparation of the highly porous urethane foam loaded with the nAl/PFPE core/shell formulation as well as bulk physical and energetic properties.



POLY 544: Epoxy based liquid crystal elastomers for shape memory materials

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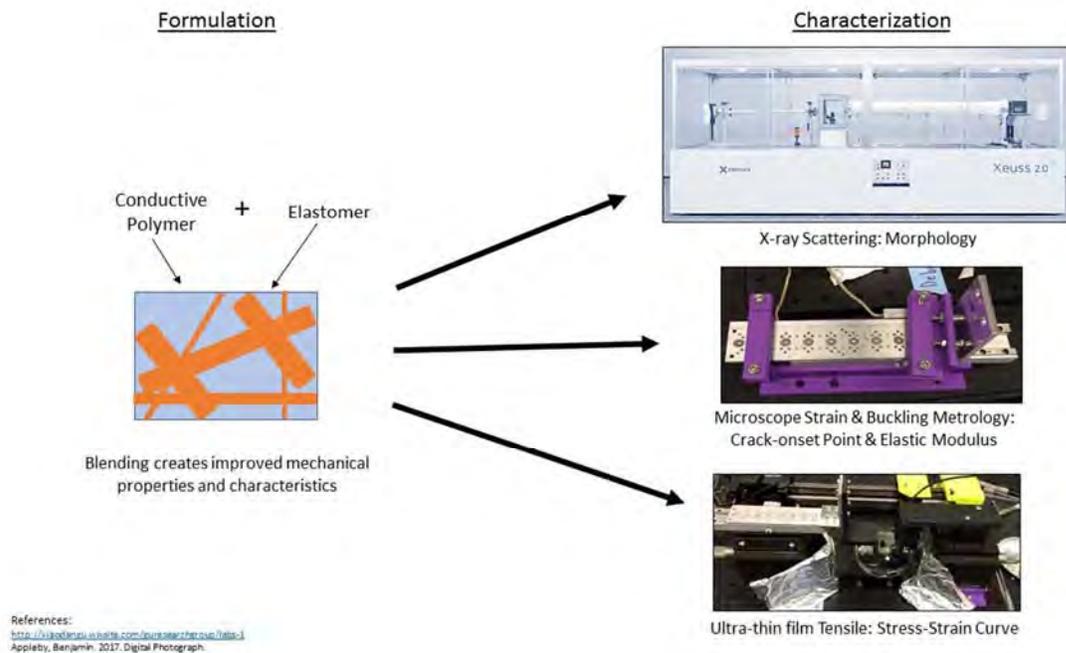
Liquid crystal elastomers (LCEs) have been receiving increased attention as a result of their shape memory properties which have far-reaching implications within materials science development that include actuatable and stimuli-responsive systems, among others. The implications of which could have reaching effects throughout the world of material science yet to be explored. In previous work, we have prepared acrylate-based LCE prepared via radical initiated mechanism which is air sensitive and requires complete penetration of the initiating energy source. This process limits scalability and reproducibility in large commercial manufacturing practices. As an alternative, we investigated a new LC elastomer via a commercial epoxide-based precursor that demonstrates insensitivity to oxygen upon curing and was shown to crosslink throughout the bulk material. A series of mechanically aligned cells of the epoxy-based polymer were produced using these materials and their optical and mechanical properties will be discussed.



POLY 545: Mechanical testing for stretchable organic thin film for electronic applications

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While mechanical testing can be completed for many polymer composites, mechanical testing of ultrathin polymer films has been limited. Specifically, conjugated polymer films used for active layers of organic electronic devices are under 200 nm. Herein, we have successfully tested the elastic modulus and crack onset strain of a stretchable organic thin film for electronic applications, and have developed a methodology for continued testing of ultrathin polymer films. To obtain both stretchability and electrical property, two polymers including a conducting polymer, P3HT (Poly(3-hexylthiophene)), and an elastomer, PIB (polysio-butylene) were blended at different weight ratios and their mechanical properties were investigated. The polymer blend was used to fabricate thin films, which were characterized through mechanical test. The thin film was floated on the water surface, then transferred onto a stress-strain tester for further stretching, which was real-time monitored by an optical microscope. In the meantime, X-ray scattering was used to determine the blend morphology, which was correlated with the mechanical performance.

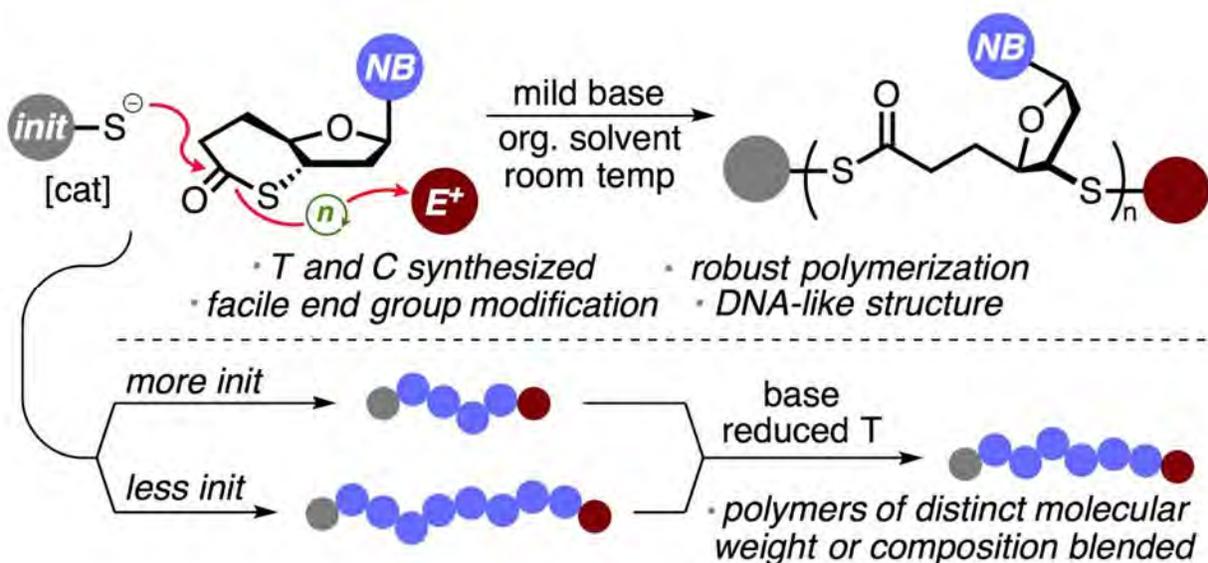


Structure-mechanical property Exploration of Stretchable Organic Ultra-thin Film for Electronic Applications

POLY 546: Dynamic, responsive DNA-like polymers

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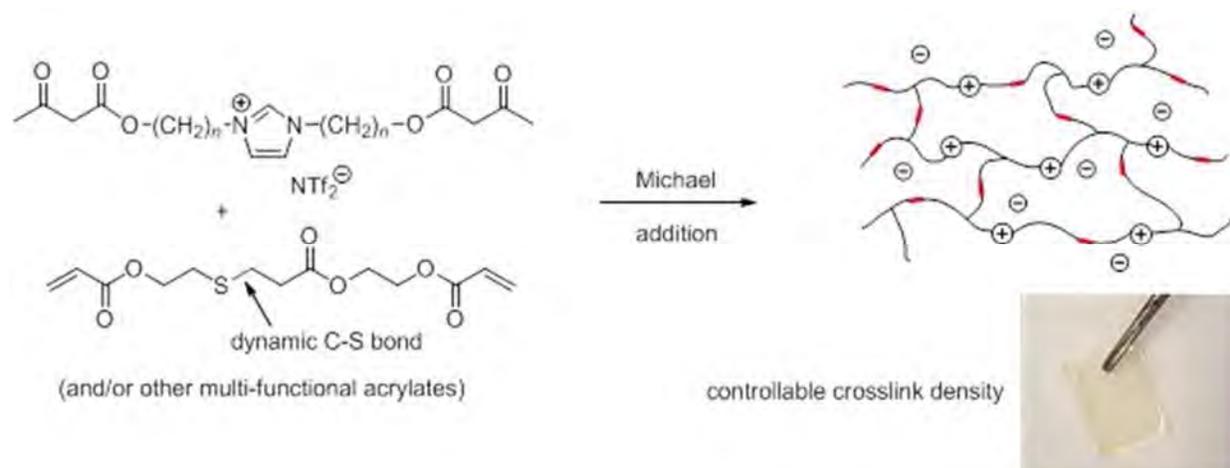
Recently we have developed synthetic routes towards the formation of thiolactone appended nucleic acids. Such thiolactones have preliminarily been shown to undergo robust ring opening polymerization to form dynamic DNA-like artificial polymers capable of rapid depolymerization, rearrangement, or responsive templation. Such polymers are anticipated, and have preliminarily been shown to bind tightly to DNA and, thus, could act as anti-sense polymers formed by template directed synthesis.



POLY 547: Dynamic thiol-Michael bonds in poly(ionic liquid) polyester networks

Samantha P. Daymon, *sdaymon@murraystate.edu*, Kevin M. Miller. Department Of Chemistry, Murray State University, Murray, Kentucky, United States

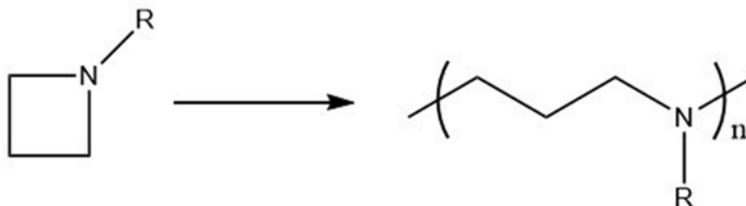
Thiol-Michael bonds have recently been shown to exhibit dynamic, self-healing properties when incorporated into non-ionic, covalently crosslinked acrylic networks. Here, a dynamic thiol-Michael bond has been incorporated into a poly(ionic liquid) polyester network in order to gauge thermoresponsive behavior as a function of mechanical and conductive properties. Base-catalyzed carbon-Michael addition polymerization between an ionic liquid-containing diacetoacetate monomer and a mixture of diacrylates (including one containing the 'dynamic' thiol-Michael bond) was employed to prepare the desired network films. Crosslink density and T_g were controlled primarily via the acrylate:acetoacetate monomer ratio. To test the rehealing potential of the materials, the films were sliced, 'rebonded' and placed in a convection oven at 100 °C for anywhere between 1-24 hours. Tensile testing (dynamic mechanical analysis) was utilized to monitor the recovery of the mechanical properties as a function of time. Several of the PILs in the study were found to break at a place away from the reseal point while recovering > 70 % of the stress and strain at break of the uncut 'original' sample. Stress relaxation and creep deformation of the rehealable PILs were also conducted and an analysis of these results will be discussed. Electrochemical impedance spectroscopy, utilizing a 4-electrode cell, indicated that the PIL polyester networks exhibited promising conductivities of 10^{-6} to 10^{-8} S/cm at 30 °C, much of which (> 80 %) was found to be recovered as a result of the rehealing process.



POLY 548: Anionic ring-opening polymerization of activated azetidines

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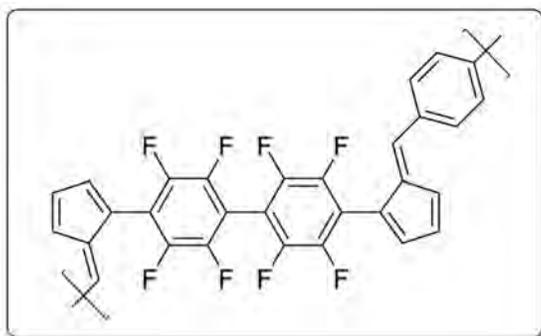
Despite their simple structure, the polymerization of strained cyclic amines is surprisingly complex. For example, azetidine exclusively polymerizes via a cationic mechanism to form hyperbranched poly(trimethylenimine) (bPTMI). In an effort to control the polymerization of azetidines, we are studying activated azetidines with electron withdrawing groups situated on the nitrogen atom. We will present data that shows that these activated azetidines undergo anionic ring-opening polymerizations to form linear polymers and these polymerizations can be controlled.



POLY 549: Fluorinated polyfulvenes for low band gap optical applications

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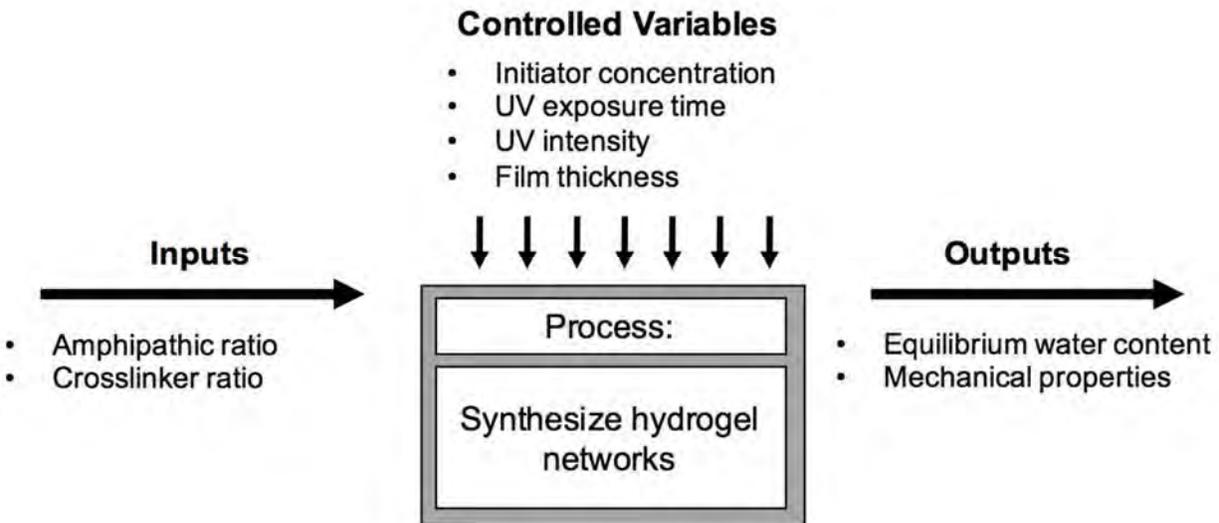
Interest in renewable energy resources has led to the continued research in highly conjugated polymeric systems as building blocks for light harvesting applications. Due to their cross-conjugated arrangement, the incorporation of intact fulvene structural units in a conjugated polymer main-chain still remains a relatively unexplored area. Small molecule studies of fulvene dyes have shown that they possess small optical band gaps. This suggests a polymer constructed of this cross-conjugated moiety could absorb the full range of UV to visible light. In this work, we have optimized a methodology to prepare partially fluorinated polyfulvenes via metal-free, step-growth coupling polymerization. The structural characterization and optoelectronic properties of these new materials will be discussed.



POLY 550: Determination of equilibrium water content in bioinspired glycopolymer hydrogel networks

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Glycopolymer-based hydrogels have potential to be used as mucosa-mimetic materials to reduce the dependency on animal tissues for drug delivery experiments. Acrylamide-based monomers functionalized with β -D-galactose saccharides (GalEAm) were synthesized by glycosylation of hydroxyethylacrylamide (HEAm) with acetobromo- α -D-galactose (AcBrGal). Dimethylacrylamide and 3-acrylamidopropyltris(trimethylsiloxy)silane was used as a model system to determine UV copolymerization parameters for crosslinking the glycopolymer hydrogels. Films synthesized under low levels of UV light intensity and shorter polymerization time (10 mW/cm² for 3 minutes) showed reduced film discoloration than films synthesized under higher UV light intensity and longer polymerization times (38 mW/cm² for 6 or 11.4 minutes) without significant changes in equilibrium water content (EWC). Based on these results, GalEAm-*co-tert*-butylacrylamide (TBA) networks with varied amphipathic ratios (90:10 GalEAm:TBA and 70:30 GalEAm:TBA) were synthesized using 10% crosslinker under a UV light intensity of 10 mW/cm² for 3 minutes. Resulting hydrogels exhibited high EWCs (86-87%) and no visible TBA domains within the films.

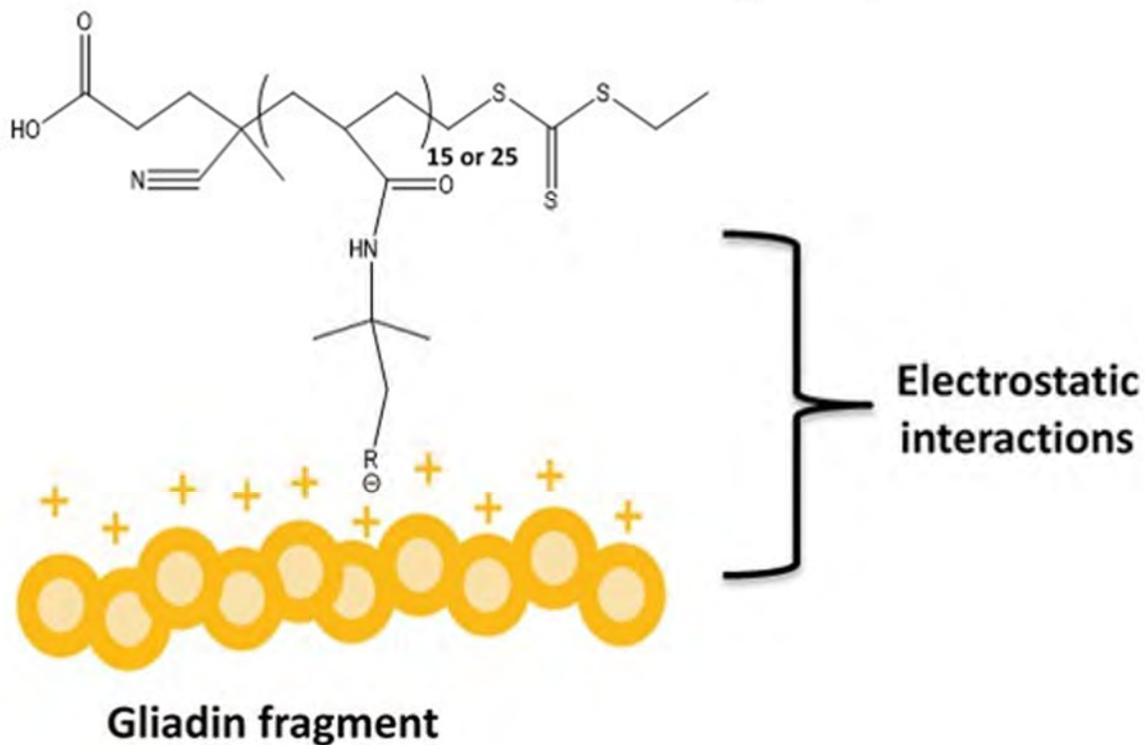


POLY 551: Synthesis of anionic acrylamide-based polymers for determination of structure/binding interactions with food-based proteins

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Onset of Celiac Disease (CeD) symptoms occurs due to an inflammatory response caused by the digestion of gluten products. Gliadin (and fragments thereof), which is a component of gluten and a known epitope, has a net positive charge at intestinal pH. While it has been reported in the literature that high molecular weight anionic polymers are able to bind to gliadin and reduce the overall inflammatory response, the mechanism of the interaction is not well understood. Previous studies in our laboratories established experimental conditions to synthesize poly(2-acrylamido-2-methylpropane sulfonate) (polyAMPS) and poly(3-methylpropyl-3-methylbutonate) (polyAMBA) at low degrees of polymerization (DP). These conditions were used to synthesize polyAMPS and polyAMBA at target DPs of 25, 15, and 5. PolyAMPS and polyAMBA were selected for use as polymer binders to gliadin and other food based proteins in order to test the effects of anionic strength and hydrophobic character on polymer/protein interactions at the molecular level for use as therapeutic agents in proteopathic diseases.

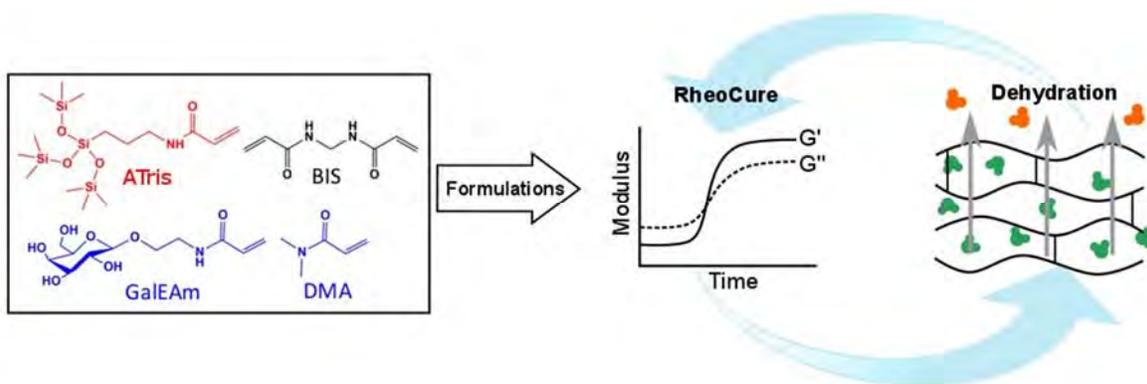
Anionic, acrylamide-based polymer, $R^{\ominus} = \text{SO}_3^{\ominus}$ or CO_2^{\ominus}



POLY 552: Monitoring the effect of crosslink density and amphipathic balance on viscoelastic property evolution in glycopolymer hydrogels using rheology

Bishal S. Upadhyay, bishalsaptusho.upadhyay@usm.edu, April L. Fogel, Sarah E. Morgan. *Polymer Science and Engineering, University of Southern Mississippi, Hattiesburg, Mississippi, United States*

Glycopolymers, synthetic analogues of naturally occurring polysaccharides that contain stereospecific pendant monosaccharide moieties, have been synthesized to mimic the inherent absorptivity and water binding propensity of naturally occurring polysaccharides. Glycopolymer hydrogels were utilized to tune structural water content in various copolymer hydrogel architectures to understand the relationship between hydrogen bonding interactions with water and the dehydration characteristics of the gels. An inverse relationship between bound water content and dehydration rate was established for these glycopolymer hydrogels. This study utilized in situ UV cure rheology to determine how the hydrogel composition influenced the evolution of the viscoelastic properties. Furthermore, the final storage modulus determined from post cure frequency sweeps was used to determine an effective crosslink density for each gel.



POLY 553: Synthesis of *p*-xylene-diisocyanide and polymerization to form poly(2,4-pyrrole-*alt-p*-phenylene)

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Polypyrrole is one example of a conjugated polymer that has many potential applications in this field, including use in batteries, organic solar cells, and chemical sensors. These polymers are very versatile; many different routes for the synthesis of polypyrroles have already been explored, and new ways to synthesize polypyrroles are constantly being developed. This work aims to synthesize poly(2,4-pyrrole-*alt-p*-phenylene) (Figure 1) using a previously unexplored method. Traditionally, polypyrroles are substituted in the 2,5 position, however this polypyrrole is substituted in the 2,4 position. This bent conformer could afford polypyrroles with unique properties. The experiment has shown successful synthesis of the diisocyanide monomer that is needed to make the target 2,4 polypyrrole. Polymerization studies are ongoing, as the right combination of ligand and copper (1) source is continuing to be tested. However, preliminary results show promise.

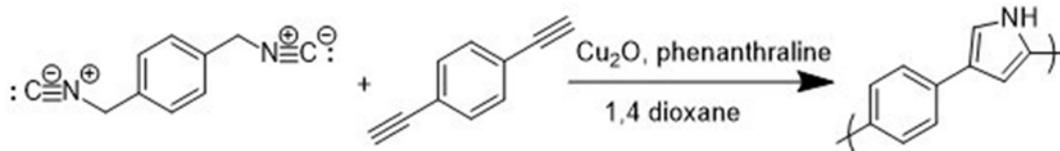


Figure 1. Proposed polymerization to obtain poly(2,4-pyrrole-*alt-p*-phenylene).

POLY 554: Synthesis of single-chain nanoparticles *via* atom-transfer radical coupling

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Atom-transfer radical coupling (ATRC) offers a method of single-chain nanoparticle (SCNP) formation using mild conditions with minimal synthetic steps. A cross-linkable monomer, dimethyl bromoethylmethacrylate (Me₂Brema), was synthesized from commercially available reagents in a one step synthesis. The monomer was then polymerized with methyl methacrylate (MMA) at 10%, 20% and 50% incorporations through reversible addition-fragmentation chain-transfer (RAFT). After polymerization, each polymer was collapsed into SCNPs *via* ATRC. Parent polymers and SCNPs were analyzed by gel permeation chromatography (GPC) in order to observe a shift in retention time. SCNPs displayed a longer retention time, indicating successful collapse of the parent polymer. Structures and incorporations of all species were verified by NMR.

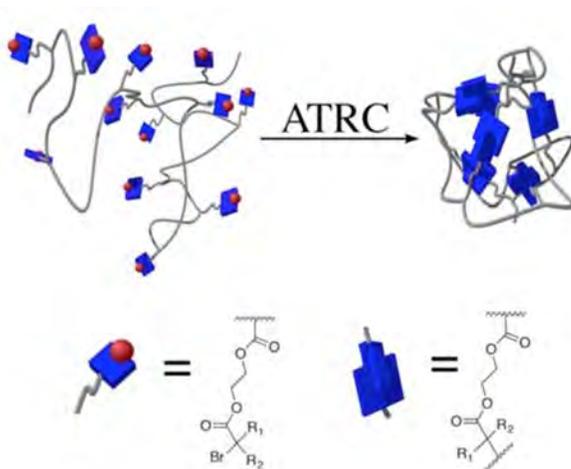
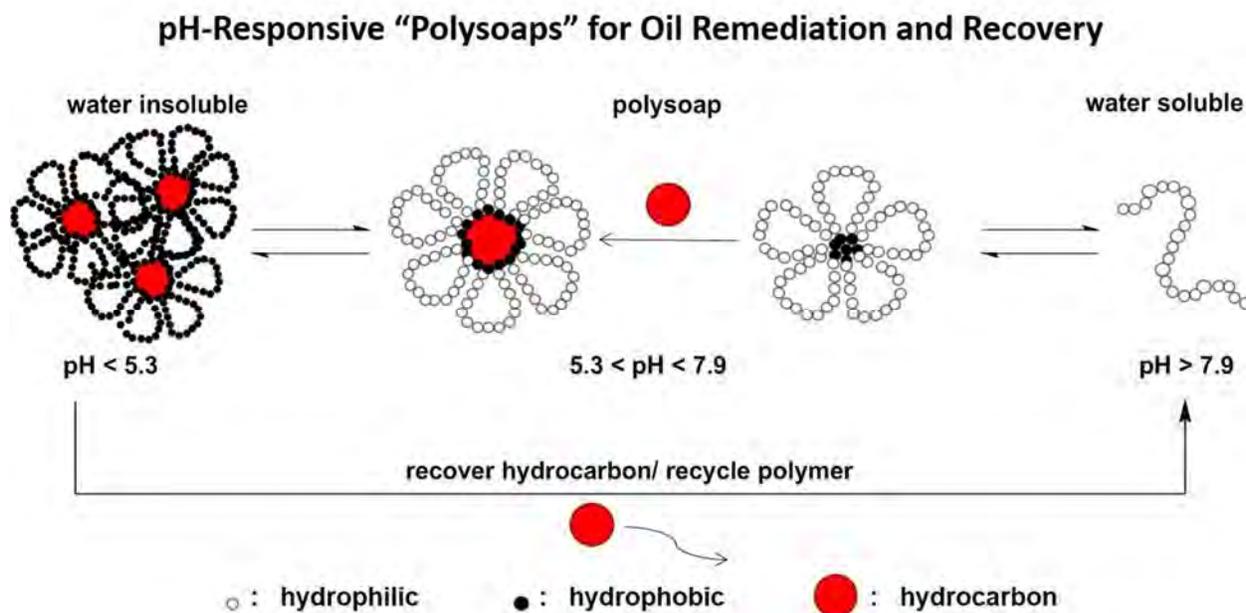


Figure 1.¹ Parent polymer with ATRC-responsive pendent groups and resulting SCNP after collapse *via* ATRC.

POLY 555: pH responsive sulfonamide-based polysoaps via RAFT copolymerization for oil remediation and recovery

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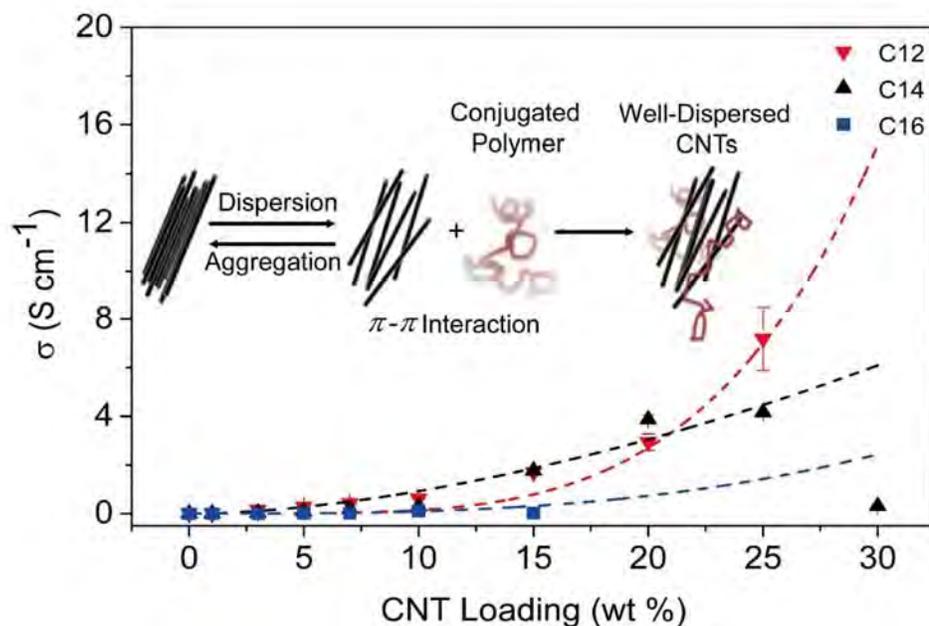
Small molecule surfactants suffer from limited efficiency in oil-spill remediation due to their inability to form micelles in dilute solution below a critical micelle concentration (CMC). Statistical amphiphilic copolymers or “polysoaps” are viable alternatives since each copolymer chain can form its own unimeric micelle with no CMC limitation. Our group has previously reported first-generation versions of these micelles capable of hydrocarbon sequestration. Those systems relied on indigenous bacteria for oil remediation and were permanently water-soluble. Our present goal is to develop second generation, stimuli-responsive systems that would allow removal of sequestered foulants as well as recycling of the “polysoaps”. In this work, we have prepared a series of “polysoaps” via the RAFT copolymerization of methacrylol sulfacetamide (mSAC) and methacrylol sulfamethazine (mSMZ). These monomers were chosen to have different pKa values (5.3 and 7.9, respectively) and thus sharp segmental solubility transitions upon ionization in water at values of $\text{pH} > \text{pKa}$. By incorporating the two sulfonamide-based monomers into a copolymer backbone, we aim to create three distinct phase responses by adjusting pH; full water solubility at alkaline pH, micelle formation at neutral pH, and phase separation at acidic pH. This tri-phasic behavior will allow for hydrocarbon sequestration and removal from water followed by hydrocarbon recovery and separation from the copolymer. The copolymer can, in principle, be recycled—potentially improving markedly the efficiency of current oil spill remediation technologies.



POLY 556: Highly conductive composites of intrinsically conductive conjugated polymers and carbon nanotubes

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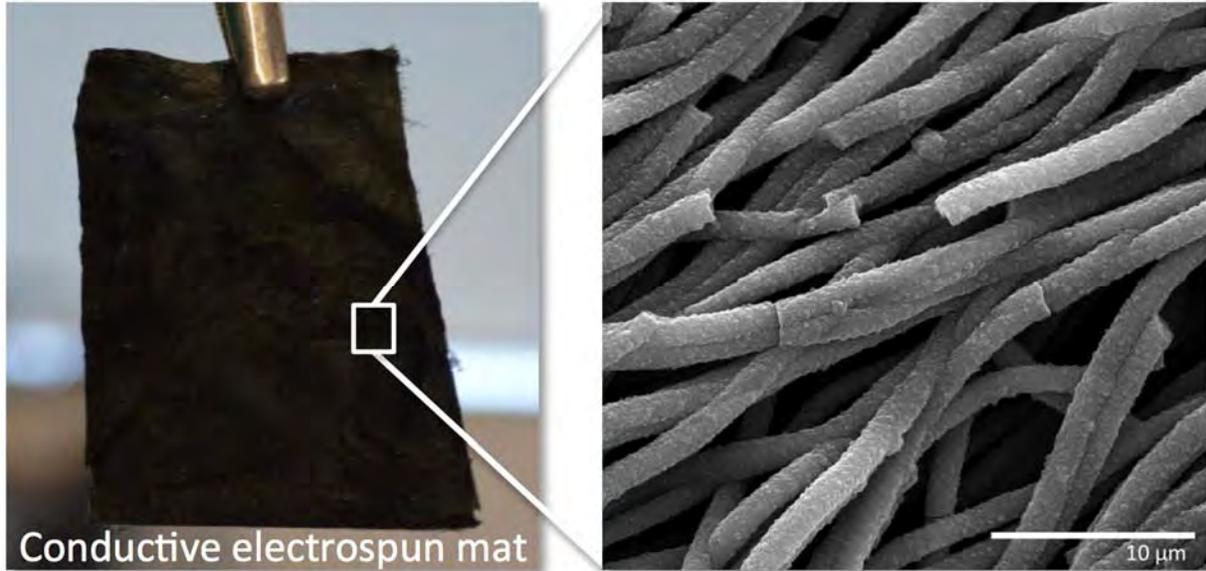
Polymer-based carbon nanotube (CNT) conductive composites are playing a pivotal role in technologies requiring light-weight structures and the integration of multifunctional properties, such as electrical conductivity, electrostatic dissipation, and electromagnetic shielding. Polymer-CNT composites often suffer from poor mechanical and electrical properties arising from electrically insulating polymer matrices with poor CNT dispersion. In this work, highly conductive composites were developed via solution processing by dispersing pristine single-walled CNTs (swCNTs) in charge neutral, intrinsically conductive polymer matrices. These composites achieved one of the highest conductivities ($\sigma = 16.5 \text{ S cm}^{-1}$ at 30 wt% swCNT) and the lowest percolation threshold ($\phi_c = 0.28 \text{ wt}\%$) reported for solution-processed neutral composites. Polymer structure-property relationships were systematically investigated by varying the polymer side chain length. Neat polymer film conductivity improved by one order of magnitude as side chain length decreased from 16 carbons ($\sigma = 0.7 \text{ mS cm}^{-1}$) to 12 carbons ($\sigma = 8.3 \text{ mS cm}^{-1}$). Moreover, these composites demonstrated unprecedented weathering stability with conductivity retained for more than one month after continuous exposure to light, air, and moisture. This work overcomes obstacles in highly conductive composite manufacturing by producing charge neutral composites with well-dispersed swCNTs and tunable electrical properties.



POLY 557: Electrospun silk fibroin for use as biomechanical actuators

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Successful implantation of engineered tissue requires that the electrical, and mechanical properties of the constructed material closely resemble that of natural tissue. Although the electrical character of conductive polymers such as poly(pyrrole) and poly(hydroxymethyl-3,4-ethylenedioxythiophene) are commensurate to the electrical character of natural tissue, the conductive polymers lack desired mechanical robustness. To resolve this issue, we have developed a method to incorporate conductive polymers into silk fibroin to form an interpenetrating network-composite of the two polymers. These composites are capable of electromechanical actuation (expand and contract), allowing the material to mimic both the structure and the function of cardiac or skeletal muscle tissue. Here, the 3D structure of silk substrates was manipulated through electrospinning to produce highly aligned, nanometer-diameter fibrous mats that are reminiscent of striated tissue. Optimization strategies will be presented that include varying polymer/dopant combinations and gold nanoparticle incorporation to improve the electrical and mechanical properties of these silk-conducting polymer composites.

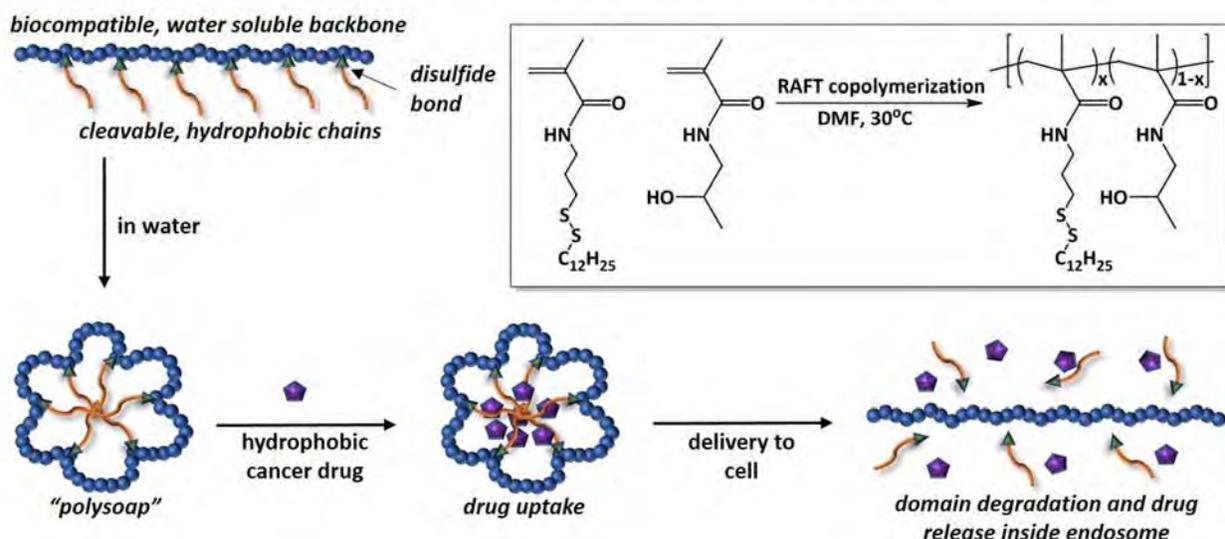


POLY 558: Responsive “polysoaps” via RAFT copolymerization to serve as therapeutic drug delivery vehicles

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Many chemotherapeutic drugs are small, hydrophobic molecules that require water-soluble, biocompatible nanocarriers for enhanced vascular circulation. Existing polymeric carriers either conjugate the drug along a copolymer backbone or sequester drugs within a protected interior domain to be delivered to specific sites in the body. Such therapeutic systems must overcome a myriad of hurdles, beginning with complex, multi-step syntheses, followed by other inherent barriers that limit the efficiency of drug delivery at the targeted site. This work aims to circumvent a number of these issues using biocompatible, stimuli-responsive polysoaps that are capable of unimeric micelle formation, hydrophobic drug delivery, and triggered release, regardless of dilution effects. These copolymers are prepared via RAFT copolymerization of N-(2-hydroxypropyl) methacrylamide (HPMA) and dodecyl disulfide propyl methacrylamide (DDPMA). This presentation will address the parameters necessary for micelle self-assembly, responsive behavior in aqueous media, and the capacity for sequestration and subsequent triggered release. The facile synthesis of these polysoaps and their ability to function at high dilution are promising indicators of their utility in future applications.

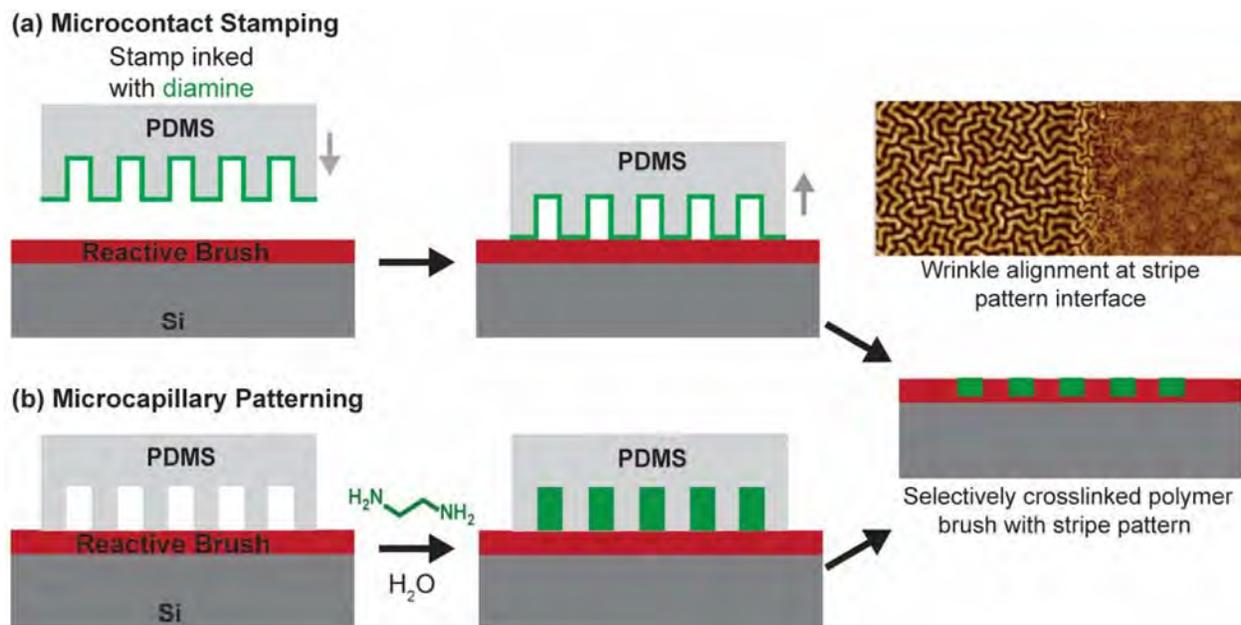
Biocompatible, Degradable “Polysoap” for Targeted Drug Delivery



POLY 559: Manipulation of wrinkle orientation in ultrathin polymer brush surfaces via soft lithography techniques

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Polymer surfaces with well-defined patterns at multiple length scales are desired for applications in controlled adhesion, hydrophobic surfaces, cell alignment, and microelectronic devices. Recently, there has been growing interest in the design of hierarchical polymer bilayer (i.e. stiff skin on elastomeric substrate) surfaces using surface wrinkling to generate patterned surfaces. The fabrication of patterned polymer surfaces has been accomplished by various techniques, such as laser ablation, etching, chemical deposition, and soft lithography. Recent efforts in our group reported a simple route to engineer wrinkled ultrathin polymer brush surfaces using post-polymerization modification (PPM), where the length scale (nanometers to microns) was tunable via post-modification reaction time. However, the application of isotropic stress to a bilayer polymer brush surface with isotropic boundary conditions typically results in the formation of wrinkles with no preferred orientations. For many applications, ordered and aligned surface structures are desired. Herein, we report our recent efforts to manipulate wrinkle orientation utilizing soft lithography techniques to template the PPM process. This presentation will highlight our efforts using microcontact stamping and microcapillary patterning techniques during the PPM reaction to guide wrinkle formation and orientation.

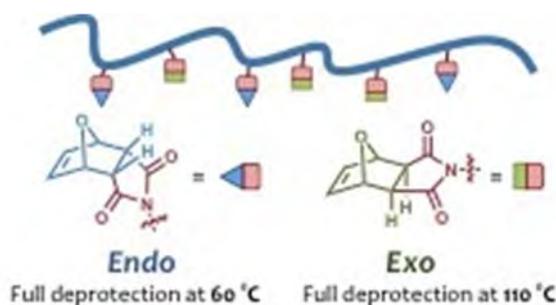


Scheme 1. Soft lithography approaches to tailor the wrinkling process in ultrathin polymer brush surfaces.

POLY 560: *Endo* vs. *Exo*: Temperature tunnable functional building blocks for highly efficient polymer modification

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The development and application of a novel *endo*-protected maleimide polymer building block is reported. The *endo* conformer undergoes deprotection at temperatures approximately 50 – 60 degree Celcius below the *exo* derivative, enabling facile and selective polymer modification. This facilitates a simple, yet powerful approach to quantitatively and selectively introduce functional maleimide handles with exceptional molecular precision via simple temperature modulation.

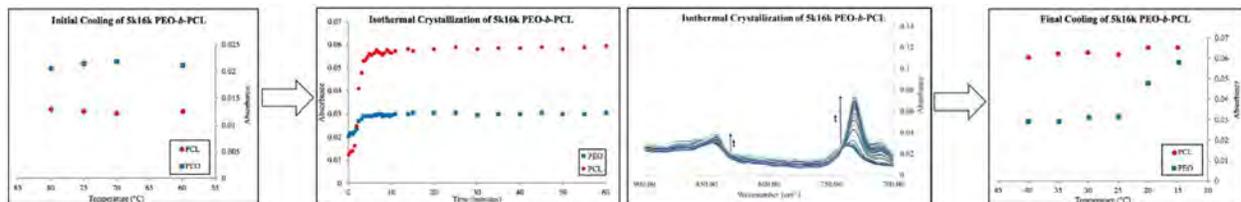


Endo vs. *Exo*: Deprotection temperatures

POLY 561: Block crystallization mechanisms of PEO-b-PCL as a function of weight fraction and isothermal crystallization temperature

Cole W. Tower, *coletower97@gmail.com*, Ryan M. Van Horn. Chemistry, Allegheny College, Meadville, Pennsylvania, United States

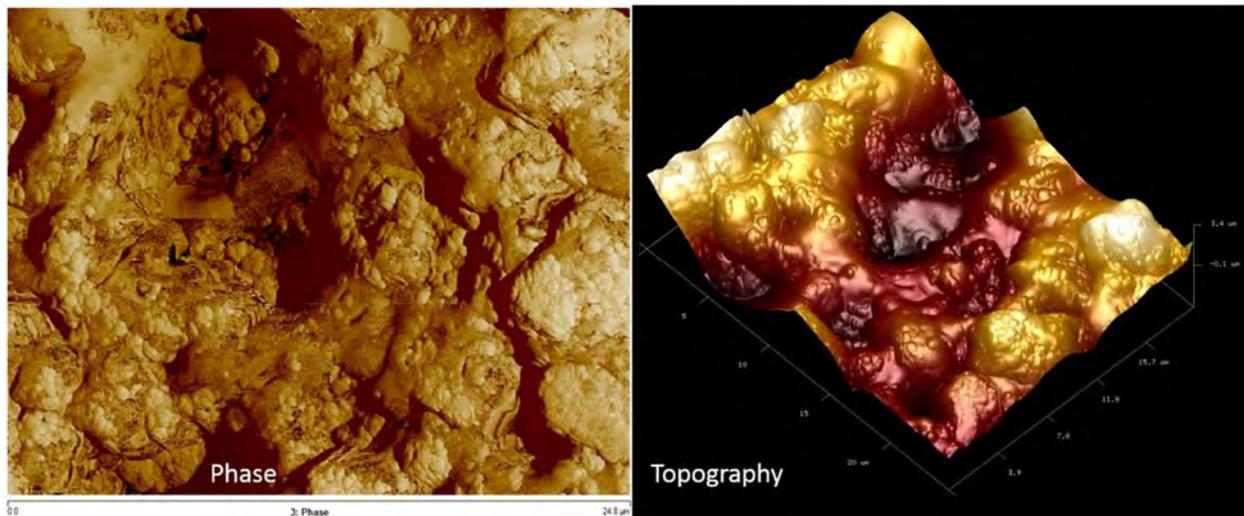
In diblock copolymer systems with blocks of similar melting temperature, such as poly(ethylene oxide)-*block*-poly(ϵ -caprolactone), the block crystallization mechanism can be manipulated by altering the isothermal crystallization temperature or relative block length. Two crystallization mechanisms exist: coincident, where both blocks nucleate and crystallize nearly simultaneously, and sequential, where the crystallization of the second block cannot crystallize under the same conditions as the first. DSC and TD-FTIR experiments were conducted using PEO-*b*-PCL samples to better understand the boundary between these block crystallization mechanisms. In each case, the sample was held at an isothermal crystallization temperature (T_c). Upon finishing the isothermal crystallization period, the sample was cooled to observe a coincident or sequential block crystallization mechanism. In symmetric and near symmetric block length systems ($w_f \approx 0.50$), coincident crystallization was observed at all T_c s. In asymmetric systems ($0.50 > w_f > 0.65$), the block crystallization mechanism may be manipulated to be sequential or coincident depending on the T_c . In largely asymmetric systems ($w_f > 0.65$), a sequential block crystallization mechanism was always observed.



POLY 562: Plasma treatment of rough polymer surfaces to achieve increased diffuse reflectance

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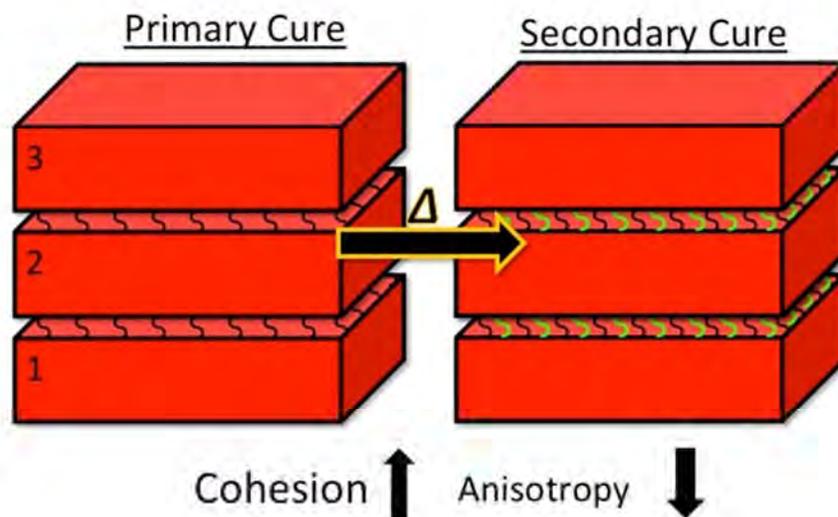
Plasma treatment has previously been employed to increase diffuse reflectance of smooth polymer surfaces. We are investigating whether plasma treatment can be employed to add additional multiscale roughness to an already rough polymer coating in order to increase the diffuse reflectance. During development of a sensor that required a flat black contrast material, several candidate coatings were identified with each having a total % reflectance of 2-3% across the wavelength range of interest. All showed some increase in total reflectance with weathering indicating likely erosion of the multiscale surface roughness that is critical for high diffuse reflectance. AFM phase and topographic data shown below for one of the coatings illustrates this multiscale roughness. Coating surfaces with and without plasma treatment were characterized with FTIR, AFM, and SEM before and after outdoor weathering. Total reflectance and diffuse reflectance were measured before and after outdoor weathering to correlate changes in surface topography and chemistry with plasma treatment condition and changes in optical properties.



POLY 563: Cohesion in layered polymer networks prepared by stereolithography

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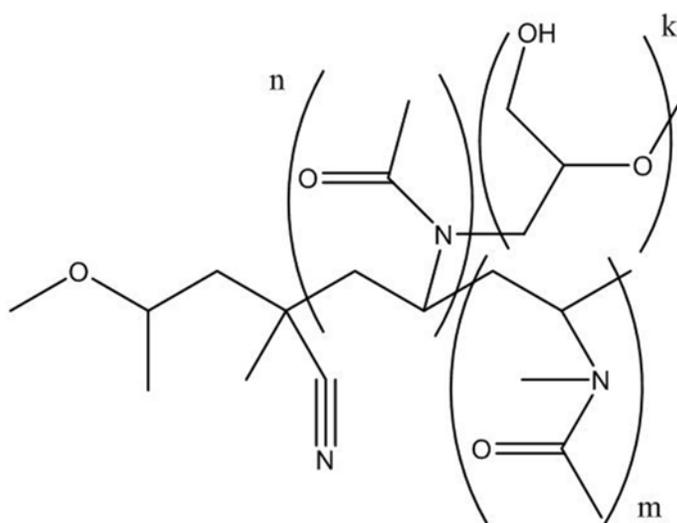
Layered polymer networks demonstrate anisotropic bulk-mechanical properties due to the layer-by-layer approach used in additive manufacturing. These layered structures have two distinct networks driving the properties: the bulk layers and the interfaces between them. Monomer loading level and number of interfaces are investigated to understand their effects on rheological and thermomechanical properties. These properties were quantified using parallel plate rheology and Dynamic Mechanical Analysis (DMA) to elucidate the difference between network properties in the bulk layers and the interface between layers. Increasing monomer loading level corresponded to increased resin viscosity. DMA showed a decrease in the $\tan \delta$ peak and a broadening β -transition peak as the number of interfaces in the sample increased. The effects of a thermal post cure on the layered polymer networks were studied using DMA and were found to reduce the intensity of the β -transition. These findings provide evidence that the bulk layers and the interface between layers exhibit distinct network properties, suggesting that DMA may serve as a method for measuring interface properties in layered polymer networks.



POLY 564: Phosphazene-base promoted ring-opening polymerization of 1,2-butylene oxide and ethoxyethyl glycidyl ether initiated by secondary amides

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We investigated the phosphazene base tBuP4 promotion of the ring opening polymerization (ROP) of 1,2-butylene oxide and ethoxyethyl glycidyl ether initiated by secondary amides. Specifically, we synthesized linear polymers and copolymers as well as grafted copolymers. Of particular interest was the range of secondary amides which could be deprotonated by tBuP4 to successfully initiate a polymerization, the presence of transfer or side reactions, and the kinetics of the polymerizations. Though there were significant differences in the polymerization rates, narrowly disperse polymers were obtained in high yield, as confirmed by size exclusion chromatography and matrix assisted laser desorption ionization time of flight mass spectrometry. Similar results were obtained for phosphazene base tBuP4 promoted initiation from copolymers.

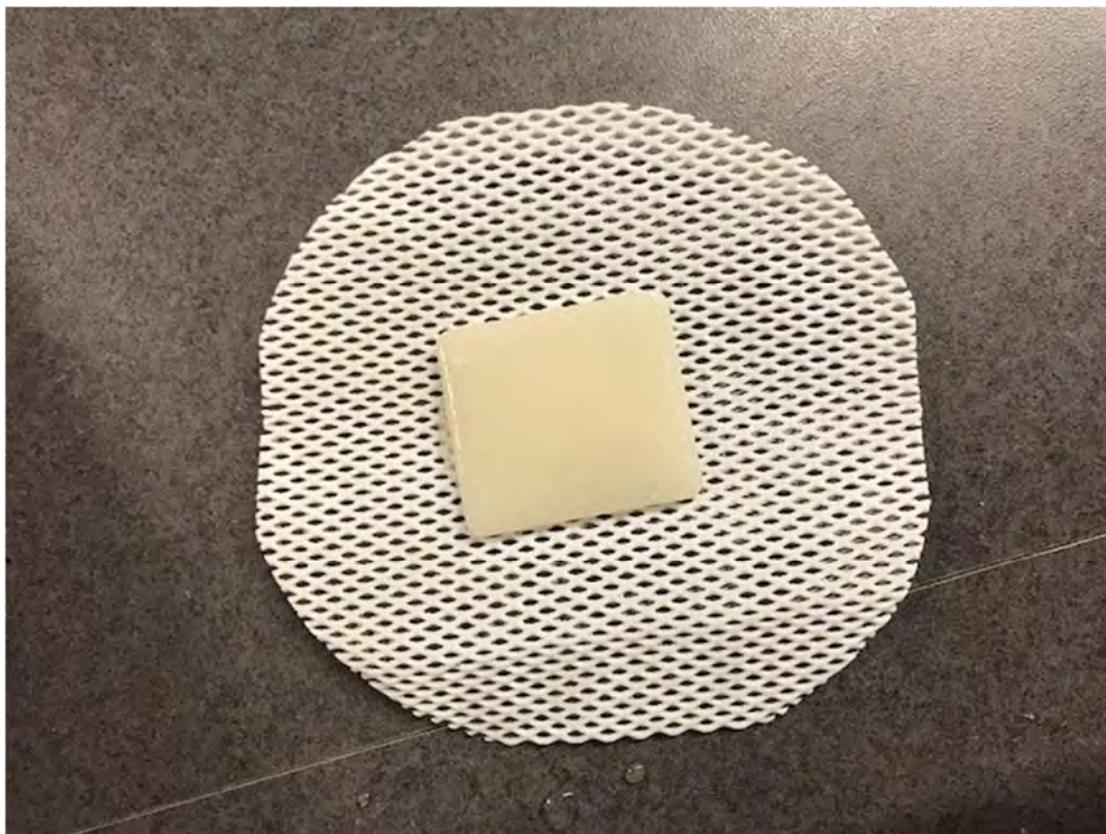


MADR-E10B-BO Grafted Copolymer

POLY 565: Zinc oxide nanoparticle composites from keratin, cellulose and chitosan: Antimicrobial properties and synthesis

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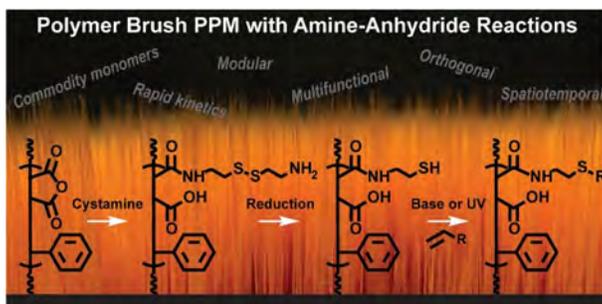
We have developed a new method to synthesize biocompatible films from cellulose (CEL), chitosan (CHI), keratin (KER) (from chicken feather, hair or wool), and Zinc Oxide nanoparticles (ZnONPs) for biomedical application. An ionic liquid, butylmethylimidazolium chloride (BMIm+Cl⁻), was used as the sole solvent to dissolve the proteins, polysaccharides and ZnO, and since used (BMIm+Cl⁻) was also recovered for reuse. The method is green and recyclable. FTIR results show that KER, CEL and CS remained chemically intact in the composites. X-ray diffraction and SEM results indicate that ZnONPs with size of 35-40 nm is homogeneously distributed in the composites. Results of bioassays indicate that the composites are effective antimicrobial against a wide range of bacteria and fungi including antibiotic resistant bacteria such as methicillin resistant *S. aureus* (MRSA) and Vancomycin-resistant *Enterococcus* (VRE). More importantly, the composites are completely biocompatible. Taken together, the composites possess all required properties for use as high performance materials including dressing to treat chronic ulcerous and infected wounds of diabetes.



POLY 566: Post-polymerization modification and wrinkling of styrene-maleic anhydride copolymer brushes

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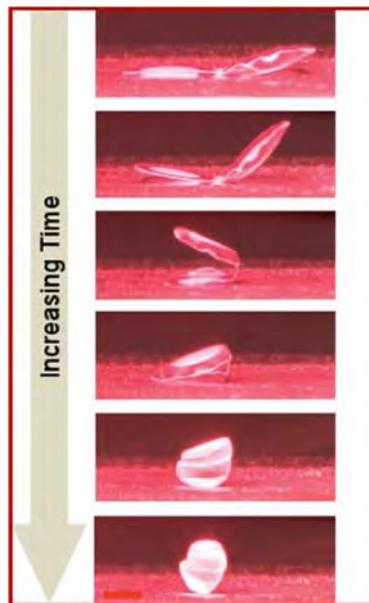
Post-polymerization modification (PPM) has been broadly employed to achieve functional polymer brush surfaces via immobilization of functional moieties on the brush using efficient organic transformations. Here, we demonstrate the amine-anhydride reaction as a modular PPM route to functional brush surfaces using poly(styrene-maleic anhydride) (pSMA) copolymer brushes as a platform. The amine-anhydride reaction on pSMA surfaces proceeds to high conversions, with rapid kinetics, under ambient reaction conditions, and exploits a readily available library of functional amines. Using cystamine as a modifier, a convenient route to thiol-functionalized brushes was developed that enables sequential PPM modifications with a large library of alkenes using both base-catalyzed thiol-Michael and radical-mediated thiol-ene reactions. The high-fidelity of the PPM reactions was demonstrated via the development of multifunctional, micropatterned brush surfaces.



POLY 567: Spheres from flat polymer sheets using only light

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Shape-changing structures have various applications ranging from devices for non-invasive surgery to deployable satellite systems. While projecting spheres onto 2D sheets is relatively straightforward (yet not flawless) – and has been practiced by cartographers for centuries – converting a flat surface to a spherical shape is a formidable challenge. We generate spheres out of flat sheets by printing ink patterns on pre-strained polystyrene sheets using an inkjet printer. These sheets are pre-strained to shrink by ~55% when heated above ~103°C, which is the material's activation temperature. Samples are heated on a hot plate to ~90°C and an IR or LED light is irradiated on the surface. The black ink on the surface of the material absorbs the light and heats up faster than the transparent regions of the polymer. Previous research has focused on patterning these sheets with black ink to locally control the material's shrinkage and produce desired shapes such as cubes, pyramids, curved panels, and grippers. This work explores the use of different ink distribution patterns to create tunable spherical structures. Potential applications include spherical encapsulation and grippers.



POLY 568: Synthesis of two fluorescent conjugated polymers with urea receptors as chemical sensors to detect fluoride ions

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Fluorescent conjugated polymers (FCPs) have gained a lot of attention because of their ability to act as sensors to detect various substances in chemical and biological systems. Their conjugated backbones provide excellent electron migration and signal amplification. These polymers fluoresce in the presence of analytes and allow determination at very low concentration. Urea receptors are known to be selective for fluoride anions thanks to the formation of hydrogen bonding with the target species. In this work, two fluorescent conjugated polymers, phenylurea-PPE and anthraceneurea-PPE, were synthesized and characterized for their use as potential fluoride sensors. Each polymer is composed of a linker monomer and a receptor site attached to the conjugate polymer molecule. Characterization of these new chemical sensors also provides insight into the photophysical properties of two different fluorophores: the phenyl ring and the anthracene unit as polymer building blocks for FCPs.

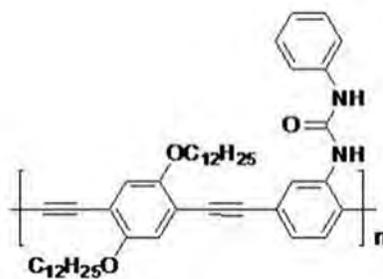


Figure 1: phenylurea-PPE

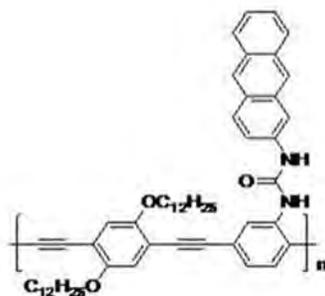


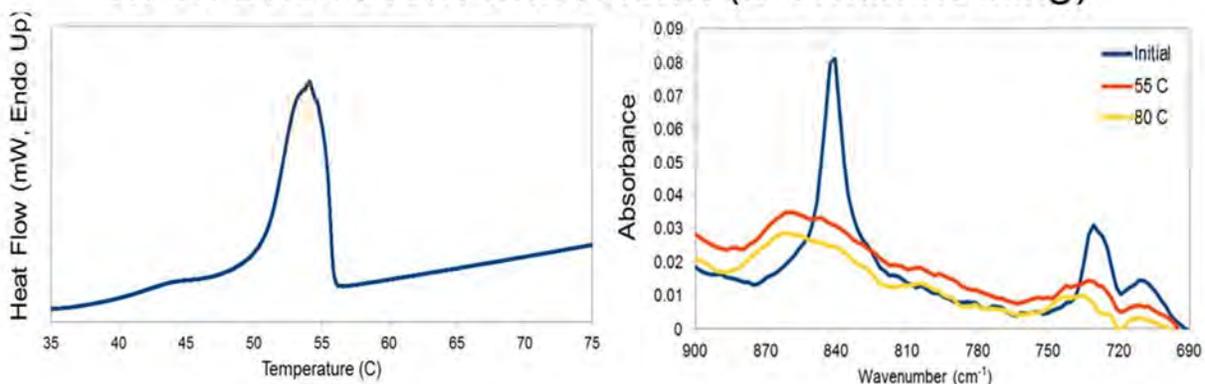
Figure 2: anthraceneurea-PPE

POLY 569: Solvent effects of melting behavior of diblock copolymers of equal weight fractions

Dana O'Connor, *deo100@msn.com*. Chemistry, Allegheny College, Meadville, Pennsylvania, United States

Recent work has been lacking in studying the behaviors of copolymers with equal weight fractions, and the melting behavior of these copolymers may be related to their crystallization properties and behaviors. Equal weight fractions (5k5k, 8k8k, and 10k10k) of the block copolymer poly(ethylene oxide)-block-poly(caprolactone-ethylene glycol) (PEO-b-PCL) were dissolved in 2% w/w solutions of several different solvents: acetone, toluene, methyl ethyl ketone (MEK), and chloroform. The samples were then melted and analyzed using both differential scanning calorimetry (DSC) and Fourier transform-infrared spectroscopy (FT-IR), both at a rate of 20°C/min. The DSC was used to determine if the blocks had separate melting temperatures in each solvent or if they melted simultaneously. Analysis of the characteristic FT-IR peaks for each block (840 cm⁻¹ for PEO and 735 cm⁻¹ for PCL) determined the melting temperature for each block and whether the melting was simultaneous or not. The melting behavior in each solvent was compared to the general crystallization behavior in each solvent. PCL melted first in acetone and MEK while PEO and PCL melted simultaneously in toluene and chloroform. Further work involved heating the samples in the solvents that had separate melting temperatures (acetone and MEK) to the lower experimental melting temperature at a rate of 20°C/min in the FT-IR and held for 15 minutes at that temperature. The spectrum was then analyzed to see if the second block would melt after being held at that temperature, which determined whether the separate melting phases were time or temperature dependent.

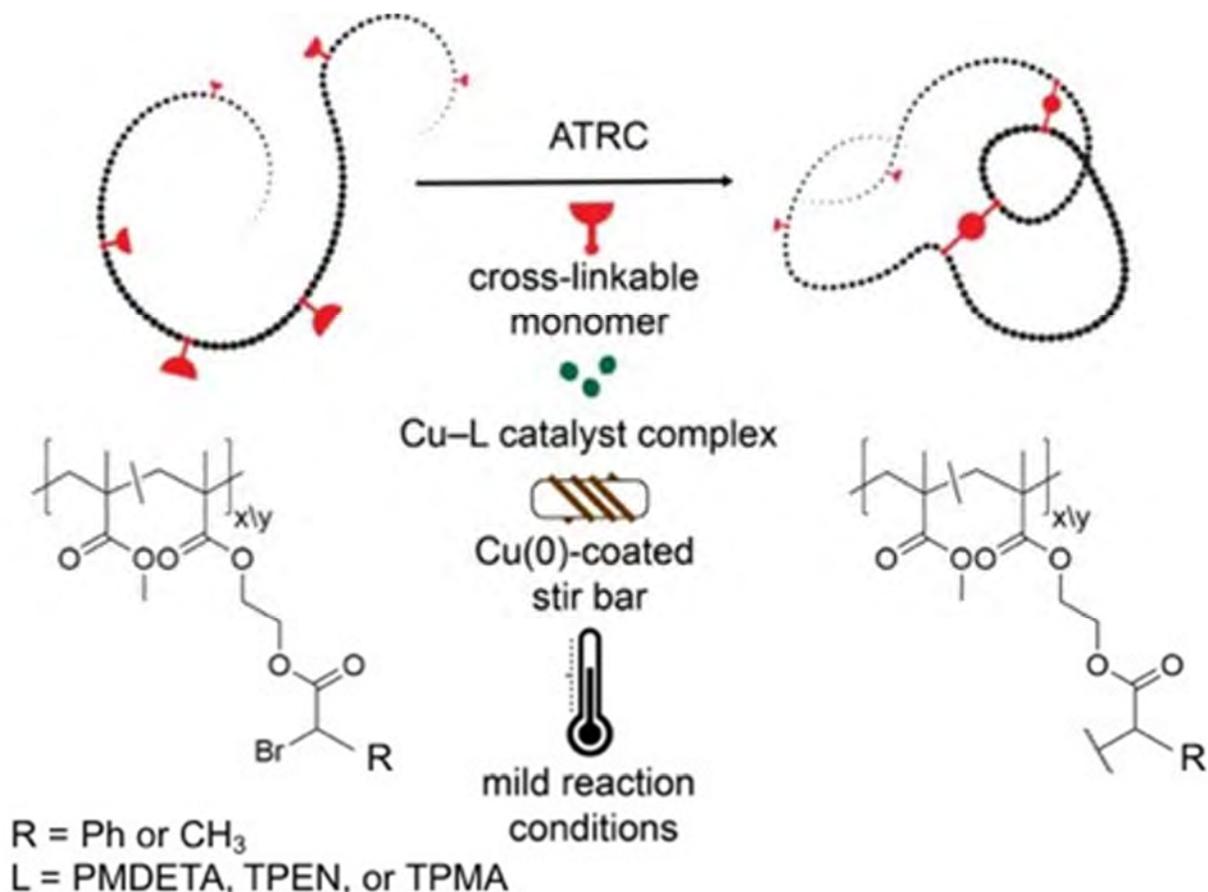
5k-5k Dried From Chloroform (2°C/min heating)



POLY 570: Synthesis of single-chain nanoparticles under various ATRC reaction conditions

Courtney Leo¹, cl2009@wildcats.unh.edu, Elizabeth R. Bright¹, Claudia Willis¹, Ashley Hanlon¹, Erik B. Berda². (1) Chemistry, University of New Hampshire, New Fairfield, Connecticut, United States (2) Department of Chemistry, University of New Hampshire, Durham, New Hampshire, United States

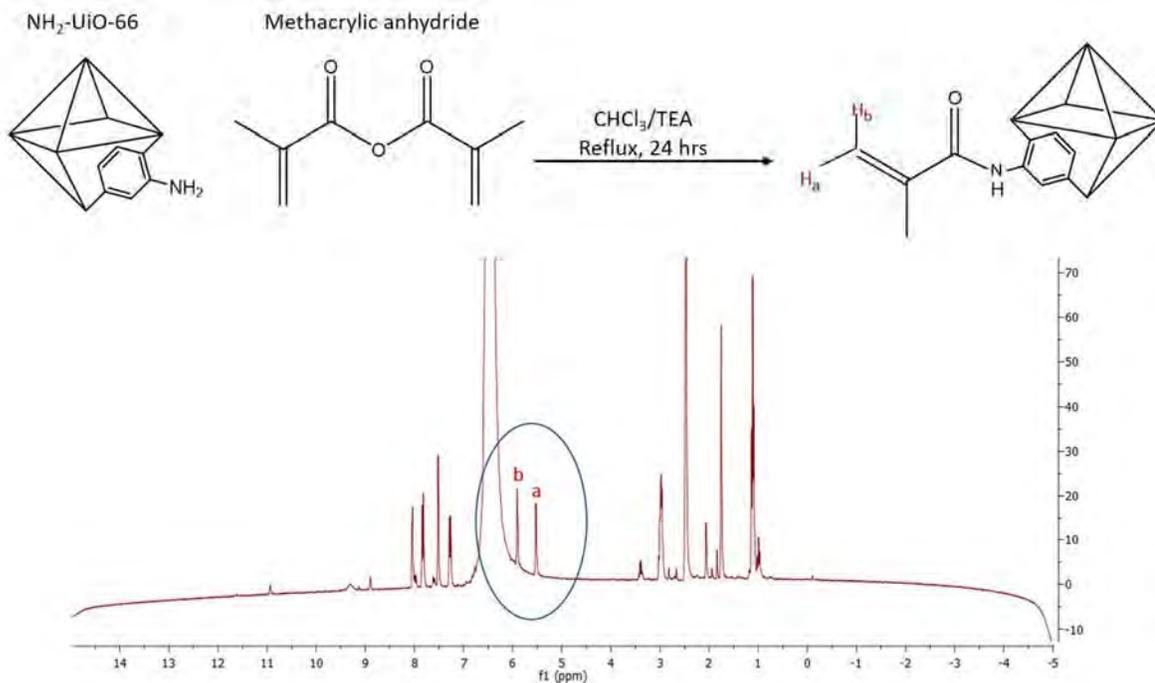
Single-chain nanoparticles (SCNP) are a class of functional nanomaterial formed by the intramolecular cross-linking of polymer chains. Atom-transfer radical coupling (ATRC) is a promising synthetic route to SCNP and other specialized macromolecules; however, limitations in our current understanding of the key design parameters and ideal reaction conditions remain a barrier to the widespread implementation of this technique. To address these concerns, we have systematically examined the formation of SCNP by ATRC, varying the chemistry of the cross-linkable unit, length of the parent polymer, and ligand for the copper catalyst. The results of this study are expected to facilitate the use of ATRC chemistry in the design of both SCNP and a broad range of controlled nanoarchitectures.



POLY 571: Investigating the relationship between MOF modification and polymer-filler compatibility in thiol-ene based mixed matrix membranes

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This project focuses on the synthesis of metal-organic frameworks (MOFs) and their implementation into thiol-ene polymer membranes to aid in the separation of carbon dioxide (CO₂) from various gases. Membrane-MOF interactions will be studied to better understand methods of improving polymer-filler compatibility in mixed matrix membranes (MMM). Conventional MOF-5, MIL-53, and UiO-66 have been synthesized as “benchmark” MOFs. Amino-functionalized analogues of each MOF have also been synthesized. Proton NMR spectroscopy confirmed the successful post-synthetic modification of amino-UiO-66 with methacrylic anhydride to yield acrylamide functionalized UiO-66. Acrylamide functionality adds the potential of grafting thiol polymer to MOF surfaces during the UV-curing process for membrane fabrication. Interfacial compatibility between MMM continuous and discrete phases will be observed through scanning electron microscopy.

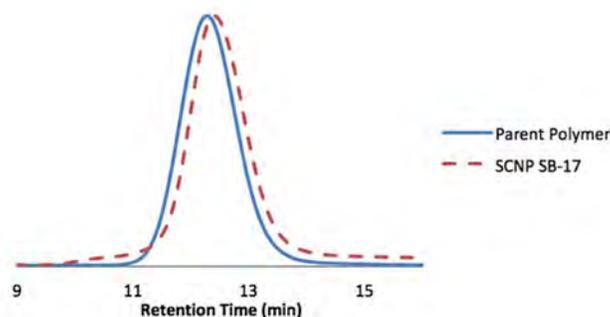
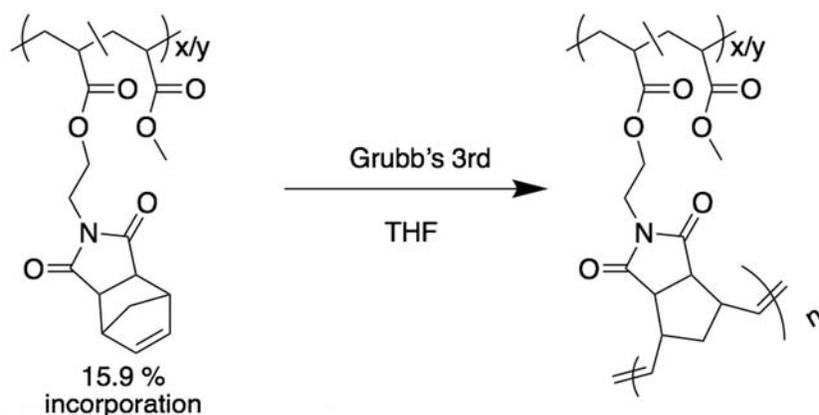


Confirmation of successful amidation reaction to modify amino(NH₂)-UiO-66.
Performed using ¹H-NMR (300 MHz)

POLY 572: Fabrication of polymer nanoparticles via intrachain ring-opening metathesis polymerizations (ROMP)

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Single-chain nanoparticles (SCNP) present a synthetic route to feature-rich macromolecules. These three-dimensional nanomaterials are prepared by the intramolecular cross-linking of polymers decorated with active pendants. This collapse process results in the reduction of the hydrodynamic radius of the polymer. In this work, a dually-functional norbornene imide monomer was prepared. The design features two orthogonal polymerizable units, the first of which can undergo reversible addition fragmentation chain-transfer (RAFT) polymerization to produce a primary polymer structure, and the second of which can undergo ring opening metathesis polymerization (ROMP) producing a secondary structure through cross-linking. The monomer was then incorporated in varying percentages to a methacrylate backbone using RAFT; examples with 15, 30, and 50 percent functional incorporation were prepared and collapsed using Grubb's 3rd generation catalyst. An increase in retention time was observed by GPC, suggesting a decrease in the hydrodynamic radius, which is consistent with the formation of SCNP. The effect of incorporation on collapse efficiency was examined.



POLY 573: Microwave assisted synthesis of polysuccinimide and polyaspartic acid for second semester organic chemistry students

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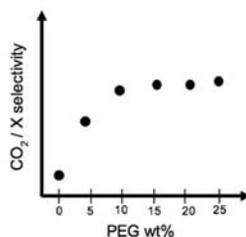
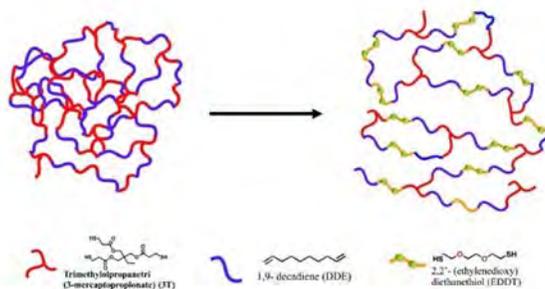
In reflection on the American Chemical Society Curriculum Guidelines on Undergraduate Degrees, the Chemistry Department at Armstrong State University has made including polymers in the undergraduate curriculum a focal point. Previously, with the assistance of undergraduate research students, we improved the safety and implementation of a second semester organic chemistry laboratory protocol for polymerizing aspartic acid (AA) into polyaspartic acid (PAA) through a polysuccinimide (PSA) intermediate. Here we report the continuation of this polymer-centric project by incorporating microwave assisted synthesis into the protocol. This adaptation will serve to expose students to state of the art equipment and additional learning objectives associated with this type of instrumentation. Since, the conversion of PAA to PSA is conveniently adapted to microwave synthesis, we focused on optimizing, with regard to student knowledge, technique and time, the polymerization of AA and subsequent workup to yield PSA. Ultimately, we found that sulfolane with a catalytic amount of phosphoric acid was suitable for efficiently converting AA into PSA in under 1.5 hours (prep and reaction time). Sulfolane turned out to be critical to the reaction due to its high boiling point, which is paramount for the polymerization to occur, and its solubility in water, which is necessary for a trituration/purification step. While there are additional details to workout, specifically with regard to time constraints, we have made and report here our promising progress towards implementing a new lab in our curriculum and hope that others find our efforts beneficial as well.



POLY 574: Thiol-ene networks containing polyethylene glycol (PEG): Determination of minimum PEG content to achieve maximum CO₂ gas solubility/selectivity

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Polyethylene glycol (PEG) based membranes have been studied and employed for separation of CO₂ from the light gases such as N₂, O₂, CH₄, H₂ etc. In addition to its high critical temperature, CO₂ can weakly interact with polar PEG moieties and these two factors result in far greater solubility and permeability of this 'acidic' gas as compared to other light gases. Previously we demonstrated the use of UV-curable thiol-ene click chemistry to prepare highly gas permeable, elastomeric network membranes which, however, contained rather large loadings of PEG varying from 38 wt% to 67 wt%. Interestingly, CO₂ gas solubility/selectivity of these membranes were comparable regardless of the PEG content used. So, we hypothesized that CO₂-philic effect of these membranes leveled off at high PEG content. The aim of this project was to determine the minimum amount of PEG which has to be incorporated to achieve the maximum CO₂ gas solubility/selectivity effect. For this purpose, an aliphatic diene was crosslinked via photopolymerization with a trifunctional ene, which was partially replaced with a PEG containing dithiol while maintaining 1:1 thiol-ene stoichiometry. This modification protocol enabled exploring the networks with lower PEG content varying from 0 wt% to 24 wt%. Gas permeation measurements demonstrated that CO₂ gas solubility/selectivity increased with PEG weight content reaching the maximum effect at about 10 wt%. Increasing PEG content in beyond 10 wt%, however, produced no further changes in CO₂ gas solubility/selectivity in accord with our hypothesis.



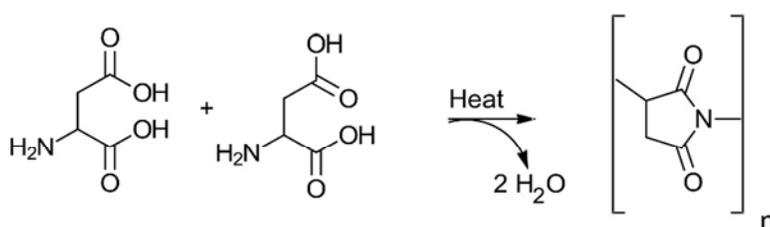
CO₂ selectivity as a function of PEG wt%

POLY 575: Poly(Aspartic Acid) PAA in the undergraduate curriculum: A multi-course approach

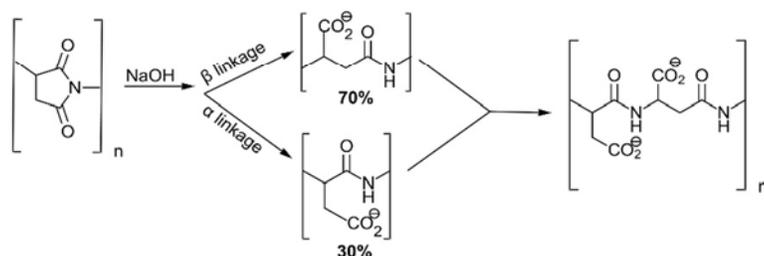
Mitch Weiland, *mitch.weiland@armstrong.edu*, Nicole Davis, Sarah E. Gray, William Hiester. Chemistry and Physics, Armstrong State University, Savannah, Georgia, United States

Recent changes to the ACS-certified bachelor's degree have called for mandatory instruction in polymers and macromolecules. In order to satisfy this requirement, we have incorporated polymeric themed laboratory exercises throughout our curriculum. One multi-course polymeric project involves the synthesis, characterization, and enzymatic degradation of poly(aspartic acid) (PAA), a biodegradable water-soluble polymer that is of interest because it has the potential to replace less environmentally friendly polymers due to its chemical and physical properties. In our curriculum, students synthesize PAA in organic chemistry and subsequently pass their products to the biochemistry and instrumental laboratories, where it serves as a substrate for poly(aspartic acid) hydrolases (PAAH) biodegradation. In the biochemistry laboratory, students express PAAH in bacteria, purify the protein using a Ni-NTA column, and characterize it by determining unit activity, temperature profiles, and enzyme activity in the presence of inhibitors. In the instrumental laboratory, PAAH degradation efficacy is assessed by characterizing the products with gel-permeation chromatography (GPC). Notably, students gain invaluable experience with techniques that are utilized in both the polymer and pharmaceutical industries. Herein, we describe these biochemistry and instrumental laboratory exercises that will allow students gain in-depth knowledge of a single polymer in a breath of courses.

Thermal polymerization of aspartic acid to form intermediate polysuccinimide.



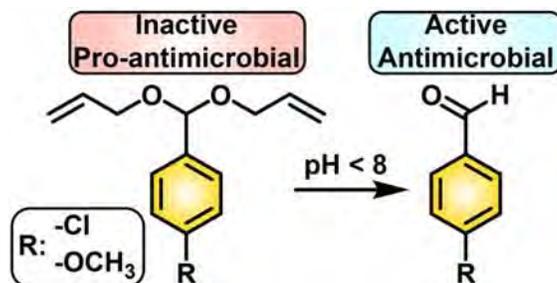
Hydrolysis of polysuccinimide to form polyaspartic acid.



POLY 576: Thiol-ene photopolymerization as a facile route to pro-antimicrobial polymer networks with degradable acetals

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Antimicrobial resistance is an escalating crisis that threatens the sustainability of public health and agricultural ecosystems. As the effectiveness of antibiotics has precipitously declined, a growing interest in alternative antibiotic scaffolds has proliferated. In this direction, aromatic terpene aldehydes – major phytochemical constituents of plant derived essential oils – are known to exhibit potent and broad spectrum antibacterial and antifungal activities. However, practical application of terpenes remains a challenge stemming from their poor water solubility, volatility, and chemical instability. Strategies have been reported to sequester or encapsulate terpenes within films or colloidal systems; however, these strategies often suffer deficiencies such as low loading, poor encapsulation efficiencies, and uncontrolled burst release profiles. The work herein describes the synthesis of pro-antimicrobial networks via degradable acetals (PANDAs) derived from para-substituted benzaldehydes using thiol-ene photopolymerization – an approach designed to address many of the challenges with sequestration of terpene aldehydes. Thiol-ene photopolymerization offers rapid cure kinetics at room temperature, low oxygen inhibition, homogeneous network formation, and high monomer conversion. Thiol-ene – as a step-addition polymerization – ensures that nearly every crosslink junction contains a degradable acetal. Therefore, PANDAs are molecularly designed to undergo complete degradation upon hydrolysis resulting in the release of a benzaldehyde as an active antimicrobial and antifungal agent, and the generation of inactive low molecular weight degradation by-products. We then incorporate this network chemistry into highly monodisperse microparticles to evaluate antimicrobial activity. The antimicrobial activity is shown to increase with increasing concentration of the acetal monomer for gram-positive (*S. aureus*) and gram-negative (*E. coli*, *P. aeruginosa* and *B. cenocepacia*) bacteria. This thiol-ene system represents a new approach for tailoring the release of antimicrobial agents from crosslinked polymeric microparticles.



POLY 577: Analyzing the nanomorphology of novel diblock copolymers for potential use as solid polymer electrolytes

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Novel diblock copolymers were synthesized via ring-opening metathesis polymerization for the potential implementation as a solid polymer electrolyte in lithium ion batteries. The first block contained a 12-unit oligomeric ethylene oxide (EO) side chain to contribute to ionic conductivity, and the second block contained a rigid phenyl block to give structural support. While both blocks contained identical oxynorbornene maleimide (ONMI)-based backbones, the percent compositions of the two blocks varied over five polymers. The bulky ONMI backbone may promote decoupling of the polymeric motion from ionic conductivity; in addition, the phenyl block may block dendritic formations that are responsible for short circuits. The copolymers were studied through atomic force microscopy (AFM) to determine what effect the composition of the polymers has on morphological order in bulk as well as with added lithium salt. Little order was seen from spin coating alone; however, solvent vapor annealing was used to induce longer range order. The addition of bis(trifluoromethane)sulfonimide lithium salt was also shown to induce order, as seen in Figure 1.

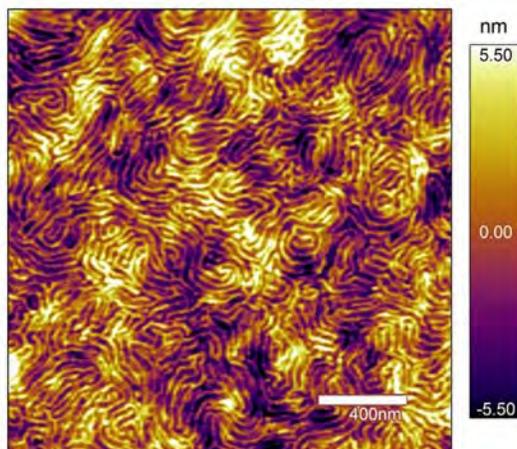
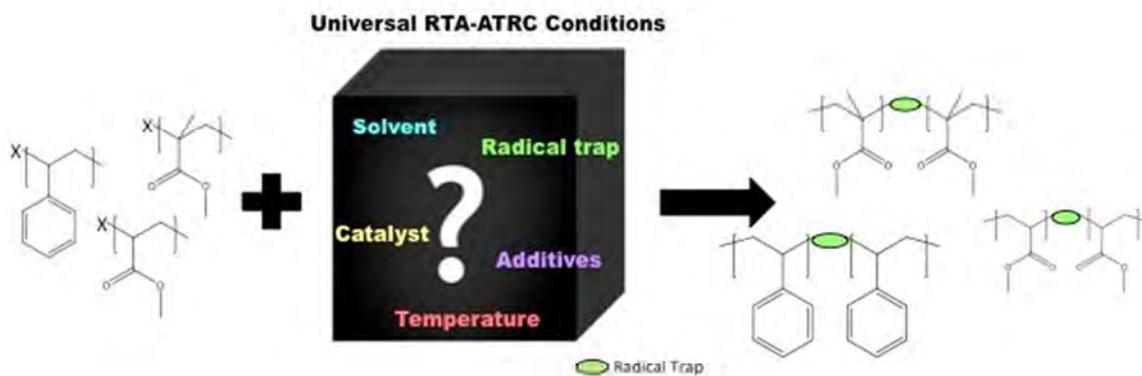


Figure 1. An AFM topographic image of a diblock polymer (50% EO monomer by mass) that contains 33.3% bis(trifluoromethane)sulfonimide lithium salt by mass.

POLY 578: Common protocol for coupling reactions of multiple classes of polymeric radicals

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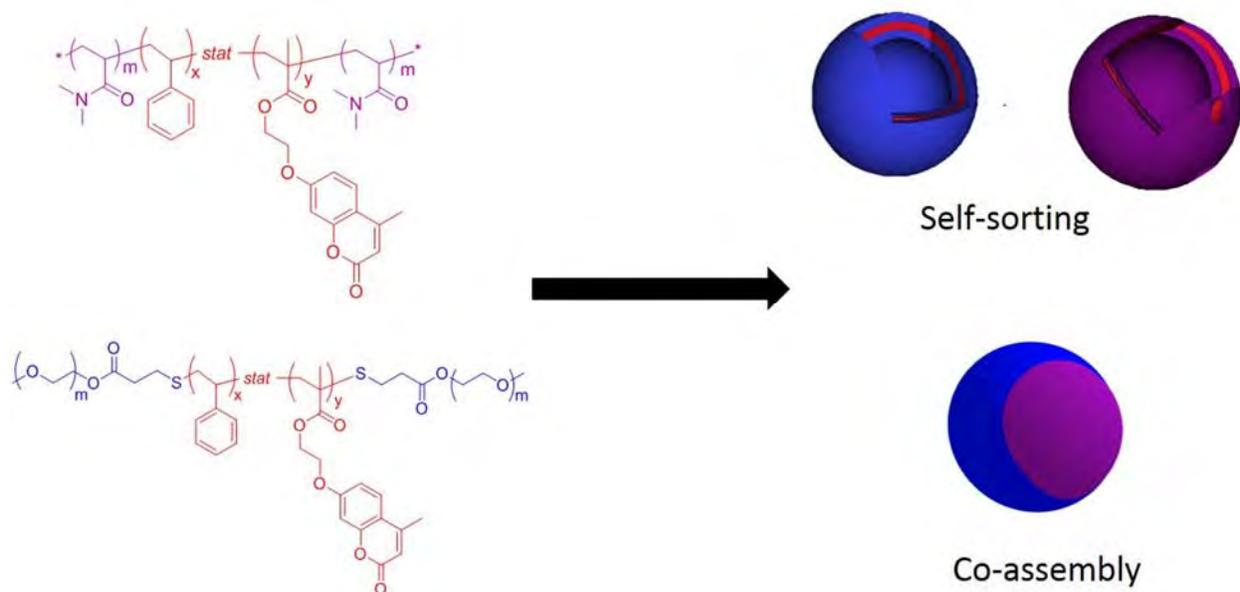
Radical trap-assisted atom transfer radical coupling (RTA-ATRC) has been demonstrated to be an efficient and simple method for coupling polymer chains with halogenated styrenic, methyl acrylate, or methyl methacrylate end groups. While coupling success has exceeded that of traditional ATRC in all cases, each polymer class has required a different set of reactants such as radical traps, solvent combinations, additives, and reaction temperature. A complete analysis of the coupling conditions that have been used in a variety of combinations of various polymers allows for the discovery of a single set of “universal” conditions that can be applied to the synthesis of topologically interesting structures whose creation relies on chain end coupling reactions.



POLY 579: Investigating the co-assembly behavior of linear amphiphilic triblocks in the fabrication of polymer vesicles

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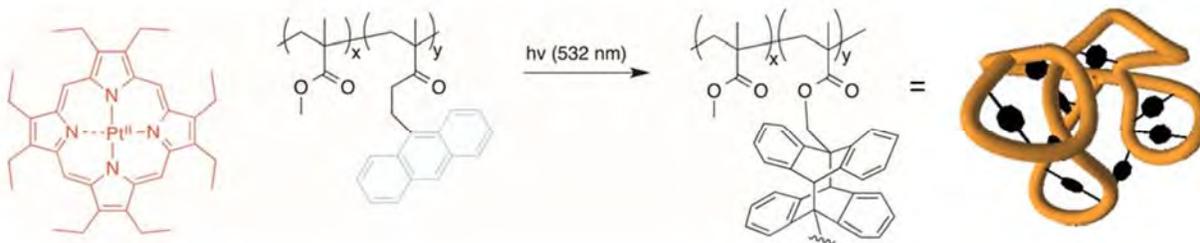
Vesicles are hollow spherical capsules formed by the self-assembly of amphiphilic block co-polymers. They bear great promise in fields such as drug delivery, imaging and diagnostics, and as nanoreactors. The hydrophobic portions of amphiphilic triblocks were synthesized by polymerizing styrene and coumarin methacrylate (P(S-*stat*-CMA)) via reversible addition-fragmentation chain transfer (RAFT) using a difunctional chain-transfer agent. P(S-*stat*-CMA) was coupled with chains of poly(ethylene glycol) acrylate via Michael addition to obtain hydrophilic blocks on both sides of the triblock. This triblock was successfully used to fabricate small and giant unilamellar vesicles by solvent displacement and electroformation respectively. A second triblock with poly(*N,N*-dimethylacrylamide) hydrophilic blocks was synthesized via chain extension RAFT polymerization from the P(S-*stat*-CMA) center block. These triblocks will be co-assembled and a comparison of how curvature affects assembly in both small and giant unilamellar vesicles will be presented.



POLY 580: Synthesis of single-chain nanoparticles through photodimerization of anthracene via triplet-triplet annihilation upconversion

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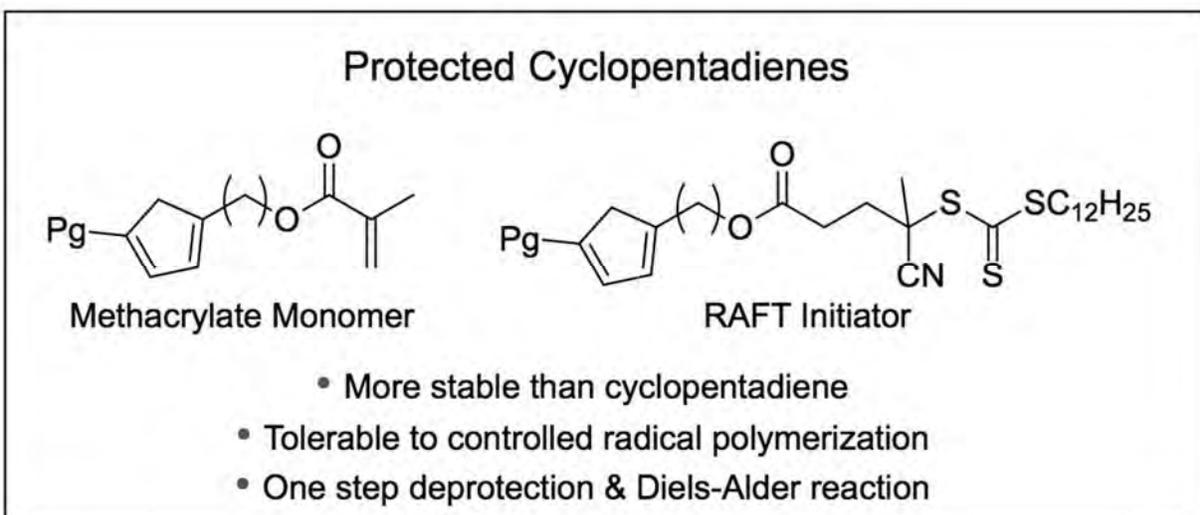
Single-chain nanoparticles (SCNPs) are architecturally defined nanostructures formed by intrachain crosslinking of a linear polymer. They have potential applications in sensing, optics and controlled release. Recently, SCNPs have been successfully synthesized by utilizing UV light to dimerize pendant anthracene moieties on methacrylic chains. Anthracene dimerization has also been shown to occur using low-energy light via triplet-triplet annihilation upconversion (TTA-UC). In this project, these concepts have been combined in an attempt to use TTA-UC to synthesize SCNPs. Irradiation of a mixture of anthracene-containing methacrylic chains and a platinum octaethylporphyrin sensitizer with 532 nm laser resulted in a decrease in the UV-vis absorbance in the 300-400 nm region, characteristic of anthracene dimerization. Atomic force microscopy (AFM), transmission electron microscopy (TEM), and size exclusion chromatography (SEC) will be used to confirm the formation of these SCNPs, while results of the reversibility of this formation will also be presented.



POLY 581: Selective deprotection of cyclopentadiene as a platform for functional polymeric materials

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Cyclopentadienes (Cp) have a multitude of synthetic applications due to their electron-rich and conformationally-locked dienes. This makes them an ideal diene in Diels–Alder reactions for conjugation chemistry and the synthesis of natural products. However, due to its high reactivity, cyclopentadiene is unstable and can dimerize or undergo an acid-catalyzed polymerization. Despite the potential of Cp for conjugation chemistry, its incorporation into polymers has been limited to end-chain modification. The synthesis of Cp-containing monomers for ATRP or RAFT polymerizations is challenging because of the rapid Diels–Alder cyclization that occurs with the vinyl functionality of the monomers. To circumvent this issue, we report the use of a protecting group on the Cp that is stable to RAFT polymerization conditions and can be easily removed after polymer isolation. The deprotection of Cp and a subsequent Diels–Alder reaction can be done in one step, forming diblock or brush copolymers. To highlight this new approach, a series of post-polymerization reactions will be described to access new functional materials.



POLY 582: Analyzing the effect of molecular weight on ionic conductivity of novel solid polymer electrolytes for use in lithium ion batteries

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Novel polymers were engineered to have a rigid oxanorbornyl backbone with an oligo(ethylene oxide) conductive side chain 'brush' to work as a solid polymer electrolyte for lithium ion batteries. These polymers were investigated due to the oligo(ethylene oxide) chain having a significant ionic conductivity and for their potential to decouple ionic conductivity from segmental motion. The effect of the molecular weight of the polymer, as well as the length of the oligo(ethylene oxide) side chain, on the ionic conductivity was measured using electrochemical impedance spectroscopy. The overall degree of polymerization (DP) of the polymers ranged from 62-370 monomer units and the length of the oligo(ethylene oxide) side chains were either $n=8$ or $n=12$. The temperature dependence on the ionic conductivity of the polymer with a DP of 62 and an oligo(ethylene oxide) side chain length of $n=12$ is shown in Figure 1. This data as well as the data of the other polymers will be compared with previously published data of polymers with shorter oligo(ethylene oxide) side chains and early results show that the data in Figure 1 have a higher conductivity than those with shorter side chains and no observed crystallization.

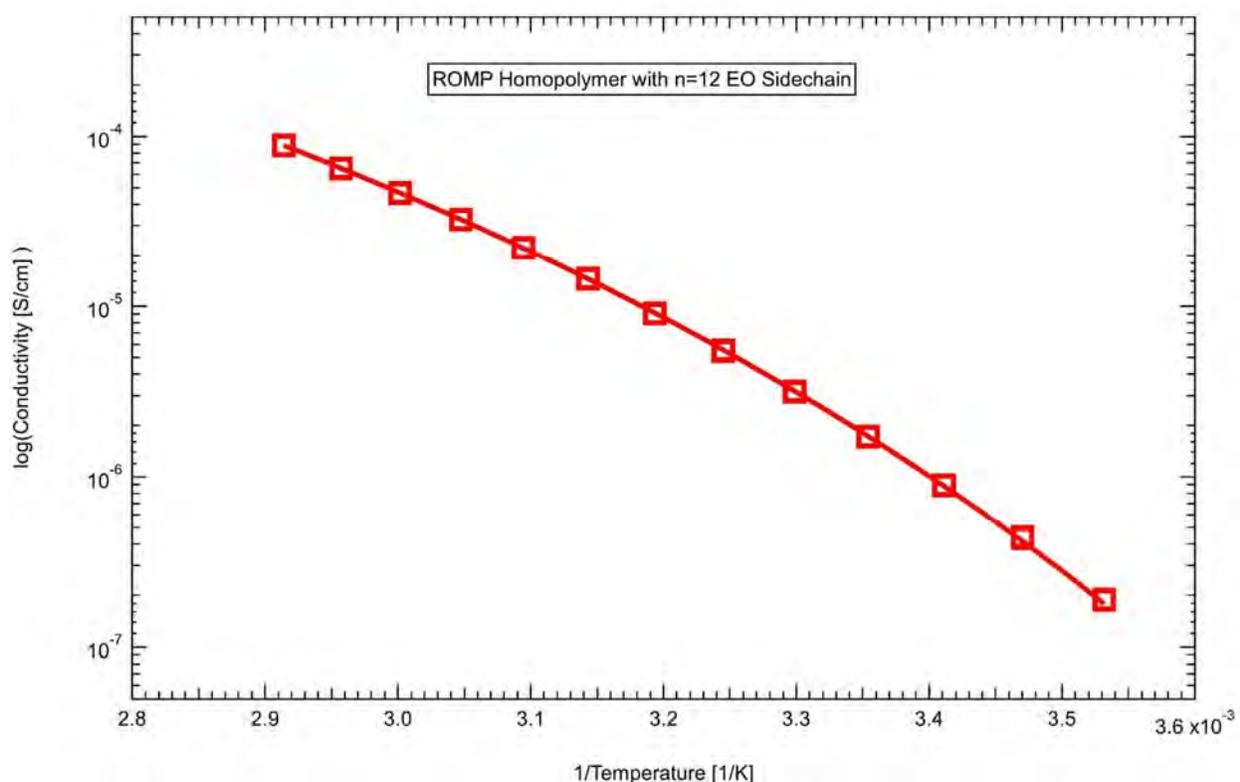
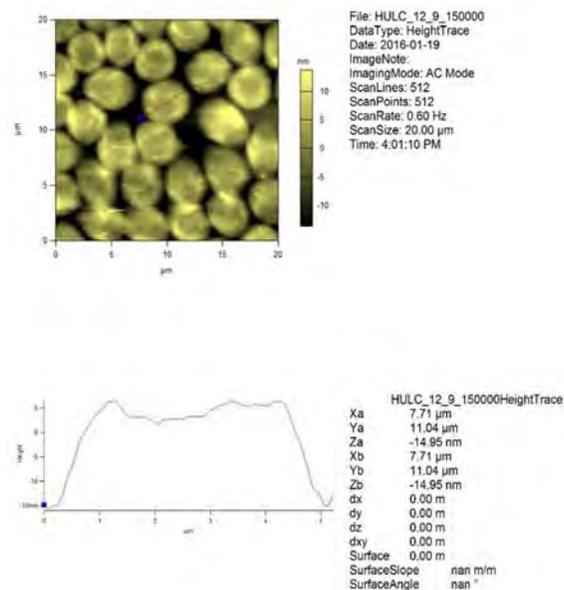


Figure 1: The logarithm of conductivity is plotted versus inverse temperature for a polymer with the oligo(ethylene oxide) side chain length of $n=12$ and a DP of 62. The solid line represents a Vogel-Fulcher-Tammann fit.

POLY 583: Analyzing the surface chemistry of polymer microgels as a function of particle stiffness

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Chemistry, Spelman College, Stone Mountain, Georgia, United States

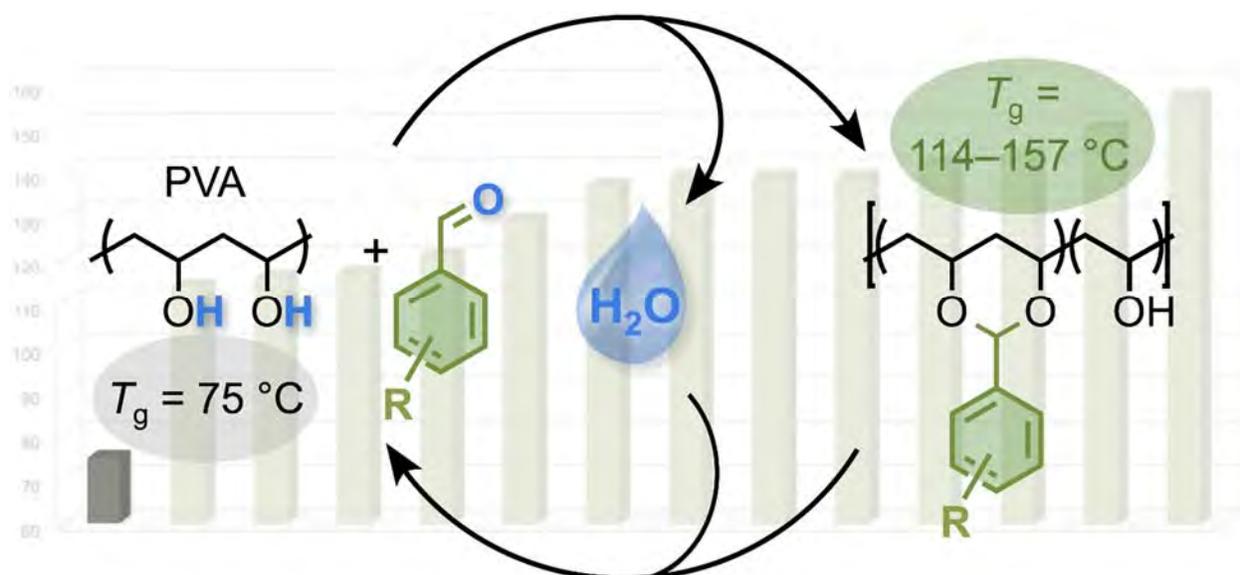
Microgel particles are being applied to a variety of nano- and microtechnologies such as biomaterials, materials for enhancing oil refinery, and catalysis. It is known that highly deformable microgel particles, dispersed in solvent, swell more than stiffer particles because stiff particles have a higher crosslinking density than deformable particles. However, in the event that these microgel particles are crosslinked to a surface, it is expected that particle-confinement will play a role in the microgel particle swelling behavior and surface adhesion. The purpose of this work was to analyze the surface adhesion of thermo-responsive microgel particles, which had been immobilized to a surface, as a function of particle deformability. The microgel particles were poly *n*-isopropylacrylamide (NIPAM) particles, synthesized via precipitation polymerization. The NIPAM microgels were crosslinked to glass substrates via ECD/sulfo-NHS crosslinking chemistry. They were then surface-functionalized with heat-treated BSA (negative control) and biotinylated-BSA (positive control). In order to examine the impact particle stiffness had on surface chemistry, surface adhesion was measured, using atomic force microscopy (AFM). The surface adhesion was measured between both BSA- and biotinylated-BSA- functionalized microgel particles, with surface-functionalized modified AFM tips (BSA- and streptavidin- functionalized tips, respectively). The BSA-functionalized surfaces were used as negative controls, and showed no evidence of adhesion, irrespective to particle stiffness. The BSA-streptavidin surfaces, showed strong evidence of adhesion, and they also evidenced many more adhesive contact points between the deformable particles, compared to stiff particles. These results will contribute toward the future development of actuating microgel coatings and films for possible applications in chemical & biomolecular sensing.



POLY 584: Obvious and non-obvious bioaromatics for polymerization

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Main-chain and side-chain functionality are critical to polymeric thermal properties and degradation behavior. This presentation will describe synthetic routes for polymerizing bioaromatics and other biogenic cyclics to yield polymers with high glass transition temperatures or high melting temperatures. Some of these monomers are already present in common biomass sources, including vanillin, coumaric acid, ferulic acid, and sinapic acid. However, some monomers are not immediately available from biomass, but can be built via facile and scalable chemistry from other biogenic molecules. These various novel thermoplastics will be discussed in the context of replacing specific fossil fuel-based packaging plastics.



POLY 585: Lignin-based functional polymers

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Lignin is an important source of synthetic materials because of its abundance in nature, low cost, stable supply, and no competition to the human food supply. The crosslinked phenolic polymer, lignin, contains a large number of aromatic groups that can be used as a substitute for petroleum-based aromatic fine chemicals. However, modification of lignin is necessary for its application in advanced materials due to its chemically inert nature and structural complexity. Polymeric modification of lignin via graft copolymerization represents an important avenue for modification because this method forms stable covalent bond linkages between lignin and synthetic functional polymers. Through the lignin graft copolymerization, lignin was integrated with synthetic polymers to obtain certain smart functions. In this presentation, we summarized our recent founding in thiol-ene lignin modification, and lignin based self-healing polymer, synthesize and special properties.

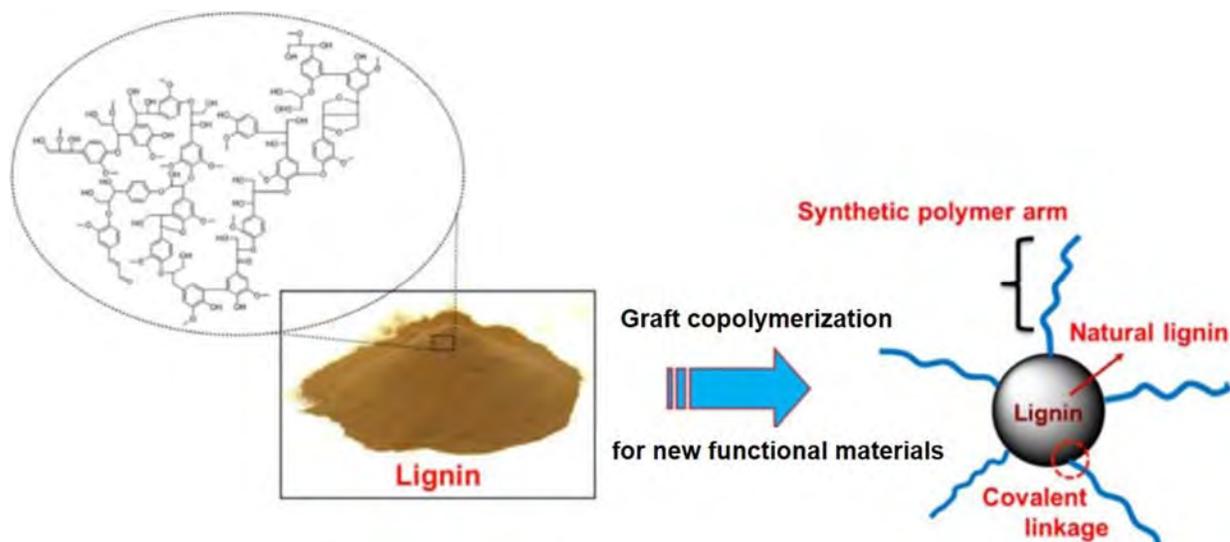
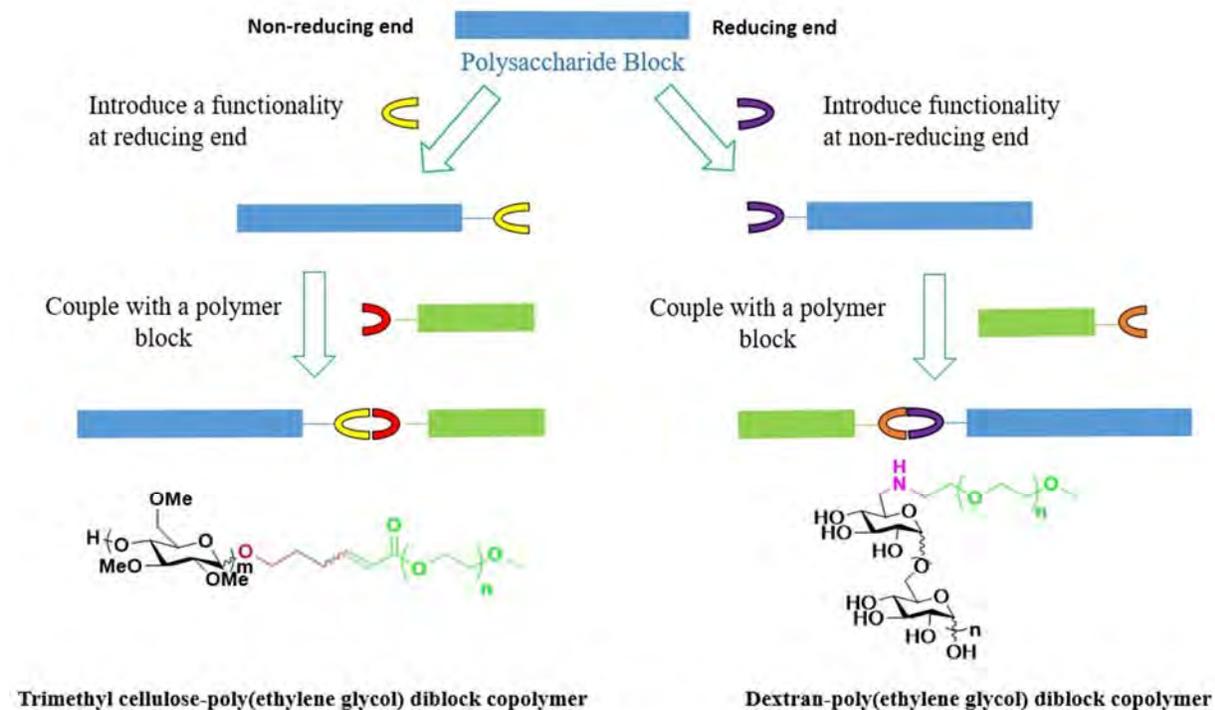


Figure 1. lignin based functional polymers synthesis schematic.

POLY 586: Novel synthetic routes to polysaccharide-based block copolymers

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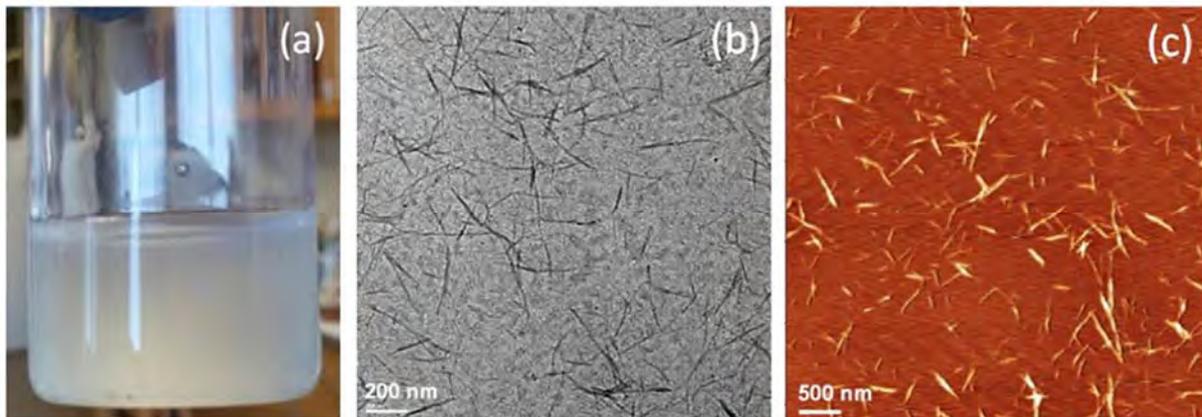
Polysaccharide-based block copolymers are attractive materials which have potential to be used widely in many practical fields including biodegradable packaging and drug delivery. Micro-phase separation of block copolymers can afford specific morphologies, leading to extraordinary properties. Many polysaccharide derivatives, including cellulose, dextran and pullulan, are good candidates for block copolymer synthesis. In spite of this potential, however, only a limited number of approaches to polysaccharide-based block copolymers have been reported. The difficulty of polysaccharide regio-selective end group functionalization can explain the limited number of studies about this new block copolymer family. We have focused on developing synthetic strategies which can regio-selectively modify the termini of polysaccharide derivatives, and from these selectively functionalized polysaccharides, build block copolymers. These approaches, including solvolysis, olefin cross-metathesis, amine alkylation and azide-alkyne cycloaddition, have generated a series of trimethyl cellulose- and dextran-based block copolymers. We will report insights into these interesting reactions, which will inform further design and synthesis of polysaccharide-based block copolymers.



POLY 587: Cellulose nanocrystals in 3D printing and aerogels: nanocomposite properties

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Renewable materials start with the use of biobased feedstocks or derived raw materials for direct utilization (little conversion or synthetic procedures). The preparation of nanocellulose materials from a variety of sources include agricultural, non-agricultural, and can vary in properties depending on the method of preparation and high fiber source. Cellulose nanocrystals (CNC) and cellulose nanofibers (CNF) have various uses for the fabrication of polymer nanocomposites, making them useful as an additive for improving thermo-mechanical properties and perhaps improving processability. In this talk, we will focus on the use of CNC derived from two sources: Abaca and coconut fibers. The mode of raw materials can be from processed pulp or directly from coconut coir. These nanofiller materials have been utilized in two types of applications: nanofiller materials for 3D printed parts via stereolithographic apparatus (SLA) and the preparation of smart aerogels with nanoclay. The former enabled strengthening of the thermo-mechanical properties of the 3D printed object and the latter results in a highly porous lightweight media useful also for oil-water separation and clean-up. The talk will discuss the methods of synthesis, fabrication, and characterization for their intended application.



POLY 588: New bio-related materials based on cardanol

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Cardanol is an agro-based raw material derived from cashew nut shell liquid, which is a byproduct of cashew nut processing. In order to extend its utility, we sought to derivatize cardanol in two ways. For the first derivative, we employed the ene reaction (a pericyclic reaction), which was facile and required only the application of heat without a catalyst. The product of cardanol and diethyl azodicarboxylate was a hydrozino-ester derivative (Figure 1, top reaction), which increased in viscosity with time and may perhaps be useful as a viscosifier in oil-based materials. Both conventional and microwave heating was shown to be effective; the latter entailed much shorter reaction time and substantial energy savings. For the second derivative, cardanol was epoxidized and then reacted with aniline with the help of an ionic liquid catalyst. The resulting aminohydrin was shown to undergo a condensation reaction with formaldehyde to form a prepolymer, which could be further reacted to form a thermosetting resin (Figure 1, bottom reaction). The reaction pathways for these reactions were fully characterized by using NMR spectroscopy.

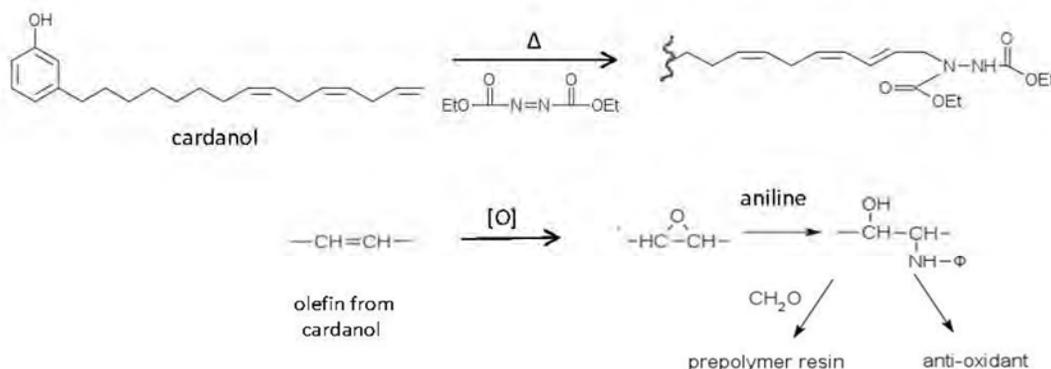


Figure 1. Top reaction: cardanol reacting with diethyl azodicarboxylate to form one of the ene reaction products. Bottom reaction: the olefin from cardanol was first converted to the epoxide, which reacted with aniline to form the aminohydrin. The reaction with formaldehyde then produced a thermosetting polymer.

POLY 589: Development of new biopolymers from renewable building blocks derived from low-molecular weight hemicelluloses

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Until recently the large majority of chemistry building-blocks are stemmed from petroleum resources. However, due to increasing scarcity of oil resources leading to a surge in raw materials prices combined to environmental concern and impact on human health, renewable and viable alternatives are urgently needed. In this purpose, the use of naturally-occurring and renewable building blocks for the chemistry in general and for the polymer science in particular are of great interest.¹ Specifically polysaccharides, such as cellulose and lignin, that are found in all plants cell are particularly good candidates for the replacement of fossil-based raw materials through their multifunctionality and are already considered as a versatile chemical platform. Among these interesting sources of raw materials, hemicelluloses represents 15% to 35% of plants and wood but is nevertheless an underexploited source of bio-based building blocks due to difficult extraction from the cell wall. Furthermore, a great majority of the extracted hemicelluloses are low-molecular weight oligomers and cannot be valorized as such. In the present work, we relate the use of low-molecular weight hemicelluloses as a renewable building-block and its use for the design and the synthesis of new biopolymers through chain extension. Molecular, thermal and thermo-mechanical characterizations of the obtained polymers will be detailed.

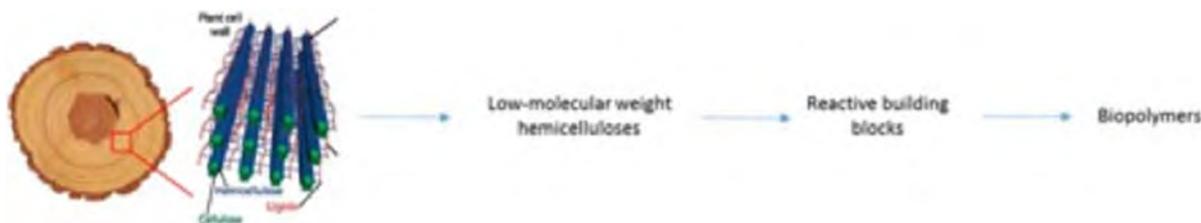
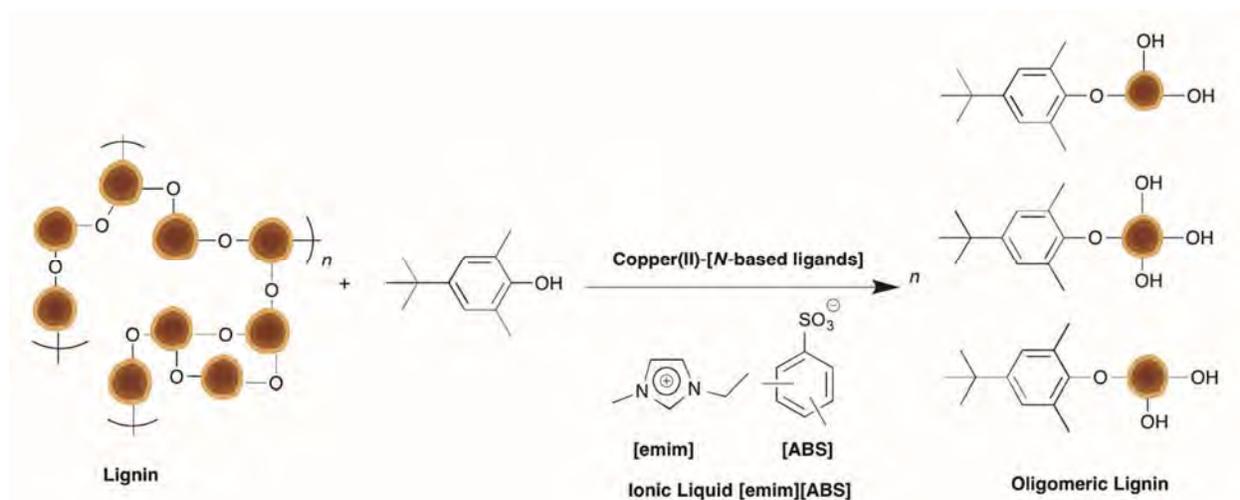


Figure 1. From hemicelluloses to new biopolymers

POLY 590: Effect of the *N*-based ligands in copper complexes for depolymerisation of lignin

Jinhua Dai, jinhua.dai@monash.edu, Kei Saito, Antonio Patti. Monash University, Oakleigh East, Victoria, Australia

Lignin has been widely studied as a sustainable source of renewable materials, particularly aromatic feedstock chemicals, which are in great and increasing need in the world. Several organic soluble *N*-based ligands and their copper complexes were firstly investigated as catalysts to depolymerise organosolv lignin in the organic solvent, dimethylformamide (DMF) and an ionic liquid (1-ethyl-3-methylimidazolium xylenesulfonate, [emim][ABS]). The results of screening depolymerisation reactions in DMF and [emim][ABS] showed that all the copper-amine complexes catalysed lignin depolymerisation more efficiently in ionic liquids than in DMF. Among the seven types of ligands, copper complexes with two types of ligands ((*E*)-*N*-(pyridin-2-ylmethylene)aniline (**L6**) and (*E*)-4-methoxy-*N*-(pyridin-2-ylmethylene)aniline (**L7**) depolymerised the lignin more efficiently than the others. These two copper complexes with *N*-based ligand were further studied to determine the most efficient conditions for the depolymerisation of the lignin. The most effective depolymerisation by conditions involved treatment at 180°C for 12 h in [emim][ABS]. Cyclic voltammetric studies were carried out to investigate the reversible potential associated with the copper centers of their complexes with these *N*-based ligands. The results suggest that two types of ligands have more positive reversible potentials than those of other copper complexes.

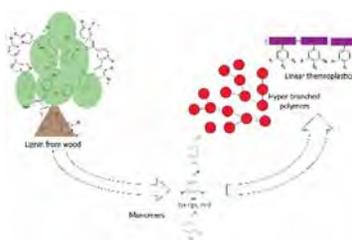


POLY 591: Thermoplastics from lignin oligomers and syringic acid derivatives

Lionel Longe², lionel.longe@monash.edu, Gil Garnier¹, Kei Saito². (1) Monash, Clayton, Victoria, Australia (2) Monash University, Malvern East, Victoria, Australia

Lignin is the second most abundant biopolymer after cellulose, and the first source of renewable aromatic compounds. Value added products from lignin have been limited to low value added blends using lignin as filler or thermosets polymer. Here, we aim at breaking down lignin into a series of specific and well characterized degradation products to serve as building blocks in the synthesis of high value lignin based thermoplastics. Lignin depolymerisation results in either oligomers or small aromatics comprising variations of syringaldehyde, vanillin and 4-hydroxybenzaldehyde. These units represent the most promising biobased building-block for synthesis of monomers, opening pathway to aromatic renewable polymers. The present work focus on syringic acid as a platform chemical for the synthesis and polymerisation of new monomers. We explored novel types of chemistry never prospected for lignin repolymerisation such as polyamides, ADMET or thiol-ene chemistry.

Here, syringic acid was used as building-block for monomer synthesis. Different strategies were investigated, including functionalisation through the acid group, through the hydroxyl group, or even demethoxylation or ring cleavage. Polystyrene-like polymer and hydroxyl terminated hyperbranched polymers had most promising results, with molecular weight of up to million and compelling thermomechanical properties. Super hydrophilic polymer obtained by thiol-ene click chemistry are also investigated. Repolymerisation of lignin oligomers obtained by lignin depolymerisation in our lab have also been investigated as a less costly process for low value added biopolymer. Physicochemical properties of the resulting polymers will also, *inter alia*, be exploited for thin-film making using coordination complexes. This presentation will summarize the success and learning of this research platform.

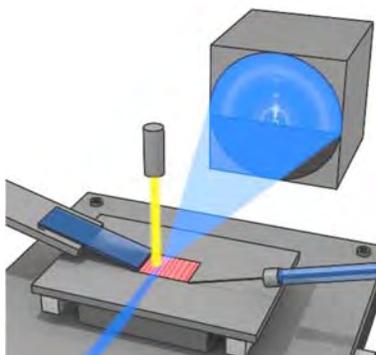


POLY 592: In-situ materials structure measurements for organic photovoltaics manufacturing

Dean DeLongchamp, deand@nist.gov. NIST, Gaithersburg, Maryland, United States

Organic photovoltaics (OPV) is a flexible electronics technology for making low-cost solar cell modules using organic active layers that are processed as inks onto substrates. Although OPV has significantly matured over the past few years, there remain significant challenges in moving from lab-scale devices to real manufacturing. We address this gap using a blade coating process as a prototype for slot-die coating and observing the structure of films in-situ as they dry. Our measurements include synchrotron-based X-ray scattering and a variety of optical methods.

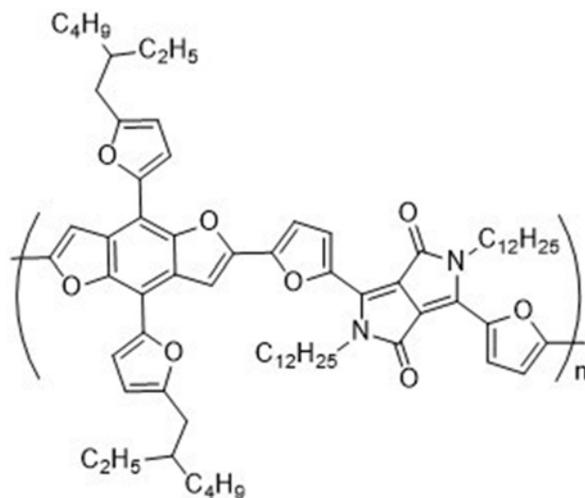
I will review our studies of OPV systems deposited by blade coating, including systems which can achieve nearly 10 % power conversion efficiency (PCE). I will emphasize commonalities and differences among systems, and attempt to classify the processing behavior of polymer-fullerene systems based on traits of the polymer such as diffraction strength (\sim crystallinity). There is a surprising diversity of solidification mechanisms among OPV systems. Some are dominated by the nanoscale crystallization of the components, whereas others appear to be dominated by liquid-liquid phase separation. Examples of good performance can be found for systems that obey many different solidification mechanisms. I will also touch on the role of additives in OPV ink formulation. There is surprising diversity in the mechanisms by which additives affect the solidification of OPV systems as well. Finally, I will address how these results might be extended to pilot-scale R2R coating by demonstrating nominally identical morphologies for both piece blade-coating and continuous-web, slot-die coating.



POLY 593: Benzodithiophene and Benzodifuran Donor-Acceptor Polymers for Organic Photovoltaics

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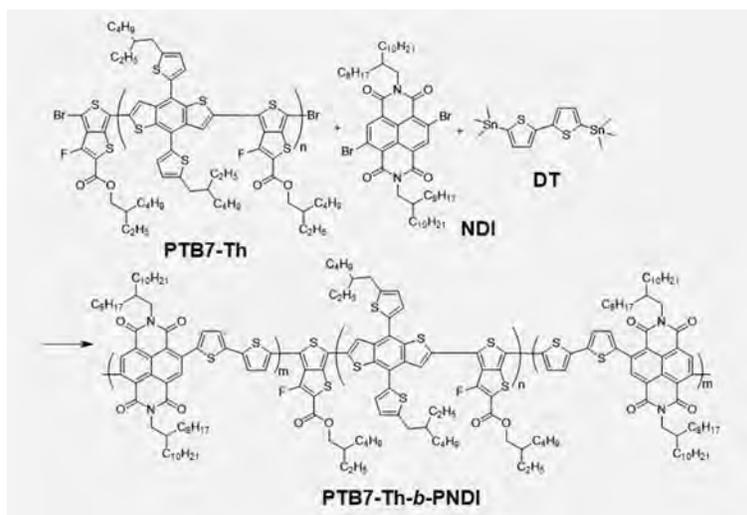
Donor-acceptor semiconducting polymers containing benzodithiophene and benzodifuran have been synthesized and tested in bulk heterojunction solar cells with [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM). The solar cells were fabricated using a conventional device structure ITO/PEDOT:PSS/polymer:PCBM/Ca/Al. The solvent employed for solution processing and concentration of blend were optimized. Tapping mode atomic force microscopy (TMAFM) and transmission electron microscopy (TEM) analysis indicated an improved phase separation between the polymer and PCBM which resulted in an increased PCE upon additive used. The highest power conversion efficiency (PCE) of 5.55% obtained was the polymer containing benzo[1,2-b:4,5-b']difuran with furan substituent as donor unit and furan-pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione as acceptor unit.



POLY 594: PTB7-Th-*b*-PNDI fully conjugated donor-acceptor block copolymers for thermal stability of photovoltaic devices

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Fully conjugated donor-acceptor block copolymers are promising candidates for photovoltaics due to their ability to microphase separate near the length scales of exciton diffusion lengths. These materials can also serve as model systems to study the relationship between molecular structure, microstructure, and optoelectronic properties of conjugated polymers. Recently, the long-term stability of organic solar cells, including both photo-stability and thermal stability, has received growing attention. As the sole active layer material and phase compatibilizer in blend systems, photovoltaic devices including donor-acceptor block copolymers are expected to display enhanced thermal stability than the corresponding blend systems. To explore the full potential of donor-acceptor block copolymers, it is necessary to develop synthetic approaches that work for various systems, including recently reported high performance polymer blend systems. The majority of high performance donor and acceptor polymers have been synthesized by cross-coupling of two different monomers through polycondensation such as Stille and Suzuki-Miyaura reactions. We prepared Poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b;4,5-b']dithiophene-2,6-diyl-*alt*-(4-(2-ethylhexyl)-3-fluorothiopheno[3,4-b]thiophene-2-carboxylate-2,6-diyl)]-*block*-Poly{[*N,N'*-bis(2-octyldodecyl)naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-*alt*-5,5'-(2,2'-bithiophene)} (PTB7-Th-*b*-PNDI) donor-acceptor block copolymer using a Stille reaction twice. Formation of block copolymers was confirmed by NMR and GPC. Solar cell devices were fabricated using the donor-acceptor block copolymer as the sole active layer material as well as with the block copolymer as an additive in PTB7-Th/PNDI and PTB7-Th/PCBM blend systems. Upon thermal stress at 80 °C for up to 168 hours, blend solar cells with addition of block copolymers exhibited enhanced thermal stability. Morphology of blends with or without addition of the block copolymer was investigated by RSoXS.

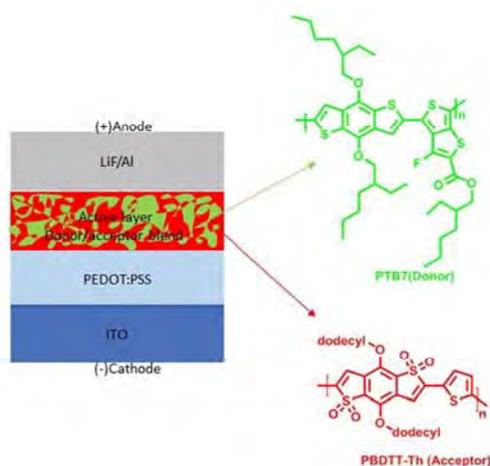


Reaction scheme for the synthesis of PTB7-Th-*b*-PNDI.

POLY 595: Synthesis and characterization of benzodithiophene-S,S-tetraoxide based donor-acceptor polymers as organic semiconductors

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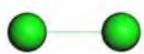
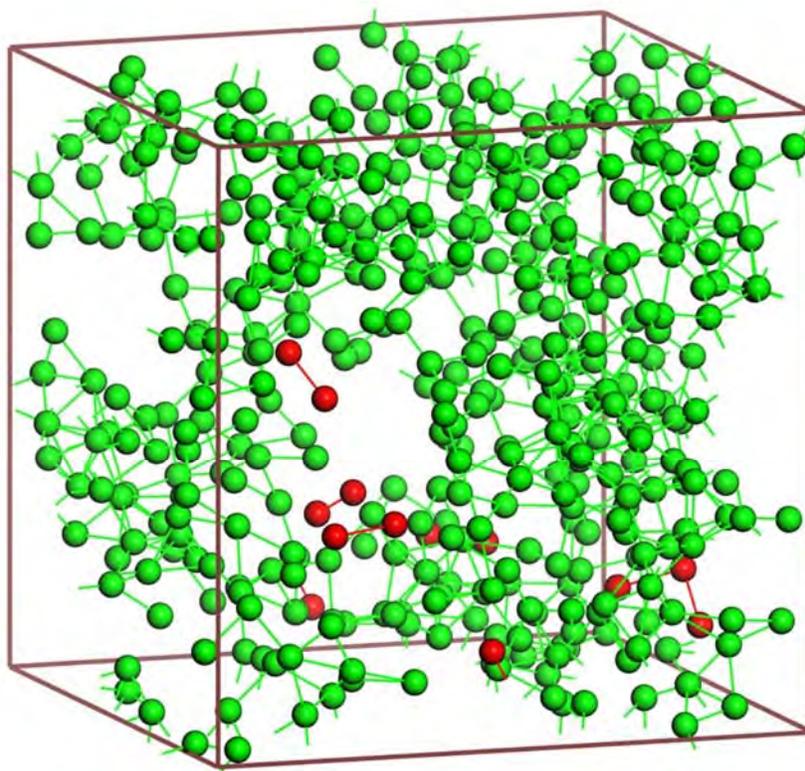
The combination of novel optoelectronic properties with ability to tailor chemical structures to achieve desired optoelectronic properties makes organic semiconductors (OSC) an attractive material in the modern technology world. Additionally, OSCs offers the opportunity to fabricate low cost, lightweight and flexible electronics and optoelectronic devices which otherwise are inaccessible using conventional semiconductor materials such as silicon. In the field of organic semiconductors, both electron donors and electron acceptor materials are equally important. However, the syntheses of electron acceptor materials lag behind the electron donor materials. This lack of electron acceptors in the field of organic semiconductors is mainly related to the stability of these materials and difficulties in the synthesis of precursor for these materials. The latter has limit the utility of electron poor heterocycle like benzodithiophene-S,S-tetraoxide (BDTT) as building blocks for the development of electron acceptor materials. In this work, BDTT was successfully functionalized by utilizing the recently developed C-H iodination reaction of electron deficient heterocycles. This functionalized BDTT molecule was then utilized to synthesize donor-acceptor polymers in good to excellent yield. In this presentation, the functionalization of BDTT molecule and synthesis and characterization of BDTT based donor-acceptor polymers for non-fullerene organic solar cells will be discussed.



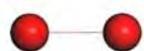
POLY 596: Polymer-acceptor bulk heterojunction solar cells: Establishing relationships among polymer chemical structure, polymer packing, and polymer-acceptor mixing

Jean-Luc E. Bredas, jean-luc.bredas@chemistry.gatech.edu. School of Chemistry Biochemistry, Georgia Institute of Technology, Atlanta, Georgia, United States

The morphology of the active layer of a bulk heterojunction (BHJ) solar cell, made of a blend of an electron-donating polymer and an electron-accepting fullerene derivative, is known to play a determining role in device performance. Interestingly, even a minor change in the chemical structure of the polymer backbone has been shown experimentally to change substantially the blend morphology. Here, taking representative systems based on benzothiadiazole-quaterthiophene polymers and PC₇₁BM, we discuss the results of molecular dynamics simulations and long-range corrected density functional theory calculations. We elucidate the molecular-scale effects that even minor structural changes to the polymer backbone can have on the "local" morphology; we focus on the extent of polymer-fullerene mixing, on their packing, and on the characteristics of the fullerene-fullerene connecting network in the mixed regions, aspects that are difficult to access experimentally.



Connected PC₇₁BM-PC₇₁BM pairs

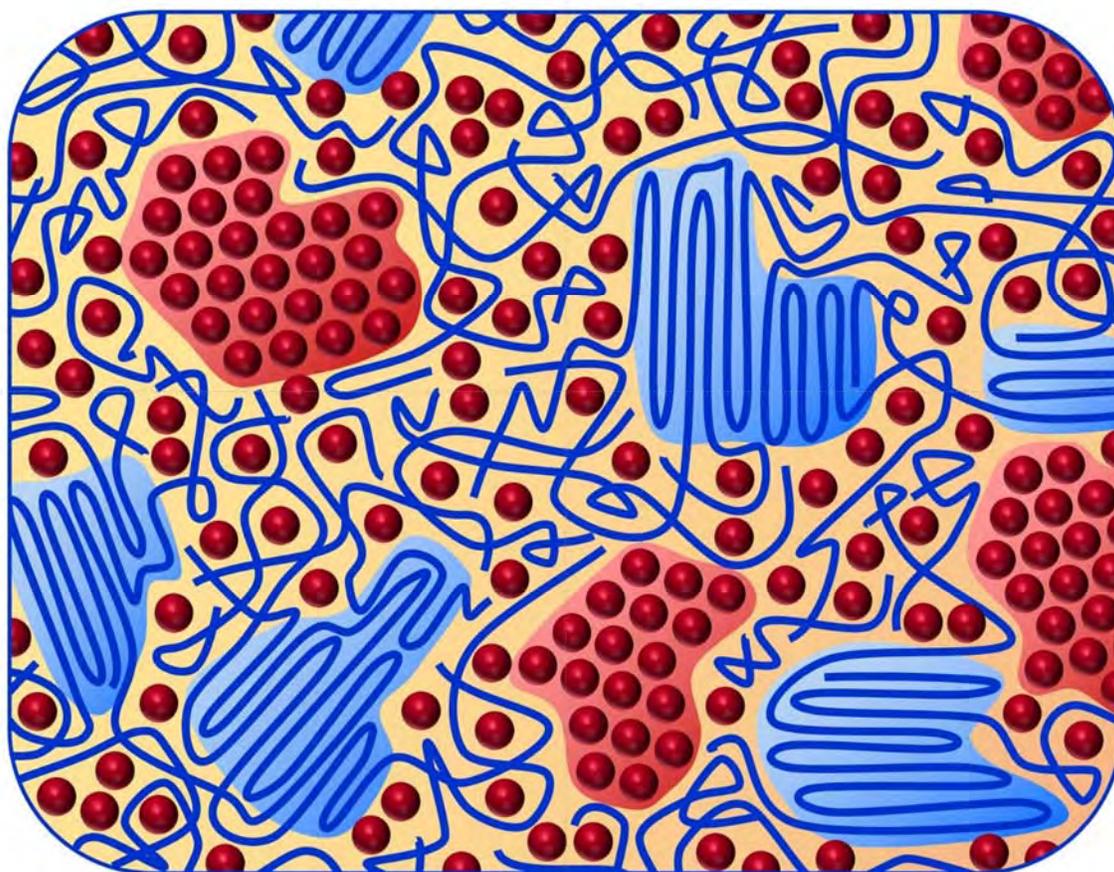


Isolated PC₇₁BM-PC₇₁BM pairs

POLY 597: Morphology in organic photovoltaics: Importance of intimately mixed donor/acceptor domains

Michael Toney, mftoney@slac.stanford.edu. SSRL, SLAC National Laboratory, Menlo Park, California, United States

In organic photovoltaics (OPVs) or “plastic solar cells”, efficient devices are bulk heterojunctions (BHJ) that are blends of a donor (typically a semiconducting polymer or small molecule) and acceptor (most often a fullerene derivative). As shown in the figure, it is by now well established that BHJs consist of nearly pure donor and acceptor domains and can consist of intimately mixed donor/acceptor domains [1-3]. These mixed regions can be important in exciton harvesting, and for carrier recombination and transport. However, we do not have a good understanding of the generality (and thus the importance) of the formation of the intimately mixed donor/acceptor for a wide range of efficient polymers, and for more recently developed, small molecules. In this talk, I show data on a range of polymer and small molecule donors with fullerene acceptors. These show that mixed domains are not necessary for good performance [4] and begin to provide design rules for controlling the amount of the mixed phase and thus the rational optimization of donor and acceptor compositions.

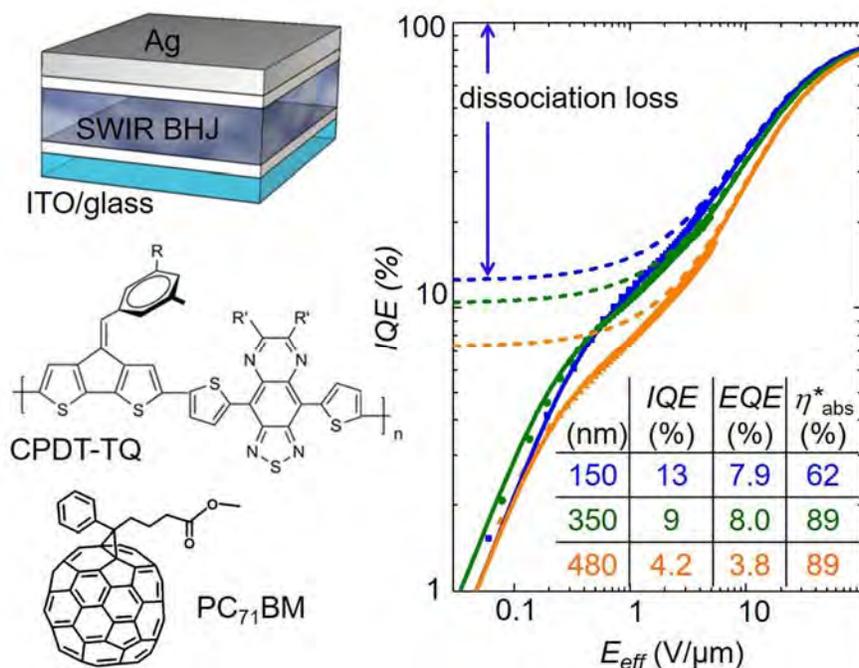


Schematic image of BHJ showing pure fullerene acceptors (red regions) and polymer donor (blue).

POLY 598: Detectivity of shortwave infrared organic photodiodes

Zhenghui Wu¹, Weichuan Yao¹, Alex London², Jason Azoulay², **Tse Nga Ng**¹,
tnn046@ucsd.edu. (1) University of California San Diego, La Jolla, California, United States (2) University of Southern Mississippi, Hattiesburg, Mississippi, United States

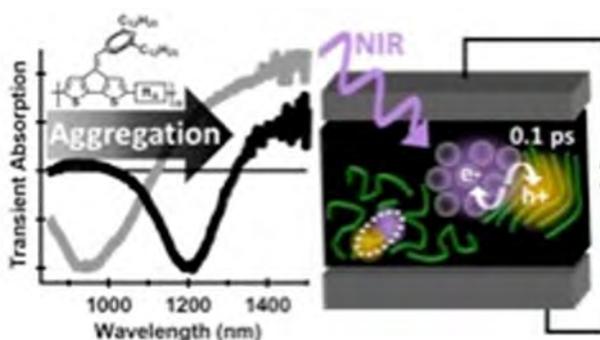
While only few organic photodiodes have photoresponse spectrum past the silicon limit of 1.1 μm , novel shortwave infrared (SWIR) polymers are emerging, and a better understanding of the limiting factors in narrow bandgap devices is critically needed to predict and advance performance. Based on state-of-the-art SWIR bulk heterojunction photodiodes that show spectral response up to 1.7 μm , this work demonstrates a new model that properly accounts for the increasing electric-field dependence of photocurrent in narrow bandgap materials. This physical model offers an expedient method to pinpoint the origins of efficiency losses, by decoupling the exciton dissociation efficiency and charge collection efficiency in photocurrent-voltage measurements. Our results indicate that the main loss is due to poor exciton dissociation efficiency, particularly significant in photodiodes with low-energy charge-transfer states. The main reasons for low charge-transfer exciton dissociation efficiency and high noise will be discussed to give a better understanding on the differences of the device physics between SWIR photodiode and those working in the visible. The optimal detectivity is obtained at zero external bias in photodiodes with film thicknesses ≤ 350 nm for the bulk heterojunction. The measured results that include all noise components show an infrared peak detectivity of 5×10^{10} Jones with a spectral range up to 1.55 μm . Several demonstrations are also conducted to show the various potential applications of organic SWIR photodiodes including distinguishing the heart pulse rate, quantifying the ethanol-water content in a mixture with 1% accuracy, and image reconstruction.



POLY 599: Ultrafast singlet exciton decay in push-pull polymers

Matthew Sfeir, *msfeir@bnl.gov*. Ctr for Functional Nanomaterials, Bldg 735, Brookhaven National Laboratory, Upton, New York, United States

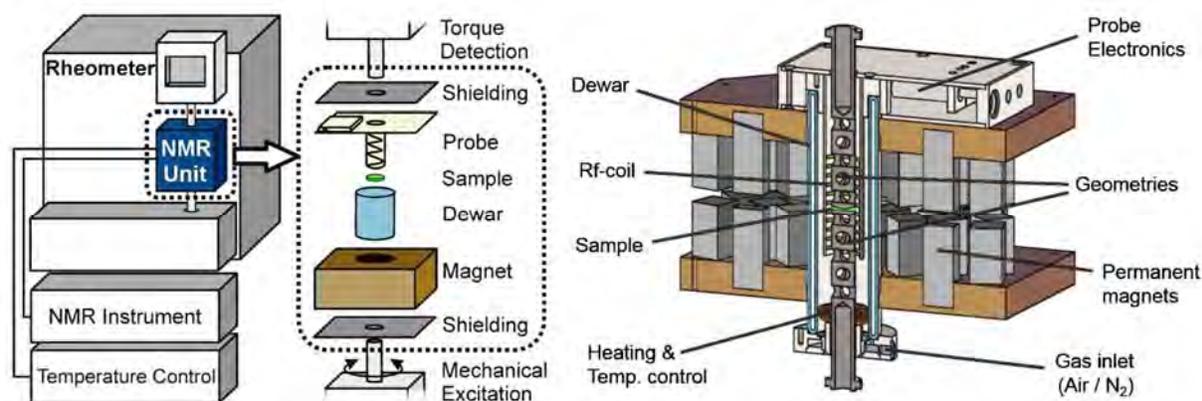
In “push–pull” polymers, electron-rich and electron-deficient monomers are alternated along the π -conjugated backbone. Strong “pull” units with high electron affinity can be employed to further decrease the optical gap for infrared optoelectronics or to develop n-type semiconducting materials. However, strong intramolecular polarity frequently results in dramatic and unexpected changes in the photophysics, including ultrafast exciton self-ionization, emergence of low-energy dark states, and singlet fission mediated by intramolecular charge-transfer character. Here, we use ultrafast spectroscopy to address issues related to utilizing narrow gap conjugated polymers in optoelectronic devices. Our measurements suggest routes to achieve efficient light harvesting, even when the intrinsic singlet exciton lifetimes are too short to permit efficient charge extraction.



POLY 600: Quiescent and flow-induced crystallization of polyolefins studied by a novel low-field RheoNMR combination

Volker Röntzsch, Mürüvvet B. Özen, Karl-Friedrich Rätzsch, Gisela Guthausen, **Manfred Wilhelm**, manfred.wilhelm@kit.edu. Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

Combining NMR and rheology has received great attention in the past 20 years because such combinations lead to correlated information on flow and molecular properties of soft matter, e.g. polymers, liquid crystals or colloids. Additionally, flow profiles (e.g. steady or oscillatory shear) both in the linear and non-linear regime can be applied to monitor and also to modify the state of a sample and measure its implications on molecular properties. Most RheoNMR designs have been realized for high-field NMR spectrometers using shear flow cells without a quantification of the rheological parameters. Here we present a low-field RheoNMR set-up based on a portable 30 MHz NMR unit that was integrated into a high end commercial strain-controlled rheometer. This unique combination can be employed to simultaneously conduct a full rheological characterization (G' , G'' , $|\eta^*|$, FT-Rheology: $I_{3/1}$, Q_0) while monitoring molecular dynamics in-situ via ^1H TD-NMR for temperatures from -15 to $+210$ °C. Possible applications include the measurement of quantitative composition in crystallizing soft matter (fats, polymers, etc.) and multiphase systems during the application of shear protocols. To display the possibilities of this new technique, studies on the quiescent and flow-induced crystallization of polyolefins are presented. A short time steady-shear protocol was applied to study flow-induced crystallization as a function of different temperatures and flow conditions, respectively.

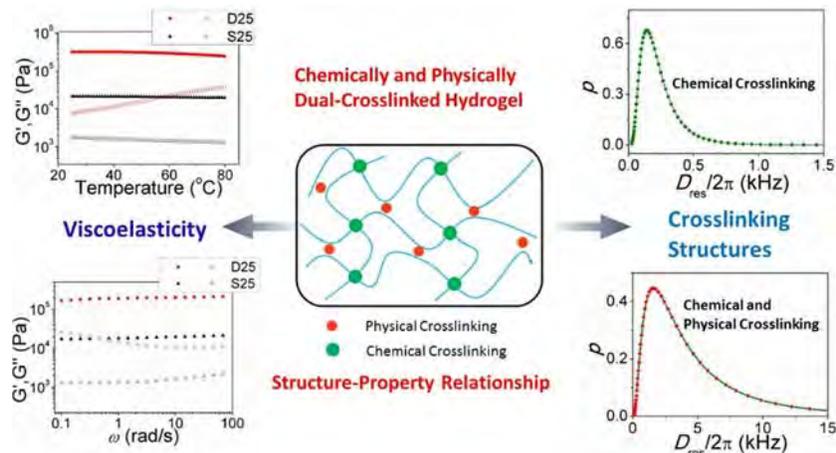


Left: Low-field RheoNMR set-up based on a portable time domain (TD) NMR unit (30 MHz) implemented in a high end strain-controlled rheometer (Rheometrics / TA ARES). Right: Cross-section of the NMR unit including a Halbach array of permanent magnets, NMR probe and temperature control elements.

POLY 601: Viscoelasticity and structures in chemically and physically dual-crosslinked hydrogels: Insights from rheology and proton multiple-quantum NMR spectroscopy

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Hydrogels have received considerable attention as an innovative material due to their widespread applications in various fields. As a soft and wet material, its mechanical behavior is best understood in terms of the viscoelastic response to periodic deformation, which is closely related to the microscopic chemical/physical crosslinking structures. Herein, a dual-crosslinked (DC) hydrogel, where a physically crosslinked network by ionic coordination (Fe^{3+}) is imposed on a chemically crosslinked poly(acrylamide-co-acrylic acid) network, was studied in detail by rheology and proton multiple-quantum (MQ) NMR spectroscopy. Rheology experiments revealed the diverse temperature- and strain frequency-dependent viscoelastic behaviors for DC hydrogels induced by the dynamic Fe^{3+} coordination interactions, in contrast to the single chemically crosslinked (SC) hydrogels. During the shear experiment, the trivalent Fe^{3+} complex with moderate/weak binding strength might transform to those with strong binding strength, and serve as permanent-like crosslinkages to resist the periodic deformation when a large strain frequency was applied. The viscoelastic behaviors of the DC hydrogels were strongly affected by the monomer ratio ($C_{\text{AAc}}/C_{\text{AAm}}$) and Fe^{3+} concentrations; however, the chemically crosslinking density did not change with $C_{\text{AAc}}/C_{\text{AAm}}$, while the physically crosslinking density was greatly enhanced with increasing Fe^{3+} concentrations. Besides, the DC hydrogels have much less content of network defects in comparison to the SC hydrogels. The heterogeneous structural evolution with increasing Fe^{3+} concentration and the monomer ratio was also quantitatively determined and elucidated by proton MQ NMR spectroscopy. In addition, the moduli (G' , G'') of the DC hydrogel were almost an order magnitude higher than that of the SC hydrogel, demonstrating the significant contribution of Fe^{3+} coordination to the mechanical behaviors. The experimental findings obtained from the rheology and proton MQ NMR experiments can be correlated with and complementary to each other.

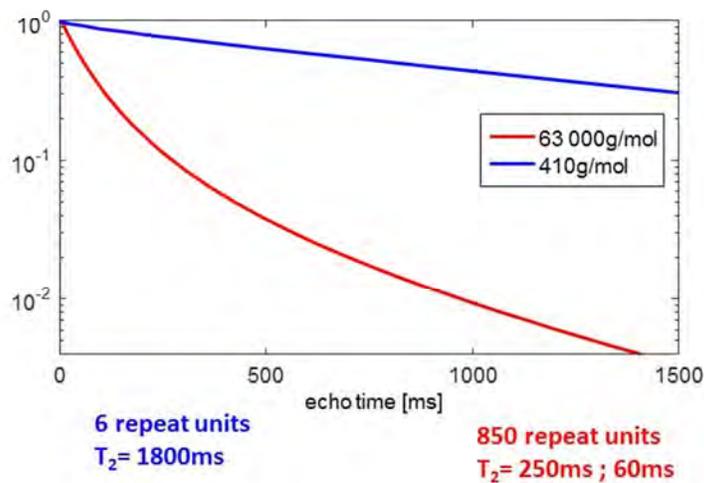


POLY 602: Polymers in electric fields and under shear studied by NMR

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In polymer melts usually a distribution of relaxation times like T_2 is observed reflecting different local mobility reflecting entanglements in polymer melts or solutions, while in an oligomer a single T_2 maybe observed. Under external shear like in a Couette cell shear-induced ordering is expected, which would lead to a shortened T_2 . Shortened T_2 is observed for oligomers only, which do not show any sign of entanglements. For longer polymers in which signatures of entanglements are found, T_2 becomes longer under shear, which indicates, that chain segment between entanglements which move more freely become longer. From the experiments it is concluded, that this is the dominating effect, ordering maybe present but less effective for the mobility relevant to T_2 .

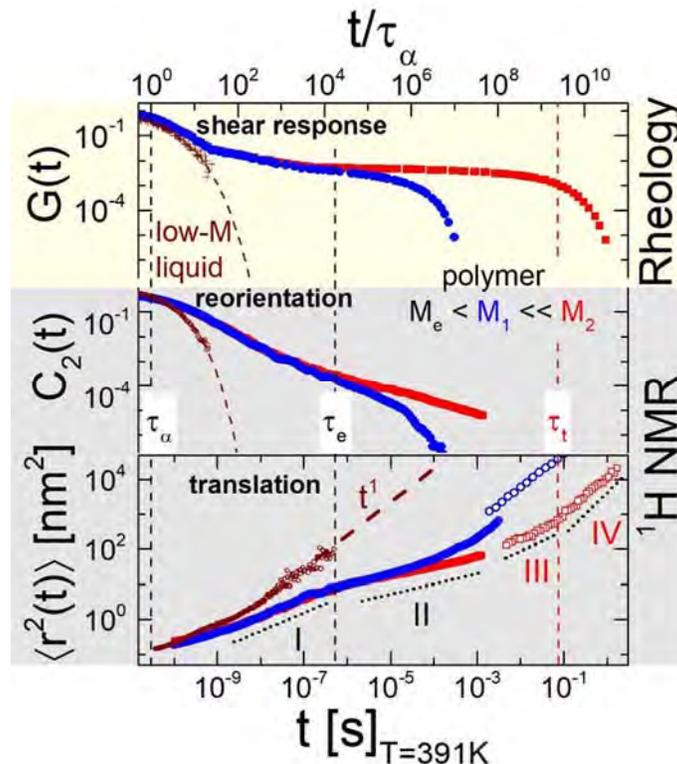
In solutions of charged polymers (polyelectrolytes) in addition the repelling force between the charges along the chain reduce entanglements. However similar effects are found for high molecular weights. To access the charge interaction along the chain, the effective charge, which is not compensated by condensed counterions is investigated by electrophoresis NMR. The effective charge at a given polymer is influenced by the ionic strength and thus at higher ionic strength more entanglements are observed. So these shear-induced effects have been observed mostly at weakly charged polyelectrolytes.



POLY 603: Field-cycling NMR as a tool of molecular rheology

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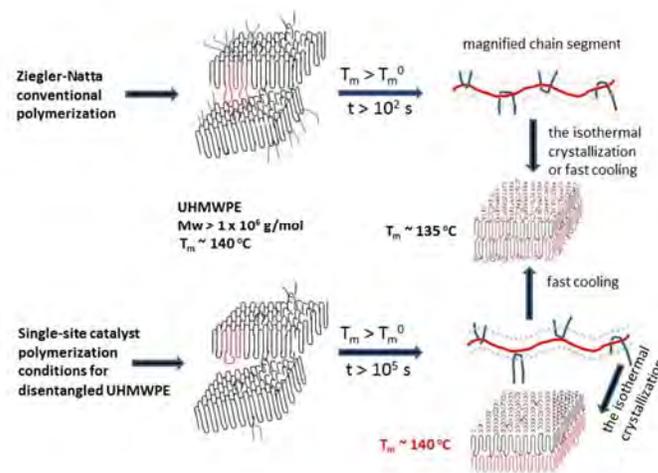
The frequency dependence (dispersion) of the spin-lattice relaxation rate, $R_1(\omega)$, provides the fluctuation spectrum of molecular dynamics in complex fluids. Employing a commercial and a home-built field-cycling (FC) relaxometer a broad frequency range of $100 \text{ Hz} \leq \omega/2\pi \leq 30 \text{ MHz}$ (^1H) is covered. In polymer melts master curve construction assuming frequency-temperature superposition allows us to extend the effective frequency range even further. Effectively, up to ten decades in frequency/time are accessed, covering the entire mode spectrum ranging from the local (α -)relaxation to chain modes and ultimately terminal relaxation. Concerning protons, relaxation is composed by an intra- and an inter-molecular contribution along $R_1(\omega) = R_1^{\text{intra}}(\omega) + R_1^{\text{inter}}(\omega)$ which we separated by isotope dilution. In the time domain R_1^{intra} and R_1^{inter} provide the reorientational correlation function $C_2(t)$ and the segmental mean square displacement $\langle r^2(t) \rangle$ respectively (Fig. 1). Those quantities are used to scrutinize polymer models. Unlike shear rheology FC NMR relaxometry allows to resolve the transition from Rouse and entanglement dynamics (Fig. 1) promoting the method as an alternative toward molecular rheology applicable to study particularly slow relaxation processes in soft matter.



POLY 604: Unlinked cyclic polymers and the non-equilibrium melt state of UHMWPE; rheological, crystallization and mechanical response

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Compared to their linear counterparts, the unlinked cyclic ring polymers are found to exhibit unique rheological and crystallization response [1,2]. The uniqueness arises because of the unconventional topological interaction between the neighboring chain segments. Retrospectively, the cyclic polymers in their melt state are reported to adopt “lattice animal” structure compared to the cross-over of the linear chains having free ends. Because of the constrained non-crystalline region, the crystalline cyclic polymers are also reported to have higher melting point compared to linear chains of similar molar masses [2]. In this presentation we will report several similarities that a disentangled UHMWPE, having number average molar mass greater than a million g/mol, draws with the cyclic ring polymers. The cause for the similarity is attributed to the low number of chain ends that the high number average molar mass UHMWPEs provide. Thus attributing to the chain segments that similar to unlinked cyclic polymer can never form the conventional topological constraints. Differences in topological constraints are found to influence crystallization, melting and mechanical response in the equilibrating and thermodynamically equilibrated polymer melt.



Influence of entangled state perceived during and after polymerization

POLY 605: Intermolecular contribution to proton spin-relaxation in polymer melts: New perspectives for experimental study of polymer melt dynamics.

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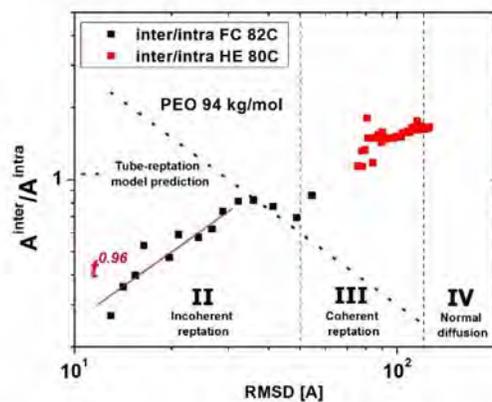
Recent progress in application of proton NMR to study of dynamics of highly molecular mass polymer melts is closely connected with reconsideration of the role of the intermolecular magnetic dipole-dipole interactions in proton spin relaxation. As it appears, the intermolecular contribution is not small and even can dominate over the contribution from intramolecular magnetic dipole-dipole interaction. After making very general assumptions, it is possible to connect the intermolecular contribution in a rather simple way with relative mean-squared displacement of polymer segments from different macromolecules. Experimental data connected with intermolecular magnetic dipole-dipole interactions obtained through combination of existing methods based on spin-lattice and spin-spin relaxation allows extracting information about polymer segment mean squared displacement in a wide time region 10^{-8} - 10^{-3} s, most of which is hardly accessible to other experimental techniques. Basic elements of corresponding theory with main assumptions allowing the mentioned application will be discussed.

$$A_p^{\text{inter}}(t) = \frac{4\pi}{9} n \tilde{W}(0;t) = \sqrt{\frac{2}{3\pi}} \frac{n}{\langle \tilde{r}^2(t) \rangle^{3/2}}$$

POLY 606: Intermolecular contribution to proton spin-relaxation in polymer melts: New experimental evidence for entanglement dynamics - does reptation really exist?

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The time-dependence of the rms displacements of chain segments in polymer melts has been a cornerstone of experimental tests of various chain motion models. Rouse and Reptation dynamics (below and above the entanglement limits for chain lengths, respectively) are described by characteristic power-laws. Neutron spin echo and gradient NMR studies have tested and confirmed these power-laws, but have also found discrepancies in some cases. The wide time gap between these two techniques is partially covered by NMR relaxometry. Again, relaxometry finds power-law relationships between NMR relaxation times and Larmor frequency, but both the dependence on frequency and molecular weight were shown to deviate substantially from tube-reptation predictions. In recent years, intra- and intermolecular spin interactions were found to possess quite different frequency dependences which makes them distinguishable. In principle, the mean-squared displacement can be obtained with the help of partial deuteration of the polymer. Latest studies have exploited the possibilities of isotopic dilution not only in relaxometry, but also in conjunction with newly developed analytical schemes employing multi-pulse encodings of dipolar interactions. Results obtained for poly (ethylene oxide) melts, when compared to PEP and PDMS, lead to the notion that an abstract, ideal-chain picture is probably insufficient to describe the NMR response, and possibly polymer dynamics themselves. While the power-law dependence predicted from the reptation model has been confirmed with these methods over an unprecedented frequency range, the relative ratio of inter- and intramolecular contributions deviates significantly from this model, providing evidence that the classical reptation picture might be incomplete.

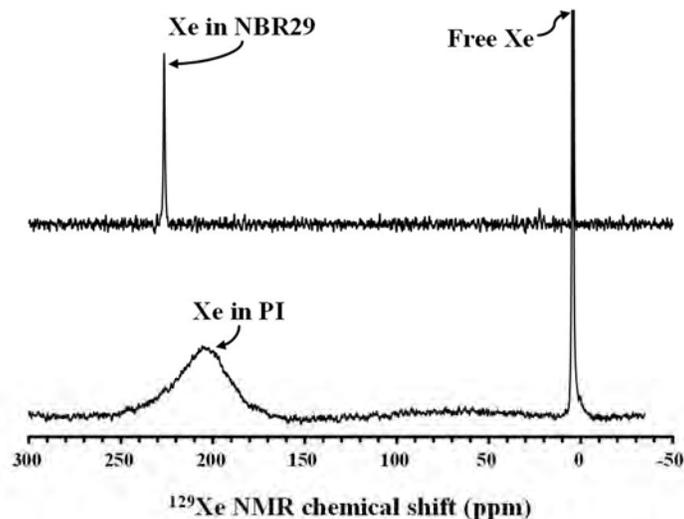


Ratio of inter- and intramolecular dipole-dipole contributions as a function of rms displacement for poly (ethylene oxide) melt of 94000 g/mol. Red and blue lines indicate the prediction of the tube-reptation model.

POLY 607: NMR observations of the gases in polymers

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The gas transport properties of polymeric materials, including sorption, diffusion, and permeation, are closely related to the structural characteristics of the polymers. As a result, the analysis of polymers exposed to certain gases by NMR spectroscopy can determine detailed correlations between gas sorption and diffusion in the polymer and high-order structures. In this study, it is discussed the NMR spectroscopy data which can be obtained from numerous gas–polymer systems, in order to demonstrate that this technique allows the characterization of the fine structures and gas transport properties of polymeric materials. ^{129}Xe NMR spectroscopy is one of the most powerful of these methods. In particular, the ^{129}Xe NMR chemical shifts of polymeric materials can provide information regarding the density of rubbery polymers or the presence of microvoids in glassy materials, on both a qualitative and quantitative basis. In addition, the spectral intensity can be converted to units of gas sorption, and the peak width (equivalent to the spin–spin relaxation time) presents a measure of diffusivity. These features are independent of the nuclei being assessed, indicating that various gases can be applied. Because peak widths are typically in the range of several tens to tens of thousands of Hz, gas diffusivity can be observed on very short timescales. Furthermore, the PFG NMR analysis of gases in polymeric materials is useful for the determination of anisotropic gas diffusion properties and molecular orientations. In conclusion, the NMR spectral observation of gases in polymeric substances has significant potential as a means of studying both gas transport properties and fine high-order structures.



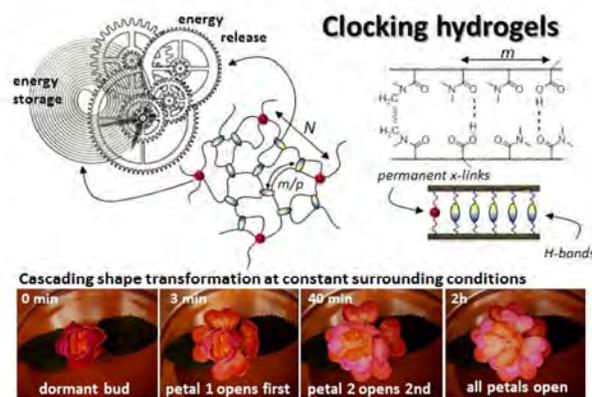
The 193.6 MHz ^{129}Xe NMR spectra of free (gaseous) Xe and the Xe in acrylonitrile–butadiene copolymer rubber (with 29 mol % acrylonitrile; NBR29) and polyimide (PI) at 0.7 (NBR29) and 0.8 (PI) MPa and 25 °C. From the chemical shift, intensity, and width of the Xe atoms in NBR29 and PI, the inter spaces between polymer chains, the amounts of Xe, and the diffusivity of Xe could be discussed, respectively.

POLY 608: Tough hydrogels for time-programmable shapeshifting

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Hydrogels are conventionally viewed as weak materials that also respond to minute variations in the surrounding environment. This presents a challenge to design gels that are mechanically tough and change properties not in response to an external trigger but as a function of time. Herein, we designed hybrid networks composed of permanent covalent cross-links and clusters of hydrogen bonds as reversible crosslinks [1]. The total high crosslink density ensures stiffness, however partitioning between the crosslinks was uneven: (i) high fraction of hydrogen bonds to provide high energy dissipation and reversible association and (ii) small fraction of permanent cross-links to implement shape control and strain recovery [2]. At 70 wt% water fraction, thus designed hydrogels display a high modulus of 28 MPa, high strength of 2 MPa, high fracture energy of $9300 \text{ J}\cdot\text{m}^{-2}$, high extensibility of 800%, excellent fatigue-resistance, and great elasticity - properties on par with that of soft connective tissues such as cartilage, skin, and ligaments.

The strain-recovery ability was further explored to design time-programmable shapeshifting materials that perform a sequence of encoded actuations without a need for external stimuli [3]. In these molecular constructs, the covalent network stores the elastic energy during deformation, while temporary hydrogen-bonds in the physical network regulate the energy-release rate after unloading. Through time-dependent reorganization of the reversible hydrogen bonds, these dual network hydrogels allows for encoding both the rate and pathway of shape transformations on time scales from seconds to hours. This generic mechanism for programing stimuli-free shape changes opens new ways to design autonomous actuators, drug-release systems, and active implants which can operate in closed or inert systems.



POLY 609: Creating tough and healable macroscale “double network” hydrogels

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The double network concept has been revolutionary in its ability to turn soft, brittle hydrogels into tough, robust materials. Double network hydrogels consist of two interpenetrating networks, where each network has a specific mechanical response: the “first network” acts as a sacrificial network, consisting of a rigid, extended network with relatively low loading percentage, and the “second network” is a globally percolated, stretchable network. When a double network hydrogel is stretched, covalent bonds of the first network break, dissipating energy. These materials possess enhanced properties, but in many cases, lack the mechanical properties to act as structural materials. Here, we attempt to utilize “double network theory” at the macroscale, by creating rigid scaffolds and embedding them in a stretchy and tough matrix, mimicking the first and second networks, respectively.

Creating hydrogel composites is difficult because of the swelling mismatch between the rigid materials and the hydrogel matrix. To overcome this problem, we utilize a low melting-point alloy (LMA) as the rigid scaffolding material inside of the hydrogel matrix. After the hydrogel reaches equilibrium, the LMA frame is melted, and the swelling mismatch between the frame and the gel is released. Beyond relieving swelling stress, these composites exhibit unique and remarkable mechanical properties. When stretched, they undergo multiple fracture processes, which results in a dramatic increase in the work of extension compared to the neat hydrogels. When stretched up to 250%, they can be cycled with 100% healing of the sacrificial network. Furthermore, these composites can exhibit shape memory, conductivity, and can act as a base for electro-chemical reactions. We believe this new technique will help create new hydrogel-based materials with properties that are unachievable with neat hydrogel materials.

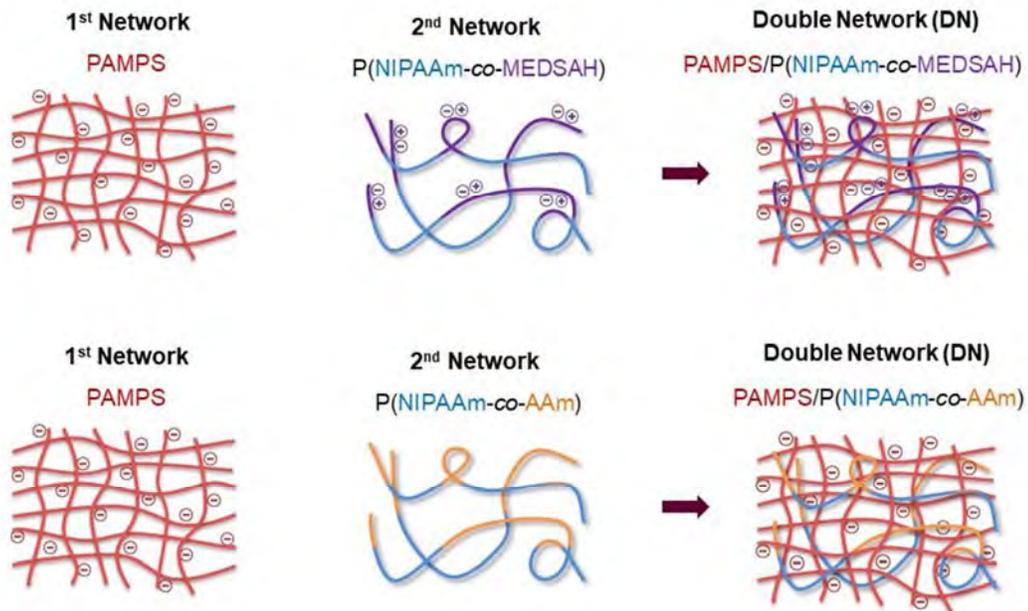


An image of an LMA-composite hydrogel.

POLY 610: Double network hydrogels with high stiffness and ultra-high strength

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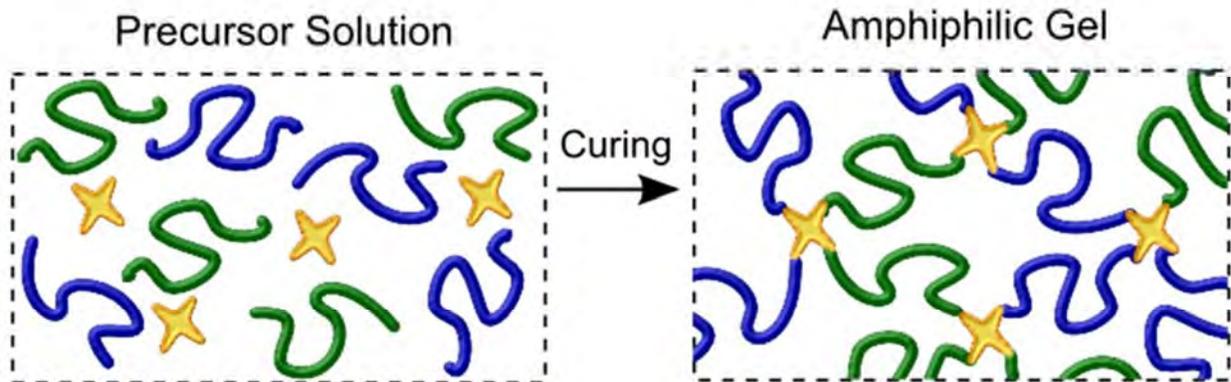
Simultaneously achieving hydrogels with high strength and stiffness is challenging. Thermoresponsive hydrogels were prepared with the unique combination of ultra-high strength (~23 MPa) and excellent modulus (~1.5 MPa). Additionally, these hydrogels undergo a volume phase transition temperature (VPTT) ~35 °C through the use of a thermoresponsive polymer, poly(N-isopropylacrylamide) (PNIPAAm). This is accomplished by employing a double network (DN) design comprised of a tightly crosslinked, highly negatively charged 1st network and a loosely crosslinked, zwitterionic 2nd network. Specifically, the 1st network is based on poly(2-acrylamido-2-methylpropane sulfonic acid) (PAMPS) and the 2nd network is based on copolymer of thermoresponsive NIPAAm and zwitterionic 2-(methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)-ammonium hydroxide (MEDSAH). The VPTT can be tuned beyond the physiologic temperature range through the incorporation of a hydrophilic comonomer, acrylamide (AAm), in place of MEDSAH in the 2nd network. This non-thermoresponsive PAMPS/P(NIPAAm-co-AAm) DN hydrogel was able to simultaneously achieve ultra-high strength (~25 MPa) and significantly high modulus (~1.2 MPa).



POLY 611: Highly resilient two component networks

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Phase-separated and self-assembled co-network materials offer a simple route to bicontinuous-like morphologies, which are expected to be highly beneficial for applications such as ion, charge, and oxygen transport. Here, a thiol-ene end-linking platform enables the systematic investigation of phase-separated poly(ethylene glycol) (PEG) and polydimethylsiloxane (PDMS) or polystyrene (PS) networks in terms of the molecular weight and relative volume fractions of precursor polymers. Small angle X-ray scattering (SAXS) shows that microphase separation of these co-networks yields disordered structures with d -spacings similar to the prediction by de Gennes of $d \sim M_n^{0.5}$. These findings demonstrate that this approach to thiol-ene co-networks is a versatile platform to create bicontinuous morphologies.

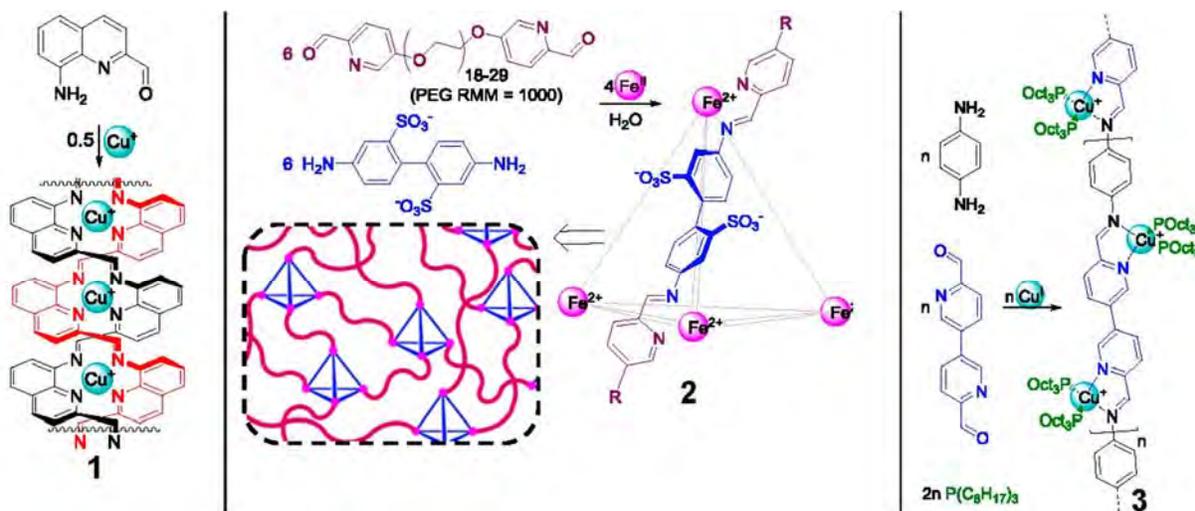


POLY 612: Functional polymers through subcomponent self-assembly

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The materials that we depend on rely upon ever-increasing structural complexity for their function. The use of chemical self-assembly as a synthetic technique can simplify materials preparation by shifting intellectual effort away from designing molecules, and towards the design of *chemical systems* that are capable of self-assembling in such a way as to express desired materials properties and functions. Below are shown the subcomponent precursors and crystal structures of three polymeric products that can form functional constituents of these systems.

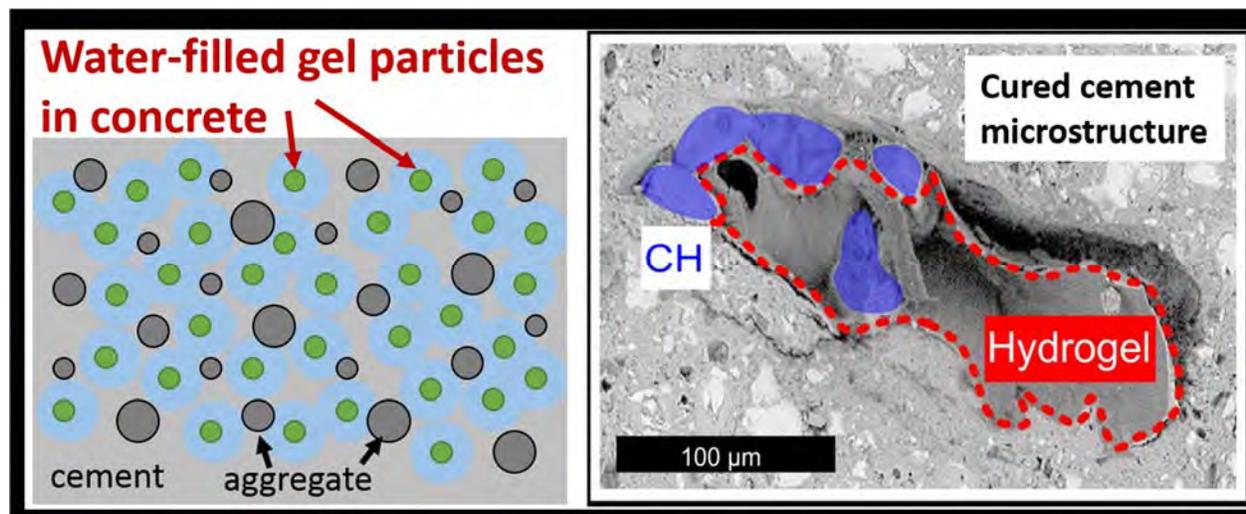
Polymer **1** self-assembles from a simple formyl(aminoquinoline) monomer and Cu^{I} , producing rigid, double-helical chains averaging 75 repeat units. It emits across the visible spectrum, with λ_{max} depending on chain length,¹ and the proximity of the copper centers within the chain may allow for extensive hole delocalization, behaving as molecular wires.² Polymer **2** is cross-linked by metal-organic cages, forming a hydrogel that contains two distinct internal void spaces: one within the aqueous hydrogel matrix, and another within the cavities of the cages themselves. Guests may be introduced and removed from both kinds of voids, independently.³ Polymer **3**⁴ and its congeners⁵ display such properties as reverse thermogelation – the formation of a gel upon increase in temperature⁴ – and blue-shifted emission upon increase in voltage when built into a light-emitting electrochemical cell.⁵



POLY 613: Swelling and mechanical characterization of poly(acrylic acid)-based hydrogel particles used as internal curing agents in cement

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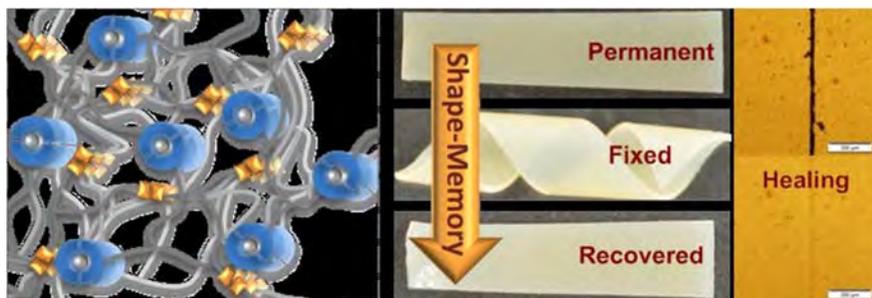
This presentation will describe the synthesis, characterization, and use of superabsorbent polymer hydrogel particles as internal curing agents in cement-based mixtures. When incorporated into cement, the swollen hydrogel particles release their stored water to fuel the hydration reaction, resulting in reduced mixture shrinkage and cracking and thus increasing cement strength and durability. However, the hydrogel's swelling performance and mechanical properties are strongly sensitive to multivalent cations that are naturally present in the alkaline aqueous phase of cementitious mixtures (including calcium and aluminum ions). To investigate polymer-ion interactions, model poly(acrylic acid-acrylamide)-based hydrogel particles with different chemical compositions were synthesized using solution and suspension polymerization techniques. Upon immersion of the particles in different salt solutions, the presence of multivalent cations significantly decreased the swelling capacity and altered the swelling kinetics to the point where some hydrogel compositions displayed rapid deswelling behavior. In solutions containing aluminum ions, a dense and mechanically stiff outer layer formed at the particle-solution interface and the internal polymer network was effectively destroyed, resulting in a water-filled capsule. It was also discovered that the presence of hydrogel particles of certain compositions encouraged the formation of specific inorganic phases within cement, including calcium hydroxide and calcium silicate hydrate phases. Ongoing work is now focused on optimizing the chemistry of the polymer hydrogels and specifically incorporating silica nanoparticles into the gels to allow for greater control of the cement microstructure.



POLY 614: Stimuli-responsive supramolecular polymer networks

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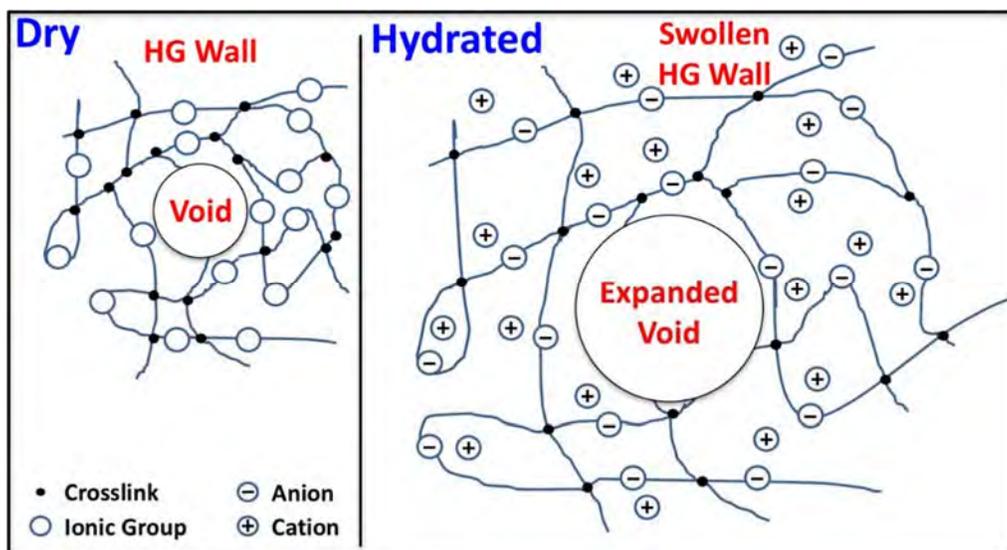
Supramolecular polymers (SPs) are formed by the self-assembly of monomeric units equipped with binding motifs that enable hydrogen bonding, metal-ligand coordination or other directional non-covalent interactions. The reversibility of these bonds can be exploited to disassemble SPs back into their monomeric species. This can be achieved in a controlled manner by the application of a specific stimulus, such as heat, light or a mechanical force, making supramolecular interactions a versatile design element for the creation of functional polymers with unusual stimuli-responsive properties. In this presentation we will discuss several recent examples of supramolecular polymer networks, which represent a scarcely investigated subset of materials based on this design. Several materials that rely on this general approach will be discussed. Interactions covered include hydrogen-bonds, pi-pi stacking, and metal-ligand binding. These non-covalent bonds can be used to assemble supramolecular monomers to create a broad range of stimuli-responsive polymers. Functions that can be achieved using this design approach include the ability to heal, (de)bonding on demand, and mechanochromic effects. This contribution will also cover new supramolecular polymer systems based on two orthogonally bound interpenetrated supramolecular networks. The crystalline hard phases formed by the two binding motifs can be selectively addressed with different stimuli, enabling mechanical switching, shape memory and “smart” healing.



POLY 615: Emulsion templated hydrogels: Superabsorbents, stimulus-responsive, double-crosslinking, and dual-response

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PolyHIPEs are porous emulsion-templated polymers that are usually synthesized using free radical polymerization within surfactant-stabilized water-in-oil high internal phase emulsions (HIPEs) [1,2]. High-porosity hydrogel polyHIPEs (HG-PHs), based on ionic and/or non-ionic monomers and crosslinked with *N,N'*-methylenebisacrylamide, were synthesized within oil-in-water HIPEs [3-6]. The extraordinary water absorbency of the HG-PHs was ascribed to a hydrogel-swelling-driven void expansion mechanism (see Figure). The water uptakes in the ionic HG-PHs were pH-responsive, while those in the HG-PHs based on *N*-isopropylacrylamide were temperature-responsive. Mechanically robust HG-PHs based on 2-acrylamido-2-methyl-propansulfonic acid exhibited unusually high water and artificial urine uptakes. The highly accessible sulfonic acid groups produced a high ion exchange capacity and rapid dye absorption. Doubly-crosslinked HG-PHs with reversible metal-coordination crosslinking were fabricated by adding FeCl₃ to covalently crosslinked HG-PHs based on acrylamide and sodium acrylate. The metal-coordination crosslinking significantly enhanced the mechanical properties but did not affect the interconnected macroporous structures or the rapid water absorption. Shape memory behaviour resulted from imposing a temporary shape through double crosslinking and then recovering the original shape by removing the double crosslinking. Other HG-PHs exhibited an anti-polyelectrolyte effect (an increase in NaCl solution uptake with increasing concentration) and a dual-response uptake with pH (decreasing from 2 to 7, increasing from 7 to 10). This work clearly demonstrates that emulsion templating amplifies the magnitude of the hydrogel network's response to the environment and accelerates its response.



POLY 616: Development of visible-light responsive and mechanically enhanced UCST double network hydrogels

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We will present an environmentally responsive hydrogel that exhibits the following features: enhanced mechanical property, upper critical solution temperature (UCST) swelling behavior, and responsiveness to visible-light. Poor mechanical properties are known challenges for hydrogel-based materials and hinder their application. By forming double network between polyacrylamide (PAAm) and poly(acrylic acid) (PAAc), the toughness of the double network hydrogel was significantly improved compared to those made of the individual polymer network (Fig.1). The hydrogen bonding dissociates and re-forms between the amide group of PAAm and the carboxylic acid group of PAAc in responding to environmental temperature and facilitates a unique UCST swelling behavior of the hydrogel. By incorporating chlorophyllin into the double network as the chromophore, the double network hydrogel demonstrated a promising response of positive swelling to the irradiation of visible-light. The effect of chlorophyllin incorporation was also observed to reduce the average pore sizes and further enhance the mechanical properties of the hydrogel (Fig.2). This double network system shows potential to serve as a new route in developing “smart” hydrogels using visible-light as a simple, inexpensive, and remotely controllable stimulus.

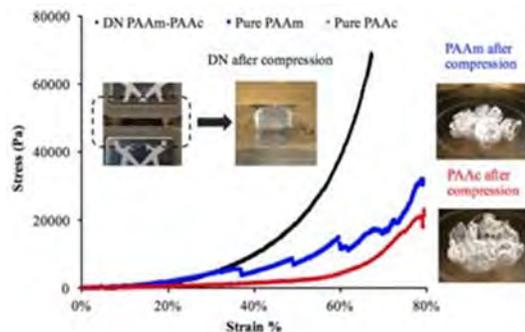


Fig 1. Compressive analysis of double network PAAm-PAAc hydrogel (black) in comparison to the single phase of pure PAAm (blue) and PAAc (red) hydrogels. Left insets: double network PAAm-PAAc hydrogel recovery to original shape after compression; Right insets: deformation of PAAm (top) and PAAc (bottom) after compression.

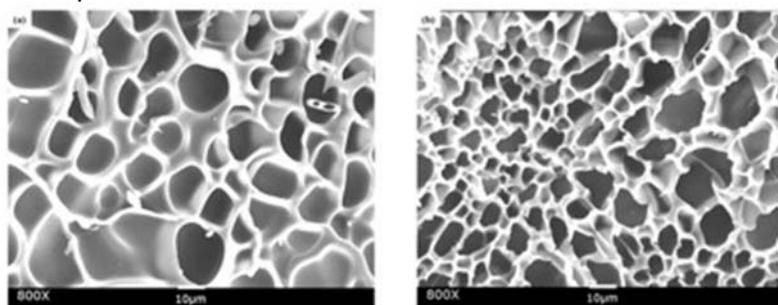
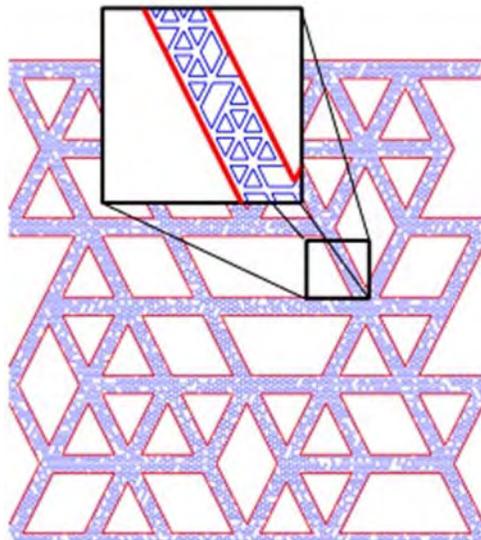


Fig 2. SEM images showing the morphology of (a) double-network PAAm-PAAc hydrogel and (b) double-network PAAm-PAAc chlorophyllin-containing hydrogel with average pore size of $16.0 \pm 4.4 \mu\text{m}$ and $9.9 \pm 4.3 \mu\text{m}$, respectively.

POLY 617: Hierarchical mechanics and assembly in hydrogels

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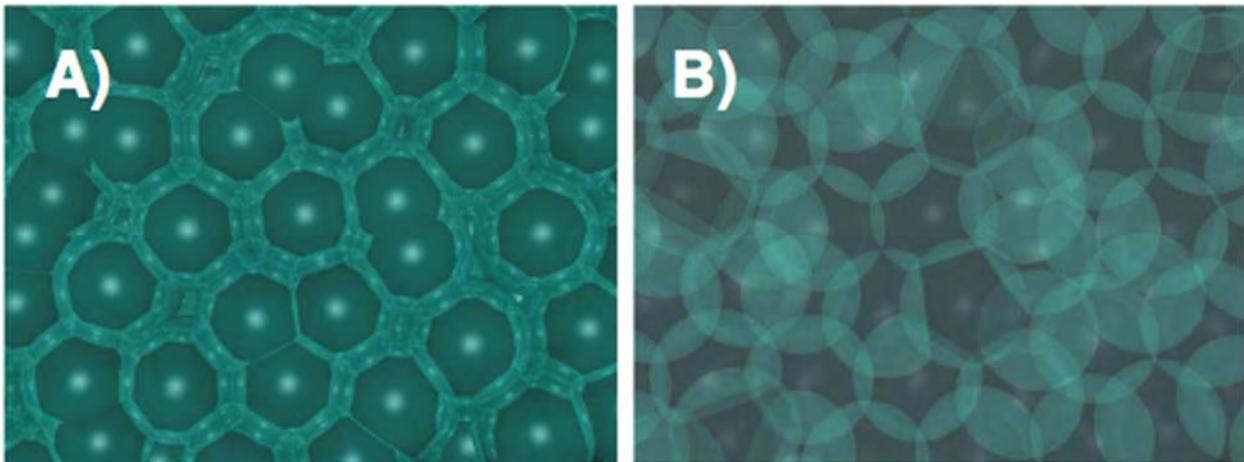
Hierarchical structures are abundant, ranging from biological materials like collagen, to engineered structures like the Eiffel tower, to suspensions of hydrogel particles. In such suspensions, cross-linked gels form micron-sized particles, which are then assembled into larger structures. The final mechanical properties of the suspension depend on structural characteristics on both gel- and particle-length-scales. In this talk, I will discuss a bottom-up approach to understand how structural hierarchy affects mechanics, as well as assembly techniques that take advantage of the hierarchical nature of hydrogel particles.



POLY 618: Soft responsive microgels at high densities

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Thermoresponsive microgels have frequently been used as model systems to study the phase behavior of colloids, and investigate the effects of softness and directional interactions in colloidal suspensions. With increasing temperature, microgels undergo a collapse transition, and change their nature from swollen, soft repulsive at low to collapsed, hard and attractive particles at high temperatures above the collapse transition temperature. This has been exploited in the past to study liquid-solid and solid-solid transitions, where often phase transitions are induced through a variation of temperature. However, in many if not most of the available studies the interpretation of the observations made is based on assumptions about the response of the particles to a highly concentrated environment and across phase boundaries, with limited experimental information existing to back up these assumptions. Here we will discuss the use of a combination of small-angle neutron and x-ray scattering, rheology, confocal and superresolution microscopy and computer simulations to study the properties of individual microgels and their effective interaction potential at high concentrations and in different states (liquid, crystalline and glassy). We will in particular highlight the influence of charges on the particle response, and also describe the effect of an external electrical field used to add an additional directional dipolar interaction.



A possible response of soft microgels to high densities, where the particles either deform or interpenetrate above close packing.

POLY 619: Hard and soft microgels: Are they different?

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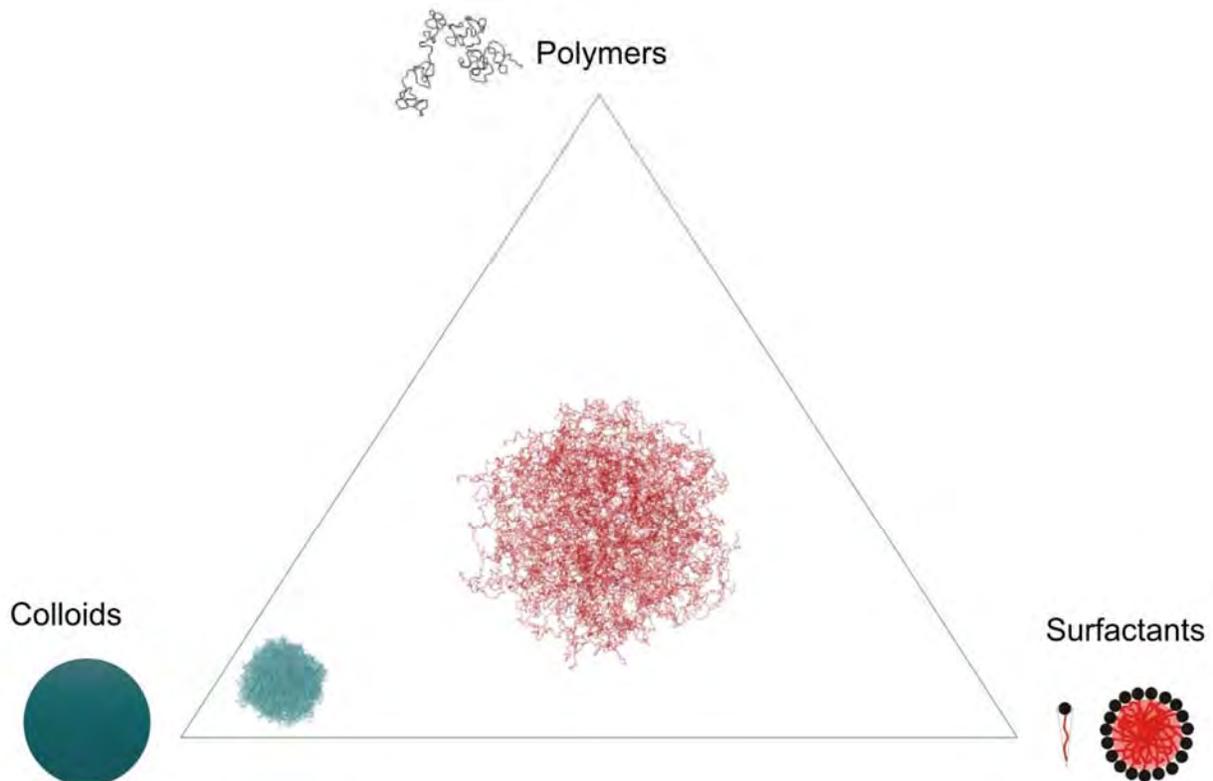
Microgels are macromolecular networks swollen by the solvent they are dissolved in. They are unique systems that are distinctly different from common systems, such as, e.g., rigid nanoparticles, flexible macromolecules, micelles or vesicles. When swollen, they are soft and have a fuzzy surface with dangling chains and the presence of cross-links provides structural integrity - in contrast to linear and (hyper-) branched polymers. Finally, microgels reveal interface activity without being amphiphilic.

The combination of being soft and porous while still having a stable structure through the cross-linked network as well as the possibility to introduce chemical functionality at different positions will allow to tune the microgels behaving as hard or soft objects.

Obviously, the degree of crosslinking is important.

We will discuss the interaction of microgels of different chemical functionality and architecture as, e.g., core-shell, hollow and multi-shell hollow microgels in bulk solution as well as at fluid interfaces.

The structure is probed by means of neutron scattering employing contrast variations as well as by (super-resolved) fluorescence microscopy. Properties of microgels at interfaces are determined by means of scanning force and electron microscopy as well as by compression isotherms and interfacial rheology. The experimental results will be compared to computer simulations.

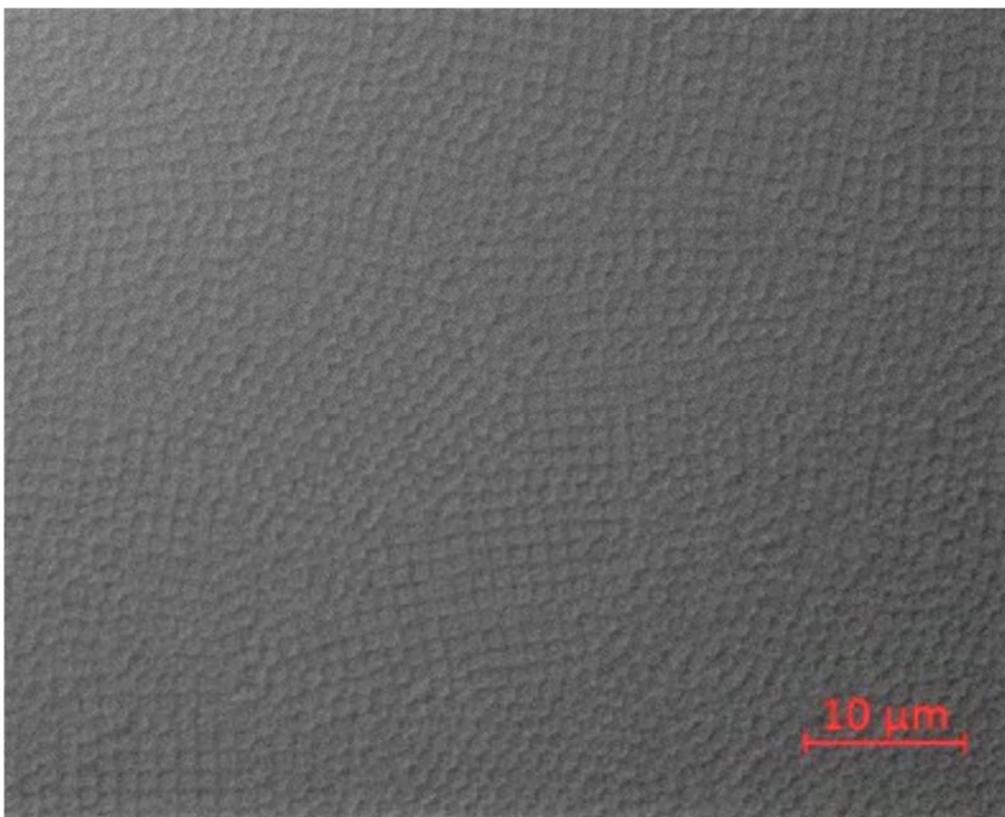


Microgels vs colloids, macromolecules and surfactants

POLY 620: Packing and defect tolerance of ultra-low cross-linked microgel assemblies

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Soft colloidal objects, such as microgels, are known to have phase behaviors that are quite different from their hard-sphere counterparts. For example, phenomena such as overpacking, self-healing, defect tolerance, and stimulus-induced annealing have all been demonstrated in colloidal crystals composed of microgels. In this contribution, we describe the phase behavior and defect tolerance of colloidal crystals composed of the softest microgels yet prepared. Using a synthetic approach that does not rely upon cross-linking monomers, but instead uses rare chain-transfer events to create the network, one can prepare "ultra-low cross-linked" (ULC) microgels. A combination of dynamic light scattering, optical microscopy, and atomic force microscopy are used to characterize the microgels and the resultant phases. Colloidal crystals prepared from these ULC microgels display all the properties described above, but in many cases the magnitude of the observed properties is significantly greater than those observed with standard cross-linked microgels. Surprisingly, observations of non-close-packed phases have also been made, suggesting that the extreme softness of the ULC microgels leads to packing phenomena not accessible using more rigid microgels.



Optical microscopy image of a polycrystalline assembly of ULC microgels.

POLY 621: Angle-independent structural colored materials by black and white components

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There are many technical and industrial applications for coloured pigments with anti-fading properties. The development of a low-cost, high-volume production method for anti-fading pigments with low toxicity and minimal environmental impact may promote their widespread use. To accomplish this goal, we need to prepare pigments using abundant and environmentally friendly chemical compounds. Here, I report on the aggregates of various colours formed by spraying fine, submicron spherical silica particles. The aggregate microstructure is isotropic with short-range order on a length scale comparable to optical wavelengths and exhibits an angle-independent structural colour due to wavelength-specific constructive interference. Interestingly, the colour saturation of these aggregates can be controlled by the incorporation of a small amount of conventional black particles, such as carbon black (CB). We demonstrate that a Japanese-style painting can be successfully drawn with this method and that an interesting effect is obtained that can be applied to steganography (Figure 1). The gel particles suspension system that display angle-independent structural color will be also described in my presentation.

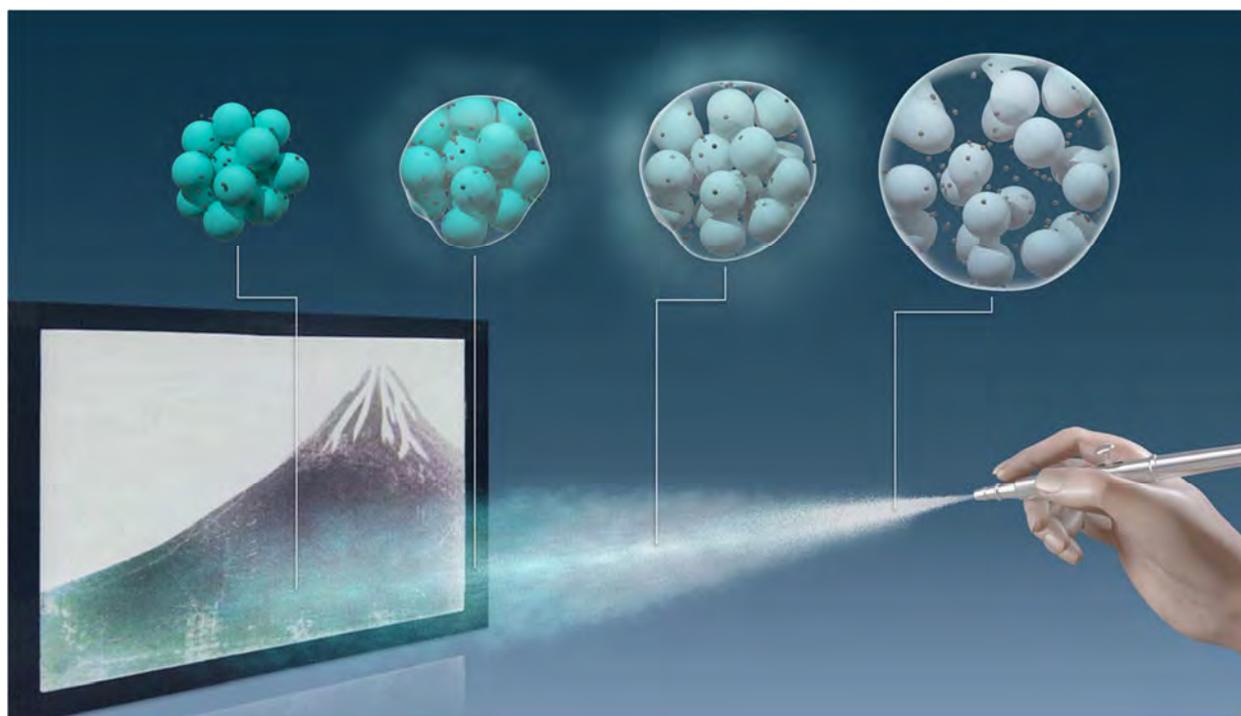
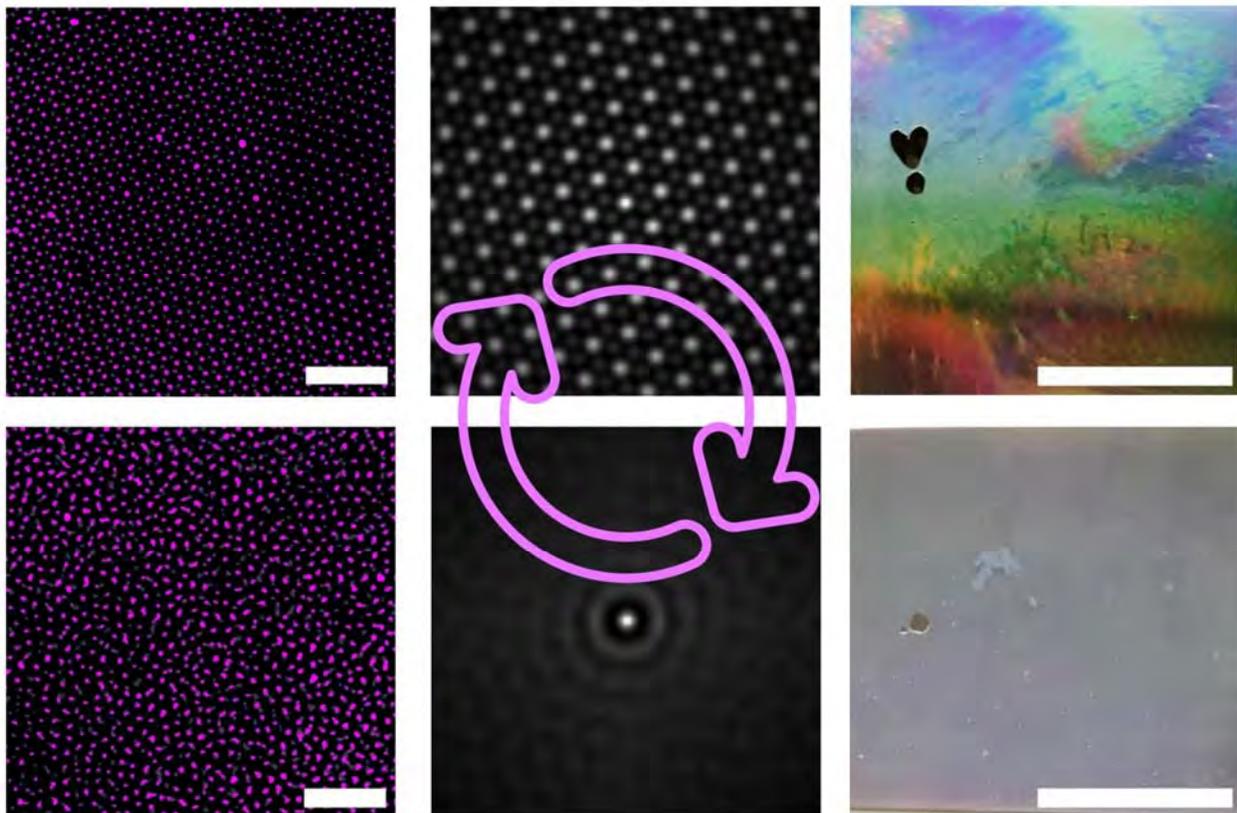


Figure 1 Demonstration of a Japanese-style painting drawn by mixing black and white particles.

POLY 622: Hard core – Soft shell microgels for reconfigurable colloidal crystal assemblies

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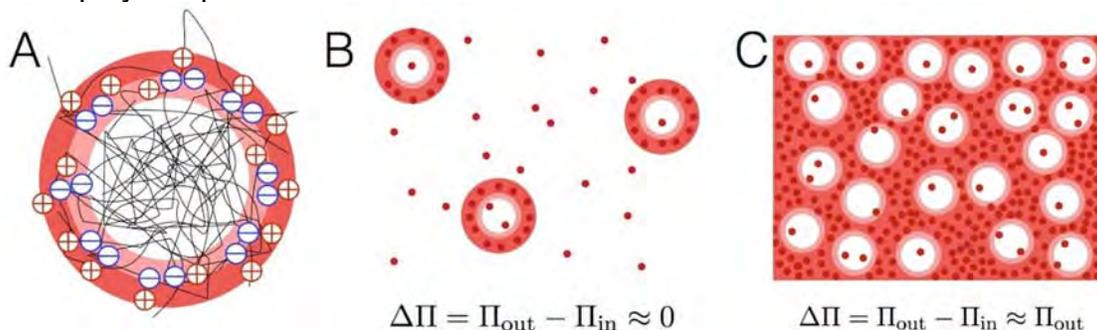
Soft microgels with hard cores can be used as reconfigurable optical components. While the swollen microgel shell has a refractive index close to the dispersing medium and can be functionalized to carry a large number of charges, the hard core can be of high refractive index and functionalized with fluorescent molecules to evoke photonic effects. When the pH of the dispersing medium is varied, the microgel shell can be charged or neutralized allowing for tuning of the interactions between the nanoscopic microgels. Here we will show how we can temporally program a crystalline microgel assembly to disintegrate and recrystallize using a lactone, which decomposes and slowly decreases the pH. Alternatively, we can also use a photoswitchable acid as a fuel to drive the system into disassembly. We will show how these complex reaction networks work and how the crystalline assemblies can be used as reconfigurable photonic components with optical bandgaps in the visible spectrum.



POLY 623: Phase behavior in polydisperse microgel suspensions controlled by spontaneous particle deswelling

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Crystallization is often suppressed by the presence of point defects due to larger atoms or impurity particles. Surprisingly, suspensions of pNIPAM microgels can overcome this limitation: Large microgels can spontaneously deswell to fit into the crystal lattice of smaller but otherwise identical microgels, thus avoiding the occurrence of point defects. We find this unique reduction of polydispersity and particle deswelling to be triggered by a difference in osmotic pressure, Π , between the inside and the outside of the microgel particles. Π is set by the counterions of charged groups on the periphery of the microgels. Although pNIPAM is uncharged, pNIPAM microgels carry charged groups (Fig. 1A) originating from the starter for the NIPAM polymerization. Most counterions are bound to the particle surface, but a small fraction can escape the attraction and sets Π of the suspension (Fig. 1B). A Π -difference between inside and outside of a microgel builds up when the counterion clouds of neighboring particles overlap. This causes an increase of Π in the space between particles, which is not compensated by an increase of Π inside of the particles (Fig. 1C). With increasing concentration, this pressure difference exceeds the bulk modulus of the softest microgels, which usually are also the largest, and makes them deswell, enabling crystallization without point defects. We find the freezing point of bidisperse pNIPAM suspensions to be linked to particle deswelling: A reduction of polydispersity due to particle deswelling of the large particles is required for crystallization. Compared to monodisperse suspensions, this causes the freezing point to shift to higher concentrations. In comparison to hard, incompressible colloidal particles, this particle deswelling mechanism fundamentally changes the role of polydispersity in microgel suspensions. We expect this mechanism to also apply for other soft polymer particles.



(A) Microgel particle and its counterion cloud that extends towards the outside (dark red shell) and the inside (light red shell) of the particle. (B) Dilute suspension where only a small fraction of the counterions can leave the particle. (C) Concentrated suspension with percolated counterion clouds. The bound counterions freely explore the volume between the microgels.

POLY 624: pH and temperature dependent swelling studies of core-shell microgels prepared with ultralow crosslinked microgels

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pH and thermoresponsive core-shell poly(*N*-isopropylacrylamide)-*co*-acrylic acid (pNIPAm-*co*-AAc) microgels were synthesized by sequential addition of shell on core microgel particles through seed and feed precipitation polymerization. The compositions of the core-shell microgels were varied by adding ultralow cross-linked shell on cross-linked core and cross-linked shell on ultralow cross-linked (ULC) core microgel. We found that the diameter of the core-shell microgels increases significantly as we adjust the pH of the microgel solution to just above the pK_a of Ac moieties present in ULC. When the pH is adjusted to 6.5, the diameter increases three-fold. This is evident from the pH and temperature dependent swelling studies by Dynamic Light Scattering (Fig. a). The Atomic Force Microscope images also confirmed this observation (Fig. b-d). We hypothesize that this extreme swelling is due to the presence of ULC shell and not restricted by the crosslinked core polymer network. This swelling behavior is very interesting and different than what we observe when ULC is present as core. Further investigations suggest that ULC-containing core-shell microgels may possess unique phase transition behaviors as compared with their cross-linked counterparts.

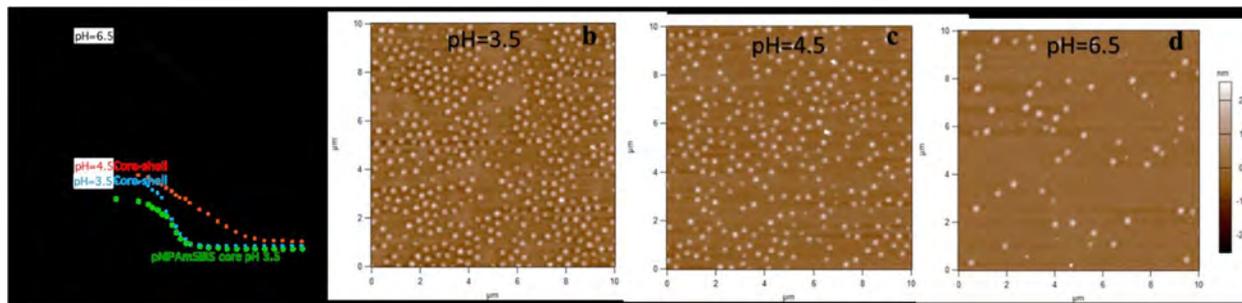
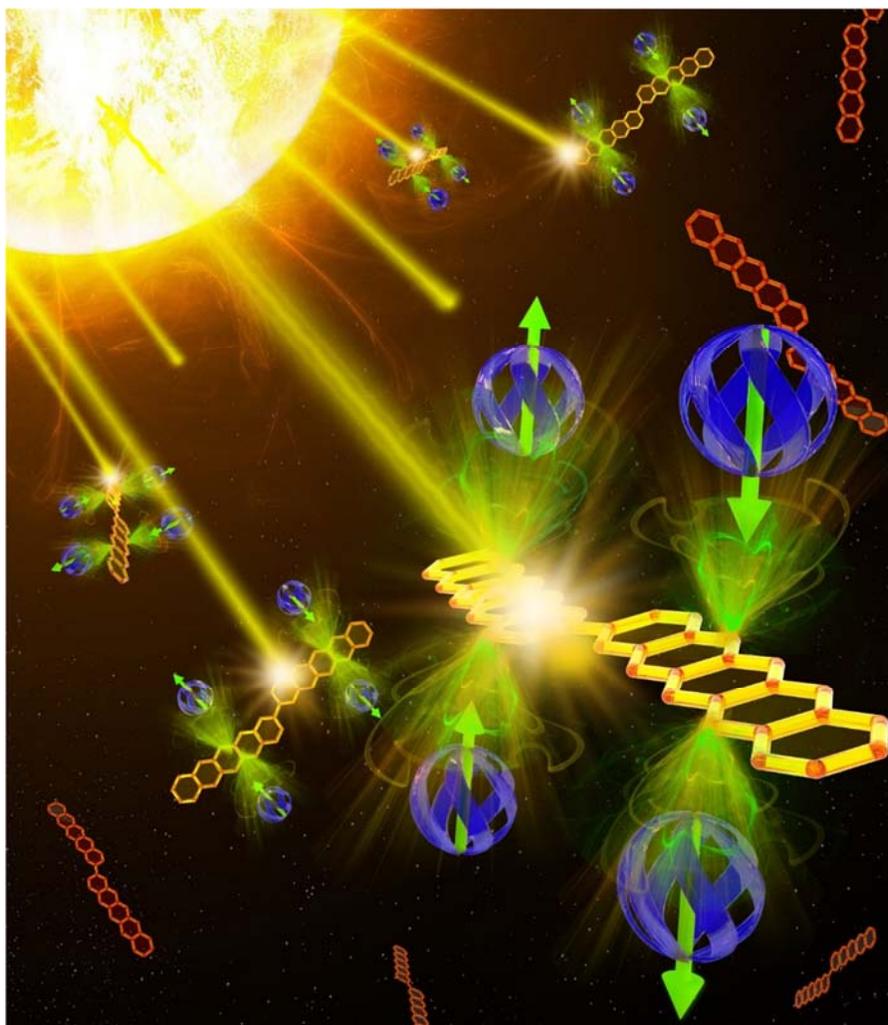


Fig. (a) pH and temperature dependent swelling studies and (b-d) pH dependent AFM images of pNIPAm core ULC shell.

POLY 625: Recent advancements in optoelectronic materials

Luis M. Campos, campos96@hotmail.com. Chemistry, MC3124, Columbia University, New York, New York, United States

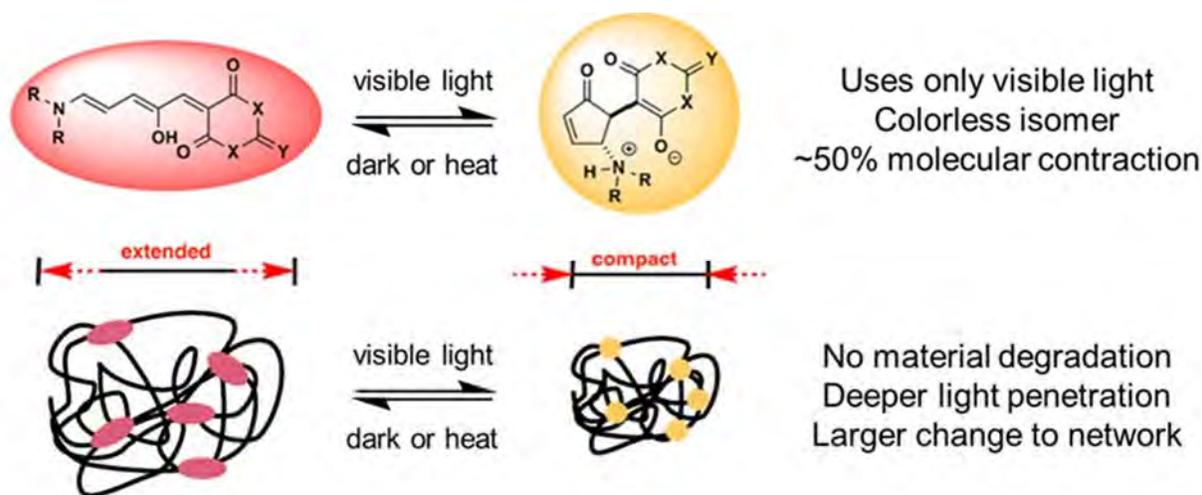
Organic materials offer a rich palette to be decorated with functional units in order to tune various properties. For example, the ability to generate multiple excitons from a single photon (singlet fission in molecular materials) has the potential to significantly enhance the photocurrent in single-junction solar cells, and thus raise the power conversion efficiency from the Shockley–Queisser limit of 33% to 44%. However, there is a paucity of materials that undergo efficient singlet fission. Our group is interested in designing building blocks that are capable of generating triplet pairs in modular small molecules and polymers. This talk will provide an overview on our approach to the design, synthesis, and evaluation of the materials.



POLY 626: DASA-based photomechanical material systems

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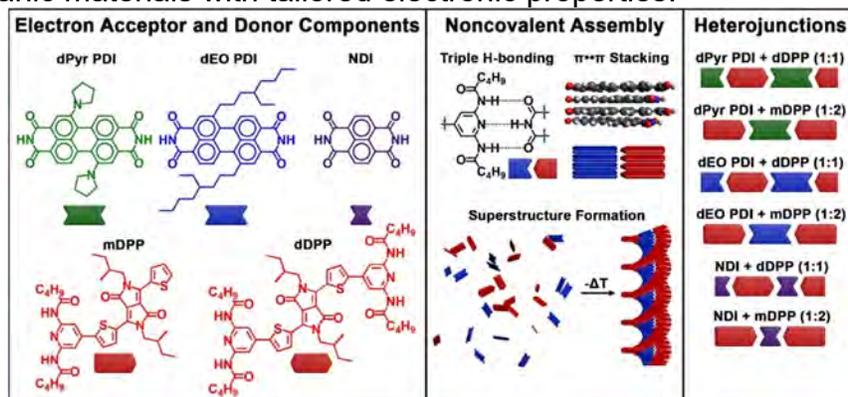
Efforts to fundamentally understand how light can be used as an energy source have led to an increased interest in stimuli induced changes to polymer gels. Photoresponsive materials offer advantages to other stimuli such as heat, electricity, and humidity because of the spatiotemporal control and direct control over intensity and wavelength that can be achieved with light. Donor-acceptor Stenhouse adducts (DASAs) are a newer class of photoswitches that convert to a compact, colorless isomer, which can allow for deeper penetration of light during photoconversion (when compared to leading photoresponsive materials) and lead to increased efficiency of these molecules as photoactuators. In this work, the incorporation of DASA photoswitches into tunable polymer networks with low dispersities is described. In addition, the use of DASA in efficiently converting light to mechanical work will be explored.



POLY 627: Interrelationships between molecular structure, hierarchical organization, and FMO energies in supramolecular heterojunctions

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The primary benefit of noncovalent assembly is that weak, reversible interactions work cooperatively to create multicomponent architectures with precise order across the molecular-to-macroscopic continuum. As a consequence, structural complexity unattainable using conventional synthetic organic chemistry can be achieved, providing emergent optoelectronic properties that are absent in individual molecular components. Here we use this order to address the challenge of light harvesting in organic photovoltaics, namely (1) the donor and acceptor components need appropriately matched frontier molecular orbital (FMO) energies to facilitate charge separation, and (2) the charges need contiguous pathways to migrate to the electrodes. As such, donor-acceptor FMO energies and assembly in films must be considered equally important aspects of design. The difficulty involved in controlling both these aspects has precluded the development of a predictive body of rules that anticipate how a given set of donor and acceptor molecules will separate light into an ion-pair that can be subsequently collected. To this end we have created a library of organic electron donors based on the diketopyrrolopyrrole (DPP) scaffold and rylene based electron acceptors that assemble into superstructures as a result of complementary H-bonding groups on the donors and acceptors, and orthogonal donor-donor or acceptor-acceptor $\pi \bullet \bullet \bullet \pi$ stacking. The two donor and three acceptor constituents of the library have subtle variations in their noncovalent bonding geometries and in their FMO levels, resulting in six unique donor-acceptor pairs that vary in their superstructures and photophysical properties. Charge separation is observed, although charge transfer processes and recombination rates are dependent on subtleties of molecular structures, assembly, and FMO levels. These results provide an increased understanding of how charge transfer dynamics manifest as a result of assembly and alignment of FMOs and could be used to design organic materials with tailored electronic properties.

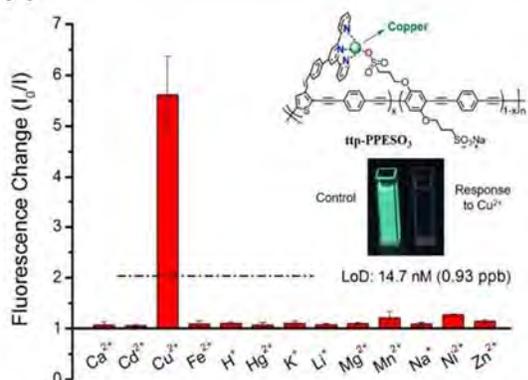


POLY 628: Design and synthesis of fluorescent conjugated polyelectrolytes as copper and fluoride sensors

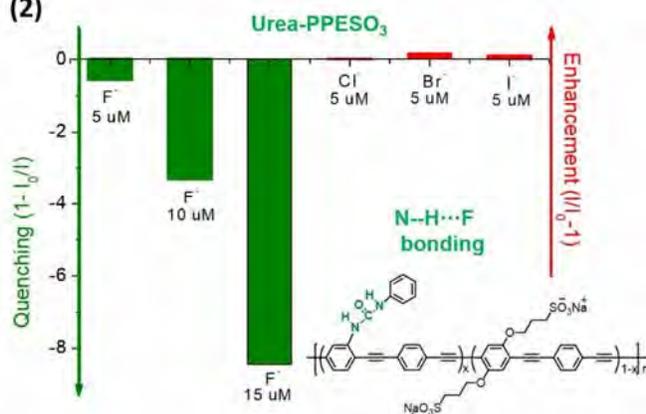
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Fluorescent conjugated polyelectrolytes (FCPEs) have drawn intense attention in manufacturing chemosensors to screen various analytes in chemical/biological systems. They are more sensitive compared to small molecular sensors due to the collective signal amplification of the molecular wire configuration. The analyte detection is interpreted on a photo-induced electron transfer (PET) or electronic-induced energy transfer (EET) basis. Thanks to the ease of structural adjustments of FCPEs, the design of next-generation sensitive and selective chemosensors has been made. In one example, a novel polyelectrolyte, ttp-PPESO₃ with terpyridine receptor and sulfonate coordination groups, was rationally assembled, and it showed great selectivity toward Cu²⁺ sensing. The limit of detection for Cu²⁺ is as low as 0.93 ppb. Another example, urea-PPESO₃ was designed specifically to detect fluoride ions. It displayed outstanding response to F⁻, at sub-ppm level, compared to the other halogenic ions. The synthesis and evaluation of these polymeric sensing materials will be discussed in this presentation.

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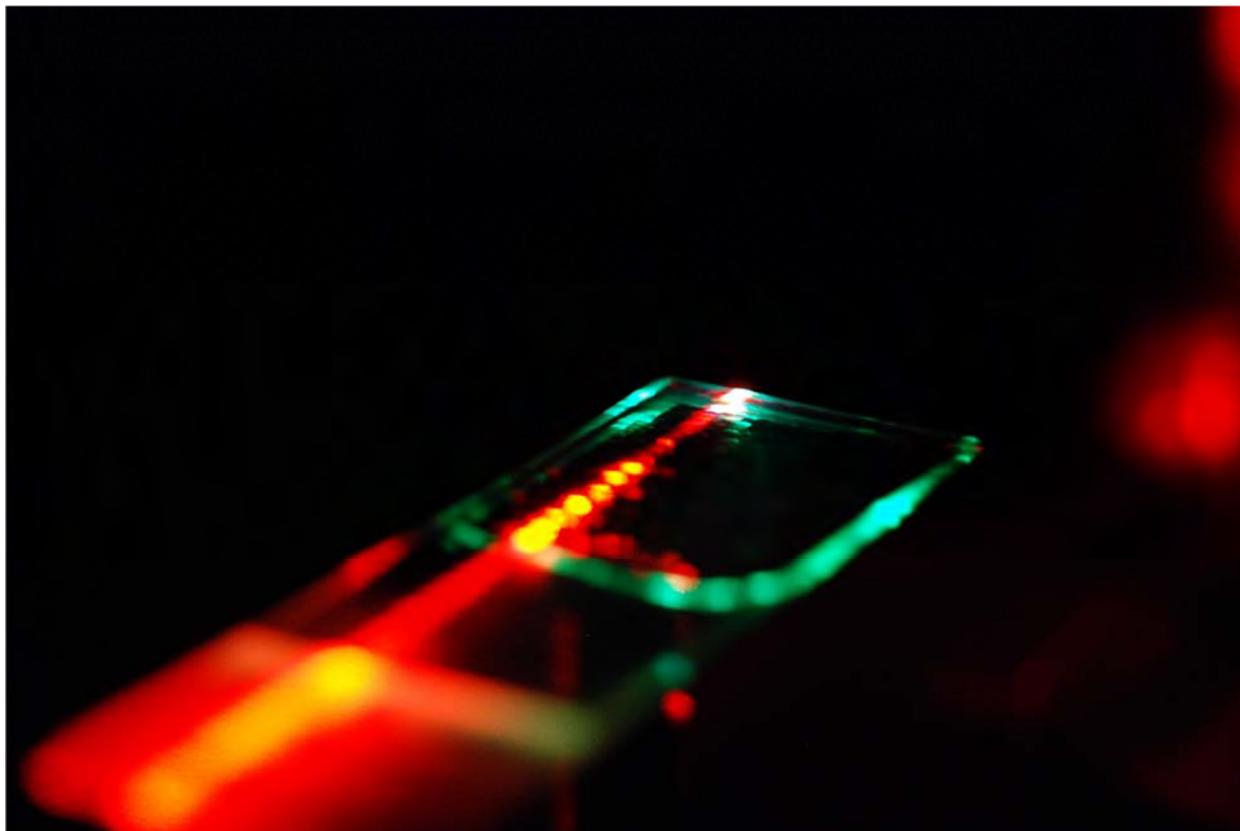
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POLY 629: Everything under the sun/light in polymers

Yoan C. Simon, *Yoan.Simon@usm.edu. School of Polymer Science and Engineering, The University of Southern Mississippi, Hattiesburg, Mississippi, United States*

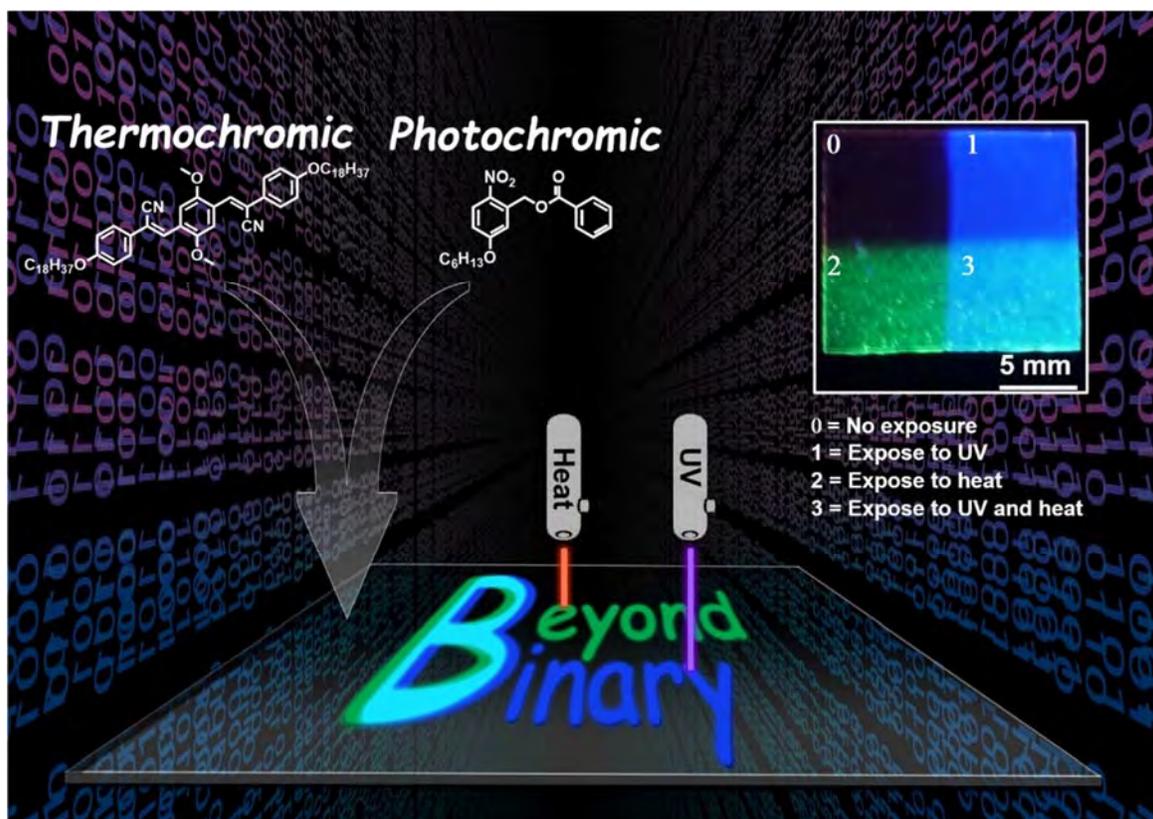
Light is a remarkable tool to induce a variety of chemical and physical processes in materials. The ability to direct polymer structure at multiple length scales down to the molecular level thanks to controlled synthetic methodologies enables the fabrication of structures that will interact with light in a predetermined and desirable fashion. Here we report some of our activities in the field of light upconversion by triplet-triplet annihilation, notably the ability to fabricate rubber and glassy polymer blends and copolymers that comprise suitable chromophore pairs along with upconverting nanoobjects, gels and nanostructured macromolecular constructs. We will additionally report on our ability to control both mechanical and shape properties of materials using light-activated processes. The data introduced will serve as a means to depict the structure-property relationships of light-responsive polymeric materials and emphasize global design principles.



POLY 630: Beyond binary: Optical data storage in a quaternary code

Emily Pentzer, ebp24@case.edu, Peiran Wei, Bowen Li, Al de Leon. Chemistry, Case Western Reserve University, Cleveland, Ohio, United States

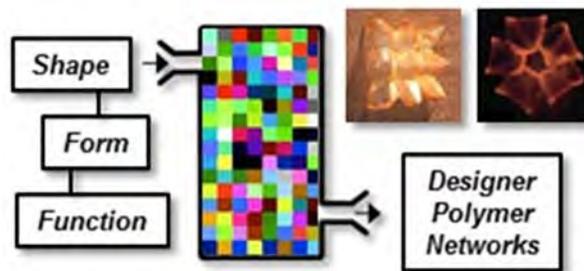
Synthetic chemistry is a powerful tool for developing new materials and dictating their properties in a bottom up approach. The Pentzer lab uses fundamental organic chemistry reactions to tune functionality and in turn the properties of small molecules, polymers, and nanoparticles with aims to improve the efficiency of the interconversion and storage of energy. This seminar will focus on the development of an optical data storage system that can store data in a quaternary code of 0, 1, 2, 3. Typically, a binary system (0, 1) is used to store data, for example, by locally changing the optical properties of the medium, as in CDs. Ongoing engineering-based approaches to increasing the density of data storage focus using multilayer films for patterning of voxels (3D pixels) or smaller data units (i.e., Blu-ray versus DVD). We will present a polymer-based system for optical data storage in which two orthogonally stimuli-responsive small molecule dyes are incorporated into a polymer matrix; one small molecule becomes fluorescent upon irradiation with UV light, and the other becomes fluorescent upon heating. Before stimulus is applied, the polymer film is transparent, colorless, and without fluorescence; photo-irradiation yields blue fluorescence, thermal irradiation yields green fluorescence, and both thermal- and photo-irradiation yields cyan fluorescence. This straightforward and scalable method enables polymer films to store quaternary information (0, 1, 2, 3).



POLY 631: Pixelated polymers: Directed self assembly of liquid crystalline polymer networks

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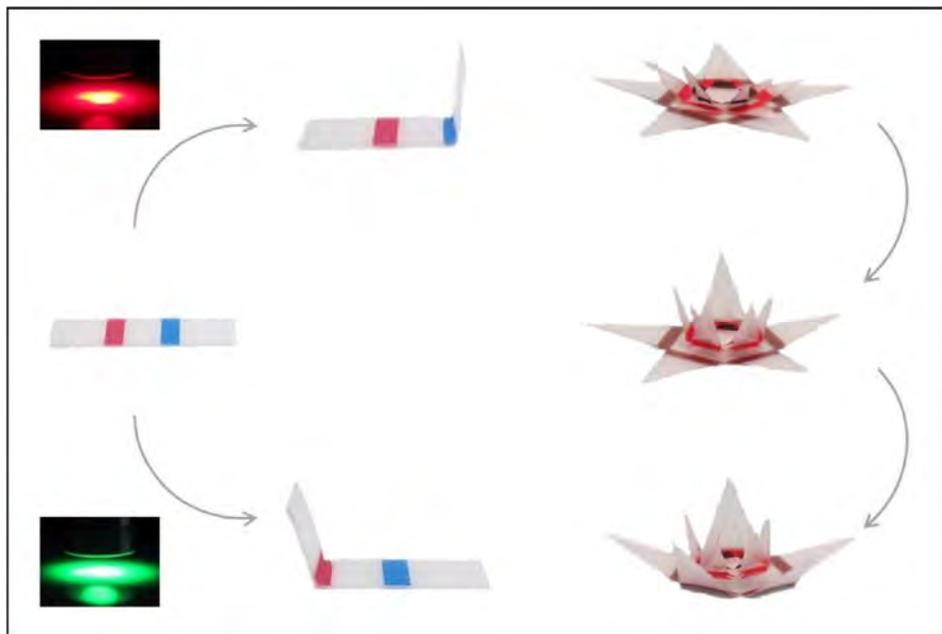
Polymeric materials are pervasive in modern society, in part attributable to the diverse range of properties that are accessible in these materials. Polymers can be stiff or soft, dissipative or elastic, adhesive or non-stick. Localizing the properties of polymeric materials can be achieved by a number of methods, including self-assembly, lithography, or 3-d printing. Here, we detail recent advances in the preparation of “pixelated” polymers prepared by the directed self-assembly of liquid crystalline monomers to yield crosslinked polymer networks (liquid crystalline polymer networks, LCN or liquid crystalline elastomers, LCE). Through the local and arbitrary control of the orientation of the liquid crystalline units, monolithic elements can be realized with spatial variation in mechanical, thermal, electrical, optical, or acoustic properties. Stimuli-induced variation of these properties may enable paradigm-shifting end uses in a diverse set of applications.



POLY 632: Using light to actuate and locally tune the properties of polymers

Michael D. Dickey, *mddickey@ncsu.edu*, Jan Genzer, Ying Liu, Robin Mays, Duncan Davis, Russell Mailen. *Chemical and Biomolecular Engineering, NC State University, Raleigh, North Carolina, United States*

This talk will describe two related projects that utilize generic light sources to induce localized changes to the physical and mechanical properties of polymers in a strategic manner. The first project utilizes photopolymerization to change the properties of the walls of microfluidic channels. Poly(dimethylsiloxane) is one of the most popular materials for microfluidics, but swells in the presence of most organic solvents and is therefore limited to handling aqueous fluids. We show that it is possible to diffuse photoinitiator into the walls of channels composed of polyvinylsiloxane to localize photopolymerization that results in a thin shell that is impervious to organic solvents due to crosslinking. The remainder of the polymer that composes the microchannel retains the desirable properties of siloxanes. The second project utilizes uniform light from a light bulb to induce self-folding of polymer films. Regions of black ink patterned on sheets of pre-strained polymer absorb the light and heat up due to the photothermal effect. The heat causes the polymer to relax and therefore shrink, which can induce self-folding. By changing the color of the ink and the wavelength of light, it is possible to control the sequence of folding to form more complex shapes. Self-folding is similar to origami but is done without direct human intervention. The appeal of this approach is that it utilizes two dimensional patterns to create a variety of complex three dimensional objects. In essence, it allows shape memory polymers to be programmed using a variety of two dimensional patterning techniques and triggered using only light. The talk will discuss the fundamental science that enables both of these projects, which are united by the importance of localized changes in polymer properties initiated by exposure to light.



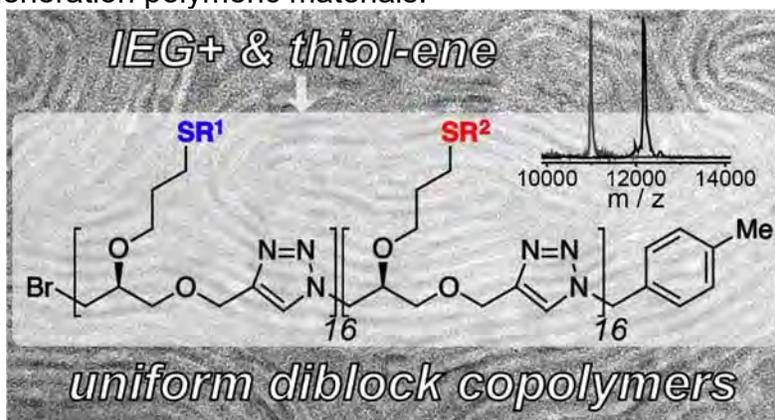
POLY 633: Iterative exponential growth synthesis of perfect triazole-based polymers

Yivan Jiang, *yivan@mit.edu*, Matthew Golder, Hung V. Nguyen, Paul Teichen, Yoshiki Shibuya, Yufeng Wang, Mingjiang Zhong, Jonathan C. Barnes, Deborah Ehrlich, Adam Willard, Jeremiah A. Johnson. *Chemistry, Massachusetts Institute of Technology, Stow, Massachusetts, United States*

Polymer chemists have long tried to replicate Nature's remarkable ability to make macromolecules of defined length, sequence, and chirality. Many new synthetic approaches have attempted to access precisely defined and diversely functionalized uniform macromolecules in useful quantities. Living statistical polymerization methods can yield polymers with precise nanoscale structures on kilogram scales, but these methods lack absolute mass control, sequence control, and stereocontrol. Solid-phase syntheses provide an extremely valuable tool for the synthesis of macromolecules with absolute structural control. However, these methods require large excesses of reagents in each step and are not yet amenable for the synthesis of polymers in a readily scalable way

We are advancing a promising alternative synthetic strategy called Iterative Exponential Growth (IEG) wherein doubly protected molecules of length L undergo cycles of orthogonal activations and couplings to yield macromolecules with length $L \times (2^n)$ cycles. Though IEG is limited to repetitive or palindromic sequences, we have used it to make unimolecular, fully sequence-controlled and stereo-controlled polymers on multigram scales.

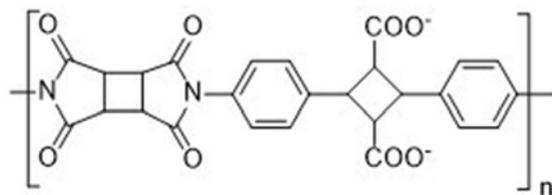
Through synthetic modification of base monomers of varying lengths, we can install many functionalities such as alcohols, electron rich and poor aromatics, free amines, and primary alkenes etc. A vast number of sequences and topologies that can be made using this system. For instance, using sequential thiol-ene click chemistry, we have synthesized unimolecular block copolymers (BCPs) of up to 12.1 kDa on a gram scale in under a week. BCPs of decane-based side chains and either triethyleneglycol- or thioglycerol-based side chains phase-segregate into hexagonal cylinder morphologies. In addition, we have found that inducing differences in tacticity, stereoisomers of these discrete block copolymers will phase-segregate differently. It is our hope that by using our IEG system, we will elucidate the structure-property relationships that will guide the design of next-generation polymeric materials.



POLY 634: Molecular design of water-soluble polyimides controlling rigidity and side chains

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Polyimides (PI) are the most vital classes of high performance polymers which can be used as high-performance plastics in various modern industries and commercial applications such as in electronic industry, adhesive, laminating resin, film or coating, and aerospace. Recently we found an efficient method to produce 4-aminocinnamic acid (4ACA) by a microorganism engineering. A photodimer of 4ACA was prepared via [2+2] cycloaddition by irradiation of ultra-violet LED lamp (300 nm), which can be regarded as a first bio-based dianilines after carboxylate groups were protected by methyl esters. The biodianilines were polymerized with diacids of amine-protected 4ACA photodimer to create transparent film with extremely high mechanical/thermal performances after the precursor poly(amic acid) was cast over dimethylformamide solution and thermally imidized. The transparent biopolyimides containing a backbone of cyclobutanyl and phenylene groups gave films with high thermal and mechanical performances even with keeping high transparency. The surface-treatment of the biopolyimide films by alkaline solution gave ionically-modified films which can attach inorganic layer such as ITO, to create bilayer organic-inorganic films. During this process, we first found the method of water-solubilization of bio-polyimides by a long term alkaline treatment. After that, we established synthetic technique to produce water-soluble polyimides containing ionic carboxylate groups and cyclobutanyl backbones, without heterogenic element heavier than oxygen. The aqueous solution of biopolyimides was cast to produce transparent films by an eco-friendly process using water.

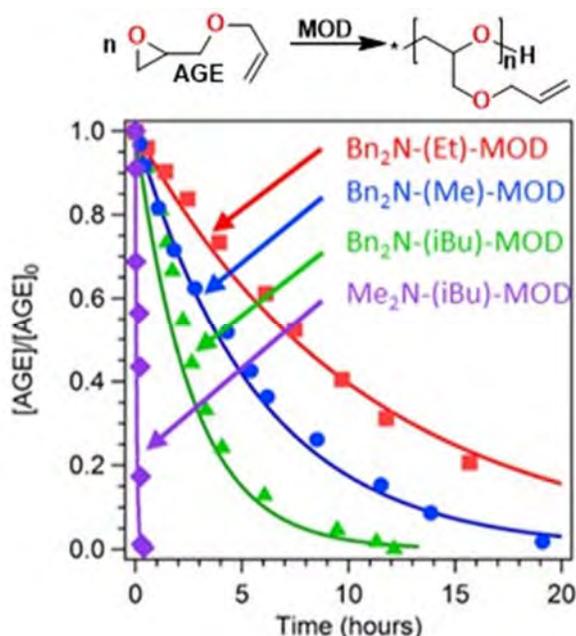


Macromolecular structure of water-soluble polyimides composed of only light elements of H C N O.

POLY 635: Structure-kinetic relationships for mono(μ -oxo)-dialuminum initiators for epoxide polymerization

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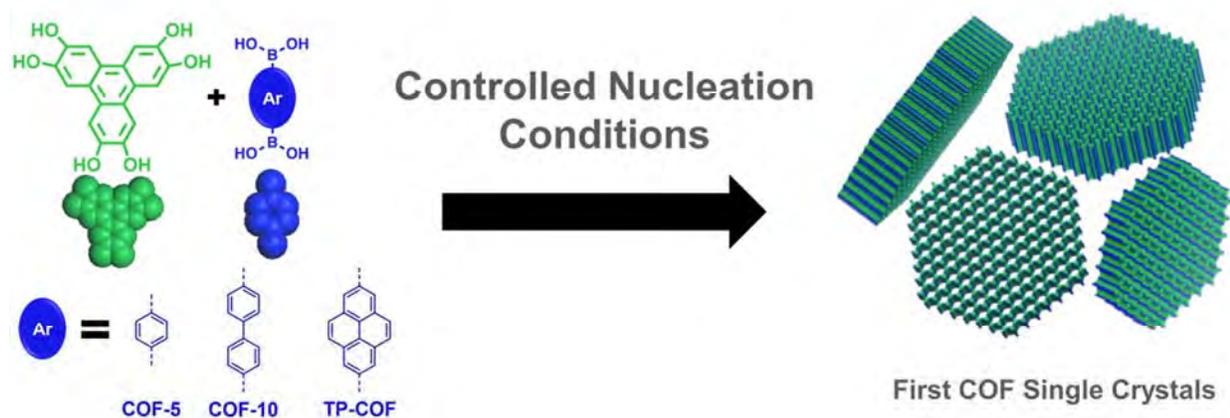
Polyethers are an adaptable class of materials due to the indiscriminate ring strain of their epoxide monomer precursors. We present a class of mono(μ -oxo)-dialuminum (MOD) initiators that are synthesized from commercially available precursors in a single step, and crystallized from the reaction medium. The MOD structures can be characterized by X-ray crystallography (XRD), and variation of MOD structure has been shown to affect polymerization rate in a mechanistically-informative manner. The original $\text{Bn}_2\text{N}(\text{Et})\text{-MOD}$ initiator had $k_p = 0.270 \pm 0.003 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ in neat allyl glycidyl ether polymerizations whereas the latest MOD initiator exhibited a nearly 400-fold increase in propagation rate under similar reaction conditions: $\text{Me}_2\text{N}(\text{iBu})\text{-MOD}$ had $k_p = 104.0 \pm 12.480 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$. MODs allow for molecular weight control, have expanded tolerance for monomer functional groups, and yield $\text{PDI} = 1.04\text{--}1.40$. Further mechanistic insight has been uncovered through the synthesis and characterization of MOD initiators and proposed analogues of polymerization intermediates. We propose that the amine substituents are near the site of monomer enchainment during propagation, which is consistent with a cyclic or cooperative polymerization mechanism. Cooperativity between active sites is supported by an exponential increase in polymerization rate with MOD concentration. The proximity of the dialkylamine to aluminum is supported based on model kinetics studies of polymerization, and by static characterization of polymerization intermediates and proposed intermediates by 2D nuclear magnetic resonance (NMR) spectroscopy studies.



POLY 636: Controlled 2D polymerizations and resultant single crystal covalent organic frameworks

Austin M. Evans², *austin-evans@utulsa.edu*, **Nathan Flanders**^{3,2}, **Lucas Parent**², **Ryan P. Bisbey**¹, **Edon Vitaku**³, **Nathan C. Gianneschi**⁴, **William Dichtel**¹. (1) Chemistry and Chemical Biology, Cornell University, Ithaca, New York, United States (2) Northwestern University, Broken Arrow, Oklahoma, United States (3) Chemistry, Northwestern University, Evanston, Illinois, United States (4) Chem M/C 0343, University of California, San Diego, La Jolla, California, United States

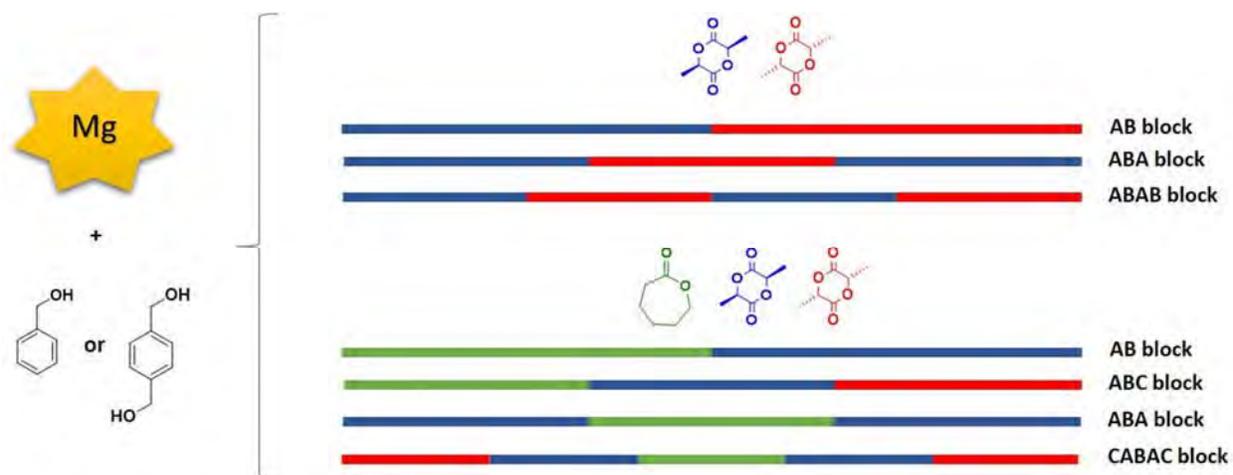
Polymerizing monomers into periodic two-dimensional (2D) networks represents an emerging frontier in polymer science. However, it remains an unsolved chemical challenge to rationally engineer and construct 2D polymers through their monomer constituents. The resulting 2D macromolecules created through these strategies are anticipated to have properties unlike those associated with linear polymers or amorphous cross-linked networks. Covalent organic frameworks (COFs) represent a class of porous, crystalline 2D networks which can be synthesized from a broad monomer scope in solvothermal conditions. However, these materials are typically obtained as microcrystalline powders or films with typical crystalline domains of less than 50 nanometers. By using a strategy to temporally separate nucleation and growth processes we are able to grow single crystal COFs. Herein, we demonstrate the first example of a controlled two-dimensional polymerization which yields multiple single-domain COF systems which are several orders of magnitude larger than those previously reported.



POLY 637: Block-stereoblock copolymers of poly(ϵ -caprolactone) and poly(lactic acid)

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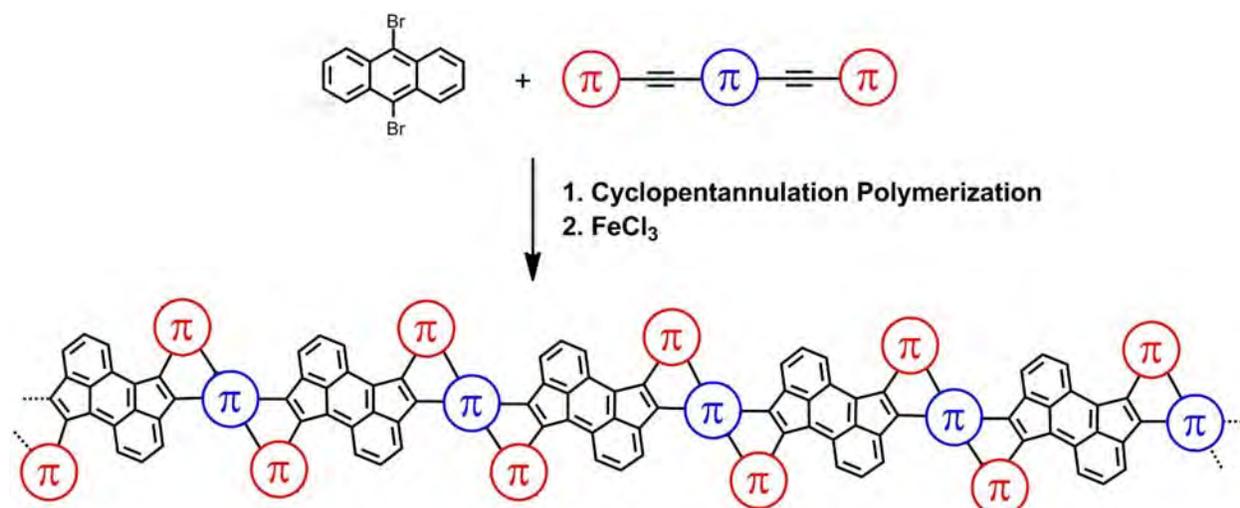
The sequential addition of monomers to a living polymerization catalyst is a promising method of copolymerization of cyclic esters, which enables the preparation of precise microstructures with predetermined block constitution and length. A suitable catalyst should lack a termination step, and not favor side-reactions such as trans-esterification between polymer chains. We have recently introduced several families of magnesium catalysts that combine extremely high activity and living nature, thereby giving access to stereoblock copolymers of poly(lactic acid) of unprecedented microstructures. In this presentation, we will describe a new variety of these catalysts, that is able to polymerize a broad scope of lactones, and in particular ϵ -caprolactone (ϵ CL). This catalyst retains the extremely high activity in lactide (LA) polymerization, as well as with ϵ -caprolactone polymerization: with loadings below 0.01%, it can fully consume both monomers under immortal conditions within minutes, with trans-esterification side reactions reduced to minimum. The preparation of the novel block-stereoblock copolymers of ϵ CL, L-LA and D-LA which feature high degrees of crystallinity and enhanced thermal properties due to stereocomplexes formation will be described. Employing different alcohols or poly-alcohols as initiators leads to diverse polymer architectures. These living magnesium catalysts show great potential in developing new and uncommon polymeric materials, which are difficult to attain by alternative approaches.



POLY 638: Conjugated polymers via cyclopentannulation strategies

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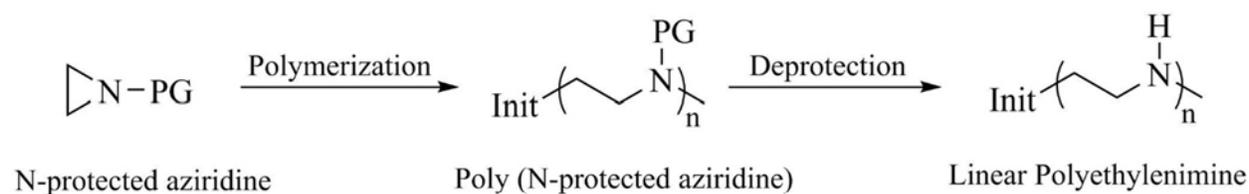
We have explored two different cyclopentafused-polycyclic aromatic hydrocarbon embedded polymer systems that have been prepared via a palladium catalyzed cyclopentannulation reaction. The first route utilized a one-step post-polymerization modification that converts three high bandgap poly(arylene ethynylene)s into low bandgap donor-acceptor copolymers. The strategy relies on a palladium-catalyzed cyclopentannulation reaction between the main-chain ethynylene functionality and a small molecule aryl bromide (6-bromo-1,2-dimethyl-aceanthrylene). The reaction installs new cyclopenta[hi]aceanthrylene electron-accepting groups between the electron rich arylenes along the polymer backbone. In a second route, a non-traditional synthesis of donor-acceptor type polymers containing a cyclopenta[hi]aceanthrylene acceptor groups can be synthesized by a palladium catalyzed copolymerization between 9,10-dibromoanthracene and a variety of bis(arylethynyl)arenes to give polymers with molecular weights (M_n) of 9-22 kDa. The bis(arylethynyl)arenes were composed of benzene, thiophene, or thieno[3,2-b]thiophene moieties, which provided access to a series of four donor-acceptor copolymers. The polymers were subjected to cyclodehydrogenation with $FeCl_3$ to access rigid ladder type polymers with the conversion investigated by ^{13}C NMR of isotopically labelled polymers. The ladder polymers possess broad UV-Vis absorptions, narrow optical band gaps of 1.17 – 1.29 eV, and p-type semiconductors.



POLY 639: Anionic polymerization of aziridines

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Polyethyleneimines (PEIs), which exist in two forms – as branched PEI (BPEI), and linear PEI (LPEI), have attracted a lot of attention due to their use in gene transfection and CO₂ capture. While BPEIs are easily obtained by electrophilic ring opening polymerization of unsubstituted aziridine with a Lewis acid catalyst, LPEIs are usually synthesized by post-modification of cationically obtained poly (2-oxazoline)s (POXs). Herein, we report a route to synthesize linear polyethyleneimine anionically through the polymerization of N-protected aziridine. The resultant poly (N-protected aziridine) showed good solubility in DMF and DMSO and can easily be deprotected under mild conditions.

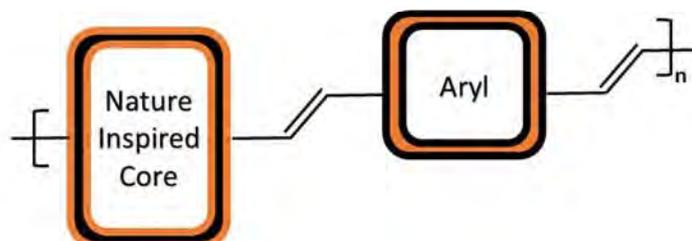


Init. : Initiator
PG : Protecting group

POLY 640: Synthesis and characterization of nature-inspired vinylene polymers

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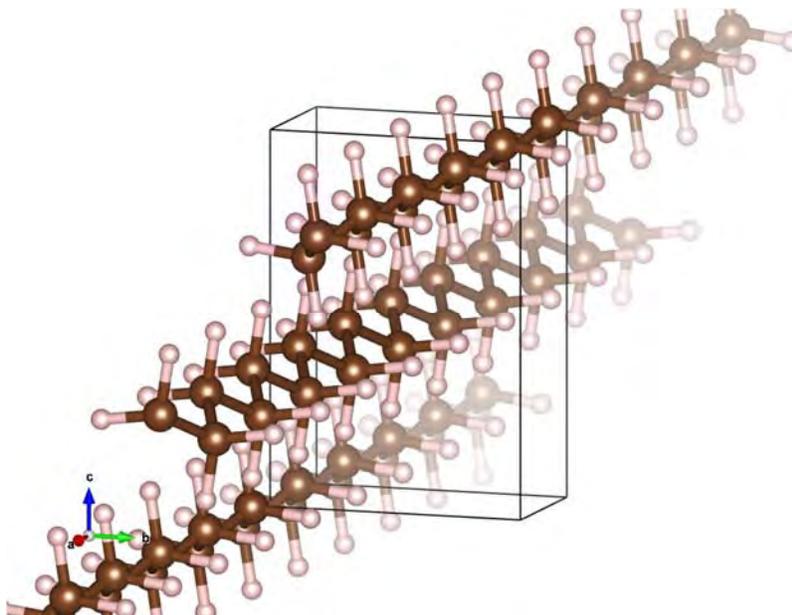
Nature is a boundless source for functionally diverse building blocks for bioinspired organic semiconductors. One such inspiration is the biopolymer, Eumelanin. Eumelanin is the black-brown variety of melanin and is thought to be a heterogeneous network produced by the oxidative polymerization of two monomers, 5,6-dihydroxyindole and 5,6-dihydroxyindole-2-carboxylic acid. These compounds are powerful radiation absorbers due to their high degree of conjugation with broadband photon absorption spectrum that extends from the ultraviolet into infrared range. Likewise, it has been shown that conjugated polymers containing vinylene and linkages possess interesting optical and electronic properties, and are being used in various organic electronic devices. The efforts toward the synthesis and characterization of nature-inspired copolymers with different arylene vinylene moieties will be presented.



POLY 641: *Ab initio* thermal conductivity evaluation of polymer systems

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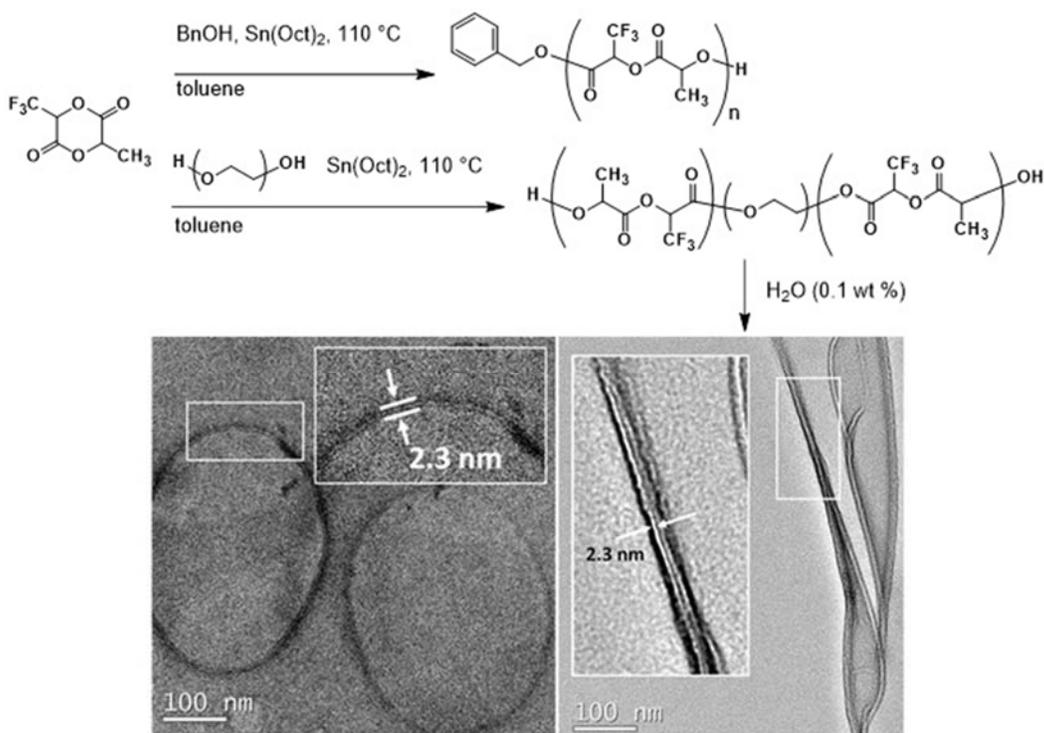
Lattice thermal conductivity (LTC) has been calculated mainly using linear lattice models and molecular dynamics simulations, but their theoretical reliability strongly depends on empirical parameters and choice of force field. With the modern advent of parallel computers, a more systematic and reliable approach to the evaluation of LTC has emerged, i.e., first-principles anharmonic lattice dynamics calculations. This approximates a LTC formula, Peierls-Boltzmann equation, based on the linearized phonon Boltzmann equation at the cubic anharmonic level and has been succeeded to predict thermal conductivity (TC) quite reasonably for several inorganic semiconductors in the broad range of TC, 1 to 10^4 W/mK. However, it has not been applied to polymer systems yet, although the LTC of polymers is one of the most important quantities for industrial purpose. This may be attributed to these two reasons: (1) It is concerted that the cubic anharmonic approximation is insufficient for polymers, because the contribution from higher order anharmonicity than cubic is pronounced for soft materials such as polymers. (2) Generally, polymer crystals have larger unit cells than inorganic crystals and hence require more computational costs. Exploiting the phono3py software, we have applied the first-principles anharmonic lattice dynamics simulations, for the first time, to a typical polymer system, polyethylene crystal (see figure), in order to evaluate the LTC value. It is established that the temperature dependence of LTC reasonably reproduces the previous experimental value. In the talk, we will report on this and show the TC of one-dimensional polyethylene chain and several typical polymers. In addition, we will make a discussion from the comparison of these results.



POLY 642: Facile synthesis of fluorine-substituted, alternating poly lactides and their amphiphilic block copolymers

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We report successful synthesis of 3-trifluoromethyl-6-methyl-1,4-dioxane-2,5-dione and ring opening polymerization of the new fluoro-lactide monomer to prepare alternating poly lactides composed of trifluoromethyl and methyl pendent groups on each repeat unit (FPLA). Molecular weights of the prepared polymers correlated well with the initial molar ratio of monomer to initiator, and were found to range from 6.6 to 22.5 kDa as determined by ¹H NMR spectroscopy. ¹H, ¹³C, and ¹⁹F NMR spectroscopy were consistent with the structures of the lactide monomer isomers, and ¹H NMR analysis was consistent with polymer backbones of alternating trifluoromethyl- and methyl-substituted lactate constituents. Additionally, we prepared amphiphilic block copolymers of FPLA and PEG (FPLA-*b*-PEG diblocks and FPLA-PEG-FPLA triblocks) by using methoxy PEG (mPEG) or PEG as alcohol initiators. We observed the formation of vesicles or worm-like micelles from the particles of FPLA-PEG-FPLA in dilute aqueous solution by TEM.

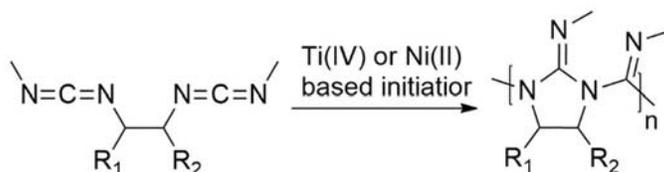


POLY 643: Cyclopolymerization of 1,2-dicarbodiimides

Chamni U. Jayarathna², *cuj140030@utdallas.edu*, **Enosha H. De Silva**¹, **Bruce M. Novak**³. (1) *Chemistry and Biochemistry, The University of Texas at Dallas, Richardson, Texas, United States* (2) *Chemistry and Biochemistry, University of Texas at Dallas, Richardson, Texas, United States* (3) *School of Natural Sciences Mathematics, University of Texas at Dallas, Richardson, Texas, United States*

Polycarbodiimides are a class of synthetic helical polymers which have been previously studied because of their large range of chiral optical properties. Carbodiimides can be polymerized using chiral catalysts to form samples that are either right or left-handed. It is from these single-screw sense samples that many of the optical properties are observed. In this study, we are polymerizing dicarbodiimide monomers that undergo cyclopolymerization. Cyclopolymerization occurs when there are no more than two carbon spacers between the two carbodiimide groups. Longer spacers lead to crosslinked materials.

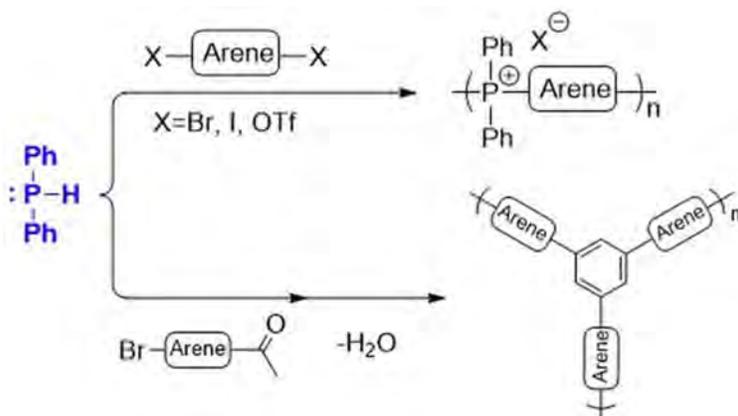
Here, we are extending the living polymerization approach used for monocarbodiimide polymerization into dicarbodiimide polymerizations using Ti(IV) and Ni(II) based initiators. The properties of the cyclic poly(dicarbodiimide) will be compared to their linear cousins. Properties that are studied will include their backbone structure, optical switching and thin film behavior.



POLY 644: Synthesis and characterization of polyelectrolytes containing tetraarylphosphonium moieties by using diphenylphosphine as commercial building block

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A new family of polymer with tetraarylphosphonium sites has been successfully developed. Tetraarylphosphonium moieties are constructed from commercial diphenylphosphine and aryl compounds bearing halogen or triflate substitutions by nickel or palladium catalyzed P-C coupling reaction. HPPH₂ is commercial starting building block to form the backbone of tetraarylphosphonium polyelectrolytes (TPELs), including linear and layered network. Properties of TPELs are tunable by simply changing the structure of aromatic segments. All new prepared TPELs have outstanding thermal stability in the range of 350-450 °C, and some of them have remarkable chemical stability in NaOH (aq). One TPEL network solid prepared via cyclotrimerization of tetraarylphosphonium salt shows physisorption with CO₂. The new synthetic protocols promise to facilitate convenient and rapid access to a wide variety of thermal/chemical stability materials as well as gas capture materials for a variety of applications.



POLY 645: Bulk and interfacial properties of acrylic emulsion-based pressure sensitive adhesives via microindentation probe tack

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Water-borne acrylic polymers are widely used in pressure sensitive adhesive (PSA) applications due to their ease of formulation, cost, and adhesion to a variety of substrates. Bulk mechanics and surface interactions both play important roles in determining the performance of a PSA. Microindentation probe tack is an elegant technique for studying both nonlinear rheological response as well as substrate dependence on the work of adhesion and cavitation profile of the adhesive. The current work has explored the use of this technique to understand the performance of double-layer pressure sensitive adhesives. Double-layer adhesives offer the possibility to optimize performance of an overall PSA film by sequentially coating two or more adhesive compositions of different compositions to more precisely control the surface interactions and bulk rheological response. These films result in very different properties than the two parent polymers separately, and the work of adhesion is strongly dependent on the order of the two adhesives.

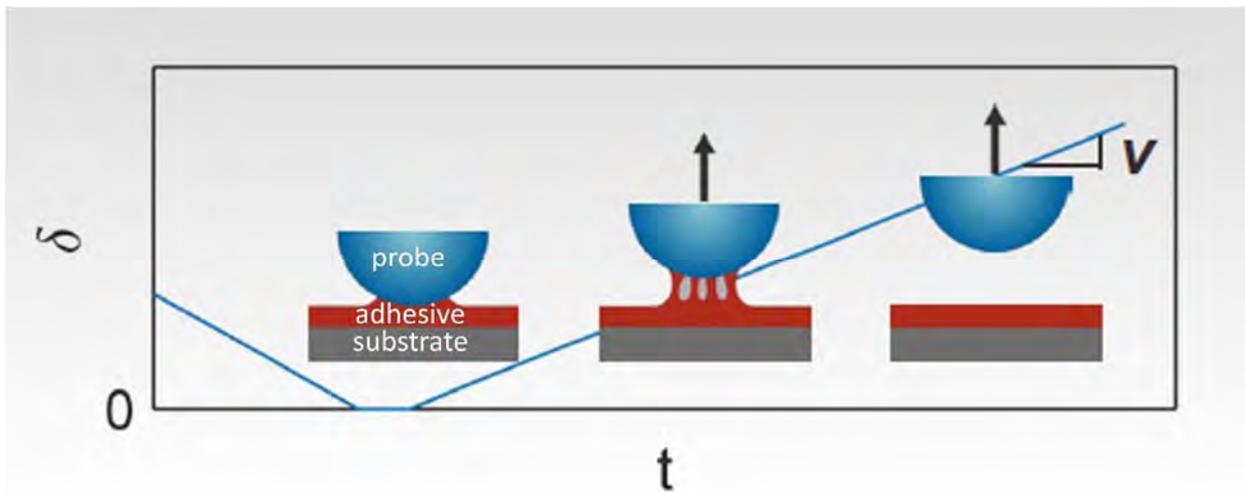
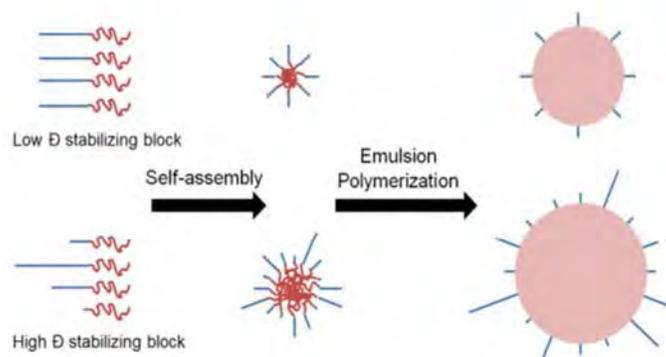


Figure 1: Schematic of Microindentation Probe Tack Measurement, where d = displacement and t = time

POLY 646: Amphiphilic block copolymers as stabilizers in emulsion polymerization: Effects of the anchoring and stabilizing block molecular weight dispersities on stabilization performance

Sean George², Gary A. Deeter¹, David P. Campbell¹, Dieter Urban³, Bernd Reck³, **Michael F. Cunningham²**, Michael.Cunningham@chee.queensu.ca. (1) BASF, Wyandotte, Michigan, United States (2) Dept Chem Eng, Queens Univ, Kingston, Ontario, Canada (3) BASF SE, Ludwigshafen, Germany

One of the key advantages of using block copolymers over traditional surfactants in emulsion polymerization is the high level of tailoring that can be done to afford the best stabilization properties; chemical structure, composition, molecular weight, and topology are all commonly optimized properties. Investigations of block copolymer molecular weight dispersity have typically focused on bulk self-assembly and melt-phase morphological behaviour. However molecular weight dispersity has not been previously studied as a design parameter for its impact on stabilization performance. Low molecular weight dispersity is generally assumed to be associated with best performance. This is the first quantitative investigation of the effects of block copolymer molecular weight dispersity with regards to stabilization performance in an emulsion polymerization. Poly(styrene)-*b*-poly(acrylic acid) block copolymers were synthesized by nitroxide-mediated radical polymerization, and employed as stabilizers in the emulsion polymerization of styrene. The effects of both the stabilizing poly(acrylic acid) block and the anchoring polystyrene block molecular weight dispersity on stabilization behavior were studied, independent of molecular weight and composition. The block copolymer stabilizers were evaluated in terms of critical aggregation concentration, dispersed phase particle size, distribution and zeta potential. Our results challenge previous assumptions concerning the need for low dispersity in block copolymer stabilizers.



POLY 647: Polymer colloids with improved re-dispersibility in alcohol based formulation

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Polymer colloids prepared from emulsion polymerization play significant role in a wide range of industrial applications. These polymer colloids are typically stabilized with protective layers through either electrostatic (anionic or cationic) interaction, or steric (non-ionic) interaction, or a combination of both electrostatic and steric interaction at their surface. The colloid stabilization can be described by the DLVO theory which considers the combined effect of the van der Waals attraction and the interaction of the electrochemical double layers between colloids. Oftentimes, they are used directly in end use application such as architecture and industrial coatings. Sometimes, they are isolated as powders in end use market such as plastics additives and construction industries. In these cases, ideally, the powders should be broken down to their primary particles either in a polymer matrix or water-containing formulation to maximize the performance benefits of the original polymer colloids. The breakdown can be assisted through a combination of shear force, heat, additional protective layer, or anti-caking agent. Recently, we are challenged with an industrial application where isolated colloid powders need to break down in anhydrous alcohol based formulation. In this paper, we investigated a variety of physical and chemical approaches to improve the re-dispersibility of polymer colloids in this type of formulation. One of the designs, as shown in Figure 1, where the polymer colloid containing two layers of surface charges with a hairy steric chain, was demonstrated to lead to the best performance.

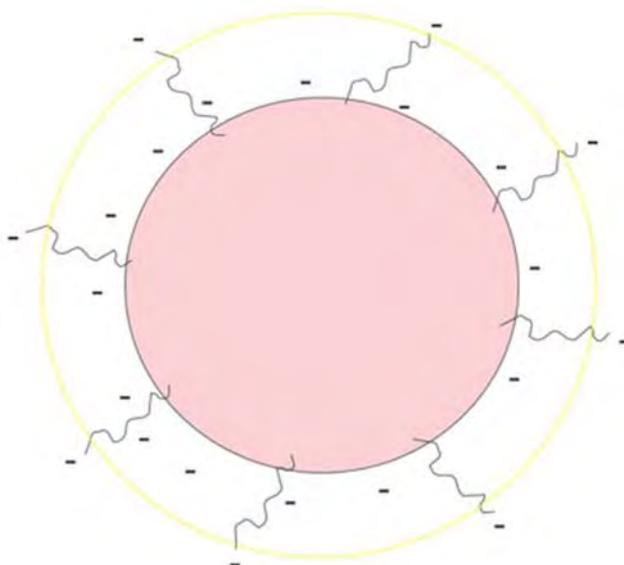


Figure 1. Design of polymer colloid with two layers of surface charges with a hairy steric chain

POLY 648: Applications of polymer colloids in Waterborne coatings: Influences of composition and process designs on coatings performance properties: Tutorial

Wenjun Wu, *wenjun.wu@arkema.com. Arkema Inc., Cary, North Carolina, United States*

Emulsion polymers have been used in a multitude of industrial applications. Many of these applications rely on the ability of discrete colloidal particles to form a smooth and continuous film in order to provide a full range of protective and functional properties. Polymer composition and particle morphology are undisputedly the most important factors in the design of polymer colloids. Examples will be given to illustrate the effects of raw material choices and synthesis parameters on the performance of waterborne coatings, for example, the surfactant employed to stabilize the polymer particles and the hydrophilic species either added or formed during emulsion polymerization. Some seemingly minor ingredients used in emulsion polymerization can also have surprisingly significant impact on coatings properties.



POLY 649: Colloidal particles for green printing technology

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Highly precise self-assembly of nanomaterials in the ink droplets along the vapor-solid-liquid three phase contact lines could be accurately achieved. Significantly, the basic units (dot, line, plane and stereo structures) via the printing technology can be precisely controlled. We achieved the silver nanoparticles assembled conductive patterns with single nanoparticle resolution. Based on the manufacturing of functional nanomaterials and controllable spreading and transferring of liquid droplets, we fabricated the superoleophilic patterns on the hierarchically structured superhydrophilic plate by ink-jet printing. Thus the image area and non-image area can be achieved on the plate, which can be directly used as the printing-plate. Our further work on assemble metal nanomaterials or colloidal nanoparticles via feasible printed process, patterned the various linear or curves 1D/2D morphologies and optimal interconnects on diverse substrates. The desirable conductive patterns contribute the remarkable application on sensitive electronic skin, transparent touch screen, multi-layer circuits, ultra-integrated complex circuits and soft actuators, as well as high performance photonic crystal sensors. These achievements on functional printing are derived and benefited from the fundamental researches on solid/liquid interfacial wettability manipulation, morphology control of dried ink droplets, as well as functional nanomaterial fabrication, which develop the research system of Green Printing Technology.

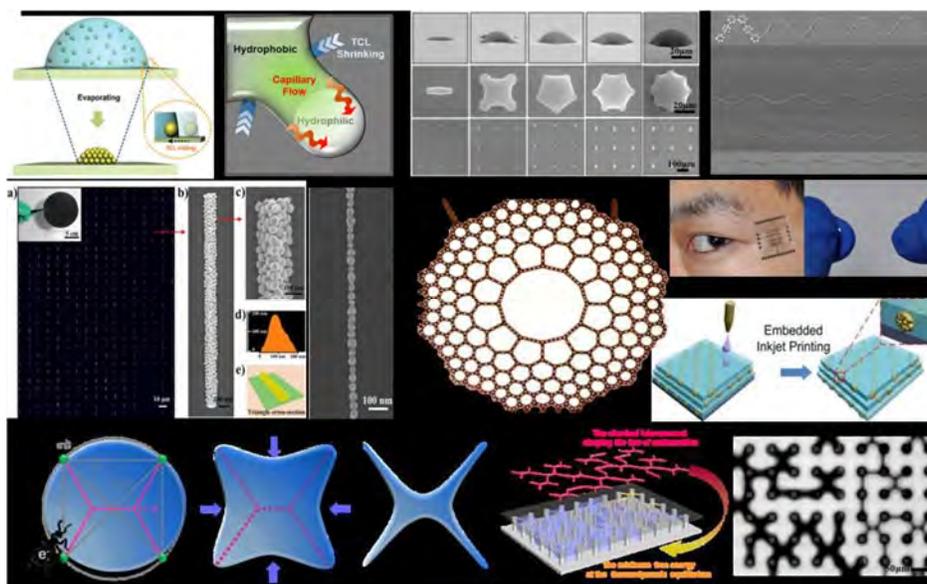
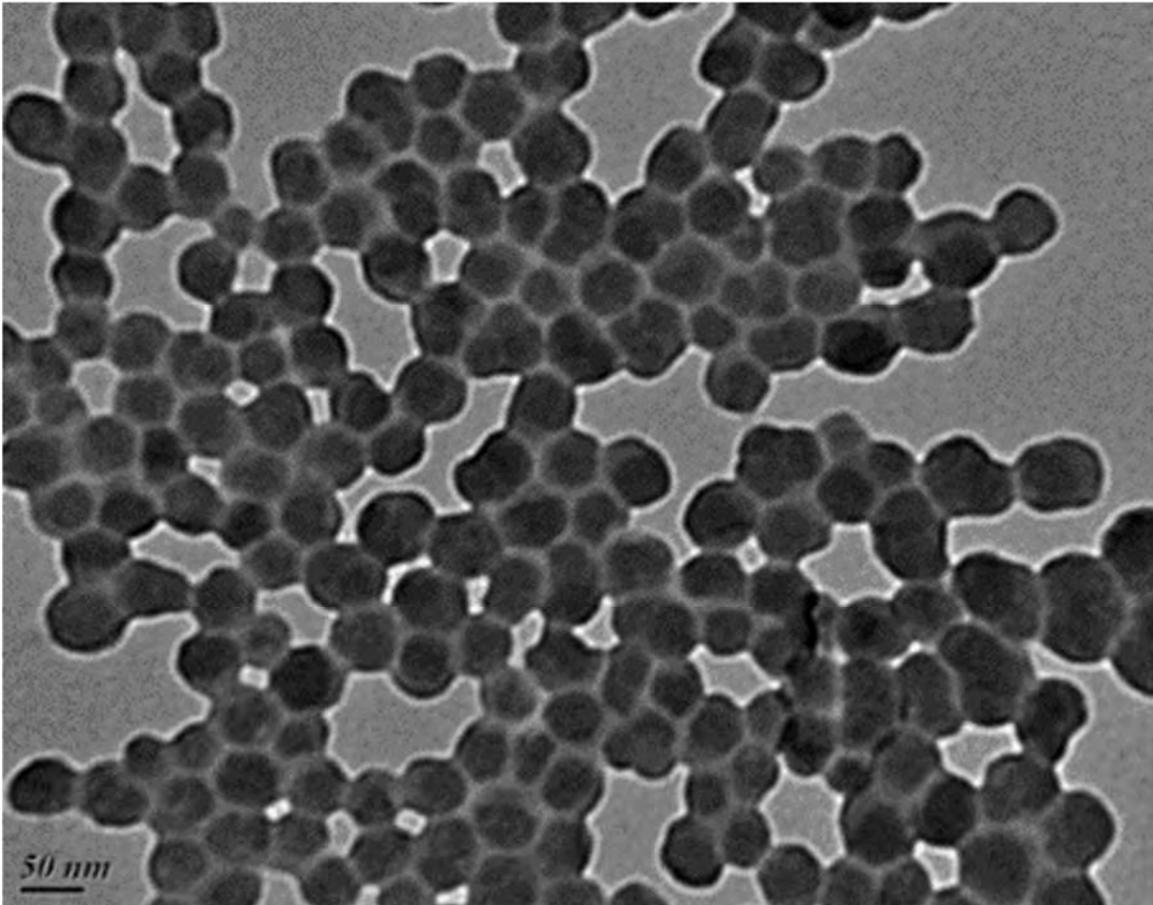


Figure 1. Based on droplet manipulation green printing technology, the remarkable variety of printed electronics could be achieved with diverse advanced applications.

POLY 650: Development of photoactive inks for application in organic electronics

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Organic conducting polymers are of increasing scientific interest and are promising candidates for various applications. Nowadays, one of the most important challenges faced by the community concerns their processability along with their long term stability. In this context, herein, I'd like to present one approach consisting in the preparation of photoactive materials stable as inks in environment-friendly phases through miniemulsification or nanoprecipitation techniques. For instance, composite particles made of the low band-gap PCDTBT polymer together with the n-type PC71BM have been prepared in aqueous media. The materials ratio was varied and the properties of composite particles were studied along with their integration.

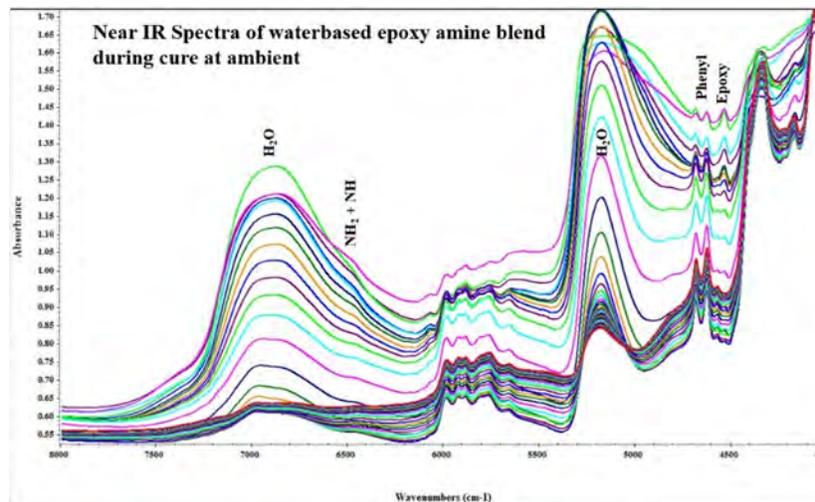


PCBM-PCDTBT composite nanoparticles made by nanoprecipitation in water

POLY 651: Property comparison between solvent-based and water-based epoxy-amine clear coatings

Monoj Pramanik, monoj.pramanik@usm.edu, Ethem Kaya, David Dellate, Michael Blanton, James Rawlins. Polymer Science and Engineering, University of Southern Mississippi, Hattiesburg, Mississippi, United States

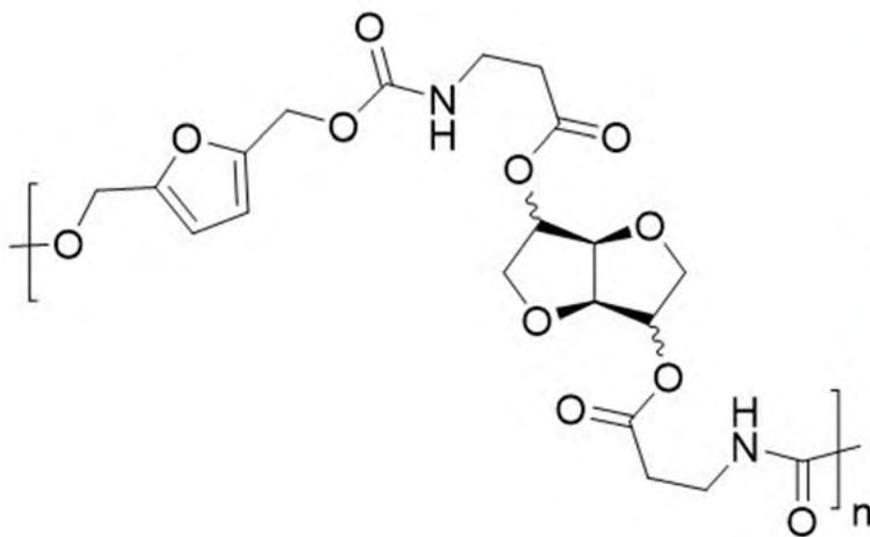
It is well established that epoxy resins (epoxide functional groups) react with amine hardeners (NH_2 or NH functional groups) to result in 2K epoxy-amine thermoset network in coatings. However, the rate of reaction between epoxide and amine is affected by water and solvent (particularly solvents having ketonic, ester, and hydroxyl moieties). Ambient curing of epoxy with amine in bulk rarely reach complete epoxy conversion in realistic timeframes from vitrification. By comparison, epoxy prepolymers when cure with amine crosslinker in water or solvent proceeds to near full epoxy conversion due to mobility of functional groups exerted by water or solvent. Often these solvation and dilution methods result in different performance attributes and the question remains, do these different routes to crosslinked results follow same or different network growth from solvent-based and water-based dilution methods as in those systems cured in bulk? How do these subtle differences, (if they are quantifiable, in network growth) between waterbased versus solventbased formulations result in differences in material performance? To test these concepts, a blend of epoxy and surfactant that has epoxy equivalent weight of ~ 260 in bulk was prepared, and a modified diamine having additives was also prepared which has amine hydrogen equivalent weight of ~ 102 in bulk. These epoxy resin and amine were blended in bulk at epoxy:amine equivalent ratio of 1.15:1 and cured which resulted in $T_g \sim 75^\circ\text{C}$. Epoxy-amine 2K clear coatings were prepared singularly from solvent-based and water-based formulations. Cure characteristics and properties in terms of mechanical, thermal, morphological, solvent resistance, and water transmission of these two coatings delivered in a different form were evaluated and compared. Epoxy-amine coatings generally have better anticorrosive performance than acrylics. Waterbased epoxy-amine and acrylic hybrid coating were thus prepared and evaluated to experience the effect of acrylic as interpenetrating network in epoxy-amine coatings and to fully understand any detectable differences.



POLY 652: Synthesis of renewable polyurethanes derived from isohexides and furans: Stereochemical effects on mechanical and viscoelastic properties

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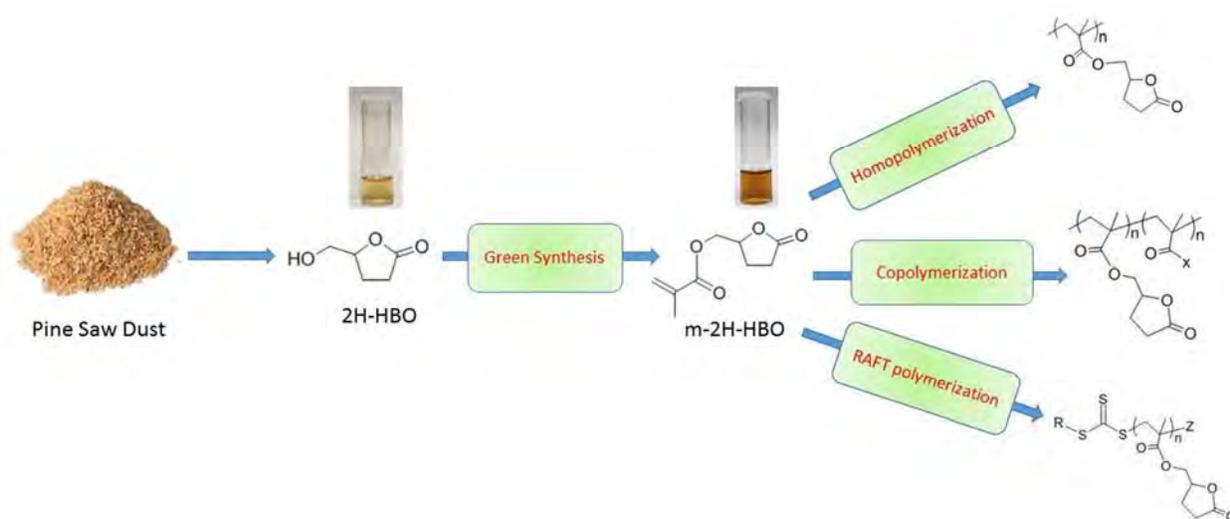
This study highlights the stereochemical effects isohexide isomer content has on the material properties of biomass derived polyurethanes. These materials were synthesized from 2,5-bishydroxymethylfuran (BHMF) and either isosorbide bis(3-isocyanatopropanoate) (ISBIP) or isomannide bis(3-isocyanatopropanoate) (IMBIP) at varying feed ratios. ¹H-NMR and optical rotation data confirm the desired isohexide feed ratios incorporated into the resulting polymers. All polyurethanes were found to be thermally stable with decomposition temperatures ($T_{d, \text{onset}}$) ~ 240 °C and glass transition temperatures (T_g) ~ 42 °C. Uniaxial tensile testing found that all materials were strong ($E > 1$ GPa) but brittle ($\epsilon < 2$ %), typical of glassy polymers. Purely isosorbide based polyurethanes were found to be lightly entangled, where isomannide polyurethanes were unentangled at similar molar masses. The presence of entanglements results in an increased density, reduced fractional free volume, and a tougher material. When the two isomers were mixed into the polymer, the resulting material showed a drastic increase in brittleness.



POLY 653: Synthesis of bio-acrylic polymers from dihydro-5-hydroxyl furan-2-one by free radical and controlled free radical polymerization.

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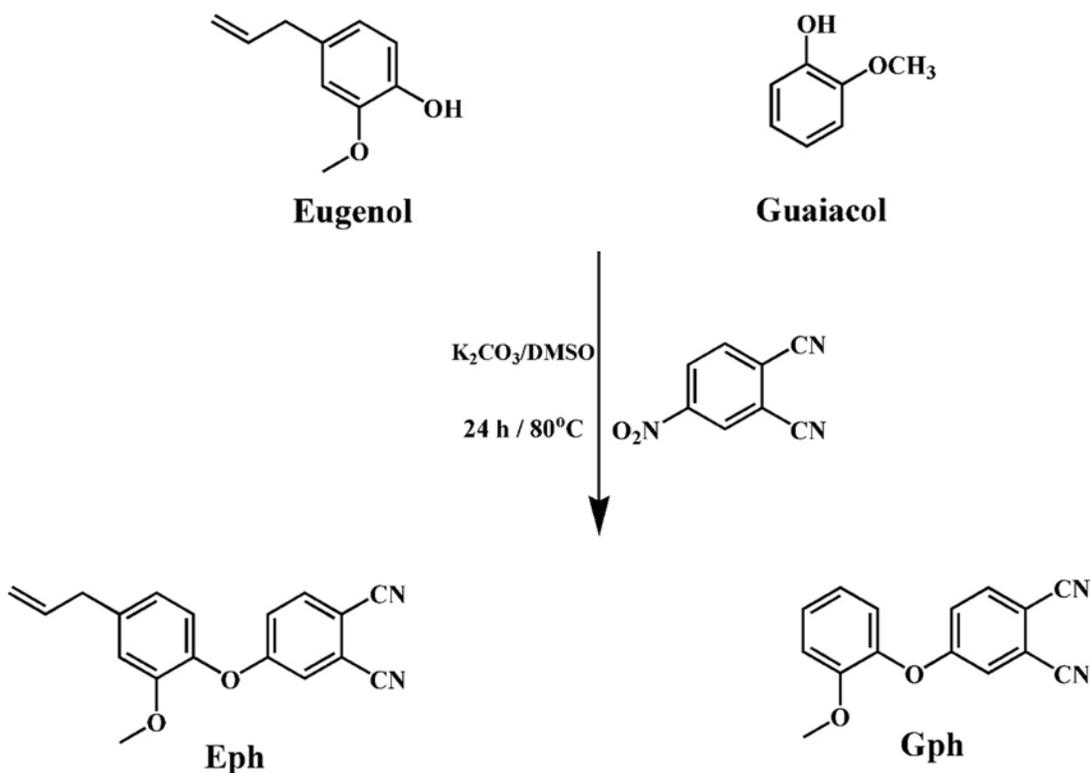
Dihydro-5-hydroxyl furan-2-one (2H-HBO), a renewable-sourced chemical containing the hydroxyl functionality is converted into its acrylic counterpart for the first time through a green chemical procedure. This newly-synthesized acrylic monomer can be polymerized using different techniques such as bulk, solution and emulsion polymerization. To check the capability of this monomer to polymerize with various other commercially-available acrylates, copolymerizations are studied based on emulsion techniques. The pendent lactone ring remains unopened during the polymerization and makes the polymer highly polar to be polymerized in a polar solvent like dimethyl sulfoxide (DMSO). This monomer is suitable to copolymerize with other commercially available acrylic monomers such as methyl methacrylate (MMA), hydroxyethyl methacrylate (HEMA), styrene, etc. RAFT emulsion polymerization is also studied with the same monomer in a simple way which gives a steady conversion (~60%) with a low dispersity of 1.06. The homopolymer produced from emulsion polymerization shows higher molecular weight from all the methods, with a glass transition temperature of around 108°C which is showing the potentiality of this monomer as an attractive, green replacement for methyl methacrylate in a certain field of applications. Along with this study, few other bio-based acrylates will be introduced and discussed.



POLY 654: Synthesis of high performance phthalonitrile resins from renewable resources

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Two bio-based phthalonitrile (PN) monomer, eugenol-based phthalonitrile (EPN) and guaiacol-based phthalonitrile (GPN), were successfully synthesized by the reaction of 4-nitrophthalonitrile with eugenol and guaiacol derived from clove and lignin, respectively, in the presence of potassium carbonate *via* nucleophilic substitution reaction. Their chemical structures were confirmed by the Fourier transform infrared spectra (FT-IR), hydrogen and carbon nuclear magnetic resonances (^1H and ^{13}C NMR), and elemental analysis. The curing behavior of the blends of PN monomers with 10 wt.% of 4-(4-aminophenoxy)-phthalonitrile (4-APN) as curing agent was evaluated by FT-IR and Differential scanning calorimetry (DSC), while rheometer was used to analyze the processability of the blends. Moreover, the dynamic thermomechanical and thermal properties of the cured blends were studied by dynamic mechanical analyzer (DMA) and thermogravimetric analysis (TGA). The results confirmed that the bio-based PN monomers and its blends show low melting temperatures, wide processing windows ($>186\text{ }^\circ\text{C}$), and low melt viscosity (inferior to $0.03\text{ Pa}\cdot\text{s}$). Also, the cured bio-based PN resins exhibited higher glass transition temperature and better thermal stability than those of typical bisphenol A-based phthalonitrile polymer.

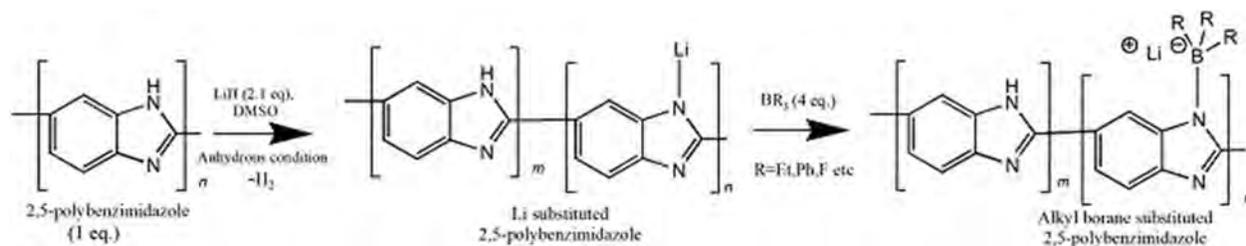


Synthetic route of the bio-based eugenol and guaiacol phthalonitrile monomers

POLY 655: Novel biomolecular design of N-boronated polybenzimidazole with single ion conductivity

Aniruddha Nag¹, aniruddhanag221991@gmail.com, Md. Asif¹, Raman Vedarajan⁴, Noriyoshi Matsum², Tatsuo Kaneko³. (1) Energy and environment area, Graduate School of Advanced Science and Technology, Nomi, Ishikawa, Japan (2) JAIST Schl of Matl Science, Ishikara, Japan (3) Jaist Sch Materials SCI, Nomi, Japan (4) Dept of Materials Science, Japan Adv Insitutute of Science Technology, Nomi Ishikawa, Japan

Polybenzimidazoles (PBIs) are a series of super high performance polymers attracting researchers' attention because of PBIs have a rigid structure of aromatic and hetero rings in their backbone to induce a good stability. Also, PBIs have active imidazole hydrogen (-NH) to receive chemical modification. However previously bio-based PBIs have ever been tried to prepare and base on such a background we have used renewable 3-amino-4-hydroxybenzoic acid (3, 4-AHBA) derived from *Streptomyces* sp. to produce bio-based PBI. Our bio-PBI showed high mechanical strength, Young's moduli, and high thermal resistance considerable comparison with commercial PBIs, owing to strong π - π stadcking interaction among aromatics and imidazole rings and H-bonding between N-H and N of imidazole ring. Imidazole ring can be easily modified by substituting the imidazole proton. Here we report N-boronation of the PBI via lithiation to be ionically conductive (scheme 1). The PBI was modified by triethylborane substitution to imidazole proton (modification degree 46 % to NH) to create anionic PBI with Li counter ion. Ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMImTFSi) was added to the anionic PBI to prepare ion gels with different concentration. Li-ion shows ionic conductivity with $1.4 \times 10^{-2} \text{ Scm}^{-1}$ at maximum whereas Li-ion transference number was obtained ($t_{\pm}=0.623$) at maximum. Ionic conductivity, Li-ion transference number, activation energy, and carrier ion number were changed with increasing ionic liquid concentration, to show maximums at a certain concentration. Further, charge-discharge measurement of the ion-gel was made by fabricating anodic half-cell composed of the ion gel as electrolyte, Si-electrode as anode, and Li-metal as cathode. The resulting value showed a good reversible capacity at discharge rates ranging 0.1 – 1.0 C. Thus, considerable electrochemical properties were confirmed which governs to use the N-boronated PBI as polymer electrolyte material in Lithium secondary batteries.

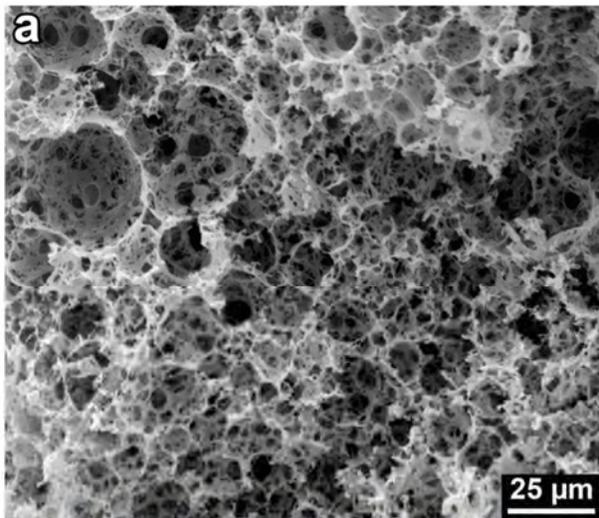


Scheme 1 PBI modification scheme to make it applicable as polymeric ionic liquid (PIL)

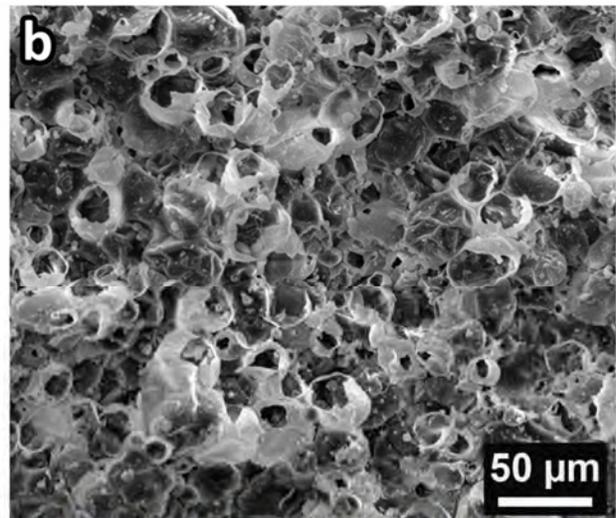
POLY 656: Emulsion-templated renewable resource polymers: Open-cell scaffolds and closed-cell encapsulation

Liraz Avraham, Liora Wienstock, Inna Berezovska, Rajashekharayya Sanguramath, **Michael S. Silverstein**, *michaels@technion.ac.il*. Department of Materials Science and Engineering, Technion – Israel Institute of Technology, Haifa, Israel

An emulsion-templated macroporous polymer, a polyHIPE (PH), is typically synthesized through free radical polymerization within the external phase of a high internal phase emulsion (HIPE), an emulsion containing more than 74% internal phase (individually dispersed droplets) [1,2]. Typically, emulsion templating generates macroporous structures with voids, ranging in size from a few micrometers to hundreds of micrometers, that are highly interconnected through holes in the polymer walls. Hydrophobic PHs are typically synthesized through polymerization of the monomers located in the organic external phase of water-in-oil (w/o) HIPEs while hydrogel PHs (HG-PHs) are typically synthesized through polymerization of the monomers located in the aqueous external phase of oil-in-water (o/w) HIPEs. Poly(urethane urea) PHs were recently synthesized using step-growth polymerization with polyols and isocyanates located in the oil phase of w/o HIPEs [3]. Most recently, PHs were synthesized using interfacial step-growth polymerization with renewable resource polysaccharides (alginate, pectin, chitosan, or dextran) or polyphenols (tannic acid or lignin) in the aqueous external phase and isocyanates in the organic internal phase of o/w HIPEs [4]. The resulting open-cell structures were successfully used as scaffolds for tissue engineering applications (a) while the resulting closed-cell structures were used to encapsulate solvents or phase change materials for energy storage and release applications (b).



Pectin-based open-cell polyHIPE.

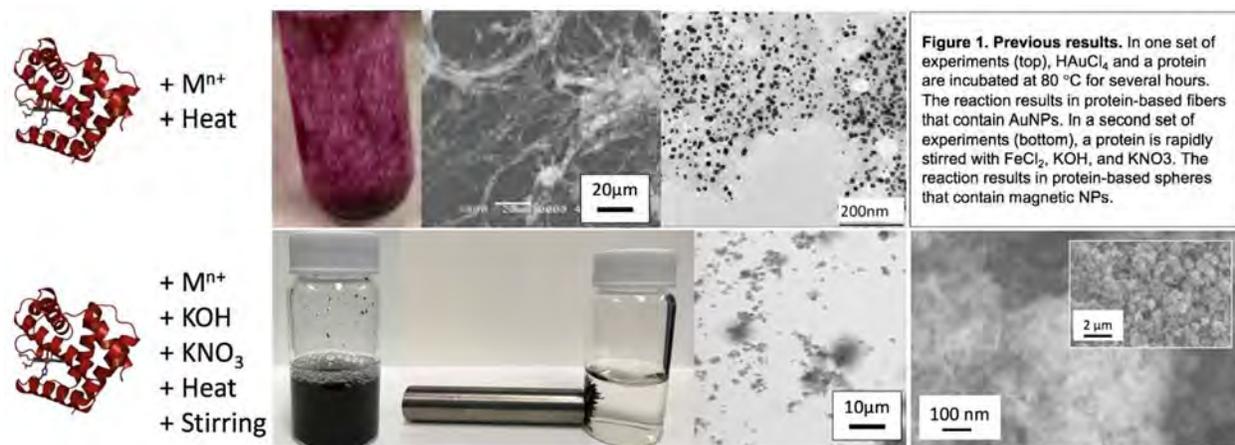


Tannic-acid-based closed-cell polyHIPE.

POLY 657: Renewable materials constructed through mimicking biomineralization

Matthew R. Hartings, *hartings@american.edu. Chemistry, American University, Gaithersburg, Maryland, United States*

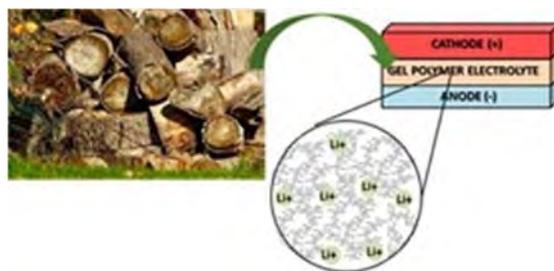
Biomimicry has been a productive means for generating new materials from renewable feedstocks. Nature, as ever, has many old tricks to teach us. One of Nature's primary means for constructing functional materials is biomineralization. In this process, proteins and mineral particles both dictate the final properties of the material produced. While composite materials have been well studied in the polymer world, the instances of researchers emulating biomineralization through the large scale organization of proteins around metal nano- and microparticles has been rare. In this talk, I will describe my group's efforts to generate protein-nanoparticle composite materials. I will discuss our observations that have come as a surprise: protein fibers are more likely to form around gold nanoparticles when using hydrophilic, rather than hydrophobic proteins. I will also discuss the applications we have targeted for some of our materials: analytes for protease detection, heavy metal removal from wastewater, and controlled drug delivery.



POLY 658: Bio-based thiol-ene polymers for use in battery applications: Synthesis and properties

Elyse A. Baroncini, baroncine0@students.rowan.edu, Joseph F. Stanzione. Dept. of Chemical Engineering, Rowan University, Glassboro, New Jersey, United States

Growing environmental and economic concerns as well as the uncertainty that accompanies finite petrochemical resources caused an increase in recent years in research and development of bio-based, renewable polymer materials. To replace petroleum-derived materials, bio-based polymers are directly produced, or, their monomers are derived from renewable sources and later polymerized. In order to determine if lignin, a highly abundant and renewable resource, could serve as a basis for bio-based conductive polymers, fractions of Kraft lignin and lignin-derived monomers were functionalized and subsequently polymerized with multi-functional thiol monomers. Powdered Kraft lignin was fractionated and characterized before imparted with allyl functionalities and used in a thiol-ene polymerization. Lignin-derived monomer vanillyl alcohol (4-(hydroxymethyl)-2-methoxyphenol) was also functionalized and UV-polymerized to yield thin, flexible polymers. Sheet resistivities of the polymers were determined according to a four-point probe method by applying a current to the thin film polymers and measuring the resulting voltage. This study adds to the list of synthesis methods of lignin-based polymers and provides insight on how to design structurally and thermally desirable bio-based polymers for battery applications.



POLY 659: Nature-derived renewable polymers to replace commodity plastics

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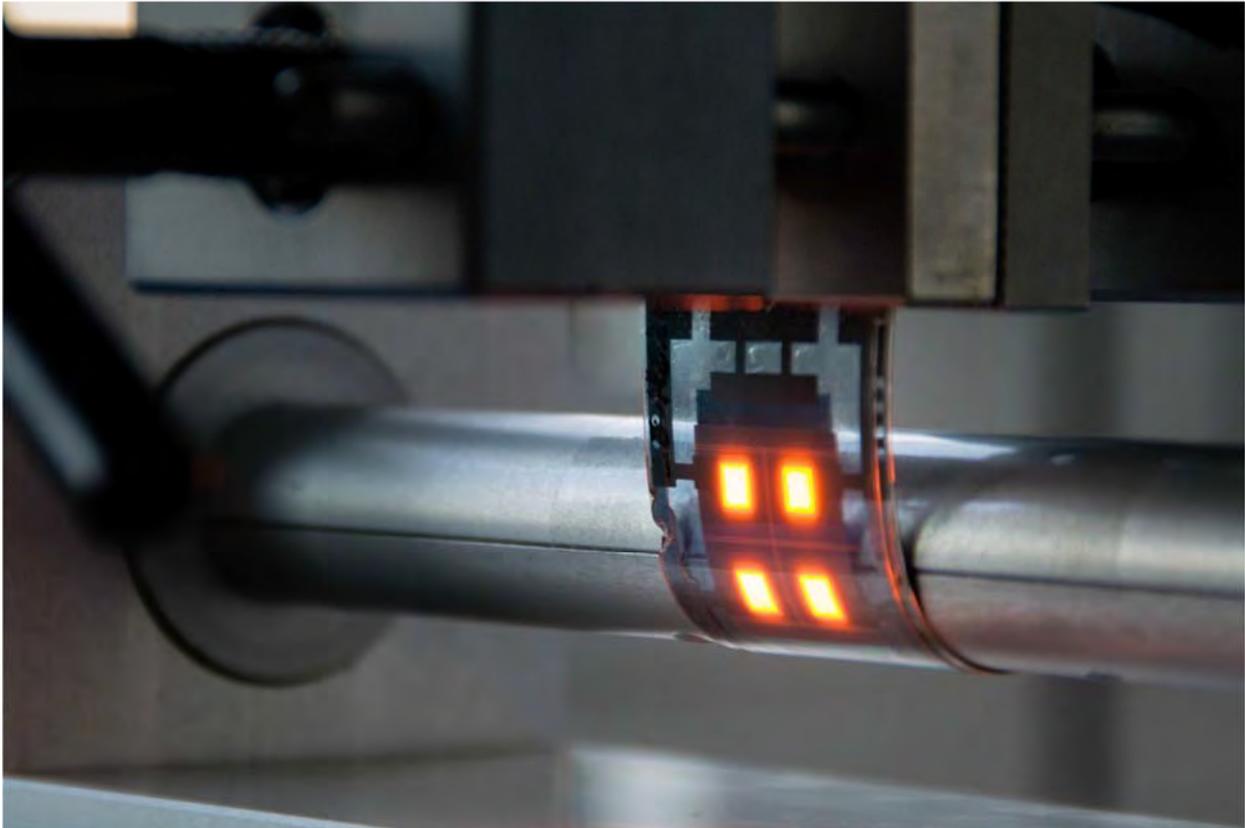
The global production of today's polymers is very dependent on fossil fuel. However, there is a progressive dwindling of these resources that new renewable sources are needed. This presentation will focus on new methods to access monomers from nature, and thus using them to synthesize renewable polymers. "Silicon acetal metathesis polymerization (SAMP)" is a methodology where silicon-based monomers and diols derived from plants are used to synthesize polysilicon acetals with glass transitions temperatures higher than that of polydimethylsiloxane (PDMS) and with high melting points. SAMP also avoids the formation of deleterious byproducts such as corrosive acid (HCl). Other nature-derived monomers have also been used with the aim of replacing non-renewable commodity plastics.



POLY 660: Development of electro-active inks for organic electronics

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Organic conducting polymers are of increasing scientific interest and are promising candidates for various applications [1]. Nowadays, one of the most important challenges faced by the community concerns their processability along with their long term stability. In this context, I'd like to present one approach consisting in the search for an alternative to polystyrenesulfonate (PSS) in the stabilization process of poly(3,4-ethylenedioxythiophene) (PEDOT) inks. A solution is for instance based on (trifluoromethanebis(sulfonyl)imide) (TSFI) side groups attached to a polystyrene backbone. This PEDOT:polyelectrolyte system showed interesting features as compared to PEDOT:PSS, for instance its rheological behavior, its doping, optoelectronic performance and long term stability. The influence of the synthesis parameters and the composition on the named properties were studied. The new PEDOT:polyelectrolyte system was finally successfully integrated as transparent electrode in OLED and OPV devices and as channel material in organic electrochemical transistors. Other systems have been more recently tested that will also be discussed.



OLED device fabricated on PET 50x35mm @Fraunhofer Institute for Organic Electronics (Dresden, Germany)

POLY 661: Strategies for triplet fusion upconversion

Andrew Pun¹, andrewbpun@gmail.com, **Daniel N. Congreve**³, **Luis M. Campos**². (1) Chemistry, Columbia University, New York, New York, United States (2) Chemistry, MC3124, Columbia University, New York, New York, United States (3) Rowland Institute at Harvard University, Cambridge, Massachusetts, United States

Triplet fusion (TF) upconversion is the process by which low energy photons are combined into one higher energy photon. This process has seen wide advancements in recent years owing to its broad scope of potential applications. However, the number of materials that can be used in TF upconversion are quite limited. Here I will discuss our groups' efforts towards expanding the library of annihilators for TF upconversion. This includes exploring new chromophores, as well as synthetic modifications to existing materials for more efficient TF upconversion. I will then discuss our groups' work in exploring the use of these new materials in several potential applications.



POLY 662: Towards supramolecular systems for efficient triplet-triplet annihilation photon upconversion

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We present an overview of our research efforts on developing new supramolecular systems for triplet-triplet annihilation photon upconversion (TTA-UC).¹⁻⁹ Our work is focused on developing well-defined supramolecular constructs, designed for efficient intramolecular triplet-triplet annihilation photon upconversions.^{4,5,9} To achieve this goal we have designed and studied new diphenyl anthracence dendrimers and polymers, as well as coordinating systems tailored for efficient energy transfer between molecular⁹ or nanoparticle² based sensitizers, e.g. Zn or Ru porphyrines. Moreover, we show that it is possible to align the upconversion systems in liquid crystals, leading to directional emission.⁶ Finally it is demonstrated that TTA-UC systems can be used to improve the efficiency of solar energy storage under idealized conditions in devices.⁸

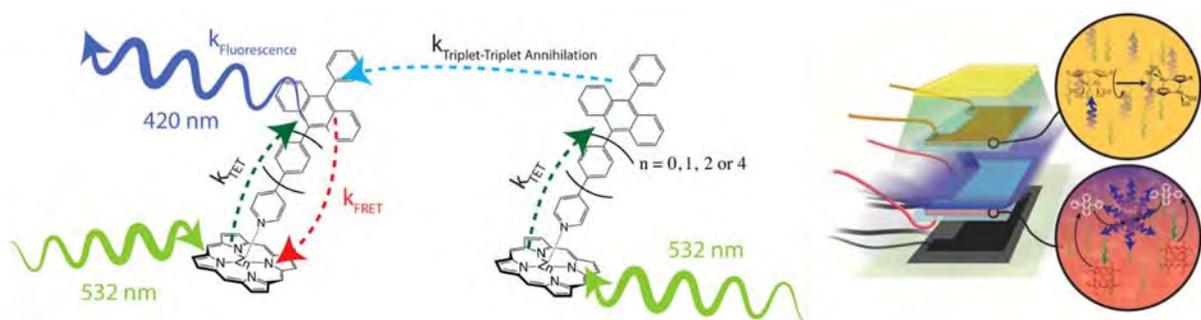


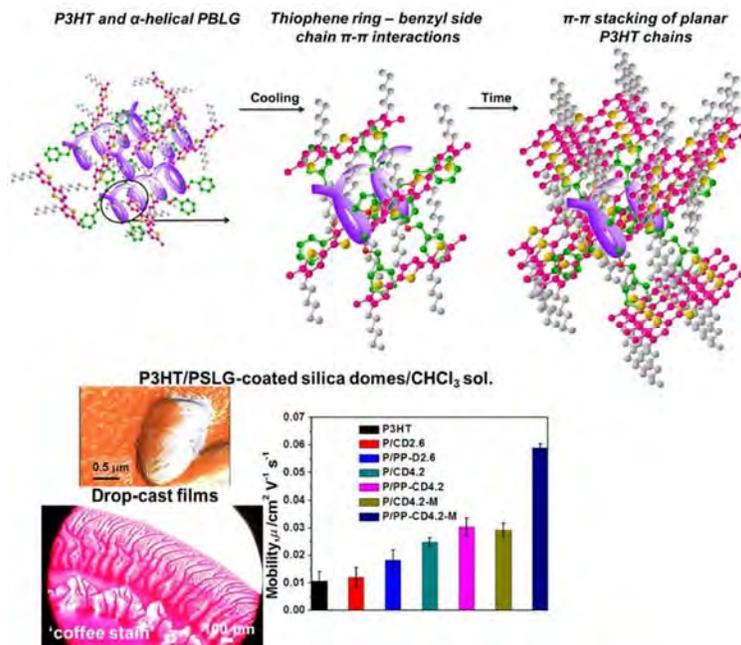
Figure 1. left) Supramolecular upconversion system⁹ right) device structure of combined energy storage/photon upconversion device⁸.

POLY 663: Polypeptide-induced organization of semiconducting polymers into hybrid electroactive materials with enhanced photo-physical properties

Cornelia Rosu^{2,3}, *cornelia.rosu@mse.gatech.edu*, **Paul Russo**^{1,3}, **Elsa Reichmanis**^{4,3}.

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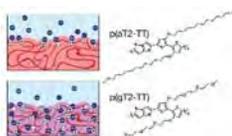
Interaction of biopolymers with organic electronic materials provides an appealing opportunity to design electroactive materials for use in many applications especially bioelectronics. Because of their biocompatibility, polypeptides facilitate easy interfacing of organic polymer semiconductors with biological systems. Polypeptides do not act just as simple bio- components; rather they effectively influence the organization of π -conjugated polymers into highly crystalline structures that allow charge transport. The first part of the talk will focus on poly(γ -benzyl-L-glutamate), PBLG, a synthetic polypeptide that forms thermoreversible three-dimensional networks. Blends with poly(3-hexylthiophene), P3HT, resulted in gel materials able to switch reversibly on and off their photo-physical properties. This behavior was observed during two cycles of heating-cooling-aging. Enhanced alignment of P3HT chains was attributed to interactions between the PBLG benzyl side chains and P3HT hexyl arms. Lastly, the properties of drop-cast films processed from dispersions of poly(γ -stearyl-L-glutamate) tethered to silica dome particles and P3HT will be described. The rational choice of axial ratio along with solution and film processing enabled electroactive materials that showed up to six times increase in charge transport when compared to pristine P3HT. Such increase was associated with enhanced alignment and assembly of P3HT that was intermediated by interactions between the alkyl side chains of the two polymers.



POLY 664: Designing organic mixed conductors for bioelectronic applications

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Direct measurement and stimulation of molecular, ionic, or electrophysiological activity is a staple of bioelectronic diagnosis and/or therapy. Such bi-directional interfacing can be enhanced by the low impedance imparted by organic electronic materials that show mixed conduction properties (both electronic and ionic transport). Many high performance bioelectronic devices are based on conducting polymers such as poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate), PEDOT:PSS. However, new structure-property and device-based design rules have led to the development of novel materials/formulations. The incorporation of glycol side chains into carefully selected backbone motifs, for example, has enabled a new class of high performance bioelectronic polymers that feature high volumetric capacitance, transconductance $>10\text{mS}$ (device dimensions ca. $5\mu\text{m}$), and steep subthreshold switching characteristics. We explore the implications of these new materials for biomolecular sensing and neural interfacing, including the effect of device operation regime on recording sensitivity and power consumption, and the role of molecular design on stability.



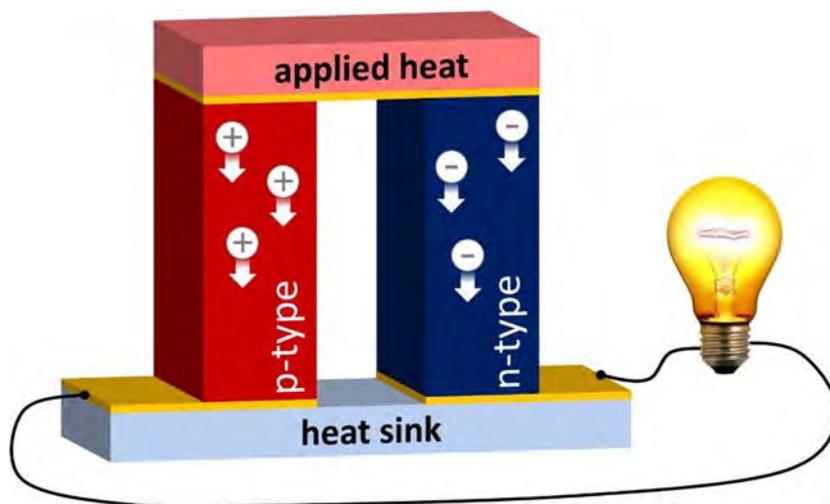
Formulation content, processing, and molecular design (shown here), can be used as a means to tune both electronic transport and ionic penetration/transport.

POLY 665: Design considerations for organic thermoelectric materials

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Over the decades, scientific evidence has mounted that the emission of anthropogenic greenhouse gases is the main reason for the increase of surface temperatures observed on Earth. Abandoning fossil fuels in the short term, however, is both technologically difficult and economically risky. Therefore, it would be advantageous to use the produced energy more efficiently thereby curbing the overall energy production and ultimately the greenhouse gas emissions. Around 60% of the energy input is lost after conversion as waste heat, of which half is so-called low temperature (<200°C) waste heat. A technology suitable to recover waste heat and transform it into usable electricity is thermoelectric generators. Due to the so-called Seebeck effect, applying a temperature differential across a suitable material will generate an electric voltage. Recovering the low-temperature waste heat however via thermoelectric generators is challenging, mainly because current technologies are based on rare, often toxic elements (*i.e.* tellurium, lead, ...); and as a result, thermoelectric modules are rather expensive and can only be efficiently operated at elevated temperatures. It is therefore paramount to develop new thermoelectric materials, able to harvest low-temperature waste heat efficiently.

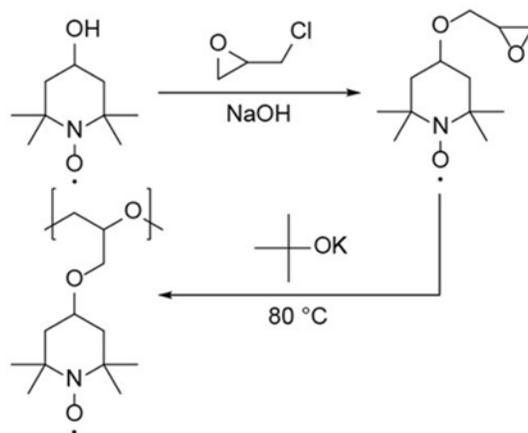
The ideal thermoelectric material possesses a high electrical conductivity, while at the same time being an excellent thermal insulator. Whereby it is relatively straightforward to find materials which fulfil one of these critical requirements, it is much more difficult to find a single material accomplishing both. Materials based on conjugated polymers, on the other hand, are attractive candidates for thermoelectric materials because they are known to be relatively good electrical conductors and at the same time excellent thermal insulators. This paper will discuss several synthetic approaches leading to better performing conjugated polymers for thermoelectric applications, thereby explicitly focussing on morphologically stable organic conductors and investigating design criteria towards more suitable n-type conductors.



POLY 666: Designing charge-neutral, non-conjugated radical polymers with high electrical conductivity values

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The oft-utilized design paradigm associated with conducting polymers is one rooted in macromolecules containing large degrees of conjugation along their backbones and the inclusion of chemical dopants that serve to change the oxidation state of the polymers. However, moving from this archetype and towards one with a single-component, charge-neutral macromolecule has significant fundamental and practical benefits, as this type of polymeric conductor should result in materials that can be designed in a less Edisonian fashion and should have longer stability when implemented in devices. In order to address this need, we have designed a series of redox-active macromolecules based on the radical polymer (i.e., macromolecules that are composed of non-conjugated backbones and have pendant groups that contain open-shell entities) design motif. Specifically, we have synthesized poly(4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl) (PTEO) using a ring-opening polymerization methodology (Figure 1) in order to form a radical polymer with a flexible macromolecular backbone and a relatively low (i.e., near room temperature) glass transition temperature. In generating a redox-active macromolecule with a flow temperature far-removed from the degradation temperature of the radical site within the polymer, thermal annealing of the radical polymer thin film resulted in the formation of localized domains with rapid charge exchange reactions. Because this material is able to obtain a local order in the glassy state, a greater than 1,000-fold increase is observed in the electrical conductivity of PTEO relative to all other reports of electrical conductivity in radical polymers. Moreover, the ultimate conductivity of $\sim 20 \text{ S m}^{-1}$ places this undoped polymer conductor in the same regime as many grades of common commercially-available, chemically-doped conducting polymers. Thus, this work implements a rarely-used design paradigm in order to generate a potentially valuable polymer electronic material.



POLY 667: Multifunctional electronic materials for thin film devices

Sang Ha Yoo, *suy60@psu.edu*, Enrique Gomez. Penn State University, University Park, Pennsylvania, United States

Organic electronics have garnered a wide range of attention for their potential advantages over their silicon counterparts. The novel characteristics of biocompatibility, large area compatibility, and multifunctionality of organic semiconductors make them suitable candidates for bioelectronics and flexible electronics applications. For bioelectronics applications, an important necessary characteristic is to have the ability to bond in a wet environment because most biological systems involve wet surfaces. Herein, we present a polymer blend thin film with semi-conductive, adhesive, and water-proof characteristics that can be utilized as an interfacial layer in three-dimensional organic-based thin film electronic devices. A phase separating behavior observed in a polymer blend film of dissimilar constituents allows for multifunctionality of the blend. By mixing a semiconducting polymer with conjugated backbone and an adhesive polymer with strong underwater adhesion, we were able to fabricate thin films that possess a strong bonding force and exhibit semiconducting behavior applicable to organic thin film transistors (OTFT). Electrical testing with OTFT structure demonstrated blend films of 50 wt% semiconductor and 50 wt% adhesive retaining ~ 85% of average saturation mobility of that of 100 wt% semiconductor films. In addition, a 73% reduction in average hysteresis was observed in the blend films compared to that of the neat semiconductor films. Characterizations under spectroscopic ellipsometry and secondary ion mass spectroscopy suggest a vertical separating behavior between the semiconducting layer and the adhesive layer, which allows for multifunctionality of the blend film.

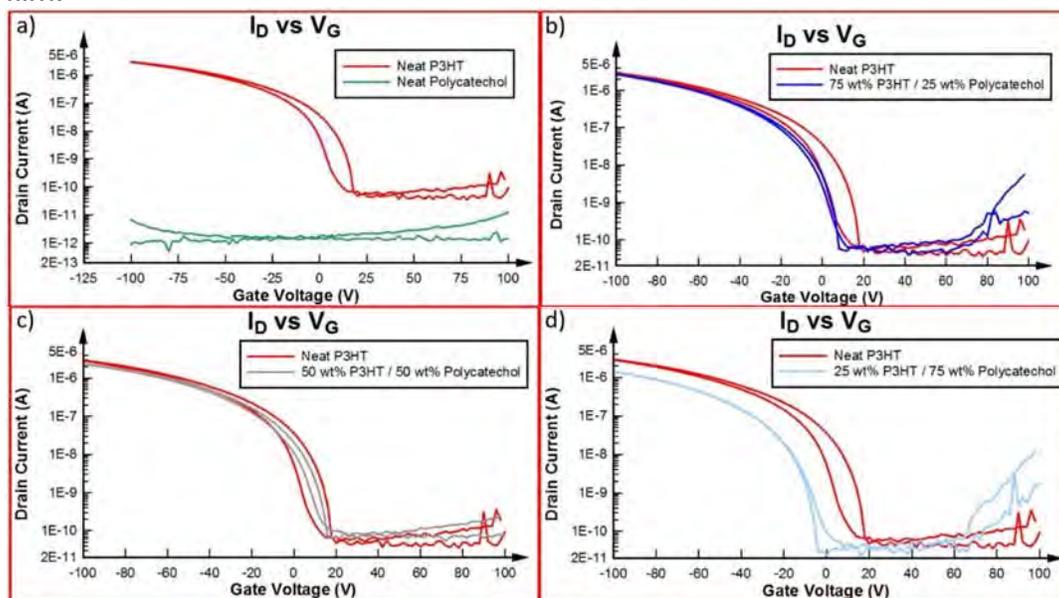
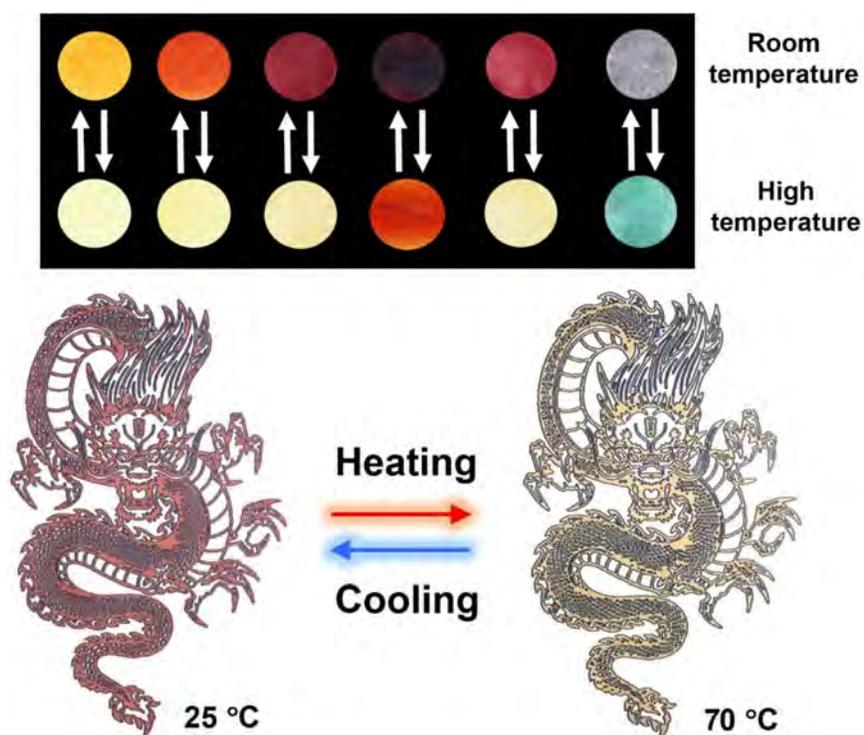


Figure 1. drain current (I_D) vs gate voltage (V_G) curves with drain voltage (V_{DS}) = 100 V and $W/L = 220 \mu\text{m} / 320 \mu\text{m}$ of TFTs with a) neat polymer films b) with 75 wt% P3HT : 25 wt% polycatechol blend film c) with 50 wt% P3HT : 50 wt% polycatechol blend film d) with 25 wt% P3HT : 75 wt% polycatechol blend film

POLY 668: Multifunctional charge transfer-based supramolecular materials with tunable thermochromism

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Stimuli-responsive materials, such as thermochromics, have found mass usage and profitability in manufacturing and process control. Imparting charge transfer-based functional supramolecular materials with tunable thermochromism, emerges as an ideal strategy to construct optically responsive multifunctional assemblies. A new series of thermochromic charge transfer-based supramolecular materials assembled in water has been developed. These assemblies are composed of a bis-bipyridinium-derived acceptor and a series of commercially available donors – namely, the neurotransmitter melatonin and its analogue bioisosteres. By tailoring the chemical structure of the donors, the strength of the charge transfer interactions can be tuned. Thermochromic aerogels and inks of these materials are prepared, with a large selection of colors, in environment-friendly solvents and demonstrate tunable thermochromic transition temperatures ranging from 45 to 105 °C. Favorable compatibility of these materials with commercial inks and inkjet printers afford excellent pattern quality with extended color options. Mechanistic studies reveal that the two types of water molecules were bound to the supramolecular complexes with different strength, and the more weakly bound water is responsible for the thermochromic transitions.



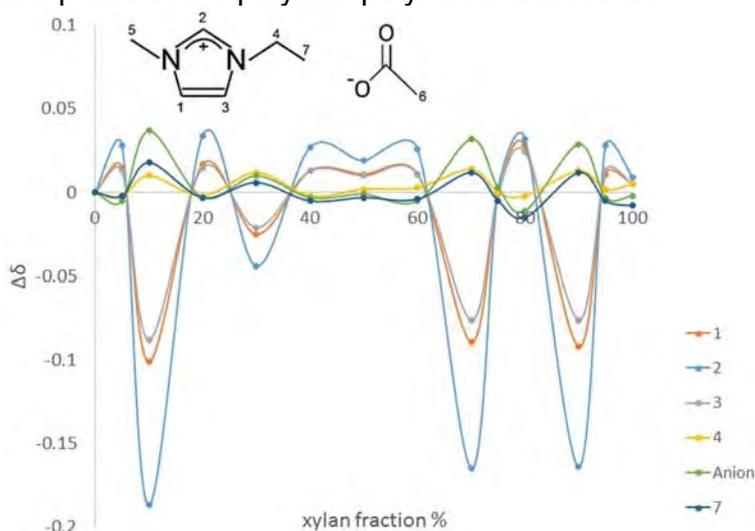
POLY 669: Diffusion and relaxometry NMR to study interactions between carbohydrates in ionic liquids

Michael E. Ries², *m.e.ries@leeds.ac.uk*, **Tatiana Budtova**¹, **Wafa Ezzawam**². (1) CEMEF/Mines ParisTech, Sophia Antipolis, France (2) Physics and Astronomy, University of Leeds, Leeds, United Kingdom

We have studied the interactions between two plant polysaccharides, microcrystalline cellulose and birch xylan, dissolved in the ionic liquid 1-ethyl-3-methyl-imidazolium acetate ([C2mim][OAc]).

Xylan in [C2mim][OAc] was investigated using rheology, NMR diffusion, spectroscopy and relaxometry for a range of xylan concentrations (0 to 15% w/w), across the temperature range 30 °C to 60 °C. These results are compared and contrasted with a similar published study on cellulose in [C2mim][OAc]. Due to the higher molecular weight of cellulose (30 kg/mol), as compared to xylan (9 kg/mol), the cellulose samples have significantly higher viscosity weight for weight. When NMR results were plotted as a function of the fraction of hydroxyl groups from each polymer, instead of their weight concentration, all the data collapsed onto one master curve.

Mixtures of xylan and cellulose in [C2mim][OAc] were then investigated using the same methods. In these mixtures the total weight fraction of carbohydrate was kept constant, at 10% w/w, whilst the composition was varied in increments from pure cellulose through to pure xylan. All the results were interpreted with reference to expected “ideal mixture” behaviour, quantifying how much the properties varied from what would be anticipated by simple additive rules. This revealed that at certain cellulose to xylan weight ratios (xylan:cellulose of 10:90, 70:30 and 90:10) there were strong interactions between the two biopolymers causing deviations in the “expected” results by ~100%. This was most clearly seen in the NMR diffusion and relaxometry where the ions are indirectly acting as a probe of the polymer-polymer interactions.



The change in ppm of the various proton resonances as a function of xylan concentration, going from pure cellulose (0% xylan) to pure xylan (100% xylan).

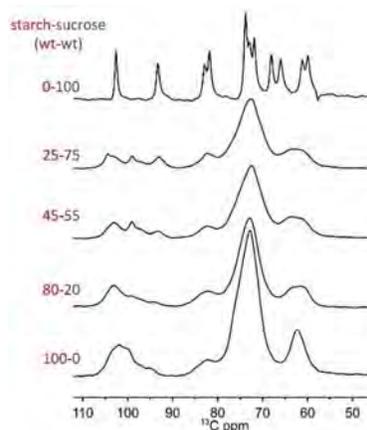
POLY 670: Starch/sucrose amorphous blends studied by low- and high-resolution solid state NMR

Marco Geppi¹, marco.geppi@unipi.it, **Francesca Martini**¹, **Giacomo Mencarini**¹, **Gabriela Badolato-Bönisch**³, **David J. Hughes**⁴, **Job Ubbink**². (1) Dept. of Chemistry and Industrial Chemistry, University of Pisa, Pisa, Italy (2) California Polytechnic State University, San Luis Obispo, California, United States (3) DSM, Kaiseraugst, Switzerland (4) University of Bristol, Bristol, United Kingdom

Biopolymer-based systems are today encountered in a wide variety of applications, since they are usually low-cost materials and respond to the actual eco-sustainable requirements of renewability and biodegradability. In particular, glassy matrices for the encapsulation and stabilization of bioactive compounds often consist of miscible blends of a carbohydrate of higher molecular weight and a low molecular weight carbohydrate or polyol. The optimization of the barrier properties of such matrices depends in a subtle way on the balance between the plasticization and antiplasticization of the high molecular weight carbohydrate by the low molecular weight compound. To this aim, understanding the phase properties, as well as the structural and dynamic features of these systems at a nanometric and sub-nanometric level is crucial to predict their final macroscopic behaviour.

In this work, the phase, dynamic and miscibility properties of modified food starch/sucrose spray dried amorphous blends were investigated by means of solid-state NMR (SSNMR) techniques. In particular, ¹H and ¹³C high and low resolution SSNMR experiments, carried out at different temperatures on blends with different modified food starch/sucrose ratios, gave interesting information on the properties of the starch and sucrose domains and on the interactions between the two components. ¹³C MAS spectra gave information about the amorphicity of the phases and the intermolecular interactions. On-resonance ¹H FID's showed evidences of the presence of domains with different degree of mobility, whose properties and relative content depend on composition. In addition, the measurement of ¹H T₁ revealed information on the phase separation of the system on the nanometric scale and on the changes induced by molecular interactions on the MHz dynamic behaviour.

The NMR results were supported by and compared with those obtained by DSC and PALS.



¹³C CP-MAS spectra

POLY 671: Insights into the heterogeneity of polysaccharides with solid-state NMR spectroscopy

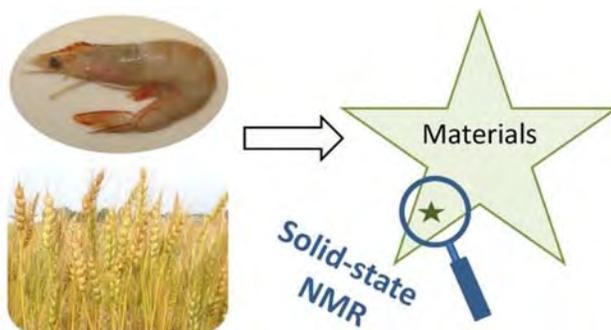
Joel J. Thevarajah^{1,2}, Matthew P. van Leeuwen^{1,2}, Maelie Heuls^{3,1}, Antoine Rouilly³, Rachelle M. Ward⁴, Elliot P. Gilbert⁵, Robert Graf⁶, Patrice Castignolles², **Marianne Gaborieau**^{1,2}, m.gaborieau@uws.edu.au. (1) Medical Sciences Research Group, Western Sydney University, Parramatta, New South Wales, Australia (2) Australian Centre for Research in Separation Sciences (ACROSS), School of Science and Health, Western Sydney University, Parramatta, New South Wales, Australia (3) Laboratoire de Chimie Agro-industrielle (LCA), Université de Toulouse, Toulouse, France (4) Yanco Agricultural Institute, NSW Department of Primary Industries, Yanco, New South Wales, Australia (5) Australian Centre for Neutron Scattering, Australian Nuclear Science and Technology Organisation, Lucas Height, New South Wales, Australia (6) Molecular Electronics, Max-Planck-Institute for Polymer Research, Mainz, Germany

Polysaccharides know a renewed interest for the production of materials owing to their renewable character. Due to their natural variability, it is important to set up methods for their advanced characterization.

Chitosan, extracted from crab and shrimp shell, is also biocompatible and biodegradable, giving it potential in biomedical applications such as membranes for cell culture. However, this application is limited due to an observed heterogeneity of cell attachment on the membranes. Chitosan's analysis in solution, hampered by solubility issues, has shown it to be heterogeneous in terms of copolymer composition. The nature of the spatial heterogeneity in the chitosan films was investigated by various two-dimensional solid-state NMR methods.

Cellulose is the most abundant polysaccharide on earth. Various processes are researched to produce materials from agricultural waste, including dissolution and regeneration, or thermocompression. The semi-crystallinity of the materials formed is crucial for their applications properties. It was characterized by XRD and solid-state NMR.

Starch is a major component of our diet. Its digestibility is crucial for the 'healthiness' of foods, however its molecular origin still eludes us. Various characteristics are assessed in starch samples grown at different temperatures or selected for their different digestibilities: branching by ¹H solution-state NMR, molecular mobility by ¹H solid-state NMR, short-range order by ¹³C solid-state NMR, crystallinity by XRD, and granular structure by SAXS.



POLY 672: NMR analysis of compositionally heterogeneous polysaccharides

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Polysaccharides are important substances used extensively for food and industrial applications. Because they are agro-based materials extracted from plants, they are often heterogeneous in composition. Thus, a conventional NMR analysis of a copolysaccharide (consisting of two types of monosaccharide residues) can only give an average value for composition. For some copolysaccharides, in addition to composition, the NMR spectra contain fine structures which can be analyzed to give comonomer sequence distribution, such as diad, triad, and tetrad sequence intensities. In these cases, it may be possible to estimate the extent of compositional heterogeneity in the copolysaccharide (Table 1). The analysis can be enhanced if fractionation data are available. Two methodologies can be used, depending on the nature of the heterogeneity. In this talk, the theoretical basis of these methodologies will be described and examples will be shown of the application of these NMR methodologies to copolysaccharides.

Table 1. Effect of compositional heterogeneity on the composition of an AB copolymer and on the triad comonomer sequence intensities

sequence	delta function ¹	symmetrical Gaussian ²	skewed Gaussian ³	bimodal distribution ⁴
A	0.400	0.400	0.400	0.400
B	0.600	0.600	0.600	0.600
AAA	0.064	0.112	0.113	0.400
AAB	0.192	0.176	0.148	0
BAB	0.144	0.112	0.139	0
ABA	0.096	0.088	0.074	0
BBA	0.288	0.224	0.279	0
BBB	0.216	0.288	0.248	0.600

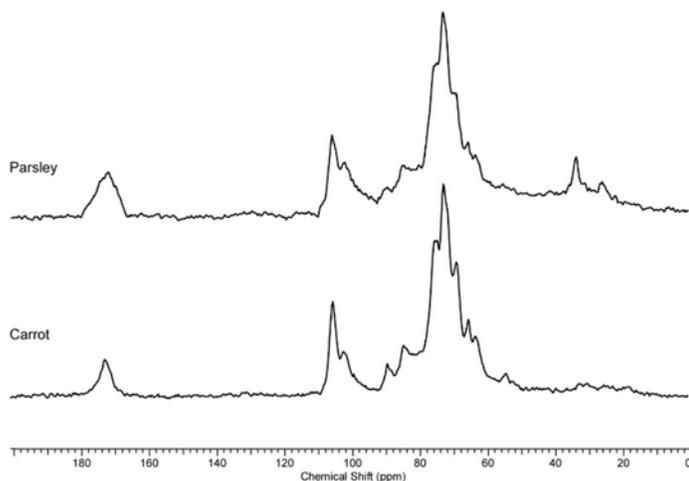
¹ Bernoullian, $P_A=0.4$. ² Bernoullian, $P_A=0.4$, $\sigma=0.2$. ³ Bernoullian, $P_A=0.37$, $\sigma=0.2$, $\tau=0.03$.

⁴ AB block copolymer.

POLY 673: Solid State NMR at high and low field for the characterization of bioplastics obtained from vegetable wastes

Roberto Simonutti¹, roberto.simonutti@mater.unimib.it, **Michele Mauri**¹, **Giovanni Perotto**². (1) Department of Materials Science, University of Milano Bicocca, Milan MI, Italy (2) Smart Materials, IIT, Genova, Italy

The valorization of vegetable waste can create opportunities to produce new valuable bioplastics, for this reason there is a great interest in developing new easy scalable processes without the use of environmentally concerning chemicals. Vegetable wastes like carrot, parsley, radish, cauliflower, spinach, orange peel and others can be converted into free standing films by a process carried out in a diluted aqueous HCl solution at room temperature. However the properties (mechanical, gas barrier, ...) of the bioplastics depend non trivially from the composition of the parent vegetable, since soluble parts can be removed in different extent and the morphology of the structural components of the bioplastics can be altered by the process. Thus it is necessary to have a comprehensive characterization of the bioplastics providing the composition and the supramolecular organization of the biomacromolecules constituting the films. ¹³C Magic Angle Spinning (MAS) NMR can provide a detailed description of the bioplastics, in terms of composition, in fact cellulose, lignin, hemicelluloses and pectins, the main components of the vegetables studied, give rise to distinctive resonances allowing to determine the fraction of each component. In all the systems studied one the most relevant component of the film is cellulose; the Cross-Polarization ¹³C MAS NMR spectra allow to determine the crystallinity of cellulose in the films. However, for a complete assignment of the spectra, due to the presence of some overlapping signals, two-dimensional experiments like ¹³C INADEQUATE MAS NMR are performed. Proton Time Domain NMR (¹H TD NMR) provides a complementary point of view on these materials that overlooks chemical detail while focusing on the chain dynamics. In particular, all bioplastic samples displayed a rigid fraction, composed by all the protons associated to crystalline cellulose but also to the rigid amorphous phase: this fraction depends on the sample origin and on the treatment.

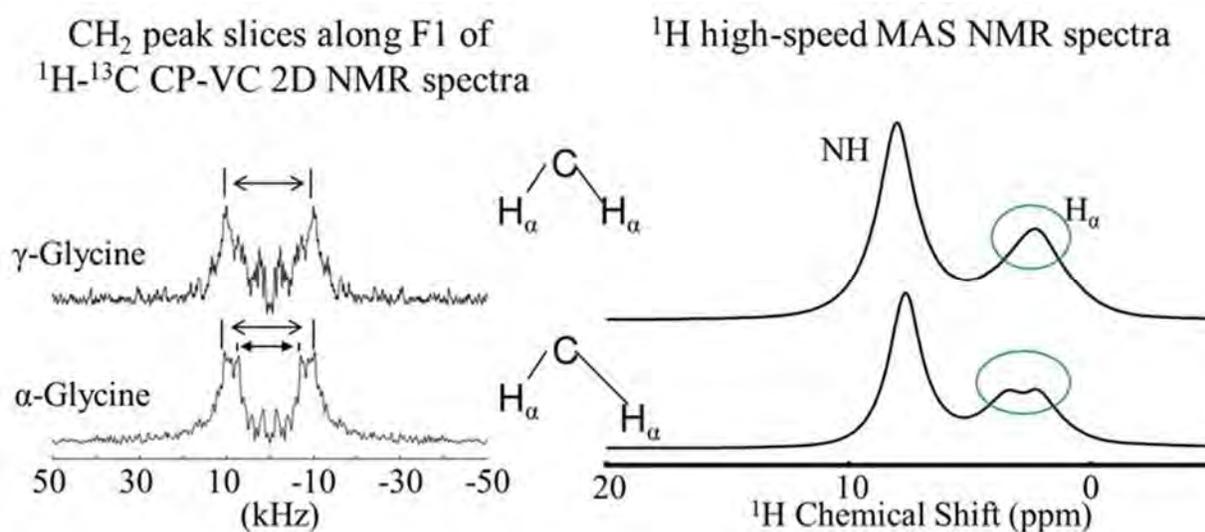


¹³C CPMAS NMR spectra of bioplastics obtained from parsley and carrot waste

POLY 674: Analysis of C-H and N-H distances of amino acids and polypeptides by CP-VC method

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The C_α-H and N-H distances of glycine in its α- and γ-crystal forms and of poly-L-alanine in two different conformations (α-helix and β-sheet) have been studied utilizing the CP-VC (Cross Polarization with Variable Contact time) method. The influence of the C_α-H and N-H distances on the ¹H chemical shift differences is also investigated for the polymorphs of glycine and the conformations of poly-L-alanine.



POLY 675: Characterization of microbial poly(γ -glutamic acid) and its polymer complex by solid NMR

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Molecular structure analysis of microbial poly(γ -glutamic acid) (γ -PGA) with different D/L ratio and its polymer complex was done by IR and solid NMR. γ -PGA is a naturally occurring biopolymer consisting of a glutamic acid, in a certain combination of D-form and L-form (γ -(D,L)-PGA), all D-form (γ -D-PGA), or all L-form (γ -L-PGA). Sodium salt of γ -(D,L)-PGA (D/L = 8/2, 7/3, and 5/5) and γ -L-PGA (D/L = 0/10) were used as received. γ -(D,L)-PGA (free form) does not dissolve in water, but its sodium salt γ -(D,L)-PGANa is water-soluble. However, γ -L-PGA (free form) and its sodium salt γ -L-PGA/Na are both water-soluble. Free form of γ -(D,L)-PGA and γ -L-PGA were obtained as a precipitate or film cast from acidic aqueous solution, respectively, in which pH is lower than pKa. Carbonyl carbon peak in ^{13}C solid NMR spectrum of γ -(D,L)-PGA differs from that of γ -L-PGA. γ -(D,L)PGA has an additional sharp peak at 171 ppm in ^{13}C solid NMR spectrum as shown in Figure 1. Sodium salt of both γ -L-PGA and γ -(D,L)-PGA do not have this peak. Both γ -L-PGA and γ -(D,L)-PGA have an absorption band at 1735 cm^{-1} in IR spectra which are not observed in their sodium salts. Carbonyl carbon peak of γ -(D,L)-PGA was curve-fitted into three peaks. At first we assigned two peaks in the higher field side to two different kinds of side-chain carboxyl groups, one for the carboxyl group which forms the strong hydrogen bonds among carboxyl groups and the other for free carboxyl group. A lowest field side peak was assigned to carbonyl carbon of main chain amide linkage. On the other hand, carbonyl carbon peak of γ -(D,L)-PGA/Na and γ -L-PGA/Na was curve-fitted into two peaks: one for main chain amide linkage and the other for free carboxyl group. Reexamination of the assignments of carbonyl carbon peaks are in progress. Structural analyses of polymer complex of γ -PGA with other polymers will also be discussed.

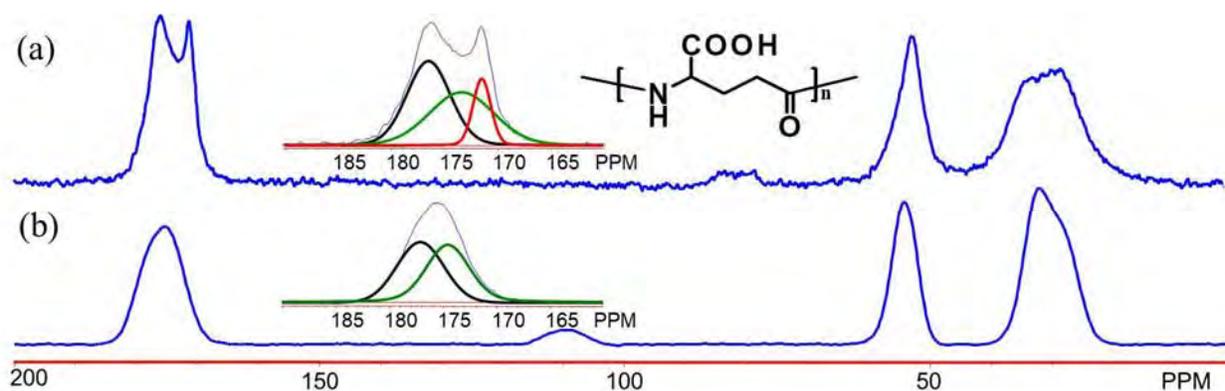


Figure 1. ^{13}C solid NMR spectra of γ -PGA with different D/L ratio of (a) D/L=7/3 and (b) D/L=0/10 prepared from acidic aqueous solution of γ -PGA Na in which pH is lower than pKa.

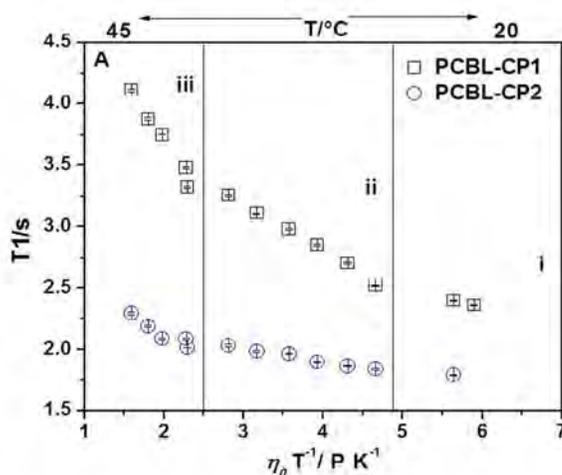
POLY 676: Investigation of polypeptide structure-property relationship by proton (^1H)/spin-lattice relaxation time (T_1) nuclear magnetic resonance and pulsed gradient spin echo (PGSE)

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Since its discovery in 1945 by Bloch and Purcell, nuclear magnetic resonance, NMR, served as one of the most important tools for chemists. This presentation will describe two examples that make use of NMR to understand the behavior of polypeptides. Self-diffusion of poly(γ -stearyl-L-glutamate), PSLG, as a function of molecular weight, M , and concentration was studied by pulsed gradient spin echo (PGSE). The self-diffusion coefficient significantly decreased with increased concentration for the medium range of molecular weight while an unexpectedly weak decrease with increasing M at given concentration was observed. In several instances, the self-diffusion measured data and fitted model suggests an approach to reptational scaling.

The second example describes a study of reversible helix-to-coil transition in *m*-cresol of poly(ϵ -carbonyloxy-L-lysine), PCBL, both as a free macromolecule and when tethered to silica particles. ^1H NMR showed the temperature range where the transition occurs. T_1 NMR experiments revealed that free PCBL shows two split modes while the tethered PCBL had only one mode displaying three domains as a function of temperature. The observed differences between the two systems were associated with the presence of random coil end fragments during folding-unfolding of PCBL chain into a rod structure.

Dedicated to the memory of our colleague and friend Dale Treleaven.



POLY 677: Self-assembly of responsive polypeptide block copolymers

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“Propose good science.”

This was the advice Tim gave me when I was starting to prepare faculty applications. At the time, combining peptide materials into block copolymers was relatively new, but this seemed like an interesting area of research for me to think outside of my ‘experimental box.’ Throughout this journey, I have been privileged to have Tim as a mentor, role model, and colleague. Congratulations for this well-deserved award!

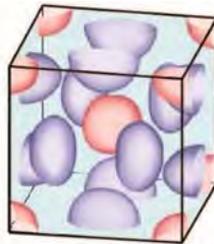
This talk will present some recent work from my group on the synthesis and characterization of peptide block copolymers, including those containing recombinant proteins. These nanostructured materials are able to self-assemble into responsive micelles and vesicles, organogels, and fractals. Assemblies are characterized using light scattering, and the addition of spectroscopic probes into these polymers gives a handle to interrogate local hydrophobicity at the interface of the assembly under different solution conditions. This work will be presented in the context of how Tim has impacted my own scientific and educational philosophy.



POLY 678: Complex lyotropic liquid crystalline sphere packings in aqueous dispersions of a diblock polymer

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Amphiphilic block polymers self assemble at high concentrations in water to form periodic supramolecular assemblies known as lyotropic liquid crystals (LLCs). Sphere-forming block polymer amphiphiles in selective solvents typically form LLCs with either high-symmetry body-centered cubic or cubic closest-packed configurations. Recently, neutral diblock polymers and aqueous LLCs of ionic surfactants have been shown to form a variety of low-symmetry micellar packings, including the tetrahedrally-closest packed Frank-Kasper A15 and σ phases with exceptional degrees of long-range translational order. The latter discoveries raise the question of whether or not these complex micellar phases can form in aqueous LLCs derived from neutral amphiphilic block polymers. This talk will focus on our recent discovery of a diblock polymer amphiphile that forms a tetrahedrally-closest packed Frank-Kasper A15 phase, with a specific emphasis on understanding the general principles underlying symmetry breaking across multiple classes of sphere-forming soft materials.



Frank-Kasper A15 phase
8 particles per repeat unit
2 discrete micelle sizes

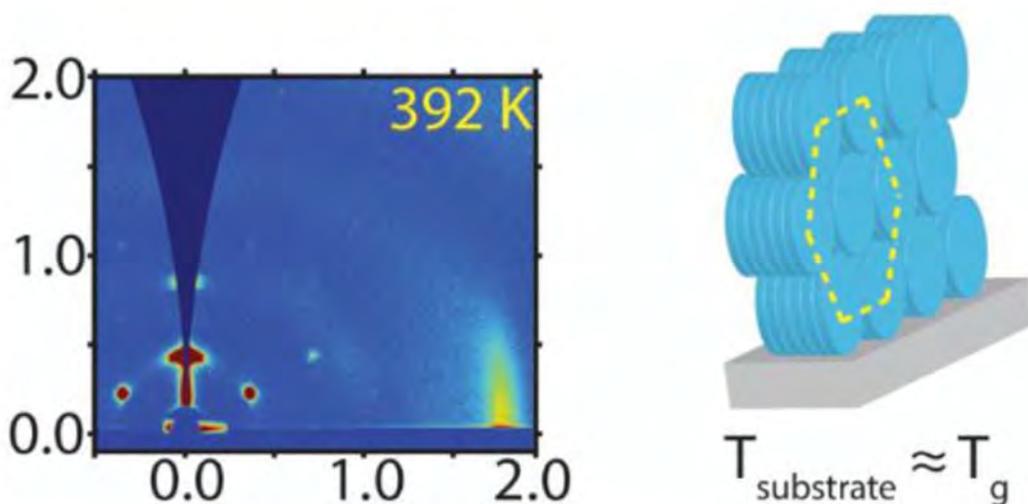
POLY 679: Using physical vapor deposition to produce structured glasses

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Glasses play an important role in technology as a result of their macroscopic homogeneity and the ability to tune properties through composition changes. These features are critical in organic light emitting diodes which utilize vapor-deposited glasses of organic semiconductors as active layers. While liquid-cooled glasses are usually isotropic, glasses produced by physical vapor deposition are generally anisotropic. This anisotropy can be manipulated to increase device efficiency.

We have shown that the substrate temperature during deposition plays a key role in controlling the anisotropy of vapor-deposited glasses. For hole transport materials such as TPD, mildly anisotropic glasses in which molecules either “lie down” or “stand up” can be prepared, as indicated by ellipsometry and grazing incidence x-ray scattering. When liquid-crystalline mesogens are deposited, much more highly organized glasses can be prepared. For the smectic mesogen itraconazole, a highly order smectic monodomain is obtained by deposition just below T_g ; everywhere in the sample the smectic planes are parallel to the free surface. For discotic mesogens, highly ordered columnar solids are obtained directly by deposition with substrate temperature allowing a switch between in-plane and out-of-plane columns. These developments present significant opportunities to design new anisotropic solids for organic electronics and optoelectronics.

The interesting properties of vapor-deposited glasses arise from the mobility of glass surfaces. During deposition, molecules near the free surface have the opportunity to sample many different packing arrangements. This leads to highly equilibrated glasses which high kinetic stability. It also leads to anisotropic glasses that have trapped elements of the anisotropic structure of the liquid/vapor interface.



POLY 680: Hydrogen bonded complex in photo-initiated cationic polymerization of epoxides and oxetanes

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We studied the thermal stability of the hydrogen bonded complex of epoxy and oxetane monomers with Brønsted acid, as being generated by photo-initiators from the UV irradiation. In particular, we investigated how its thermal stability affects the induction period in the photo-initiated cationic polymerization. The molecular structure of the monomers having methylene ether bonds connected next to epoxy and oxetane groups is a key structural motif for the formation of the hydrogen bonded complex, which stabilizes the photo-acid and is responsible for the induction time in the cationic photopolymerization. Using temperature-controlled FTIR with in-situ UV irradiation, we performed a series of real-time FTIR (RT-FTIR) experiments to support that the induction time is originated from the thermal stability of the hydrogen bonded complex that is strongly influenced by the heat conduction environment for the study of photopolymerization. Specifically, we focused on temperature-controlled RT-FTIR studies for the photocationic polymerization of bis(1-ethyl(3-oxetanil)methyl) ether (“di-oxetane”, DOX) (Figure 1). The super-acids generated from UV irradiation are immediately captured by DOX and become inactive in a form of hydrogen bonded supramolecular complex at $T < 30\text{ }^{\circ}\text{C}$. On the subsequent heating after UV irradiation at room temperature, the hydrogen bonded complex of DOX loses its thermal stability at $\sim 50\text{ }^{\circ}\text{C}$ and the autocatalytic cationic polymerization of DOX occurs.

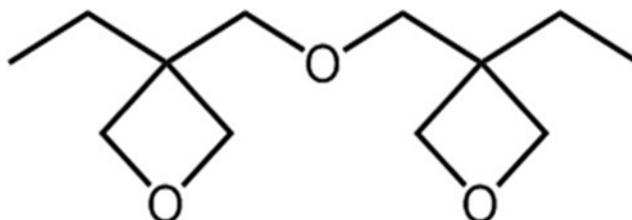
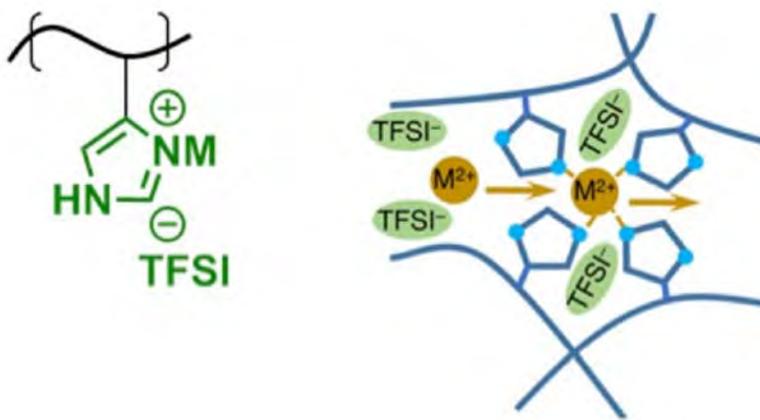


Figure 1. Chemical structure of DOX.

POLY 681: Functional polymeric ionic liquids

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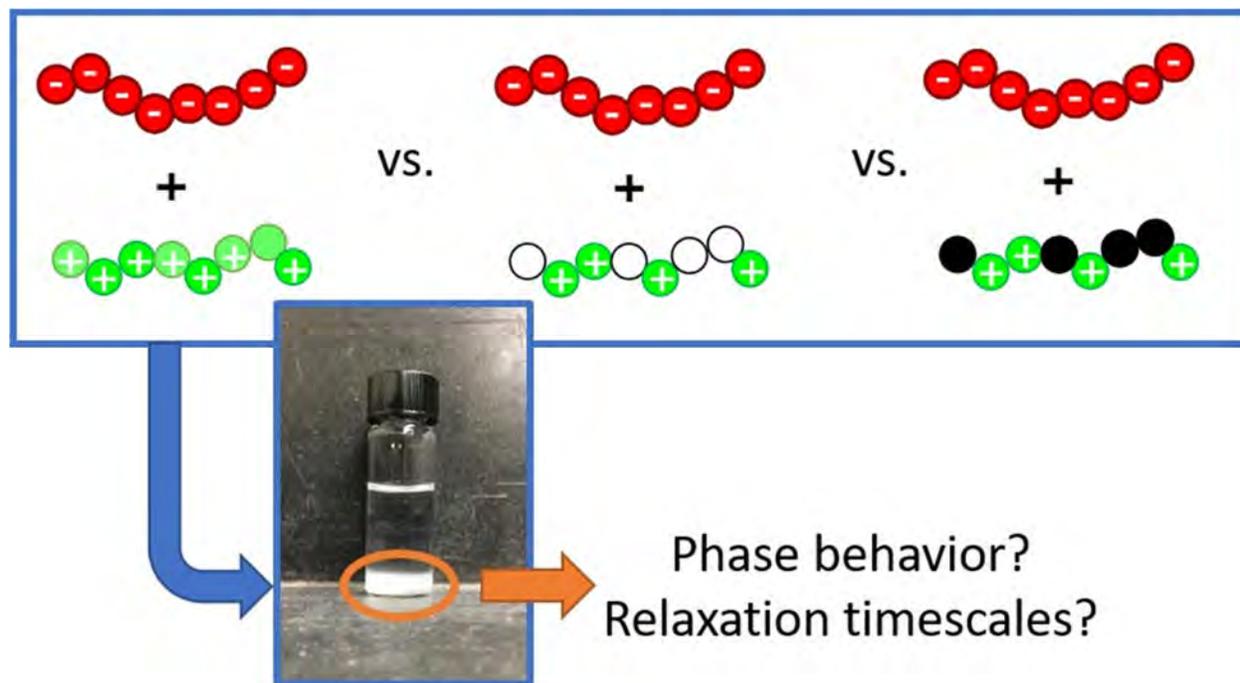
Polymers that contain ionic liquid constituent retain many of the properties of ionic liquids including ionic conductivity. We have recently found that a polymerized cation (such as imidazolium) is an excellent host for any associated anion. As a result, polymeric ionic liquids are not just solid counterparts to IL's, but are excellent vectors for the inclusion of a variety of functionalities ranging from multi-valent ions for batteries to magnetic anions. Moreover, PIL block copolymers allow orthogonal control over mechanical and morphological properties, ultimately leading to a conceptual framework for processable, tunable, multifunctional materials. In this talk, I will discuss a class of protic polymerized ionic liquids (PILs) based on imidazolium cations which exhibit high ionic conductivities in the solid state. Further, I will also discuss PIL's that are useful for applications ranging from magnetic materials to thermoelectrics



POLY 682: Composition-dependent dynamics in polyelectrolyte complex coacervates

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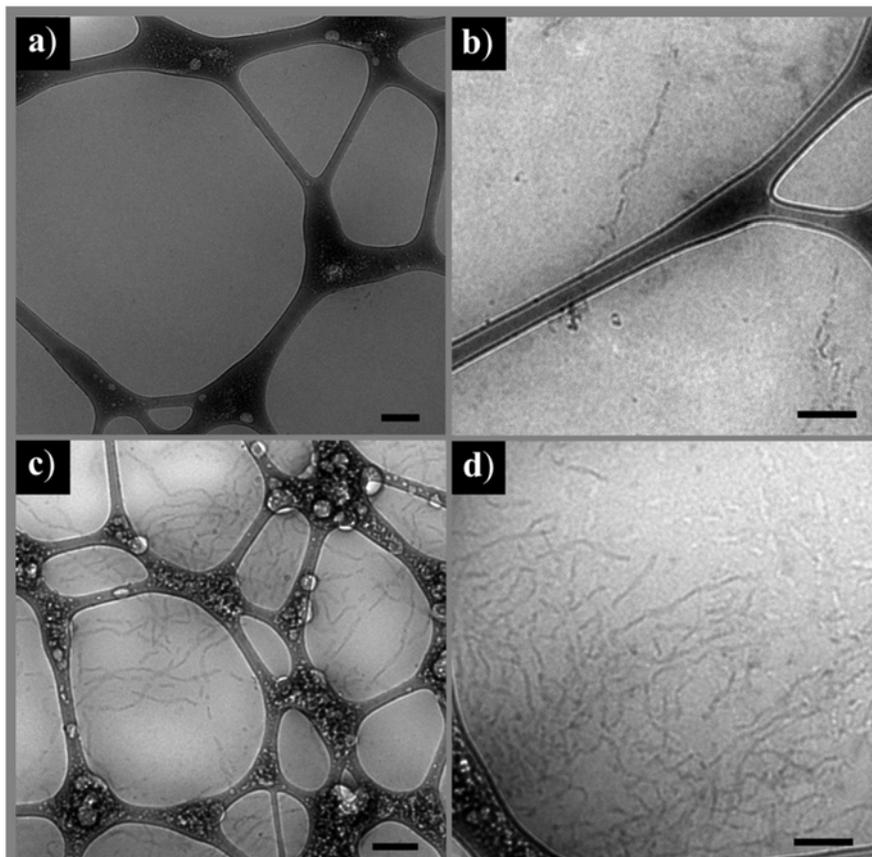
We investigate the roles of charge density and hydrophobicity in determining the properties of polyelectrolyte complex coacervates using two model systems. In the first, we investigate coacervates of poly(dimethylamino ethyl methacrylate-*stat*-di(ethylene glycol) methyl ether methacrylate) (P(DMAEMA-*stat*-DEGMA)) with polyacrylic acid (PAA). Rheological measurements on a polymer library in which the polycation charge density is varied while maintaining the same average number of charged sites per chain allow us to probe the role of cooperative interactions between adjacent charged sites, and provide a quantitative test of the sticky Rouse model for the relaxation timescales of these materials. In the second model system, we instead use post-polymerization functionalization of poly(N-acryloxy succinimide) to maintain identical charge densities and degrees of polymerization across samples while changing the sidechain hydrophobicity. Characterizing the composition-dependent phase behavior and viscoelasticity of the resulting coacervates allows us to identify the compositional windows in which electrostatic and hydrophobic interactions each dominate the coacervate properties, and illustrate their potential as design parameters for controlling the stability and viscoelasticity of these materials.



POLY 683: Thermoreversible gelation of methylcellulose: Confounding what we teach in Polymers 101

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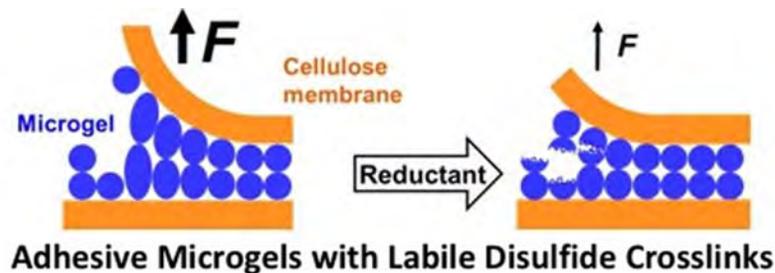
It is well established that aqueous solutions of methylcellulose (MC) can form hydrogels on heating, with the rheological gel point closely correlated to the appearance of optical turbidity. We recently discovered that MC chains associate into fibrils on heating. The fibrillar structure was precisely quantified with a powerful combination of (real-space) cryogenic transmission electron microscopy (cryo-TEM) and (reciprocal space) SANS and SAXS techniques. The cryo-TEM images reveal that MC chains associate into fibrils with a remarkably uniform diameter of 15 ± 2 nm over a range of concentrations and molar masses. The fibrillar nature of the gel structure was confirmed by fitting the scattering data with a model based on the form factor for flexible cylinders. However, there are still many puzzles unresolved. For example, why do macromolecules that are extremely heterogenous in molar mass, and containing a statistical distribution of eight repeat units, form such regular structures? Why do structures form at all, when the Flory-Huggins parameter is less than 0.5?



POLY 684: Adhesive microgels

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Over the last decade we have explored the use of aqueous microgels as adhesives for wet cellulose surfaces. The technological motivation is to expand the applications of wood fiber based materials in agricultural production and in food packaging with a view to finding greener replacements for non-renewable materials. From a scientific perspective, microgels permit the design of well-defined polymer networks in adhesive joints. In the early work, we prepared polyvinylamine (PVAm) microgels that were superior adhesives compared to linear PVAm. More recently we have focused on classical carboxylated-PNIPAM microgels. Without modification, these microgels have no adhesive properties on wet cellulose. However, the carboxylated microgels become adhesive when coated with adsorbed or grafted adhesive polymers such as PVAm or polyamide-epichlorohydrin (PAE) polymers commonly used in the paper industry. We have supported the experimental work with a peel delamination model that simulates the influences of microgel coverage (mass/joint area), diameter and crosslink density. Finally, we have developed adhesive microgels with labile disulfide crosslinks, facilitating recycling after use.



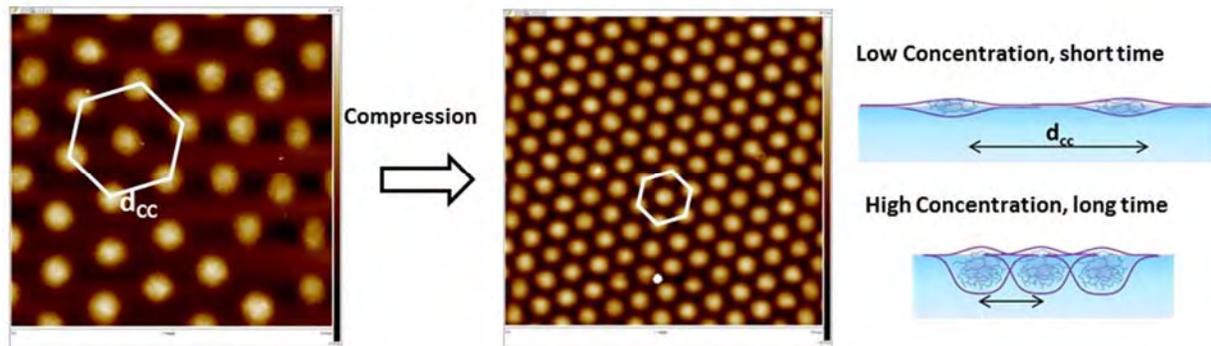
POLY 685: Soft microgels at liquid interfaces: model surfaces and emulsions

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Microgels are soft, deformable water-swollen cross-linked polymeric particles, which have the ability to undergo volume phase transition upon various stimuli. Some of them, such as poly(*N*-isopropylacrylamide) (pNIPAM), are amphiphilic and adsorb at liquid interfaces. Hence, they can stabilize Pickering emulsions [1] or foam films [2] in good solvent conditions. Due to their softness, these particles can deform and adopt various conformations at the liquid interface, which are translated into different macroscopic properties of the resulting emulsions, in particular in their flow behavior. The conformation depends on microgel structural parameters and also processing conditions.

Studying microgel adsorption at flat interfaces gives better insight into the link between microgel organization, their deformation and interfacial mechanical properties. This was achieved by two complementary methods: the spontaneous adsorption and the forced compression [3, 4]. Both equilibrium and kinetics aspects were studied. Using a systematic approach, we deciphered the role of structural parameters, in particular the cross-linking density and of electrostatics.

This knowledge can be further exploited to design new stimuli-responsive emulsions, with tailored properties.



AFM images of microgels ($10 \times 10 \mu\text{m}^2$) transferred on solid substrate after being compressed at the air-water interface and scheme of their profile view in the different conformations

POLY 687: Interface-mediated self-assembly of multifunctional core-shell microgels

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The encapsulation of inorganic nanoparticles by cross-linked polymers yields core-shell microgels that spontaneously self-assemble at air/liquid interfaces forming highly ordered monolayers. Transfer of these monolayers from the interface to macroscopic solid supports allows the fabrication of hexagonally ordered superstructures with large single crystalline domains. Depending on the thickness of the polymer shell such structures possess inter-core distances from a few up to several hundred nm. Multiple depositions on one substrate or deposition to substrates with different contact angles gives access to a broad range of complex superstructures including non-hexagonal 2D Bravais lattices.

In this contribution we will demonstrate the structural diversity that is accessible by interface-mediated self-assembly of hard-soft core-shell microgels. Furthermore, we will show how assembly of particles with plasmonic cores can lead to superstructures that show collective optical responses that differ strongly from the single particle behavior. The observed diffractive/plasmonic coupling can be reversibly tuned by addressing the refractive index environment through changing the swelling state of a responsive hydrogel matrix. This way fully reversible resonance tuning becomes possible by either solvent exchange or temperature (see figure 1).

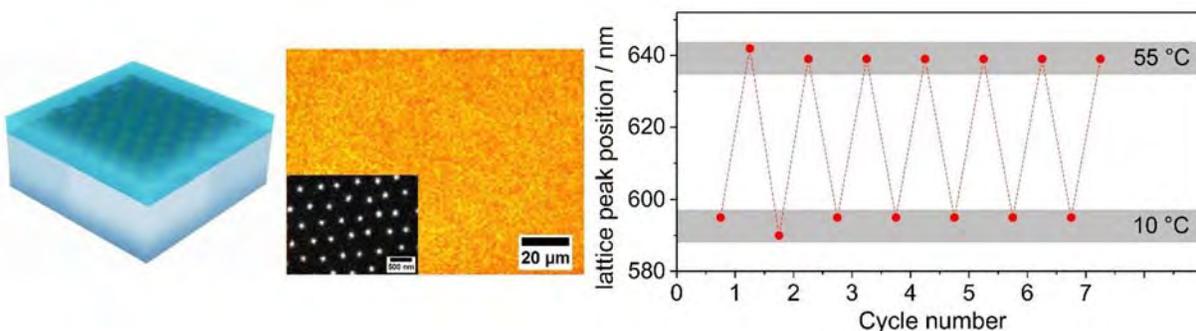


Figure 1. Left: Schematic depiction of a self-assembled plasmonic monolayer on glass (grey) embedded in a hydrogel matrix (light blue). Middle: Optical microscopy image as well as SEM image (inset) of an experimental hydrogel-embedded monolayer sample. Right: Temperature response of the resonance peak (diffractive/plasmonic coupling) for repeated heating/cooling cycles. Adapted from [3].

POLY 688: Smart nanomembranes by electron beam cross-linking of copolymer microgels

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Stimuli-responsive surfaces are of interest for a multitude of applications such as sensors[1], anti-fouling coatings [2] and cell culture substrates [4]. For the latter, coatings made of thermoresponsive Poly-(*N*-isopropylacrylamide) pNIPAm microgels have been found to allow reversible switching of cell adhesion upon heating and cooling [3-5]. In these works the microgel layer had to be deposited on the substrate intended for use by printing or spin-coating. Hence, the dimensions and material properties of the substrate can strongly influence the adsorption of the microgel particles. The present contribution will briefly review our efforts in this area.

Moreover, the preparation of free standing transferable membranes from cross-linkable microgels will be presented. Such membranes exhibit a thickness of about 100 nm in the dry state and can be transferred to different surfaces. This overcomes problems arising from direct deposition of microgels. The approach is based on the deposition of microgels, containing aromatic moieties, by spin-coating the particles on a sacrificial-polyelectrolyte or gold layer. A suitable comonomer was identified and different comonomer contents were used to make cross-linkable microgels.

Atomic force microscopy (AFM) was used to study the surface coverage, topography and the thickness in addition to ellipsometry measurements. Both methods for the characterization of the surface were applied to the dry and wet state to determine the thermoresponsive properties of the layers. The layers are subsequently cross-linked by e-beam irradiation. It is shown that the obtained microgel layers can be used to control ion-flow in electrochemical cells by changing temperature crossing the LCST of PNIPAM.



Schematic drawing of the principle of electron-beam-cross-linking between two functionalized microgel particles adsorbed at a surface.

POLY 689: Macroscopic aqueous foams stabilized by PNIPAM microgels

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Aqueous particle stabilized foams can be found in many technical applications and food products.

In these systems the particles adsorb at the air-liquid interfaces of the foam and stabilize them. When altering the properties of the particles like their hydrophobicity, the properties of the produced foams can be changed. Typical particles are modified silica nanospheres, but also soft colloidal particles like proteins, especially in food-related systems.

Another class of soft colloidal particles are cross-linked, short-chained poly-N-isopropylacrylamide (NIPAM) polymers, which have attracted much attention during the last years and were studied with various techniques and in the context of multiple possible applications. Since these microgels are responsive to external stimuli like temperature, materials made from them can be considered “smart” materials. A prominent example are thermo-responsive emulsions stabilized by microgel particles adsorbed at the water-oil interface. In these systems the emulsion stability can be controlled by changing the temperature.

In this contribution we report on our experiments with aqueous foams, which are stabilized by PNIPAM microgel particles.

We present how microgel properties like size, cross-linking density and particle concentration can influence the properties of macroscopic foams prepared with them. In addition we try to shine light on the interactions in microgel-loaded thin liquid films by analyzing disjoining pressure isotherms recorded with a Thin Film Pressure Balance (TFPB).

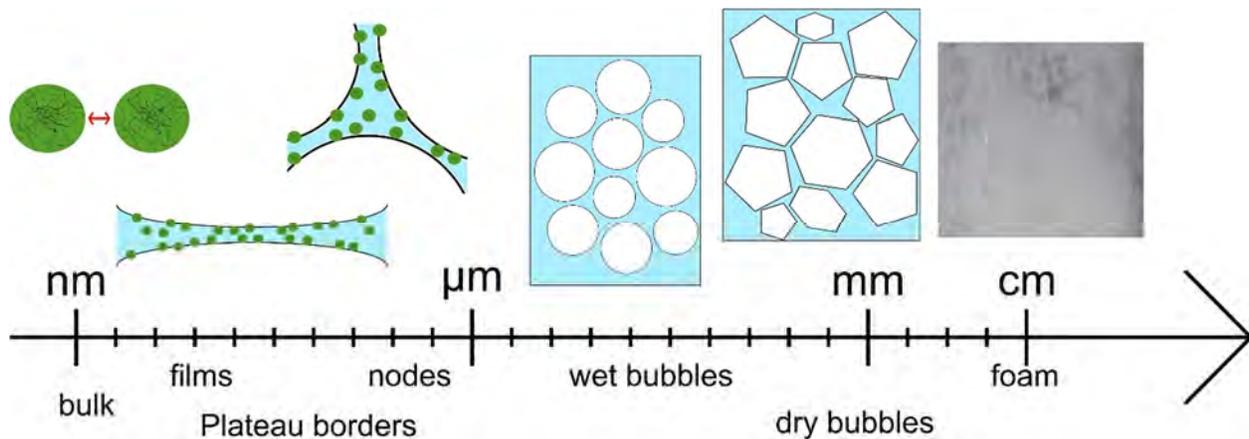


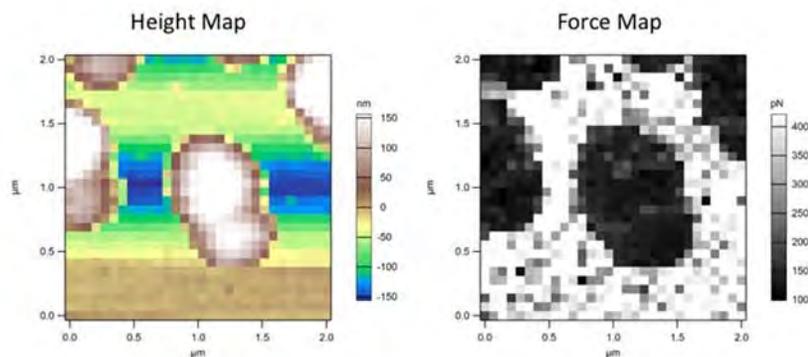
Figure 1: Structure of particle stabilized foams on different length scales.

POLY 690: Mechanical characterization of single microgels using atomic force microscopy nanoindentation

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Microgels are an active area of both basic and applied research, in part due to their unique deformability and ability to be functionalized with therapeutic compounds for biomedical applications. Additionally, microgel properties such as size, charge, and stiffness can be modulated by varying synthesis conditions and chemical composition. For example, common formulations such as poly(*N*-isopropylacrylamide) (pNIPAM) microgels can be co-polymerized with acrylic acid (AAc) to introduce negatively charged groups and convenient sites for functionalization. Traditionally, pNIPAM microgels are synthesized with an exogenous crosslinker such as *N,N'*-methylenebisacrylamide (BIS). However, in the absence of added crosslinker, ultralow crosslinked (ULC) pNIPAM microgels can still be formed through rare chain transfer reactions localized to the core of the microgel, resulting in even softer microgels.

Previous work has reported the Young's modulus of individual pNIPAM microgels through the deswelling transition. Atomic force microscopy (AFM) nanoindentation has also been used to report the Young's modulus of ULC pNIPAM-co-AAc microgels deposited in a packed monolayer on glass. This work builds on that foundation by more thoroughly defining the mechanical properties of pNIPAM microgels. Using two techniques of AFM nanoindentation, the shear and bulk moduli of the microgels can be determined. In the first, the microgel's shear modulus is probed at a sufficiently high velocity to avoid deswelling, simulating a mechanical response in the absence of volume change. The second technique involves "dwelling" at set indentations to allow for force measurements after equilibration of deswelling. The characterization of bulk and shear moduli may be particularly important to understand the behavior of microgel particles in blood flow, where they are exposed to both shear forces from fluid flow and compressive forces from other blood components.



Height (left) and force (right) maps of pNIPAM microgel particles using AFM nanoindentation.

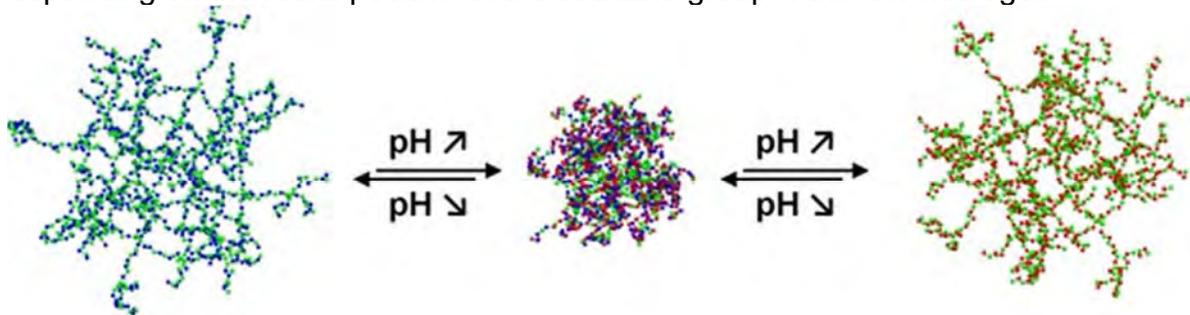
POLY 691: Monte Carlo simulations of weak polyampholyte microgels: pH-dependent ionization and volume change

Cornelius Hofzumahaus, Christian Strauch, **Stefanie Schneider**, schneider@pc.rwth-aachen.de. Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany

For weak polyelectrolytes (PE) as well as for weak polyampholytes (PA), not only the pH- pK_0 value but also the local electrostatic environment of the ionizable group determines the degree of ionization and structural properties of the polymer. The proximity of already ionized groups, which is enforced by the interconnectivity of the polymer chain, influences the probability of additional groups to become ionized. Therefore, the degree of ionization for polymers with different architectures differs from the ideal value, obtained for monomers at low concentrations. PA with a network topology are interesting, because of their possible applications for pH-triggered uptake and release of guest molecules.

In this work, we investigate PA networks with different distributions of titratable groups within the network. We employ a bead-spring model of the polymers with ionizable beads, explicit counterions and implicit solvent. The model is solved using Monte Carlo simulations and we involve a special titration step, which includes both the intrinsic probability of ionization for the isolated monomer as well as the interaction of the charge with its environment in the acceptance criterion of the trial move. We assess the degree of ionization as well as the structure of the polymer in dependence of the $pK_{A,base}$, $pK_{A,Acid}$ and pH values of the system for homopolymer polyelectrolyte networks as well as for ampholytic copolymers with different spatial distributions of acidic and basic monomers. Counterion distributions and the effective charge of the microgel were investigated as well.

It is seen, that the degree of ionization can either be reduced or enhanced depending on the type and distribution of the monomers of different type in network. In accordance with experiments, two titration steps are found for polyampholytic polymer networks with relatively close $pK_{A,acid}$ and $pK_{A,base}$ values. The degree of ionization differs, depending on the radial position of the titratable group within the microgel.



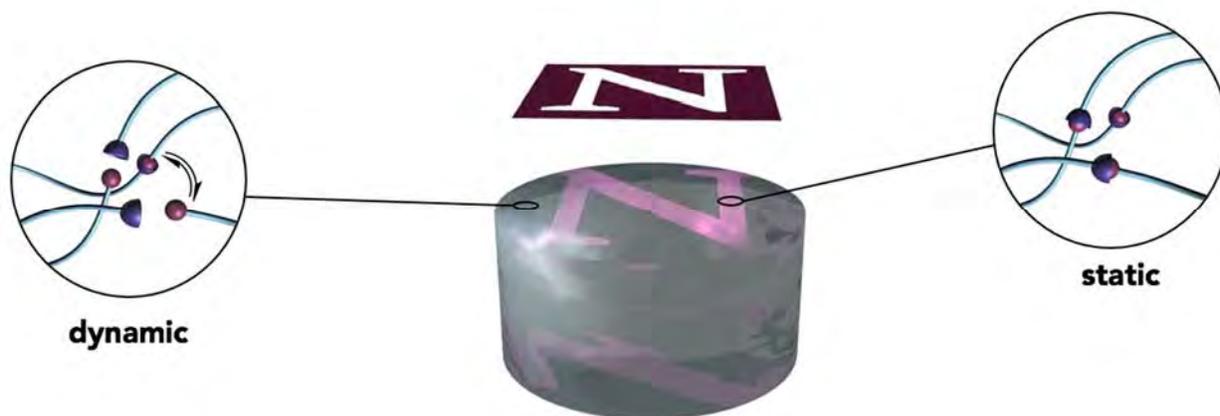
Snapshots of PA networks with a random distribution of acidic and basic groups at low (left), intermediate (center) and high (right) pH. Charged beads are depicted in blue (positive) and red (negative) and neutral beads are drawn in green.

POLY 692: Photocontrol of crosslink exchange kinetics in hydrogels and vitrimers

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The macroscopic properties of polymers emerge from a combination of molecular (covalent and noncovalent associations, van der Waals forces) and macromolecular (entanglement, reptation) interactions. Light uniquely offers precise, tunable, and external spatiotemporal control over molecular interactions, which can be translated into macroscopic responses. Photochemical crosslinking and cleavage allow precise tailoring of the *structure* of elastic polymer networks.

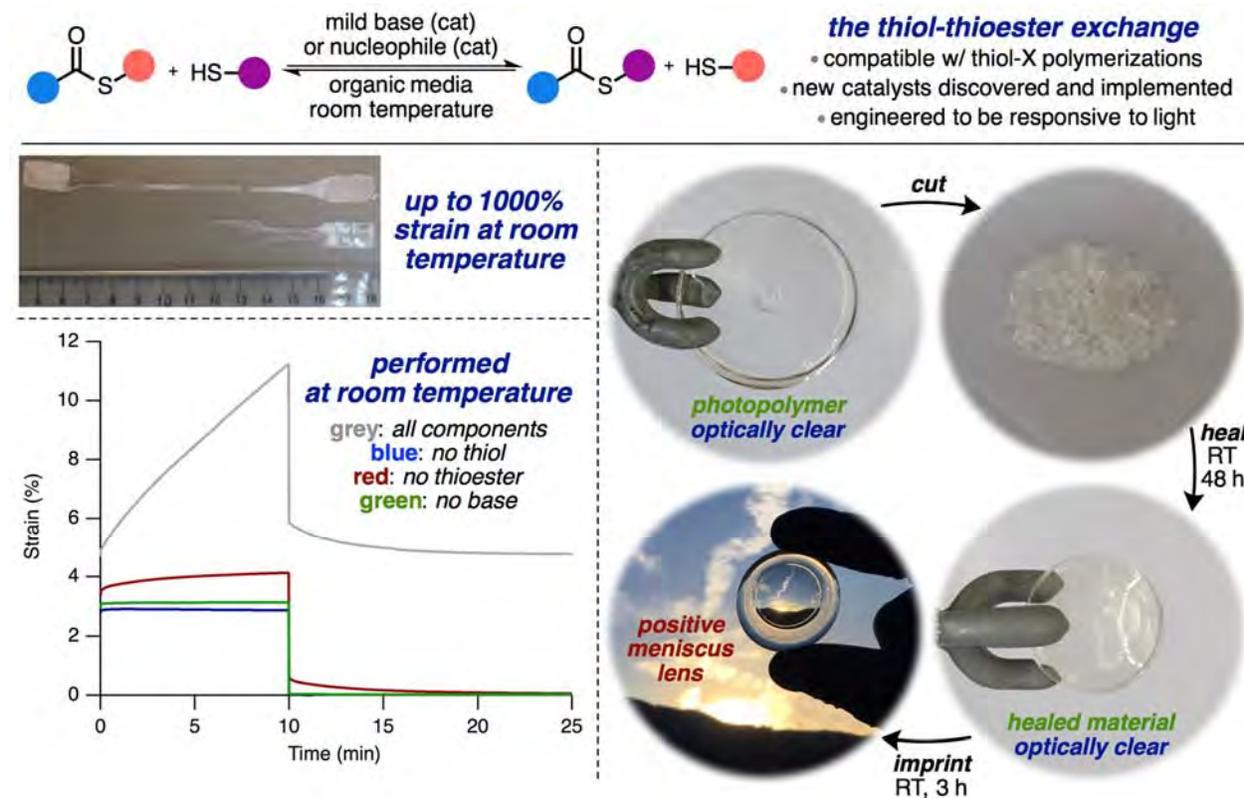
Recently, researchers have developed strategies to tune the *temporal* properties of viscoelastic networks that rely on changes in the composition and structure of the crosslinks, accessing multiple timescales for stress relaxation. I will describe my group's design of photoswitchable dynamic covalent crosslinks that enable *external*, *spatiotemporal*, and *reversible* control of viscoelasticity in hydrogels and vitrimers. We have observed reversible photocontrol of both the stiffness of these materials and the crossover frequency. I will discuss our efforts to elucidate the molecular mechanism underlying these macroscopic changes, as well as rational optimization of the photoswitch to enable applications in 3D cell cultures and recyclable elastomers.



POLY 693: Photo-switchable plasticity in (photo)polymerized network polymers

Christopher Bowman², christopher.bowman@colorado.edu, Brady Worrell¹, Matthew K. McBride¹, Gayla Berg¹, Chen Wang¹, Lewis Cox¹. (1) Chemical and Biological Engineering, The University of Colorado at Boulder, Boulder, Colorado, United States (2) UCB 596, Univ of Colorado, Chemical Biological Eng, Boulder, Colorado, United States

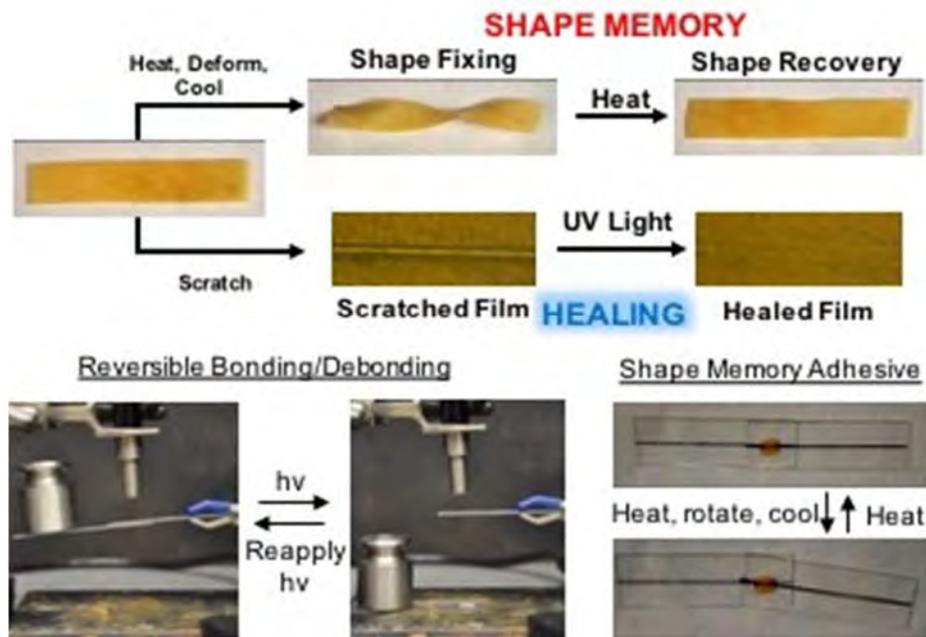
Network polymers containing covalent crosslinks cannot, generally speaking, be remolded, reshaped, or repurposed following fabrication. We have challenged this dogma by the addition of a dynamic thioester crosslink that is capable of being seamlessly introduced into mature polymerization techniques while subsequently engaging in dynamic thiol-thioester exchange. These network polymers were discovered to be easily remolded or repurposed at room temperature, effectively maintaining the polymer's optical clarity. As thiol-thioester exchange was hinged upon incorporation of three components, namely thiol, thioester, and a suitable catalyst (base or nucleophile), we devised a switchable material, capable of turning ON or OFF plastic behavior *in situ* via delivery or consumption of the catalyst, respectively. Nearly perfect temporal and spatial control over plasticity in these polymers is demonstrated with potential uses for this platform being shown.



POLY 694: Photo-sensitive multi-responsive structurally dynamic polymers

Stuart J. Rowan^{1,2}, stuartrowan@uchicago.edu. (1) Institute for Molecular Engineering, University of Chicago, Chicago, Illinois, United States (2) Department of Chemistry, University of Chicago, Chicago, Illinois, United States

The dynamic bond can be defined as any class of bond that selectively undergoes reversible breaking and reformation, usually under equilibrium conditions. The incorporation of dynamic bonds (which can be either covalent or non-covalent) allows access to structurally dynamic polymers. Such polymers can exhibit macroscopic responses upon exposure to an environmental stimulus, on account of a rearrangement of their polymeric architecture. In such systems, the nature of the dynamic bond not only dictates which stimulus the material will be responsive to but also plays a role in the response itself. Thus, such a design concept represents a molecular level approach to the development of new stimuli-responsive materials. We have been interested in the potential of such systems to access new material platforms and have developed a range of new mechanically stable, structurally dynamic polymer films that change their properties in response to a given stimulus, such as temperature, light or specific chemicals. The main focus on this talk is how we have used this concept to access photo-sensitive/responsive materials through judicious choice of the dynamic bond incorporated onto the polymer architecture and how this has allowed access to multi-stimuli, multi-responsive materials. Such adaptive materials have been targeted toward applications that include healable plastics, responsive liquid crystalline polymers/actuators, shape memory materials and reversible adhesives.



Multi-functional shape-memory and photo-healable polymers can be used as shape-memory, photo-responsive adhesives

POLY 695: Strong underwater adhesion of low modulus polyester adhesives is achieved with photochemical control of cohesive bonds

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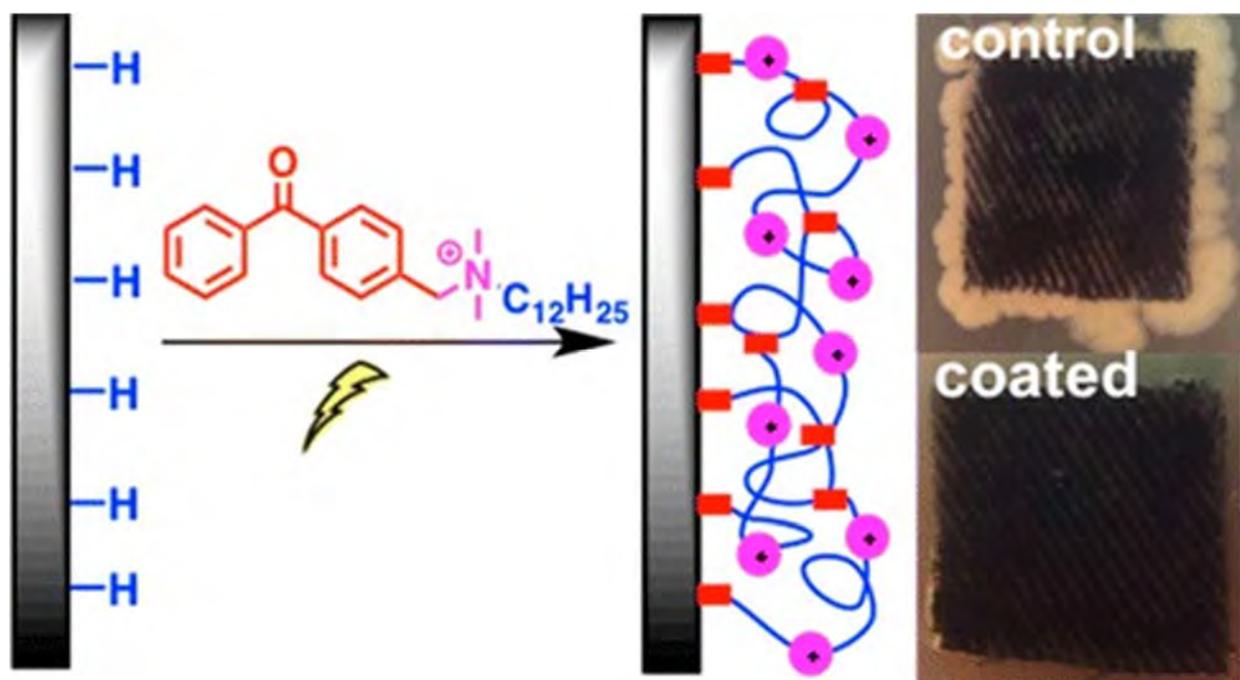
Mussel adhesion has fascinated scientists for their ability to adhere to underwater substrates. They do this by the secretion of adhesive proteins underwater in a temporal fashion. The mixture of proteins secreted by mussels are tuned to provide both adhesive and cohesive interactions with the substrate. Synthetic adhesives in comparison are for the most part are compromised in an aqueous environment due to their inability to prevent water penetration into the adhesive interface. We will present our work on the design and evaluation of synthetic polyesters that demonstrate strong underwater adhesion. The polyester is designed to flow at room temperature that enables application without any solvent. Catechol units of the polymer provide adhesive contacts with the substrate. The applied polymer is subsequently cured to a crosslinked polymer providing cohesive interactions. Lapshear measurements show strong adhesion even when the polymer is applied underwater and cured. Our current results indicate that the hydroxyl groups of catechol play a role in adhesion and that a hydrophobic environment is necessary for synthetic adhesives to show good performance in wet environments. Fundamental studies regarding the nature of the adhesive interface is being carried out using sum frequency generation spectroscopy and JKR measurements.



POLY 696: Photochemical grafting of functional copolymers with high abrasion resistance

Jason J. Locklin, jlocklin@uga.edu. Univ of Georgia Riverbend Rsch, Athens, Georgia, United States

This talk will highlight a variety of functional copolymers that can be permanently grafted to any substrate containing C–H bonds to form a durable polymeric film within 1 minute. The general strategy for polymer design includes copolymers of: (1) a functional component (anti-ice, anti-foul, antimicrobial, superlubricating, oleophobic, etc.), (2) a wetting agent for improved surface/substrate uniformity, and (3) a benzophenone moiety that, under mild UV irradiation, generates a densely cross-linked network with covalent attachment to a variety of substrates, including plastics, fabrics, and alkyl-modified glass surfaces. Through molecular design of the chromophore, the kinetics of crosslinking were observed to be one order of magnitude faster than that of previously reported benzophenone-associated cross-linkers, which makes the photochemical crosslinking more attractive for industrial coating applications. In this talk, we demonstrate functional coatings that have excellent durability that are used in a wide variety of applications.



Example of photochemical crosslinking to generate durable antimicrobial coatings.

POLY 698: Preparation of micro-patterned surfaces by the use of light-sensitive alkoxyamines

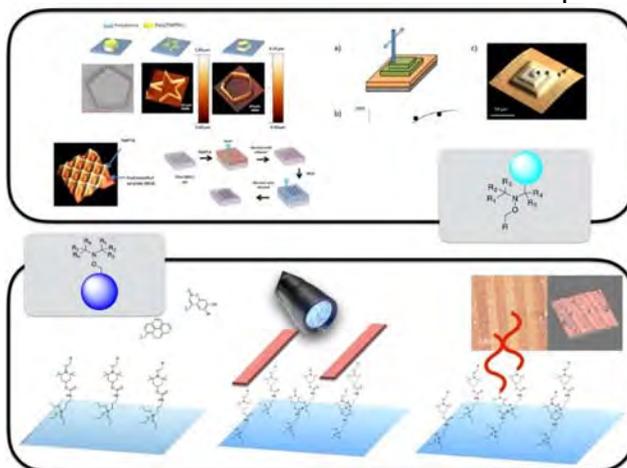
Yohann Guillaneuf, yohann.guillaneuf@gmail.com. Aix-Marseille University, Marseille, France

The spatially controlled functionalization of surface is currently widely investigated for several applications (biomaterials, sensors, micro/nano-fabrication, etc). Two techniques could be used to prepare such micropatterns. The first one is a photopolymerization from the surface whereas it is also possible to couple polymers onto surfaces by efficient ligation methods.

Since ten years, we are working on the development of light-sensitive alkoxyamines as a efficient method to generate alkyl and nitroxide radicals with both temporal and spatial control. The position of the chromophore is a key parameter for its use. If located on the nitroxide moiety, it will allow to perform Nitroxide Mediated Photopolymerization (NMP2). Using both mask and direct laser writing, we showed that reinitiation of a polymerization from a surface prepared using a first monomer could occur and that patterns with another monomer having different properties could be obtained. It is also possible to tune the height of the pattern with the irradiation time (microstructure thickness from few tens of nanometers to few micrometers). The influence of the nitroxide design will be highlighted in this presentation.

Secondly, in recent years, several methods for the light induced formation of reactive groups on surfaces have been developed which avoid the loss of spatial resolution through diffusion of the photoactive component. Functional groups can be utilized for the highly efficient ligation of an appropriate reaction partner but require specific end-group for both partners. As the combination of alkyl radicals and nitroxides could be seen as a clean “click” reaction, we thus prepare light-sensitive alkoxyamines but with the chromophore on the alkyl moiety to selectively trigger the release of the nitroxide. Using an alkoxyamine covalently bound on surface, it is thus possible to generate patterns of nitroxides that could be coupled with a variety of alkyl radicals to prepare interesting micropatterns.

The two approaches will be discussed in term of micropatterning potential.



POLY 699: Opacifying polymer imaging: a new strategy for thermal printing

Andrew Hejl, AHejl@dow.com, **Brian Einsla**, **Chao-Jen Chung**. *The Dow Chemical Company, Collegeville, Pennsylvania, United States*

Thermal printing is a technology with growing use worldwide for the production of receipts, labels, tickets and tags. Conventional thermal printing uses an imaging system containing a leuco dye and an acidic developer such as bisphenol A (BPA) that, when heated, changes color from light to dark. The widespread use of BPA and its potential effects on human health are a topic of growing concern and replacement imaging technologies are desirable. We have developed an alternative thermal imaging system that uses opacifying polymer particles coated over a colored layer. The opacity is obtained from a hollow polymeric latex that upon drying forms air voids sized to scatter visible light. Upon exposure to heat during thermal printing these hollow particles undergo collapse losing their opacity and exposing the colored layer underneath. Emulsion polymerization techniques to control the void size and chemistry of the polymeric shell are critical to achieve the desired printing performance. The resulting thermal papers can be used to print a permanent image without the use of dyes or developers. The technology described here was awarded the 2017 U.S. EPA Presidential Green Chemistry Challenge Award.

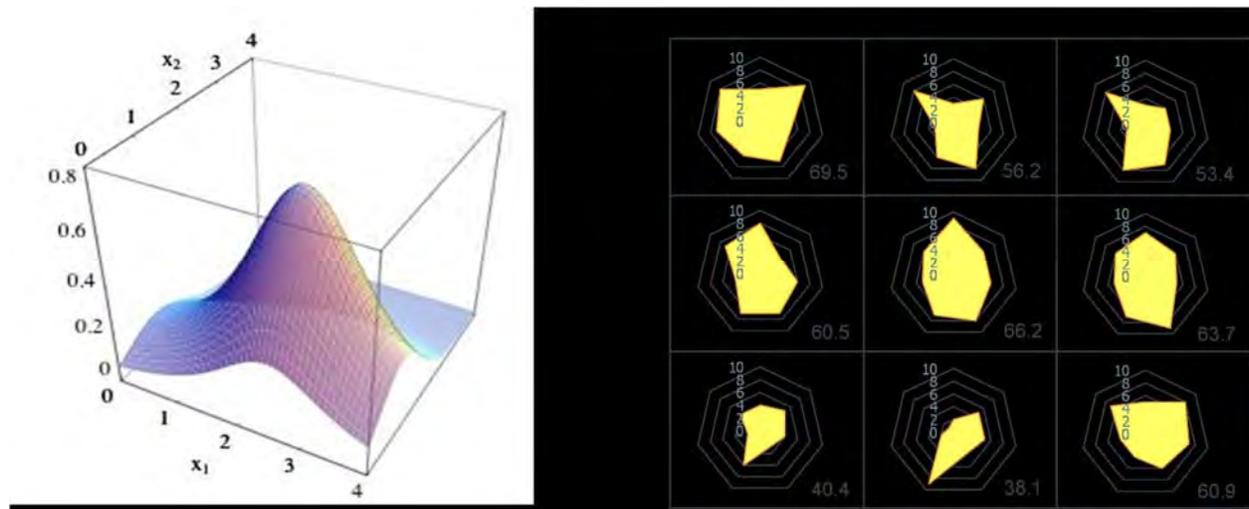


Thermal printing mechanism using opacifying polymer layer

POLY 700: Waterborne coating formulations with poly (vinyl acetate) and acrylic latex blends utilizing design of experiments and high-throughput methodology

Partha S. Majumdar¹, PSMajumdar@dow.com, Melinda H. Keefe², Keith Alderfer¹, Brandon Rowe³, Kevin Oleksiak¹, Michelle Toth¹, Kevin Henderson¹, Jeff Sweeney². (1) Coatings & Performance Monomers, Dow Chemical, Collegeville, Pennsylvania, United States (2) Research & Development, The Dow Chemical Company, Willow Grove, Pennsylvania, United States (3) DowFood, Pharma & Medical, The Dow Chemical Company, Collegeville, Pennsylvania, United States

Blending multiple latexes to formulate waterborne architectural paints is often practiced targeting a better balance of properties compared to the formulations containing individual latexes. Unfortunately, mixing numerous combinations of individual latexes with structural incompatibility can decrease miscibility resulting in an unacceptable degradation of one or more desirable properties. The interaction of these latex blends with formulation parameters such as additive package, volume solids, and pigment volume concentrations also significantly impacts the paint performances. This study utilized design of experiments (DOE) and high throughput methodologies in its approach to investigate the impact of blending poly (vinyl acetate) latexes with acrylic latexes on multiple paint properties. I-optimal DOE was conducted for estimating Taylor-Series Expansion models involving main effect and up to three factor interaction terms. After data collection and analysis, predictive models were developed for each property to estimate the trends and associations with the variables. Predictive models were also utilized for optimizing multiple responses in order to achieve desired performance balances.



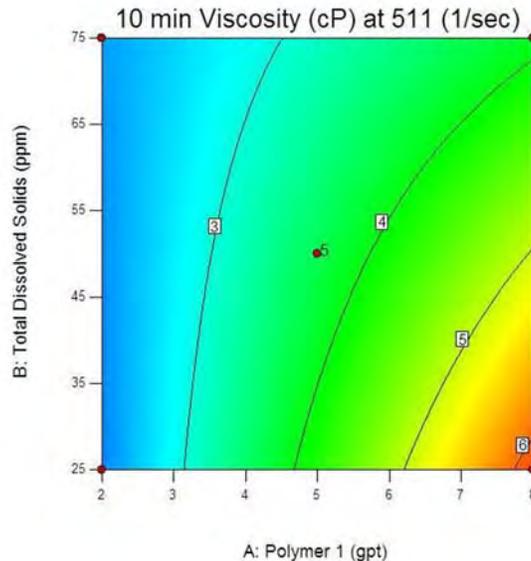
POLY 701: Altering friction reducer viscosities by controlling polymer concentration, brine composition and mixing energy

Carl Aften, caften@flotekind.com. Flotek Chemistry LLC, Magnolia, Texas, United States

Friction Reducers (FRs) are traditionally utilized to decrease the horsepower required to move a hydraulic fracturing fluid at a fixed flow rate. Viscosity is not a crucial factor in proppant transport when FRs are used before the perforations in slick water applications, however viscosity becomes a greater factor in proppant transport from the perforations into the formation. Viscosity becomes an important qualifying criterion with the advent of High Viscosity Friction Reducer (HVFR) systems that require higher loadings than traditional FRs.

The viscosities of four FRs applying eight variables were studied using response surface methodology. Establishing consistent hydration with unique apparatus design and viscosity measurement verification were the initial criteria. Viscosity was measured at a shear rate of 511s^{-1} on an Ofite 900 and tracked over periods ranging from 3 to 60 minutes. Once established, this method studied the effects of 1:1, 2:1, 2:2, and 3:2 salts singularly or in various concentrations and combinations. In addition, experimental designs were conducted under fresh water conditions in which FR loading, (1.0 to 6.0gpt), blender RPM, (600 to 12,000) and blender mixing time, (0.5 to 8.7 minutes) were varied. Viscosities were measured from 200 to 6000s^{-1} using a microchip viscometer.

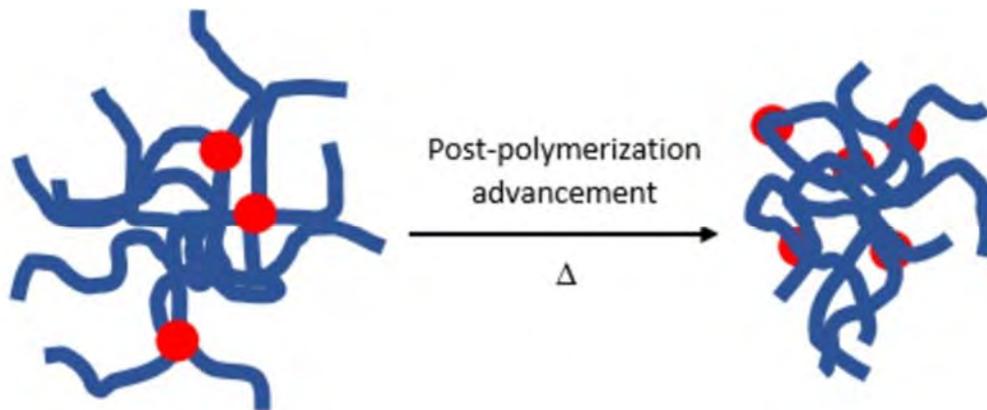
The response surfaces correlated highly with consistent trends noted depending upon the specific FR and salt matrix tested. The total dissolved solids (TDS) and hardness had a minor to major influence on the viscosity based upon FR examined. Brines were predominately antagonistic; however, some were synergistic with respect to viscosity. The influence of mixing and FR dosage correlate highly to the viscosity of the FR. For certain combinations the effect of time had no influence at long durations which indicates a viscosity reduction limit.



POLY 702: Post-polymerization molecular weight advancement in an acrylic latex adhesive and its effects on adhesive properties

Kimberly Schultz, kcmschultz@mmm.com, Corinne Lipscomb. 3M Company, Saint Paul, Minnesota, United States

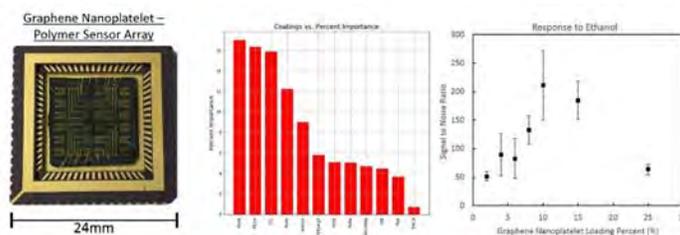
Post-polymerization advancement in the molecular weight and gel content of an acrylic latex initiated with a redox pair has been observed upon processing and storage conditions at elevated temperatures. This phenomenon has implications for acrylic latex products where a cure time, finishing tank, or hold tank are utilized. Samples of a C8/acrylic acid copolymer were prepared and characterized to study this effect and its impact on adhesive properties. Methods of controlling the molecular weight and gel content build will be presented.



POLY 703: Optimization of polymer-graphene nanoplatelet chemiresistive sensors for detection and discrimination of chemical warfare agents

Michael S. Wiederoder¹, *michael.wiederoder@gmail.com*, **Matt Weiss**², **Eric C. nallon**^{3,4}, **Randy Paffenroth**², **Vincent P. Schnee**³, **Collin J. Bright**³, **Shannon K. mcgraw**¹, **Joshua R. Uzarski**¹. (1) US Army Natick Soldier Research, Development and Engineering Center, Boston, Massachusetts, United States (2) Department of Mathematical Sciences, Worcester Polytechnic University, Worcester, Massachusetts, United States (3) Night Vision and Electronic Sensors Directorate, United States Army, Fort Belvoir, Virginia, United States (4) Black Cow Analytics LLC, Charlottesville, Virginia, United States

Rapid detection systems for chemical warfare agents (CWA) are needed to reduce exposure threat. Current technologies are limited by the use of selective sensors that require pre-determined targets and an inability to adapt to environmental conditions. Electronic nose systems overcome this by utilizing multiple semi-selective chemical sensors simultaneously with conductive polymer-colloid materials of particular interest due to their response diversity and commercial availability. Previously, detection and discrimination of 5 CWA simulants and 8 interferent compounds was demonstrated with an array of chemiresistive sensors consisting of polymer-graphene nanoplatelet (GNP) composite coated interdigitated electrodes. Using 12 unique polymer-GNP coated sensors 95-100% classification accuracy was achieved. First the effect of these 12 polymers on classification accuracy was evaluated for down selection to reduce future device complexity. Using a random forest analysis the optimal polymers were identified for detection of the CWA simulants, interferents, and all analytes. Next the coating deposition, formulation, and thickness of sensor coatings with these down selected polymers was evaluated to improve sensor sensitivity and repeatability. All coatings were airbrushed to improve dispersion, uniformity, and sensor repeatability compared to dropcast and spin cast films. The optimal GNP-polymer weight ratio was investigated using 3-18% (w/w) solutions deposited on an interdigitated electrode array. Coatings were evaluated by measuring the response magnitude and signal to noise ratio (SNR) upon exposure to ethanol and dimethyl methylphosphonate (DMMP). Maximum response occurred near the percolation coefficient with the maximum SNR at a greater weight percent. The effect of thickness was evaluated by depositing solutions with different solids content. Thinner films maximize response magnitude due to the increased surface area to volume ratio for the sorption based reactions. However SNR is maximized with a slightly thicker coating by minimizing coating variations across the electrodes. The results demonstrate methods to optimize conductive polymer-colloid sensors for sensitive, robust CWA detection systems with applications to other analyte types.



POLY 704: Plenary lecture: Skin-inspired polymer electronic materials and devices

Zhenan Bao, zbao@stanford.edu. *Chemical Engr Dept MC 5025, Stanford University, Stanford, California, United States*

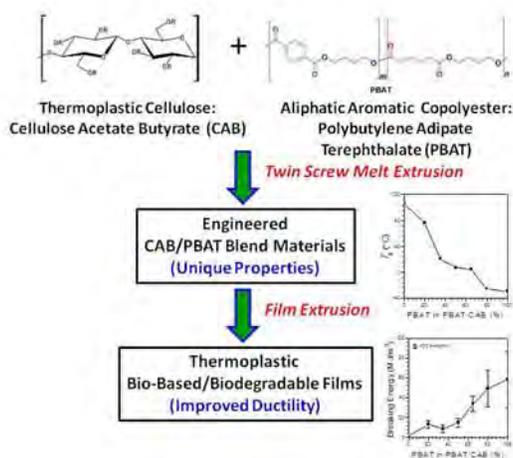
Skin is the body's largest organ, and is responsible for the transduction of a vast amount of information. This conformable, stretchable and biodegradable material simultaneously collects signals from external stimuli that translate into information such as pressure, pain, and temperature. The development of electronic materials, inspired by the complexity of this organ is a tremendous, unrealized materials challenge. However, the advent of organic-based electronic materials may offer a potential solution to this longstanding problem. In this talk, I will describe the design of organic electronic materials to mimic skin functions. These new materials enabled unprecedented performance or functions in medical devices, energy storage and environmental applications.



POLY 705: Cellulose ester and biodegradable polyester blends having improved properties

James H. Wang, jameswang.sshy@sinopec.com, Bing Zhou. SINOPEC, Appleton, Wisconsin, United States

Renewable biopolymers are important feedstocks for developing sustainable materials to address the global climate change. As the most abundant biomass on earth, cellulose and its derivatives can play a critical role in manufacturing the second generation biofuels, biopolymers, and biochemicals. This paper reports our research in developing biodegradable polymer blends containing a cellulose ester and a biodegradable polyester. A series of cellulose acetate butyrate (CAB) and poly(butylene adipate terephthalate) (PBAT) blends ranging from 20% to 80% by weight of CAB were prepared by a melt extrusion process. It was found that CAB and PBAT had good compatibility over the composition range, exhibiting a single glass transition temperature (T_g). The crystallization of PBAT was suppressed by the presence of 50% or more CAB. The blends containing from 35% to 65% of CAB unexpectedly had better thermal stability than pure CAB or PBAT. The CAB/PBAT blends showed unexpected and interesting rheological properties, the blends showed up to 34% reduction in melt viscosity at a shear rate of 100 s^{-1} and up to 32% viscosity reduction at 1363 s^{-1} . The change in melt rheology has improved the melt processability of CAB for a broad range of applications requiring low viscosity. The films made from the polymer blends containing 80%, 65% and 50% of CAB had low ductility (26% to 57% Elongation at Break) and high modulus (585 to 1080 MPa), these blends also had low melt elasticity. The ductility of the films increased with the PBAT content, reaching 250% at 80% of PBAT. The melt ductility of the CAB/PBAT blends were also significantly improved over that of pure CAB, enabling successful fiber spinning from the CAB/PBAT blends. The results of this research have demonstrated the potential to develop materials from cellulose derivatives having processability and mechanical properties in the range of typical synthetic polymers, this provides a technical foundation for the development of these cellulose-based polymer blends for sustainable packaging and other applications.



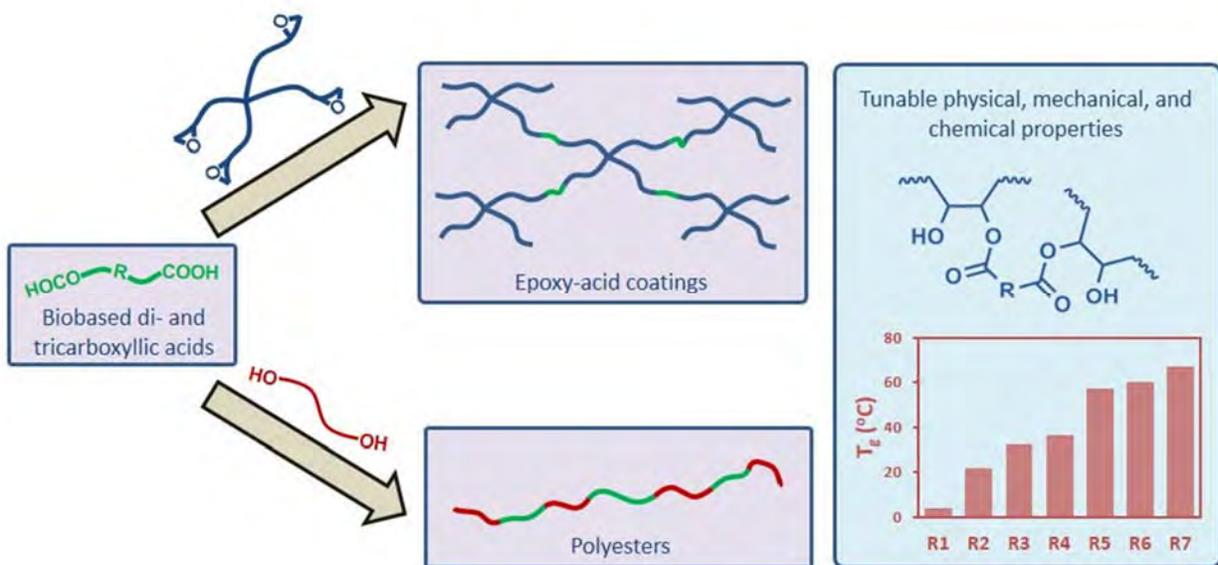
POLY 706: Bio-based carboxylic acids as components of sustainable coating systems

Ivan Hevus, Ivan.Hevus@ndsu.edu, Dean C. Webster. Coatings and Polymeric Materials, North Dakota State University, Fargo, North Dakota, United States

Aliphatic carboxylic acids manufactured from petrochemicals are widely used today as building blocks for several types of coating systems, including hardeners for epoxy resins and components of polyesters. The chemical structure of the acid has a significant effect on the coatings properties. Today, the focus in chemical manufacturing is shifting from traditional synthesis of chemicals from petrochemical feedstock towards development of chemicals from bio-based raw materials using either chemical or biological processing. This method of manufacturing not only enables more sustainable products, but also allows us to utilize many new and novel chemical structures that have not been commercially available before.

As more new polycarboxylic acids become available from renewable feedstock, their use in coatings applications could prove advantageous because of the unique properties they can provide. Thus, the use of new bio-based carboxylic acids as components of polyester or epoxy-acid systems could lead to coatings with improved adhesion, durability, hardness, flexibility/ductility, and corrosion performance.

A set of new functional bio-based di- and tricarboxylic acids that can be useful as components of sustainable coatings and can be produced from renewable feedstock on a commercial scale have been identified. Using selected acids in polyesters and epoxy-acid coating formulations, we developed a series of novel sustainable coatings. The physical, chemical, and mechanical properties of the developed materials can be adjusted over the broad range by varying the nature of the acid component.



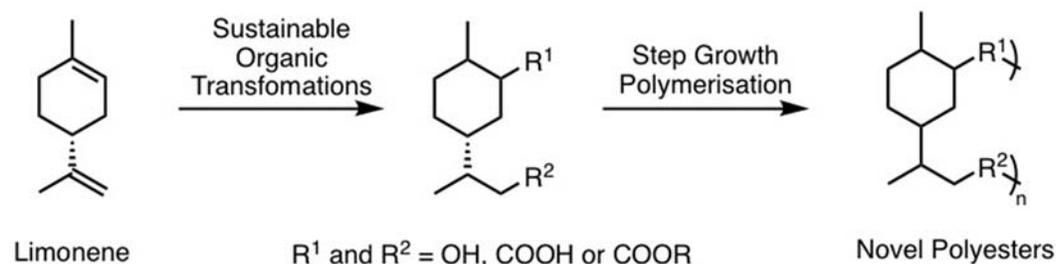
POLY 707: Polymerisation of limonene and α -pinene derived monomers for the synthesis of novel renewable polyesters

Megan Thomsett, *pcxmt4@nottingham.ac.uk*, Steven M. Howdle, Robert A. Stockman.
Chemistry, University of Nottingham, Nottingham, United Kingdom

Environmental issues surrounding petrochemical derived plastics have provided a driving force for scientific research that aims to alleviate our dependence on polymers derived from fossil fuels.¹ Terpenes, terpenoids and resin acids are a group of non-polar small molecules typically produced biosynthetically by many classes of trees and plants.² The terpenes are a vast family of naturally occurring compounds, which show enormous structural diversity and provide a source of hydrocarbon rich biomass. They are abundant, inexpensive and do not directly compete with food sources, making them ideal small molecule building blocks for many applications including the area of renewable polymers.

This research aims to transform limonene and α -pinene into useful, functionalised, terpene derived monomers, which have the potential to undergo polymerisation for the synthesis of renewable polymers. The project focused on synthesising new monomers for step growth polymerisation for polyester synthesis.

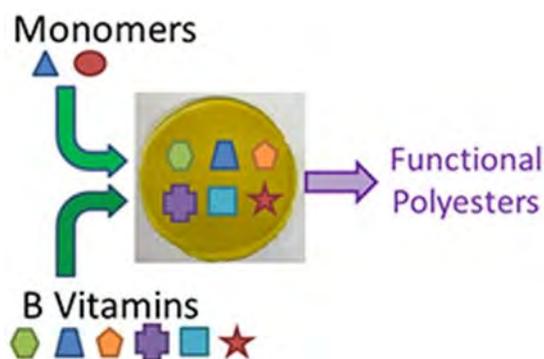
The functionalisation of limonene and α -pinene to enable the synthesis of a renewable monomer which can undergo step-growth polymerisation is presented. More specifically, sustainable oxidation chemistry was used to synthetically modify limonene into a hydroxy-acid which can self-condense to form a polyester. The limonene derived monomer was subsequently polymerised in bulk to yield a low molecular weight novel polyester with a high percentage of the mass originating from renewable biomass.



POLY 708: Attaching multiple B vitamins to polyesters

Robert T. Mathers, *rtm11@psu.edu*. Chemistry, Pennsylvania State University, New Kensington, Pennsylvania, United States

Covalent attachment of multiple B vitamins (B₁, B₂, B₅, B₆, B₇, B₉) opens new opportunities for functional polymers. Traditionally, B vitamins, like B₇ and B₉, have been conjugated with polymers in solution via carbodiimide (DCC) reactions or click chemistry. This presentation describes a melt polymerization strategy with citric acid and diglycerol that allows attachment of multiple B vitamins in a single step. Based on numerous control experiments with UV/Vis and FTIR spectroscopy, LC/MS, and GPC, covalent attachment occurred by means of Fischer esterification.



Multiple B Vitamins Conjugate to Polyesters via Fischer Esterification.

POLY 709: Preparation and characterization of bio-based polyesters and polycarbonates derived from xylochemicals

Silvio Curia, *curia@rowan.edu*, Joseph Mauck, Alexander Bassett, Joseph F. Stanzione. Dept. of Chemical Engineering, Rowan University, Glassboro, New Jersey, United States

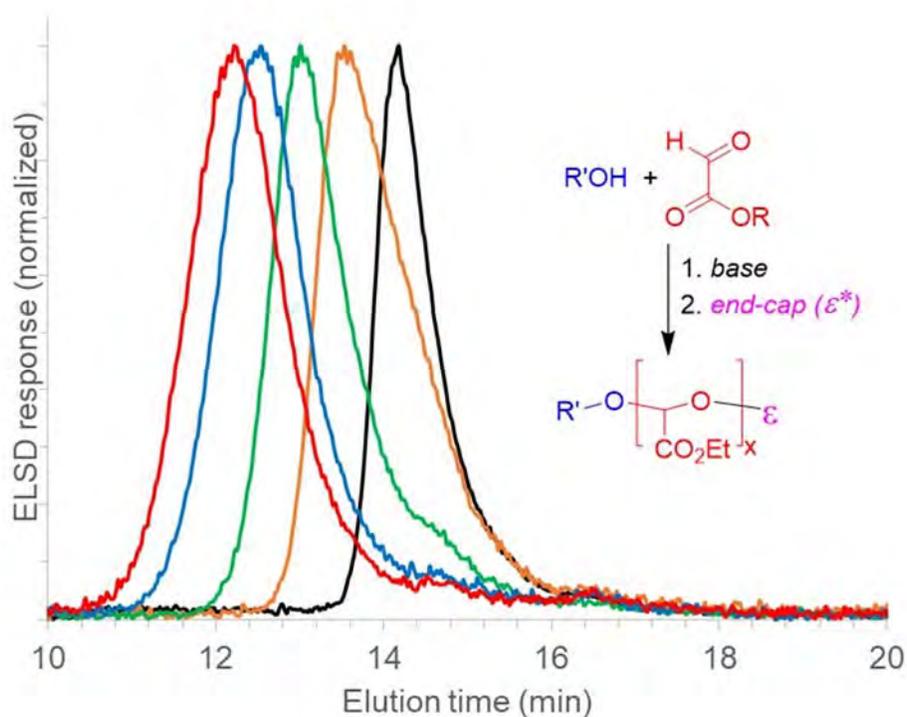
The utilization of wood-derived building blocks (xylochemicals) to replace fossil-based precursors is an attractive research subject of modern polymer science. The continuing development of new bio-based feedstocks opens opportunities to increase the resource base from which chemical and materials engineers can draw to meet specific polymer property requirements. Recently, significant efforts have transpired to obtain bio-based polymers and copolymers with enhanced thermomechanical properties for a wide variety of applications. In continuing these efforts, we have prepared and examined novel linear polyesters and polycarbonates derived from xylochemicals. Bio-based bisphenolic analogues were synthesized *via* electrophilic aromatic condensations of lignin-based building blocks. These bisphenolics were subsequently polymerized with multiple diacid chlorides/diacids to prepare a series of polyesters with varied and well-defined thermomechanical properties. Additionally, the same monomers were used for the synthesis of polycarbonates. These novel thermoplastics were characterized to assess their structure-property relationships and compared to industrial, fossil-based “equivalents”. The results of our study illustrate that these new polymers are valid alternatives to petroleum-based materials currently employed in the plastics industry.



POLY 710: Glyoxylate-containing block copolymer materials

David Hewitt, **Robert B. Grubbs**, robert.grubbs@stonybrook.edu. State University of New York, Stony Brook, New York, United States

Glyoxylic acid is a naturally occurring acid that can be prepared from a range of precursors, including carbon dioxide. Polymerization of glyoxylic acid and its esters results in polyacetals with properties dictated by the nature of the side group that can easily be degraded in the presence of acids. Controlled polymerization of glyoxylate esters from hydroxyl-terminated macroinitiators can be used to prepare a range of block copolymers with a degradable polyglyoxylate block, including polymers that form hydrogels. We will discuss aspects of the synthesis, characterization, and degradation of these polymers.

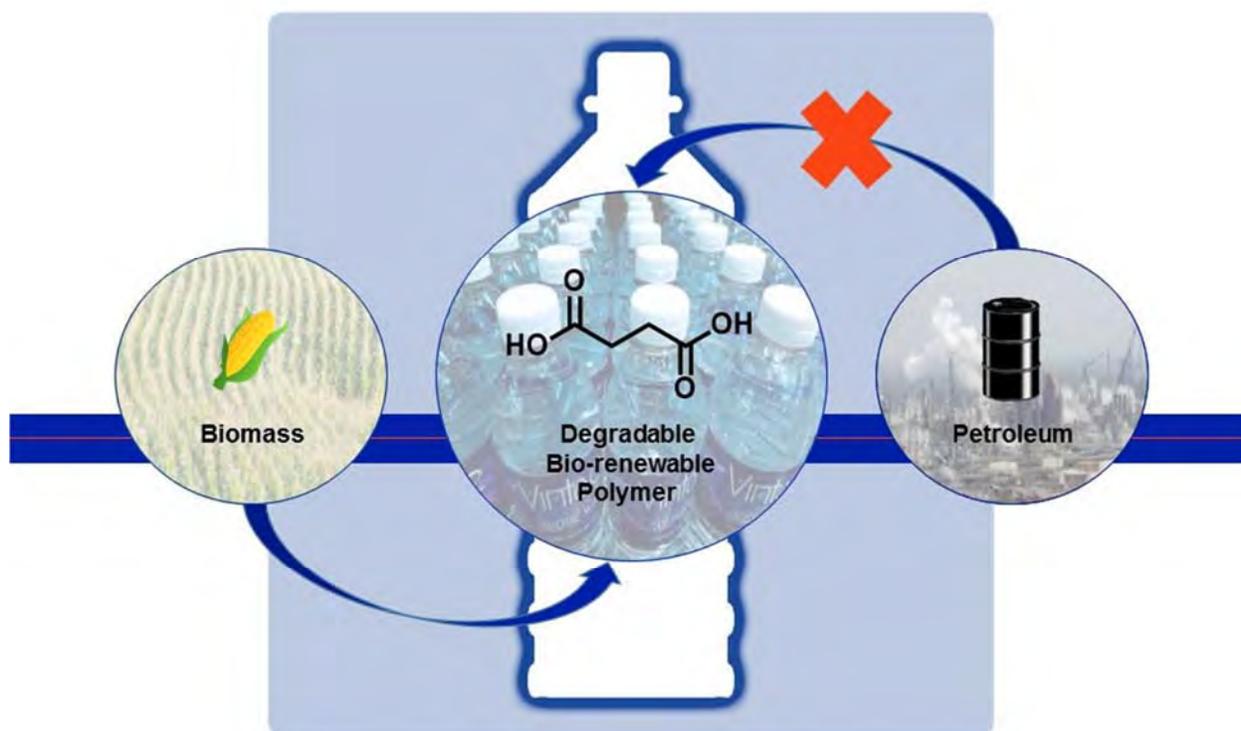


Comparative SEC traces for poly(ethylene oxide)-block-poly(ethyl glyoxylate) diblock copolymers prepared with increasing amounts of ethyl glyoxylate relative to poly(ethylene oxide) monomethyl ether initiator.

POLY 711: Poly(ethylene terephthalate) mimics based on naturally derived starting material

Gabriel Short, gabriel@taclabs.org, Haley Donow, Ha Thi Hoang Nguyen, Stephen A. Miller. Chemistry, University of Florida, Gainesville, Florida, United States

In today's market, single use disposable packaging account for a significant amount of commodity plastics. These plastics are generally fossil fuel dependent and non-degradable resulting in an accumulation of waste. This presentation will focus on polymer series derived from abundant renewable biomass aiming to replace the commodity plastic poly(ethylene terephthalate) (PET). Polymers based on an aromatic bio-cycle and diols of differing length, yield polyesters with high glass transition temperatures comparable to PET while increasing degradability.



POLY 712: Characteristic of biodegradable polyester PHBH and water-soluble poly(vinyl alcohol) blend nanofibers

RINA AFIANI A. REBIA¹, 17st117h@shinshu-u.ac.jp, Toshihisa Tanaka². (1) Department of Bioscience and Textile Technology, Shinshu University, Ueda-shi, Nagano, Japan (2) Faculty of Textile Science and Technology, Shinshu University, Ueda-shi, Nagano, Japan

Poly[(R)-3-hydroxybutyrate-co-(R)-3-hydroxyhexanoate] (P(3HB-co-3HH), PHBH) is a copolymer, developed from poly[(R)-3-hydroxybutyrate] (PHB), the basic homopolymer in polyhydroxyalkanoates (PHA) which are a family of biodegradable polyesters produced by bacterial fermentation. PHBH has a lower melting point, highly ductile properties and is more flexible than PHB. However, some deficiency such as low crystallinity and poor mechanical properties, made PHBH to limited application. One approach to improve properties of PHBH is blending with the other polymers. Poly(vinyl alcohol) (PVA) is a water-soluble polymer, biocompatible, high crystalline, flexible and also it is used in a wide range of industrial, and medical applications. The advantage of this research is to provide the potential of PHBH/PVA biodegradable blend nanofibers for wound dressing as medical application which discovering the characteristic of different ratio of materials. In this study, Pure PHBH, pure PVA, and blend PHBH/PVA were dissolved in HFIP or mixed solvents to prepare 1 wt% homogeneous solutions. The different compositions comprised of 100/0, 90/10, 70/30, 50/50, 30/70, 10/90, and 0/100 PHBH/PVA electrospun nanofibers were prepared by electrospinning. We investigate about characteristic and miscibility for PHBH/PVA blend nanofiber by SEM, FTIR, DSC and analyse for crystalline phase, surface wettability, and the water absorption. Moreover, we report about *in vitro* enzymatic biodegradation and *in vitro* cell adhesion for blend nanofibers. From the result, PHBH/PVA blend nanofibers were successfully prepared and fabricated by electrospinning from 1 wt% of solution in HFIP and mixing solvent. PHBH/PVA blend nanofibers were exhibited a smooth surface, uniform diameter, and without beads along their length (Figure 1). The fiber diameter of nanofibers was decreased with the increase of PVA ratio. The degradation of PHBH/PVA blend nanofibers was performed in lipase solution at 37°C for 4 weeks. Figure 2 shows the weight loss for electrospun nanofibers after enzymatic degradation *in vitro*. It exhibited that the nanofibers degraded with time by enzyme. PVA content in nanofibers have been influenced on the degradation rate of blend nanofibers, which is greatly improved.

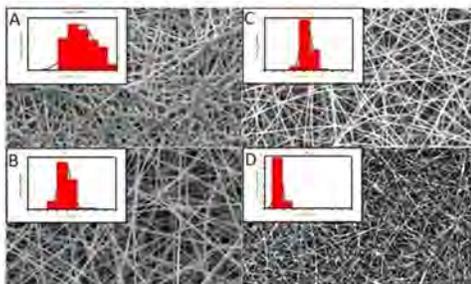


Figure 1 SEM micrographs of the electrospun nanofibers 1wt% of pure PHBH (A), pure PVA (B), blend PHBH/PVA (C) 70/30, and (D) 30/70.

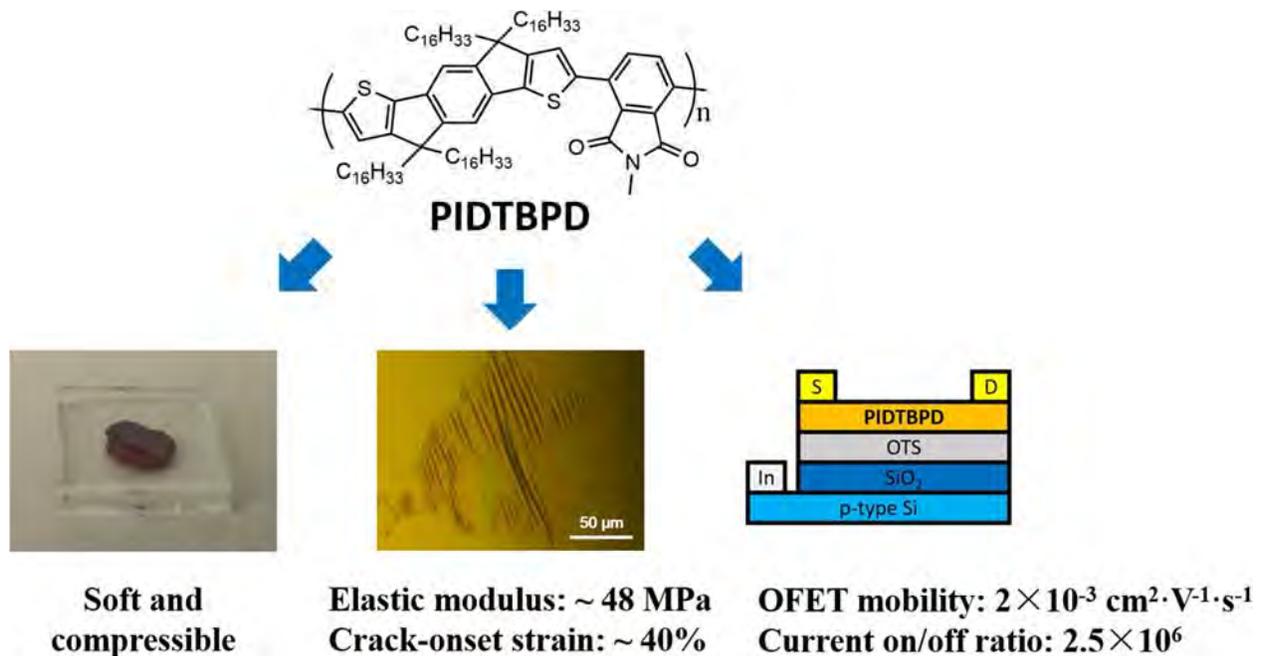


Figure 2 *In vitro* degradation for electrospun nanofibers of pure PHBH, ratio PHBH/PVA of 90/10, 70/30, 50/50, and 30/70 in PBS containing enzyme lipase.

POLY 713: Designing high ductility polymers for stretchable electronics

Christine K. Luscombe, luscombe@u.washington.edu. Materials Science and Engineering, University of Washington, Seattle, Washington, United States

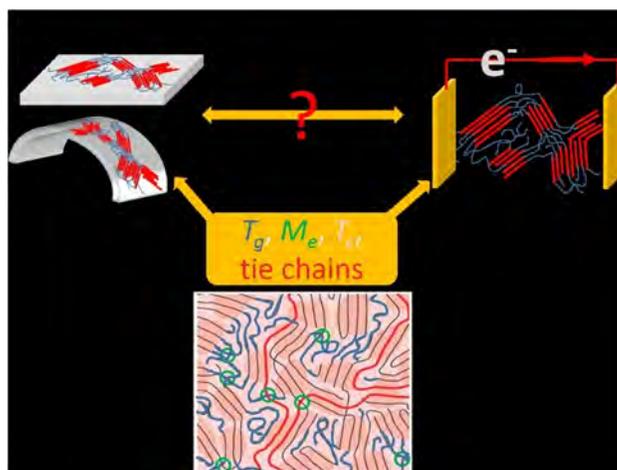
Organic semiconductors have been the focus of scientific research because of their interesting (opto)electronic properties and solution processability. They have been successfully employed and extensively studied in the fields of organic photovoltaics (OPVs), organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs) and organic thermoelectrics (OTEs). As their practical applications have extended into the health and life sciences areas (e.g., electronic skins and artificial muscles), the mechanical compliance (i.e., low stiffness and high ductility) has become increasingly important. This in turn requires one to establish an understanding of the relationship between polymer structure and their mechanical properties as well as their (opto)electronic properties. In this presentation, the synthesis of a series of indacenodithiophene-based semiconducting polymers will be discussed along with the feasibility of using these polymers in stretchable devices.



POLY 714: Understanding polymer physics of conjugated polymers for future deformable semiconductors

Renxuan Xie³, rux102@psu.edu, **Ralph H. Colby**², **Enrique Gomez**¹. (1) Penn State University, University Park, Pennsylvania, United States (2) Materials Science Engineering, Penn State University, University Park, Pennsylvania, United States (3) Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania, United States

The fundamental polymer physics of conjugated polymer, including the tie chains, the entanglement molecular weight (M_e) and the molecular weight dependences of glass transition temperature (T_g) and the liquid-crystal-to-isotropic transition temperature (T_c), are lacking. These microstructural parameters ultimately connect the charge transport and mechanical flexibility of conjugated polymer. The molecular weight dependence of T_g is studied using regioregular (RR) and regiorandom (RRa) Poly(3-hexylthiophene-2,5-diyl) (P3HT) by oscillatory shear rheometry. We find two T_g 's for both RR and RRa P3HT. The higher T_g , T_α , is associated with the backbone segmental motion and depends on the molecular weight, such that the Flory–Fox model yields $T_\alpha = 22$ and 6 °C in the long chain limit for RR and RRa P3HT, respectively. For RR P3HT, a very different molecular weight dependence of T_α is seen below $M_n = 14$ kg/mol, suggesting this is the typical molecular weight of intercrystal tie chains. In addition, coupled with the absolute molecular weight distribution, M_e of P3HT is extracted by fitting the linear viscoelastic data using tube reptation model. Furthermore, this linear viscoelasticity study is expanded to other conjugated polymers, such as poly-((9,9-dioctylfluorene)-2,7-diyl-alt-[4,7-bis(thiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl) (PFTBT), poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene] (PBTTC-C14), to locate T_c and identify the type of liquid crystalline phase, which is verified by polarized optical microscopy and X-ray scattering. Therefore, this fundamental polymer physics study provides a pathway towards being able to predict and design the molecular structure of conjugated polymers with desired mechanical and conductive properties as deformable semiconductors in the future.



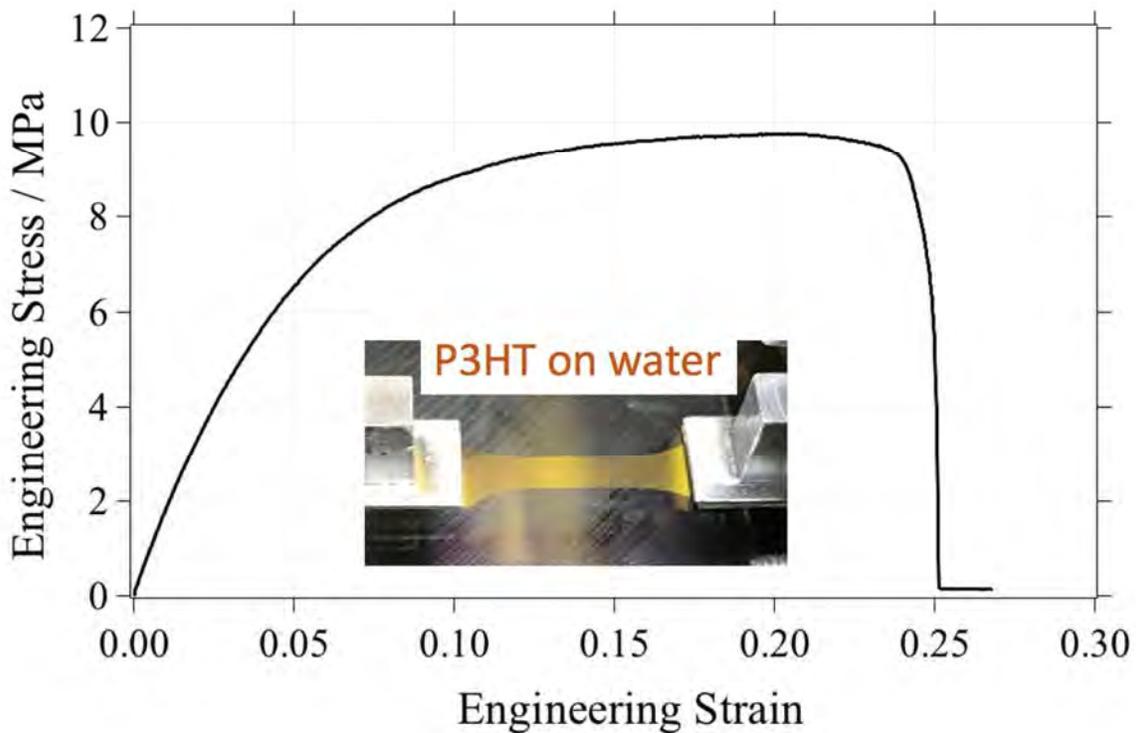
Connecting the mechanical and conductive properties of conjugated polymers with microstructural parameters obtained by fundamental polymer physics study

POLY 715: Directly measuring the complete stress–strain response of ultrathin organic electronic films

Xiaodan Gu, Xiaodan.gu@usm.edu, Song Zhang. Polymer Science and Engineering, Univ. of Southern Mississippi, Hattiesburg, Mississippi, United States

Printed wearable electronics routinely involve bending, twisting and stretching of the ultra-thin organic film during the roll-to-roll manufacture and under use. To date, the most widely adopted method to measure the mechanical property of thin film relies on a buckling metrology developed by Stafford et al. The Young's modulus is simply linked to the wrinkling phenomenon of the polymeric thin film on elastomer substrate under compression. In this talk, we will discuss an alternative route to use a pseudo-free standing tensile tester to directly measure the full stress-strain curve for an ultra-thin film (i.e., film thickness less than 50nm). At this length scale (i.e., < 50nm), the mechanical property of the thin polymeric film is known to deviate from its bulky due to the free polymer/air interface or polymer/substrate interaction. This study is aiming to provide a direct insight into the mechanical property for flexible electronics at the nanoscale.

Strain-strain curve for P3HT ultra thin film

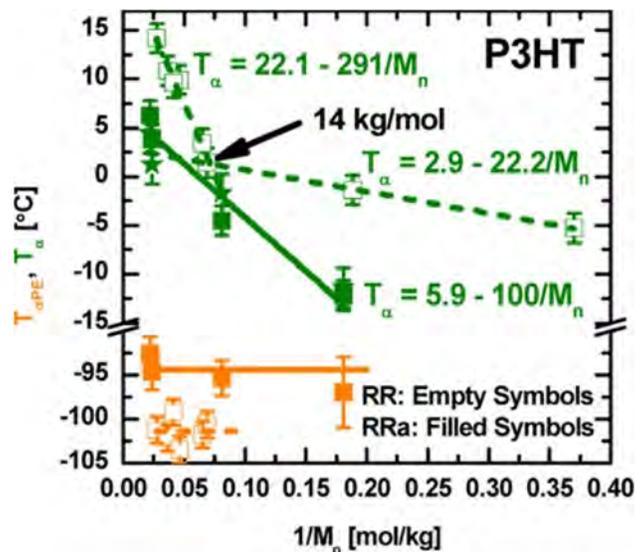


Tensile tester for P3HT thin film on water

POLY 716: Relationships between chain properties of the active layer and performance of polymeric electronic devices

Enrique Gomez, *edg12@psu.edu*. Penn State University, University Park, Pennsylvania, United States

Polymers may play an important role in various emerging optoelectronic applications because they can combine the chemical versatility of organic molecules and the flexibility, stretchability and toughness of polymers with dielectric or semiconducting properties. Nevertheless, in order to achieve the full potential of polymers for electronic applications, a clear description of how their structure, morphology, and macroscopic properties are interrelated is needed. We propose that the starting point for understanding conjugated polymers includes a description of chain conformations and phase behavior; unfortunately, further efforts to measure these crucial parameters are needed. Predictions and measurements of the persistence length of various conjugated polymers have significantly refined our intuition of the chain stiffness, and have led to predictions of the nematic coupling parameter and nematic-to-isotropic transitions. We show that the consequence of stiff backbones is a ubiquitous alignment layer near interfaces. Rheological measurements have led to refined estimates of the entanglement molecular weight and the glass transition temperature of both poly(3-alkylthiophenes) and push-pull copolymers, leading to new ways of thinking about how crystallites are interconnected within semicrystalline structures. Exploring mixing between conjugated polymers and small molecules or other polymers has demonstrated tremendous advancements in attaining the needed properties for various optoelectronic devices. Current efforts continue to refine our knowledge of chain conformations and phase behavior and the factors that influence these properties, thereby enabling the prediction of novel optoelectronic materials based on conjugated polymers.



Rheology measurements of conjugated polymers reveals the MW dependence of T_g for both regioregular and regiorandom materials. The break in slope is attributed to the onset of tie chains.

POLY 717: Hydrogen bonding in semiconducting polymers: Effect on self-assembly and mechanical properties

Thi Hai Van Nguyen, Michael U. Ocheje, Brynn P. Charron, **Simon Rondeau-Gagne**, *srondeau@uwindsor.ca*. Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, Canada

Organic electronics involves materials that are inherently easy to tailor, allowing for functionalities inconceivable before for conventional electronics. In particular, flexibility and robustness toward mechanical stress are now required for many applications such as wearable electronics and flexible/stretchable sensing devices. Despite the fact that solution-processed materials with excellent charge transport ($>10 \text{ cm}^2/\text{Vs}$) are now been achieved, these materials (and related devices) can suffer from mechanical stress which limit their use in modern technologies. Thus, new strategies to obtain semiconductors that can tolerate extreme environmental conditions are highly desirable.

This presentation will focus on the recent approaches used by our group to develop and design novel conjugated polymers with both high charge carrier mobility and improved mechanical properties. A recent strategy we utilized relies on the incorporation of hydrogen bonding side-chains in conjugated polymers. Not only the hydrogen bonds can drastically influence the charge transport properties of π -conjugated materials, but these supramolecular interactions can also act as sacrificial bonds upon strain, thus significantly affecting the mechanical properties. The complete characterization of our new conjugated polymers and their utilization in organic field-effect transistors (OFETs) will be discussed. Moreover, the influence of hydrogen bonding on molecular stretchability will also be highlighted.

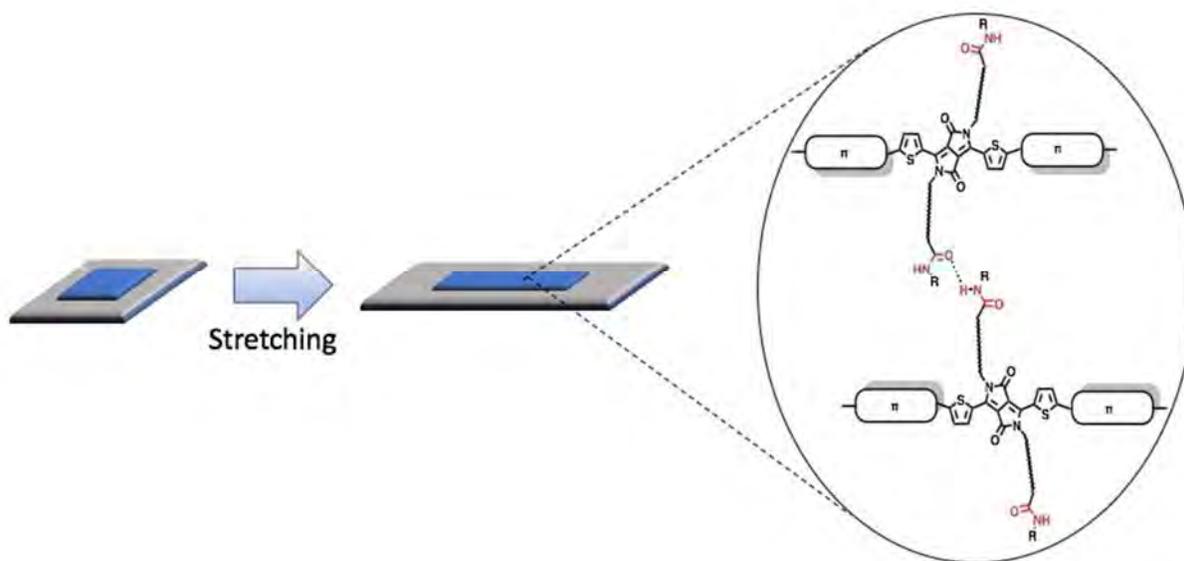
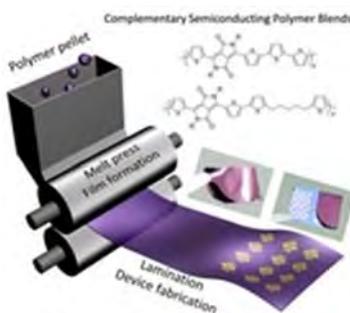


Figure 1. Stretchable conjugated polymers through hydrogen bonding side-chains

POLY 718: Melt-processable semiconducting polymer blends

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Organic semiconductors have gained enormous attention as an alternative or replacement for conventional inorganic semiconductors. Solution processing has been a promising and primary technology for organic semiconductor thin film formation for organic electronics. Presumably, it can potentially deliver low cost, fast roll-to-roll printing processing. As an alternative, melt processing involves a reversible liquefaction-solidification process. It is broadly used in industry to produce plastic thin films, but little progress has been achieved in organic semiconductor thin films. In this presentation, I will talk about our latest efforts on how to make semiconducting polymer melt processable, while how we can retain their excellent optical and electronics properties.

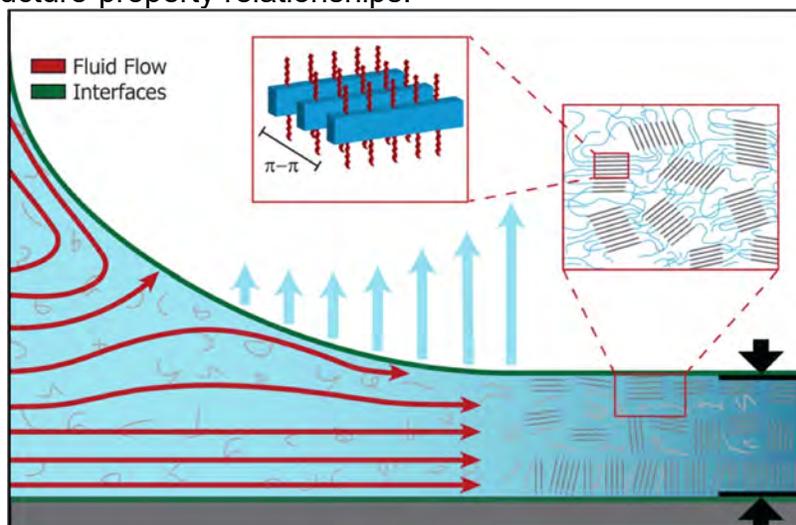


POLY 719: Printing semiconductor polymers to order: Critical roles of interfaces and fluid flow

Ying Diao, yingdiao@illinois.edu. Chemical and Biomolecular Engineering, University of Illinois at Urbana Champaign, Urbana, Illinois, United States

Organic electronic and optoelectronic materials that are light-weight, flexible and can be manufactured using energy-efficient and high-throughput methods. The solution printability at near ambient conditions enables deposition on flexible polymer substrates to create wearable, stretchable, imperceptible (opto)electronic devices for use in applications unimagined before. On the other hand, key challenges remain: how does molecular assembly proceed during solution printing and how to control the resulting thin film morphology? The significance of this challenge lies in the fact that charge transport in printed thin films is highly sensitive to their morphological parameters from molecular, mesoscopic to device scale. Addressing this challenge can open up new avenues for attaining high (opto)electronic performances, facilitating the much needed structure-property relationship studies in polymer-based electronic devices.

In this talk, we present several strategies we recently developed for controlling multi-scale assembly of conjugated polymers that are directly compatible with solution printing. In particular, we highlight the critical roles of multiphase interfaces and fluid-flow in directing the non-equilibrium assembly process. We developed a new concept of dynamic templating to expedite polymer nucleation and the ensuing assembly process, inspired by biomineralization templates capable of surface reconfiguration. Molecular dynamic simulations reveal that surface reconfigurability is key to promoting template-polymer interactions, thereby lowering polymer nucleation barrier. Using this method, we achieved high degree of global and local alignment over large area. In certain cases, we even observed small-molecule-like morphology for high molecular weight conjugated polymers, which has been rarely observed before. With high degree of control over thin film alignment, molecular packing and mesostructures, we further correlate these morphological characteristics with anisotropic charge transport properties towards establishing structure-property relationships.

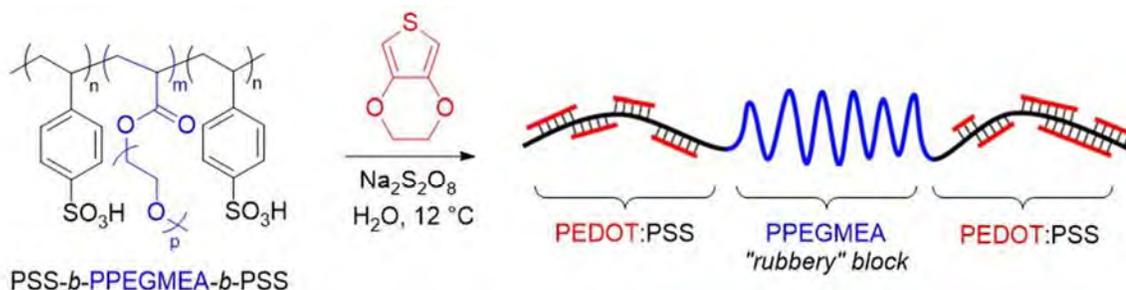


POLY 720: Synthesis of water-soluble ionic elastomers for stretchable organic electronics

Laure V. Kayser, *laure.kayser@mail.mcgill.ca*, Madeleine D. Russell, Alexander N. Stein, Darren J. Lipomi. NanoEngineering, University of California, San Diego, San Diego, California, United States

The recent development of highly flexible and stretchable organic electronics has prompted novel applications in wearable and bio-integrated electronics where skin-like properties (stretchable, soft, self-healing) are desirable for an intimate contact with the human body. But, organic semi-conducting and conducting polymers which are both electronically performant and mechanically compliant remain challenging to obtain. In particular, the polyelectrolyte complex poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), which has been extensively used as a conductive material in organic electronics, undergoes a brittle fracture at only 5 % strain. While the stretchability of PEDOT:PSS can be improved by using additives (Zonyl, Triton X, ionic liquids), concerns about the biocompatibility and toxicity of these additives have been raised. Another strategy to improve the stretchability of PEDOT:PSS is to blend it with an elastomer (PDMS, polyurethane), but the incorporation of the composites in electronic devices proved difficult due to the poor solubility of the elastomers. Alternatively, our approach is to use a water-soluble and intrinsically stretchable PSS-based triblock copolymer as a matrix for the in situ polymerization of 3,4-ethylenedioxythiophene (EDOT).

PSS-based ionic elastomers are typically synthesized via the sulfonation of polystyrene triblock copolymers using sulfuric acid. While effective, this approach requires harsh reaction conditions and doesn't achieve complete sulfonation, which ultimately leads to defects and poorly water-soluble polymers. Instead, we are using an aqueous reversible addition-fragmentation chain transfer (RAFT) polymerization of sodium 4-styrenesulfonate and poly(ethylene glycol) methyl ether acrylate (PEGMEA) for the one-pot synthesis of well-defined block copolymers of "hard" PSS and "rubbery" PPEGMEA. The resulting ionic elastomers can easily serve as a matrix for the in situ oxidative polymerization of EDOT. We are currently investigating the use of the obtained water-soluble conductive elastomers in wearable strain sensors, stretchable organic solar cells, LEDs and electrotactile devices.



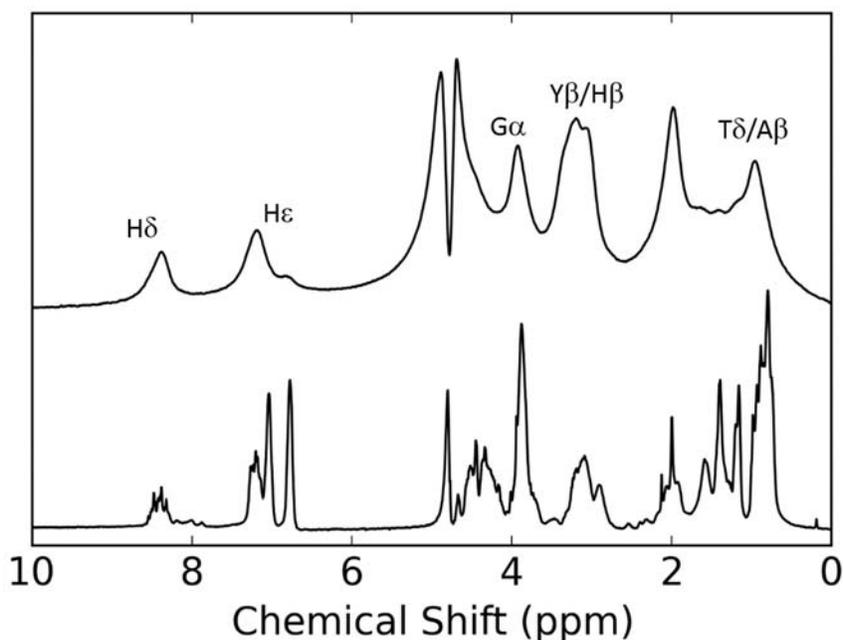
Synthesized by RAFT Polymerization

Water-Soluble Conductive Elastomer

POLY 721: Structure and dynamics of protein hydrogels

Peter A. Mirau, *peter.mirau@us.af.mil*, Maneesh Gupta, Patrick Dennis. AFRL, Wright Patter, Ohio, United States

Protein hydrogels are of interest as biocompatible scaffolds or interfaces in sensors. We have used NMR methods to determine the structure and dynamics of protein hydrogels prepared from recombinant proteins selected for their mechanical and transport properties. The properties of hydrogels strongly depend on the crosslinking method, the degree of crosslinking and amino acid composition. The proteins of interest, suckerin 12 and reflectin from squid and the worm jaw protein NVJP1, are disordered in solution but have a tendency to self-assemble through β -sheet formation. The hydrogels were crosslinked using both selective and non-selective enzymatic methods. The effect of crosslinking with horseradish peroxidase, for example, is visible in the NMR spectra by a change in line widths, relaxation times and the disappearance of selected peaks in the swollen hydrogels. These effects allow the identification of crosslinking sites in hydrogels crosslinked with enzymes or metals. The dynamics of protein hydrogels were measured from the relaxation times and the rate of water diffusion through the gels. Suckerin 12 is of particular interest as a self-assembling hydrogel because of it is constructed of repeating sequence domain structures that resemble block copolymers. The role of the domains in self-assembly is examined by comparing the proton NMR spectra for the hydrogels with the amino acid probabilities. The spectra show narrow lines from the histidine, threonine and alanine that are most prevalent in the M1 domain and demonstrates that crosslinking occurs predominantly through the M2 domain. The properties of protein hydrogels are related to both the sequence and amino acid probabilities.



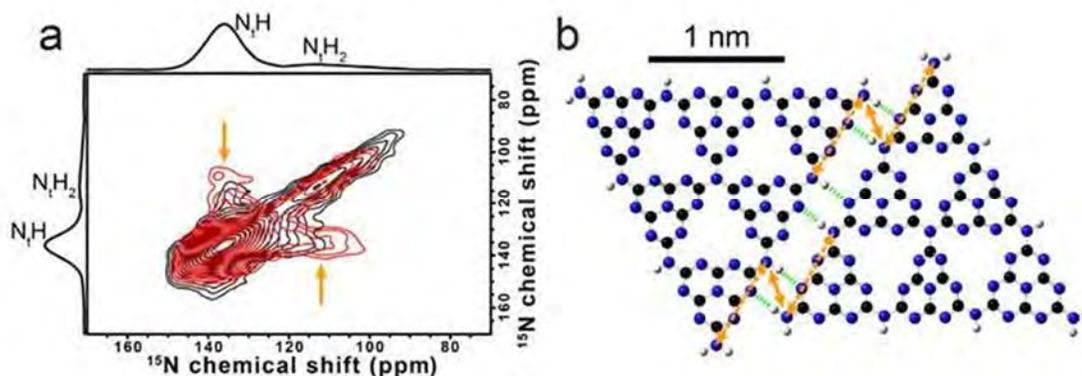
The NMR spectra of suckerin 12 without (bottom) and with (top) crosslinking

POLY 722: Solid-state NMR studies of graphene-based systems and nano-mole-scale protein solid-state NMR using ultra-fast MAS

Yoshitaka Ishii, ishii@bio.titech.ac.jp. School of Life Science and Technology, Tokyo Institute of Technology, Yokohama, Japan

This work involves two separate topics on solid-state NMR (SSNMR) applications to graphene-related nano-materials and protein nano-assemblies associated with Alzheimer's disease (AD). First, we present SSNMR structural studies on graphene- and graphite-based nano materials. It is demonstrated that SSNMR is a powerful tool to analyze the structures and chemical reactions for graphite oxide (1,2) and other graphene-based systems. We also discuss our recent work on SSNMR analysis of two-dimensional (2D) graphitic carbon nitride (g-C₃N₄). Our SSNMR analysis presented direct evidence of 2D assemblies of melem oligomers in g-C₃N₄ via inter-molecular hydrogen bonding for the first time.

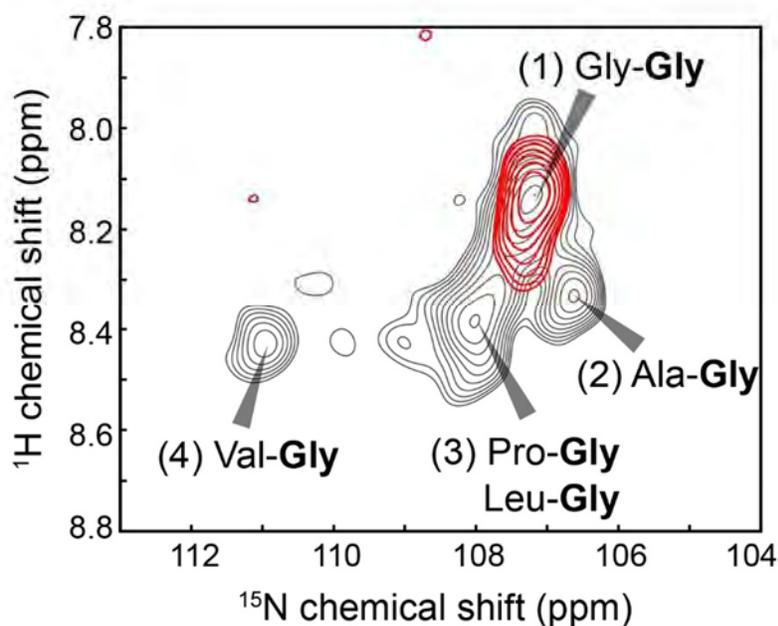
Second, we discuss resolution and sensitivity enhancement in ¹H and ¹³C biomolecular SSNMR under ultra fast magic angle spinning (UFMAS) conditions (≥ 80 kHz) in a high magnetic field (¹H frequency: 750-800 MHz). Major challenges in biomolecular SSNMR are limited sensitivity and resolution. As a general strategy for sensitivity and resolution-enhanced SSNMR, we discuss protein SSNMR using ¹H detection and paramagnetic condensed data collection (PACC) method (3,4) in a high field. Our data on protein microcrystal GB1 and amyloid-β (Aβ) fibril show that traditionally time-consuming 3-4D biomolecular SSNMR is feasible for signal assignments and structural elucidation of sub-mg of proteins with this approach. We also present an approach for extremely fast data collection of 2D SSNMR data (< 1 min) for a nano-mole scale protein sample (10–25 nmol) by using ¹H detected SSNMR in an ultra-fast MAS condition at 90–100 kHz and paramagnetic condensed data collection (PACC) method. The current sensitivity limit of multi-dimensional SSNMR is discussed with other subjects related to SSNMR experiments using UFMAS.



POLY 723: Targeting repeating subunits in elastin with strategic enrichment and solid-state NMR spectroscopy

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To-date, the complete structural characterization of a protein by solution or solid-state NMR spectroscopy has typically implemented a series of experiments to assign chemical shifts (and, hence, secondary structure) to each amino acid in the sequence. Although feasible for a growing number of proteins and peptides, such is not the case for elastin. Elastin is assembled from its soluble precursor, tropoelastin, which is a high-molecular weight protein with numerous repeating sequences. Indeed, the polymeric character of both tropoelastin and elastin required a different approach, which is described in this talk. Our strategy combines enrichment of the key amino acid types in elastin with NMR experiments that target specific pairs of amino acids. Specifically, the crosslinking and hydrophobic domains are distinguished by the abundant Ala-neighboring-Ala and Gly-neighboring-Gly, respectively. With multiple populations of Gly and Pro, selection via ^{13}C - ^{15}N and ^{13}C - ^{13}C dipolar and/or J couplings was employed to unambiguously identify the targeted 2-aa sequences. These results and their implications for the understanding of elastin's elasticity will be discussed.

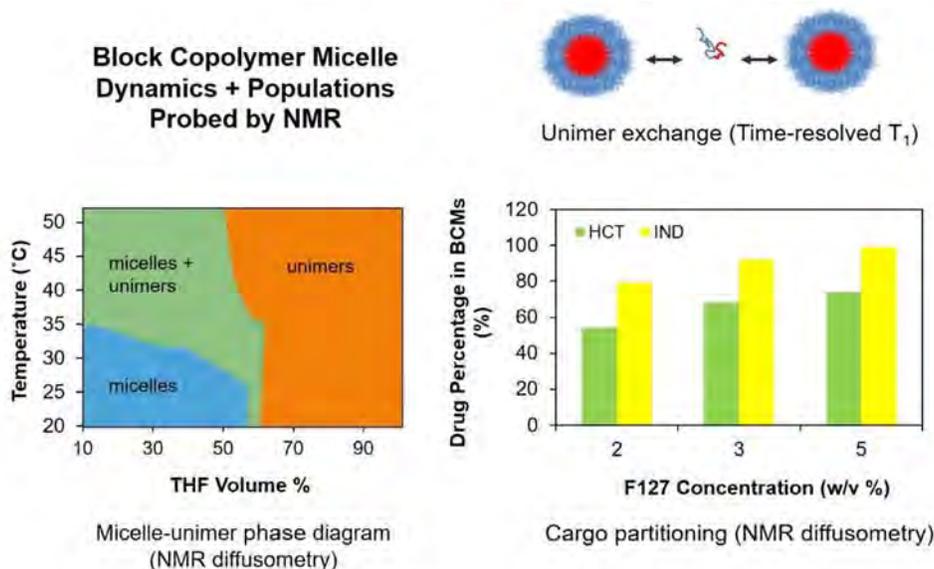


2D ^1H - ^{15}N rINEPT-HETCOR (grey contours) and $\{^{13}\text{CO}\}$ - ^{15}N - ^1H HETCOR (red) spectra of hydrated $[\text{U-}^{13}\text{C}, ^{15}\text{N}\text{-Gly}]$ elastin

POLY 724: Understanding block-copolymer micelle dynamics and molecular partitioning for tunable cargo encapsulation and delivery

Xiuli Li¹, lix@vt.edu, **Bryce E. Kidd**¹, **Tyler J. Cooksey**², **Megan L. Robertson**², **Louis A. Madsen**¹. (1) Department of Chemistry and Macromolecules Innovation Institute, Virginia Tech, Blacksburg, Virginia, United States (2) Department of Chemical and Biomolecular Engineering, University of Houston, Houston, Texas, United States

Block-copolymer micelles (BCMs) can carry molecular cargo in a nanoscopic package that is tunable using polymer structure in combination with cargo properties. For example, BCMs are used in targeted anticancer drug delivery due to their biocompatibility, in vivo degradability and prolonged circulation time. We are using NMR spectroscopy and diffusometry combined with SANS to investigate diblock poly (ethylene oxide)-b-(caprolactone) (PEO-PCL) and commercial triblock (PEO-PPO-PPO) micelle systems. We quantify the populations and diffusion coefficients of coexisting micelles and free unimers over a range of temperatures and solvent compositions by NMR diffusometry (figure – lower left). We present evidence for dominance of the insertion-expulsion mechanism of unimer exchange in these systems, and map micelle-unimer phase diagrams versus temperature and solvent composition. We have also developed a novel time-resolved NMR spin-lattice relaxation (T_1) measurement (figure – upper right) by mixing protonated and ^2H -labeled micelle solutions to determine unimer exchange rates using common NMR spectrometers. Finally, we can quantify cargo (e.g., drug) partitioning in BCMs (figure – lower right), and we observe that more hydrophobic cargos have a higher partition coefficient. In summary, our NMR studies shed light on how intermolecular interactions fundamentally affect cargo partitioning and release, unimer exchange and the tuning of micelle structure and dynamics.



POLY 725: NMR of silk

Tetsuo Asakura, **Akio Nishimura**, fy3461@go.tuat.ac.jp. Dept of Biotechnology, Tokyo University of Agriculture and Technology, Tokyo, Japan

Our group has been studying the structure and the dynamics of several kinds of silks for a long time. At present, silks continue to attract the attention of researchers in biology, biochemistry, biophysics, analytical chemistry, polymer technology, textile technology and biomaterials because of their excellent mechanical properties such as high strength, high toughness, and biocompatibility.

In this paper, we will present our recent research on a wild silkworm (*Samia cynthia ricini*) silk fibroin and spider dragline silk (including recombinant spider silk) using NMR spectroscopy. Common primary structure with the two types of silk is the tandemly repeated sequences made of polyalanine and glycine-rich regions. The difference in the crystalline polyalanine region is the length of polyalanine $(Ala)_n$, where $n \sim 6$ for spider dragline silk and about $n \sim 12$ for *S.c.ricini* silk. We could clarify for the first time significant differences in the packing arrangements of polyalanine regions from detailed solid-state NMR analyses and molecular dynamics calculations. Thus, the packing arrangement is mainly rectangular together with staggered for spider dragline silk, but exclusively staggered for *S.c.ricini* silk (Figure).

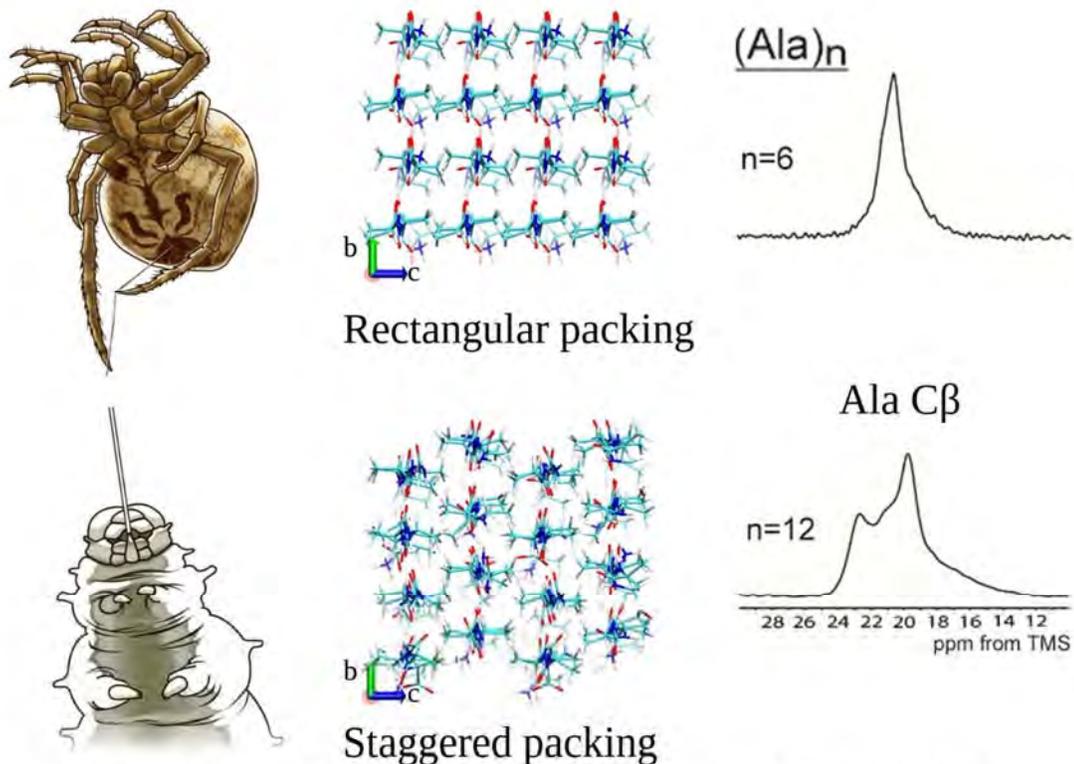


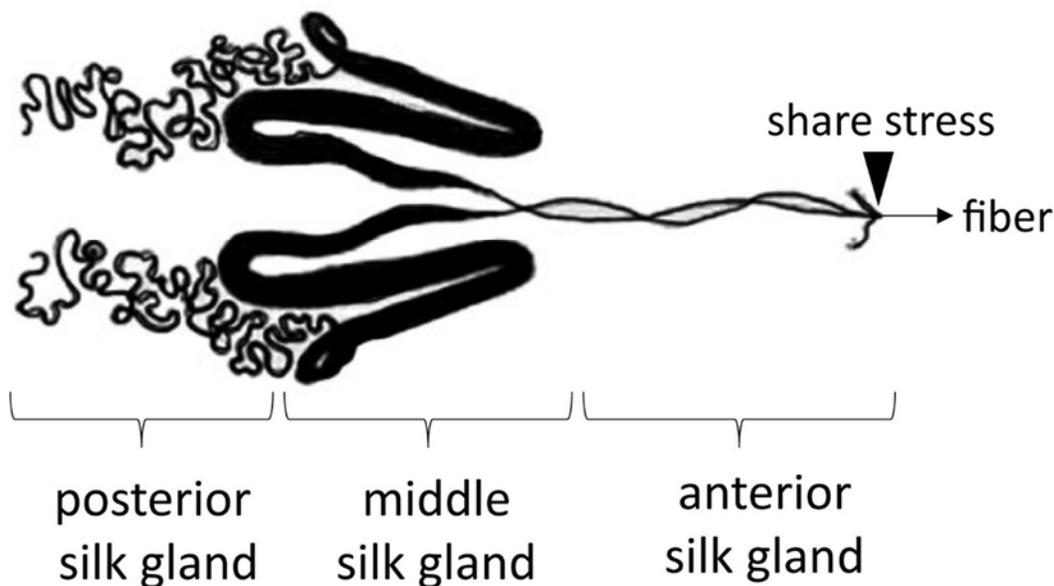
Figure: Spinings of silk fibers (left) and two different packing arrangements of polyalanine regions in the silks (center) of spider (upper) and *S.c. ricini* silkworm (lower), respectively. The Ala C β CP/MAS NMR peaks (right) of $(Ala)_6$ and $(Ala)_{12}$, which are the typical models of polyalanine regions in spider and *S.c. ricini* silks, respectively.

POLY 726: Conformation and dynamic properties of silk fibroin in a silk gland

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Silk fibroin from the *Bombyx mori* silkworm is an attractive material owing to its excellent mechanical properties, including high strength and high toughness. In addition, because of its excellent biocompatibility, it has been used as a biomaterial. *B. mori* silkworms produce silk fibroin fibers from an aqueous silk fibroin solution by applying shear stress within the spinneret under ambient temperature. This process can be used for developing sustainable fiber-processing technology. However, to completely elucidate the fibroin processing mechanism, the structures of fibroin before and after spinning need to be determined. The fibroin molecule, which comprises a heavy chain of 390 kDa and a light chain of 26 kDa connected by a disulfide bond, is secreted into the posterior silk gland of a silkworm as an aqueous solution. Then, the silk fibroin stored in the middle silk gland is spun out through the anterior silk gland and converted into silk fibers. Silk fibroin with very high molecular weight and a high concentration of about 30% in aqueous solution should have the appropriate conformation and/or orientation to form antiparallel β -sheet rich fibers. The pH gradient is reported to probably regulate the assembly of silk fibroins in the aqueous solution and the formation of fibers. To evaluate the transition of silk fibroin in the silk gland, the conformation and dynamic properties of silk fibroin extracted from each part of the silk gland are studied using NMR.

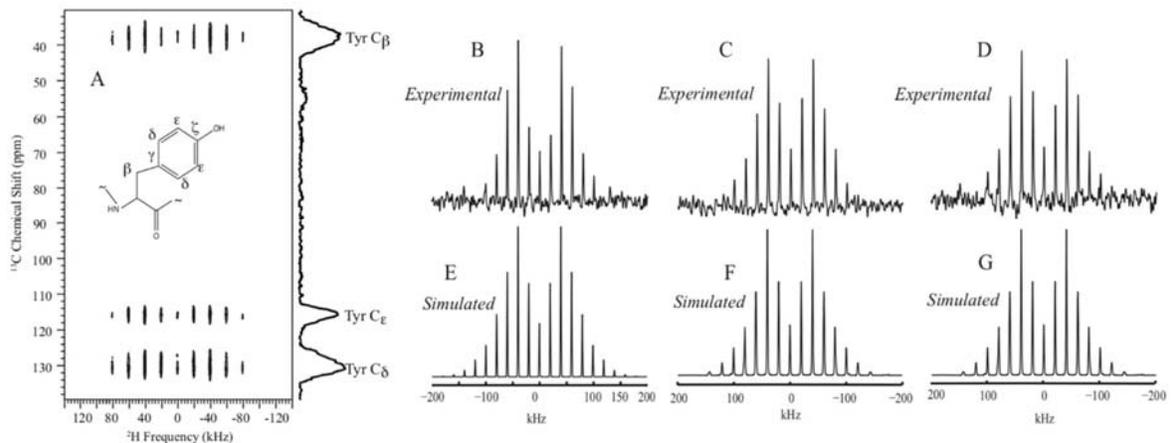
Image of the *B. mori* silk gland



POLY 727: Using magnetic resonance techniques to probe the structure and dynamics in synthetic & natural spider silks

Jeffery L. Yarger, jyarger@gmail.com, Xiangyan Shi, Chengchen Guo, Aleksandar Lazaric, Brian Cherry. Magnetic Resonance Research Center, Arizona State University, Tempe, Arizona, United States

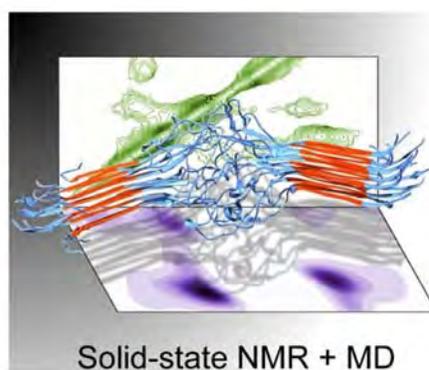
Understanding the molecular structure and the hierarchical organizations in spider silk proteins is critical to the goal of producing a protein-based synthetic material with properties similar to that of natural spider silk fibers. Our research group is exploring the molecular structure, protein-protein interactions, and hierarchical structures formed in major ampullate silk proteins (dragline and web-building). Advanced solid-state NMR allows for complete assignment of spider silk spectra and elucidate all secondary structure elements in spider silk fibers that have been isotopically ($^{13}\text{C}/^{15}\text{N}$) enriched. Furthermore, recently developed $^2\text{H}/^{13}\text{C}$ 2D NMR techniques to interrogate the molecular dynamics of spider silk proteins will be presented (representative $^2\text{H}/^{13}\text{C}$ 2D NMR data is shown in the figure below). All together, these studies produce an unprecedented level of detail into the molecular and hierarchical structures of natural spider silk fibers.



POLY 728: Using NMR to probe the structure, dynamics and assembly of spider silk fibers

*David Onofrei, Dillan Stengel, Giavana Valdez, Alex Villalba, Bennett Addison, **Gregory P. Holland**, gholland@mail.sdsu.edu. Department of Chemistry and Biochemistry, San Diego State University, San Diego, California, United States*

Over 400 million years spiders have evolved to produce six different silks. Spider silks are comprised almost entirely of protein and are used for a diverse range of applications such as web construction, egg case production and wrapping prey. The silks vary dramatically in their mechanical and physical properties with the major ampullate silk (dragline) exhibiting a strength that exceeds steel by weight and a toughness greater than Kevlar while, the flagelliform silk has extensibility comparable to rubber. Our lab is focused on understanding the molecular structure and dynamics of the proteins that comprise the various spider silk fibers. It is the folded structures and hierarchical organization of these proteins that imparts spider silks their impressive yet, diverse mechanical and physical properties. Our research team has been developing and applying a suite of solution, diffusion and solid-state NMR techniques to probe secondary structure (see Figure 1), hydrogen-bonding, side chain dynamics, and oligomeric protein assembly all of which are crucial to understanding spider silk formation and the resulting fiber properties. Recently, we have focused on understanding the protein-rich fluid within the various silk producing glands to determine the conformational structure and dynamics prior to fiber formation and elucidate the important biochemical triggers responsible for converting the gel-like liquid to fibers with unparalleled properties. Insights into the state of the protein in the gland are being gained from a combination of diffusion NMR and cryo-electron microscopy (EM) that is providing evidence for supramolecular silk protein organization prior to fiber spinning. It is our belief that a better fundamental understanding of the spider silk protein molecular structure and assembly process will accelerate the ability to mimic and reproduce similar biologically inspired fibers in the laboratory.



POLY 729: Elastomer organogels: Generating motion through crystallization of the swelling solvent

Kevin A. Cavicchi, *kac58@uakron.edu. University of Akron, Akron, Ohio, United States*

This talk will work on the fabrication of shape morphing materials (e.g. shape memory polymers and bilayer actuators) by the blending of an elastomer and crystalline small molecule, such as a fatty acid or wax. The main advantage of this approach is the facile ability to convert commodity polymers into responsive materials. It will be shown that shape memory can be generated by swelling elastomers and foams in fatty acids. The fatty acids are able to form structure spanning load-bearing networks that resist the elastic restoring force of the deformed elastomer. Upon heating and melting of the fatty acid, excellent elastic recovery of a deformed shape is observed. In a second example, the fabrication of bilayer actuators composed of a passive polymer and a wax filled active elastomer layer will be shown. Here the wax is used an internal dilating agent whose volume can be reversibly cycled through the heating and cooling of the bilayer resulting in large bending motion.

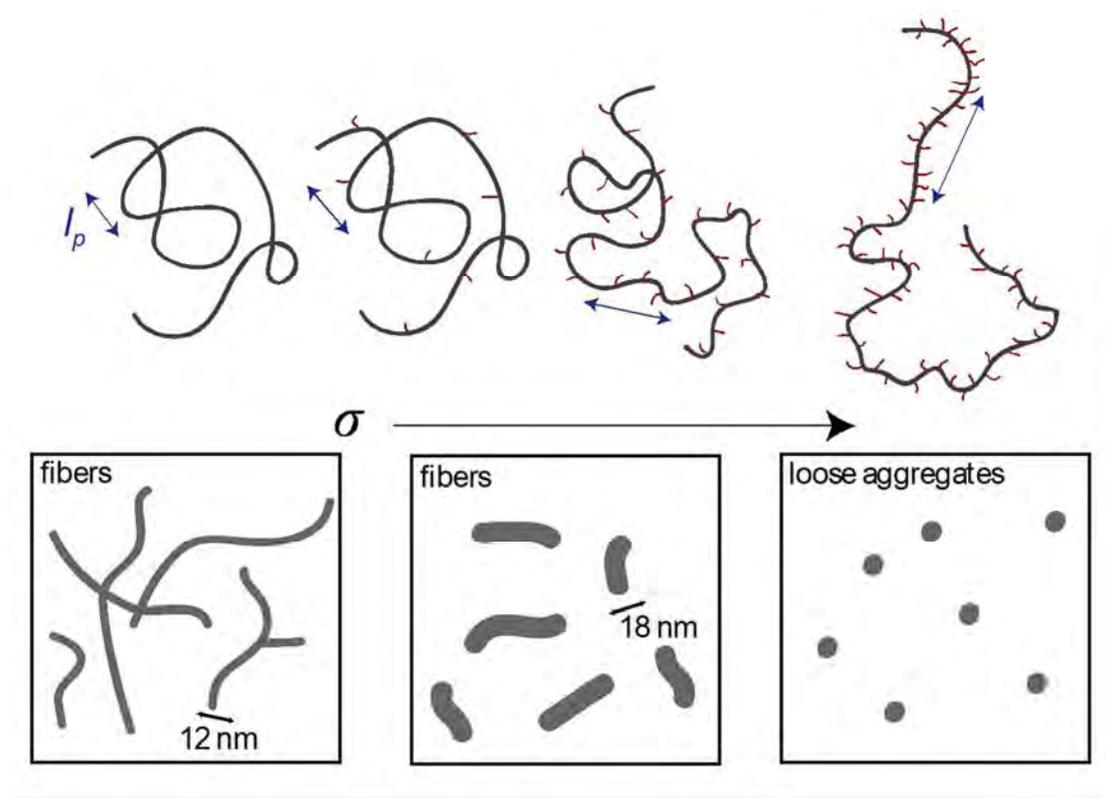


Stearic acid swollen shape memory polyurethane foam

POLY 730: Effects of poly(ethylene glycol) grafting density on the thermoreversible formation of a fibrous methylcellulose network

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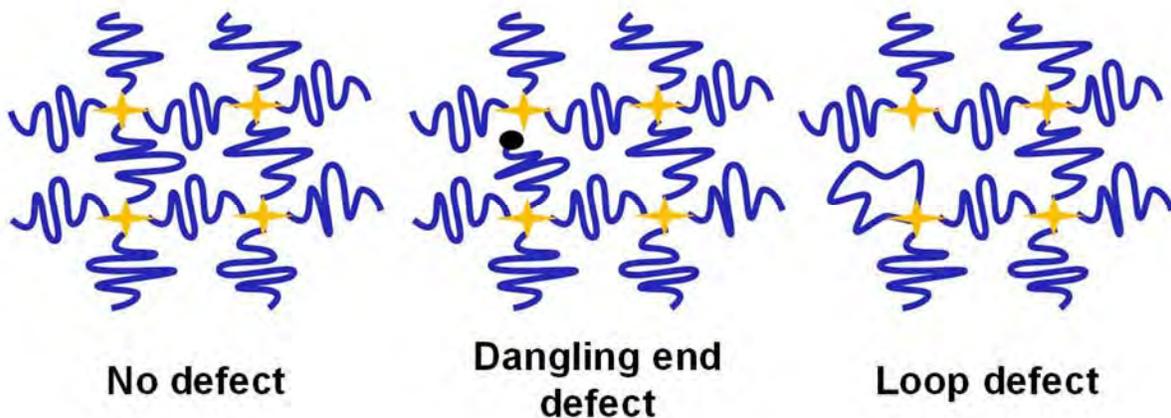
Methylcellulose (MC) is used in an impressively wide variety of commercial products due to its ability to reversibly form highly elastic fibrous networks upon heating. To investigate the effects of chain stiffness on the fiber and network structures, we have grafted short poly(ethylene glycol) (PEG, $M \sim 800$ g/mol) chains onto the backbone of MC at grafting densities ranging from 0.7 to 33% (grafts per anhydroglucose unit). Static and dynamic light scattering reveals that the overall radius of the chain increases systematically with graft density, in a manner in excellent agreement with theory. As the contour length remains unchanged, it is apparent that grafting leads to an increase in the persistence length of this semiflexible copolymer, by as much as a factor of four. Upon heating, at grafting densities below 10%, MC still forms fibrous networks. The diameter of the fibers increases as a function of grafting density from 12 to 18 nm, but the fibers are shorter and lead to weaker gels. Above 10% grafting, AFM and SAXS show that the anisotropy is broken, and that the elastic modulus of these gels is much lower than the modulus of ungrafted MC at 80°C. Instead of fibers, MC-g-PEG forms loose aggregated structures. We discuss the results in terms of MC chain flexibility and its effect on fiber formation.



POLY 731: Networks from telechelic macromonomers with tailored defects

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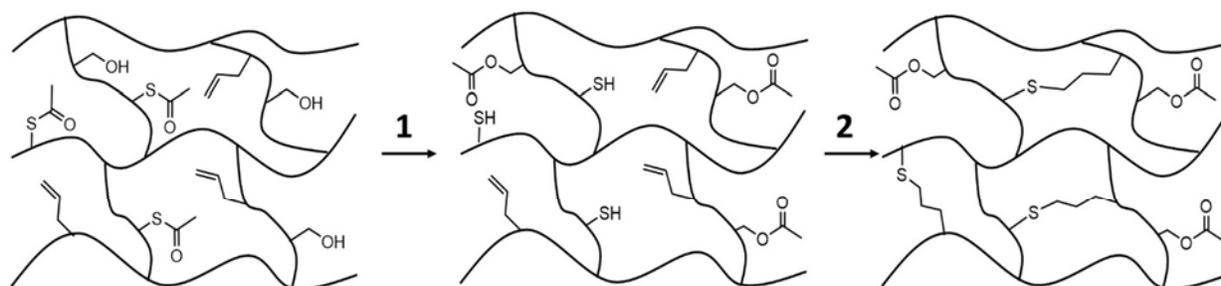
Every polymer network contains defects, most commonly dangling ends and loops, in the network structure that affect its performance. Some techniques such as synthesizing networks from telechelic macromonomers have been used to reduce defects compared to typical free radical crosslinking reactions; end-linking prevents heterogeneous crosslinking which can trap reactive sites and produce many defects. The same end-linking technique can also be used to intentionally introduce defects into the network through methods such as the addition of monofunctional macromonomers during network formation to produce dangling end defects or the reduction in concentration during network formation to produce loop defects. Series of networks with increasing amounts of defects were synthesized by the photo-initiated crosslinking of norbornene-functional macromonomers with small molecule thiols. The few previous studies that systematically introduced defects focused mainly on the effect of loops on network performance, so this study focused more on the equally common network defect of dangling ends. The synthesized networks were characterized to determine the gel fraction, swelling, and mechanical properties under tension and compression. Analysis of the data quantified the reproducible effect the defects had on the networks' properties and assists in refining existing network elasticity theories.



POLY 732: Metamorphosis within polymer networks: Stress relaxation, network shape control and second-stage functionalization reactions

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The objective of this work was to evaluate the efficiency of the thioester-hydroxyl exchange reactions within a variety of acrylate and methacrylate polymer networks. Upon the acyl transfer from the thioester to hydroxyl, thiol groups are freed and rendered accessible for further functionalizations/reactions. Depending on the exchange temperature, choice of the catalyst as well as the initial thioester content, stress relaxation, bulk shape control and subsequent functionalization reactions within the networks were demonstrated. As exchange catalysts different nucleophiles and bases were used. It was found that 1,1,3,3-tetramethylguanidine (TMG) facilitates the OH-thioester exchange at ambient conditions. On the other hand, 4-dimethylaminopyridine (DMAP) was shown to be the most efficient catalyst for exchange at elevated temperatures. Over 60 % stress reduction was observed in one hour at the temperature above T_g in materials containing DMAP. Because of self-limiting character of this dynamic exchange process, desired and quick post-polymerization transformations are possible leading to materials with unprecedented properties and broad applications.



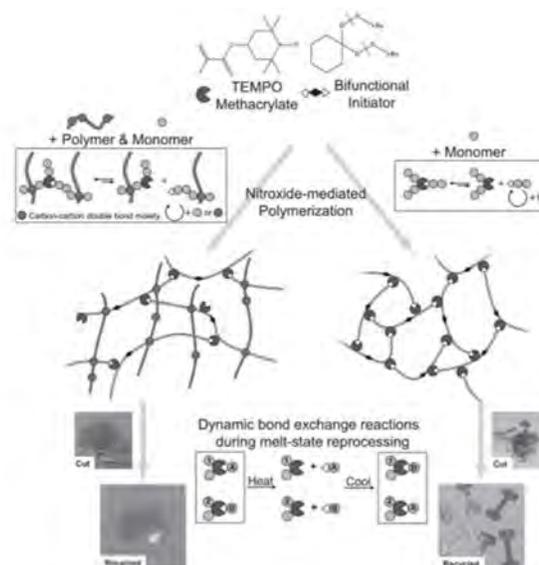
1: metamorphosis: acyl transfer to hydroxyl group 2: second stage thiol-ene crosslinking

Schematic of thioester-OH exchange and subsequent thiol-ene reaction

POLY 733: Polymer networks with reversible and/or exchangeable cross-links: Complete property recovery associated with cross-link density leading to fully reprocessable, recyclable networks and an approach to suppress creep in vitrimers

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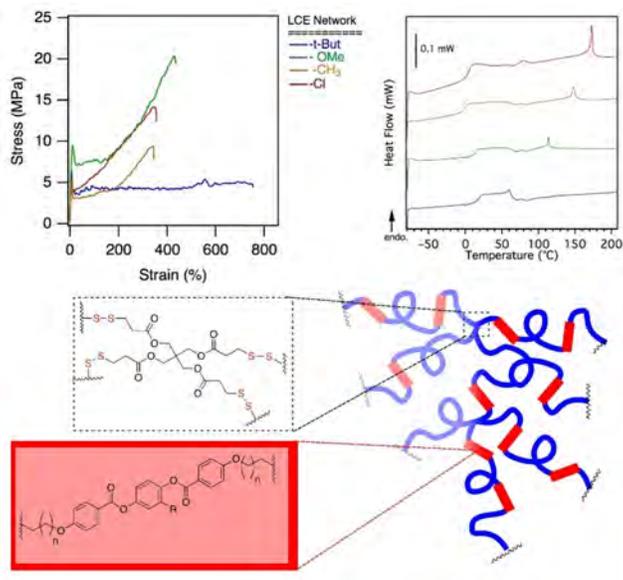
Thermosets are cross-linked networks that cannot be recycled by melt processing because the percolated network prevents the polymer from undergoing flow in the melt state. Significant, recent research has focused on making networks melt-reprocessable or malleable via cross-links that are reversible as a function of temperature or that can undergo exchange reactions (e.g., trans-esterification). While progress has been made, relatively little success has been reported after reprocessing in achieving full property recovery associated with cross-link density. Here, we describe results of two studies in which we achieved full property recovery associated with cross-link density. The first exploits nitroxide-mediated polymerization to achieve cross-linked polybutadiene and polyisoprene (with and without substantial carbon black filler) as models for rubber tires. The rubbery state modulus reflects cross-link density, and the modulus was reproduced within error for multiple recycling steps. (See Jin et al., Adv. Mater. 2016, 28, 6746.) The second demonstrates that, under appropriate catalyzed reprocessing conditions promoting reversible and exchange reactions, polyhydroxyurethane (PHU) networks can achieve full property recovery associated with cross-link density after multiple reprocessing steps. Such PHUs are potential substitutes for polyurethane networks that cannot achieve effective property recovery. We also describe work aimed at suppressing creep in networks that are reprocessable due solely to exchange reactions, a class of materials coined as "vitrimers". Because of the presence of exchange at temperatures exceeding the vitrification temperature, vitrimers can undergo creep when subjected to load. We have developed a novel approach to reduce creep in vitrimers and have quantified conditions under which our approach can be used.



POLY 734: Dynamic stimuli-responsive liquid crystal elastomers as actuating adhesives

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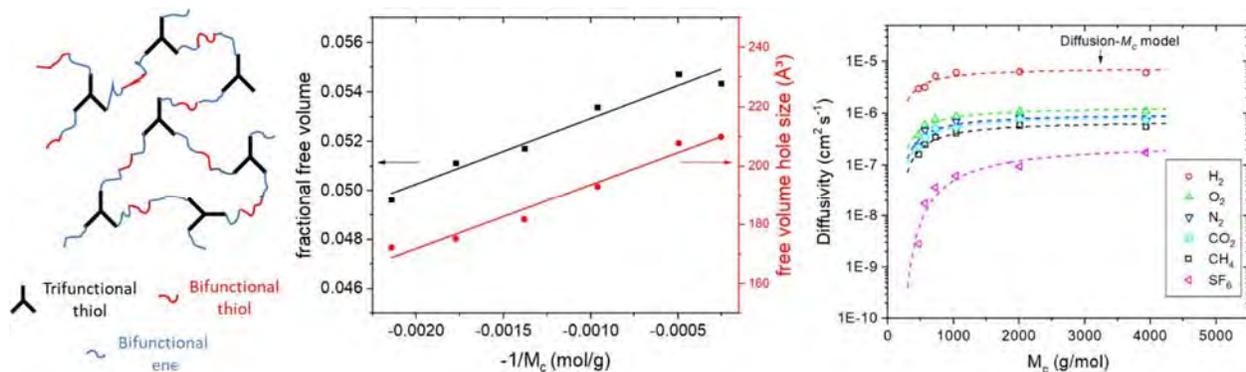
An enduring challenge in polymer science is to create materials endowed with the inherent ability to react to a multitude of stimuli, with each eliciting a unique macroscopic physical response. However, the design of these *smart materials* requires judicious selection of which combination of chemical functionalities to embed within the material. We have created a family of liquid crystalline elastomer networks (LCNs) that can respond reversibly to a number of different stimuli (UV and visible light, metal ions, and heat). These materials are synthesized using a facile two-step process where thiol telechelic prepolymers are first prepared in a step-growth polymerization and subsequently oxidized in the presence of a tetrathiol crosslinker. The presence of disulfide bonds (dynamic at $T > 150\text{ }^{\circ}\text{C}$ or upon exposure to UV light) at the junctions of the network makes these materials adhesives that are both self-healing and reprocessable. Additionally, the incorporation of one or more liquid crystal mesogens in the backbone of the prepolymer causes network to adopt an ordered liquid crystalline phase, with a melting temperature and liquid crystal to isotropic transition temperature dependent on the structure of the prepolymer used. Conveniently, changes to the mesogen or combination of mesogens in the prepolymer can be used to tune the thermal, mechanical, and rheological properties of the LCN. Knowledge of these structure-property relationships can be used to design advanced materials tailor-made for specific applications. As a specific example, I will describe a shape-memory elastomer that can be used as a reversible actuating adhesive with heat as the only external trigger.



POLY 735: Free volume and gas transport studied in model elastomeric thiol-ene networks: Effect of crosslink density

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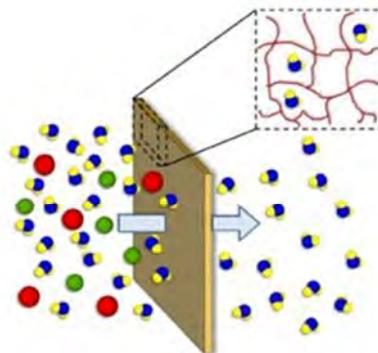
The effect of crosslinking on free volume in rubbery networks can be complex. According to the classical Fox and Loshaek theoretical approach, the fractional free volume in networks ought to change linearly with the concentration of crosslinks or inversely with the molecular weight (M_c) between the crosslinks. However in reality, changing the crosslink concentration often results in simultaneous altering of the polymer polarity which itself affects the free volume of a polymer. It seems that in this work we uniquely managed to overcome this obstacle and by using the advantages of thiol-ene click chemistry designed and synthesized a family of model networks with largely different concentration of crosslinks but very similar polarity. The model polyethylene glycol (PEG) based thiol-ene networks, in which the concentration of crosslinks varied by one order of magnitude, was prepared by gradually decreasing the ratio of PEG containing trifunctional to bifunctional (telechelic) thiol monomers in the presence of unchanged molar amount of PEG containing telechelic ene monomer while maintaining 1:1 thiol:ene stoichiometry. Dielectric spectroscopy studies revealed very similar dielectric permittivity values for the networks at high frequencies which experimentally confirmed that their polarities were indeed very similar. High pressure dilatometry studies were performed to study the effect of temperature and pressure on specific volume of the networks (PVT analysis). Simha-Somcynsky equation of state (EOS) was used to fit the PVT data in order to extract the fractional free volume. Fractional free volume (FFV) of the networks changed linearly with the concentration of crosslinks or with $1/M_c$, thus experimentally confirming the Fox and Loshaek model assumption. In addition to FFV assessment, average volume of the molecular holes (v_h) in the network polymers was probed by positron annihilation lifetime spectroscopy and v_h exhibited a similar linear trend with the concentration of crosslinks or $1/M_c$. Gas diffusion was also studied in the network films and showed a vivid dependence with M_c . A free model based model was developed and explained well this behavior.



POLY 736: The coupling of polymer dynamics and water transport in cross-linked polymer membranes

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Polymer transport membranes that facilitate or inhibit ion transport are critical for fuel cells, flow batteries, ion exchange columns, electrochemical sensors, getter materials for encapsulation, gas separations, and clean water. A common thread that spans nearly all of these applications is that their function is coupled to the transport of water or some other small molecule penetrant through the membrane. There is a significant need to understand the nature by which small molecule penetrants move through the membrane. In this presentation, I will focus on the general case of water diffusion through three types of membrane materials with very different network structures: tightly cross-linked epoxy resins that are used in structural composites and exhibit very little swelling, loosely cross-linked polyamide membranes that are used as the active layer in a reverse osmosis desalination membranes and exhibit moderate swelling upon hydration, and ion containing block copolymer alkaline fuel cell membranes that contain transient ionic cross-links and swell significantly with water. A combination of three techniques will be used to characterize the swollen structure and dynamics of the membrane materials relative to their transport behavior. Positron annihilation lifetime spectroscopy will be used to quantify the intrinsic “free volume” or intermolecular packing efficiency in the material, small angle neutron scattering will be used to quantify the microstructure of the water-rich domains in the hydrated materials, and quasielastic neutron scattering will be used to quantify both the fast polymer dynamics of material and the dynamics of the water molecules diffusing through the membranes. The insights from these measurements will be used to discuss the different mechanisms that are used to describe water transport in these materials ranging from solution-diffusion to pore-flow transport.

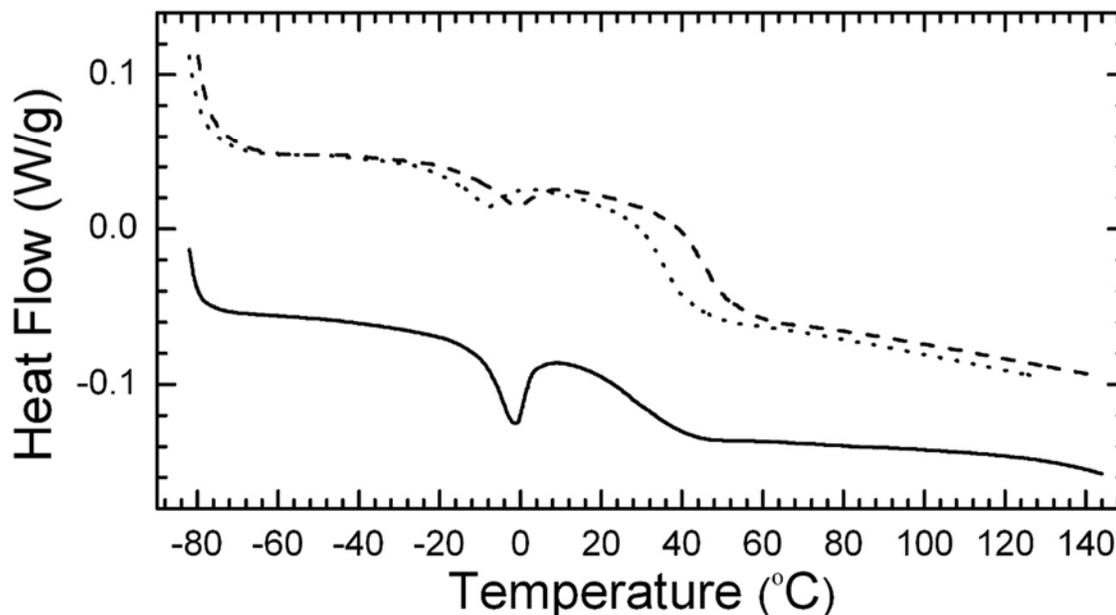


Water permeating through a cross-linked membrane

POLY 737: Stimuli-responsively porating gels: Melting below glass transition

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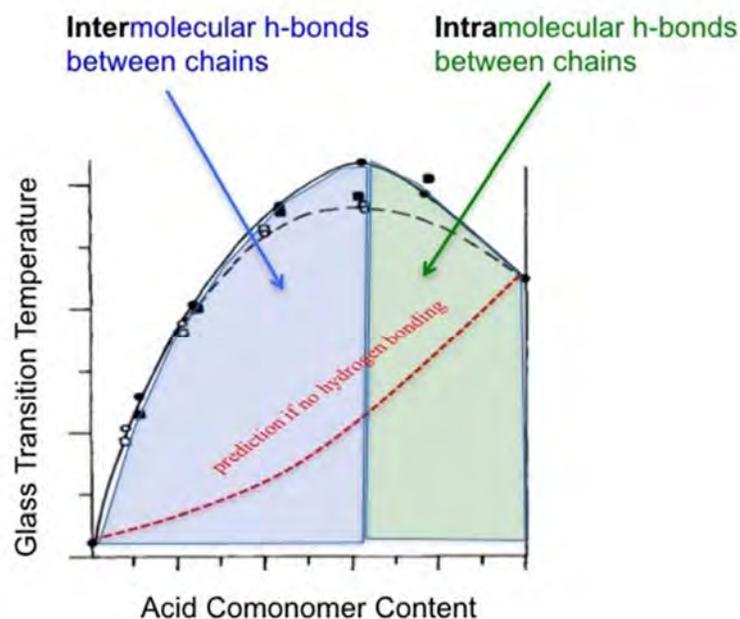
A stimuli-responsive resin incorporating a reactive ionic-liquid (IL) monomer, 1-methyl-3-[11-hydroxyundecyl]imidazolium bromide (HOC₁₁C₁ImBr), has been prepared by condensation addition polymerization to show that stimuli-responsive polymerized ionic liquids (PIL) are not confined to preparation by free radical chain polymerization. This particular resin was prepared from glycerol and hexamethylene diisocyanate with one third equivalent corresponding to the IL, and a control resin was prepared without IL. Both materials exhibit the interesting property of melting and solidifying below their respective T_g 's. The PIL exhibits reversible poration in response to hexafluorophosphate and in response to DMSO/water solvent exchange. The incorporation of the IL imparts an expected plasticizing effect, with a T_g at about 28°C, while in the control we have a T_g at about 37°C to 49°C, depending on the density of the phase measured.



POLY 738: Mechanistic insights into topological network impact on glass transition temperature

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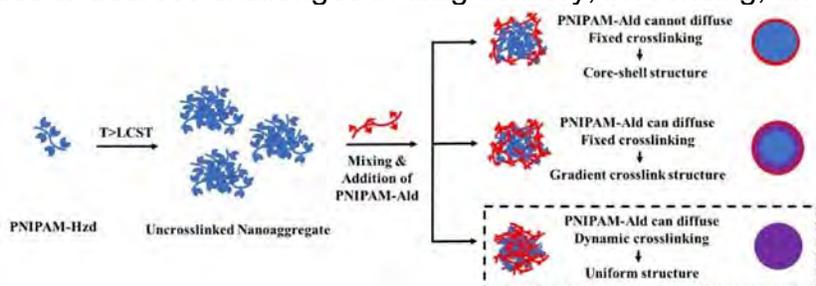
Correlation between a specific crosslinker and impact on glass transition temperature (T_g) is difficult to determine as the topological network formed can differ widely with respect to reaction conditions. Here, we present our experimental and analytical approaches to the pursuit of isolating the individual contribution of a particular crosslinking comonomer to T_g through linear copolymerization (via protection of a pendent vinyl group), intramolecular network formation (via single-chain nanoparticle formation) by a temperature induced stimulus, and intermolecular network formation (via a concentrated reaction environment, post-deprotection) by the same temperature trigger to crosslinking. Moreover, covalent crosslinking (via divinyl comonomers) will be contrasted with pseudo-crosslinking by hydrogen bonding functional groups (via carboxylic acid based comonomers) again in attempt to unravel these complex contributions to the polymer glass transition temperature. In this second scenario, the measurement of T_g is especially challenging as the acid groups are complicated to fully dry and suffer (at least partial) conversion to anhydrides at temperatures relevant to their glass transition. Moreover, those same temperatures can break the intermolecular hydrogen bonds that define the network itself. This talk aims to highlight the care necessary to properly characterize networks based on hydrogen bonding and to showcase insights into topological network architecture from meticulous measurement of the glass transition temperature.



POLY 739: Degradable homogeneous microgels via self-assembly of reactive poly(N-isopropylacrylamide) oligomers

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Conventional poly(N-isopropylacrylamide) (PNIPAM) microgels prepared via precipitation polymerization have been used in many applications due to their ability to dynamically change their diameter, hydrophobicity, pore size, and surface charge as a function of temperature. However, in the context of practical biomedical use *in vivo*, the lack of degradability of conventional PNIPAM microgels creates challenges in that conventional microgels cannot be cleared effectively from the body. In response, we have developed a self-assembly method in which well-defined hydrazide and aldehyde functionalized PNIPAM oligomers are used to form microgels linked by hydrolytically degradable hydrazone crosslinks. Hydrazide-functionalized oligomers are pre-heated above their lower critical solution temperature, after which the aldehyde-functionalized oligomer is added to induce crosslinking. Microgels can be fabricated within minutes on the size range of ~180-300 nm and with high monodispersity and degradability (particularly in acidic conditions) while maintaining the same reversible temperature-responsive swelling properties of conventional PNIPAM microgels. Interestingly, while conventional microgels have a dense core/diffuse shell structure due to the faster polymerization rate of the crosslinker used, a combination of surface force measurements, small angle neutron scattering, and ultrasmall angle neutron scattering confirmed that these self-assembled microgels have a homogeneously cross-linked internal structure. This somewhat surprising result is attributed to a combination of the dynamic nature of the hydrazone crosslinking chemistry and the assembly conditions used that promote polymer interdiffusion. Coupling the predictable diffusive and refractive properties enabled by the homogeneous internal structure with the degradability enabled by the assembly chemistry, we anticipate that these microgels offer opportunities to address challenges in drug delivery, biosensing, and optics.



Scheme 1: Schematic of self-assembly process and anticipated structures of resulting microgels depending on the diffusibility of the PNIPAM-Ald crosslinker and the permanence of the crosslinks formed. The homogeneous morphology is consistent with the structural characterization results.

POLY 740: Pathway-controlled complexity of metastable DNA microgels based on sequence-defined multiblock copolymers

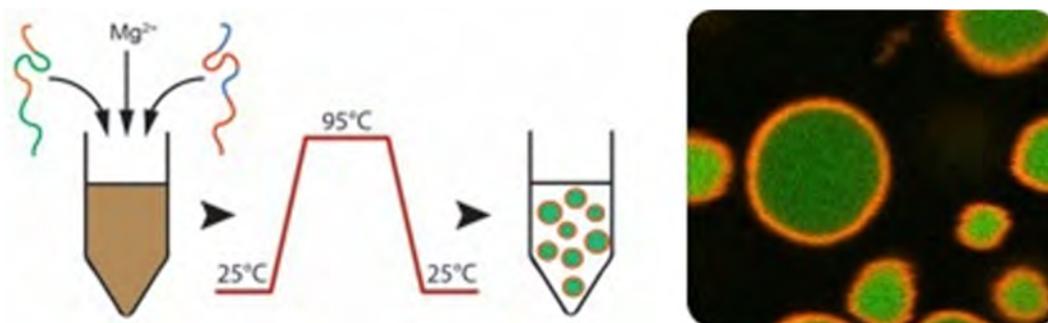
Andreas Walther, andreas.walther@makro.uni-freiburg.de, Remi Merindol, Sebastian Loescher. University of Freiburg, Freiburg, Germany

Microgels are traditionally formed from synthetic polymers, and elaborate architectures, such as core/shell or Janus type morphologies, typically require tedious multistep reaction pathways. Here, we embark on an entirely different way and use pathway complexity in self-assembling DNA multiblock copolymer systems to structure metastable all-DNA microgels with complex architectures using a controlled heating pathway. The resulting architectures include simple microgels, microgel capsules and most importantly core/shell microgels with tunable dynamics of the encapsulated DNA. Interesting protocell architectures with liquid DNA encapsulated in a hydrogel DNA shell can be prepared and varied to the extent to change the internal dynamics to a full core/shell microgel/microgel structure.

Origin of this complex phase behavior is the fact that we discovered a DNA LCST phenomenon (the polymer character), which can be overlaid with classical DNA hybridization (the supramolecular character). Both processes - phase segregation and hybridization - oppose each other during heating and cooling, and act on vastly different time, energy, and length scales. Based on elaborate kinetic control over these parameters it is possible to develop outstandingly defined and diverse morphologies.

We finally show that even plasmonic nanoparticles can be integrated to achieve photothermal and spatiotemporally controlled release of DNA of core/shell microgel capsules, and demonstrate approaches for condensation into cellular hydrogels.

The emphasis of this talk will be on the fundamental elucidation of the kinetics, pathway control and structural diversity of this new type of hierarchically structure DNA microgels.

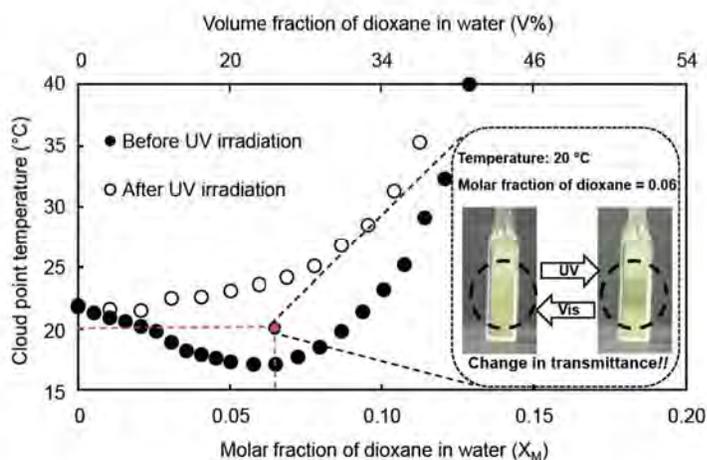


POLY 741: Responsive and thermo-lockable hydrogels and nanogels

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In the late 1980's, Irie reported that the phase transition temperature of random copolymers of NIPAM and N-(4-phenylazophenyl)acrylamide in water can be altered through irradiation of the solution with UV light, thereby creating one of the first light/temperature "doubly-responsive" system. To obtain triple responsive azobenzene-PNIPAM systems, a property of either the chromophore or the polymer chain must be modified reversibly by a stimulus other than heat or light. For instance, irradiation of α,ω -di-azobenzene-PNIPAM in mixed water/1,4-dioxane leads to cloud-point temperature enhancements as high as 7 °C upon small changes in solvent composition, as a consequence of the cononsolvency of PNIPAM in water/1,4-dioxane and the preferential solvation of the azobenzene moiety by 1,4-dioxane. Supramolecular interactions, also, can affect the responsiveness of azobenzene-modified PNIPAM. Irradiation of interlocked cyclic PNIPAM/ α -cyclodextrin (α -CD) rings or "charm-bracelets", induce a shuttle motion of the α -CD along a PNIPAM ring section upon trans/cis isomerization of the azobenzene.

Recently, we devised several approaches towards triple responsive hydrogels and water-dispersible nanogels. Temperature/pH/light responsive crosslinked PNIPAM nanogels were obtained by RAFT polymerization of NIPAM using a chain transfer agent with a few acrylate units. The nanogels were used as stabilizers/actuators of responsive high internal phase (HIP) oil-in-water Pickering emulsions. Hydrogels formed via supramolecular interactions of α,ω -di-(α -CD)-poly(ethylene glycol) chains (linker) with star-PNIPAMs where each arm has an azobenzene end group exhibit a fast shrinkage upon heating, disintegrate upon light-induced expulsion of the azobenzene from the α -CD cavity, and expand upon cooling, unless the complexes are locked chemically.



Cloud points of α,ω -di-azobenzene-PNIPAM in water/1,4-dioxane mixtures

POLY 742: Stimuli-responsive supramolecular microgels

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Microgels are functional macromolecules with unique properties like porous structure, tunable chemical functionality and swelling in solvents. Development of new synthesis methods that allow controlled integration of chemical functionalities into microgels opens new ways to generate functional polymer systems with unique functions like stimuli-responsiveness, re-shaping, switchability and adaptability.

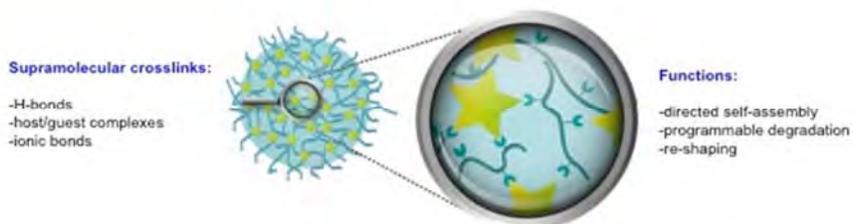
This contribution will focus on synthesis methods to obtain microgels exhibiting non-covalent dynamic crosslinks based on host-guest complexes, ionic bonds or hydrogen bonds and characterization of their properties in aqueous solutions.

Reactive mono- and multi-functional cyclodextrins were synthesized and selectively incorporated into microgels using precipitation polymerisation approach.

Supramolecular cyclodextrin-based crosslinkers provide degradability of microgels provoked by molecular triggers. Cyclodextrins in combination with catalytically active gold nanoparticles play a role of binding domains improving the selectivity of the catalytic processes in microgels.

Recently we developed facile synthesis method to obtain aqueous supramolecular temperature-responsive microgels using tannic acid as multifunctional physical crosslinker. The precipitation polymerization of *N*-vinylcaprolactam in the presence of tannic acid leads to the formation of well-defined stimuli-responsive microgels cross-linked by hydrogen bonds formed between the tannic acid and carbonyl groups of the polymer chains. We demonstrate that obtained microgels exhibit reversible temperature-triggered swelling/deswelling and undergo pH-triggered degradation in aqueous solutions.

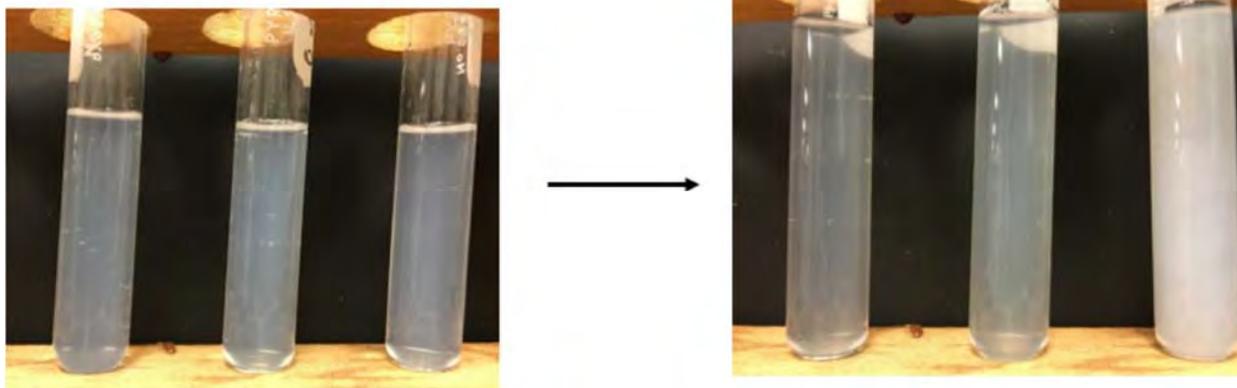
Monodisperse colloiddally stable microgels with a high amount (> 30 mol-%) of zwitterionic groups were synthesized using W/O miniemulsion approach. High contents of zwitterionic groups in microgels led to the formation of dynamic reversible ionic crosslinks along with permanent covalent crosslinks generated by bisacrylamide. Obtained microgels exhibit temperature-triggered swelling/deswelling behavior and co-existence of UCST- and LCST-type transitions in aqueous solutions.



POLY 743: Biodegradable and stimuli-responsive autodispersing polyurethanes

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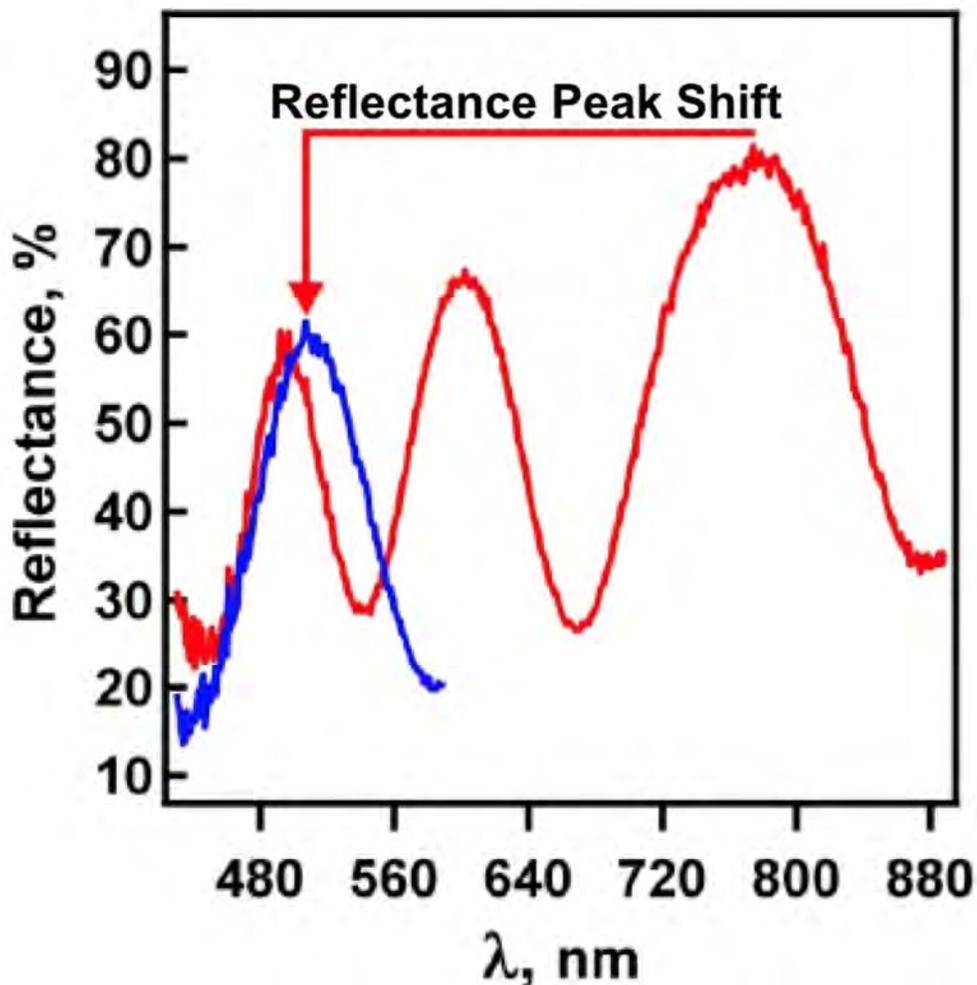
Polyurethanes derived from di-OH telechelic poly(ethylene oxide) and poly(propylene oxide) provide a biodegradable backbone when condensed with diisocyanates. Addition of hydroxyl-functionalized ionic liquids as chain terminating agents provide solvent-exchange and anion-exchange stimuli-responsiveness. We demonstrate that condensation polymers derived from such monomers can be tuned to form autodispersing nanogels and microgels, and that tuning the hydrophilicity ratio of the poly(alkylene oxide) components allows one to modify the sequestering ability of such hydrogels. Anion exchange can also be used to tune inter-particle attractions, and to tune destabilization kinetics of such gels in dispersion.



POLY 744: Sensing and biosensing with nanogel-based optical devices

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Stimuli-responsive nanogels have been used to generate nanocavities that exhibit color, and multippeak reflectance spectra. The optical properties are a result of constructive/destructive interference of light resonating in the nanogel-based cavity, which depends directly on the nanocavity's dimensions. By careful manipulation of their chemistry, nanogels capable of changing size in response to their surroundings can be synthesized. Likewise, nanocavities capable of changing their dimensions, and optical properties, in response to their surroundings can be fabricated. This presentation will highlight our most recent efforts to generate nanocavity-based sensors and biosensors.



26.5 °C (red) and 38.5 °C (blue). At high T, the peaks in the red spectrum blue shift as the nanogels collapse. Only a single peak at 38.5 °C is shown for clarity. Similar responses can be used to detect a variety of analytes.

POLY 745: A responsive nanogel probe for ratiometric fluorescent sensing of pH and strain in hydrogels

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In this study a new pH-responsive nanogel probe containing a complementary non-radiative resonance energy transfer (NRET) fluorophore pair is investigated and its ability to act as a versatile probe of network-related changes in three hydrogels demonstrated. Fluorescent sensing using NRET is a powerful method for studying relationships between Angstrom length scale structure and macroscopic properties of soft matter. Unfortunately, inclusion of NRET fluorophores into such materials requires material-specific chemistry. The nanogel probes (NG_{Ph/An}) were prepared by copolymerization of methyl methacrylate (MMA), methacrylic acid (MAA), ethyleneglycol dimethacrylate (EGDMA), (9-phenanthryl)methyl methacrylate (Ph) and (9-anthryl)methacrylate (An). The NG_{Ph/An} dispersions were pH-responsive (Fig. 1a) and also showed changes in their photoluminescence (PL) as the particles swelled (Fig. 1b and c) as a consequence of NRET. The intensity ratios also showed reversibility that was not affected by aggregation (Fig. 1d). Ratiometric PL data for the gels labelled with the nanogel probes enabled pH-triggered swelling and de-swelling to be studied as well as Ca²⁺-triggered collapse and solute release. PL measurements during compression of a nanogel probe-labelled nanocomposite gel demonstrated mechanochromic behavior and strain sensing. The new nanogel probes have excellent potential for provide a versatile ratiometric fluorescent platform for studying pH and strain within gels.

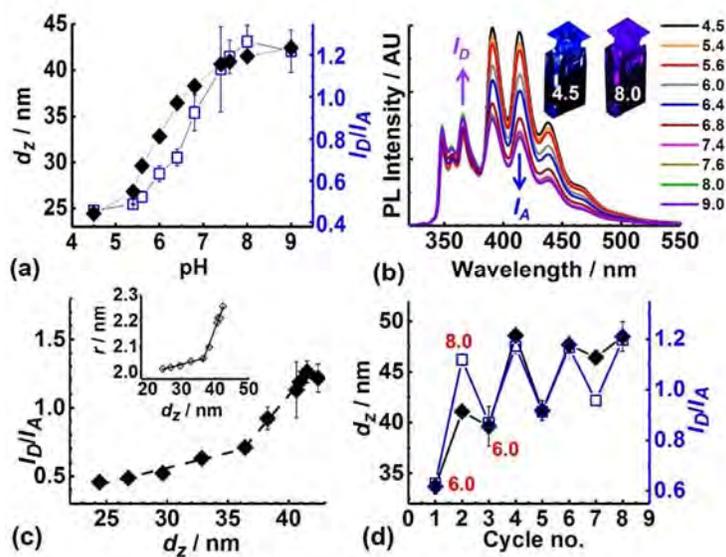
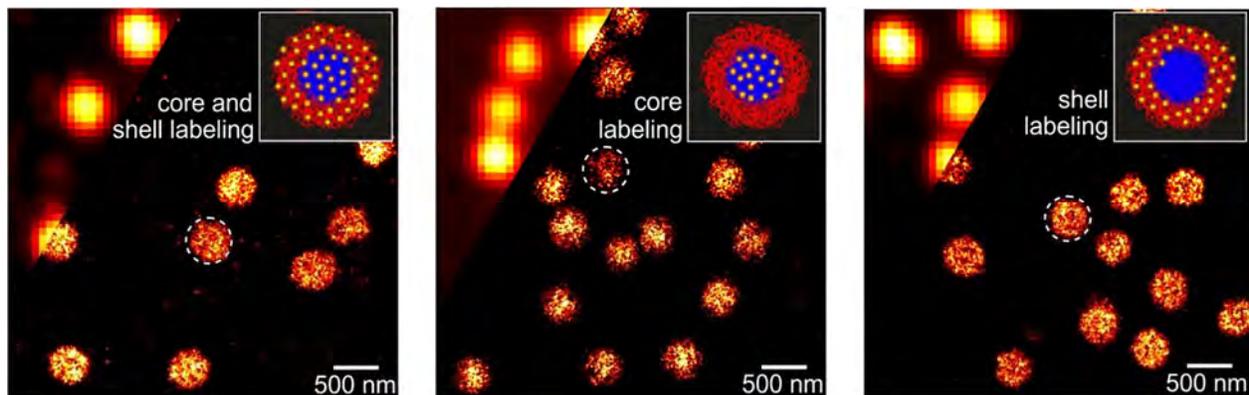


Figure 1. (a) Variation of z-average diameter (d_z) and PL intensity ratio of the donor and acceptor peaks (I_D/I_A) with pH for an NG_{Ph/An} dispersion. (b) PL spectra for the NG_{Ph/An} dispersions. The inset shows cuvettes of the dispersions irradiated with UV light. The pH values are shown. (c) Variation of I_D/I_A with d_z . The inset shows the calculated average separation between the Ph and An. (d) Data from repeated cycling between pH 6.0 and 8.0.

POLY 746: Superresolution fluorescence microscopy for the *in situ* visualization of compartmentalized microgels / nanogels

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The elucidation of the structure of compartmentalized microgels (nanogels) and microgel structures is challenging since they do not possess strong contrast for electron microscopy, and since classical fluorescence microscopy fails due to the fact that their structures are significantly smaller than the diffraction limit of optical light. However, modern superresolved fluorescence microscopy methods such as dSTORM (direct stochastic optical reconstruction microscopy) reach resolutions down to typically 10-30 nm and, therefore, are highly suited to fill this gap of structural *in situ* imaging. In this contribution, the success of superresolution fluorescence imaging methods to address research questions concerning microgels and their application in determining the spatial distribution of implemented functionalities will be demonstrated. In addition, the challenge to gain reliable 3D information in fluorescence and transmission electron microscopy (TEM) imaging will be discussed.

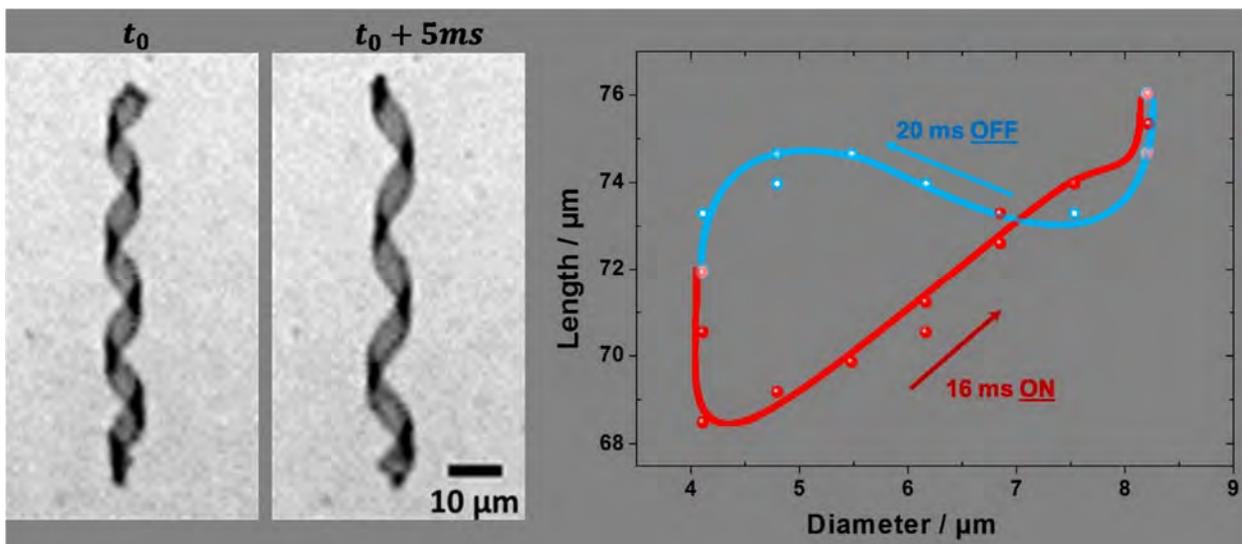


Superresolved dSTORM images of microgels with different core and/or shell labeling schemes as sketched in the upper right drawing of each of the three images. In the upper left corner, the diffraction limited images are presented. The microgels sizes as determined by light scattering are representatively shown as dashed white circles.

POLY 747: Non-reciprocal shape shifting microgels engine

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Motion is essential to life and its control is a key issue in the design of artificial microrobots and micro-machines. A topical challenge in microscale locomotion is the development of synthetic materials that sustains self-propulsion by body shape deformation akin to microorganisms. Mechanical actuation also in nature is frequently caused by swelling and deswelling of hydrogels. In cases like the hydraulic opening and closing of a pine cone. Intrigued by these examples, an increasing interest has developed in artificial hydrogel actuator systems that exploit swelling/deswelling in response to an external stimulus. Mostly these systems utilize the volume phase transition of polyacrylamide derivatives and focus on the shape variance between end states in equilibrium. In this work the focus is on temperature responsive thin poly(*N*-isopropylacrylamide) microgel bodies that undergo bending and torsional motions upon swelling and deswelling. Very fast temperature jumps localized to the volume of the thin microgel body are achieved by near IR-light and heat has been engineered to enable temperature jumps. Because the heating is restricted to the inner volume of the small microgel, they also cool down quickly due to the fast heat transfer to the surrounding bath once the heating is ceased. Because swelling and shrinkage are diffusion controlled and cannot follow in time the fast temperature changes, the volume change can be effectuated out of equilibrium. As a consequence volumetric changes of anisometric gels tend to be inhomogeneous. The resulting stress results in shape deformations and the accumulation of elastic energy that is released with a delay. In principle, all these different effects can be well controlled. Mastering the nonequilibrium response provides control of the complex motion of a soft microrobot, which goes beyond what has been so far reported for hydrophilic microgels.



The non-equilibrium actuation of the microgel helix in response to strobe irradiation by NIR light causes repetitive cycles of unwinding and winding of the helix, resulting in a net rotational motion.

POLY 748: Photoactive BODIPY polymer-based systems: Polymersomes for PDT and 2D & 3D micrometric surface patterning

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Herein we show two examples of BODIPY variants with particular regard to polymeric systems. Boron dipyrromethene difluoride (BODIPY) dyes are a popular class of chromophore. Properties are readily tunable synthetically, and variants spanning a wide gamut of colours can be obtained from the visible to NIR, with both high absorption and emission quantum yields. Additionally, we recently showed structural homologues, comprising a meso-N in place of a C atom - AzaBODIPY, gives rises to extremely photostable NIR AzaBODIPY fluorochromes, certain variants also showing promise in terms of photosensitization of singlet oxygen production.

In a first case, as part of an ongoing research effort in developing photoactive polymersomes, amphiphilic block copolymers covalently-grafted with a heavy-atom containing AzaBODIPY was seen to form discrete polymersomes. Under photoirradiation, singlet oxygen was efficiently produced, evidenced by trapping experiments and NIR luminescence. Tests of photodynamic therapy (PDT) was carried out on two different cancer cell lines in vitro and a correlation of activity with regard to induced cancer cell death and positioning of the chromophore (periphery/middle of polymersome bilayer) was tested. To this end, an asymmetric multifunctional AzaBODIPY was synthesized and inserted at specific locations in polypeptide-based rod-coil amphiphilic block copolymers. This study aimed to aid optimization of the design of synthetic therapeutic nanomedicines with low photosensitive molecule loading.

Equally, an azido-BODIPY prototype was synthesized, which upon irradiation undergoes a photochemical cleavage reaction. This generates a reactive intermediate, which ultimately leads to a photoregulated homopolymerization yielding fluorescent polymeric brushes on surfaces. This approach was adapted to produce well-defined patterns on glass slides with micrometric precision in x, y and z-directions using laser excitation in a confocal fluorescence microscope set-up.

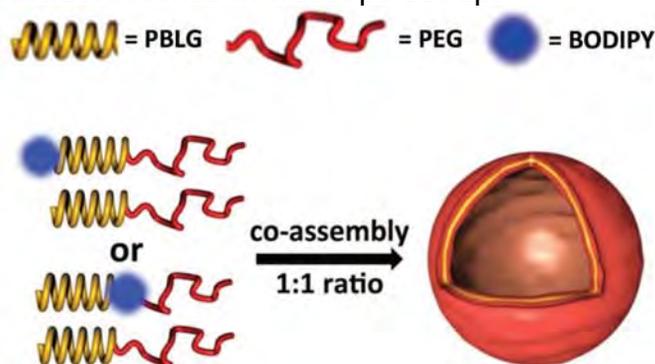
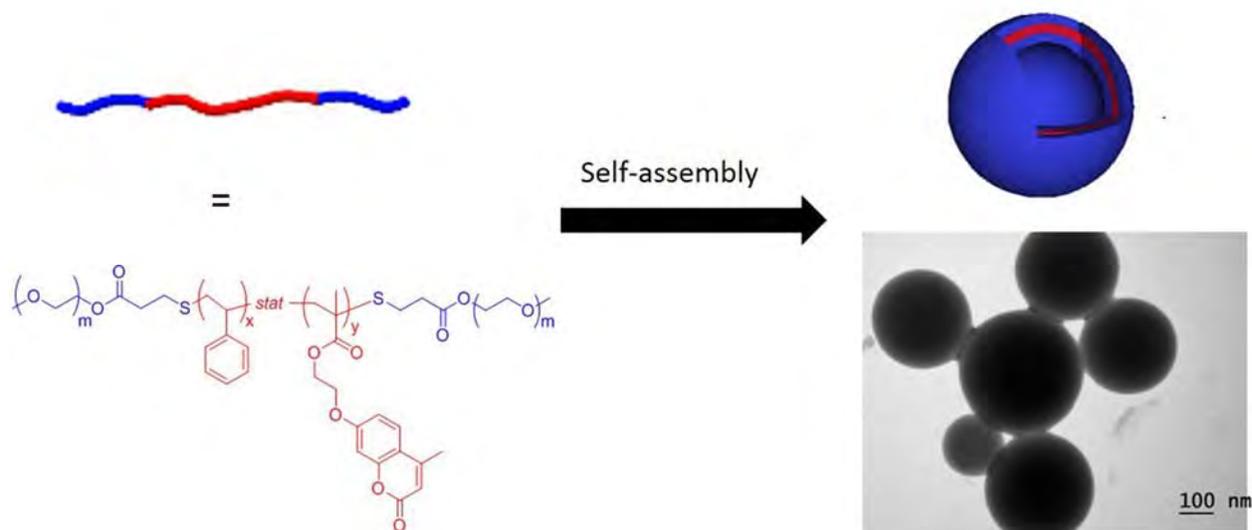


Figure: Block copolymers integrated with BODIPY photosensitizers self-assemble to give photoactive polymersomes exploited in vitro for PDT with 2 cancer lines.

POLY 749: Design and fabrication of mechanically stable polymer vesicles from crosslinkable linear amphiphilic triblock copolymers

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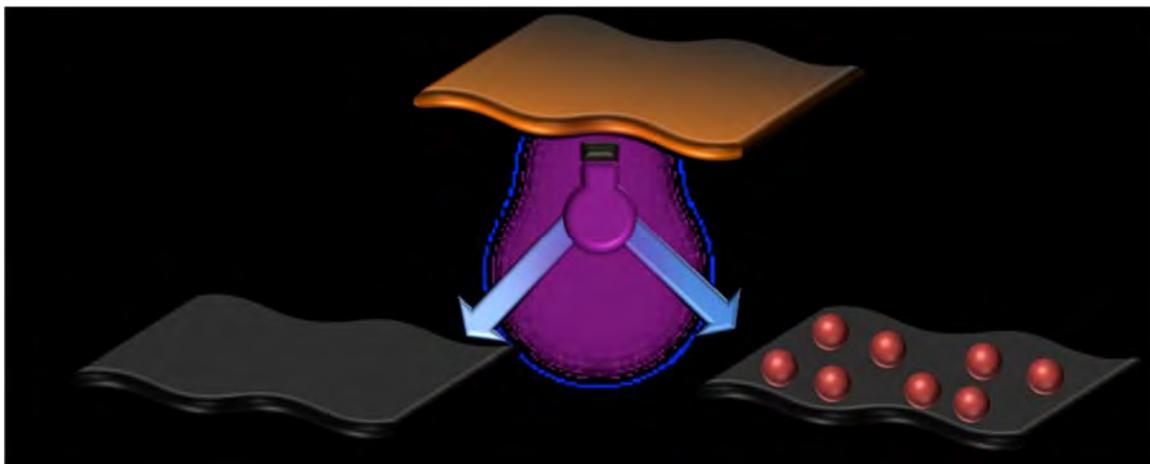
Linear amphiphilic triblock copolymers, methoxy-end-terminated poly((ethylene glycol)-*block*-(polystyrene-*stat*-coumarin methacrylate)-*block*-poly(ethylene glycol)) (mPEG-*b*-(PS-*stat*-PCMA)-*b*-mPEG) were synthesized with varying hydrophobic weight percentages using reversible addition-fragmentation chain transfer polymerization and subsequent end-group modification. At hydrophobic weight compositions approaching 90%, these amphiphilic triblocks self-assembled in aqueous solution to form nanoscale vesicles (<200 nm diameters), which maintained their structure after UV-induced crosslinking via [2+2] cyclodimerization of the coumarin moiety. Giant unilamellar vesicles (GUVs) (>20 μm) were also successfully fabricated via electroformation using these polymers. The effect of crosslinking on the mechanical stability and permeability of both GUVs and nanoscale vesicles will be reported, as well as a study of their potential use as stable cargo carriers.



POLY 750: Polymer nanocomposites: In-situ photoconversion to nanoparticles with ketyl radicals

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The synthesis of metal nanoparticle (NP) materials involve the use of colloidal methods and ligands/surfactants that result in either micellar, block copolymers, and nanoreactor configurations to control the growth kinetics of NPs. This results in control of size, shape, polydispersity, and surface functionality or core-shell geometries of these nanomaterials. Equally important is their dispersion in polymer materials hosts in the form of coatings, gels, bulk shapes, and layered systems, etc. Very often, the NPs are prepared first and then mixed with the polymer hosts resulting in poor dispersion methods and unoptimized properties. This talk will highlight the in-situ fabrication of polymer nanocomposites by the photoconversion of nanoparticles using ketyl radicals and metal nanoparticle precursors (Au, Pt, Pd, etc.) based on the selective incorporation of radical generators that facilitate reduction of these precursors to metal[0]. The mechanism of this photoconversion will be discussed. The result is that nanocomposites can be prepared based on the synthesis and blending of these precursors and radical generators which can be selectively activated by UV irradiation and converted onto patterns or metalized films. Such methods will offer an alternative to the fabrication of metal NP loaded fibers, coatings, films, etc. that can be processed first followed by a non-heating conversion procedure.



POLY 751: Light-responsive polymersomes for spatially and temporally controlled release

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Polymersomes are robust artificial vesicles resulting from the self-assembly of amphiphilic copolymers. Over the past decade, polymersomes have become a popular research topic in the fields of nanomedicine and biotechnology. They can be engineered and customized to meet various specifications for a variety of biomaterials-related areas such as drug delivery, nanoreactors, or gene therapy. One major challenge is to design stimuli-responsive systems that can release loaded species in a controlled manner, at a precise time and location. Among all the possible triggers that can be applied, light is widely considered as a versatile approach. In this context, our aim was to design light-sensitive polymersomes which can undergo rupture upon irradiation, for specific cargo release.

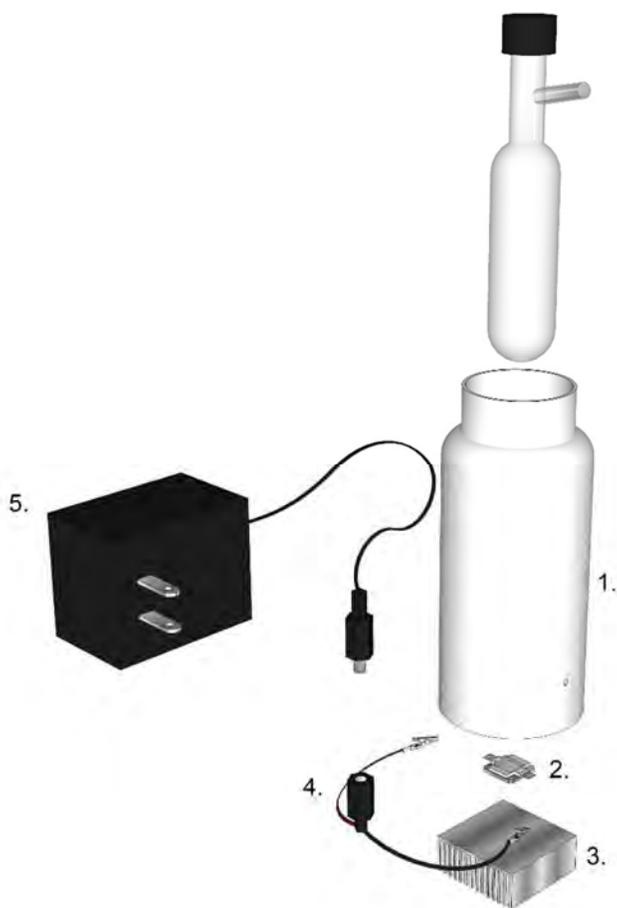
In the present work, we developed a coumarin derivative molecule as a linker between two polymers to yield an amphiphilic diblock copolymer with photo-responsive properties. Coumarin undergoes heterolytic bond cleavage after irradiation, leading to a separation of the two blocks causing the vesicle leakage or rupture. This photosensitive molecule has attractive features such as a high molar absorption coefficient, good chemical stability, fast release rates and fluorescence, which allow facile monitoring. Additionally, two functional groups on this coumarin derivatives was designed in such a way that a wide variety of polymers can be grafted, offering a large range of versatile light-sensitive block copolymers. We specifically report here on the coumarin synthesis followed by grafting of poly(trimethylene carbonate) (PTMC) and poly(ethylene oxide) (PEO). PTMC and PEO have been widely studied as materials for biomedical applications due to their low toxicity and biocompatibility. In addition, the self-assembly properties and the light-mediated rupture mechanism of the polymersomes were studied.



POLY 752: Making and breaking polymers with light: Blue-light-mediated photoiniferter polymerization and polyketone degradation

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Light can be harnessed for both polymer synthesis and degradation. For polymer synthesis, we designed a simple, inexpensive photoreactor for conducting blue-light mediated photoiniferter polymerization using thiocarbonylthio compounds (common chain transfer agents in RAFT polymerization). Using this photoreactor, we show that bottlebrush polymers can be prepared using the grafting-from method. For polymer degradation, we prepared a series of ABA triblock copolymers containing soft polybutadiene segments with incorporated ketone units and hard polylactide (PLA) segments. These bio- and photodegradable thermoplastic elastomers have good mechanical properties and degrade in response to UV light.



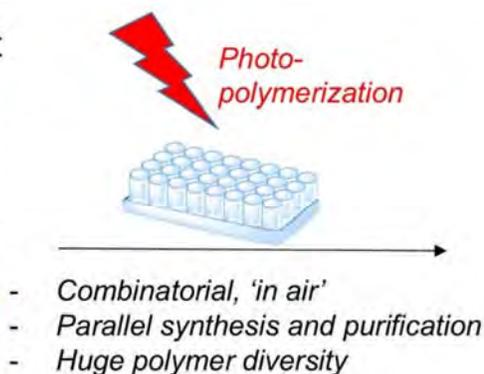
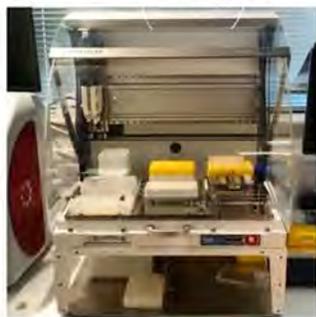
POLY 754: Photochemical combinatorial discovery of antimicrobial polymers

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Kingdom

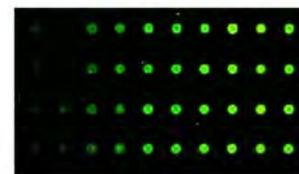
The identification of polymers with emergent properties is a major challenge; a huge range of monomers exist which can be combined in near unlimited combinations. Any strategy to maximise chemical space, particularly for biomedical applications, should enable access to 100's, if not 1000's of unique polymers. The synthesis method should be robust, and purification/isolation should also be high-throughput and preferably accessible using robotics. Finally, the handling steps should be compatible with high-throughput screening using e.g 96 or 384 well plates. (Controlled) radical polymerization is accessible and recent advances enable 'in air' polymerization where a light source is used to provide the radical flux, removing the need for degassing.

Here we report the use of photo-initiated 'in air' polymerization using liquid handling robots to enable the discovery of new anti-microbial materials. Each step is performed in a parallel. We show that this enables reproducible (co)polymer synthesis in low volume. Using this strategy, a range of monomers are (co)polymerised together and the resulting polymers screened to identify new structures which have increased antimicrobial, and in particular, anti-mycobacterial, activity relative to homopolymers. The screening process was essential with only a small sub-set showing enhanced antimicrobial (10 fold) activity, and low toxicity.

Liquid handling robot



Array-based screening



Identification of function

↓
New polymers

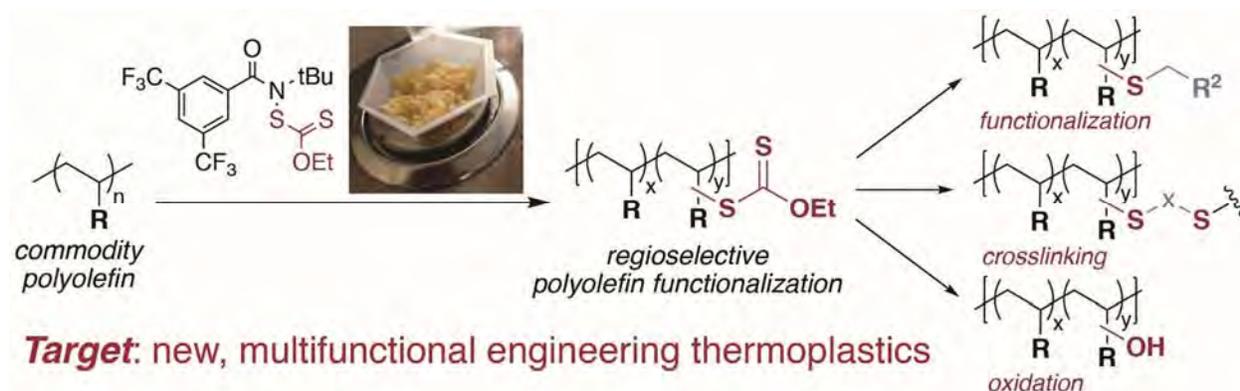
Photo-chemical enabled discovery of new materials.

POLY 755: Regioselective, C–H xanthylation as a platform technology for polyolefin functionalization

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Polyolefins are high-volume, low-cost engineering thermoplastics with high tensile strength, low density, attractive chemical resistance, and excellent processability. Currently, polyolefins constitute nearly 60% of world polymer production. For their ubiquity, however, these hydrocarbons do not interface with other materials, drastically limiting their ability to form composites, coatings, adhesives, or to be used in high-performance engineering applications. Imparting functionality onto these materials without comprising the desirable properties of the parent material would uncover new and unusual properties not typically associated with polyolefins. There is a considerable unmet need to develop chemistry that transforms these abundantly available commodity polymers into functional materials without resorting to *de novo* synthesis.

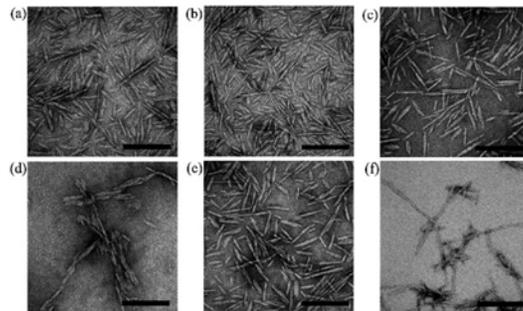
Developing methods to transform polyolefins into the functional materials of the future will require polymer chemists to rethink their approach to post-polymerization modification, seeing C–H bonds as potential points of diversification rather than unreactive functionality. To address this challenge, we propose to use the modern toolkit of photochemical formation of amidyl radicals to generate new, functional, and high-value materials from readily available precursors. Our lab is pursuing the photoinitiated xanthylation of aliphatic C–H bonds to enable the regioselective functionalization of branched polyolefins without an erosion in polymer molecular weight. This “late-stage” methods are amenable to both a commodity polymer precursor (homogeneous functionalization) or the surface of a pre-fashioned plastic object (heterogeneous functionalization) and will use simple chemistry to enhance the thermal, mechanical, and/or surface properties of a variety of materials. The anticipated outcomes are twofold: new methods for the selective introduction of valuable functionality into a range of commodity polymers, and new materials with a greatly expanded scope of physical properties for next-generation engineering applications.



POLY 756: Cellulose nanocomposites

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Cellulose nanomaterials have gained a lot of notice recently owing to their impressive mechanical and thermal properties, environmental benefit, low toxicity and relatively low cost. Of these materials, cellulose nanocrystals (CNCs) are semi-commercial and have been used in nanocomposites for a variety of applications. However, CNCs also have issues related to dispersion in hydrophobic resins due to the highly hydroxylated and sulfate ester CNC surface. Here, we detail our efforts at preparing CNC nanocomposites, their properties, and potential applications.

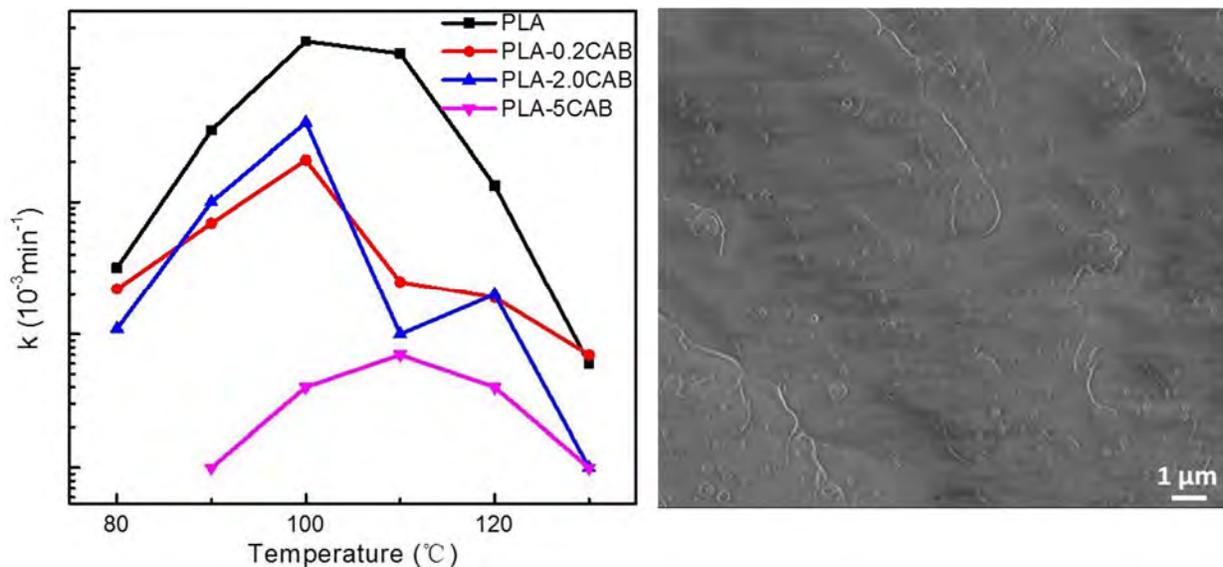


Cellulose Nanocrystals after surface modification.

POLY 757: Effects of cellulose acetate butyrate on the crystallization of polylactic acid

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The effects of cellulose acetate butyrate (CAB) on the crystallization of PLA (composed of 98.6 weight % L-lactide and 1.4 weight % D-lactide) was thoroughly investigated. The neat PLA and its blends were isothermally crystallized at various temperatures, and the kinetic parameters were determined with Avrami approach. PLA and its blends exhibited similar values of the Avrami exponent, while the kinetic constant varied drastically with the crystallization temperature and the CAB concentration. At high crystallization temperatures such as 110 °C and 120 °C, the presence of only 0.2 weight % CAB significantly reduced the rate of crystallization of PLA. Further increasing the CAB concentration in the blends did not show such a significant impact. While at low crystallization temperatures of 90 °C and 100 °C, substantial decrease of the kinetic constant was observed at the CAB concentration higher than 5 weight%. Combined with analysis by Scanning Electron Microscopy (SEM) and polarized optical microscopy, we were able to conclude that at high crystallization temperatures at which nucleation is the rate-determining step, low concentration of CAB (< 0.2 wt%) acts as an anti-nucleating agent which causes a reduction in the rate of PLA crystallization. While at low crystallization temperatures, a CAB percolation network is formed by uniformly dispersed nanoscale CAB phase (~160 nm) at a higher mass fraction (of about 5 weight %), the network effectively obstructs the movement of PLA segments and consequently decreases the crystalline growth rates of PLA.



The crystallization kinetic constants of PLA and its blends at different temperature (left), the SEM image of PLA-5CAB (right).

POLY 758: Splitting of meniscus at air-LC interface of megamolecular polysaccharide and its theoretical evaluation

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The drying interface is a dynamic modal and has been widely studied in the context of a drying droplet and convective self-assembly of colloidal particles. The analysis of the shape of the meniscus curve has been the focus of many research articles but has only been considered from the viewpoint of surface interactions. Also, this field has been limited to spherical particles with little information about anisotropic particles.

In this regard, we have researched an exopolysaccharide, *sacran*. The LC unit of *sacran* was observed to be huge rod, 1-2 μm in diameter with length greater than 20 μm showcasing self-assembling characteristics. It is extracted from *Aphanothece sacrum*, a cyanobacteria indigenous to Japan. It has a M_W greater than 10^7 gmol^{-1} , shows critical liquid crystalline concentration $\sim 0.2 \text{ wt\%}$ and exhibits the ability to form anisotropically swelling hydrogels. It was also recently reported that drying *sacran* solution in a container with thickness less than the capillary length leads to deposition of a highly oriented vertical membrane. In this study, the meniscus curve of the drying interface has been mathematically analyzed so as to clarify the rationale behind this vertical deposition (**Fig.1**).

From the standard equation of a meniscus, the splitting of meniscus during the drying process of 0.5 wt% *sacran* solution could be justified. Accordingly, evaporating the solution from a confined space (1 mm) leads to development of a dense structure and subsequent formation of a skin layer at the air-LC interface. This suppresses the escape of water and creates an imbalance in the system. Splitting of the interface followed by vertical deposition of *sacran* solves this problem. Additionally, providing twice the surface area for evaporation as compared to the normal one in the whole process. We foresee that optimizing drying conditions and concentration of solution, other polymeric materials can also split meniscus and form highly oriented vertical deposition.

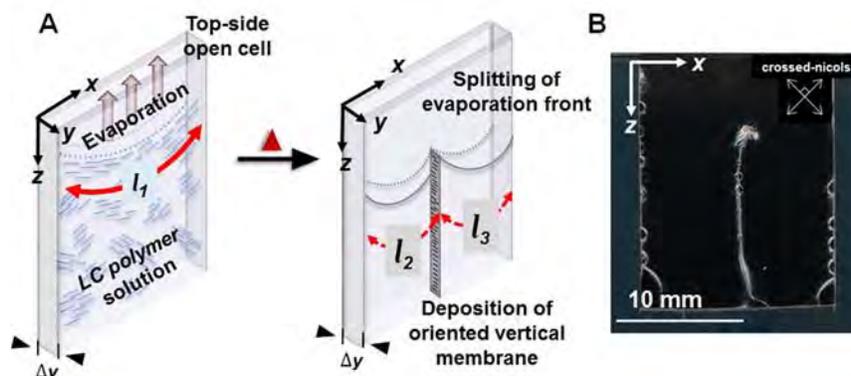
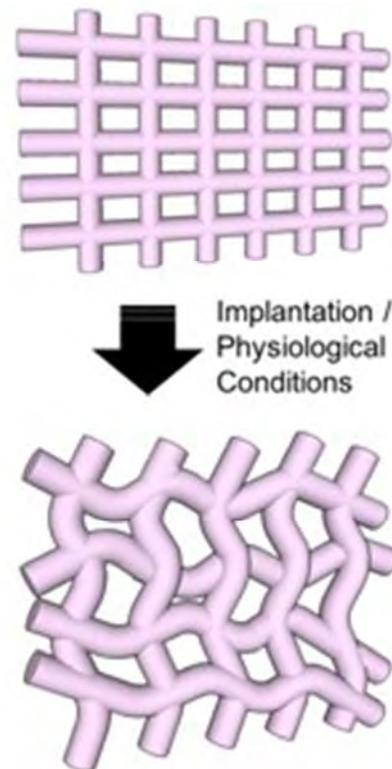
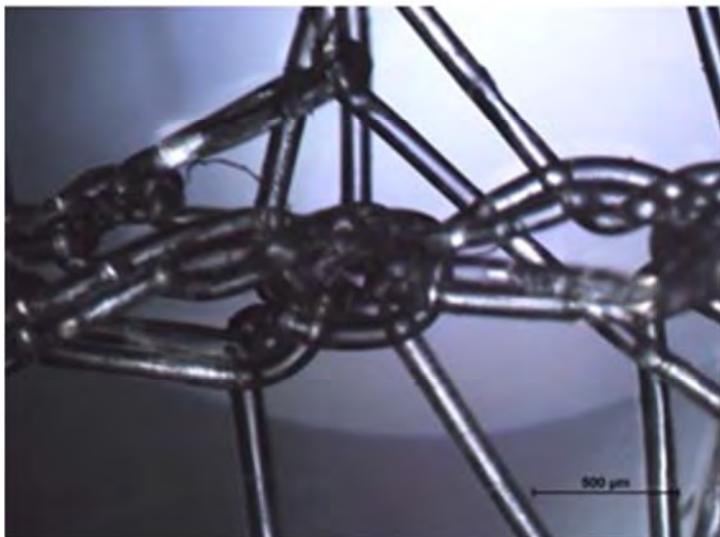


Figure 1. **A.** Schematic illustration of the meniscus splitting during drying of the LC polymer solution so as to provide surface area for evaporation. **B.** Actual image of the deposited *sacran* membrane after drying inside a cell.

POLY 759: Stimuli responsive materials for personalized implants

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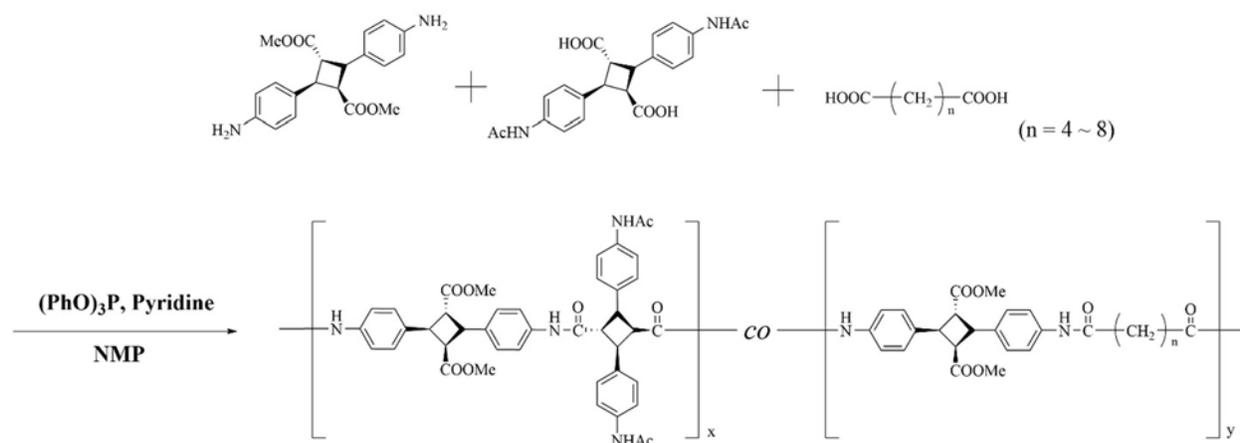
The incorporation of small amounts of high-stiffness, high-aspect-ratio nanometer-sized fillers into polymers is a design approach that has rapidly emerged as a broadly exploited framework for the creation of new materials with tailored mechanical properties. Crystalline cellulose nanocrystals (CNCs) are attracting significant interest in this context, mainly due to their intriguing mechanical properties and the abundance of cellulose in the biomass. These nanocomposites show dynamic mechanical behaviour, which is achieved through regulation of the molecular interactions, and therewith the stress transfer, between adjacent nanocrystals. We will present our experimental research, targeting the design and processing of 3D printable polymer/CNC for implantation into the human body. We investigate how different processing methods affect the morphology and mechanical properties of nanocomposites made from polyurethane and renewable fillers. Comparisons are made between traditionally made solution cast samples, and materials were printed into implantable meshes.



POLY 760: Structure-property relationships of bio-based polyamides with super-high mechanical toughness

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4-Aminocinnamic acid derived from microbial resources must be one of the most expected monomers for application in high-performance bio-plastics. Especially, a bio-based polyamide which had been synthesized by 4-aminocinnamic acid derivatives showed high mechanical strengths as high-transparent plastics. Moreover, the mechanical strengths were enhanced by the addition of adipic acid as a third monomer to synthesize co-polyamide. Significantly, strain energy density of this co-polyamide was also enhanced by the addition of adipic acid which probably affects both flexibility and strength of co-polyamide. However, there still have the possibilities to improve these mechanical properties by controlling the selection of third monomers and of their composition ratio. Moreover, the structural advantages of that co-polyamide were not clear so far. From above, we focused on the mechanical properties of a series of co-polyamides which had been synthesized by 4-aminocinnamic acid derivatives and various kinds of aliphatic dicarboxylic acids with controlling their composition ratio. Additionally, structural analyses of these co-polyamides were carried out by means of FT-IR and other analysis methodologies. As a result, obtained co-polyamide showed higher elongation at break (140 % at max) and strain energy density (250 MJ/m³ at max) which contained higher ratio of aliphatic dicarboxylic acids. The maximum mechanical strength was about 530 MPa when pimelic acid (C=7) was contained with 25 mol%, which was 60 MPa higher than that of reported co-polyamide in our research group. Furthermore, the result of *in-situ* FT-IR measurement indicated tautomerization throughout tensile test. From this tautomerization, the cyclobutene rings in the co-polyamides were deformed from V-shaped non-plain structure to plain one, which reduces stress concentration in main-chain throughout tensile test.

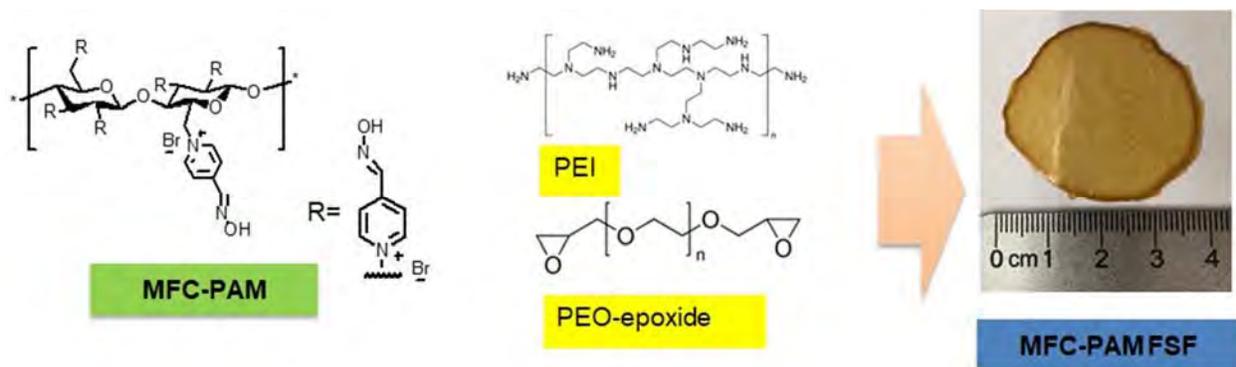


Scheme 1. syntheses of a series of co-polyamides derived from 4-aminocinnamic acid

POLY 761: Bioproduct derived protective layers: Self-exfoliating reactive layers

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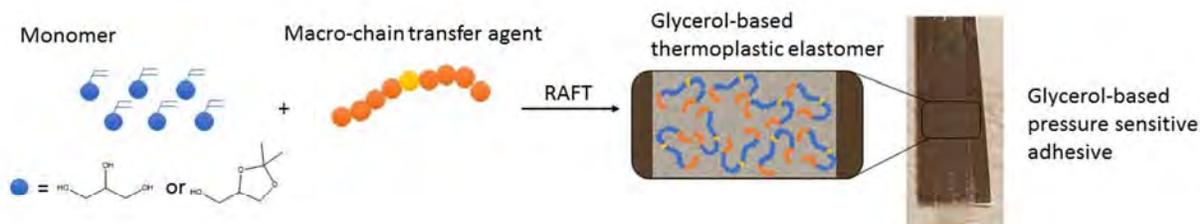
Nanocellulose is an interesting material with unique properties and chemistry. We have worked to exploit these characteristics to develop new functional thin films and aerogels. To enhance the comfort and protection of warfighters in the battlefield and during operations in diverse climates, new technologies and material assemblies are required for the fabrication of advanced multifunctional garments that allow high water vapor transport rates (breathability) while blocking toxic chemicals and biothreats. In particular, for in-the-field military-personnel protection from chemical and biological (CB) agents, smart dynamic biological-agent-blocking materials are highly desirable that exhibit a reversible, CWA-triggered, rapid transition from a breathable state to a protective state. Cellulose materials, cellulose nanocrystals and microfibrulated cellulose (CNC and MFC, respectively) were functionalized with both oxime and pyridine aldoxime (PAM) nucleophilic units. New films based on MFC-PAM, PEI, and crosslinker were prepared. Studies of the neutralization of a CWA simulant, DFP, by various solid films were performed. Surface-enhanced Raman spectroscopy (SERS) has also been explored as a method to allow visualization of CWA diffusion through the films.



POLY 762: Glycerol-based pressure sensitive adhesives: Synthesis and application

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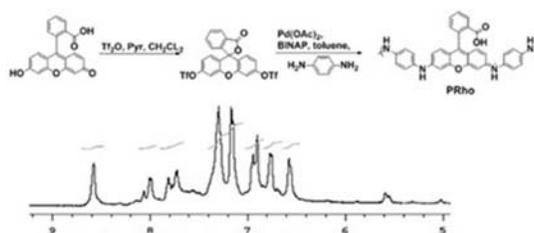
In the global drive to cut down on the reliance of petroleum feedstocks due to fluctuations of price and availability, biorenewables have shown potential as viable alternatives. Glycerol is a good candidate among biorenewable resources because of its low cost and wide availability as the byproduct from the transesterification of triglycerides in the biodiesel process. Herein we present tackifier-free pressure sensitive adhesives (PSAs) derived from glycerol-based thermoplastic elastomers (TPEs) synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization. To obtain desired functionality for RAFT polymerization, the proper acrylation of solketal, a glycerol derivative, is achieved through transesterification with acrylates. The mechanical properties of TPEs are enhanced by the aid of glassy macro-chain transfer agents. The final properties of glycerol-based TPEs are tunable depending on the structure of glycerol derivatives. By following different synthetic routes, both hydrophobic and hydrophilic TPEs can be obtained. In this contribution we describe the synthetic process as well as the performance of the final PSA products through dynamic shear rheology and peel testing.



POLY 763: Polyrhodamine: Towards the design of a new optical chemical sensory material

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Polyaniline (PANI) stands out as one of the most widely employed polymer, with commercial applications in printed circuit board manufacturing, antistatic and electrostatic dispersive (ESD) coatings, and corrosion protection. PANI also has great potential for applications in many other fields such as supercapacitors and batteries, electronic devices as hole-injection layers, solar cells, biosensors, and toxic metal recovery. Polyaniline (PANI) is one of the most explored conducting polymer (CP) material for biosensors and chemosensors, as it acts as an electron transfer mediator during redox and enzymatic reactions, and also as a substrate for the adsorption of biomolecules. Unfortunately, practical use of PANI is plagued by the material's aging effect, optical and electrochemical instability, and the lack of standard/optimized deposition methods. We present a new conducting polymer based on the rhodamine dye towards the development of a series of new conducting polymer as efficient bio- and chemosensors towards pH, ROS and other biological analytes. Our model polymer (polyrhodamine, PRho) was prepared from a Buchwald/Hartwig synthesis of fluorescein ditriflate with p-phenylenediamine to give the polymer in good yield (80 %) and high molecular weight ($M_n = 47000$). The polymer was shown to have good optoelectrical properties consistent with the rhodamine dye and good chemical and electrical stability. The polymer can be cycled between acid (pH ~ 1) and base (pH ~ 12) solution without any noticeable change in the absorption spectrum. The cyclic voltammogram of a 100 cycle scan shows two redox peaks that were reversible even after 100 scan, with only a small change in the current for the second redox cycle. We will also present data on the effect of pH, ROS and other biological analytes on the optoelectrical properties of the PRho.

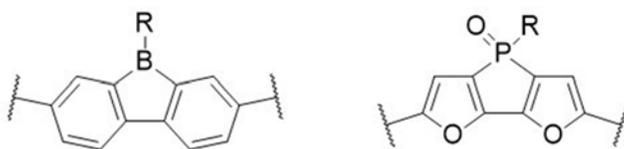


Synthesis of our Polyrhodamine

POLY 764: Conjugated polymers containing boron and phosphorus

Paul Rugar, paul.rugar@gmail.com. Chemistry, University of Alabama, Tuscaloosa, Alabama, United States

The incorporation of inorganic elements into conjugated compounds is a powerful technique to create materials with novel properties and functionalities. We currently are studying boron and phosphorus containing conjugated polymers and small molecules. Their role as electron accepting materials, sensors, and rapidly tunable moieties will be presented. Their properties and performance will be compared and contrasted to common organic conjugated materials.



POLY 765: Synthesis and optoelectronics of coplanar ladder polymers

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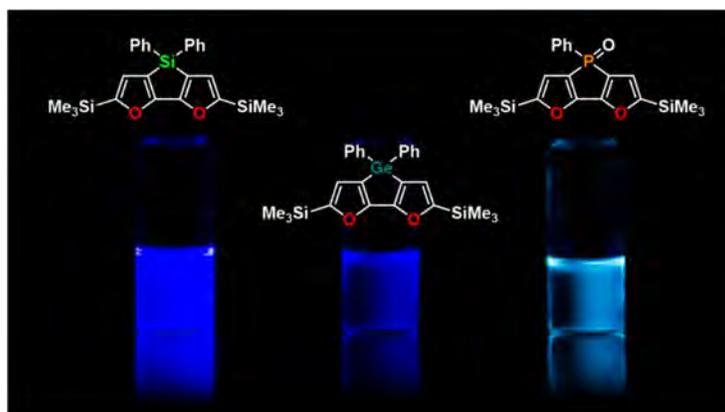
Coplanar torsional conformation plays a key role in shaping the optoelectronic properties of conjugated organic macromolecules. It is still an elusive task, however, to control the desired coplanar yet rigid conformation for materials performance. We aim to establish general synthetic methodology and comprehensive structure-property correlations of rigid coplanar pi-systems, through synergistic approaches combining chemical synthesis, process engineering, and optoelectronic characterization. In order to achieve this goal, we designed and implemented multiple chemical strategies, including the incorporation of non-covalent bridging bonds, the use of dynamic covalent reactions, and the employment of highly efficient annulation reactions. Efforts were also made to solve the major challenges associated with low solubility of rigid coplanar macromolecular materials for characterization and processing. Unique optical, electronic and mechanical properties of these new materials are investigated and optimized for advanced applications.



POLY 766: Synthesis of stable difuran derivatives with p-block elements bridge

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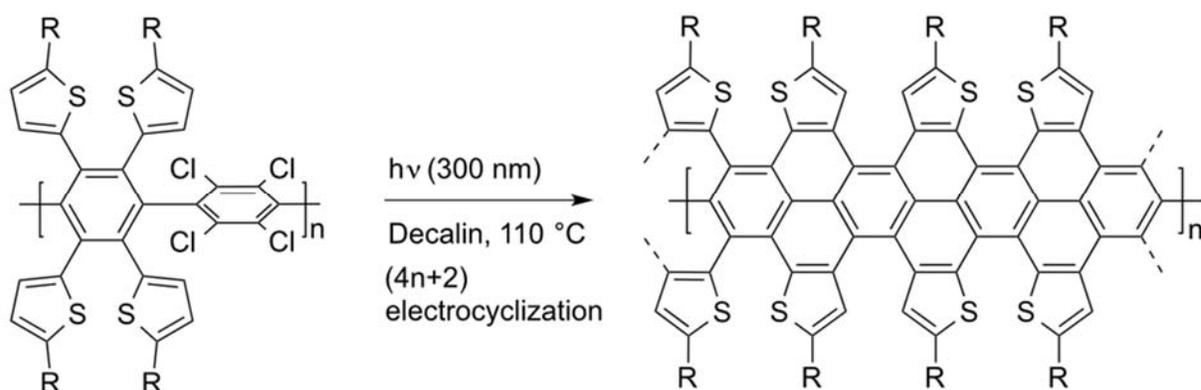
Thiophene-based materials have been widely used in in optoelectronic devices such as photovoltaic cells (PVCs), organic thin film transistors (OTFTs), organic light-emitting diodes (OLEDs), and sensors. However, furan containing materials, the oxygen analogs of thiophenes, have received significantly less attention in the literature due to light- and oxygen-induced decomposition.¹ Herein, we report the synthesis of several difuran-based small molecules with different p-block elements such as Si, Ge, P and B.² The heteroatoms play a crucial role in determining the optical and electrochemical properties, as well as enhancing their stability.



POLY 767: Functionalized graphene nanoribbons as semiconducting materials for organic electronics

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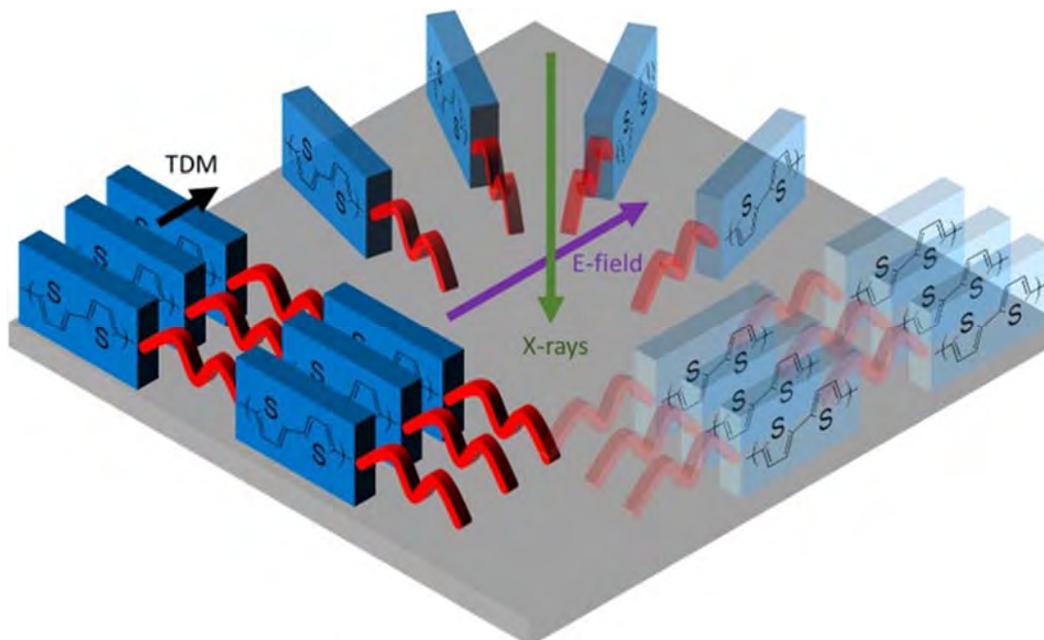
Nanographenes (NGs) and graphene nanoribbons (GNRs) are very promising materials for electronic applications. However, NGs and GNRs produced by physical methods do not allow control over size, shape and functionalization of GNRs, leading to undefined electronic and physical properties. Thus, methods to prepare such materials using the solution-phase bottom-up approach have been proposed. Yet, none of them has been proven as efficient for the introduction of electron-rich and electron-poor units on the edges of GNRs, thus limiting the modulation of their electronic properties. In this regard, our group has revisited and used a photochemical method, called the cyclodehydrochlorination reaction (CDHC), for the regioselective, mild and metal-free synthesis of NGs and GNRs from polychlorinated precursors [1,2]. Although this method is very useful for the synthesis of all-phenyl molecules, very few examples have been reported for the synthesis of heterocycle-fused NGs and GNRs. In this presentation, we will show how the CDHC reaction, a $(4n+2)\pi$ electrocyclization reaction, can be used to prepare well-defined linear and helical NGs and GNRs based on electron-rich heterocyclic motifs such as thiophene, pyrrole and ullazine and electron-poor units such as pyridine and benzothiadiazole. We also show how the CDHC reaction has been used to prepare ladder conjugated polymers (CLPs) with both electron-rich and electron-poor units, thus creating a permanent dipole within the polymer backbone. Carbon nanotubes wrapping, field-effect transistor (OFETs) and bulk heterojunction solar cells (BHJSCs) testing of these new materials will also be presented.



POLY 768: Polarized soft X-ray scattering reveals chain orientation and domain size of conjugated block copolymer lamellae

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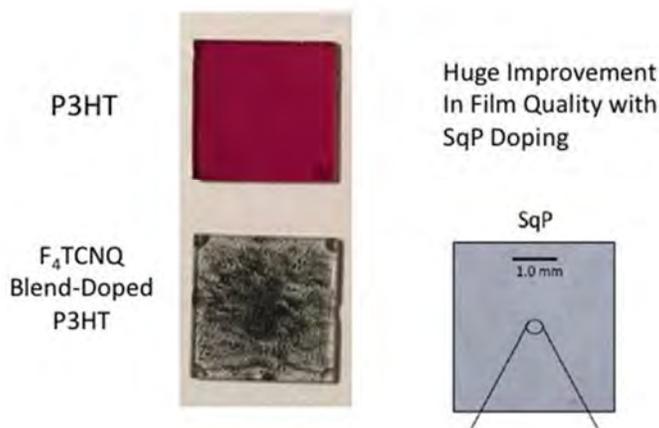
Fully conjugated block copolymers, consisting of covalently bonded donor and acceptor blocks, can serve as the active layer in organic photovoltaics and other organic electronic devices. The use of Resonant Soft X-ray Scattering (RSoXS) allows for studies into the molecular orientation and domain spacing of the polymers by tuning the X-ray energy and polarization to examine various components of block copolymers. Using the conjugated block copolymer system of poly(3-hexylthiophene)-*block*-poly((9,9-dioctylfluorene)-2,7-diyl-alt-[4,7-bis(thiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl), P3HT-*b*-PFTBT, and PFTBT derivatives, we can examine the effects of various polymer blocks on the differences of morphology between the donor and acceptor. Polarized Soft X-Ray Scattering (PSoXS) allows us to quantify the type and the degree of orientation of chains within block copolymer domains in thin films. Further examination of the anisotropy in PSoXS data provides a clear signature of the block copolymer microstructure. Radial distribution and Fourier transform calculations of model polymer structures corroborate this concept of block copolymer domains. Simulated scattering helps predict size, orientation, inhomogeneity, and interfacial width within conjugated block copolymers. Based on our early finding, we believe that within our P3HT-*b*-PFTBT block copolymer films, the crystalline P3HT blocks orient parallel to the block copolymer interface, and we confirm that the domain spacing extracted from PSoXS scales with the end-to-end distance of the blocks. Additionally, there is a correlation between block copolymer device performance and the strength of the anisotropy of the film, as measured by the PSoXS data.



POLY 769: Optoelectronic properties of sequentially-processed, chemically-doped, controlled crystallinity conjugated polymer films

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Chemistry and Biochemistry, UCLA, Los Angeles, California, United States

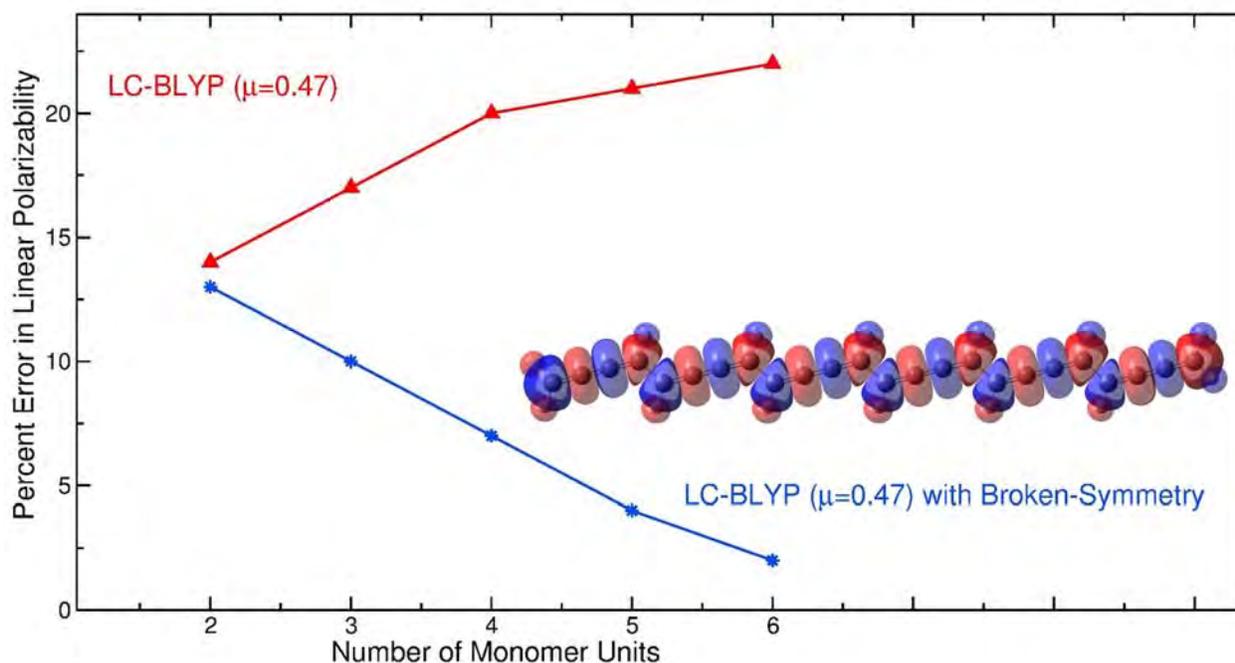
Conjugated polymers are usually doped by mixing an oxidizing agent with the polymer. Typically this is done in solution prior to casting a film of the doped polymer, but as the polymer becomes charged in solution it also becomes less soluble, leading to poor film morphology. We have developed an alternate method for chemically doping polymers that we refer to as sequential processing (SqP). In SqP, a film of the pristine conjugated polymer is cast first, and then the dopant is introduced in a second casting step using a solvent that swells but does not dissolve the underlying polymer. The degree of dopant penetration can be controlled by changing how the solvent in the second step swells the polymer, and the resultant doped film quality is as good as that of the original pristine polymer film. The excellent film quality allows us to easily make electronic measurements, including AC Hall Effect, for understanding carrier concentrations and mobilities. Moreover, since crystalline regions of the polymer do not swell, the crystallinity of the polymer can be controlled in the first casting step and then preserved through the doping process, allowing doping to be studied with a controllably tunable polymer morphology. We present results for a series of conjugated polymers, including P3HT, with a series of molecular dopants. We find that the degree to which the polarons delocalize depend directly on the crystallinity of the polymer film, providing a direct means to tune the carrier mobility and film conductivity. Spectroscopy measurements show that the polaron delocalization and mobility depend on how strongly the dopant anions interact with the polarons; if we choose dopants where the countercharge is kept far from the polymer backbone, we can greatly improve polaron delocalization, mobility and conductivity. At the highest doping levels, we are able to drive many conjugated polymer systems to form bipolarons, whose properties we investigate with ultrafast transient absorption measurements.



POLY 770: Polarizabilities of π -conjugated polymers revisited: Improved results from broken-symmetry, range-separated DFT

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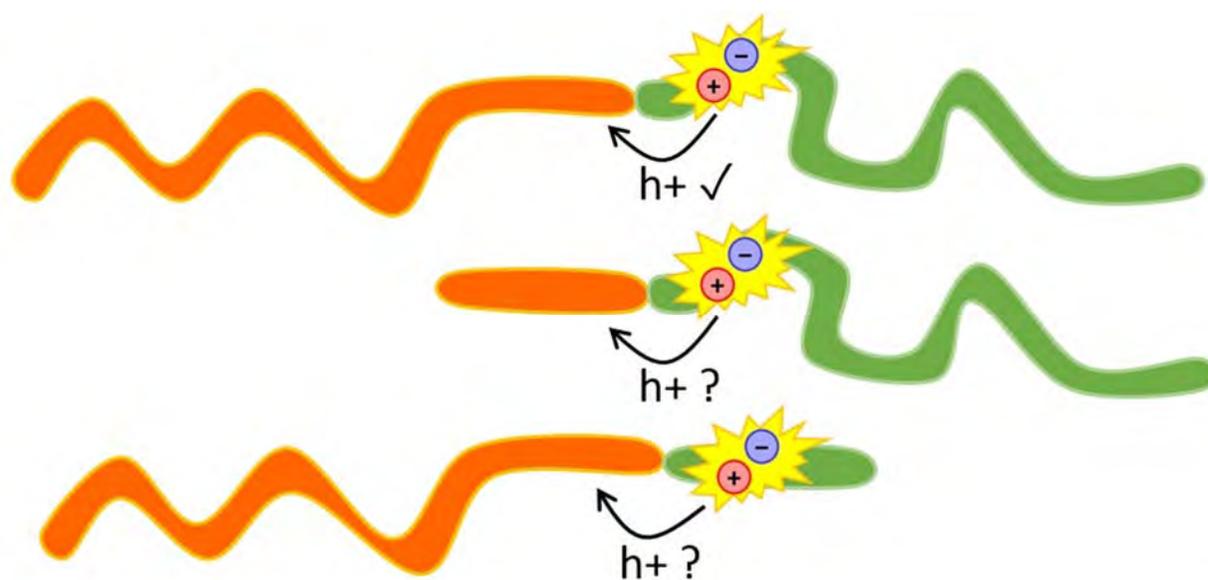
We present a detailed analysis of nonempirically tuned range-separated functionals, with both short- and long-range exchange, for calculating the static linear polarizability and second hyperpolarizabilities of various polydiacetylene (PDA) and polybutatriene (PBT) polymers. Contrary to previous work on these systems, we find that the inclusion of some amount of short-range exchange does improve the accuracy of the computed polarizabilities and second hyperpolarizabilities. Most importantly, in contrast to prior studies on these oligomers, we find that the lowest-energy electronic states for PBT are not closed-shell singlets, and enhanced accuracy with range-separated DFT can be obtained by allowing the system to relax to a lower-energy broken-symmetry solution. Both the computed polarizabilities and second hyperpolarizabilities for PBT are significantly improved with these broken-symmetry solutions when compared to previously published and current benchmarks. In addition to these new analyses, we provide new large-scale CCSD(T) and explicitly correlated CCSD(T)-F12 benchmarks for the PDA and PBT systems, which comprise the most complete and accurate calculations of linear polarizabilities and second hyperpolarizabilities on these systems to date. These new CCSD(T) and CCSD(T)-F12 benchmarks confirm our DFT results and emphasize the importance of broken-symmetry effects when calculating polarizabilities and hyperpolarizabilities of π -conjugated polymers.



POLY 771: Using conjugated block copolymers to examine the dependence of charge transfer on conjugation length

Melissa P. Aplan, mpa150@psu.edu, Enrique Gomez. Chemical Engineering, Penn State University, University Park, Pennsylvania, United States

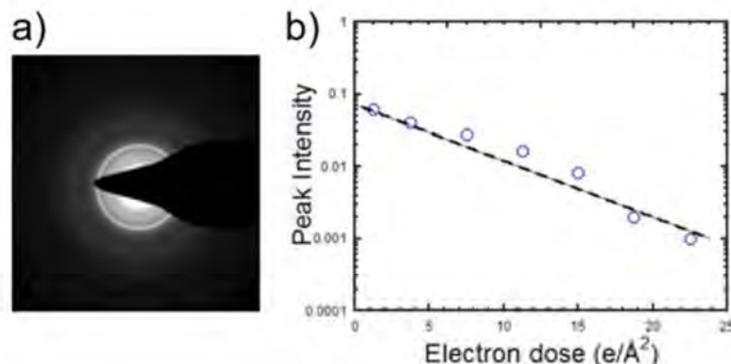
Organic photovoltaics (OPVs) is an exciting field that could have a significant impact on everyday life. Nevertheless, relatively low device efficiencies prevent OPVs from reaching their true potential. The mechanism for photocurrent generation is not fully understood. As it stands, it is challenging to rationally design new high-performing materials. Fully conjugated block copolymers, consisting of an electron donor block and an electron acceptor block, can be used as model systems to examine fundamental processes of charge generation in organic materials. The block copolymers can be fully dispersed in solution, decoupling electronic properties of the material from morphological properties of a thin film. We synthesized a series of fully conjugated block copolymers consisting of a poly(3-hexylthiophene) (P3HT) electron donor and a push-pull polymer electron acceptor, poly-((2,5-dihexylphenylene)-1,4-diyl-alt-[4,7-bis(3-hexylthiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl) (PPT6BT). By altering synthetic conditions, the molecular weight of each block is systematically tuned. Dynamic light scattering confirms that the synthesized block copolymers can be fully dispersed in dilute solutions, enabling studies of photoluminescence quenching within individual chains. The absorption and emission spectra of the block copolymers are deconvoluted to extract the contribution from each block, enabling us to quantify the yield of intramolecular charge transfer states. Taking the data from all block copolymers together, we find a critical conjugation length of the P3HT block required to generate charge transfer states. Interestingly, charge transfer is largely independent of PPT6BT chain length, suggesting that the push-pull character decreases the requirement on conjugation length for efficient charge transfer.



POLY 772: Minimizing beam damage with antioxidants to enable high resolution imaging of conjugated polymers in the electron microscope

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Transmission electron microscopy (TEM) of conjugated polymers has remained a challenge because resolution is limited by the electron dose the sample can handle. We have characterized the effects of beam damage on poly(3-hexylthiophene) (P3HT), poly(3-dodecylthiophene-2,5-diyl) (P3DDT), and poly[(5,6-difluoro-2,1,3-benzothiadiazol-4,7-diyl)-alt-(3,3''-di(2-octyldodecyl)-2,2';5',2'';5'',2'''-quaterthiophene-5,5'''-diyl)] (PffBT4T-2OD) via electron diffraction and scanning TEM electron energy-loss spectroscopy (STEM-EELS). Critical dose D_c values were calculated from the decay of diffraction and low-loss EELS peaks as a function of dose rate, temperature, and the addition of antioxidants. At room temperature, D_c was observed to first increase then decrease with increasing dose rate, whereas at cryogenic conditions this dose rate dependence becomes less pronounced and the overall critical dose increases. D_c is also higher for polymers with higher glass transition temperatures. Altogether, these results suggest that the main mechanism for beam damage in conjugated polymers is diffusion of free radicals. Thus, we show that the addition of free radical scavengers such as butylated hydroxytoluene (BHT) mitigates radiation damage. At room temperature, the addition of BHT increases the critical dose because the diffusion of radicals is halted by BHT, despite the fact that BHT does not incorporate into the polymer crystals where damage is measured. At cryogenic conditions, BHT does not increase the critical dose because diffusion is already suppressed. We predict that the addition of BHT is important to enable high-resolution experiments without cryogenic conditions, such as in-situ experiments under electrical bias. In addition, STEM-EELS beam damage experiments not only reveal that the electronic structure of conjugated polymers decays before the crystal structure but also establish dose limits for high resolution low-loss spectrum imaging of conjugated polymers.



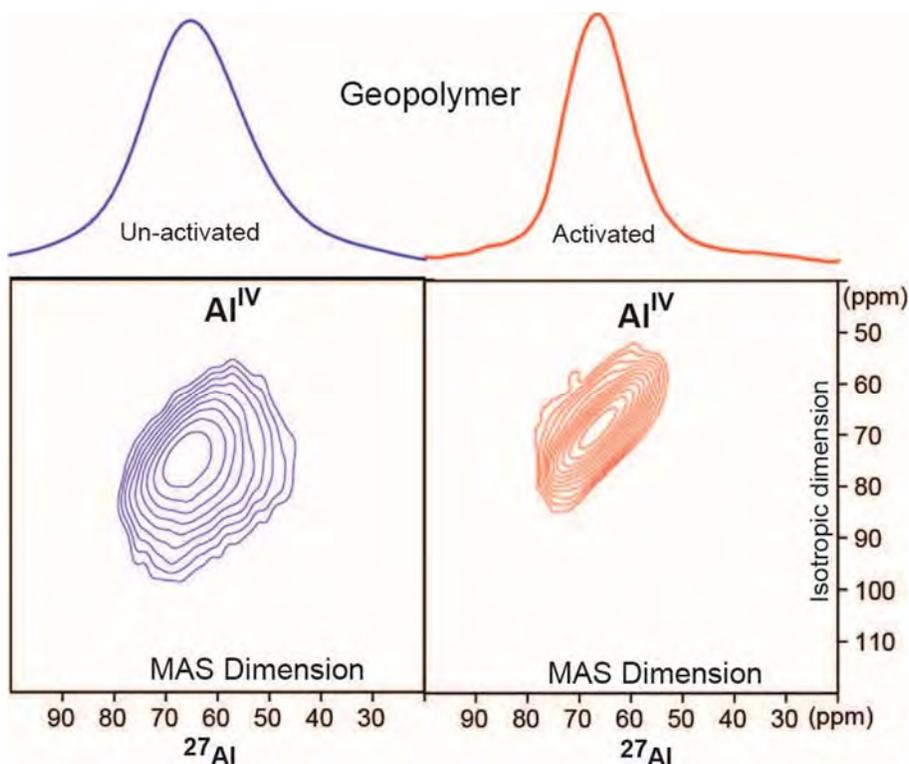
π - π peak intensities extracted from electron diffraction (a) are plotted against electron dose to determine critical dose, as demonstrated in (b) for PffBT4T-2OD at 1 $e/\text{Å}^2$ s (intensities are plotted on a log scale).

POLY 773: Polymers from earth and space

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Inorganic geopolymers and organic interstellar dust analogues are two novel families of complex polymeric materials. Geopolymers are condensed aluminosilicates, synthesized by the alkali activation of waste slag and fly-ash. Interest in these materials stems from their potential as a zero-carbon alternative to ordinary Portland cement. Here we present a detailed multinuclear (^{29}Si , ^{27}Al , ^{23}Na and ^1H) and multidimensional NMR investigation of the structure of two distinct geopolymers synthesized from slag and fly-ash. Insights from NMR are coupled with different microscopy and diffraction techniques to reveal unparalleled details of their local and long range structure.

The space between stars, known as the interstellar medium, is filled at a low density of $\sim 10^3$ atoms/cm 3 , of which $<1\%$ comprises carbon. However a high photon flux ionizes small organic molecules such as acetylene, which condense to form large and complex polymeric structures known as interstellar dust, whose structure is a subject of much debate. By synthesizing interstellar dust analogues (ISDA) in an ionization chamber which mimics the conditions of the interstellar medium, NMR is able to yield novel insights on their structures. Here we present for the first time detailed ^{13}C NMR investigations of ISDA synthesized from acetylene and isoprene precursors, and elucidate the distinct structures formed from these two materials.

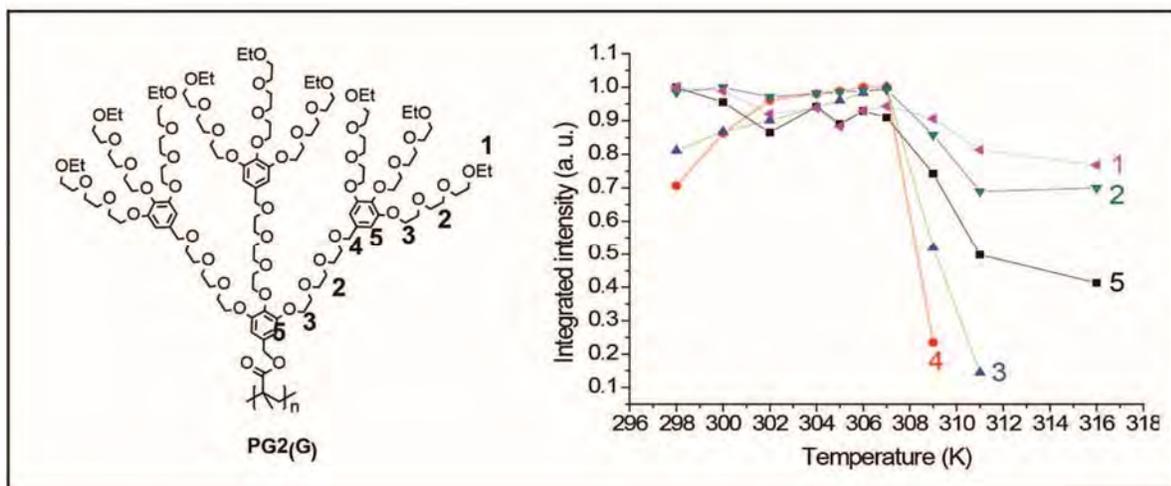


^{27}Al MQMAS of a neat and activated geopolymer.

POLY 774: Solution properties of thermally sensitive macromolecules studied by high resolution NMR and MD simulations

Cheng Zhang², Wen Li¹, Lianxiao Liu¹, James Reid², Stefano Bernard², Debra J. Searles², Hui Peng², Afang Zhang¹, **Andrew Whittaker²**, a.whittaker@uq.edu.au. (1) Department of Polymer Materials, Shanghai University, Shanghai, China (2) AIBN, The University of Queensland, St Lucia, Queensland, Australia

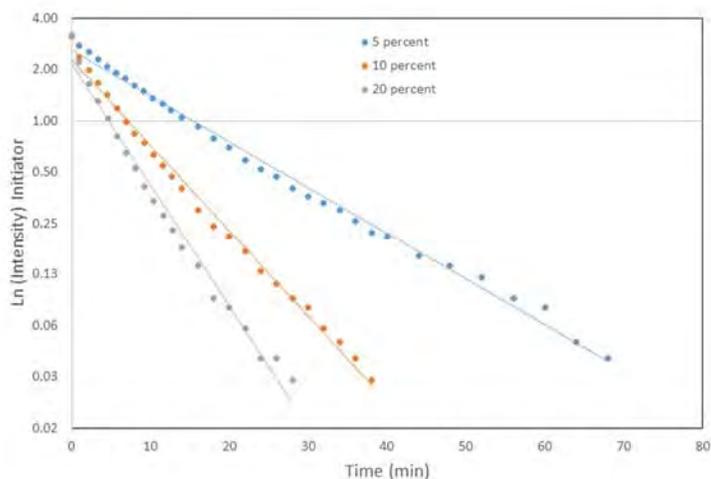
The conformations that synthetic macromolecules adopt in solution are of intense interest particularly in the domain of biomedical research. For most applications in that field, interactions between the synthetic materials and endogenous species within the body are especially critical in determining properties, performance and ultimate fate of the macromolecule. One class of macromolecule intensely exploited in that field over the past several decades are the thermally responsive polymers. In this presentation I will discuss studies of polymer conformation in aqueous solution using high resolution NMR correlation spectroscopy supported by MD simulations, focussing on two classes of materials. Thermoresponsive dendronized polymers, in which pendant dendrons are attached at each repeat unit along the main chain of the polymer, show LCST behaviour, have extremely sharp thermal transitions and negligible thermal hysteresis. Our studies shed new light on the dehydration processes occurring across the LCST. Copolymers of oligoethyleneglycol methacrylate (OEGMA) which also may pass through an LCST on heating, are increasingly seen as an alternative to polymers of N-isopropylacrylamide (NIPAAm) for use in biomedical devices and nanoconstructs. The extent of dehydration of the pendant side chains is much lower in OEGMA polymers compared with PNIPAAm, and as a consequence particles of these polymers retain large-scale segmental mobility. The implications for properties such as biocompatibility and drug release will be discussed.



POLY 775: Characterization of photo-initiated living radical polymerization kinetics with *in-situ* NMR spectroscopy

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Controlled/living radical polymerizations are a facile way to make polymers of well-defined architecture for advanced applications. However, photo-initiated living polymerizations are not as common commercially, as say anionic polymerizations, due to lingering non-ideal behavior of many initiator systems. We have used NMR spectroscopy to follow the fate of many mono- and di-functional xanthate and dithiocarbamate initiators in the polymer chain. The NMR analysis included consumption of the initiator, MW as a function of conversion, and end group analysis to determine the kinetics for initiation of polymer chain growth in the second direction for di-functional initiators. From the end group analysis, some undesired side reactions were also identified. Preliminary studies were done with aliquots taken from the polymerization at different times. This procedure is tedious, and it is difficult to adequately space the time points without prior knowledge of the kinetic rates. In order to obtain more detailed kinetic profiles, an *in-situ* setup was developed using a 365 nm LED light source with a fiber optical cable to directly irradiate the sample in the NMR spectrometer while acquiring data. Using the *in-situ* NMR characterization, detailed kinetic rates were obtained for several initiators to evaluate the fidelity of the living radical process. A number of parameters were varied including UV intensity, temperature, and %solids to assess their impact on the kinetic profiles and undesired side reactions.



POLY 776: NMR analysis of the stereoregularity of poly(lactic acid) through the use of selective solvents

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The physical properties of poly(lactic acid) (PLA) are largely influenced by its stereoregularity and stereosequence distribution. NMR is regarded as the best method to study polymer stereoregularity, and many NMR studies of the stereosequence distribution of PLA have been previously reported. Most of these NMR analyses were carried out in deuterated chloroform at the tetrad level for CH proton and carbon, and partially at the hexad level for the carbonyl carbon. Thus far, no detailed ¹H or ¹³C NMR assignments of CH₃ group have been reported [Fig.1(a)]. In this study, enhancement of the peak separation has been attempted by changing NMR solvents. We found out that pyridine showed a remarkable solvent effect on the NMR spectra (due to ring current effect) and as a result, well-resolved peaks of the methyl proton were successfully obtained [Fig.1(b)]. The peak assignment has been partially made and more work is in progress. Several methods will be employed to enhance our understanding of the NMR spectra of PLA, including the analysis of the relative peak intensities of individual tetrad sequences for PLA samples prepared under different polymerization conditions, monitoring of the peak behavior by changing the ratio of mixed solvents, and two-dimensional NMR experiments.

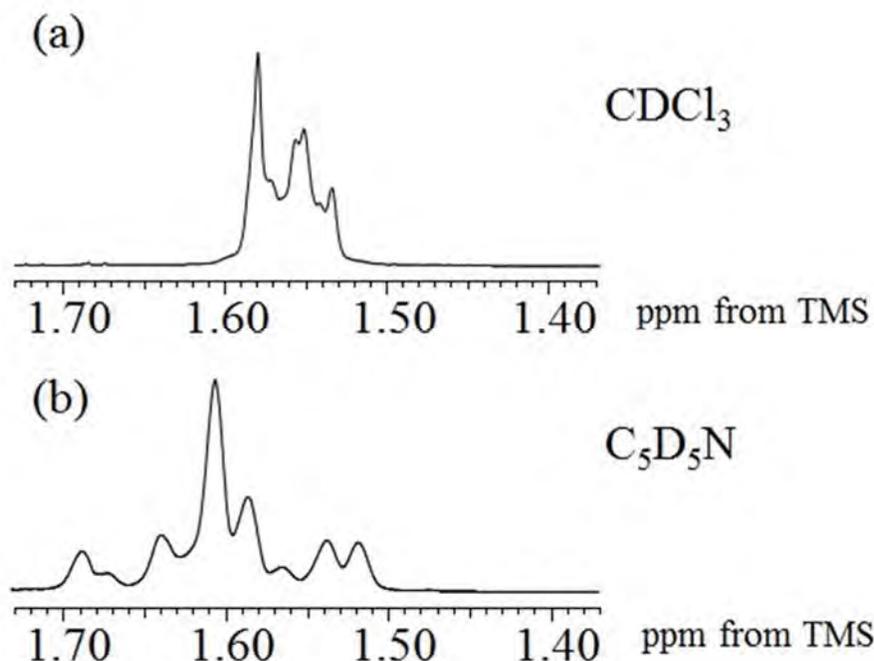
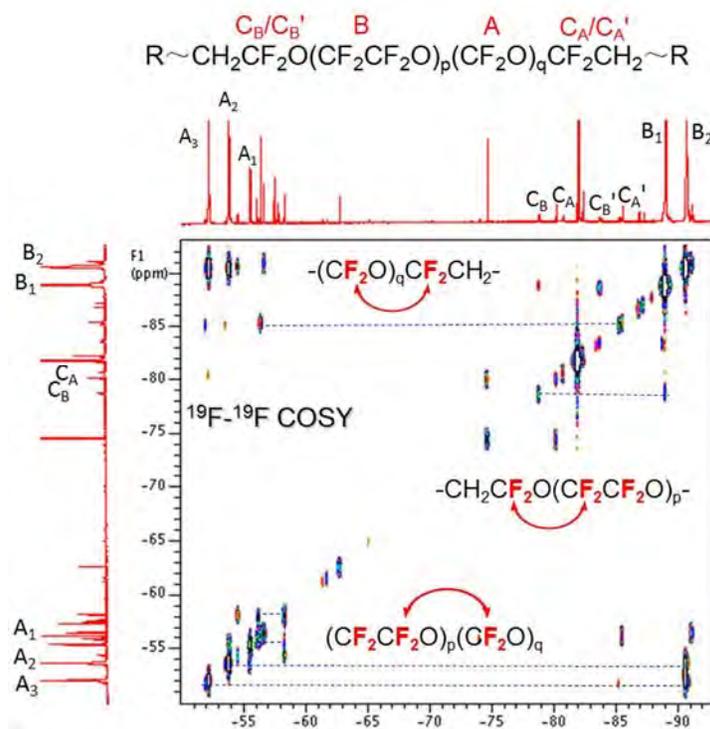


Fig.1 600MHz ¹H NMR spectra of copolymer derived from PLLA and PDLA (the CH₃ proton region).

POLY 777: Multidimensional NMR studies of perfluoropolyether

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 (1) Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, Jiangsu, China (2) Dept. of Chemistry, University of Akron, Akron, Ohio, United States

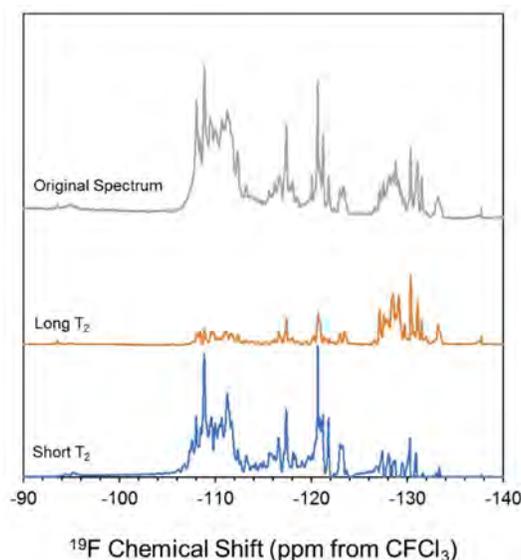
Perfluoropolyether (PFPE), also known as perfluoroalkylether (PFAE) or perfluoropolyalkylether (PFPAE), is a synthetic polymer consists of carbon, oxygen and fluorine atoms. Its excellent lubricant characteristics and lifetime stability, even when exposed to extreme conditions of temperature, pressure and chemically reactive species make it an outstanding material in extensive applications. The exact structure of PFPE plays an important role in affecting the polymer's morphology and physical properties. Thus it is of great interest and importance to understand PFPE's structural characteristics such as monomer- and stereo-sequence effects, chain end and branching structures. A series of PFPE commercially available samples have been studied with multidimensional NMR spectroscopy. The selective regions of $^{19}\text{F}\{^{13}\text{C}\}$ gHSQC and ^{19}F - ^{19}F selective Exo-COSY produced ultra-high resolution of 2D-NMR spectra for PFPE samples. Signals can be resolved from the complex mixture of monomer- and stereo-sequences present in the polymers. The chain-end structures and possible isomeric fractions have been identified. It provides a reliable means to study the primary and microstructures of PFPE fluoropolymers, which gives valuable information about polymerization conditions, physical properties and structure-property relationships.



POLY 778: Advanced NMR methods for determining sequence distributions in fluoropolymer elastomers

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The fluoropolymer elastomer Kelf-800 and its replacement FK-800 are synthesized by the radical co-polymerization of polychlorotrifluoroethylene (PCTFE) and polyvinylidene fluoride (PVDF) in a nominal 3:1 ratio. The resulting random monomer distribution produces a complex ^{19}F NMR spectrum of hundreds of overlapping, broad peaks that make sequence distribution assignment impossible without the aid of advanced 2D or 3D NMR spectroscopic methods. The $^{19}\text{F}\{^{13}\text{C}\}$ HMQC data sets of these materials still produce NMR contour maps containing hundreds of cross peaks. In this submission, we illustrate the use of T_2 filtering and covariance NMR methods that allow us to greatly simplify complex 2D NMR spectral data and allow us to begin making assignments to discrete monomer sequences. In this system, the strong cross relaxation effects from ^1H in the VDF monomer exhibit a strong effect on the T_2 decay of neighboring ^{19}F species. This effect produces two discrete populations of ^{19}F peaks that can be extracted by bulk fitting of ^{19}F spectra collected as a function of T_2 decay. These components can be used in covariance methods where they are transformed into pseudo-2D data sets and used to filter $^{19}\text{F}\{^{13}\text{C}\}$ HMQC and HSQC data sets. Comparison data will be presented from other ^1H containing fluoropolymer co-polymers in addition to Kelf-800/Fk-800

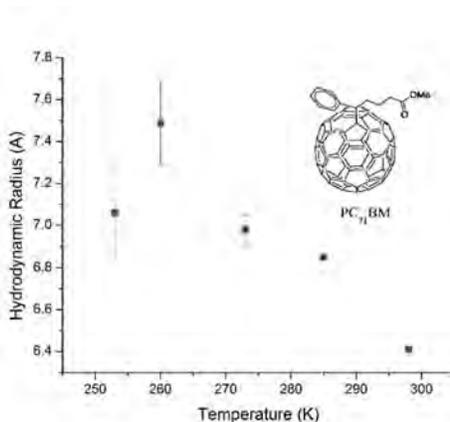


Stacked ^{19}F NMR spectra from a sample of FK-800. Top spectrum is as collected. The bottom two represent the short and long T_2 filtered data

POLY 779: Making NMR more accessible

Weiguo Hu, *weiguo_hu@yahoo.com*. University of Massachusetts, Amherst, Massachusetts, United States

This presentation attempts to supply some thoughts on the persistent disconnect between the vast power of NMR and the relatively small fraction of it that is tapped by the broad research community. From the educational aspect, both solution- and solid-state NMR classes could be taught to non-NMR-experts without invoking quantum mechanics while retaining the academic rigor. Several examples will be discussed in which the NMR techniques involved are simple enough for beginning NMR users to navigate yet generate impactful insights: (1) The hydrolytic degradation mechanism of poly(*p*-phenylene-2,6-benzobisoxazole) (PBO) fiber, the strongest commercial fiber yet suffering from a crippling degradation problem, by ^{31}P NMR; (2) using diffusion NMR to study the association behavior of photovoltaic molecules in solution and the molecular weight of polymers.

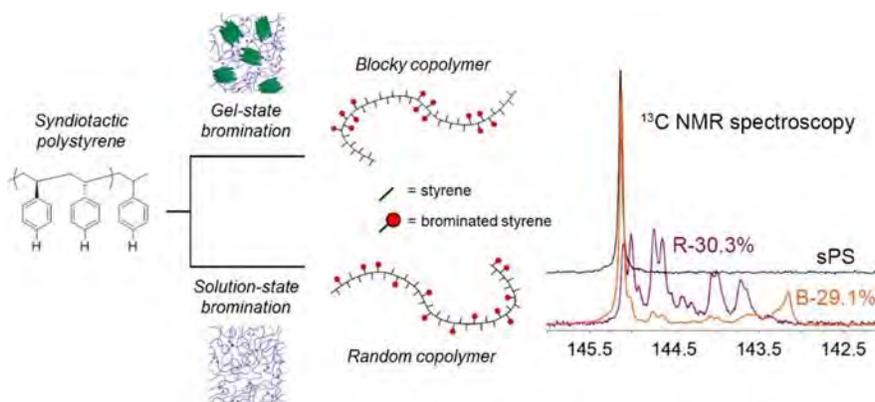


Hydrodynamic radius of PC₇₁BM in toluene as measured by NMR.

POLY 780: Evaluating co-monomer sequence distribution in brominated syndiotactic polystyrene (sPS-Br) copolymers using ^{13}C NMR spectroscopy

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^{13}C NMR spectroscopy has been used to evaluate co-monomer sequence distribution in brominated syndiotactic polystyrene (sPS-Br) copolymers prepared via a post-polymerization functionalization method carried out in solution and in a heterogeneous gel state. Bromination in solution produces sPS-Br copolymers with random architectures, while gel-state functionalization is expected to produce copolymers with blocky architectures through selective bromination of the amorphous polymer chain segments that interconnect the gel's crystalline domains. NMR spectroscopy experiments were used to characterize the microstructural differences between solution-state and gel-state sPS-Br copolymers, prepared in a matched set with degrees of bromination ranging from 6-30 mol% Br. Here, I will discuss assignment of the carbon resonance spectra of random and blocky sPS-Br copolymers to triad and pentad co-monomer sequences using 1D and 2D NMR spectroscopy experiments. Co-monomer sequence distributions were found to be in excellent agreement with Monte Carlo-type simulations of 2000 statistical sPS-Br copolymer chains.



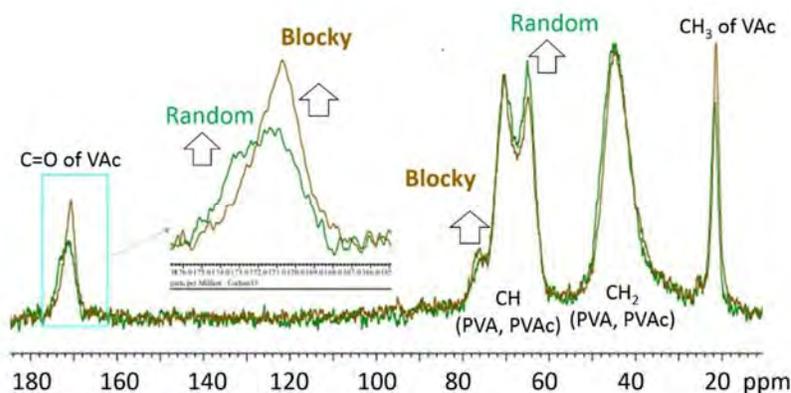
POLY 781: Structure analysis of blockiness controlled poly (vinyl alcohol-co-vinyl acetate) by NMR

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Poly (vinyl alcohol -co-vinyl acetate) (VA-VAc copolymer) is an industrially important polymer used for various applications such as polarizing films, water-soluble films and scaffolds for cells. VA-VAc copolymer has many hydroxyl groups in its structure, which affects the higher order structures forming hydrogen bonds, resulting in a large change in solubility, elastic modulus and thermodynamic properties. Therefore, the effect of blockiness of this copolymer on the higher order structure is important and interesting. Recently, we have found a method to control blockiness of VA-VAc copolymer by using ate complex which is a transesterification catalyst. This technique can easily change only the blockiness of copolymers with constant molecular weight and composition ratio. By changing only blockiness, it's possible to analyze the correlation between blockiness and higher order structure.

In this study, we prepared several VA-VAc copolymer samples with controlled blockiness and analyzed their primary structures using solution ¹H NMR. As a result, it was found that copolymers with different blockiness were obtained depending on the treatment time with the ate complex. Using some copolymers as raw materials film samples were prepared, and the higher order structures were analyzed using solid state ¹³C NMR. From the CP/MAS spectra, it was found that the state of formation of hydrogen bonds in the film and the molecular motion are different due to the change of blockiness. From the water solubility test of these films, a large difference in water solubility was observed due to varied blockiness.

In the presentation, we'll also introduce correlation analysis between the primary structure and higher order structure using two-dimensional correlation spectroscopy (2D-COS).



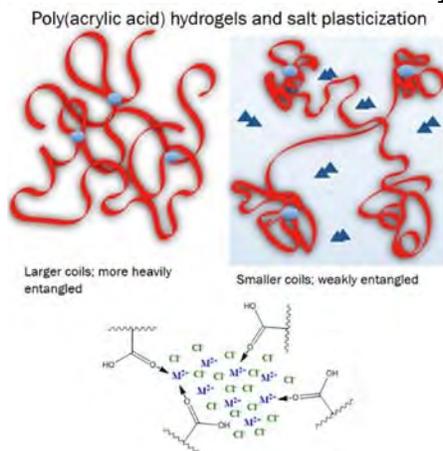
Comparison of ¹³C CP/MAS spectra of blocky copolymer and random copolymer. Changes in CH and carbonyl peaks appear depending on blockiness.

POLY 782: Enhanced elasticity and property modification of poly(acrylic acid) and other polyelectrolytes: Studying and modeling the effects of salts and ionic liquids added during synthesis on material behavior

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Polyelectrolyte gels, namely poly(acrylic acid) (PAA), synthesized in the presence of high-molarity salts or ionic liquids exhibit fascinating behaviors that are much different from PAA gels synthesized without salt, even when the latter are incubated in high-molarity salt solutions. The most prominent feature of these materials is a marked enhancement in mechanical strength and high elongation, with near-complete recovery. The enhanced mechanical properties of these high salt-loaded gels significantly diminish upon washing the materials with water to remove the salt, and cannot be restored upon incubation in solutions containing equivalent concentrations of salt, indicating that the addition of salts or ionic liquids during synthesis is critical to property enhancement. This enhanced elasticity is thought to be brought about by phase-separated regions of salt acting as a plasticizer and modulating intermolecular interactions between AA units. As no base is employed during or after synthesis to neutralize AA units, the gels are believed to be substantially unionized, leading to unique polymer-polymer and polymer-solvent interactions when in the presence of salt.

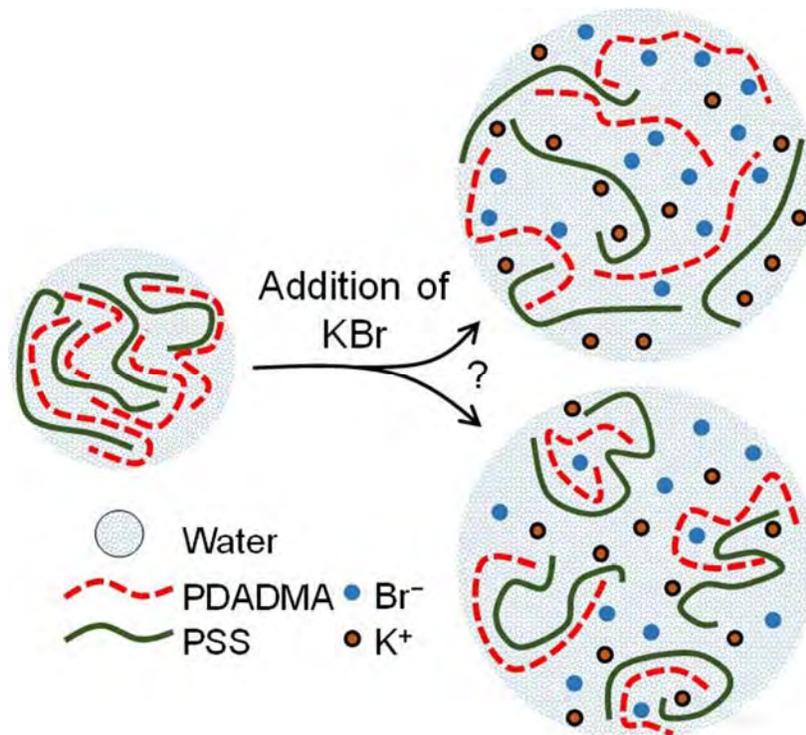
This study focused on the addition of a wide variety of salts during synthesis, including chloride salts of cobalt, zinc, lithium, rubidium, and sodium. Besides chloride salts, carbonate, nitrate, sulfate, and bromide salts, as well as ionic liquids, have been studied. In addition to characterizing the changes exhibited by these materials, this phase of the project has focused on analyzing the structure of these materials and to understand the cause of the enhanced properties. Techniques such as x-ray scattering, including x-ray absorption fine structure (XAFS), neutron scattering, and atomic force microscopy have been used to probe these systems to develop a more complete understanding of the unique molecular interactions that they exhibit.



POLY 783: Chain conformation in polyelectrolyte complexes, from solids to gels

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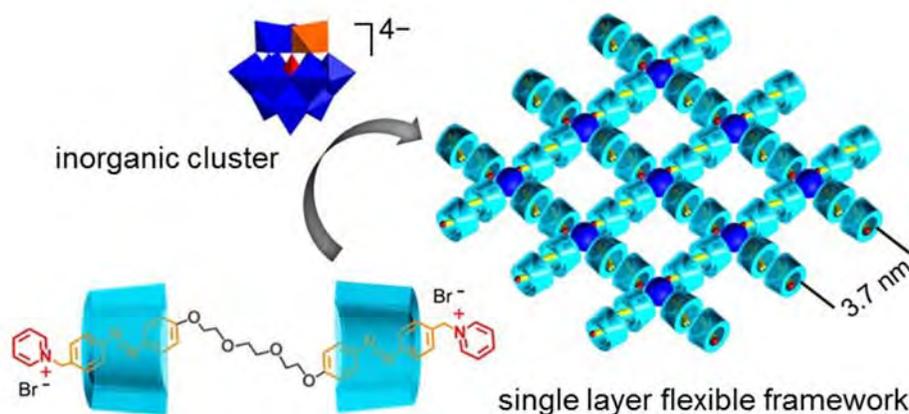
Mixing oppositely charged polyelectrolytes in solution results in stoichiometric precipitates. These products of polyelectrolyte complexation are usually porous, brittle, and challenging to put into use, but can be processed further to obtain a wide range of materials. By adding salt, a full spectrum of partly associated complexes can be accessed from rubbery solids to coacervates. Coacervates are phase-separated solution mixtures made of a gel-like phase and a liquid phase. Using complexes made from a well-known polyelectrolyte pair, poly(diallyldimethylammonium) (PDADMA) and poly(styrenesulfonate) (PSS), chain conformation was probed in a wide spectrum of assemblies, ranging from solids to decreasingly viscous gels. Neutron scattering was employed to investigate the coil dimensions of deuterated PSS inserted in specific quantities in the PDADMA/PSS complex prepared with KBr. Through contrast matching, the PSS chain is isolated from, but observed in, its complex environment. The polyanion was found to maintain a constant radius of gyration and an ideal Gaussian conformation in the solid material. However, as more KBr was added, the chain size started to shrink. A comparison was made with the same polyanion in the presence of salt alone using light scattering, excluding the effect of the polycation. The analysis reveals details about the internal structure of these complexes and a better understanding of polymer dynamics in polyelectrolyte assemblies.



POLY 784: Gels and frameworks comprising of organic linkers and polyanionic clusters via non-covalent bonding towards membranes for filtration and separation

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Nanoporous structures within two and three dimensions have attracted huge interest over recent years because of their potentials as advanced materials in fundamental research and for industrial applications. The main drawbacks are the difficulties to mold thin membrane in large scale because of the coordination interaction and/or covalent bond. To improve the combination, flexible binding such as electrostatic force should be considered if the non-saturation and non-preferential binding angles can be controlled. Fortunately, polyoxometalates (POMs) as a family of nanosized polyanionic clusters have demonstrated good merits in fabrication of hybrid self-assemblies due to their diverse composition and topology. Importantly, multi-negative charges around the surface of POMs are delocalized, making the clusters ideal candidates as the nodes for soft framework architectures through flexible intermolecular interaction. In this presentation, we succeed in creating flexible single molecular layer ionic POM cluster organic frameworks (shown in Figure) with unprecedented uniform orthogonal pores in large area. The bola-form cations with azobenzene and flexible spacer are used as the stick bridging POMs via charge compensation. The soft membrane bearing well-defined framework structure can be prepared feasibly and the pore size can be modulated for precise size-selective separation of quantum dots. Detailed characterizations and discussions support the proposed understanding. Following the results, we introduced the host-guest interaction to realize the construction of network structure in organic phase. The formed organic gels spreading on the support also perform the membrane function for separation of organic solution from aqueous phase. The present idea is illuminative in supramolecular polymers and porous materials because the obtained single layer ionic cluster-organic framework also demonstrates potentials in absorption-separation, catalysis, and bio-filtration.



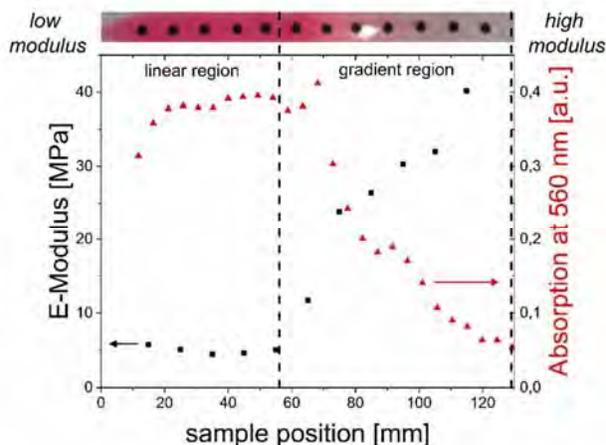
Assembly structure of flexible single layer framework via electrostatic interaction

POLY 785: Soft-hard polymer gradient materials based on thermoreversible urea-siloxane networks

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(AB)_n-segmented poly(urea-siloxane)s are thermoplastic elastomers (TPE), composed of urea-hard segments and poly(dimethylsiloxane) (PDMS) soft segments. These TPEs form stable elastic networks at room temperature due to hydrogen bonding of the urea units. Upon heating, the physical crosslinks disaggregate and melt processing of the material is possible. Poly(urea-siloxane)s are synthesized via polyaddition of diisocyanates and PDMS-diamines with different chain length in order to provide polymers with different transition temperatures, melt viscosities and mechanical properties. The melt viscosity was further tuned to process the polymers with our melt gradient setup by adjusting the molecular weight.

Bulk polymer gradient materials (PGM) are materials which change their composition and consequently at least one property continuously along one axis. So far PGMs are mainly based on low viscous fluid prepolymers which form covalent irreversible crosslinks upon photo- or thermal polymerization. In order to fabricate PGMs from the melt, a heated syringe pump setup for melt processing up to 200 °C was installed. This setup includes two heatable syringes being connected via metal capillaries to a heated static mixer. From each syringe one molten component can be pumped into the static mixer and finally being extruded into a Teflon mold. The gradient is generated by applying a certain flow profile, resulting in an elastic material with a gradually changing modulus. For the PGM we used two poly(urea-siloxane)s differing in their Young's modulus, which are based on 1,6-hexamethylene diisocyanate and PDMS-diamines with different chain length. The fabricated PGM was optically visualized via UV-Vis measurements by adding an UV-active dye to the soft component. Determination of the Young's moduli at distinct measuring points along the sample axis proved the continuously changing modulus from a soft to a stiff material.

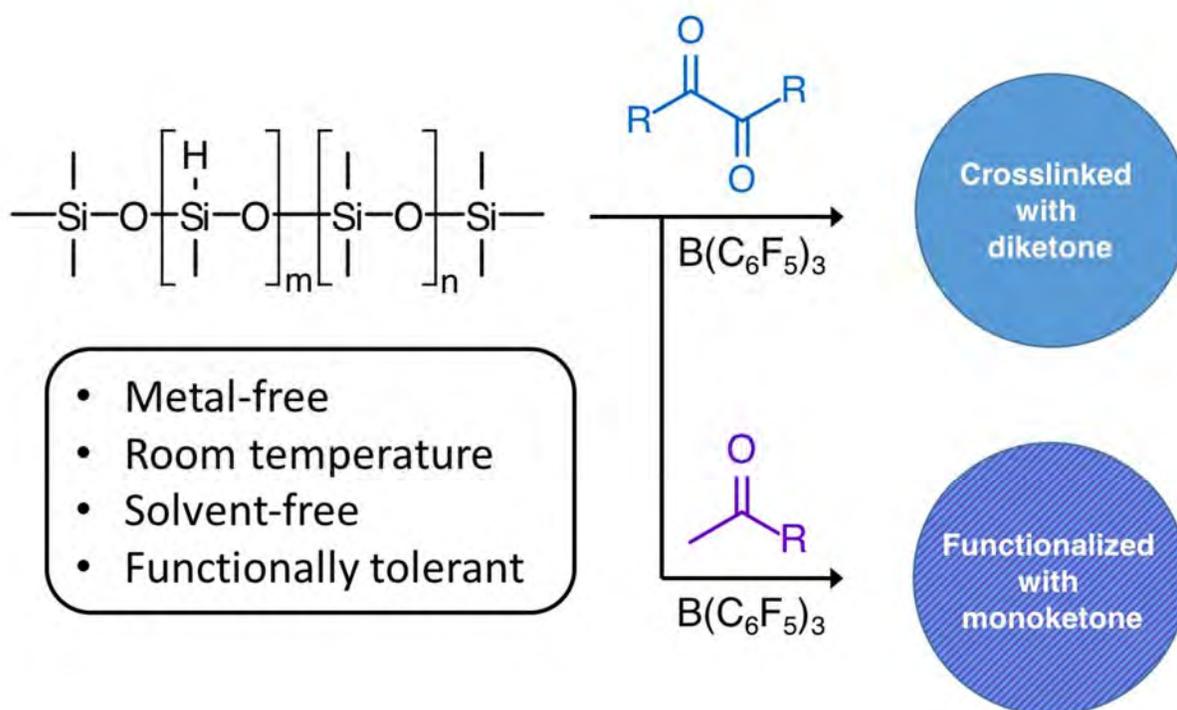


Optical visualization and mechanical characterization of PGM based on urea-siloxane TPEs, starting from a low modulus (5 MPa) to a stiff modulus (40 MPa).

POLY 786: Metal-free borane hydrosilylation as a mild route to diverse silicones

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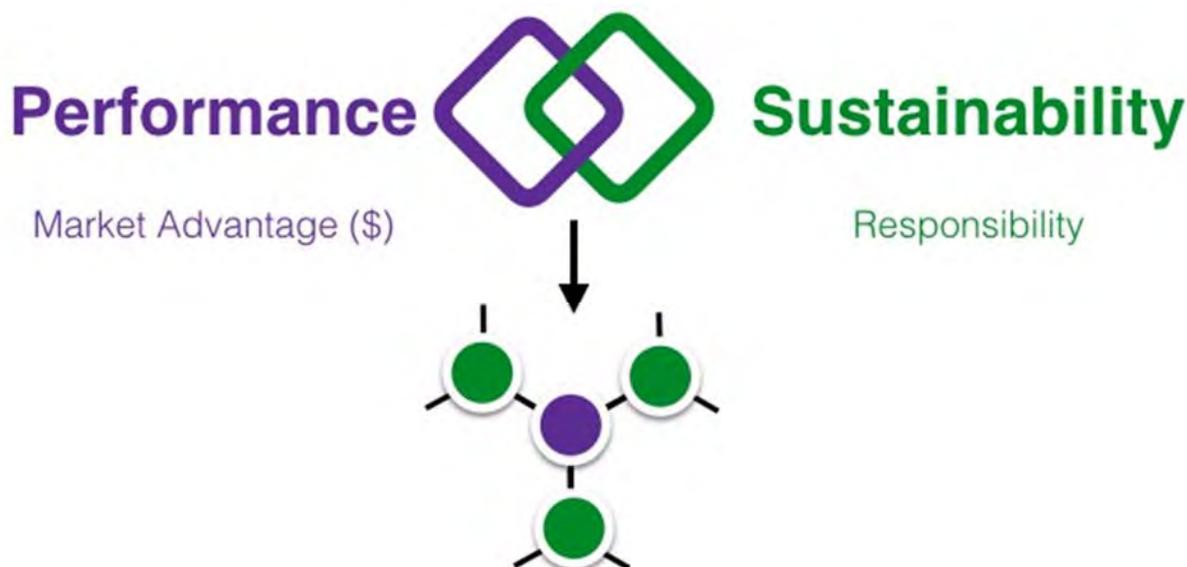
Silicone elastomers have wide utility due to their high thermal and chemical stability, excellent processibility, and good biocompatibility. Current strategies to achieve room temperature vulcanization rely on the use of tin or platinum catalysts, which, while effective, are limited by their toxicity or high cost, respectively. We present a novel route to silicone elastomers that takes advantage of environmentally friendly, low-cost borane chemistry to vulcanize siloxanes via metal-free hydrosilylation using commercially available siloxanes and diketones. This technique can be used to produce silicone elastomers with tailorable mechanical properties as well as to introduce chemical handles for post-vulcanization functionalization.



POLY 787: Molecular design strategies for recyclable, high-performance networked polymers based on new dynamic covalent bonding motifs

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Networked polymeric materials that incorporate dynamic covalent bonds exhibit useful, reconfigurable character. Here I will describe our recent efforts in understanding and controlling the fundamental physiochemical aspects of such dynamic bonds, with a particular focus on new "clickable" dynamic covalent bonding motifs. Our polymer networks overcome many of the challenges in the field of vitrimers, particularly regarding activation barriers to bond exchange, glass transition temperature, and reprocessing (e.g., de-polymerization). Our work suggests that we are only at the beginning of a revolution in smarter polymers designed for both high performance, durability, and sustainability.

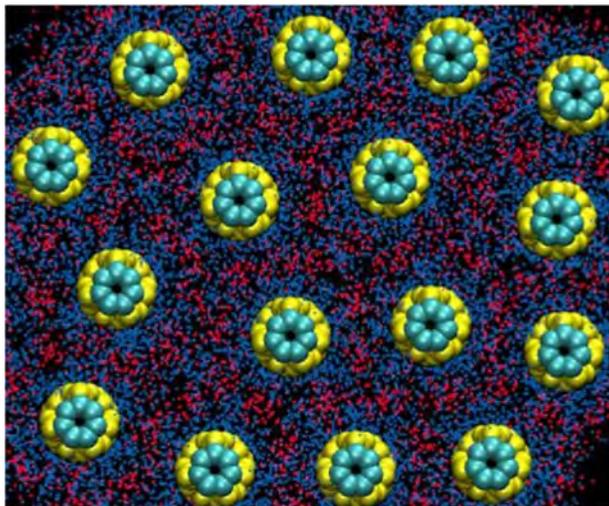


POLY 788: Molecular ionic composites: Stiff solids with liquid-like ions inside

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The interplay of massively collective non-covalent interactions can give rise to surprising bulk material properties. I will describe a new type of solid material that simultaneously possesses a high mechanical stiffness and yet free (liquid-like) ion motions inside. We build this material from a rigid-rod ionic polymer (essentially sulfonated Kevlar) and a strongly correlated liquid (an ionic liquid). We call this new class of materials “molecular ionic composites” (MICs).

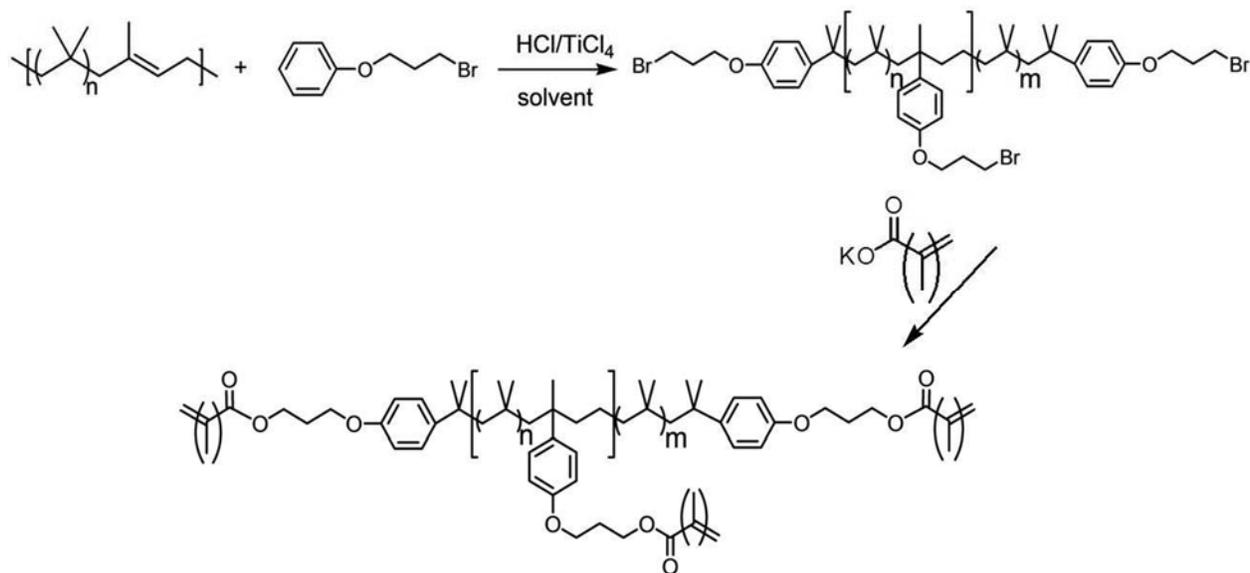
By contemplating the non-covalent forces and anisotropy present in these systems, we can understand the correlated “electrostatic network” that arises in MICs. The figure shows an MD simulated view of a MIC, looking down the polyanion rod axes (yellow sulfonates and turquoise polymer backbones), which are surrounded by correlated clouds of ionic liquid cations (blue) and anions (red). The sulfonated rigid-rod polymer forms a helical dimer that helps provide a rigidity persistence length of ~ 100 nanometers along the rod axis. The high stiffness (E' up to 3 GPa), high thermal stability (up to 300 deg. C), high conductivity (up to 8 mS/cm), and anisotropic properties of MICs show promise for enabling safe and higher density rechargeable batteries as well as other electrochemical devices. This talk will overview our attempts to understand and design the behaviors of MICs from atomic to bulk length scales by combining NMR spectroscopy and diffusometry, MD simulations, dielectric spectroscopy, shear rheology, tensile testing, X-ray diffraction, and a host of other characterization techniques.



POLY 789: Photocured networks from polyisobutylene macromers

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Isobutylene containing polymers have been used in a wide variety of specialized applications such as adhesives, sealants, and strength modifiers due to their low gas permeability, excellent damping characteristics, and resistance to harsh solvents and stress cracking. To impart mechanical stability, crosslinking is desirable in many applications. However, polyisobutylene (PIB) homopolymers cannot be crosslinked without some modification either along the backbone or at the chain termini. Traditionally this has been done by copolymerization with isoprene (butyl rubber) to create a sulfur-vulcanizable rubber. As an alternative curing process, we have recently described photocurable (meth)acrylate macromers obtained by end quenching of living carbocationic PIB. Herein, we describe the constructive degradation of butyl rubber to provide PIB based photocurable macromers containing both side-chain and terminal (meth)acrylate moieties. We will compare the curing kinetics, viscoelastic properties, and calculated crosslink densities of these systems to those previously obtained by the end quenching approach.

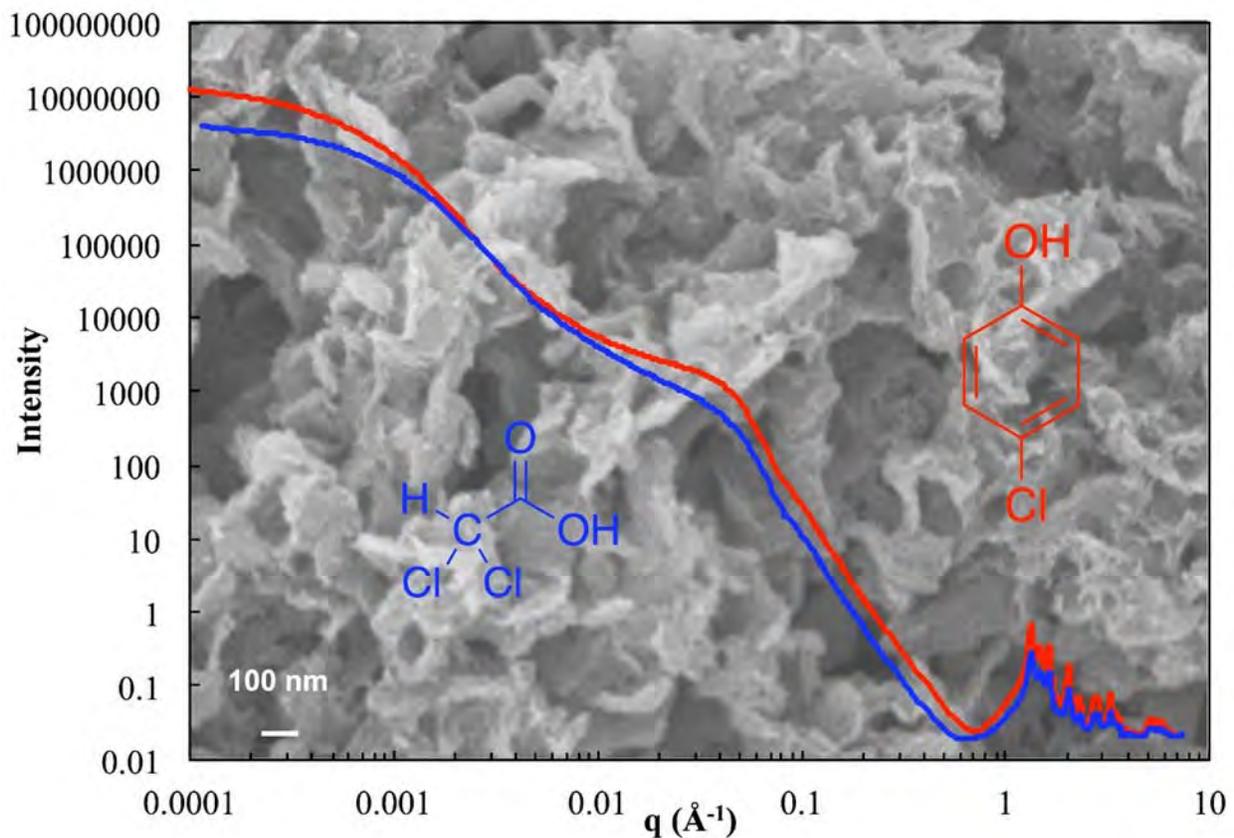


Synthetic outline towards photopolymerizable PIB macromers via constructive degradation.

POLY 790: Influence of processing conditions on morphological features in poly(ether ether ketone) gels and aerogels

Samantha Talley, *sjtalley@vt.edu*, Robert B. Moore. Virginia Tech, Blacksburg, Virginia, United States

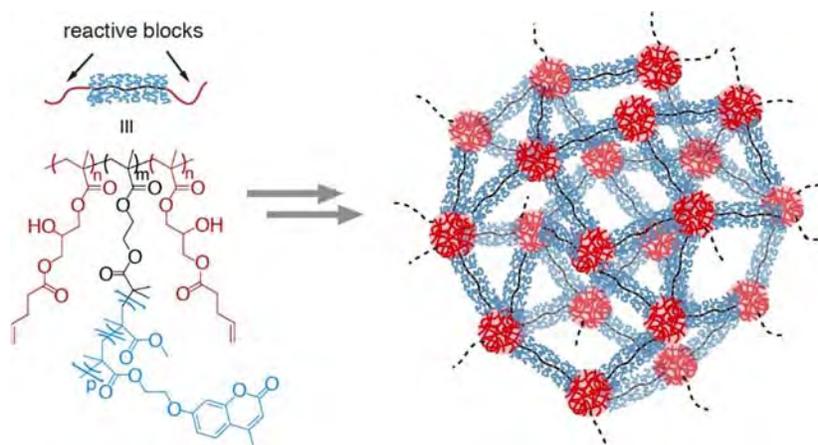
Poly(ether ether ketone) (PEEK) is of particular interest as an engineering thermoplastic due to its high temperature thermal transitions, high crystallizability, mechanical strength, and low chemical reactivity. The effort to find new solvents capable of dissolving PEEK has produced relatively few solvent options, and, only recently, solvents in which PEEK will form stable gels, hydrogels, and aerogels following solvent exchange. In this report, small angle x-ray scattering and scanning electron microscopy are utilized as complementary techniques to characterize the hierarchical nanostructure of PEEK gels. The form and spatial distribution of the morphological features are correlated to processing conditions such as solvent selection, drying technique (freeze-drying versus supercritical CO₂ extraction), and gel concentration.



POLY 791: Synthesis of mesoporous polymer frameworks from end-reactive bottlebrush copolymers

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Molecular framework approaches allow for the fabrication of nanoporous materials with pore dimensions limited to the length scale of the utilized rigid molecular building blocks (< 5 nm). The inherent flexibility of linear polymers precludes their utilization as long framework connectors for the extension of this strategy to larger length scales. We developed a method for the fabrication of mesoporous frameworks by using bottlebrush copolymers with reactive end blocks serving as rigid macromolecular interconnectors with directional reactivity. Orthogonally cross-linkable functionalities placed at bottlebrush ends and side chains were used for network formation and reinforcement of bottlebrush bridges connecting the network junction points. Dual-reactive bottlebrush copolymers with pendant alkene functionalities and photoactive coumarin side chains were synthesized by a combination of controlled radical polymerization and polymer modification protocols. Polymer networks were constructed by Ru-catalyzed cross-metathesis cross-linking of bottlebrush copolymers where isolated cross-linked domains were interconnected with bottlebrush copolymer bridges. Mesoporous polymer frameworks with average pore diameters of 9-50 nm were obtained by simple solvent removal without necessitating templating, chemical etching or supercritical drying. Pore dimensions were conveniently tunable by the length of the utilized bottlebrush copolymer building blocks. The materials fabrication strategy described in this work expands the length scale of molecular framework materials and provides access to mesoporous polymers with a molecularly tunable reticulated pore structure.

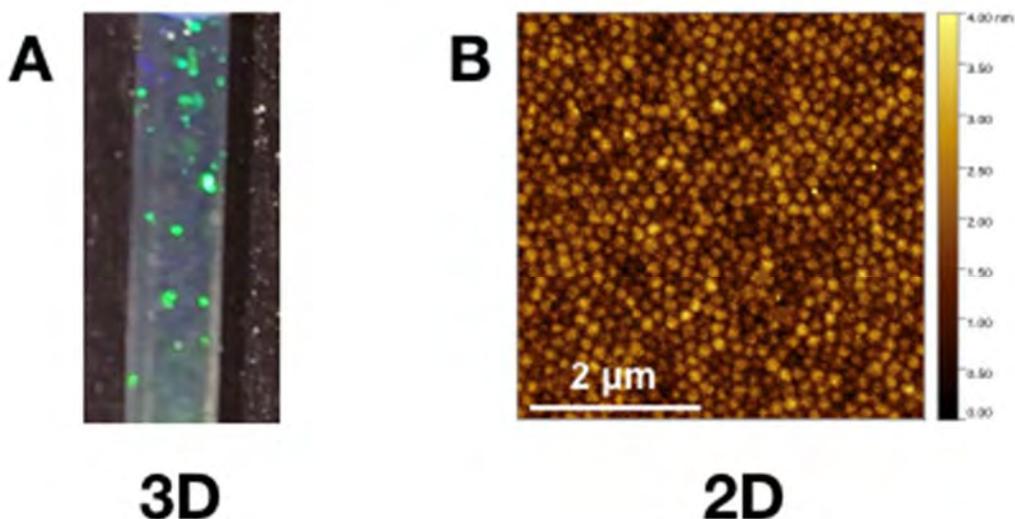


POLY 792: Ultra low crosslinked microgels are ordered in bulk and disordered in two-dimensions

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The interplay between softness and liquid-to-solid transition is one of the more general problem in nature. In this contribution we present the phase behavior of water suspensions of ultra low crosslinked poly(*N*-isopropylacrylamide) microgels is studied in three and two-dimensions. In three-dimensions the phase behavior is comparable to the one of regular crosslinked microgels: Coexistence between crystals and liquid and fully crystalline samples are observed (Fig. 1A). Small-angle neutron scattering measurements of the single particle form factors show no failure of the spherical shape, both in crystalline and disordered, overcrowded samples. At the oil-water interface, the compressions isotherms and the analysis of the atomic force microscopy images of depositions at different concentrations of the microgels reveal that in two-dimensions the crystallization is suppressed (Fig. 1B). The reason for this is the wide variation of the particle bulk moduli together with the reduced mobility of the particles due to the confinement. Furthermore, the degree of compression can be used to switch the property of the depositions from the linear polymer-like to the one of a suspension of colloidal particles.

Fig. 1 A) Crystals formed by the ultra low crosslinked microgels in water suspensions, three dimensional. B) Disordered arrangement of microgels imaged with atomic force microscope after deposition, two dimensional.



POLY 793: Cationic, anionic, or amphoteric dual pH/temperature-responsive degradable microgels via self-assembly of oligomeric precursor polymers for drug delivery

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“Smart” microgels based on poly(N-isopropylacrylamide) (PNIPAM) have attracted interest in many biomedical and environmental applications given that they can shrink and/or aggregate upon heating. By copolymerizing acidic or basic comonomers, pH-responsiveness can be introduced to create dual responsive microgel systems useful for ion exchange, drug delivery, environmental sorption, and other applications. In particular, the capacity of dual responsive microgels to deswell and/or aggregate at a specific pH/temperature combination indicative of cancerous tumors (which are generally slightly warmer and more acidic than healthy tissues) offers unique potential for physically targeting drug delivery to cancer microenvironments. However, conventional precipitation-based PNIPAM microgels are non-degradable, limiting the utility of such microgels in drug delivery applications. In response, we have developed a novel approach to overcome this limitation by creating degradable thermosensitive microgels by the controlled precipitation of well-defined hydrazide and aldehyde-functionalized PNIPAM oligomers. This thermally driven self-assembly approach enables the formation of a hydrolytically-labile hydrazone cross-linked network that can break down over time into oligomeric by-products of molecular weights below the renal filtration limit. By functionalizing either oligomer with anionic (acrylic acid) and cationic (N,N-dimethylaminoethyl methacrylate) comonomers and performing self-assembly, microgels with cationic, anionic, and amphoteric charges can be prepared. The resulting microgels exhibit the same pH and temperature-responsive particle sizes and zeta potentials as conventional microgels (Fig. 1). Furthermore, by adding a moderately water soluble drug (dexamethasone) into the pre-assembly solution, direct drug loading into the microgel during self-assembly can be achieved with high encapsulation efficiencies (>95%) and slow drug release. These results, coupled with the degradability of these microgels, suggest improved performance in applications demanding dual pH/temperature specific drug delivery.

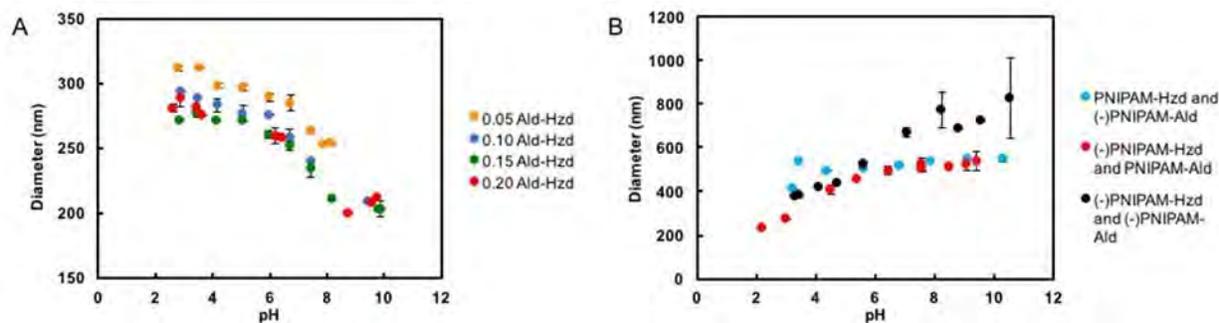
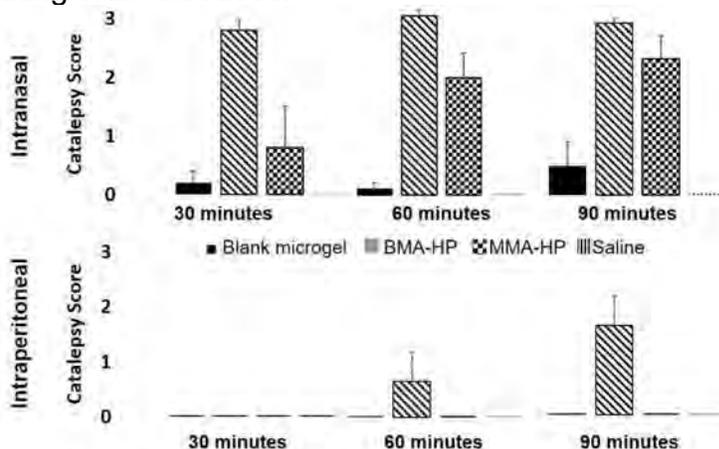


Fig.1: Diameter versus pH for single-charged PNIPAM self-assembled microgels; (A) cationic (at different crosslinker ratios) and (B) anionic (at different combinations of anionic pre-polymers)

POLY 794: Hydrophobically-modified poly(oligoethylene glycol methacrylate)-based nanogels for the delivery of anti-psychotic drugs to the brain

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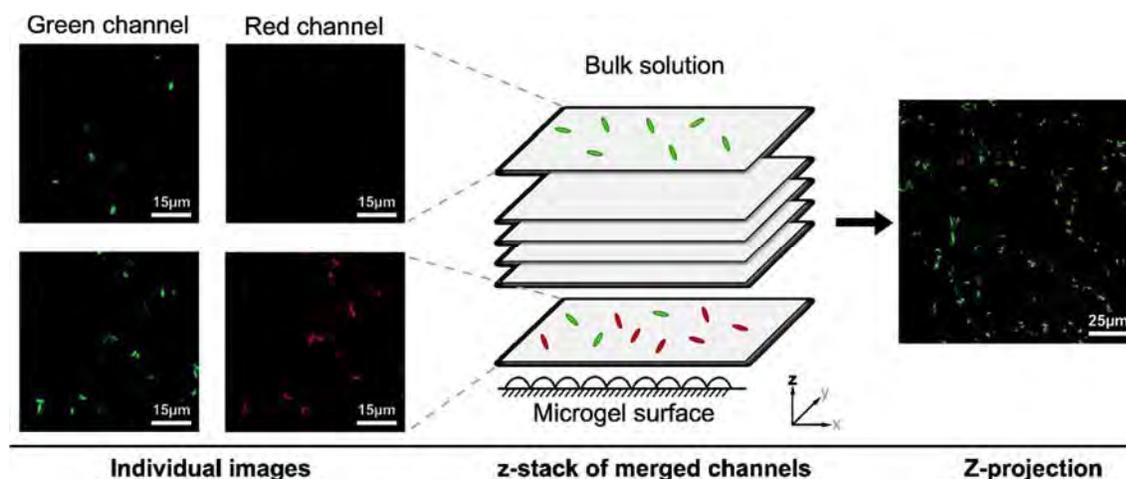
Nanoparticles have attracted significant attention as drug carriers because their chemistry and structure can be tuned to target certain tissues, control drug release and decrease the dose required for effective therapeutic intervention. Nanogels have the additional advantage of being mechanically deformable, enabling their passage through tight junctions like the blood-brain barrier. However, the hydrophilicity of nanogels limits their ability to uptake most anti-psychotic drugs like haloperidol, which are highly hydrophobic and thus have poor bioavailability as well as negative side effects at therapeutic doses. Herein, we present a method to synthesize hydrophobized nanogels using protein-repellent poly(oligoethylene glycol methacrylate) (POEGMA) to promote long-term circulation. The nanogels were synthesized by precipitation polymerization using either butyl methacrylate (BMA) or methyl methacrylate (MMA) as the hydrophobic comonomer. All nanogel formulations have diameters <100 nm with narrow polydispersities (<0.1). Quantification of drug uptake indicated that (1) MMA nanogels load more haloperidol than the more hydrophobic BMA nanogels and (2) increasing the fraction of hydrophobic monomer too high decreases the amount of drug encapsulated, suggesting that both nanogel swelling and drug partitioning are important in drug loading. *In vivo* response was assessed by administering drug-loaded nanogels via intraperitoneal injection or intranasally to male Sprague-Dawley rats. Catalepsy was examined by placing the front paws on a bar and scoring the length of time the rats held this position (Figure 1), while locomotion suppression was studied using computerized cages that record multidirectional movements. Both BMA and MMA nanogel formulations induced catalepsy and showed locomotion impairment; however, BMA nanogels consistently produced higher scores than MMA nanogels despite having lower drug loading, a result attributed to their smaller size and thus improved transport to the brain via the intranasal route. Thus, hydrophobically-modified nanogels offer attractive properties for treating brain diseases.



POLY 795: Peptide-loaded microgels as antimicrobial surface coatings

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Microgels are weakly cross-linked polymer colloids, which can be made responsive to various stimuli. In the context of drug delivery, microgels are of particular interest as carriers for biomacromolecular drugs, such as peptides and proteins, offering both protection against enzymatic degradation and triggered release. While microgel suspensions are becoming increasingly understood, much less is known about surface-bound microgels. Addressing this, we here report properties of electrostatically triggered surface-bound microgels, as well as their use as delivery systems for antimicrobial peptides (AMPs). In doing so, we investigate effects of microgel charge density, pH, and ionic strength on microgel volume transitions at surfaces, surface-induced microgel deformation and nanomechanical properties, as well as consequences thereof for peptide loading and release, using a battery of experimental techniques, including AFM PeakForce QNM, QCM-D, ellipsometry, and confocal and cryoTEM microscopy. We also report *in vitro* studies on AMP-loaded surface-bound microgels, notably on the interplay between surface- and release-related effects for the antimicrobial properties of such systems.

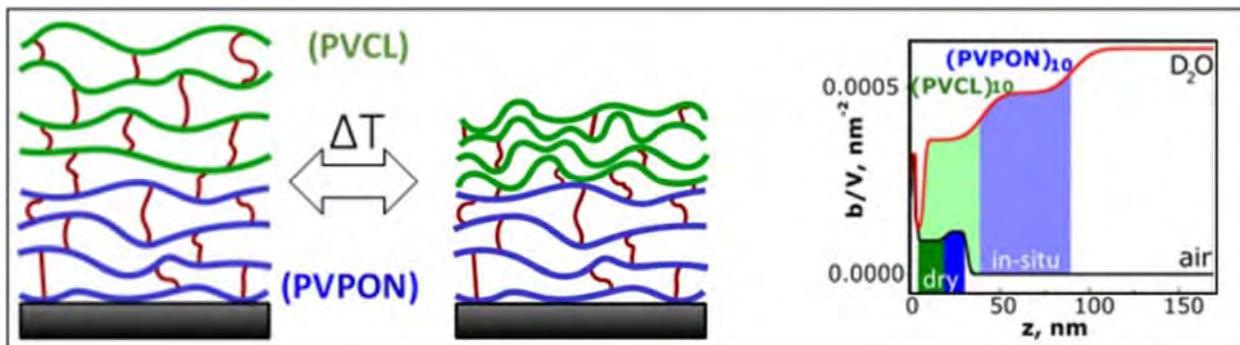


Schematic of confocal microscopy imaging of LIVE/DEAD-stained *E. coli*, showing the distance dependent bactericidal properties of peptide-loaded surface-bound acrylic acid-based microgels.

POLY 796: Stratified hydrogels and architectural control of temperature response

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This work studies the effect of hydrophilicity and layered architecture on temperature-response and surface morphology in non-ionic crosslinked layer-by-layer films. The films are prepared as hydrogen-bonded multilayers and later crosslinked. Hydrophilic poly(N-vinylpyrrolidone) (PVPON)_n is integrated with temperature-sensitive poly(N-vinylcaprolactam) (PVCL)_m, which transits from coil to globule above ~35°C. Layer hierarchy is imposed during fabrication, with n/m reflecting the number of layers of each polymer in a stratum. Stratum thickness and deposition order significantly influence film hydration; (PVCL)₂₀ shrinks from 58nm to 37nm in H₂O at 50°C. The (PVCL)_m(PVPON)_n film with PVCL bottom stratum swells less at 25°C and shrinks more at 50°C, compared to PVPON stack on bottom. Neutron reflectometry shows distinct strata of PVPON and PVCL in dry films, with respectively higher and lower scattering length densities. Hydration increases with the amount of PVPON in the film, which suppresses the temperature response. In (PVPON)_n(PVCL)_m, PVPON stratum shows a larger shrinkage suppression than that for (PVCL)_m(PVCL)_n which is explained as the (PVCL)_m stack being sandwiched between two adjacent aqueous interfaces of hydrated (PVPON)_m and bulk water. These results yield new insights into control of temperature response and surface characteristics in nanostructured polymer networks, relevant to fundamental and applied research on stimuli-responsive polymers.

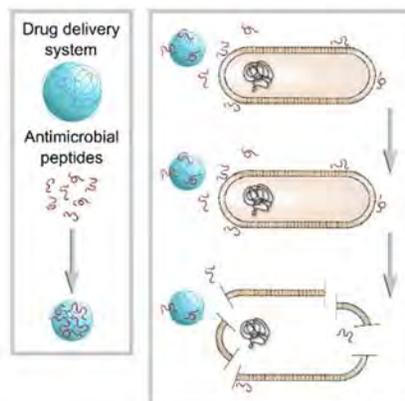


POLY 797: Poly(acrylic acid) microgels as carriers for antimicrobial peptides

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Due to increasing resistance development against conventional antibiotics, antimicrobial peptides (AMPs) are receiving considerable attention as potential therapeutics. Through lysis of bacterial membranes, AMPs provide fast and broad-spectrum antimicrobial effects. While there have been considerable efforts to identify potent and selective AMPs, drug delivery aspects of such compounds have been less studied. For example, infected tissue is often characterized by high proteolytic activity. Thus, administration of AMPs is likely to result in rapid degradation of the peptide and corresponding activity loss. Furthermore AMPs bind to serum proteins and are rapidly cleared from bloodstream, which can translate into reduced efficacy, as well as toxicity effects, related to accumulation in the reticuloendothelial system. In these and other contexts, it would be advantageous to combine AMPs with delivery systems designed for the application at hand.

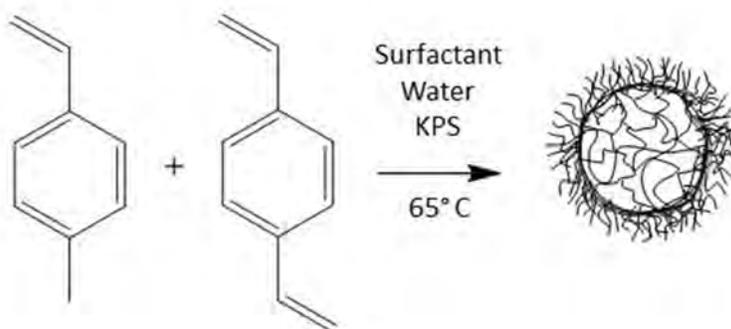
Microgels are lightly cross-linked polymer colloids, displaying dramatic volume transitions in response to different stimuli. They are of particular interest as carriers for biomacromolecular drugs since they offer a water-rich environment, thus reducing detrimental conformational changes, at the same time as providing protection against enzymatic degradation and allowing controlled or triggered release. In order to elucidate key properties of AMP-loaded microgels, we here investigate effects of microgel charge density on AMP loading and release, using a library of poly(ethyl acrylate-co-methacrylic acid) microgels, investigated with ellipsometry, particle size- and z-potential measurements. In addition, membrane interactions of peptide-loaded microgels are addressed, translating from biophysical studies with ellipsometry and liposome leakage to investigations of functional consequences, including antimicrobial activity, cell toxicity and proteolytic stability.



POLY 798: Synthesis and functionalization of polymer nanoparticles

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With a growing variety of nanoparticles available, research probing the influence of particle deformability, morphology, and topology on the behavior of polymer nanocomposites is increasing. The incorporation of soft polymeric nanoparticles in polymer nanocomposites has displayed unique behavior, but their precise performance depends intimately on the internal structure and morphology of the nanoparticle. With the goal of providing guidelines to control the structure and morphology of soft polymeric nanoparticles, we have examined monomer starved semi-batch nano-emulsion polymerizations that form organic, soft nanoparticles, to correlate the precise structure of the nanoparticle to the rate of monomer addition and crosslinking density. The synthesis method produces 5-20 nm radii polystyrene nanoparticles with tunable morphologies. Small angle neutron scattering (SANS) results correlate synthetic conditions to the structural characteristics of soft polystyrene nanoparticles. These results show that the measured molecular weight of the nanoparticles is controlled by the monomer addition rate, the total nanoparticle radius is controlled by the excess surfactant concentration, and the crosslinking density has a direct effect on the size of each nanoparticle. Furthermore, poly(4-methyl styrene) nanoparticles with brominated chain ends (66%) were successfully synthesized. Due to the presence of benzyl bromide, one can readily functionalize the soft polymer NPs. Particularly, poly(isoprene) synthesized via living anionic polymerization was grafted to the brominated poly(4-methyl styrene) nanoparticles and their morphological behavior as well as viscoelastic properties were investigated. The dependence on the molecular weight of poly(isoprene) and the living chains length in correlation with the grafting density was examined in detail.



POLY 799: Hydrogel microspheres for selective separation of halogen compounds

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We have investigated the molecular separation behavior of hydrogel microspheres (microgels).¹ In this study, the microgels allow the selective separation and release of halogen-containing compounds. The delivery and/or removal of halogen-containing compounds is of particular importance in the context of drug delivery or the decontamination of drinking water. For the latter, metallic materials, such as layered double hydroxides (LDHs), are usually employed, even though this methodology is not without flaws, as the adsorbed halide anions need to be released from the LDHs prior to the reduction of the anions, which is accompanied by a release of chloride anions into the solution.

We developed a new concept that is based on water-immiscible poly(2-methoxyethyl acrylate) (pMEA) as the halogen bonding acceptor, which is incorporated in swollen hydrogels in order to increase the specific adsorption volume and dispersion stability. Due to the properties of the soft and swellable microgels, it is thus possible to control the amount of adsorbed halogen-containing compounds that is released (**Figure**). Thus, these nanocomposite microgels resolve a variety of problems associated with, e.g., the removal of halogen compounds from wastewater, or with the delivery of halogen-containing drugs.² Moreover, we found that the other polymers also have halogen bonding ability, and the bonding strength can be controlled. Thus, the detailed results will be discussed at the session.

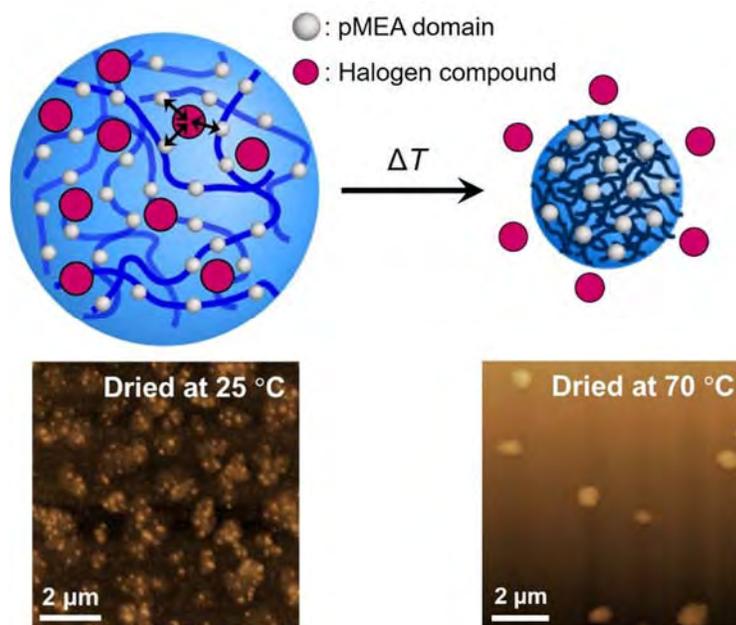
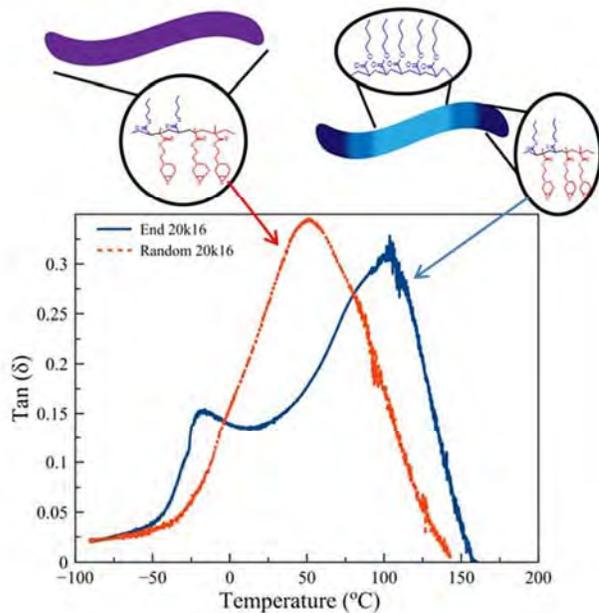


Figure. Schematic diagram of the swollen nanocomposite microgels in the presence of halogen compounds (top), and AFM images of the microgels dried at 25 C and 70 C (bottom).

POLY 800: Controlling photo-induced phase separation through kinetics and polymer architecture

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Many photocurable formulations utilize relatively small molar mass reactive diluents and large molar mass reactive oligomers. One important facet of these large molecules is their ability to govern the bulk properties of the photocured thermoset. This work examines how prepolymer architecture, specifically reactive group placement, leads to structure property relationships concerning network formation. Nitroxide Mediated Polymerization (NMP) was used to synthesize prepolymers with photocurable epoxide groups incorporated with butyl acrylate located predominantly at the chain ends of the large prepolymer. It was found that the presence of homo-butyl acrylate between the end-functionalized prepolymers induced the formation of multiple domains within the network compared to a randomly functionalized control. The formation of multiple domains was also tuned by altering the relative crosslink density of the prepolymer molecules and the ratio of prepolymer to reactive diluent. The presence of both high and low T_g domains within the polymer networks produced materials with significant increases in Young's modulus while maintaining a high elongation at break. End functionalized materials also increase resistance to prolonged stress exposure on the network and provides a facile method of targeting thermomechanical properties without altering the chemical composition of a photocurable formulation.

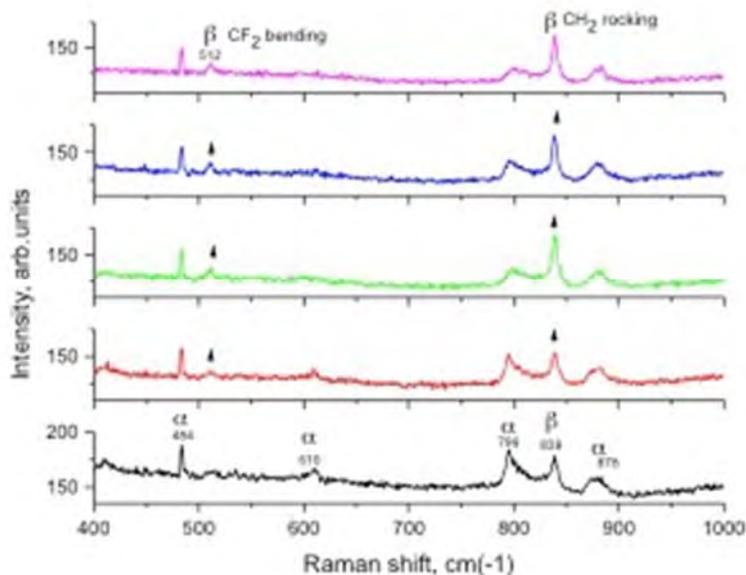


Phase separation as directed by oligomer architecture

POLY 801: Light intensity induced phase transitions in graphene oxide doped polyvinylidene fluoride

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The coupling of high frequency electromagnetic radiation (light) with low-frequency functionalities of dielectrics and liquid crystals is a long-standing problem of fundamental and applied science. An ability to turn “on” and “off” the pyro-, piezo-, or ferro-electric properties of materials on demand by optical means leads to fascinating device applications and is central to modern photostriction, where material strain is generated by light. In this work, we report on the interesting finding of the light intensity induced phase transitions observed in 0.05 % weight GO doped piezoelectric PVDF films with 100 μm thicknesses. Two effects were discovered in the Raman studies with wavelength of incident beam 532 nm: (i) an alternated modulation of integrated intensities of 797 and 840 cm^{-1} as a function of time, where wavenumbers stand for vibration modes of CH_2 rocking of α non-piezoelectric and β piezoelectric phases, respectively and (ii) reversible switching between α and β phases depending on the light intensity (power within the range of 10 – 40 mW). We provide a hypothesis on the mechanism and origin of observed effects within the framework of pyroelectricity of GO doped PVDF.

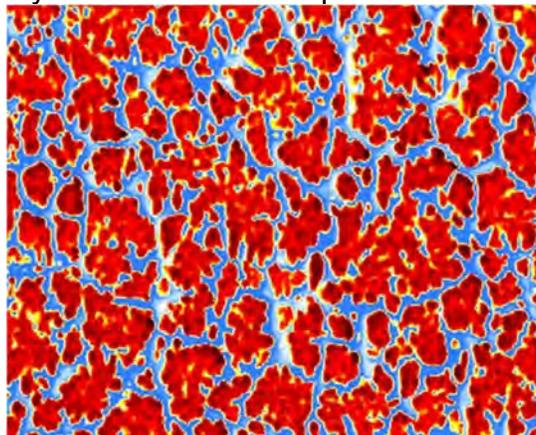


PVDF phase transformation under laser light illumination

POLY 802: Light-controlled phase separation using different monomer compositions of a radical/cationic system

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Photopolymerization-induced phase separation (PhIPS) is a technique capable of combining the properties of different constituents into a single polymer by controlling the polymer morphology. PhIPS will lead to distinct nano/microstructured domains, generating materials with unique physical and mechanical characteristics such as increases in material toughness. In this study, we investigate the effect of light intensity on the polymer morphology and thermomechanical properties for different monomer formulations. Phase separation was induced using a hybrid radical/cationic system comprised of butyl acrylate (BA) and di-functional oxetane (DOX). Our investigation revealed that the irradiation intensity had a small effect on the degree of phase separation for formulations with low concentrations of BA. On the other hand, the nano/microstructure domains were significantly dependent on the light intensity for formulations with concentrations of BA on the same order as of DOX which resulted in higher modulus and up to a four-fold increase in toughness. This behavior was attributed to the changes in the continuity and size of each polymeric phase. To investigate the creation of different domains, atomic force microscopy (AFM) was used in a tapping mode. AFM revealed that the BA softer domain was continuous at low light intensity (10 mW/cm²), contributing to weak mechanical properties. However, at the intermediate light intensity (100 mW/cm²), the continuous domain switched to harder DOX domain. At an even higher light intensity (1500 mW/cm²), the domain size became smaller, increasing the crosslink density. To confirm that the enhanced mechanical properties were caused by the changes in polymer morphology, the conversion of both BA and DOX was maximized by post thermal curing at 90 °C for four hours. These results demonstrate the ability to control the morphology and properties through PhIPS by altering the light intensity and monomer composition.

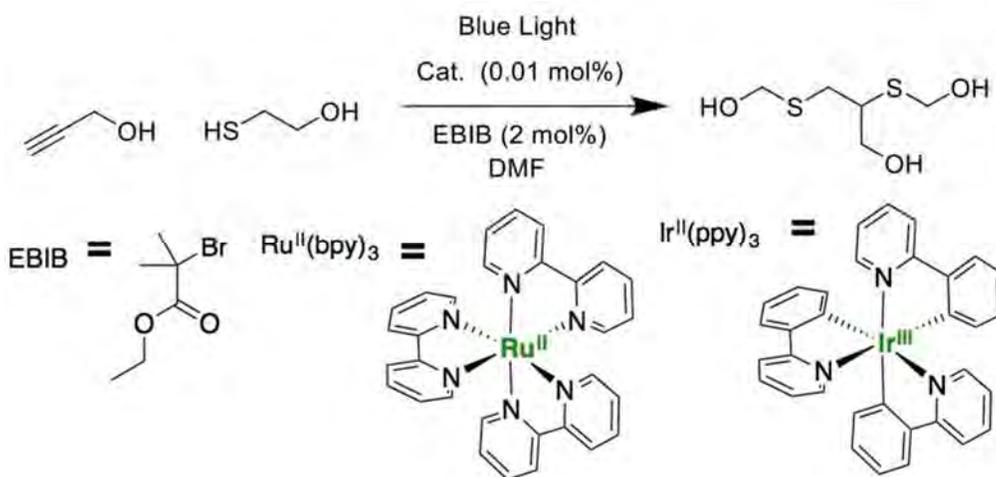


Surface image of a phase-separated polymer

POLY 803: Photoredox chemistry for efficient thiol-alkyne coupling and polymer synthesis

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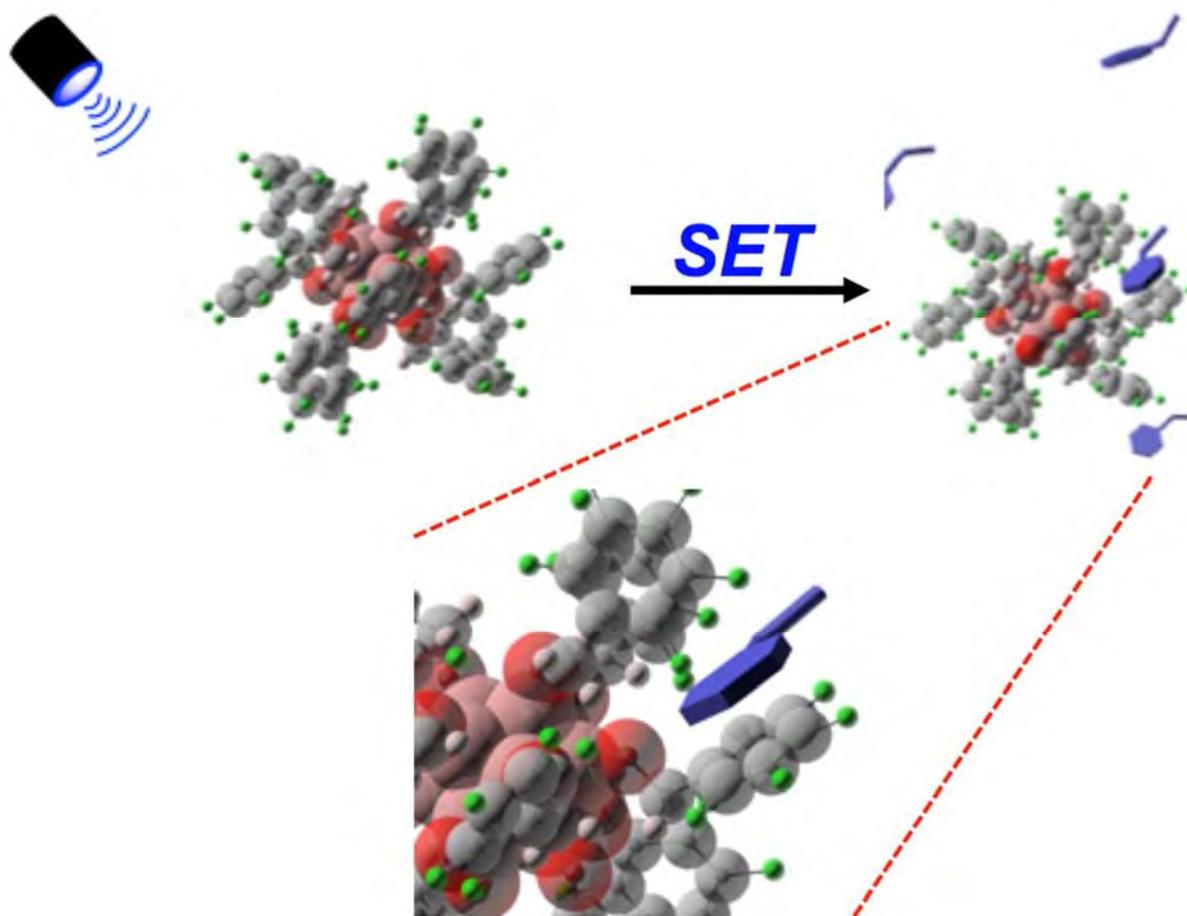
Thiol-alkyne (thiol-yne) coupling is a powerful tool for the synthesis of surfaces and macromolecules, since it enables two thiol functionalized moieties to be attached to one alkyne. This creates an ideal scaffold for functionalization and post polymerization modification with high modification density. Typically, thiol-yne coupling falls into one of two categories, nucleophilic and radical thiol-yne reactions. The radical pathway often uses a UV-photoinitiator to provide the radicals needed to drive the reaction forward. Here, we wish to investigate the impact of visible light photoredox catalysts to create a cycle where thiol-yne chemistry can be initiated using visible light. Two distinct types of photoredox catalysts are used, $[\text{Ir}(\text{ppy})_3]$ and $[\text{Ru}(\text{bpy})_3]^{2+}$, under conditions that either promote the oxidation or reduction of the metal catalyst. A detailed mechanistic study is performed, to understand the impact of the light source, and the reaction conditions on the efficiency of the thiol-yne reaction. Under optimized, efficient modification of alkynes with two thiols is observed within 30 min, using an ATRP initiator, ethyl α -bromoisobutyrate, as partner reagent in the photoredox process using blue light to initiate the process. Further, the thiol-yne reaction is applied to polymer synthesis and modification, for instance in the synthesis of hyperbranched polymers with high degrees of branching under visible light. This method could be applied in the future to generate a library of materials with advanced architecture and high density of grafted functional groups.



POLY 804: Boron cluster photosensitizers and dopants

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In 2016¹ we reported that perfunctionalized dodecaborate clusters ($B_{12}(OBn)_{12}$) are powerful photooxidants. We showed how these species, photo-excited with a bench-top blue LED source, can exhibit excited-state reduction potentials as high as 3 Volts and can participate in electron-transfer processes with a broad range of styrene monomers, initiating their polymerization. Furthermore, these molecules can be used to photoinitiate polymerization aliphatic olefins using blue light at cluster loadings as low as 0.05 mol%. This presentation will focus on detailing mechanistic insights pertaining to the previously disclosed photoinitiation process. Specifically, we will present structure-function relationships showcasing how the functional groups appended on the cluster affect the initiation efficiency. These and other studies suggest that charge transfer interactions occurring initially between the cluster and monomer are important for photoinitiation and subsequent polymerization efficiency. The last portion of the talk will be devoted to showcase our most recent findings how these clusters can be used as dopants with conjugated polymer materials.



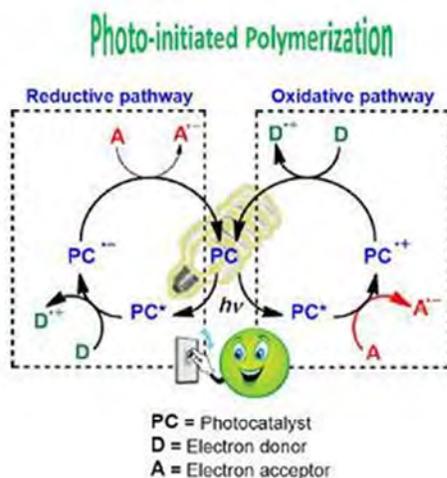
POLY 805: PhotoRedox catalysts in polymerization reactions: Towards to high performances systems

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A short review on the role of photoredox catalysts (PC) as initiators in photopolymerization reactions is presented. A special emphasis is done on photoinitiators that behave as photoredox catalysts leading to i) high performance initiating systems for polymerization upon low light intensity for the use of light emitting diodes (LEDs) and/or visible light or ii) dormant species and re-initiation that can be triggered by light. **Some examples for 3D printing applications will be given.**

[Scheme 1 must be here]

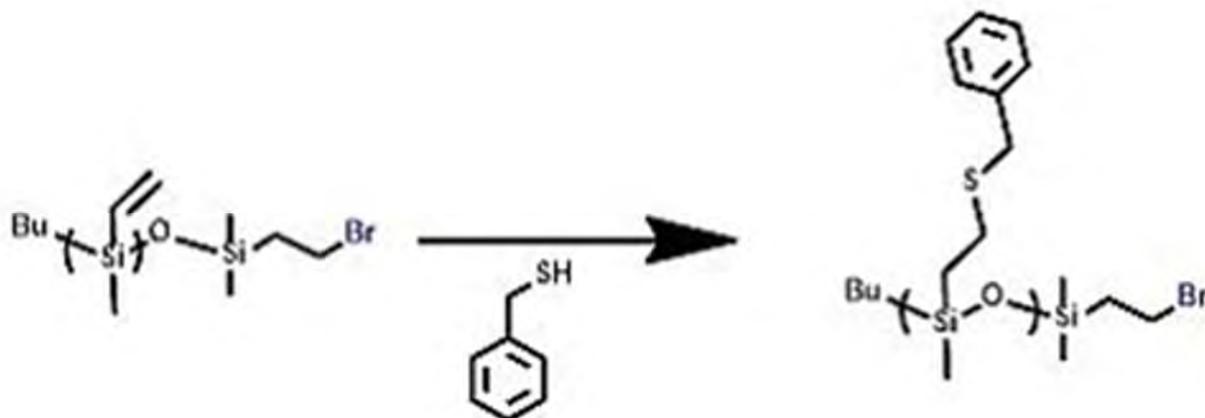
Scheme 1. Reductive and oxidative photoredox catalytic mechanisms.



POLY 806: Synthesis and kinetic studies of thiol – ene post-polymerization modification of poly(vinylmethylsiloxane)

Sourav Chatterjee¹, schatter@tulane.edu, Bo You³, Andrew S. Raymond², Julie N. Albert¹. (1) Tulane University, New Orleans, Louisiana, United States (3) Yale University, New Haven, Connecticut, United States

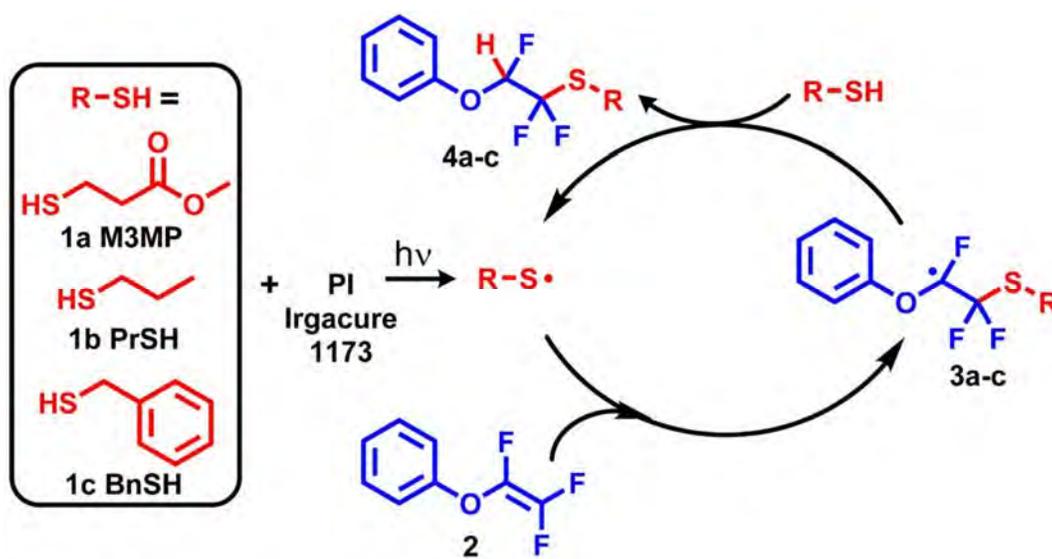
The field of photopolymerizations has been one of the most widely and rapid growing industries in recent years. Thus, these materials have found widespread use in coatings, imaging materials, photoresists, and many other products. Most of the thiol – ene photopolymerization reactions make use of a photoinitiator, which has the advantage of shortening reaction times but the disadvantages of possible side reactions and faster material aging. We have applied the thiol-ene synthetic strategy to the post-polymerization modification of poly(vinylmethylsiloxane) (PVMS) and studied the reactivity of the vinyl groups on PVMS toward different thiols, as different chemical modifications are desirable for different applications. Due to the disadvantages of using a photoinitiator, we focused on the reaction kinetics without a photoinitiator. The kinetics of these reaction were studied via proton nuclear magnetic resonance (¹H-NMR) spectroscopy and gel permeation chromatography (GPC).



POLY 807: Thiol-trifluorovinyl ether (TFVE) photopolymerization: An on-demand synthetic route to semi-fluorinated polymer networks

Brian Donovan, Jason Ballenas, **Derek L. Patton**, derek.patton@usm.edu. School of Polymer Science and Engineering, University of Southern Mississippi, Hattiesburg, Mississippi, United States

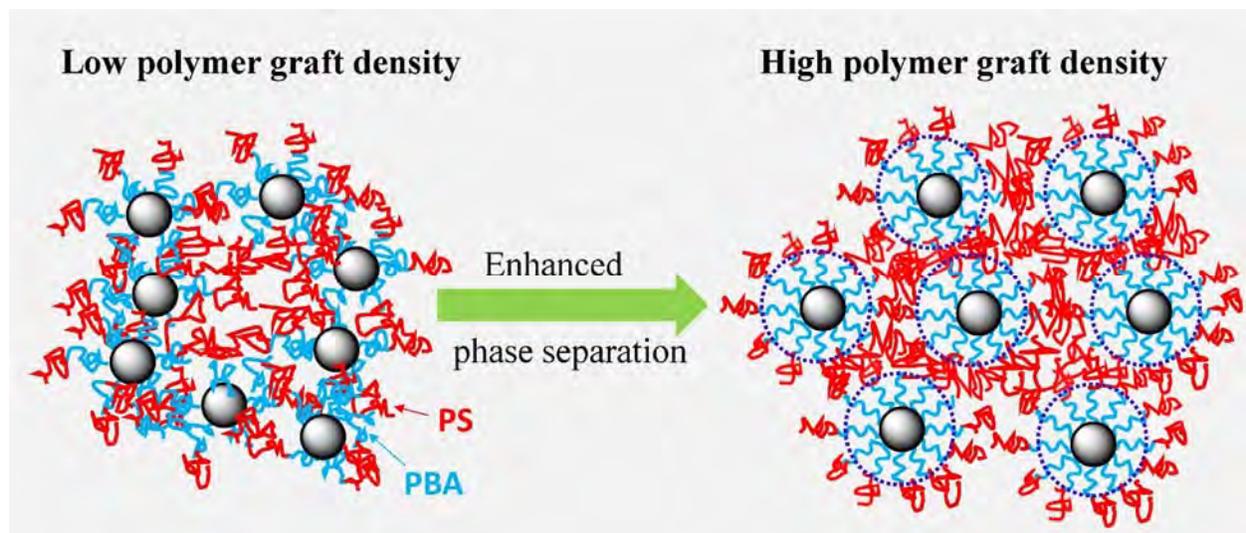
This presentation will focus on our recent efforts to develop thiol-trifluorovinyl ether (thiol-TFVE) photopolymerization as a facile, cure-on-demand synthetic route to semi-fluorinated polymer networks. The thiol-TFVE reaction – which proceeds via anti-Markovnikov addition of a thiyl radical to the TFVE group – was elucidated using model small molecule reactions between phenyl trifluorovinyl ether and thiols with varying reactivity. These model reactions, characterized by ^{19}F NMR, ^1H NMR, and FTIR, also provided evidence of an oxygen-induced degradation pathway that may be circumvented by performing the reactions under an inert gas atmosphere. Photopolymerization of difunctional TFVE monomers with multifunctional thiols occurred with rapid kinetics and high conversions as observed with real-time FTIR, and provided homogeneous semi-fluorinated polymer networks with narrow glass transitions as observed with dynamic mechanical analysis. The semi-fluorinated ether/thioether linkage incorporated into the polymer network yielded hydrophobic materials with increased and tunable T_g , a 2-fold increase in strain at break, 4-fold increase in stress at break, and more than 5-fold increase in toughness relative to a thiol-ene material composed of a structurally similar hydrogenated ether/thioether linkage. The increased T_g and mechanical toughness are attributed to the higher rigidity, hydrogen-bonding capacity, and stronger carbon-carbon bonds of the semi-fluorinated ether/thioether relative to the hydrogenated ether/thioether. We anticipate that the simplicity and rapid cure kinetics of the thiol-TFVE photopolymerization coupled with on-demand access to tunable and enhanced materials properties will provide a framework for the design of new semi-fluorinated polymer thermosets for a range of applications.



POLY 808: Thermoplastic elastomers from one-component block copolymer grafted nanoparticles via surface-initiated RAFT polymerization

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Thermoplastic elastomers (TPEs) have broad applications in a variety of fields. The traditional and widely used TPEs are made from triblock copolymers such as poly(styrene-block-butadiene-block-styrene) (SBS) and poly(styrene-block-isoprene-block-styrene) (SIS), which are synthesized by living anionic polymerization. Herein we report on thermoplastic elastomers formed by block copolymer grafted silica nanoparticles without additional polymer matrix. The block copolymer, poly(styrene-block-(n-butylacrylate)) (PS-b-PBA), tethered to 15 nm silica nanoparticles was prepared by RAFT polymerization using a grafting-from strategy. The ultimate tensile stress and elastic modulus increased with increasing PS chain length. The dispersion of the silica NPs and the microphase separation of the block copolymer in the matrix-free polymer nanocomposite were investigated using small-angle X-ray scattering (SAXS), transmission electron microscopy (TEM), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA). The higher polymer graft density TPEs exhibited better microphase separation of the block copolymers and more uniform silica NP dispersion than lower polymer graft density TPEs with similar polymer chain length and composition. This versatile strategy to prepare thermoplastic elastomers by block copolymer grafted nanoparticles broadened the design of new TPEs, which introduces a new parameter, polymer chain graft density, as a new tool to enhance microphase separation and hence to tune the mechanical properties of TPEs.

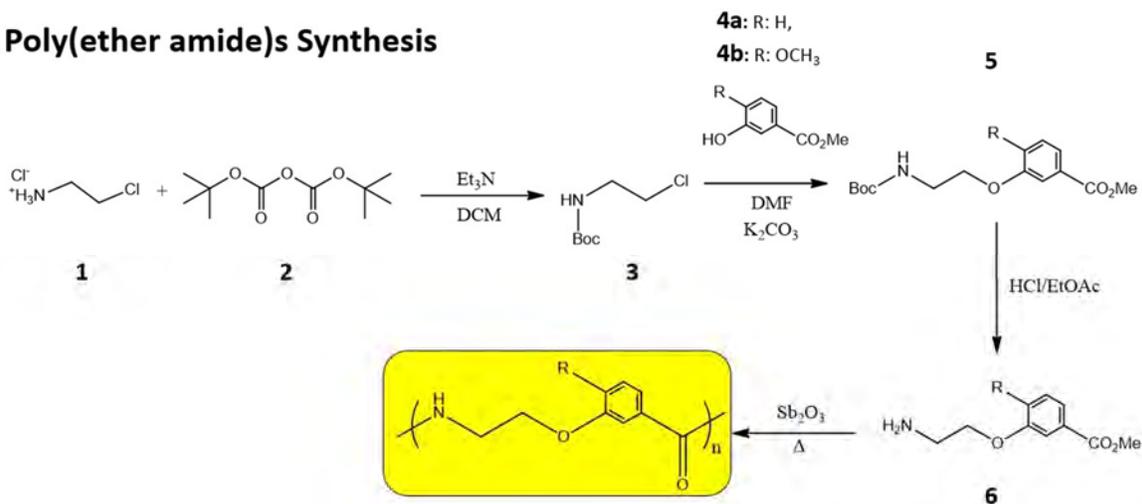


POLY 809: Synthesis of novel biorenewable poly(ether amide)s

Guery Saenz, *gs938@msstate.edu*. Chemistry, Mississippi State University, Starkville, Mississippi, United States

Petroleum-based products have dominated the commercial market for many decades. However, there have been a push to replace petroleum-based products due to the unsustainability of petroleum source with those from renewable sources such as lignin. Novel and sustainable poly(ether amide)s were synthesized by melt polycondensation of two lignin-derived monoaromatic compounds: methyl 4-hydroxy-3-methoxybenzoate and methyl 4-hydroxybenzoate with 2-chloroethylamine. In this work we describe the synthesis and characterization of two new poly(ether-amide)s as alternative thermoplastics from lignin-based raw materials. The results show that the glass transition temperature (T_g), melting temperature (T_m) and the temperature for 50% mass loss, range from 90–120 °C, 180–190 °C, and 270–320 °C, respectively. We explored the structure/property relationship with respect to hydrogen bonding and its effects on the thermal and physical properties of these polymers. It was shown that hydrogen bond interactions appear to play an important role to define the thermal properties of the two poly(ether amide)s synthesized.

Poly(ether amide)s Synthesis

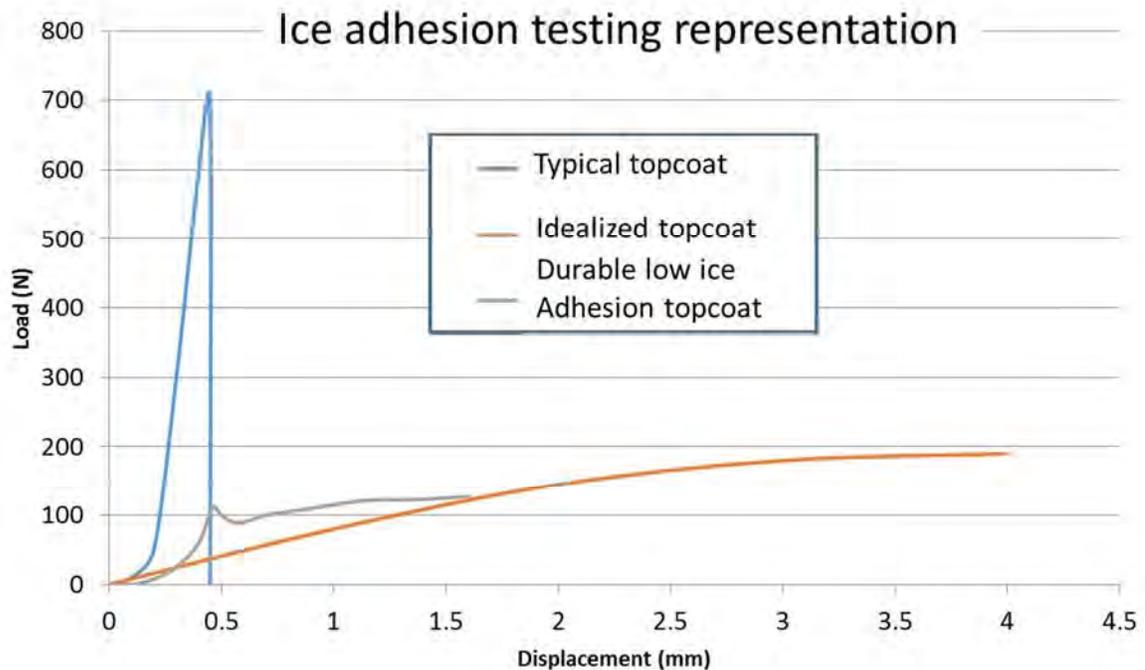


Synthesis of novel poly(ether amide)s by melt polycondensation of lignin-derived monoaromatic compound.

POLY 810: Durable coatings with low ice adhesion

Scott J. Moravek, moravek@ppg.com. PPG Industries, Inc., Allison Park, Pennsylvania, United States

Various strategies have been explored to mitigate ice adhesion to surfaces but the challenge of creating durable polymeric coatings with low ice adhesion remains. The current state of work toward polymeric thermoset coatings that are both durable and have low ice adhesion will be presented.

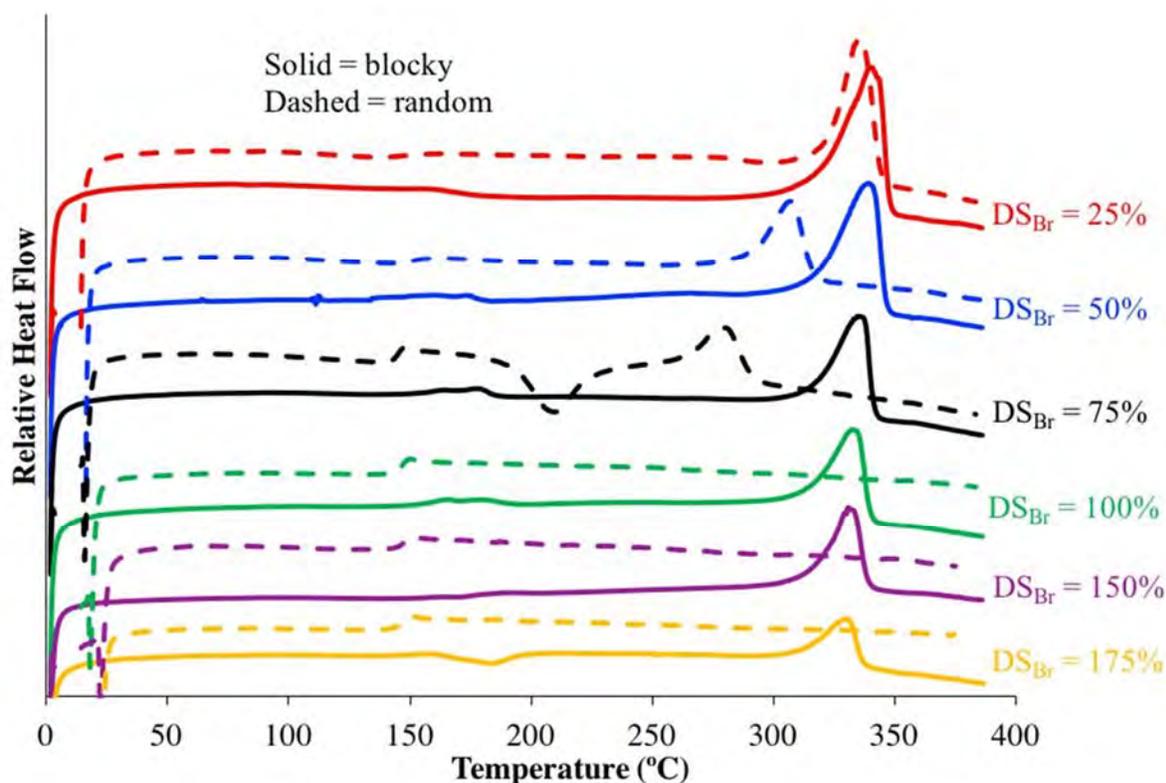


Simulated data showing the behavior of different coating compositions and the variation in the ice adhesion failure mode.

POLY 811: Blocky bromination of poly(ether ether ketone) in the gel-state as a platform for further functionalization

Lindsey Anderson², ljande91@vt.edu, **Robert B. Moore**¹. (1) Virginia Tech, Blacksburg, Virginia, United States (2) Chemistry, Virginia Tech, Blacksburg, Virginia, United States

Post-polymerization bromination is a useful technique to modify existing homopolymers and provide functional handles for further substitution. Most methods of bromination occur in the homogeneous solution-state and yield random copolymers. Recently, however, functionalization in the semicrystalline gel-state has been shown to produce blocky copolymer architectures through selective functionalization of the amorphous domains. In this work, the bromination of poly(ether ether ketone) using N-bromosuccinimide is explored and compared in the solution-state and the gel-state. The BrPEEK copolymers were fully characterized using ¹H NMR, FTIR, DSC, DMA, and SAXS to determine the influence of architecture on crystallizability and morphology. Following bromination, two further reactions were explored. First, Ullmann reactions were investigated to attach superacid side chains to the PEEK backbone. Second, the functionalization of blocky BrPEEK was investigated to produce blocky brominated, sulfonated PEEK copolymers. By utilizing the initial gel-state reaction, novel PEEK block copolymers are obtainable using facile post-polymerization techniques.



POLY 812: Combination of anionic ring-opening and condensation reactions for the synthesis of aliphatic-aromatic copolyamides

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Polyamides are one of the major engineering thermoplastics. Their properties can be tuned by a number of techniques like copolymerization, incorporation of fillers, or blending with other polymers.^{1,2} The variety of polyamides offers a lot of industrial applications in textile, medicine, or automobile industry. In composite materials, some polyamides are considered nowadays as an alternative to epoxy or polyester thermosets as far as their properties and processing can be adapted for the production of parts at low price.

Polycondensation and anionic ring-opening polymerization are the main methods used to prepare such materials.^{3,4} The need to find new synthesis methodologies is actual and is expected to propose new materials and properties.

The discussion will focus on the combination of anionic ring-opening polymerization of ϵ -caprolactam and condensation polymerization of aminobenzoate derivatives for the synthesis of aliphatic-aromatic copolyamides.⁵ Thermal characteristics of some polyamides will be discussed.



Scheme 1. Anionic-based strategy proposed for the synthesis of Aliphatic-Aromatic Copolyamides

POLY 813: *n*-Heterocyclic carbene organocatalyzed ring-opening polymerization of *n*-tosyl aziridines using functional initiators and amino-alcohols as bifunctional and double headed initiators

Camille Bakkali-Hassani¹, *camille.bakkali-hassani@u-bordeaux.fr*, Joan Vignolle¹, Stephane Carlotti¹, Daniel Taton¹, Elisabeth Rieger², Frederik Wurm². (1) ENSCPB, University of Bordeaux, Pessac, France (2) Max Planck Institute, Mainz, Germany

N-Heterocyclic carbenes (NHCs) have received increasing attention over the last past 20 years because of their particular steric and electronic properties. They have recently emerged as organocatalysts in the context of polymer chemistry, allowing the precise synthesis of a wide range of macromolecules by chain- or step-growth polymerization processes¹⁻³.

Generally, aziridines polymerize via a cationic pathway, affording non-controlled hyper-branched poly(ethylene imine). Interestingly, it was recently shown that aziridines could be activated toward anionic ring-opening polymerization (AROP) by *N*-tosylation^{4,5}. In this work, the ring-opening polymerization of activated aziridines catalyzed by a NHC, namely 1,3-bis(isopropyl)-4,5(dimethyl)imidazol-2-ylidene, have been investigated in presence of various initiators^{6,7}. In the proposed approach, different activated *N*-sulfonyl amines, non-activated secondary amine, trimethylsilyl azide as well as amino-alcohols can be used as an initiator and molar masses are controlled by adjusting the initial monomer/initiator feed ratio. Characterizations by SEC, NMR and MALDI-ToF MS are consistent with a living/controlled organocatalytic ROP of *N*-tosyl aziridines.



Figure 1 : NHC-organocatalyzed polymerization of *N*-tosyl aziridines in presence of various initiator

POLY 814: 3D printing of polymers: Form, filler, functionality

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The new types of polymers that have been used for 3D printing have been limited to a number of commodity polymers. Very often the different methods of 3D printing dictate the class of polymers or monomers that can be used to match with the process and reactivity. This talk will highlight the match in form, filler, and function of different classes of 3D printing methods (FDM, SLA, SLA, VSP, etc.) with the eventual polymers classes, thermoplastics, thermosets, and elastomers. The Advincula research group has focused on the use of nanofiller materials as well improving the properties of polymers used in 3D printing. This includes polyurethanes, polysiloxanes, PEEK, polyamides, over traditional polymers used predominantly with FDM and SLA. The group will demonstrate the intended form- applications from actuator switches, electric motors, molds, and separators. The use of thermo-mechanical testing methods is important for determining the performance of these materials for actual parts replacement and not just prototyping.

