Division of Polymer Chemistry (POLY)

Graphical Abstracts

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Division of Polymer Chemistry (POLY)

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POLY 1: Poly(phthalaldehydes) as stimuli-responsive, depolymerizable materials that are capable of providing amplified responses

Anthony M. DiLauro, antdilauro@gmail.com, Scott T. Phillips. Chemistry, The Pennsylvania State University, State College, Pennsylvania, United States

CD$_r$ polymers, or polymers that are capable of continuous depolymerization mediated by a reaction-based detection unit, represent an emerging class of stimuli-responsive materials that are characterized by their ability to provide an amplified response to specific chemical or physical signals. This presentation will focus on poly(phthalaldehydes), a poly(acetal) CD$_r$ polymer that is unique in its ability to completely depolymerize to monomer in seconds to minutes both in solution and in the solid state. Specifically, we will discuss our work to develop poly(phthalaldehyde) derivatives with improved properties and to apply poly(phthalaldehydes) as stimuli responsive materials, including as responsive microcapsules, as shape changing materials, and as reagents that provide signal amplification in the context of diagnostics.
Our group has a long-standing interest in polymers that mimic naturally occurring sugar polymers found in the body, specifically heparin. Heparin is an important actor in preventing thrombosis and blood clots. In order to probe the role of structure and functional groups in our synthetic polymers we have prepared a range of polyureas. This material set has yielded important information on what structural features are required for effective heparin mimicking. Recently, we have extended these studies into focusing on the materials science aspects of the polymers, specifically by preparing “smart” polymers that possess shape-memory properties. In this presentation I will show we designed heparin-mimicking polymers that possess a tunable glass transition temperature ($T_g$) and shape-memory behavior close to physiological temperatures.

Anti-IIa and clotting time results of heparin-mimicking polymers
Nature broadly employs supramolecular chemistry to construct complex, responsive, and smart biological structures, including deoxyribonucleic acid (DNA). Complementary hydrogen bonding and pi-pi stacking of nucleobases are crucial to stabilize the double helix structure and store genetic information. Our recent efforts have demonstrated the potential of synthetic nucleobase-containing supramolecular polymers in advanced, smart material fabrications. Nucleobase-functionalized acrylic monomers enabled facile synthesis for a series of supramolecular polymers with well-defined architectures and tailorable properties. Nucleobase-containing random copolymers afforded pressure sensitive adhesives with enhanced peel and sheer strength compared to bench-mark controls. Symmetric ABA triblock copolymers with nucleobase-functionalized external blocks self-assembled into microphase-separated, free-standing films. Morphological and thermo-mechanical analysis elucidated the effect of processing conditions on block copolymer self-assembly in presence of nucleobase noncovalent interactions. A supramolecular blend with complementary nucleobase pairs exhibited microphase-separated morphology with extended plateau window. The robust complementary hydrogen bonding of nucleobase pairs shows potential in solving the paradox of enhancing materials' mechanical performance while maintaining usable processibility. Preliminary results on the asymmetric ABC triblock copolymers with complementary nucleobase-functionalized external blocks revealed remarkably ordered microphase-separated morphologies. Nucleobase pairing assisted in block copolymer phase separation and self-assembly. These nucleobase-containing supramolecular polymers are emerging as next generation smart materials with enhanced thermo-responsiveness, mechanical performance, and processibility.
Modern needs in materials science and bioapplications are manifold: From hydrophobic matrices for tissue engineering to water-soluble protein therapeutics a great variety of polymers is employed to fit to each application. We seek to establish a unique modular protocol to fulfill the demands in these modern needs. The incorporation of uncharged phosphates or phosphonates within the polymer backbone is a unique handle to tune the materials properties both along the main chain but also at the side chains. A key feature of poly(phosphoester)s (PPEs) is the pendant group that is attached to every phosphorus along the backbone.
POLY 5: Light-degradable polymers: amplification strategies, response to new wavelengths, and application to a clinical challenge

Jason Olejniczak, Carl-Johan Carling, Viet Anh Nguyen Huu, Arnold Garcia, Jing Luo, Kang Zhang, Adah Almutairi, aalmutairi@ucsd.edu. UC San Diego, La Jolla, California, United States

This presentation will cover several recent advances in the development of light-degradable polymers as tools for biological research and drug delivery, including a strategy for chemically amplifying the light signal to accelerate degradation, a polymer responsive to visible rather than UV or near infrared light, and application of a previously reported polymer to the treatment of disease. The chemical amplification strategy relies on phototriggered unmasking of acidic groups that hydrolyze adjacent ketals, which overcomes ketals' requirement of low pH for efficient degradation. Particles composed of the photocaged-acid/ ketal polymer degrade rapidly upon brief irradiation. The diversification of wavelengths useful for triggered degradation of soft materials involves a photocage not previously used in responsive materials, which cleaves in hydrophobic environments (unlike coumarins), and absorbs light from 400-500 nm. Particles composed of this polymer, when subcutaneously injected and irradiated through tissue, release sufficient drug to significantly reduce carrageenan-induced paw inflammation in mice. Finally, we have evidence that a UV-degradable polymer (Fomina et al., J Am Chem Soc 2010) may be useful for the delivery of anti-angiogenics to treat macular degeneration. This strategy would preserve clinician control over dose timing while reducing the frequency of intravitreal injections. UV-degradable particles are stable in the eye for months and release a therapeutically effective dose of a small molecule anti-angiogenic; the irradiation required for release is well-tolerated by the eye.
POLY 6: Folding single polymer chains

Christopher Barner-Kowollik, christopher.barner-kowollik@kit.edu, Johannes Willenbacher, Ozcan Altintas. Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

The lecture will present our latest advances in the field of folding single polymer chains into defined nanoparticle structures. Initially, the so-called 'selective point folding' approach will be discussed on several examples, evidencing that single polymer chains can be folded and unfolded via independent and orthogonal interaction points not unlike naturally occurring biomacromolecules. Specifically, orthogonal additional binding principles beyond hydrogen donor/acceptor systems will be discussed in the context of single chain folding. Secondly, single chain polymer folding via so-called 'repeat unit folding' will be explored and avenues towards inherently fluorescent as well as catalytically active single chain nanoparticles will be discussed. A special focus will be placed on using photochemical approaches to collapse single chains. In addition, analytic approaches towards evidencing single chain nanoparticle formation will be shown with an emphasis on DOSY and DLS methodologies.
POLY 7: Poly(β-methyl δ-valerolactone) as a scalable and renewable soft segment for aliphatic polyester block polymers

Marc A. Hillmyer, hillmyer@umn.edu. Department of Chemistry, University of Minnesota, Minneapolis, Minnesota, United States

Renewable aliphatic polyester block polymers hold tremendous promise as advanced sustainable materials that can compete with their petrochemically-derived analogs in terms of mechanical performance, environmental impact and cost. One obstacle to broad implementation of such hybrid materials is the economical production of a low glass transition temperature aliphatic polyester that can be readily incorporated as a soft midblock into ABA triblock copolymers for use in, for example, thermoplastic elastomers, tough plastics, and adhesives. Through a metabolic engineering approach, our research team in the Center for Sustainable Polymers at the University of Minnesota has developed an efficient and scalable route to a cyclic ester that can be polymerized in a controlled fashion and combined with hard poly(lactide) A end blocks to give ABA triblock copolymers with tunable mechanical properties. β-methyl δ-valerolactone was prepared by dehydration and hydrogenation of mevalonate produced in high titers from sugar by an engineered microorganism. Ring-opening transesterification polymerization of this cyclic ester using an organocatalyst was used to generate the corresponding block polymers in a controlled fashion. In this talk I will cover the discovery and development of these and related materials for the preparation of next generation sustainable block polymers.
In 2011 we discovered that both Atom Transfer Radical Polymerization (ATRP) and Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization evidently suppress the gel point in the polymerization of acrylated epoxideized soybean oil (AESO) such that polymerized AESO (PAESO) could be isolated as a thermoplastic rubber at > 80% yield. This discovery opened a completely new realm for biopolymer applications based on thermoplastic poly(AESO) rubbers; moreover, sequential polymerization of PAESO with styrene yields styrenic block copolymers with many properties reminiscent of the Kraton SBS family first commerized over forty years ago. In this talk I will share our experiences in bringing these materials to market, beginning with their synthetic details of and their basic rheological properties. Like SBS polymers, PS/PAESO block copolymers showed early promise as asphalt modifiers: a simple high volume application with relatively few barries to market entry. Moreover, technoeconomic analysis suggests that—even with new capital expenditures—PS/PAESO can be cost advantaged over SBS analogues at full scale production. Over the past two years we have cultivated a combination of strategic partnerships between academic, government, and industrial entities that continues to push PS/PAESO (and its successors) out of the laboratory and into the marketplace.

A major milestone 2 years in the making: Ground-breaking for a 500 kg per day pilot scale biopolymer production facility at the BioCentury Research Farm of Iowa State University.
In view of continuing interest in the utilization of agricultural by-products, we have converted cellulose, wheat straw, barley straw, and rice hull into carboxymethylcellulose (CMC), using both conventional heat and microwave-assisted synthesis. The application of microwave technology has enabled an improved synthesis of CMC to be conducted, with similar degrees of substitution as conventional heat (3 h) but reduced reaction times (30 min). The CMC obtained can be acetylated to form carboxymethylcellulose acetate (CMC acetate). The FT-IR and solid state $^{13}$C NMR spectra of these materials have been characterized. With variations in the degrees of substitution of carboxymethyl and acetyl groups, a family of CMC acetate products can be made. These materials may perhaps find applications as filtration membranes, functional fillers in polymers, and additives in commercial formulations.
Organocatalytic Ring-Opening Polymerization provides an attractive strategy for the generation of renewable polymers. With James Hedrick of IBM, we have developed a family of organic catalysts for selective ring-opening polymerization reactions. We have also discovered a class of selective Pd catalysts for the oxidation of biomass-derived polyols to chemical intermediates and monomers. These advances have enabled an integrated catalytic strategy for the conversion of renewable resources into new materials. Mechanistic and theoretical investigations of these catalytic oxidation and ring-opening polymerization reactions have provided opportunities for the generation of renewable polymers and functional materials.
Melanins are a class of naturally occurring pigmentary macromolecules found in mammals. These compounds have a high degree of conjugation rendering them a powerful radiation absorber with broadband photon absorption spectrum that extends from the ultraviolet into the infrared region. The black-brown variety of melanin is known as eumelanin and is thought to be a heterogeneous network produced by oxidative polymerization of the two monomers, 5,6-dihydroxyindole and 5,6-dihydroxyindole-2-carboxylic acid. Groundbreaking work by McGinness and Proctor on electrical switching established that eumelanins were organic semiconductors. Currently, we have synthesized a eumelanin-inspired indole core, methyl 4,7-dibromo-5,6-dimethoxy-N-methyl-1H-indole-2-carboxylate from the plant extract, vanillin, which can serve as new building block for organic semiconductors. The design, synthesis, and characterization of eumelanin-inspired conjugated polymers from this indole core will be presented.
Phenolic acids are sustainable, plant-derived chemicals found in a variety of natural sources such as fruits and vegetables. Phenolic acids are advantageous sources for polymers due to their aromatic rings, which provide mechanical strength, and the presence of carboxyl and hydroxyl groups, which provide routes to polymerization. In this study, crosslinked thiol-ene networks were derived from phenolic acids. Polymer films synthesized through thiol-ene chemistry are found in a variety of applications including adhesives, soft touch coatings for electronic devices, protective coatings on floors and wires, among others. Fundamental relationships between the molecular structure of the phenolic acids and the thermal and mechanical properties of the resulting polymer films have been developed. Such knowledge is an important first step toward the widespread implementation of biobased phenolic acids in thiol-ene polymer film applications.
Poly(ethylene 2,5-furandicarboxylate) (PEF) is a promising biobased polyester whose chemical structure is analogous to poly(ethylene terephthalate) (PET). Despite the similarity in chemical structure, PEF is often reported to have a higher glass transition temperature than PET. Therefore we conducted an in-depth analysis of the glass transition dynamics to understand and explain this difference from the point of view of molecular motion. The dynamic of the cooperative relaxation process of PEF was examined by means of multi-frequency temperature modulated differential scanning calorimetry (TOPEM®) and dynamic mechanical analysis (DMA) (Figure 1). Fraction (RAF) and the average sizes of the cooperative rearranging region (CRR) in the glass transition region were determined for PEF with different degrees of crystallinity. It is shown that CRR size decreases when crystallinity increases, due to the amorphous phase confinement by the crystals. The DMA measurements are in good agreement with the TOPEM results. The glass transition temperature and the half-high width were obtained from the loss modulus curve and allowed calculation of the characteristic volume of cooperativity. The dynamic relaxation phenomena have shown a frequency dependent behavior and the activation energy of the glass transition was determined for the amorphous and crystalline samples and the differences will be discussed.
This presentation will describe the preparation of hydrophilic polymers substituted with oligopeptides, zwitterions, and 'reverse zwitterions', with additional discussion of the use of these polymers in materials chemistry and in conjunction with live cells.
POLY 15: Mimicry of photosynthesis: for the synthesis of well-defined polymers
Sivaprakash Shanmugam, Jiangtao Xu, Cyrille Boyer, cboyer@unsw.edu.au. School of Chemical Engineering, UNSW Australia, Sydney, New South Wales, Australia
Since cyanobacteria inhabited on Earth 3.4 billion years ago, Nature had developed efficient chemical processes, including photosynthesis, capable to convert solar energy into chemical energy, which could be used by the bacteria or plants to produce natural polymers (polysacharide). Researchers have tried to mimic such process. In this work, we present a new method of polymerization, named Photoinduced Electron Transfer - Reversible Addition Fragmentation Chain Transfer Polymerization (PET-RAFT) (Scheme 1), which presents some similarity with the photosynthesis reaction (especially with Photosystem II). Here, we investigated a range of highly efficient photoredox catalysts, including metallo base catalysts, organophotoredox catalysts and a new bioresource photocatalyst capable of controlling the polymerization of methacrylates, acrylates and acrylamides in the presence of thiocarbonylthio compounds to afford the synthesis of complex macromolecules. This polymerization technique can be performed in a closed vessel in the presence or absence of air. The polymerization kinetics was investigated using on-line Fourier transform near-Infrared spectroscopy (FTNIR) which was employed to monitor the monomer conversions (Scheme 2). Interestingly, this polymerization technique can polymerize a large range of conjugated and unconjugated monomers under air to yield well-defined polymers (PDI < 1.20). Finally, we will show different applications of this technique and we will give its current limitations.

Scheme 1. Proposed mechanism of a photoinduced living polymerization using fac-[Ir(ppy)3] as photoredox catalyst.

Scheme 2. Exemple of monomers.
POLY 16: New methodology for controlled supramolecular polymerization
Xi Zhang, xi@mail.tsinghua.edu.cn. Tsinghua University, Beijing, China

Study on supramolecular polymers has gained significant advancement, but it remains a big challenge to realize control over supramolecular polymerization. In this presentation, I will introduce two strategies to fabricate supramolecular polymers towards molecular weight and structural control. It is aimed to enrich methodologies of fabricating supramolecular polymers, leading to combing molecular architectures with functional assemblies.

One strategy is multi-step self-assembly, which includes covalent preparation of ditopic monomers and supramolecular polymerization of these monomers. In order to obtain high molecular weight polymers, we have introduced a rigid or bulky linker into the monomer to suppress dimerization and cyclization during supramolecular polymerization. To this end, we have established a new methodology of supramolecular polymerization promoted and controlled by self-sorting. It is highly anticipated that a similar methodology can be used to fabricate supramolecular polymers with linear, branched or hybrid topologies and different self-sorting systems could also be utilized.

Another strategy involves so-called mixed strategy, referring to non-covalent preparation of supramonomers and covalent or non-covalent polymerization of them. For example, supramonomers are fabricated on the basis of host-guest interactions, and then supramolecular polymers are produced by click polymerization of the supramonomers. In this way, the fabrication of supramolecular polymers may become controlled by choosing appropriate methods of covalent polymerization. In addition, we have demonstrated that the similar concept can be extended to fabricate supramolecular polymers by non-covalent synthesis of the supramonomers as well.

References
POLY 17: Sequential one-pot organocatalytic polymerization of epoxides and cyclic esters/carbonates

Junpeng Zhao\textsuperscript{3}, junpeng.zhao@kaust.edu.sa, David Pahovnik\textsuperscript{2}, Yves Gnanou\textsuperscript{4}, Nikos Hadjichristidis\textsuperscript{1}. (2) National institute of chemistry, Ljubljana, Slovenia (3) Physical Sciences and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia

Abstract

At first glance, the sequential ring-opening polymerization (ROP) of epoxides and cyclic esters seems facile and the synthesis of the corresponding block co-/ter-/quarto-polymers appears straightforward. However, initiating/catalytic systems that work for epoxides, typically alkali alkoxides, provoke chain transfer reactions in the case of cyclic esters, and those that are appropriate for the latter, typically tin or aluminum alkoxides, are irrelevant for the former. The same is valid in the case of organocatalysts such as phosphazene bases. For example, \(t\)-BuP\(_4\), one of the strongest phosphazene bases, is well suited for the polymerization of epoxides but brings about extensive chain transfer reactions in the case of cyclic esters. By using a mild phosphazene base (\(t\)-BuP\(_2\)), as the common catalyst and monohydroxyl compound or water as initiators, we were able to synthesize in one-pot well-defined triblock and pentablock terpolymers of ethylene oxide (EO), \(\varepsilon\)-caprolactone (CL) and L-lactide (LLA). The drawback of this strategy is the long polymerization time of EO (three days) and that no other (substituted) epoxides can be polymerized by \(t\)-BuP\(_2\). On the other hand, strong organic acids, such as diphenyl phosphate (DPP) have been employed to afford well-controlled ROP of cyclic esters/carbonates via either a monomer activation mechanism or a monomer/chain end dual activation mechanism. By combining the ideal superbase catalyst (\(t\)-BuP\(_4\)) for epoxides and the ideal organic superacid catalyst (DPP) for cyclic esters/carbonates into a novel “catalyst switch” strategy, where DPP acts as both base neutralizer and catalyst (excess), we were successful synthesizing in one-pot well-defined co-/ter-/quarto linear and 3-arm star polymers.

References


Figure. Sequential organocatalytic ring-opening polymerization of epoxides and cyclic esters/carbonates using (a) a mild phosphazene base (\(t\)-BuP\(_2\)) and (b) a "catalyst" switch strategy
Poly(2-vinyl-4,4-dimethylazlactone) (pVDMA) is emerging as an extremely versatile reactive platform in synthetic polymer chemistry. Post-polymerization modification of pVDMA (co)polymers with judiciously chosen primary and secondary amines is a convenient route for the preparation of novel responsive (co)polymers sensitive to a range of applied stimuli. In this talk we demonstrate the ability to access libraries of new thermoresponsive polymers with sharp and tuneable cloud points, how to reversibly induce self-assembly as a function of temperature or pH and how to prepare series of stimulus responsive hydrogels all from well-defined pVDMA (co)polymers prepared via reversible addition-fragmentation chain transfer (RAFT) radical polymerization.
POLY 19: Self-immolative polymersomes for high-efficiency triggered release and programmed enzymatic reactions


Stimuli-triggered disassembly of block copolymer vesicles or polymersomes has been conventionally achieved via solubility switching of the bilayer-forming block, requiring cooperative changes of most of the repeating units. Herein we report an alternative approach by incorporating hydrophobic blocks exhibiting stimuli-triggered head-to-tail cascade depolymerization features. Amphiphilic block copolymers bearing this motif self-assemble into self-immolative polymersomes (SIPsomes). By modular design of terminal capping moieties, visible light, UV light, and reductive milieu can be utilized to actuate SIPsomes disintegration into water-soluble small molecules and hydrophilic blocks. The design of SIPsomes allows for triggered drug co-release and controllable access towards protons, oxygen, and enzymatic substrates. We also demonstrate programmed (OR, AND and XOR-type logic) enzymatic reactions by integrating SIPsome encapsulation and trigger/capping moiety-selective cascade depolymerization events (Scheme 1).

Scheme 1: Schematics of the construction self-immolative polymersomes and relevant characterization data
Cartilage provides a smooth and nearly frictionless contact surface for joint movements. Aggrecan is a biologically important naturally occurring polyelectrolyte, whose complexes with hyaluronic acid provide the osmotic resistance of cartilage. It has a bottlebrush architecture consisting of a core protein to which many chondroitin sulfate and keratan sulfate chains are covalently attached. These charged side chains (bristles) are distributed along well-defined regions of the protein core. The molecular mass of the chondroitin sulfate chains varies from 20 to 30 kDa, while the molecular mass of the keratan sulfate chains is between 4 and 8 kDa. Light scattering and small angle neutron scattering (SANS) measurements are reported for aggrecan in near physiological salt solutions. These techniques probe the length scales that govern the osmotic response of the system. At low values of the scattering vector $q$, SANS and static light scattering measurements reveal that the aggrecan solution contains assemblies of aggrecan subunits. Dynamic light scattering yields a relaxation rate that varies as $q^3$, arising from the internal modes of the motion inside the aggrecan assemblies. In the presence of hyaluronic acid (HA) light scattering measurements indicate complex formation between aggrecan and HA molecules. The supramolecular aggrecan/HA complexes provide the osmotic properties necessary for the cartilage to resist deswelling under compressive load.

The experimental results discussed in the presentation illustrate that
(i) The structure and function of cartilage involve specific interactions between the major macromolecular constituents of the extracellular matrix, and
(ii) Combination of static and dynamic measurements probing the mechanical properties over a broad range of length and times scales yield new insights into the functional properties of cartilage.

![Figure 1](image-url)

Figure 1. Small-angle neutron scattering profiles of aggrecan in near physiological (100 mM NaCl) salt solutions.
POLY 21: Drug-functionalized cell-penetrating peptides for enhanced delivery and binding in myotonic dystrophy type 1 treatment

Yugang Bai¹, baiyugang@outlook.com, Lien Nguyen², Ziyuan Song³, Jianjun Cheng³, Steven C. Zimmerman⁴. (1) University of Illinois at Urbana-Champaign, Urbana, Illinois, United States (2) Chemistry/ RAL Box 41-5, UIUC, Urbana, Illinois, United States (3) Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States (4) Chemistry, University of Illinois, Urbana, Illinois, United States

Small molecules that were known to bind to (CUG)n repeat were conjugated onto the side chains of cell-penetrating peptides (CPPs) by click-chemistry. The CPPs greatly improved the water-solubility of the hydrophobic drug, preventing aggregation, and effectively transporting them into the cells. In addition, the resulting multi-valent drug polymers could have dramatically improved binding affinity towards (CUG)n repeat, as well as reduced cellular toxicity. The helical polypeptide could expose all the drug moieties on the exterior of the rod-like conformation, making them all available for binding. Peptides with different length, drug loading and helicity were evaluated using model cells. Overall, the exceptionally high binding affinity and efficient drug delivery allowed very low dosage in affinity, foci dispersion and splicing reversal studies. Short RNA-cleaving peptide could potentially be conjugated onto the CPPs as well, granting the conjugates the ability to degrade the toxic RNA.
POLY 22: Novel biodegradable, biocompatible and biofunctional block copolymer scaffolds for tissue engineering applications

Patrizia P. Smith¹, pasmith@mines.edu, Amanda L. Rightler², Brook K. McConnell³, Fang Zhang³, Sven O. Streubel³, Shi-Long Lu³, Daniel Price⁴, Stephen G. Boyes¹. (1) Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado, United States (2) Department of Chemistry and Biochemistry, University of Tulsa, Tulsa, Oklahoma, United States (3) Department of Otolaryngology, University of Colorado Denver, Denver, Colorado, United States (4) Columbine High School, Littleton, Colorado, United States

Polymers such as poly(lactide) (PLA) and other polyesters possess advantageous properties such as biodegradability, biocompatibility and good mechanical properties which has led to their use as scaffold materials for tissue engineering applications. Scaffolds serve as a temporary artificial extracellular matrix (ECM), thus polymers functioning as scaffolds should be reasonably hydrophilic and aid cell adhesion, proliferation, differentiation, and new tissue formation. PLA homopolymers are inherently hydrophobic and modification procedures to render them more hydrophilic generally result in the breakdown of the polymer backbone and in a decrease in the mechanical integrity of the scaffold. Furthermore, it has been a challenge to functionalize PLA-based scaffolds since control over the loading of bioactive agents is rather limited. We thus report the development of amphiphilic PLA-based block copolymers such as poly(lactide)-block-poly(polyethylene glycol ethyl ether methacrylate) (PLA-b-PPEGEEMA) which can be transformed into core-shell type fiber scaffolds using electrospinning and phase separation techniques. Contact angle and wetting studies show that the block copolymer scaffolds exhibit highly improved hydrophilicity, suggesting that the PPEGEEMA block is located on the surface of the fibers. Furthermore, preliminary cell studies using IMR90 cells show that the PLA-b-PPEGEEMA scaffolds favor cell adhesion compared to the PLA homopolymer scaffolds. Lastly, the incorporation of poly(N-methacryloxyxysuccinimide) (PmAOS) allows for biofunctionalization of the block copolymer with peptides or growth factors and the synthesis of novel biocompatible, biodegradable and biofunctional polymer scaffolds is currently under way.
POLY 23: Protein:polymer conjugates via graft-from ring-opening metathesis polymerization

Sergey A. Isarov1,2, s.isarov@gmail.com, Jonathan K. Pokorski1. (1) Department of Macromolecular Science and Engineering, School of Engineering, Case Western Reserve University, Cleveland, Ohio, United States (2) Department of Physiology and Biophysics, School of Medicine, Case Western Reserve University, Cleveland, Ohio, United States

The conjugation of polymers to therapeutically-useful proteins is an effective way to improve their stability as well as to protect them from degradation in vivo. These modifications ultimately increase circulation lifetime and bioavailability. Unfortunately, existing methods for the fabrication of such conjugates are ‘graft-to’ approaches that have considerable kinetic limitations. In this work, we describe the first modification of proteins via ‘graft-from’ ring-opening metathesis polymerization (ROMP) under physiological conditions. ROMP chemistry is extremely powerful due to its ability to quickly form low-dispersity polymers of targeted molecular weights and architectures, while being exceptionally tolerant of a variety of functional groups. A water-soluble ROMP ruthenium carbene catalyst was prepared and immobilized onto the protein surface to form a stable macroinitiator. This macroinitiator subsequently facilitated the growth of polymers directly from the protein surface resulting in high-molecular-weight protein:polymer conjugates. Finally, reactive block copolymers were grown from the protein surface and shown to react post-polymerization to form fluorescent conjugates.
Poly lactic acid as a biodegradable polymers in packaging materials reduce the environmental pollution caused by plastic wastes. These natural polymer are widely seen as a biopolymer has poor mechanical strength that need to use nanoparticle. Natural cellulosic fibers were used in long form as a reinforcement to fabricate green composites. The objective of this research is to investigate and improve mechanical and thermal properties of PLA by developing PLA composites reinforced with natural fibres. Mechanical and physico-chemical properties of the composites have been investigated as a function of fiber loading. Fiber/matrix interaction between the polymer and reinforcement has been analyzed and the composites fabricated showed an increase in properties with fiber loading up to 20%.
POLY 25: N-heterocyclic carbenes in the organopolymerization of N-substitued N-carboxy-anhydrides to polypeptoid

*Laura Falivene*¹, *lfalivene@hotmail.it*, *Miasser Alghamdi*², *Luigi Cavallo*³. (1) KCC, KAUST, Jeddah, Saudi Arabia (2) KAUST, Thuwal, Saudi Arabia (3) King Abdullah Univ of Science Technology, Thuwal, Saudi Arabia

The use of “new” catalytic systems working in reactions that were previously known to be possible only by transition-metal complexes has attracted growing interest. Organocatalysis, a catalytic approach based on using small organic compounds, such as N-heterocyclic carbenes (NHC), to promote reactivity, has become a powerful tool in organic synthesis, polymer synthesis and other areas, thanks to several advantages it can offer, as compared to other modes of catalysis. Following our work in the NHC promoted polymerization of cyclic and acyclic acrylates [1-2], here we present an account of theoretical studies into the mechanism of polymerization of polar cyclic monomers promoted by N-heterocyclic carbenes (NHC). In particular, the mechanism of polymerization of N-substitued N-carboxy-anhydrides to poly(a-peptoid), promoted by NHC has been investigated, see Chart 1. The general mechanism goes through the monomer activation carried up by the NHC species, acting like an initiator; afterwards the propagation occurs on the anionic center. In each step one monomer is added and one molecule of CO₂ is released [3-4]. Recent experimental findings strongly suggested the presence of two initiation pathways. Encouraged from these experimentally results, a DFT investigation has been performed with the aim to rationalize the possible occurring activation, propagation and termination mechanisms, figuring out which is the mechanism energetically favored.

![Chart 1](image)

Cellulose is one of the most abundant biopolymers on earth and is the cornerstone of products such as paper, cardboard and clothing. However, due to the excellent material properties of cellulose, such as high strength and low weight, it is foreseen that with proper modification, cellulose could be employed in various other applications. An interesting approach to cellulose modification is through long chain grafting, a topic that has been extensively studied since the 50’s. One particularly interesting polymerization method for this purpose is ring opening polymerization (ROP), as it can be initiated from the hydroxyl groups on the cellulose backbone and hence no modification of the cellulose is necessary in order to form grafts. There exist several reports in the literature on the grafting of both PCL and PLA utilizing ROP from cellulose surfaces. Herein, the surface-initiated ROP of trimethylene carbonate (TCM) and hexamethyldicyclotrisiloxane (HMCS) employing organocatalytic systems, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), has been investigated. The ability to control the grafting length of the polymer from the surface was demonstrated by either altering the time of the polymerisation or the ratio of free initiator to monomer. TBD was a highly efficient catalyst, both for TCM and HMCS, resulting in hydrophobic paper in as little as one minute. However; when DBU was employed for the ROP of HMCS, no polymer was formed. This polymerisation route provides milder conditions than conventional metal-catalysed ROP, greatly reducing reaction times and thus is an attractive method for modification of natural biopolymers compared to previously described methods.

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Recently, we developed a light-induced polymerization method based on the copper-catalyzed alkyne azide cycloaddition reaction (photo-CuAAC). Photo-CuAAC polymerizations have proven to be ideal for preparing polymers with high glass transition temperature, mainly due to the stiff triazole linkages that are the products of CuAAC reactions. In order to implement photo-CuAAC polymerizations for rapid curing and hydrolytic stability, the design of non-degradable monomers is essential. Herein, we evaluated the effects of monomer structures on the conversion and the rate of photo-CuAAC polymerization. Di-functional azides and tri-functional alkynes were synthesized with variability in core structures (linear, cyclic and aromatic) and backbone functionalities (carbamates and ethers). The polymerization kinetic was monitored via FTIR. Increases in polymerization rates and final conversion were observed as we reduced the stiffness of core structures and backbones. For example, when the core structure of azides was changed from methylenediphenylene to cyclohexane, the average initial polymerization rate increased from 33±6 to 60±6 % conversion per minutes, and the final conversion increased from 75±3% to 95±1% when curing at 50°C. In conclusion, we demonstrated that structural elements of monomers are crucial for controlling both the polymerization rate and the maximum conversion in photo-CuAAC polymerizations.

POLY 28: Chemical modification reactions of polysaccharides studied in real time by light scattering and viscometry-based methods

Vivian C. Spier², Alina M. Alb¹, aalb@tulane.edu. (1) Physics, Tulane University, New Orleans, Louisiana, United States (2) Chemistry, UFPR, Curitiba, Parana, Brazil

Polysaccharides, in natural or chemically modified form, have become recently increasingly attractive to both research and industrial communities, mainly due to their good solubility in water, high chemical reactivity, and high solution viscosity, at low cost and low toxicity. Among the extensively used chemical modification reactions, oxidation reactions of polysaccharides, represent a promising route to extend the range of applicability since they lead to anionic polyelectrolytes with higher solubility in aqueous media.

In this study, the TEMPO-mediated oxidation of xyloglucan and the subsequent alkylation of the intermediate reaction products using dodecylamine are followed in real time by light scattering-based unique methodologies together with traditional methods. The effects of various factors such as pH, reaction temperature, and polysaccharide structure on the degree of oxidation and on the grafting efficiency and degree of alkylation are investigated. Changes in polymer characteristics (molecular weight distribution, size) during the oxidation reactions and the gradual conversion to polyelectrolyte are illustrated in the evolution of the computed electrostatic and hydrodynamic parameters. Monitoring viscosity and light scattering signatures during both types of reactions offer complementary means to highlight conformational differences between the grafted and starting polymers allowing quantitative assessments to be made about degree of grafting and efficiency of the reactions. It is hoped that the knowledge gained from these studies will offer efficient tools for enhancing targeted material properties.

Online monitored TEMPO-mediated oxidation of xyloglucan
The objective of polymer drug-delivery is to preferentially accumulate at the diseased site and deposit a large payload of therapeutic. If these requirements are met, polymer-therapeutics have the potential to increase drug efficacy, reduce side effects and improve patient compliance. Current state-of-the-art techniques used to monitor the in vivo behavior of polymers involve qualitative fluorescence imaging, several blood draws, and the sacrifice of numerous animals followed by arduous analysis of harvested tissue. These techniques are extremely invasive and give a one-time “snapshot”, which only provides rudimentary information of the absorption, distribution, metabolism, and elimination (ADME) of the material. Therefore, a rapid, non-invasive technique that provides real-time, continuous feedback of the interaction between a polymer and the body is necessary to optimize drug-delivery. Positron Emission Tomography (PET) and Single Photon Emission Computed Tomography (SPECT) are used to non-invasively visualize how polymers navigate through the body. Furthermore, tomographic imaging provides real-time kinetic information on the pharmacokinetic (PK) and pharmacodynamic (PD) behavior of each polymer. We evaluate two key pharmacokinetic parameters for each polymer: blood circulation, and tumor accumulation. Factors such as molecular weight, charge, and biocompatibility were investigated for enhance circulation and tumor accumulation.

Figure 1. Dynamic Positron Emission Tomography of a Polymeric Delivery System Labeled with Copper-64

Figure 1. Dynamic Positron Emission Tomography of a Polymeric Delivery System Labeled with Copper-64
In this contribution, we have investigated a series of polymerization reactions using a thermal camera. The aim of this study was evaluating this approach to obtain a time- and spatially-resolved image on the course of polymerization reactions. Indeed, thermography allows for recording heat evolvement/time plots combined with spatial resolution on the surface of macroscopic samples. Heat distribution within the formulation and transfer across the interface area can be monitored and evaluated (see figure). Accordingly, we became able distinguishing between the influence of bulk and the interface area. Additionally, undesired side reactions like oxygen inhibition in radical polymerizations can be trapped. Our results indicate that using appropriately designed reaction chambers, thermography offers beneficial insights into the evolution of polymerization reactions.

Figure. Heat evolvement, recorded with a thermal camera, indicating start of the ring opening metathesis polymerization of dicyclopentadiene depending on the volume of the reaction chambers. An identical formulation of dicyclopentadiene and a Grubbs 2nd generation-type initiator was filled in three differently shaped reaction chambers (3.14 mL: 20 mm Ø x 10 mm; 2.01 mL: 16 mm Ø x 10 mm; 1.13 mL: 12 mm Ø x 10 mm).
Hydrogels are currently being studied in great depth for a multitude of applications in medicine due to their high water content by mass. The conventional brittle single network hydrogel has been successful in meeting many needs of the medical industry, particularly in low-load bearing applications, however it fails to perform in mechanically demanding applications such as those encountered by tissue or cartilage. The brittleness of conventional single network hydrogels comes largely from the heterogeneous nature created during synthesis. This heterogeneity causes regions of high stress throughout the polymer with few or no mechanisms available for distributing load effectively throughout the system. Modern dual-network hydrogel platforms focus on combatting this inhomogeneity—and thus, brittleness by transferring load to a secondary network in such a way as to reduce the number of covalent bond breakages and prevent crack propagation. However, they are often prone to hysteresis as one of the networks is often sacrificial, making them unsuitable for cyclic loading. Our unique system comprised of AB diblock and ABA triblock copolymer has been tuned to form a highly homogeneous network of 20nm spheres (A blocks) which are tethered mechanically during melt-state self-assembly. Through increasing the triblock copolymer content in this hydrogel platform to levels above 40 mol% we have been able to produce single network systems able to compete mechanically, while often having a higher water content by mass, with many dual-network and composite systems. This simple and highly tunable platform, which can also undergo high cyclic loading with low levels of hysteresis, may have significant implications for the future of synthetic soft tissue design.
POLY 32: Smart polymers for on-demand drug delivery

Yanfeng Zhang3, Kaimin Cai2, Jianjun Cheng1, jianjunc@illinois.edu. (1) Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States (2) Materials Science Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States (3) University of Illinois at Urbana-Champaign, Urbana, Illinois, United States

Smart materials that are stable under ambient conditions but can degrade rapidly in response to external triggers may have broad applications. Triggers such as light, changes in pH and temperature, enzymes, redox agents, and ultrasound have been employed in the design of smart polymers. Self-immolative polymer is one such trigger-responsive material prepared with aniline derivatives bearing a methylalcohol substituent in the para- or ortho-position as key building blocks. The aniline monomers self-condense to form polymers with a urethane backbone and a terminal amine protected by a trigger-responsive protecting group. Once the removal of the protecting group is triggered, degradation by means of a 1,6- or 1,4-elimination reaction is initiated from one chain end and propagates spontaneously through the polymer backbone to the other end. Here, we report the redesign of self-immolative polymers by creating a class of polymers that can undergo degradation in a more controlled manner. Specifically, we designed 2,6-bis(hydroxymethyl)anilines (BHA) bearing protecting groups sensitive to UV light, acid, or base, and used the two hydroxyl groups of BHA for condensation polymerization with active bis-acyl co-monomers for the synthesis of polymers bearing trigger-responsive domains controlling the polymer degradation. Application of triggers to remove the protecting group of polymers resulted in elimination reactions at each repeating unit. We used this polymer to prepare drug-containing nanoparticles from which the encapsulated cargos can be rapidly released upon trigger-induced degradation.
Size exclusion chromatography, SEC, (gel permeation chromatography, GPC) is at present the most common method for molecular characterization of synthetic polymers in terms of their molar mass averages and dispersities (distributions). Usefulness of SEC/GPC is enormous because besides quantitative molar mass data of linear macromolecules, it enables fast estimation of molecular parameters of complex polymers such as copolymers and branched polymers, as well as assessment of sizes of isolated macromolecules in solution. The extent of aggregation and association of macromolecules, and also of (preferential) interactions in polymer systems can be judged. Unfortunately SEC/GPC is often used improperly because several phenomena that can badly affect the quality of results are unknown, underestimated, or deliberately ignored by some researchers. SEC/GPC results are intentionally misinterpreted and sometimes even misused to support incorrect conclusions. Basics of SEC/GPC will be briefly outlined and the unconventional applications of method elucidated. The drawbacks, shortages, and pitfalls of SEC/GPC will be discussed more in detail with the aim to furnish information to the method users who may want to ameliorate quality of their results and seek explanation of some unexpected outcomes of their measurements. The role of column porosity, enthalpic interactivity, as well as their history will be demonstrated. The effect will be discussed of experimental conditions, especially mobile phase type and purity, injected sample concentration and volume on the quality of data obtained. It will be manifested that SEC/GPC still needs further development and that the standardization of sample preparation, measurement, and processing of results is necessary.
The need for even better insights into polymer structure-property relationships to support process and application development continues to drive improvements in analysis techniques. Simultaneous determination of polymer chemical composition and molecular weight can be achieved using a two-dimensional coupled gradient polymer elution (GPEC) – size exclusion chromatography (SEC) system with traditional UV, RI, or light scattering detectors. This approach becomes even more powerful when an information-rich mid-infrared spectroscopic detector is incorporated. Current LC-IR instrumentation enables IR spectra to be collected that cover nearly the full spectral range (4000 – 700 cm\(^{-1}\)) after solvent elimination. This offers the potential to have a full FTIR spectrum for every point in the chromatogram, thereby enabling the identity and composition of specific chromatographic peaks to be determined. In addition, advanced data processing techniques often are employed to analyze the resulting datasets. Baseline algorithms are utilized to remove excess noise from the data prior to subsequent interpretation and analysis, such as better identifying an unknown chromatographic peak via an FTIR spectral library search or generating functional group-specific molecular weight distributions. More sophisticated approaches, such as multivariate curve resolution by alternating least squares (MCR-ALS), are used to mathematically resolve co-eluting polymers whose spectra lack isolate, unique IR bands, as shown in the figure for SAN and PS. This presentation will provide examples, using commercial polymers, of two aspects of utilizing a solvent elimination IR detector after the chromatographic separation: method development data analysis.

A): Weight percent of acrylonitrile as a function of elution time for a styrene-acrylonitrile (SAN) copolymer sample.
B): MCR-ALS resolved chromatographic profiles for the SAN copolymer (Blue) and residual polystyrene monomer (Red)
C): MCR-ALS resolved IR spectra. (Left, Blue) SAN copolymer, (Right, Red) Residual polystyrene monomer.
Chemical heterogeneity, defined as the change in average chemical composition as a function of copolymer molar mass, affects processing and end-use properties of copolymers such as toughness, brittleness, and biodegradability. In one-dimensional size-based macromolecular separations (e.g., size-exclusion or hydrodynamic chromatography, or flow field-flow fractionation), chemical heterogeneity is usually determined with via multiple detection, employing a series of detectors with different sensitivities (e.g., refractometry combined with UV spectroscopy), or using chemically-sensitive detection methods such as infrared (IR) or, less commonly, nuclear magnetic resonance spectroscopy. To date, Raman spectroscopy appears to have been overlooked as a potential macromolecular separations detection method for the purposes of determining copolymer chemical heterogeneity. This, in spite of the fact that Raman presents a number of advantages over, e.g., IR, especially as regards the characterization of water-soluble copolymers. Here, we examine the feasibility of coupling size-exclusion chromatography (SEC) to Raman detection in continuous off-line fashion, akin to the way SEC is coupled to IR using a solvent elimination interface. Results of our heart-cut experiments, which involved a gradient random copolymer of styrene and methyl methacrylate, were compared to chemical heterogeneity information for the same copolymer obtained via on-line SEC/MALS/UV/DRI. Our results demonstrate that continuous off-line Raman detection for macromolecular separations is feasible and, furthermore, that this type of coupling should be possible employing the same or similar hardware to that currently used for continuous off-line IR detection in size-based macromolecular separations.
POLY 36: Probing serum phase oligomer in acrylic emulsion polymerization process by GPC-RI/MS

Tianlan Zhang, Tianlanzhang@dow.com, Wei Gao, Ralph Even, Debra Kline. The Dow Chemical Company, Collegeville, Pennsylvania, United States

In free radical emulsion polymerization, water soluble initiator radicals are generated by either a thermal or redox process. The free radicals in the aqueous phase will react with soluble monomers until they reach a composition (z-mer radical) 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 before such adsorption events, forming serum oligomers which can be found in the final product. It is apparent that understanding the serum phase oligomers is not only important to probe the aqueous phase reaction during emulsion polymerization, but also to ascertain their impact on the final performance of emulsion products.

A gradually fed, seeded butyl acrylate/acrylic acid emulsion with redox activated persulfate initiator was studied. The serum phases of in-process samples were analyzed by GPC-RI/MS to determine the concentration, the molecular structure, and the formation mechanism of the serum phase oligomer as well as soluble radicals during the emulsion polymerization. The z-mer radicals captured by 4-hydroxy-TEMPO were also identified in the analysis and their composition is in good agreement with the composition of sulfate anion free radical adducts suggested by Maxwell, I. A. et al. based on hydrophobic free energy of absorption.


Figure 1: GPC-RI Chromatograms: in-process sampling serum phase of acrylic emulsion
Styrenic thermoplastic elastomers (TPEs) are of great importance in both academic research and industrial applications. However, high temperature applications, such as use in tires, cannot be achieved by styrenic materials due to the glass transition temperature of polystyrene ($T_g=100^\circ$C). To address this need, we have carried out the synthesis and characterization of triblock copolymers polybenzofulvene-b-polyisoprene-b-polybenzofulvene (FIF). Detailed morphological characterization and mechanical testing are currently underway and will be reported at the conference.
POLY 38: Ultrahigh performance size exclusion chromatography of synthetic polymers
Miroslav Janco¹, MJanco@dow.com, James N. Alexander¹, Edouard S. Bouvier², Damian Morrison². (1) Analytical Sciences, Dow Chemical, Collegeville, Pennsylvania, United States (2) Waters Corp, Milford, Massachusetts, United States

Size Exclusion Chromatography (SEC) is the preferred method for the determination of the molecular weight parameters of synthetic polymers as a result of its universality, reliability, reproducibility and low sample consumption. To achieve sufficient resolution of separated species, the column sets are composed of at least two, and more often, three analytical columns (300 x 7.5-10 mm ID). Typical flow rates are 1 - 2 mL/min in order not to damage the column packing by exceeding its back pressure limit. Therefore, resulting SEC separation run times are often in range of 30 to 60 min. Substantial acceleration of SEC separations remains difficult to achieve due to column packing pressure limitations. Short and wide diameter SEC columns (50 x 25 mm ID) that allow high eluent flow rates (typically 5 to 10 mL/min) while still running at moderate backpressure are the only present solution to speed up SEC separations¹). A limitation to this approach is lower column resolution.

Ultra high performance size exclusion chromatography (UHP SEC) is a newly developed disruptive technology allowing separation of synthetic polymers with very short analysis times and improved resolution²). Using a Waters ACQUITY UPLC® H-Class system and BEH SEC columns packed with 1.7-2.5 μm particles with pore size ranging from 45 to 900 Å, size based separations of polystyrene and poly(methyl methacrylate) standards in tetrahydrofuran and poly(ethylene oxide) standards in 20 mM ammonium acetate in methanol are achieved within two to six minutes. The speed of analysis is about ten times faster than conventional SEC separations, and greater resolution is achieved (Figure 1). Average molecular weights of selected commercial polymers have been determined using UHP and conventional SEC. Average M data of analyzed samples are in good agreement using the two approaches. An inherent limitation of SEC in UHP mode is the characterization of very high M polymers (above ca. 2 million Daltons) due to the deformation and/or mechanical shearing of large molecules at high flow rates.

Figure 1. UHP SEC chromatogram of 16 component mixture of PS standards obtained on three BEH XT columns (150x4.6 mm id) packed with 2.5 μm BEH particles in THF using RI detection. Flow rate: 1ml/min.
POLY 39: Advanced polymer chromatography: Method development tools for SEC polymer analysis

Damian Morrison, Damomorrison@verizon.net, Michael O'Leary. Chemical Materials, Waters Corp, Milford, Massachusetts, United States

Traditionally, size exclusion or gel permeation chromatography (SEC/GPC) is used for the characterization of polymeric material, specifically their molecular weight distribution. In order to resolve polymeric species, long column lengths and banked column configurations are commonly used, resulting in lengthy analytical test cycle times as well as the associated consumption of costly and often hazardous solvents. Additionally, many test sets suffer from minimal replicate data points due to the typical analysis time resulting data with limited statistical weighting.

In this paper the benefits of a comprehensive systematic approach for polymer molecular weight characterization will be presented. Waters® ACQUITY® Advanced Polymer Chromatography® (APC™) System, with its innovative and robust ACQUITY APC™ column technology, allows for improved resolution of polymer distributions with significantly shorter chromatographic total analysis cycle times. Additionally, we will describe some of the tools that are available to develop stable and impactful test methods that result in richer data sets based on more stable operating conditions, and replicate analyses that are easily obtained within minutes and not hours.
POLY 40: Progress towards the efficient synthesis of polymers with precisely defined mass, sequence, and stereochemistry

Jonathan Barnes², Deborah Ehrlich², Frank Leibfarth², Timothy F. Jamison¹, Jeremiah A. Johnson², jaj2109@mit.edu. (1) Chemistry/18-590, MIT, Cambridge, Massachusetts, United States (2) MIT, Massachusetts Institute of Technology, Boston, Massachusetts, United States

Mother Nature achieves remarkable functional diversity from macromolecules with precisely defined structures built using only a few monomers. Despite numerous recent advances towards the goal of precision polymer synthesis, there are still very few examples of non-amide- or non-phosphate-based synthetic polymers that simultaneously possess precise mass, sequence, and stereochemistry. In cases where these features are present, the requisite synthesis is not amenable to facile diversification or scale-up. This talk will describe the development of a synthetic strategy for the efficient synthesis of macromolecules with precise atomic structure. The approach makes use of the seldom-used iterative exponential growth process, which allows for rapid molecular weight increase through iterative monomer activation and coupling reactions. A few critical modifications of this method have allowed us to synthesize precisely defined polymers on preparative scale. The synthesis, properties, and applications of new families of precise macromolecules will be presented.
The programmed synthesis of block copolymers can be achieved by a number of controlled polymerization methodologies. Using ATRP novel amphiphilic diblock copolymers have been prepared starting from PEO-based non-ionic surfactants having an aliphatic end-group. The resultant styrenic block copolymers have been synthesized and fully characterized. The block copolymers show intriguing crystallization in the solid state, and self-assembly behavior in aqueous solution. The PEO block in all of the prepared samples was found be amorphous, which contrasts with the PEO surfactant precursor, MeOPEO-b-PS and fluorinated DNPEPEO-b-PFMAs (Macromolecules 2013, 46, 3737–3745). These results indicate the profound influence of the end-group to direct physical properties. Block polymer particles (BCPs) with mesoporous internal structures are formed by self-assembly in THF/water solutions. The transformation of internal and surface structures of these BCP as a function of water content and temperature were investigated by TEM, SEM and DLS. The internal mesoporous structures of the BCPs were richly varied, and could be interesting materials for catalysis, templating and delivery applications. The influence of end-groups to afford the ability to direct, or program, structure in solution or the solid state will be discussed.
The security printing industry struggles continuously to outwit counterfeiters employing measures that are difficult to reproduce without special knowledge, resources, and equipment. Although fluorescent inks have emerged as powerful anti-counterfeiting technologies, we lack methods for creating high-security features such as real-time color tuning. We have developed a fluorescent ink by installing large rings around fluorophores by means of the cooperative capture synthesis.1–3 This system’s complex equilibria, rapidly tunable solid-state fluorescence, and non-linear response to ink concentrations lay the foundations of a strategy for encrypting images that are difficult to reproduce, even given access to the ink’s components. Not only is this modular system reversible, it is also complemented by simple chemical authentication protocols. These attributes set this system apart from conventional fluorophores and render it appealing for applications in high-security protection technologies.

References:
This presentation will highlight recent advances in our investigation of stimuli-responsive materials that rely on reversible covalent interactions. By constructing branched macromolecules and hydrogels that are crosslinked via dynamic-covalent bonds, we are able to prepare materials capable of responding to changes in their surrounding environment. Single chains and polymeric nanoparticles that contain these linkages are able to reconfigure their macromolecular structure and/or dissociate into smaller components by reshuffling their covalent crosslinks. Hydrogels crosslinked via reversible linkages are able to heal themselves by crosslink exchange across their failure interface. This presentation will cover our recent results in each of these areas.
We demonstrate that chirality determines the phase state of polyelectrolyte complexes formed from mixing dilute solutions of oppositely charged polypeptides. In these systems, the physical state of the resultant complex is determined by the combination of electrostatic and hydrogen bonding interactions. The formation of fluid complexes occurs when at least one of the polypeptides in the mixture is racemic, which disrupts backbone hydrogen bonding networks. Pairs of purely chiral polypeptides, of any sense, form compact, fibrillar solids with a β-sheet structure on mixing. Analogous behavior occurs in micellar cores formed from polypeptide block copolymers with polyethylene oxide, where microphase separation into discrete, self-assembled aggregates with either solid or fluid cores, and eventually into ordered phases at high concentrations, is possible. Chirality is an exploitable tool for manipulating material properties in systems based on polyelectrolyte complexation. Its role in these systems gives insight into polyelectrolyte complex phase behavior more broadly. Work performed in collaboration with Sarah L. Perry, Lorraine Leon, Kyle Q. Hoffmann, Matthew J. Kade, Dimitrios Priftis, Katie A. Black, Derek Wong, Ryan A. Klein, Charles F. Pierce III, Khatcher O. Margossian, Jonathan K. Whitmer, Jian Qin, Juan J. de Pablo.

Brightfield optical micrographs showing the liquid coacervates or solid precipitates resulting from the stoichiometric electrostatic complexation of L, D, or racemic (D,L) poly(lysine) with L, D, or racemic (D,L) poly(glutamic acid) at a total residue concentration of 6 mM and 100 mM NaCl. Liquid coacervate droplets are only observed during complexation involving a racemic polymer. Scale bars are 25 μm.
POLY 45: Responsive polypeptide-based star and triblock copolymers: Smart function through morphology transitions

Greg A. Strange, Ashley J. Johnson, Ian Smith, Jacob G. Ray, Daniel A. Savin, dsavin1973@gmail.com. Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, Mississippi, United States

The self-assembly of amphiphilic block copolymers is dictated primarily by the balance between the hydrophobic core volume and the hydrophilic corona. In these studies, amphiphilic diblock, triblock and star copolymers containing poly(lysine) (PK) and poly(glutamic acid) (PE) were synthesized and their solution properties studied using dynamic light scattering, circular dichroism spectroscopy and transmission electron microscopy. These materials exhibit hydrodynamic size that is responsive to pH, due in part to the helix-coil transition in the peptide chain, but also due to changes in curvature of the assembly and chain density at the interface. This talk will present some recent results in solution morphology transitions that occur in these materials as a result of the helix-coil transition and associated charge-charge interactions. We exploit the responsiveness of these materials to encapsulate and release therapeutics such as doxorubicin and demonstrate the potential to achieve triggered release as a function of pH due to morphology transitions.
Isosorbide and succinic acid are promising biobased feedstocks for the preparation of biorenewable materials. Some studies on isosorbide-succinate polyesters had previously been reported, but the properties of monomeric materials derived from these two building blocks were unknown. We designed a diisocyanate that is prepared from isosorbide and succinic acid in a short reaction sequence featuring a Curtius rearrangement. The diisocyanate synthesis does not require any stoichiometric petroleum-based reagents and has been scaled past 100 grams. This diisocyanate allows polyurethanes with up to 100% bio-content to be prepared, and the thermo-mechanical characterization of representative polyurethanes is ongoing. We also discovered that a synthetic precursor to the diisocyanate is a promising tackifier. Characterization of a family of related tackifiers revealed that simple structural changes allow the temperature at which the material is most tacky to be adjusted without reducing the level of maximum tack.
POLY 47: Benzyl chloride functionalized polycarbonates: A versatile platform for the synthesis of functional biodegradable polycarbonates

Robert Ono¹, ono@utexas.edu, Shao Qiong Liu⁴, Shrinivas Venkataraman², Willy Chin⁴, Yi-Yan Yang³, James Hedrick¹. (1) IBM, San Jose, California, United States (2) Inst of Bioeng and Nanotech, Singapore, Singapore (3) Inst Bioengr Nanotech, Singapore, Singapore (4) Institute of Bioengineering and Nanotechnology, Singapore, Singapore

An aliphatic polycarbonate containing pendant benzyl chloride groups was synthesized by organocatalytic ring opening polymerization (ROP) of a cyclic carbonate monomer (MTC-OCH₂BnCl). Facile post-polymerization modification of the resultant polymer with various nucleophiles facilitated access to a functionally diverse variety of biodegradable polycarbonate materials in high yield, including those that contained diethanolamine, phosphonium, and azide groups. The azide-functionalized polycarbonates could be further elaborated via Cu-catalyzed click chemistry with alkynyl-functionalized poly(ethylene glycol) (PEG) or pyrene to form the corresponding PEG- or pyrene-grafted polymers. Finally, preliminary results wherein the abovementioned post-polymerization functionalization of poly(MTC-OCH₂BnCl) is utilized to modulate the physical properties of self-assembled nanoparticles will be discussed in the context of therapeutic delivery applications.
POLY 48: Synthesis, characterization, and bimodal blend studies of renewable biobased epoxy resins from vanillyl alcohol

Eric D. Hernandez¹, hernan23@rowan.edu, Joshua M. Sadler², John J. La Scala², Joseph F. Stanzione¹. (1) Chemical Engineering, Rowan University, Glassboro, New Jersey, United States (2) Army Research Lab, RDECOM, Aberdeen Proving Ground, Maryland, United States

Polymers derived from renewable resources are becoming considerably attractive as sustainable alternatives to their petroleum-derived counterparts. Lignin is a natural and abundant raw material made up of cross-linked aromatics that could potentially be broken down to yield renewable bio-based monomers for applications in high-performance thermosetting resins. Vanillin, a lignin-derived aromatic molecule, can be reduced to yield an aromatic diol, vanillyl alcohol. Vanillyl alcohol is a promising monomer for the synthesis of epoxy pre-polymers. In this work, diglycidyl ether of vanillyl alcohol (DGEVA) was synthesized and its chemical structure was confirmed by ¹H-NMR, ¹³C-NMR, FT-IR, and GPC. Bimodal resin blends of diglycidyl ether of bisphenol A (DGEBA) with varying weight ratios of DGEVA as well as other single aromatic epoxies were prepared and cured with a diamine to investigate their structure-property relationships. Thermogravimetric and viscoelastic properties of the cured resins were characterized and compared using TGA and DMA, respectively. The vanillyl alcohol based epoxy-diamine system possesses a higher glass transition temperature \( T_g \) (106 °C) than the other single aromatic epoxy-diamine systems as well as a higher storage modulus \( E' \) at 25 °C (3 GPa) than the petroleum-based DGEBA-diamine resin.
Selective organic catalysis in the synthesis of materials from sustainable resources by ring-opening polymerization

Andrew P. Dove, a.p.dove@warwick.ac.uk. Univ of Warwick, Coventry, United Kingdom

Organic catalysts have become powerful alternative to metal-based salts and complexes in ring-opening polymerization (ROP). In addition to providing easy-to-use and low cost commercially available species that can mediate such polymerizations, organocatalysts have presented opportunities to polymerize monomers that are hard to polymerize in a controlled manner by other routes. Amongst these discoveries, the ability to control the polymerization of a wider range of monomers derived from sustainable resources has resulted. Our work in this area has focused on the development of organocatalytic species and the polymerization of monomers derived from renewable sources. The application of these polymers in elastomeric materials and 3D-printed scaffolds presents new application opportunities.
Polylactide (PLA) is one of the most ubiquitous plastics based on renewable resources. It is used in a variety of applications and is often found in biodegradable packaging. However, it is also used in hydraulic fracturing where it serves the role of a proppant delivery agent.

In this talk, a brief overview of hydraulic fracturing is presented in order to provide the context for how PLA is employed in this important field of natural resource development. Subsequently, PLA hydrolysis reactions are discussed and data is used to develop a simple kinetics model. Application of this model to varying reservoir conditions is discussed and prospects for future use of biodegradable polymers is given.

The use of PLA and other biodegradable polymers in hydraulic fracturing provides an excellent example of putting renewable polymers to work.
A new non-toxic soybean-based polymeric surfactant (SBPS) for personal-care products was developed and extensively characterized, including an evaluation of the polymer surfactant performance in model shampoo formulations. Foaming and cleaning ability of model formulations were compared to those with only sodium lauryl surfate (conventional low molecular weight surfactant, SLS) as a surfactant, as well as to SLS-free shampoos. The obtained results show that the presence of SBPS improves cleaning and foaming of model shampoo formulations. Their physico-chemical properties and performance are comparable to commercially available shampoos. Examination of SBPS/SLS mixtures in model shampoos showed that the presence of the SBPS enables the concentration of SLS to be significantly reduced without sacrificing shampoo performance.

In addition, it appears that the presence of SBPS promotes a conditioning effect as indicated by the reduction in protein loss from treated hair tresses. This positive influence of the soy-based surfactant ingredient is even more pronounced when the common conditioning agent, Aloe Vera extract, is present in the shampoo. Overall, the obtained results indicate that SBPS reduces damage to the hair during wet combing. Model SBPS-based shampoos were found to be comparable with the commercial shampoos used for the study. Major requirements of multifunctional shampoos - mild detergency, foaming, good conditioning and aesthetic appeal - are all met by SBPS-based model shampoo formulations.
Increasing performance requirements in a variety of markets and regulations toward more sustainable products and processes globally has led to high interest and investment in the chemical industry to research the properties of bio-based feedstocks as a sustainable and economical alternative to petroleum. This talk will review Elevance’s Biorefinery process that prepares building blocks from renewable feedstocks using a cross metathesis with olefins as shown in Figure 1.

The biorefinery outputs include olefins and esters that offer significant synthetic versatility. Figure 2 shows some examples of the molecular architectures that have been designed to obtain desired properties for a broad range of applications. Data will be presented comparing Elevance’s polymer and monomer technology to conventional technology, ranging from a recently commercialized functionalized poly-a-olefins that have shown improved lubricant properties versus conventional and metallocene PAOs to Elevance newly commercialized monomer, octadecanedioic acid that has shown improved water and chemical resistance versus shorter chain alternatives.

These examples and other potential advantages that metathesized building blocks can provide across multiple market segments and application areas will be presented.
New technology to produce an ever growing portfolio of renewable feedstocks continues to rapidly develop. Advances in catalysis and separations have made possible the production of a wide variety of high value monomers from commodity agricultural sources. These include both new molecules with unique properties not accessible from petrochemical derivatives as well as improved routes to existing chemicals of commerce. Understanding coproducts, safety, feedstock logistics and application needs is essential to successful commercialization of these technologies. Here we present a number of bioderived development opportunities including new monomers for polyesters, polyurethanes, polycarbonates, and epoxies and additives ranging from plasticizers to lubricants.

Example polymer feedstocks that can be derived from agricultural resources
POLY 54: Polysaccharide circuit boards for epidermal electronics

Michael A. Daniele¹, michaelangelo.daniele@gmail.com, Jeffrey S. Erickson¹, Adrian J. Knight², Stephen A. Roberts², Kathryn Radom², Scott Walper¹, Jonathan Yuen³. (1) Center for Bio/Molecular Science & Engineering, US Naval Research Laboratory, Arlington, Virginia, United States (2) Naval Research Enterprise Internship Program, US Naval Research Laboratory, Washington, District of Columbia, United States (3) ASEE Postdoctoral Fellow, US Naval Research Laboratory, Washington, District of Columbia, United States

Much can be learned about a person's fitness and environment by direct sensing at the skin's surface. The capabilities of such sensors are determined by the material properties of the substrate that interfaces the skin and electronics package. These substrates must provide the following: (1) tough and conformal contact with the skin, and (2) transmission of chemical, mechanical or electronic signal from the skin to the electronics package. Polysaccharide composites are ideal for developing epidermal bioelectronics because they can exhibit a high strength/weight ratio, and their functional surface chemistry provides facile routes to tailor electronic activity and analyte transmission across the biological-electronic interface. Demonstrating a capability to fabricate conformal, biocompatible substrates with tunable chemical permeability and electronic properties is essential for truly integrating biology and electronics across the epidermal surface.

Our current research is exploring the chemical, mechanical, and electronic properties of conformal circuit boards to develop polysaccharide substrates that enable epidermal bioelectronics. The molecular weight and crystallinity of the polysaccharides are critical components in determining the resultant chemical and mechanical properties of the material. Side-chain modification of the basic polysaccharides have provided the requisite toughness to form an epidermal substrate — thin enough to adhere by van der Waals forces but robust enough avoid failure of the electronics package due to mechanical deformation. Novel trace architectures and materials are being explored for stretchable electronic devices.

Polysaccharide circuit boards (PCB) are laminates composed of a bioderived sugars — nanocellulose and pullulan. The PCB and decal transfer are a bio-active material system for supporting electronic devices capable of conforming to biological surfaces.
Nature provides endless examples of precisely engineered macromolecules; proteins, for instance, which contain amino-acid side-chains that are accurately positioned, often in a way that determines the proteins’ roles. Chemists are remarkably proficient at directing the synthesis of small molecules, but fine-tuning the structures of large molecules, such as those found in polymers, is far more taxing. Despite many years of research, the field of macromolecular engineering i.e. the preparation of large molecules with strict control over their 2D / 3D structure and chemical groups has many challenges yet to overcome.

The lecture will describe new synthetic paths to design macromolecules showing excellent control over their topology and functionality. We have combined organic synthesis, polymerisation processes and supramolecular chemistry to design polymeric nanostructures showing a hierarchical structure, from controlled monomer sequence (1D) to architectures (2D) to self-assembly (3D). The exploitation of these nanostructured materials will be discussed, with examples of applications in the material and biomedical fields.
POLY 56: Sequence-controlled polymerizations: The Holy Grail is near

Jean-Francois Lutz, jflutz@unistra.fr. Precision Macromolecular Chemistry, Institut Charles Sadron, Strasbourg, France

The development of sequence-controlled polymers is an important emerging topic in polymer science (Figure 1). Progress in that area of research has been particularly significant during the last five years. Indeed, innovative strategies for regulating comonomer sequence distribution in chain-growth and step-growth polymerizations have been reported. In addition, new polymerization pathways involving tailor-made soluble supports, macromolecular templates, and molecular machines have been described in the literature. In this lecture, I will summarize the advances that have been made and discuss the last hurdles that need to be overcome to achieve perfect sequence-regulation. This discussion will be illustrated by recent examples obtained in my laboratory. For example, the synthesis of monodisperse sequence-defined polymers using accelerated iterative protocols will be discussed in details.
Proteins-polymer conjugates are widely used as therapeutics. All of the Federal Drug Administration (FDA)-approved protein conjugates are modified with poly(ethylene glycol) (PEG). We have developed several polymer structures that can be utilized as alternatives to PEG. These polymers have the benefits of PEG, along with additional advantages such as enhanced thermal stability or degradability (Fig 1). The conjugates are prepared by (a) first synthesizing the polymers with protein reactive end groups and conjugating to proteins or (b) polymerizing from proteins. This talk will discuss various classes of conjugates prepared by grafting to and grafting from methods and their applications as therapeutics for various diseases.
POLY 58: Synthesis of protein-polymer conjugates with controllable activity through site-specific conjugation

Xin Li, Lei Wang, Yuanli Cai, Lin Yuan, Hongwei Wang, Gaojian Chen, Hong Chen, chenh@suda.edu.cn. Soochow University, Suzhou, China

Control of protein activity is a critical issue for human health and treatment of disease. Conjugation to synthetic polymers is an effective method to control protein activity at different levels, providing new opportunities for therapy, molecular diagnostics, and tissue engineering. In this work we generated a mutant pyrophosphatase (PPase) with a substituted cysteine residue near the active site by site-directed mutagenesis. This was used for conjugation to sulfhydryl modifier p-chloromercuribenzoate (PCMB) and to pyridyl disulfide-functionalized poly(2-hydroxyethyl methacrylate) (pHEMA) via the “grafting to” method, resulting in a clear and reversible decrease or entire loss of catalytic activity of PPase due to conformational change. This approach provides a new strategy for efficient control of protein activity at different levels by site-specific conjugation of a small molecule and a polymer. We also prepared protein–polymer conjugates via the “grafting from” method by visible light assisted reversible addition-fragmentation chain transfer (RAFT) polymerization at ambient temperature. This polymerization is fast and can be conveniently controlled via irradiation time. By site-specific polymerization of N-isopropyl acrylamide (NIPAAm) from the protein surface, activity is retained and in certain cases provides a conjugate with on-off-switchable properties in response to temperature.

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Schematic illustration showing strategies for control of protein activity through site-specific conjugation of polymer.
POLY 59: Entropy driven chain effects on ligation

Christopher Barner-Kowollik\textsuperscript{4}, christopher.berner-kowollik@kit.edu, Albena Lederer\textsuperscript{2}, Michelle Coote\textsuperscript{3}, Ganna Gryn'ova\textsuperscript{3}, Kai Pahnke\textsuperscript{4}, Friedrich G. Schmidt\textsuperscript{5}, Josef Brandt\textsuperscript{1}, Nathalie Guimard\textsuperscript{4}. (1) Leibniz-Institut Polymerforschung Dresden e.V., Dresden, Germany (2) Leibniz-Institute of Polymer Research Dresden, Dresden, Germany (3) Chemistry, Australian National University, Canberra, Australian Capital Territory, Australia (4) Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany (5) Evonik Industries, Marl, Germany

Fundamental entropic chain effects enable the tuning of modular ligation chemistry – for example dynamic Diels–Alder (DA) reactions in materials applications – not only classically via the chemistry of the applied reaction sites, but also via the physical and sterical properties of the molecules that are being joined. The lecture will discuss our findings that evidence a significant impact of not only chain mass and length with a difference in the degree of debonding of up to 30 % for different lengths of macromonomers of the same polymer type but – remarkably – also a chain stiffness effect with a difference in bonding degrees of nearly 20 % for isomers. Entropic chain effects govern every reversible ligation chemistry and indeed every cleavage reaction. The lecture will evidence these effects on several examples.
Our laboratory uses a materials genome approach to the discovery and prediction of programmed primary structures that are instructed to undergo intramolecular and intermolecular self-assembly, self-organization and the other sequences of events involved in the emergence of complex-homochiral biological functional systems. Materials genome uses the first principles employed in biology to design the tertiary structure responsible for a particular function. Since the mechanism of transfer of structural information is not understood, theoretically the primary structures responsible for the creation of complex functional systems characterized by adaptation, self-control, self-organization, self-repair, etc. cannot be designed. This lecture will discuss the discovery of programmed primary structures that will provide new mimics of complex biological cell membranes and of their programmable glycan ligands. Their biomedical applications, including programmed glycan-ligand topology binding to sugar-binding proteins (lectins) and other, will be discussed.
Since the first report on the solid-state preparation of polydiacetylene (PDA) in 1969, extensive research efforts have been devoted to this classic type of conjugated polymers. PDAs have found widespread applications in non-linear optics, organic conductors and sensory materials. Despite a large number of examples, PDAs reported to date have been synthesized exclusively from a single type of reaction, i.e., irradiation induced topochemical polymerization of diacetylene (DA) monomers. Such reactions occur efficiently only if the DA monomers are able to pack into periodic structures within very strict geometrical boundaries. As a result, few types of DA monomers, typically having alkyl spacers between DA cores and functional side-groups, can be successfully polymerized.

We report herein novel polydiacetylenes (PDAs) bearing alkyl and phenyl substituents synthesized, for the first time, by solution polymerization using acyclic enediyne metathesis. The resulting polymers are soluble in common organic solvents and show distinct physical and photophysical properties both in solutions and as thin films, caused by different steric and electronic effects from the side-groups. Bulk heterojunction solar cells employing these PDAs have been fabricated and evaluated, which out-performed, by more than 100 fold, the only previous example of solar cells employing PDAs from solid-state polymerization.

POLY 62: Very long, linear polymers from tandem isomerization/alternating ring-opening metathesis polymerization (i-AROMP)

Li Tan, Kathlyn A. Parker, Nicole S. Sampson, nicole.sampson@stonybrook.edu. Chemistry Dept, Stony Brook University, Stony Brook, New York, United States

Ring-opening metathesis approaches can provide non-conjugated polymers with sidechains that bear a variety of functional groups. ROMP polymers from cyclopentene/cyclooctene and norbornene/cyclooctene pairs are known to show a preference for alternation with appropriate catalyst selection. Here we describe a surprising, tandem, isomerization - alternating ROMP protocol that gives very long, linear copolymers with rigorous sequence alternation. A cascade based on bicyclo[4.2.0]oct-7-ene-7-carboxamides of primary amines and cyclohexene provides efficient entry to well-controlled copolymer architectures that can display diverse functional groups. The bicyclo amides are isomerized in the presence of (3-BrPyr₂)Cl₂(HIMes)Ru=CHPh to the corresponding bicyclo[4.2.0]oct-1(8)-ene-8-carboxamides in which the olefin is tetrasubstituted. Upon addition of cyclohexene, the isomerized amides undergo alternating ring-opening metathesis polymerization to provide long (MW >100 kDa) and linear copolymers with backbones that contain alternating unsaturated amides and 1-alkylidene-2-alkylcyclohexanes.
Ring-opening metathesis polymerization (ROMP) is an industrially important and academically interesting method of synthesizing polymers.\textsuperscript{1,2} Most practical ROMP processes are strain-driven reactions,\textsuperscript{3-5} but larger macrocycles, which present greater possibilities for the selection of functional groups on the monomer, can also undergo ROMP via an entropically driven (ED) polymerization.\textsuperscript{4,6} ED-ROMP is a more difficult process because it requires a higher concentration of the cycle and this normally results in incomplete reactions.\textsuperscript{5} Here, we present our strategy for ED-ROMP; it is based on the pre-concentration of macrocyclic olefins in micelles. We take a closer look at the effects of surfactant selection on the size and the polydispersity index of the polymerization. We will present a comparison of the use of various commercially available surfactants, two different Grubbs catalysts and two synthesized Grubbs-modified amphiphiles.

Figure 1: Ring opening metathesis polymerization reaction via emulsion polymerization.
POLY 64: Accessing hydroxystyrene-containing block copolymers using living anionic polymerization of 3- and 4-(2-tetrahydropyranyloxy)styrene

Steve R. Larson¹, 9larsons@gmail.com, Daniel P. Sweat¹, Xiang Yu², Padma Gopalan². (1) Organic, University of Wisconsin-Madison, Madison, Wisconsin, United States (2) Materials Science & Engineering, University of Wisconsin-Madison, Madison, Wisconsin, United States

Living anionic polymerization allows for facile synthesis of block copolymers with a high degree of control over the volume fraction of each block and overall polydispersity. Because this method subjects monomers to highly basic conditions, many functional groups are unable to be used. This work reports the synthesis of an acetal protected hydroxystyrene, 4-(2-tetrahydropyranyloxy)styrene (4OTHPSt), that is able to undergo living anionic polymerization and chain extension with a variety of other monomers (styrene, tert-butylstyrene, DMS, POSS). Quantitative deprotection achieved with catalytic HCl or through thermal annealing at elevated temperatures (180°C for 2h). The influence of change in substitution of OTHP group from 4- to 3- position in the monomer on the anionic polymerization and the thermal properties of the resulting polymer is also explored and discussed. For both P3HS-PtBuSt and P4HS-PS bulk assembly with minimum feature sizes in the sub-10nm is demonstrated. More notably, poly(3-hydroxystyrene) [P3HS] exhibits a lower T_g, at 167°C (T_g [P4HS] = 182°C) leading to more accessible conventional thin film processing methods, particularly useful for block copolymer lithography.
We describe the synthesis and characterization of a novel set of conjugated polymers that may be doped through simple post-polymerization acid/base chemistry. Dopability arises from incorporation of aryl-imidazole units which are easily protonated or deprotonated (pKa’s of ~6.4 and 12) placing a positive or negative charge in conjugation with the polymeric backbone. We hypothesized that acid-doping would increase the system’s electron affinity while base-doping would decrease the ionization potential. This hypothesis came about by drawing analogies between our system and the inorganic Group IV semiconductors where p-doping effectively creates holes just below the conduction band (LUMO) and n-doping adds electrons to the system in electronic states just above the valence band (HOMO). Indeed, these materials show interesting opto-electronic properties upon doping, including highly variable band structures and fluorescence emission profiles. We quantify the effects of doping through cyclic voltammetry and a variety of spectroscopies including: UV/Vis, fluorescence, and $^1$H NMR. Previously, the effects of doping have been attributed to steric collisions affecting backbone planarity; we demonstrate through the synthesis and characterization of vinylene and ethynylene linked polymers that there is more to the observed phenomena than changes due to sterics, lending credibility to the concept of inducing electronic changes upon doping.
POLY 66: Pushing the limit of the RAFT process: One-pot preparation of multiblock copolymers

Guillaume Gody¹, g.gody@warwick.ac.uk, Sebastien Perrier¹,². (1) Department of Chemistry, University of Warwick, Coventry, United Kingdom (2) Faculty of Pharmacy and Pharmaceutical Sciences, Monash University, Melbourne, Victoria, Australia

Biopolymers, such as proteins and poly(nucleic acids), play key roles in living organisms. Their highly specialised functions arise from their perfectly controlled primary structures (i.e. sequence regulation of repeat units along the polymer backbone), which direct the folding of a single polypeptide chain into a precise three-dimensional structure. By analogy, synthetic sequence-defined polymers could play an important role in modern advanced materials science. However, the ability to control the monomer sequence in a single polymer chain so as to be able to anticipate its resulting conformation is an as yet unrealised dream and lies outside the scope of existing synthetic tools.¹ Alternatively, synthesizing sequence-defined block copolymers – i.e. multiblock copolymers, whereby the chain structure at the monomer level does not play a key role – is a more accessible approach for designing new soft materials capable of self-assembling into ordered structures.²

Over the past decade, the synthesis of block copolymers has enjoyed considerable progress with the advent of reversible deactivation radical polymerization (RDRP). The preparation of high-order multiblock copolymers has already been achieved by Cu(0) mediated radical polymerization.³ However, the use of reversible addition-fragmentation chain transfer (RAFT) polymerization to create these structures at scale has often been considered a close to insurmountable challenge.

Here we report a breakthrough that allows for the synthesis of complex multiblock copolymers by one-pot, multi-step sequential RAFT polymerization with yields >99% and fine control (Fig.1).⁴

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References
POLY 67: RAFT polymerization of tertiary amine-based methacrylate pH-responsive monomers for smart MRI contrast agents

Liping Zhu, lzhu@mines.edu, Samantha Powell, Stephen G. Boyes. Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado, United States

Well-defined tertiary amine-based methacrylate pH-responsive homopolymers and block copolymers were synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization using a dithioester or thiosulfinate based RAFT agent for homopolymers and poly(ethylene glycol) (PEG) macro-RAFT agents for block copolymers. $^1$H NMR and gel permeation chromatography results confirmed the successful synthesis of these homopolymers and block copolymers. A detailed study of the polymerization kinetics for each of these systems indicated that the formation of both the homopolymers and the block copolymers was well defined. The pH-responsive properties of these homopolymers and block copolymers were also studied by determining the pKa values using titration-based techniques and also monitoring the hydrodynamic volume and zeta potential of the polymers in solution via dynamic light scattering (DLS). The pKa titration experiments suggested that the homopolymers and the related block copolymers have a similar pKa. The DLS investigation showed that all of the block copolymers underwent a sharp transition from unimers to micelles around their pKa and the hydrodynamic diameter ($D_h$) was not only dependent on the molecular weight but also on the composition of the block copolymers. These copolymers have then been used to modify gadolinium (Gd) nanoparticles to design a smart contrast agent for magnetic resonance imaging (MRI), which will potentially allow for enhanced diagnostics in the treatment of cancer.

RAFT Polymerization of pH-responsive monomers
POLY 68: Stille catalyst-transfer polycondensation using palladium catalysts for the synthesis of well-defined conjugated materials

Yunyan Qiu, yunyanq@andrew.cmu.edu, Tomasz Kowalewski, Kevin J. Noonan. Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States

The emerging potential of catalyst-transfer polycondensation (CTP) to synthesize defined π-conjugated polymers is just beginning to be realized. Functional semiconducting polymers such as poly(3-hexylthiophene) can be obtained with control over molecular weight and chain-end functionality by appropriate combination of monomer and catalyst. Palladium catalysts have arisen as a promising alternative to nickel for expansion of Kumada and Negishi CTP. In this presentation, the development of a Stille CTP approach to synthesize poly(3-hexylthiophene) will be discussed. A comparison of Stille and Suzuki-Miyaura methods with various Pd catalysts will also be provided with respect to their “living” chain-growth behavior (molecular weight control, dispersity and well-defined chain-end functionality).

Palladium catalyzed chain-growth polycondensation of poly(3-hexylthiophene) by a A-B monomer design
Sequence controlled polymers are defined as macromolecules whose monomer arrangements are in precise order. In traditional copolymers the distribution of monomers is usually uncontrolled or statistically controlled. In natural polymers such as proteins, the primary sequence of proteins is polypeptides, which is synthesized using 20 amino acids as building blocks. Additionally, the order/arrangement of amino acids in polypeptide chains direct the folding information, which guides the polypeptide to fold into defined secondary/tertiary structures to achieve specific functions of proteins. Here, to mimic the biopolymer synthesis in nature, we developed a strategy that combines “thiol-ene” and “thiol-Michael” addition click chemistries to synthesize sequence controlled polymers. We successfully synthesized polymers whose sequences are analogs of oligonucleotides in nature, these polymers exhibit binding activity towards complementary DNA strands. Since our polymers have neutral backbones in the structures, the CNA/DNA hybrids have higher melting temperatures as compared to natural DNA double strands. Moreover, the hybridization between our CNA and DNA has been used in materials science such as surface modification and hydrogel formation.
Along with a growing demand on functional polymers in a wide range of interdisciplinary applications, polymers with readily clickable groups received increasing attention because of their robust and reliable ability to produce functional materials without painful procedures. A number of click type reactions have been employed in order to expand the scope of functional materials obtained by post-polymerization modification. This includes thiol-ene, thiol-maleimide, nucleophile-isocyanate, activated ester-amine reactions, and Cu(I) catalyzed and metal-free 1,3-dipolar cycloaddition reactions between organo-azides and acetylenes, which all realize practically quantitative conversions during the post-polymerization modification step. Despite a high efficiency of click reactions, intrinsic and inevitable synthetic limitations of above mentioned click reactions exist. To be precise, the limitations are 1) the number of installable functional units is only one per a monomeric unit and 2) the bonding generated by click reactions along with an installation of desired molecules show no functionality themselves. In order to accelerate the production of polymeric materials via post-modification process based on click reactions, these synthetic limitations should be overcome. In this context, the author paid attention to a renovation of post-modification processes by introducing highly efficient organic transformation reactions into polymer chemistry. When turning attention to a development of organic chemistry, a series of multicomponent reactions (MCRs) have appeared as an innovative synthetic methodology. Although multicomponent reactions triggered new chemistry and applications, a few attentions have been paid in the field of polymer chemistry. In this presentation, the author will show a new synthetic possibility of post-modification reactions by employing MCRs and applications thereof for producing highly functionalized polymers (Scheme).
The application of conducting polymers in electronic devices has received rapidly growing attention due to their potential low cost fabrication, light weight, facile processing and flexibility. In recent years, various conducting polymers have been developed or are currently under investigation for electronic applications. In particular, heteroatom containing conjugated polymers exhibit interesting optical and electronic properties. Acyclic Diene Metathesis (ADMET) has emerged as a promising synthetic approach, due to its ability to be used with a wide range of architectures using functional group tolerant catalyst systems. We have successfully used ADMET in a unique way to access a library of conjugated polymers containing distinct electro-optically active aromatic segments. Structure/property relationships were investigated, specifically electronic interactions between the aromatic conjugated segments and their influence on the electro-optical material characteristics. Polymers are exclusively trans-configured at the internal vinylene bonds. The structural details of polymers have been characterized by $^1$H, $^{13}$C and 2D NMR spectroscopy. The opto-electronic properties were studied by UV-vis and Fluorescence spectroscopy. HOMO and LUMO levels were obtained via Cyclic voltammetry. TGA and DSC analysis were used to investigate the thermal behavior of the compounds.

Figure. UV-Vis and PL spectra of monomer (1) and polymer (P1)
POLY 72: Synthesis and polymerization of new 2-substituted vinylimidazolium salts

Darren Smith, dmssch@rit.edu, Timothy Muzio, Thomas W. Smith. School of Chemistry and Materials Science, Rochester Institute of Technology, Webster, New York, United States

The glass transition in polymers derived from tetrasubstituted 1-butyl-2,3-dimethyl-4-vinylimidazolium salts has been found to be surprisingly invariant as compared to that in polymers derived from corresponding salts of trisubstituted 1-ethyl-3-methyl-4-vinylimidazolium or disubstituted 1-ethyl-3-vinylimidazolium monomers. It is believed that this invariance is a result of greater steric separation between the tetrasubstituted imidazolium moiety and its counter anion. If this is the case, similar invariance in glass transition characteristics may be observed in polymers derived from other trisubstituted and tetrasubstituted imidazolium monomers. In the present research, new trisubstituted ionic liquid imidazolium monomers, have been synthesized. The most straight forward synthetic option for synthesis of 1-butyl-2-methyl-3-vinylimidazolium salts is alkylation of commercially available 2-methyl-1-vinylimidazole. However, given the very high price of this monomer it was necessary to synthesize this intermediate in-house. Vinylation of imidazole with acetylene is the most preceded option for the synthesis of 2-methyl-1-vinylimidazole. Unfortunately, vinylation with acetylene is not a reaction that is well-suited for execution in academic laboratories by undergraduate researchers. The aza-Markovnikov addition of 2-methylimidazole with vinylacetate to form the acetoxy imidazole derivative, 1-(2-methyl-1H-imidazol-1-yl)ethyl acetate provided an answer to this conundrum. The acetoxy derivative was pyrolized to yield 2-methyl-1-vinylimidazole from which the 1-butyl-2-methyl-3-vinylimidazolium salt was prepared. An alternative route to either 1-butyl-2-methyl-3-vinylimidazolium or 1-methyl-2-butyl-3-vinylimidazolium salts that was developed in our laboratories involved the lithiation of the 2-position of the imidazole ring in 1-vinylimidazole with subsequent methylation or butylation of the 2-lithio imidazole intermediate.

2-Substituted Imidazolium Polymers
POLY 73: Aza-Diels–Alder route to polyquinolines

David J. Dibble, djoshdibble@gmail.com, Mehran Umerani, Amir Mazaheripour, Young Park, Alon A. Gorodetsky. Department of Chemical Engineering and Material Science, University of California, Irvine, Irvine, California, United States

Polyquinolines have been studied since the early 1970s due to their favorable chemical, optical, electrical, and mechanical properties. These materials have shown particular promise for applications in organic electronic devices, such as light emitting diodes. However, there are few synthetic strategies available for the preparation of polyquinolines, including transition metal catalyzed Suzuki and Sonogashira couplings, oxidative polymerizations, and the Friedlander synthesis. We have developed a new synthetic route to polyquinolines based on the aza-Diels–Alder (Povarov) reaction. Our approach furnishes polyquinolines with a unique architecture and connectivity in only two synthetic steps from inexpensive, commercially available reagents. The resulting products have been extensively characterized with chromatographic and spectroscopic techniques. Our strategy may represent a welcome addition to the polymer chemist’s toolkit by providing ready access to a diverse library of polyquinoline-type materials.
POLY 74: Size and composition-based nanoparticles separations and analyses using field-flow fractionation

Kim R. Williams, krwillia@mines.edu. Colorado School of Mines, Golden, Colorado, United States

Field-flow fractionation (FFF) is used to separate and characterize various nanoparticles ranging from functionalized Si quantum dots to polymeric core-shell nanoparticles. Flow and thermal FFF are the techniques emphasized in this presentation. These two fields interact with different physicochemical properties of the nanoparticles leading to different types of separations and characterization.

Flow FFF utilizes a fluid flow to induce migration of nanoparticles to a sample accumulation wall. Separation is based on differences in diffusion coefficients which can be related to hydrodynamic diameters using the Stokes-Einstein equation. Hence, size-based separations and size distributions are obtained. Thermal FFF utilizes a temperature gradient to effect separations. The magnitude of thermal diffusion of analytes is dependent on factors such as their composition and interfacial interactions with the carrier liquid. Consequently, composition-based separations and information may be obtained.

Several nanoparticle systems and studies will be discussed to highlight the capabilities of flow and thermal FFF. Using flow FFF, functionalized Si quantum dots were separated and TEM and photoluminescence (PL) measured for each collected ‘monodisperse’ size fraction. This enabled a comparison of the measured maximum PL wavelength for different size fractions (F1, F2, F3) with theoretical predictions as shown in Figure 1. This work also demonstrated flow FFF’s ability to simultaneously remove excess reagents that interfere with PL measurements. Gold nanorods have been separated and characterized by flow FFF. The collected fractions represented size and shape ‘standards’ that were then used to elucidate information about the diffusion of rod-shaped nanoparticles. Thermal FFF’s sensitivity to composition is demonstrated using polymeric core-shell nanoparticles and inorganic and metallic nanoparticles.

While this presentation focusses on nanoparticles, it should be noted that both these FFF techniques are also used to separate and analyze polymers.
Tailored biomolecular materials gain rising attention as bio-sensors, artificial enzymes, light harvesting systems, photonics and nanoelectronic devices. Thus, the formation of higher order molecularly organized structures is widely explored, in particular to gain more control over shape, size and function. In this work artificial supramolecular structures of dendronized glycopolymers are investigated. The self-aggregation properties of these worm-like polymers were found to be dependent on pH value, molar mass and concentration. The shape of the aggregates is changing strongly as a result of changing H-bonding interactions. Additionally to dendronized polymers, block-copolymers self-organization in polymersome structures was studied for the complexation and transport of enzymes. Their shape and activity dependence on the pH value is significant. Complementary application of filed flow fractionation coupled to several detectors and AFM, cryo-TEM or TEM tomography show the high potential of combined separation techniques for scaling and interaction properties investigation of biomolecular systems.
Asymmetric flow field-flow fractionation (AF4) is a particle-size based fractionation technique, which uses an open-channel design, thus eliminating analyte loss as a result of irreversible adsorption on column packing materials. AF4 can be coupled online to various detectors, such as UV-Vis and fluorescence spectrometers, multiangle light-scattering (MALS), dynamic light-scattering (DLS) and refractive index detectors. AF4 is a powerful tool to characterize macromolecular complexes, polymeric nanoparticles, and biopolymers, such as proteins, polysaccharides, and oligonucleotides. Presented here are two AF4 analyses carried out in our laboratories.

In one study, AF4 was used to characterize the complexes formed between poly(acrylates) and polyclonal immunoglobulin G (IgG) in its native conformation and after heat-stress. The AF4 protocols developed allowed the fractionation of solutions containing free poly(acrylates), native IgG monomer and dimer, poly(acrylates)/IgG complexes made up of one IgG molecule and a few polymer chains, and larger poly(acrylates)/IgG aggregates.

In a second study, AF4 was used to characterize polymersomes formed by polymethylloxazoline-b-polydimethylsiloxane-b-polydimethyl-oxazoline and mixed systems formed by the triblock copolymer and dimyristoyl-phosphatidylcholine liposomes. The encapsulation of the drugs in liposome, polymersome and the “binary-somes” was also evaluated using a fluorescent probe as the model.

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Interactions of polymers with vesicles and proteins investigated by asymmetric flow field-flow fractionation
POLY 77: Measurement of size and certain structural features of sub-nanokilometer particles in suspension

Philip J. Wyatt, pwyatt@wyatt.com. Wyatt Technology Corp, Santa Barbara, California, United States

The Rayleigh-Gans (R-G) approximation to light scattering theory has long been used to interpret the scattering from a wide range of particles in order to extract their size. Most successful has been the application to ensembles of spheres, rods, random coils, and disks following their separation by liquid chromatography means. The restrictions of the approximation have long thwarted thoughts of measuring particles well outside of the requirements for the application of R-G theory which are:

\[
|n/n_0 - 1| = |m - 1| \ll 1 \quad \text{and} \quad 2ka|m - 1| = x|m - 1| \ll 1,
\]

where the particle refractive index is \( n \) and that of its suspending medium \( n_0 \), \( k = 2\pi n_0/\lambda_0 \), and \( \lambda_0 \) the wavelength of the incident light in free space. The particle “diameter” is assumed to be \( 2a \) where, for a sphere, its radius is \( a \), for a rod, its length \( l = 2a \), etc. These requirements are shown to be overly restrictive and a R-G-based approximation may actually be used to characterize particles well outside of these restrictions.

Starting with measurement of the so-called “mean square radius”, \( <r^2> \), a very large range of particle classes well outside of the R-G strictures may be measured to accuracy better than 10%. The \( <r^2> \) values expressed as a function of their structural parameters for variety of particle classes are described and examples presented. These include PSL spheres with diameters of 1000nm. These \( <r^2> \) values are often not obvious and some analyses are generally required. An interesting set of PSL are shown in Fig. 1.
Asymmetric flow field flow fractionation, AF4, is an emerging versatile tool used to obtain high-resolution information on size, molecular weight and stability of nanoscale particles in liquid media. Coupled to multi-angle light scattering detection, AF4-MALS has been used to analyze, characterize and separate polysaccharides, liposomes, and spherical and nonspherical particles. In the work to be described, AF4-MALS was used to evaluate and improve (by fractionation) the size and stability of silica colloids. As shown in the accompanying figure, it is easy to identify particles that are too large or too small from the main population. Weakly basic conditions alter the shape of the silica particles over time, and AF4-MALS was able to resolve these particles according to their shapes. This finding was confirmed by dynamic light scattering and transmission electron microscopy. Degraded silica colloids were easy to separate by fractionation because of the AF4-MALS high resolution and its ability to sample large numbers of particles. Not only spherical colloids were accurately characterized by AF4-MALS, but also anisotropic particles. Supported by Polymers Program, NSF DMR 1306262.
POLY 79: Semipreparative asymmetric flow field-flow fractionation for nanoparticle characterization

Carmen Bria, cbria@mines.edu, Akram Ashames, Patrick Skelly, S. Kim R. Williams. Colorado School of Mines, Golden, Colorado, United States

The ability to characterize nanoparticles by asymmetric flow field-flow fractionation (AF4) has impacted a broad range of fields from biotechnology to nanotechnology. However, the availability of sufficiently large amounts of purified analytes is critical for conducting investigative studies concerning their fundamental properties and function. Precipitation and centrifugation have been used to isolate nanoparticles in quantities suitable for additional testing. However, precipitation may cause irreversible aggregation and sample collection after centrifugation is tedious. The development of a semi-preparative asymmetric flow field-flow fractionation (sP-AF4) method has the potential to overcome these limitations.

The scale-up from an analytical to a semi-preparative channel means larger sample amounts can be introduced into the channel. However, increased channel size and sample amounts can impact separation resolution, destabilize channel flow rates, and increase potential membrane contamination. Separation performance metrics such as resolution and reproducibility are compared for analytical and sP-AF4 channels. Results showed that resolution is maintained in sP-AF4. Additionally, destabilization of flow rates and additional membrane contamination is not observed in the sP-AF4 channel.

Purification of biological samples often results in low concentrations of the desired sample component making further analyses and studies difficult. A cancer-derived exosomes sample was fractionated using the sP-AF4 channel and SDS-PAGE of the collected fractions showed an abundance of exosome associated proteins. Fractionation of exosomes also revealed a distinct subpopulation of larger particles which may suggest the presence of non-exosome contaminants or exosome aggregates. The sP-AF4 channel was also used to produce more narrowly dispersed nanoparticles for subsequent investigations of enhanced nanoscale properties.
POLY 80: Synthesis and characterization of functional polymer nanoparticles via sonogashira coupling

Alka Prasher¹, ahk23@wildcats.unh.edu, Danming Chao³, 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 (3) Chemistry, Jilin University, Changchun, China

We discuss the synthesis of single-chain nanoparticles via a palladium catalyzed Sonogashira Coupling reaction (Fig 1). Intra-chain cross-linking of various linear polymer chains was achieved by using either an external cross-linker or a built-in cross-linking. The resulting nanoparticles were characterized via triple detection size exclusion chromatography (SEC) where MALS detector gives the absolute molecular weight and viscometric detector gives the particle size. Particle size can be tuned through polymer molecular weight and by degree of cross-linking. Comparing similar reaction conditions with different polymer architecture elucidates the best arrangement for the effective chain folding.

Figure 1: Synthesis of Single-chain Nanoparticles via Sonogashira Coupling
Mechanochromism, defined as a color change in response to a mechanical deformation, is a phenomenon observed in many functional polymer gels. The ability for mechanochromic materials to visually sense local deformation via a color change makes them potentially useful for measuring separation modes of pressure adhesives, traction forces of cells, tissue deformation during surgical procedures, blast damage in body armor, as well as failure for building infrastructure. An interesting class of polymer gels that displays mechanochromism is block copolymer photonic gels (Figure 1). These polymers are nanostructured materials engineered with a photonic stopband or color whose mechanochromic properties can be tuned with the addition of solvents, diluents, polymers and nanoparticles. This presentation will demonstrate block copolymer photonic gels as sensors for detecting interfacial mechanics relevant to pressure sensitive adhesion. The block copolymer gels discussed are styrenic-based diblock copolymers preferentially swollen with a favorable solvent to enhance both their optical and mechanical properties. We show several applications of block copolymer photonic gels as sensors for detecting different modes of mechanical deformation and present a simple mechanical model that relates the observed color shifts to structural changes of the block copolymer photonic gel.
POLY 82: Development of mechanochemical and thermal triggers for release of small organic molecules

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

Our research focuses on the development of macromolecular materials capable of releasing small organic molecules in response to mechanical or thermal stimulus. We will discuss new classes of mechanophores capable of either direct release of small molecules or triggering a cascade release by initiating head-to-tail depolymerizations. Recent findings on new thermally-responsive materials will also be presented, which will focus on the use of oxazines as linkers for small molecule attachment and thermally-activated release.
Photonic structures—giving rise to interference of light upon reflection from periodically structured dielectric media—can be found widely in nature as a simple means to robust and tunable coloration. We have studied the preparation of multilayer films from photo-crosslinkable polymers and found this approach to yield well-defined structural colors that can easily be tailored due to the ability to independently control the properties of each layer. However, the modest contrast in refractive index provided by common polymers means that many layers are required to achieve highly efficient reflection. Thus, the incorporation of high refractive-index inorganic nanoparticle species represents an attractive means to improve performance while simplifying fabrication. We describe the preparation and characterization of such nanocomposite sensors, and compare their behavior to those of all-polymer multilayers.
Liquid crystalline materials are ubiquitous stimuli-responsive materials that are the basis of the $2B display industry. Here, we report on our recent efforts to explore stimuli-induced mechanical adaptivity in liquid crystalline polymer networks. Previous examinations of these materials have reported dramatic planar shape change exceeding 400% strain. We describe our recent efforts to digitally program the self-assembly of both glassy and elastomeric liquid crystalline polymer networks to yield monolithic, shape-changing structures triggered with both heat and light. Through control of the molecular alignment of the liquid crystalline polymer network, complex three-dimensional shapes can be generated where the direction and type of actuation can be locally controlled.
In this talk, I will present our work on developing stretchable electronic polymers, understanding the design principles and the use of these polymers for stretchable devices, such as transistors and solar cells.
POLY 86: Applying reconfigurable networks of charge-transporting polycyclic aromatic hydrocarbons to problems in energy storage

Brett A. Helms, bahelms@lbl.gov, Peter D. Frischmann, Laura C. Gerber, Sean E. Doris, Changyi Li. The Molecular Foundry, Lawrence Berkeley National Lab, Berkeley, California, United States

I will report our recent work in understanding and controlling adaptive charge-transport behaviors in reconfigurable molecular networks of polycyclic aromatic hydrocarbons in non-aqueous electrolytes. I will also include a detailed look into their network forming ability as a function of concentration and imposed state of charge. The unique attributes of this class of materials have the potential to impact a variety of energy storage devices, and will be discussed in the context of a hybrid Li-S flow battery.
Christine K. Luscombe, luscombe@u.washington.edu. Materials Science and Engineering, University of Washington, Seattle, Washington, United States

π-Conjugated polymers are being used in the fabrication of a wide variety of organic electronic devices such as organic field-effect transistors (OFETs), organic photovoltaic (OPV) devices, and organic light-emitting diodes (OLEDs). Since the seminal work on the conductivity of polyacetylene by Heeger, MacDiarmid, and Shirakawa was published in 1970s, the field of organic electronics has grown exponentially. We have now reached a stage where the quantum efficiencies of OLEDs outperform those of inorganic LEDs, the highest charge mobilities obtained for polymers reaching 8.5 cm²/Vs, and OPVs now have a power conversion efficiency (PCE) of 9% (single cell), 10.6% (tandem cells). The advances made in organic electronics have been driven by the syntheses of π-conjugated polymers with increasingly complex structures but have heavily relied on an Edisonian approach. Despite these advances, there are many contradictory reports in the literature about our understanding of the performance of π-conjugated polymers in many applications.

Our group has been studying and developing techniques to grow semiconducting polymers using a living polymerization method. This has allowed us to synthesize polymer architectures that we haven’t been able to access till now including polythiophene brushes, star-shaped P3HT, as well as hyperbranched P3HT. In this presentation, our work towards creating brush polymers will be presented where a series of fully conjugated graft copolymers containing poly(3-hexylthiophene) (P3HT) side chains and a p-type carbazole-diketopyrrolopyrrole (CbzDPP) donor–acceptor backbone were synthesized via a graft through Suzuki polymerization. The macromonomers were formed by externally initiating P3HT growth from a boronic ester-functionalized carbazole via Kumada catalyst transfer polycondensation. Subsequently, this macromonomer was copolymerized with a DPP monomer via a graft through Suzuki polymerization to yield the final graft copolymers.
POLY 88: High performance cement via cellulose nanocrystal addition

Jeffrey P. Youngblood\textsuperscript{1}, jpyoungb@purdue.edu, Robert Moon\textsuperscript{3}, Jason Weiss\textsuperscript{2}, Pablo Zavattieri\textsuperscript{2}, Yizheng Cao\textsuperscript{2}. (1) School of Materials Engineering, Purdue University, West Lafayette, Indiana, United States (2) Purdue University, West Lafayette, Indiana, United States (3) Forest Products Laboratory, Madison, Wisconsin, United States

Research will be presented on strength and plasticity enhancement of cement by cellulose nanocrystal (CNC) addition. CNCs are an attractive material class for possible applications in nanocomposites reinforcement, nanomaterials and biomedicine as they have high strength and stiffness, yet are renewable, biodegradable, non-toxic, and cheap. Here, we will detail efforts to utilize these materials in cementitious composites. CNCs are highly surface active on the cement particles and act to stabilize in dispersion, thus lowering yield (increasing plasticity). As well, increases in strength are observed due to hydration increases. These effects will be presented and explained.

Schematic showing cellulose nanocrystal (CNC) enhanced hydration of cement.
Surface-initiated controlled radical polymerizations (SI-CRP) in polar media, especially water, are often observed to be accelerated in comparison to those in nonpolar media. Moreover, the adsorption of neutral polymers onto charged colloids has a pronounced effect on their zeta potential due to excluded volume in the electrical double layer (EDL). Cellulose nanocrystals (CNCs), derived from natural resources, offer a highly charged interface to examine possible electrical double layer effects on SI-CRP in aqueous media. Here, we monitored copper-mediated SI-CRP from partially charged CNCs in aqueous media by way of zeta potential measurements. To this end, we utilized a hydrophilic uncharged monomer, namely N,N-dimethylacrylamide (DMAM), and copper complexes with N-type ligands. We further characterized PDMAM brushes grafted from CNCs via FTIR and TGA. Molecular weight of PDMAM brushes was determined by GPC analysis of hydrolytically cleaved polymers. We emphasize the role of surface chemistry on the accelerated growth of polymer brushes from CNCs in water and expand a model of the interfacial region during polymer brush propagation.
POLY 90: Can hemicelluloses be used for durable wood adhesives?

Eva E. Malmström¹, mavem@kth.se, Emelie Norström¹, Linda Fogelström¹, Petra Nordqvist², Farideh Khabbaz². (¹) Fibre and polymer technology, KTH Royal Institute of Technology, Stockholm, SE-100 44, Sweden (²) Casco Adhesives, AkzoNobel, Stockholm, Sweden

Wood adhesives are mainly derived from petroleum-based resources. It is therefore desirable to develop new binder systems which, in full or partly, originate from renewable resources. However, it is not possible to cut back on adhesive properties such as bond strength, water and heat resistance. Protein obtained from milk (casein) was used already in ancient Egypt and more recently other proteins, such as soy protein isolate and wheat gluten, have been evaluated with positive results. (Frihart, 2005) (Nordqvist et al., 2010) None the less, the protein-based binders suffer from the non-despicable fact that proteins are a food source.

Building on this we investigated the use of gums, a class of polysaccharides used as thickeners in the food industry, as wood adhesives. Water dispersions of locust bean gum (LBG), guar gum or tamarind gum show promising adhesive properties without any modifications. Good water resistance was found for adhesives from LBG-dispersions. (Norström et al., 2014)

Inspired by this, we directed our attention towards hemicelluloses (HC) as another class of very interesting polysaccharides. HC are today mainly considered as byproducts from the pulping process and are often incinerated. From environmental and economic perspectives it is desired to make use of all constituents in wood.

In this study, water dispersions of HCs were prepared and evaluated as wood adhesives, according to EN 204 and EN 14257. Not surprisingly it was found that the HC itself gave too poor adhesive properties why the effects of crosslinkers and/or dispersing agents were evaluated. It was found that wood bonded with a HC dispersion containing a dispersing agent and a crosslinker resulted in very good bond strength, water resistance and heat resistance. This paper will discuss the most recent findings.

The interphase, shown below in the FRET efficiency map, is the volume of polymer adjacent to an interface, and it can comprise up to 30% of the polymer in a polymer nanocomposite. It controls the effectiveness with which the nanoparticle and polymer interact to produce enhanced properties, but it remains a poorly characterized phase. Specifically, the characterization of dynamics of the polymer in the interphase is necessary to enable intrinsic toughening mechanisms. The development of measurements capable of probing polymer dynamics on length scales comparable to that of the interphase (1 nm to 200 nm) is necessary to develop the fundamental structure property knowledge needed to create high performance nanocomposites. This presentation will report on our efforts to use various fluorescence microscopy tools such as FRET, FLIM and mechanophores to enable imaging of the interphase in polymer nanocomposites.
Cellulose nanocrystals (CNCs) are high-aspect ratio, mechanically stiff fibers which can serve as both a bio-renewable reinforcing agent in nanocomposites, as well as a handle for adding stimuli responsiveness. CNCs can be extracted from a wide range of natural cellulosic materials, with characteristics such as crystal structure, crystallinity and aspect ratio fluctuate widely between sources. Here, we report small molecule functionalized cellulose prepared for sustained delivery in a variety of environments. Moieties attached to the surface of cellulose nanocrystals show that both irreversible and reversible changes can be induced by application of an external stimuli. Moreover, we present our research focused on the design and fabrication of structured cellulose nanocrystals foams and nanocomposites for implantation. These specifically designed materials are mechanically tunable, matching the intended implantation site.
As sustainability is widely recognized as a major global challenge, the scientific and industrial communities around the world are actively searching for effective strategies and pathways to reduce the environmental impact of products, processes, and lifestyles. It is important to develop viable raw materials with reduced carbon footprints. Among the available renewable raw materials, cellulose is highly attractive due to low cost, abundance, and wide availability around the world. From a material application standpoint, utilizing cellulose as a starting material for making thermoplastic polymers is highly preferred over food-based feedstocks such as starch, vegetable oils, plant proteins, etc.

Cellulose has been made into films (cellophane) and fibers (rayon), but the technologies used are high-cost and high-environmental footprint processes which involve multiple-steps to produce soluble cellulose derivatives first and then regenerate cellulose. Utilization of cellulose as a thermoplastic material was rarely explored since cellulose is not thermoplastic. In this paper, cellulose derivatives possessing limited thermoplastic properties were investigated for developing renewable materials. The thermal properties and rheological properties of cellulose esters were evaluated. The thermoplastically processed cellulosic films had high tensile strength but low ductility. In order to improve the mechanical properties of the films, a series of polymer blends with a biodegradable polymer were prepared. It was found that the films made from the polymer blends exhibited improved ductility over the cellulosic films. Interesting changes in properties substantially different from the starting polymers were found. This research has demonstrated the potential for developing thermoplastic renewable materials from non-food based cellulose, but significant research is still needed to fully understand the structure-property relationship and application potential.

![Figure 1. Transforming cellulose to thermoplastics](image-url)
POLY 94: Renewable thermoplastics from lignin

Amit K. Naskar, NASKARAK@ORNL.GOV, Chau D. Tran, Anthony S. Bova. Materials Science Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States

Here we report a method to produce lignin-derived, industrial-grade plastics with properties rivaling current petroleum-derived alternatives. Lignin, a biomass constituent and a byproduct from the paper and biorefining industries, is a promising feedstock. In recent years, researchers have demonstrated that lignin can be used directly to create a number of novel plastic resins, but most have used low lignin loading, required energy-intensive chemical modification, and had poor mechanical properties. Each of these factors severely hinders the commercialization potential of a robust family of lignin-based polymers. In our recent work, we have tailored a range of thermoplastic, recyclable polymeric materials with ≥ 50% lignin content, mechanical properties similar to high-strain thermoplastic elastomers, commodity thermoplastics, and engineering plastics. By understanding the interfacial chemistry of lignin and a range of matrix polymers and optimizing the use of compatibilizers we have produced these materials in batch and continuous production processes using solvent-free, reactive processing using traditional polymer blending and extrusion equipment. The resulting polymer exhibit multiphase morphology and shear thinning melt-rheology.

![Tensile stress-strain profiles of processed polyblends.](image)
Polymeric nanofibers are attractive for a number of tissue engineering applications. Nanofibers can be generated easily via electrospinning, and their morphology and dimensions can be tuned easily with solvent, concentration and processing conditions. Apart from the physical characteristics of nanofibers, the biochemical effects that are induced from the bioactive motifs presented on the surface of nanofibers also play an important role in the resulting behavior of cells on the materials. Efficient chemical methods aiming at efficient modification of electrospun fibers are needed to enhance their bioactive properties in vitro and in vivo. In our research, 4-dibenzocyclooctynol (DIBO) and its derivative were used as initiators for the ring-opening polymerization of a number of different monomers to generate functional polymers like DIBO-PBLG, DIBO-PCL, DIBO-PLA, DIBO-(P(CL-co-OPD)) and so on. The presence of a DIBO group at the chain end of the polymers enables efficient and metal-free functionalization post-electrospinning (Figure 1). Combined with other types of efficient chemical methods, di-functionalized and tri-functionalized nanofibers were also constructed for the study of synergistic effects in tissue engineering.

Figure 1. Efficient post-fabrication functionalization by copper-free click chemistry
Development of the polymerization methodology termed inverse vulcanization has enabled the direct polymerization of elemental sulfur with a divinyllic comonomer into chemically stable high sulfur content polymeric materials exhibiting useful electrochemical properties. These sulfur plastics have demonstrated promising electroactivity versus Li for next generation battery technology. While initial successes utilizing these sulfur-rich copolymers as polymeric cathode materials have been demonstrated, the materials exhibit an exceptional electrical resistivity prohibiting ideal performance as an electrode and requiring the use of conductive carbon fillers. Furthermore, extension of inverse vulcanization to include the copolymerization of elemental sulfur with monomers bearing pendant functionality has not been established. We demonstrate expansion of the scope of inverse vulcanization to incorporate multifunctional styrenics with post-electropolymerizable side chains into high sulfur content copolymers. Upon oxidative polymerization of the pendant electroactive moieties, conjugated polymer pathways are successfully installed through the inverse vulcanizate efficaciously augmenting the electrical properties of the high sulfur content copolymer. These novel polymeric materials composed of majority by mass sulfur have promising application for next generation secondary Li batteries.
Polymers with π-conjugated backbones have diverse applications as organic electronic and stimuli-responsive materials. Researchers are able to tune the electronic and material properties of these polymers through molecular design of both the polymer backbone and pendant moieties. The installation of these desired units into the polymer, however, often poses synthetic challenges. One method, direct arylation polycondensation, relies on C–H activation and circumvents the functionalization steps required for traditional Stille- or Suzuki-type polymerizations. Another solution is to utilize well developed polymerization techniques such as ring-opening metathesis polymerization (ROMP) followed by efficient post-polymerization modification. We will discuss the application of both techniques for the protection against chemical warfare agents and synthesis of electron-accepting conjugated systems derived from readily available starting monomers.
Poly(ionic liquid)s (PILs) are a subclass of polyelectrolytes with ionic liquid as the repeating unit, which have attracted much attention due to their unique properties. Well-defined PILs homopolymers or block copolymers were synthesized by normal atom transfer radical polymerization (ATRP) and activators regenerated by electron transfer (ARGET) ATRP with ppm copper catalyst. A simple and universal gel permeation chromatography technique was developed for precise molecular weight characterization of PILs. Both AB and ABA type PIL block copolymers were synthesized by ATRP using various macroinitiators. The amphiphilic poly(acrylic acid) (PAA)-b-PILs self-assembled in THF/H₂O mixture to form nanoscale cuboidal shaped particles with bicontinuous cubic phase under optimized conditions by a bio-inspired hierarchical self-assembly process. Free-standing PILs membranes were prepared for CO₂/N₂ gas separation, including PIL random copolymers, PIL block copolymers, and PIL bottlebrushes.
Hydrazide and blocked isocyanate chemistries are useful for post-polymerization modification (PPM), and have been underutilized for obtaining polymers with controlled architectures. Blocked isocyanates are generated by an equilibrium reaction between isocyanates and, commonly, N-based heterocycles, which can then be reversed thermally or by direct nucleophilic displacement. In this research, we demonstrate the synthesis and use of blocked isocyanate methacrylate-based monomers in RAFT polymerizations to mitigate the sensitivity of isocyanates to water, while maintaining mild, room temperature reactions. By changing the identity of the blocking agent to adjust deblocking conditions, we show that direct nucleophilic displacement of blocking agents occurs readily at room temperature – a result that maintains the salient features of isocyanate reactivity while reducing sensitivity to water.

Hydrazone linkages, a class of dynamic covalent chemistry, are also established through a thermodynamic equilibrium which is controlled by pH. We have investigated the synthesis of hydrazide-containing monomers and the polymerization of these monomers directly by aqueous RAFT polymerization, which, until now, has yet to be achieved. Direct polymerization of hydrazide monomers opens doors to libraries of polymers that can shuffle or exchange pendent groups thereby enabling the design of new dynamic combinatorial polymer libraries for a wide range of applications. The dynamic nature of both the blocked isocyanates and hydrazone functional polymers promotes facile and versatile post-polymerization modification.
POLY 100: Sequencing in step-growth polymerization: Influence of segment length on thermomechanical properties of polysulfone-containing segmented polyesters

Joseph M. Dennis\textsuperscript{2}, jmden88@vt.edu, Gregory B. Fahs\textsuperscript{1}, Robert B. Moore\textsuperscript{1}, Sam R. Turner\textsuperscript{2}, Timothy E. Long\textsuperscript{1}. (1) Virginia Tech, Blacksburg, Virginia, United States (2) Macromolecules and Interfaces Institute, Virginia Tech, Blacksburg, Virginia, United States

The enhanced thermal, hydrolytic, and chlorine stabilities of polysulfones enable high performance membranes for water purification technologies. However, poor solvent resistance, which is attributed to the lack of crystallinity, limits the potential commercial impact of polysulfones. On the other hand, semi-crystalline polyesters exhibit superior solvent resistance compared to polysulfones, and copolymerization of polysulfones with semi-crystalline polyesters suggests an unprecedented family of high performance, multiphase thermoplastics. A solvent-free, melt polycondensation to afford segmented polysulfone-containing polyesters involved quantitative end-capping of phenol-terminated polysulfone (PSU) with ethylene carbonate to generate telechelic oligomers with primary hydroxyl functionality. Subsequent melt transesterification of dimethyl terephthalate and 1,4-butanediol in the presence of end-capped, PSU oligomers yielded high molecular weight segmented block copolymers with alternating PSU and poly(butylene terephthalate) (PBT) sequences. The PBT segment length and thermomechanical properties were dependent on PSU incorporation. Complementary DSC, SAXS, and WAXD revealed a miscible amorphous PSU and PBT phase, while PBT crystallinity was maintained below 80 wt.% PSU. Furthermore, the incorporation of PSU segments significantly affected crystallization and thermomechanical properties; DMA revealed a crystallinity-dependent plateau above the composition-dependent glass transition temperature ($T_g$). As a result, the addition of a semi-crystalline morphology into PSUs maintained thermal stability, obtained higher temperature operating windows, and offer potential impact as chemically resistant, high-temperature thermoplastics.
POLY 101: Olefin cross-metathesis, a mild, modular and efficient approach towards functionalized cellulose esters

Xiangtao Meng¹,³, xiangtao@vt.edu, John B. Matson¹,², Kevin J. Edgar¹,³. (1) Macromolecules and Interfaces Institute, Virginia Tech, Blacksburg, Virginia, United States (2) Chemistry, Virginia Tech, Blacksburg, Virginia, United States (3) Department of Sustainable Biomaterials, Virginia Tech, Blacksburg, Virginia, United States

Functionalization of polysaccharides are of great interests in enhancing the desired properties of polysaccharide derivatives for purposes as diverse as drug delivery, antimicrobial, and coating. However, such efforts have relied extensively on conventional synthetic approaches such as esterification and etherification. While the convention methods have indeed contributed to most commercially important polysaccharide derivatives, the diversity of these derivatives are, however, limited by these methods due to harsh conditions they require, and/or accessibility of reagents. Olefin cross-metathesis (CM) has, for the first time, been used for polysaccharide modification (cellulose in particular), and proven a mild, modular and wide in scope approach. Generally, cellulosic backbones were appended with terminally olefinic side-chains as handles (e.g. cellulose acetate undec-10-enoate), which was then reacted with a CM partner via CM, and thus functionalized with corresponding functional group (Figure 1). By switching to a variety of different acrylic acid-based CM partners such as acrylic acid and acrylates, efficient, modular and wide in scope side-chain functionalization of cellulose can be achieve. This chemistry is so mild and efficient that under room temperature nearly 100% of terminal olefin can be converted to CM adducts within 1 h in most reactions. Considering that the α,β-unsaturation may lead to crosslinking of the CM products due to a free radical mechanism, we explored reactions including hydrogenation that reduce the unsaturation and thus eliminate the potential instability. With this chemistry in the toolkit of polysaccharide chemists, we believe more and more polysaccharide derivatives with diverse functionalities and facile synthetic pathways will be obtained.

Figure 1. General three-step synthetic method for functionalized cellulose esters via olefin cross-metathesis. Note that structures are not meant to imply regiospecificity; particular positions of substitution in all schemes are only for convenience of depiction and clarity.
Development of sustainable and biodegradable materials is essential for future growth of the chemical industry. For a renewable product to be commercially competitive, it must be economically viable on an industrial scale and possess properties akin or superior to existing petroleum-derived analogs. To address this challenge, we have developed an efficient semisynthetic route to the branched lactone, $\beta$-methyl-$\delta$-valerolactone ($\beta$M$\delta$VL), which can be transformed into an amorphous, low glass transition temperature polymer. We determined poly($\beta$M$\delta$VL) may be used as a macroinitiator for the polymerization of lactide, resulting in well defined ABA polyester triblock copolymers with tunable mechanical properties that can rival styrenic block copolymers. This promising strategy offers an economically viable approach to bioderived plastics and elastomers for a broad range of applications.

We use an efficient semisynthetic route to produce a branched lactone, $\beta$M$\delta$VL, from glucose. Renewable ABA triblocks synthesized from $\beta$M$\delta$VL and lactide exhibit tunable mechanical properties akin to styrenic block polymers.
Composite membranes of two or more polymers have recently become popular for many applications. The integration of chemical and physical properties of the contributing polymers lead to higher quality and performance characteristics of composite membranes. Cellulose acetate (CAc) and poly (vinyl alcohol) (PVA) is electrospun from one solution in DMSO as a low volatile solvent, for the first time. The electrospun membranes are characterized by Scanning Electron Microscopy (SEM) and Thermal Gravimetric Analysis (TGA). CAc is a derivative of the naturally abundant and cheap polysaccharide, cellulose, an environmentally friendly polymer which is a popular candidate in the production of an array of materials with different applications such as filtration, protective clothing, electronics, biomedicine, wound dressing, and drug delivery. As a versatile starting material, CAc can be processed into fibers, membranes, and films. PVA has unique physical and mechanical properties that are beneficial in many applications including the production of electrospun fibers and membranes. It can also serve as a carrier polymer to assist in the electrospinning of CAc. The co-electrospinning of CAc and PVA from one solution results in a membrane containing fibers of both polymers while reducing the steps of preparing composite membranes, which are typically prepared by electrospinning one polymer solution on top of the other, followed by crosslinking of separately spun membranes; or by coaxial or multijet electrospinning of two or more separate polymer solutions.. DMSO was found to be a suitable solvent for the co-electrospinning of CAc and PVA, based on the solubility of CAc and PVA in DMSO. SEM images and TGA plots show that the resulting membranes have a uniform fiber distribution and considerable heat resistance.
POLY 104: Assessing gas permeability in polymer nanolaminates

Erik Dunkerley, Daniel F. Schmidt, Daniel_Schmidt@uml.edu. Plastics Engineering, U. Mass. Lowell, Lowell, Massachusetts, United States

Polymer nanocomposites have attracted interest for many years due to their enhanced barrier properties. This has translated into commercial applications from food packaging to fuel storage, and has sparked interest in barrier modeling. While simplifying are often invoked and microstructural changes ignored, the commonly invoked tortuous path models nevertheless show the ability to capture some of the behavior of these materials.

More recently, nanolaminates consisting of a majority of highly oriented nanolayers held together by a minority of a polymeric binder have attracted significant attention thanks (among other things) to their extreme barrier properties. Their performance is generally far in excess of what is seen in melt-blended polymer nanocomposites, and inspires significant practical interest. From a scientific standpoint, these materials also offer a clear opportunity to better understand the factors controlling nanocomposite permeation behavior.

We report on efforts to develop such an understanding. Polystyrene has been combined with two different nanoclays, one compatible, the other incompatible. Homogeneous, fully dense films based on both nanoclays and containing 0% to 100% polystyrene were prepared via automated spray deposition. Nanolaminate structure was assessed via 2D x-ray diffraction and scanning electron microscopy, with composition and density also confirmed and consistent with expectations.

An in-depth investigation of the oxygen permeability of these materials is presented, with emphasis on the effects of composition and intercalation. Common analytical models are applied both as-is and orientation-corrected, and additional results from nanolaminates based on other amorphous polymers are presented as well. The range of applicability of various analytical models is clarified and important parameters controlling barrier properties are identified, with clear implications for polymer nanocomposites in general.

A free-standing spray-deposited nanolaminate thin film displaying its flexibility and transparency
In many cases, electronics packaging requires electrical conductivity and barrier to oxygen, even under humid conditions. These two properties have simultaneously been realized through the use of surfactant-free aqueous layer-by-layer (LbL) processing, in the form of a polymer composite nanocoating. By layering graphene oxide (GO) with polyethyleneimine (PEI), a ‘nano brick wall’ structure has been created, imparting gas barrier properties to the film. Reducing the graphene oxide with a thermal treatment further demonstrates continued high oxygen barrier in humid conditions (0.0217 cc/m²/day/atm) and imparts high electrical conductivity (1750 S/m). These thin (<400 nm) films are flexible relative traditional coatings (e.g. ITO), and processing occurs under ambient conditions with water as the only solvent.
POLY 106: Stretchable gas barrier achieved with partially hydrogen-bonded multilayer nanocoating

Kevin M. Holder¹, kevin.m.holder@gmail.com, Fangming Xiang¹, Benjamin R. Spears², Molly Huff³, Morgan Priolo³, Eva Harth², Jaime C. Grunlan¹, jgrunlan@tamu.edu. (1) Texas A M Univ, College Station, Texas, United States (2) Vanderbilt Univ, Nashville, Tennessee, United States (3) 3M, Saint Paul, Minnesota, United States

Super gas barrier nanocoatings have recently been demonstrated by combining polyelectrolytes and clay nanoplatelets with layer-by-layer deposition. These thin films match or exceed the gas barrier of SiOₓ and metallized films, but they are relatively stiff and lose barrier with significant stretching (≥ 10% strain). In an effort to impart stretchability, hydrogen-bonding polyglycidol (PGD) layers were added to an electrostatically bonded thin film assembly of polyethylenimine (PEI) and montmorillonite (MMT) clay. Hydrogen bonding allowed the film to retain barrier at 10% strain. More recently, a 20 BL all-polymer film of poly(acrylic acid) (PAA) and poly(ethylene oxide) (PEO) was able to survive 100% strain, while maintaining a 5X improvement in the gas barrier of 1.5 mm thick natural rubber. The ability to prevent cracking and preserve gas barrier at such high strains provides a tremendous opportunity for reducing weight and improving barrier of elastomeric materials.
This lecture summarizes our research in the area of particulate filled multilayer polymer composites.

Continuous layer-multiplying coextrusion is a method by which two or more dissimilar polymers are combined into microlayer or nanolayer laminates. Typically, the total number of layers ranges from tens to thousands of layers. Multilayering is an attractive approach for creating designed structures from particulate-filled polymers. If the particles are anisotropic, for example platelets, flakes, tubes or short fibers, the geometric constraints imposed by layer multiplying ensure orientation of the particles in the plane of the layers. Furthermore, filled and unfilled layers can be alternated. Mineral particles, in particular platelets, can be added to increase barrier properties. It can be shown that for barrier enhancement it can be advantageous to alternate filled and unfilled layers. Furthermore we demonstrated that thermally stimulated interdiffusion of a polymer pair with strong mismatch of diffusion coefficients in microlayers can be employed to increase the concentration of inorganic particles. In recent years the work focused on concentrating nanoplatelets such as organically modified montmorillinite (MMT), synthetic mica and graphene. Multilayers containing high aspect ratio nanoplatelets displayed noticeable enhancement of gas barrier and fire retardant properties.
In the past 30+ years, polymer membranes have emerged as a viable and widely used technology to separate gas mixtures and purify water via desalination and filtration of, for example, wastewater. In desalination, for example, reverse osmosis membranes are the dominant technology for desalinating seawater, displacing thermally driven processes in much of the world. In gas separations, polymer membranes are widely used for air separation and hydrogen purification, and they are increasingly being used for natural gas separation.

In recent times, focus on grand challenges facing mankind, including development of energy-efficient methods to provide clean water in both the developed and developing world and mitigate carbon dioxide levels in the atmosphere, have driven research into new platforms of membranes in our laboratories. Additionally, the strong and often competing connections between water, energy, and food production, coupled with the shale gas and shale oil revolution currently under way in the United States, are providing new opportunities for low-energy separations.

This presentation will focus on two stories, each illustrating pathways beginning from fundamental molecular engineering of polymers to tune their properties for specific separations, followed by scale-up and commercial deployment. In one case, membrane materials were developed with a specific affinity for CO₂, resulting in membranes that are currently used for CO₂ removal from H₂ in H₂ production and in large-scale field tests for post-combustion carbon capture. In the second case, beginning from Office of Naval Research sponsored research in the 1990’s, focused on separation of oil/water emulsions in bilgewater about Navy ships, porous membranes used for water filtration were surface modified to improve their lifetime and performance (i.e., resistance to fouling). Systematic tuning of the chemistry and application of these nanometer-thick surface modification coatings led to fouling-resistant, energy-efficient membranes now in commercial production for the oil and gas industry (purification of flowback water from hydraulic fracturing, desalination of water for fracking operations), municipal wastewater purification, and rural desalination. Finally, the presentation will provide a short section on a forward-looking view of the bright future emerging for fundamental science to drive innovation in polymer membranes for both new and existing applications.
To allow advanced separation devices to be competitive for use in large scale separation processes, both low costs per unit of separation contact area and compact module sizes are desirable. In fact, polymer based membrane and sorbent fiber modules easily satisfy this low cost requirement; however, separation efficiency is also important for ultimate success in competition with less energy efficient traditional approaches. Unfortunately, pure polymer membranes and sorbents often fail to meet separation efficiency requirements for applications like CO₂ removal from flue gas and from natural gas, or for olefin-paraffin separations. This presentation discusses strategies to meet the dual needs of low cost and high efficiency using fibers based on composite materials. Such materials, comprising separate domains of intrinsically different materials types, e.g., polymers with embedded zeolitic, porous silicas or metal organic frameworks, can address a spectrum of application needs. Practical approaches for both membrane and sorbents will be discussed to illustrate material types and processing approaches to enable devices based on composite materials.
POLY 110: Biomaterial-based barrier materials and composites: A review on how to prevent unwanted water interactions and water-induced property deterioration

Per Larsson\textsuperscript{1,2}, per.larsson@polymer.kth.se, Lars Wagberg\textsuperscript{1,3}. (1) Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden (2) BiMaC Innovation, KTH Royal Institute of Technology, Stockholm, Sweden (3) Wallenberg Wood Science Center, KTH Royal Institute of Technology, Stockholm, Sweden

Our ecological footprint is steadily increasing and our society is facing one of its greatest challenges: the inevitable transition into a society where resources are replenished at the same rate as they are consumed. At the same time there are increasing demands on both price and performance of the materials we use in our everyday life, making this transition even harder. Lignocellulosic biomass and other carbohydrates are abundant and renewable resources that naturally are potential candidates to replace non-renewable materials such as petroleum-based plastics. However, biomaterials in general, and lignocellulosics in particular, have a thermodynamic propensity to interact with water, which severely limit, or even completely diminish, their applicability in advanced construction materials, barriers and packages. The aim of this presentation is therefore to review the current state-of-the-art research in which biomaterials have been used as gas barriers, in mechanically strong and durable composites or other advanced applications where water or water vapour is present, and outline where and how biomass indeed can be used to replace or even outperform non-renewable materials, and, if necessary, how to modify the material to possibly overcome its thermodynamically inherent shortcomings in the presence of moisture.

Moisture content, gas permeability and strength as functions of relative humidity for carbohydrate-based materials.
Natural polysaccharides and their derivatives are complex materials. They are naturally polydisperse and often contain ultra-high molar mass (M > 10^7 g/mol) components and supra-molecular structures. The nature of these properties strongly influences the behavior and function of the polysaccharides in many applications, and thus characterization is of critical importance. Very few methods of analysis are suitable for this task, having various drawbacks which can cause artifacts. Asymmetric flow field flow fractionation (AF4), coupled to suitable detectors such as multi-angle light scattering (MALS) and differential refractive index (dRI) detection has proven its strength in this area. However, AF4 experimental work and method development can be demanding due to the complexity of the material with regards to polydispersity, large size and ultra-high molar mass. Success, thus, depends on systematic approaches to analysis and experimental work.

The purpose of this presentation is to give an overview of what AF4-MALS-RI can deliver for the characterization of polysaccharides and their derivatives with regards to characterization in terms of mass, size, structure/conformation, interactions with other compounds, etc. The presentation will also cover some challenges and possible limitations related to AF4-MALS-RI analysis of very large, highly polydisperse and aggregated polysaccharides.
POLY 112: Asymmetrical flow FFF coupled with light scattering for the separation and the structural characterization of glucopolymers with various branching patterns

Agnes Rolland-Sabate1, Agnes.Sabate@nantes.inra.fr, Florent Grimaud2, Romain Iraque2, Sophie Guilois1, Denis Lourdin1, Jean-Luc Putaux3, Gabrielle Potocki-Véronèse2, Alain Buléon1. (1) BIA, INRA, Nantes, France (2) INSA, Toulouse, France (3) CERMAV, Grenoble, France

Polysaccharides generally extracted from plants, algae or produced by microbial fermentations are widely used as texturizing agents. They are also interesting biodegradable materials that could be used for packaging. This work describes a detailed investigation of the macromolecular structure of branched glucose-based biopolymers presenting different structures: glycogens, amylopectins and dextrans synthesized in vitro by dextranucrase mutants. Our approach was based on the determination of the structural heterogeneity of these biopolymers, notably by determining their complete size distributions. As these branched polymers are not well fractionated by means of classical size exclusion chromatography, their structure and size were investigated using NMR and asymmetrical flow field flow fractionation (A4F) coupled with multi-angle laser light scattering (MALLS). The calculated macromolecular conformation and shape in solution were discussed as a function of their branching degree. The branching degree varied from 6 to 8%, 3 to 20% and 3 to 5% for glycogens, dextrans and amylopectins, respectively. Glycogens and dextrans had very broad molar masses and size distributions whereas an antagonistic trend was observed for amylopectins. The molar mass ranged from 5.2 x 10^6 to 1.8 x 10^7 g.mol⁻¹, 7.6 x 10^7 to 6.0 x 10^8 g.mol⁻¹, and 1.2 x 10^8 to 4.2 x 10^8 g.mol⁻¹ for glycogens, dextrans and amylopectins, respectively. Glycogens and amylopectins exhibited a spherical conformation in solution with a Rg/Rh ratio characteristic of dendritic and hyperbranched structures, respectively, whereas the series of dextrans exhibited more extended conformations from hyperbranched to quasi-linear comb-like structures. These macromolecular characteristics are compared to their thermal properties and film-forming ability to open new perspectives for the design of biosourced materials for food or non-food applications.
X. M. Liu, x.michael.liu@gmail.com, E. Peter Maziarz, edmundpeter.maziarz@pfizer.com. Global R&D, Materials and Product Chemistry, Pfizer, Glen Allen, Virginia, United States

The physicochemical properties and biocompatibility/biological functions of biopolymers heavily depend on their molecular weights, molecular weight distributions, and molecular structures. Detailed understanding of these biopolymers used for medical materials becomes increasingly important in the pharmaceutical and consumer healthcare industries. Frequently such detailed information needs a combination of analytical techniques. In this study, we fully characterize different molecular weights of hyaluronic acid and polymeric cationic hydroxyethyl cellulose derivatives (i.e. Polymer JR) using on-line size exclusion chromatography with light scattering, differential viscometer, and differential refractive index detector. For the analysis of Polymer JR, we evaluate the effect of solvent systems on the separation, polymer solution behaviors, and characterization. Four solvent systems of varying pH, ionic strength, buffers, and level of organic solvent content were assessed. The absolute molecular weights, molecular weight distributions, radius of gyration, and solution conformation of both hyaluronic acid and Polymer JR are obtained. Finally the intrinsic viscosity and intrinsic viscosity distributions of the polymers are obtained and compared.

Schematic of size exclusion chromatography with triple detection (SEC-TD)
Cellulose ether materials find widespread use in numerous applications including oil and gas, personal care, industrial, pharmaceutical and food. Many of these applications rely on key properties of cellulose ether materials including water retention, thermogelation, rheology and film formation. Cellulose ether properties depend on the molecular structure of the materials. In addition to substitution chemistry, bulk substitution levels and substitution distributions, cellulose ether molecular weights and molecular weight distributions (MWD) are critical structural parameters impacting properties. Size exclusion chromatography (SEC) is the most widely used technique for characterizing MWDs of polymers, including cellulose ethers. SEC is a dilute solution technique requiring unimolecularly dissolved chains and separations conditions that are strictly controlled by entropic exchange of solutes between the mobile phase and stagnant liquid within the pores of the column packing material. For many applications, amphiphilic cellulose ethers yield the best properties. Amphiphilic materials tend to self-associate in solution making SEC analysis a challenge. In this talk, two examples of amphiphilic cellulose ether materials, namely hydrophobically modified hydroxyethyl cellulose and hypromellose acetate succinate will be discussed. The challenges associated with SEC characterization of these materials will be highlighted, and the strategies used for successful molecular weight characterization will be presented.
POLY 115: New approach to overcome hydrophobic interaction in cellulose ethers for reliable molecular weight characterization

Yongfu Li¹, ylli@dow.com, David M. Meunier¹, David Redwine¹, Meinolf Brackhagen², Roland Adden². (1) Analytical Sciences, The Dow Chemical Company, Midland, Michigan, United States (2) Dow Pharma & Food Solutions, Bomlitz, Germany

Cellulose ethers are derived from cellulose, the most abundant polymer in the nature. Aqueous-soluble cellulose ethers have been widely used as thickeners, binders, film formers and water-retention agents in the applications of food, cosmetics, pharmaceuticals, latex paints, constructions and ceramics products to provide unique properties such as thermogelation, rheology and film formation for the application. The properties of cellulose ethers depend on their chemical structure such as molecular weight, substitution group, level and distribution. Aqueous size-exclusion chromatography (SEC) is widely used for determination of molecular weight distributions (MWD) of cellulose ethers. However, it is a challenge to obtain reliable MWD data for cellulose ethers having low thermal gelation temperatures. Under typical aqueous SEC conditions, these materials self-associate resulting in lower water solubility and bi-modal chromatograms. In this talk, it will be shown that the ultrahigh molecular weight materials observed in dilute cellulose ether solutions are self-associates driven by inter-chain and intra-chain hydrophobic interactions as studied by the influence of Hofmeister series salts and their concentration. Hydrophobic interactions in cellulose ether solutions can be controlled by salt type and concentration. Therefore, addition of salt provides a viable strategy to defeat self-association in these materials for a successful molecular weight characterization.

Figure 1. Influence of Hofmeister series salts on self-association of cellulose ethers having low thermal gelation temperatures.
Electroactive polymers (EAPs) provide an exciting method of creating next-generation smart materials. EAPs demonstrate a change in size or shape upon application of a voltage, and conversely generate a voltage upon deformation. One common manifestation of an EAP consists of an ionically conductive polymer membrane (e.g., Nafion) sandwiched between two electrodes. Typically, these electrodes consist of precious metals such as platinum or gold. Upon the application of an external electric field, these ionic polymer-metal composites (IPMCs) demonstrate significant bending. Applications for such IPMCs include artificial muscles, flexible energy harvesting devices, lightweight dynamic sensors, and robotic controls. While IPMCs are a very promising smart material, the use of expensive rare-earth metals as electrodes is undesirable. In this work, we demonstrate the first ionic polymer composites incorporating electrospun carbon nanofibers. These devices, referred to as ionic polymer carbon composites (IPCC) utilize easy to manufacture, low-cost electrodes. The electrospun carbon nanofibers demonstrate high surface area (45-450 m²/g), porosity (96%) and electrical conductivity (0.8-6 S/cm). To create the IPCC, two carbon fiber electrodes are impregnated with Nafion and then assembled into a multi-layer composite with a melt-press. The electrospun electrodes offer several advantages compared to similar actuators. In addition to the low cost and ease-of-production of the electrodes, the nanofabrication procedure allows for control of several different electrode properties. We demonstrate actuation properties of ±1 cm under an alternating 5V amplitude square wave with a 0.2 Hz frequency. Upon manual mechanical bending, the IPCC demonstrates a piezoelectric response of 1.3 mV/mm of thickness.
New materials that contain both organic and inorganic components have potentially new chemical and physical properties that can even lie outside those bracketed by their constituents. In our ongoing investigations of the relationships between structure and thermal properties of materials, we have investigated several composite systems in which polymers are one component. These include poly(ethylene oxide)/nanozeolite composites, carbon nanotubes/polystyrene composites, PMMA/alumina composites, and negative thermal expansion materials as composites with polymers. These systems allowed investigation of the influence of confinement of the polymers on degree of crystallinity and glass transition temperature, and the influence of composition and morphology on thermal conductivity.

How does a physical property of an inorganic-polymer composite compare with the properties of its components?
Hybrid materials that integrate inorganic and organic components at the nanoscale provide the potential for combining the properties of the constituents. The presence of a few weight percent of clay can enhance the mechanical strength, thermal stability, and barrier properties of a polymer if the individual layers of the clay are well dispersed in the polymer matrix. However, control of nanoscale integration of the inorganic and organic components can be difficult to achieve. Our approach involves a “grafting from” preparation of polymer brushes on synthetic hybrid clays. Lamellar magnesium organosilicates with covalently linked organic moieties provide initiation sites for \textit{in situ} growth of end-tethered polymer. The variety of available organosilicate groups renders this strategy suitable for a range of living polymerization systems. The ability to control both initiator site packing density and polymer chain length affords a high degree of tailorability to the resulting nanocomposites, which suspend as individual brush-like lamellae in solution or have an exfoliated nanocomposite structure in the solid state. The synthesis, characterization, and properties of these covalently linked polymer brush–clay nanocomposites will be described.
Supramolecular chemistry is a powerful tool to build complex molecules through non-covalent interactions under high yield, mild reaction conditions. Ionic interactions can be used to couple a wide range of oppositely charged molecules, such as hydrotropes, surfactants, ionomers and polyelectrolytes to build polymers with more complex architectures. The presence of ion pairs in these polymers can result in new physical properties due to the dissociation or aggregation under different environmental conditions. This talk will discuss efforts in our laboratory to prepare elastic polymer networks using ion-pairs as inter-chain crosslinks. Both synthesis efforts by controlled radical polymerization and bulk mechanical characterization by oscillatory and steady shear rheology will be discussed. It will be shown that ion-pair crosslinks yield mechano-responsive elastomers that are stable at low frequency over a wide temperature range, but can be deformed at high strain. This has potential applications in functional elastomers including shape memory and self-healing systems.
Vitrimers are a new class of permanently cross-linked networks that contain dynamic covalent bonds that can undergo associative exchange reactions. As a result, the topology of these networks can be dynamic under certain conditions, which allow these materials to relax stress or to be reshaped and recycled just like thermoplastic while being insoluble like thermosets even at high temperatures. The concept of vitrimer was first introduced with epoxy-based systems relying on transesterification of beta-hydroxy ester as associative exchange reaction.\textsuperscript{1-3} We have been exploring recently the possibility to extend this concept both to other associative exchange reactions and polymer matrices. We present here our latest results on vinylic vitrimers and describe the synthesis and complete characterization of this new class of vitrimers.

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Reshaping and recycling of a permanently cross-linked vinylic network
POLY 121: Combined hydrophobicity and mechanical durability through surface nanoengineering

Paul R. Elliott¹, Stephen P. Stagon², Hanchen Huang³, h.huang@neu.edu. (1) Department of Mechanical Engineering, University of Connecticut, Storrs, Connecticut, United States (2) Department of Mechanical Engineering, University of North Florida, Jacksonville, Florida, United States (3) Department of Mechanical and Industrial Engineering, Northeastern University, Boston, Massachusetts, United States

Polymer, in combination with nanorods, provides a means of engineering surfaces. This presentation reports combined hydrophobicity and mechanical durability through the nanoscale engineering of surfaces in the form of nanorod-polymer composites. Specifically, the hydrophobicity derives from nanoscale features of mechanically hard ZnO nanorods and the mechanical durability derives from the composite structure of a hard ZnO nanorod core and soft polymer shell. Experimental characterization correlates the morphology of the nanoengineered surfaces with the combined hydrophobicity and mechanical durability, and reveals the responsible mechanisms. Such surfaces may find use in applications, such as airplane windshields, that benefit from hydrophobicity and require mechanical durability.

Schematic of nano-composite surface, showing a silicon substrate (dark), ZnO nanorods (white), and polymer (grey); with a water droplet (blue). Not to scale.
POLY 122: Sustainable carbon sources for the chemical industry: CO₂ is becoming a direct and indirect component in polyurethane plastics

Christoph Guertler¹, christoph.guertler@bayer.com, Karsten Malsch¹, Matthias Wohak², Aurel Wolf⁴, André Bardow⁵, Niklas von der Assen⁵, Walter Leitner³, Thomas E. Mueller². (1) Bayer MaterialScience AG, Leverkusen, Germany (2) CAT Catalytic Center, Aachen, Germany (3) Inst of Tech and Macro Chemistry, Aachen, Germany (4) Bayer Technology Services, Leverkusen, Germany (5) LTT, RWTH Aachen University, Aachen, Germany

Dream Production – scheduled to deliver commercial products soon
Carbon dioxide is much too valuable to just be released into the atmosphere - it can, at least partly, replace petroleum, a traditional source of carbon. Bayer MaterialScience wants to exploit this possibility and has become a pioneer of using CO₂. The Dream Production project, well established for some time now, focuses on using carbon dioxide to produce polyols, a crucial component of polyurethane foam. The new material is scheduled to be launched in 2016. The first target product: mattresses with a CO₂ content in the new polyol of about 20 percent.

Dream Polymers – follow up with a two-pronged approach
Now the experts at BMS in Leverkusen are taking the next step. Funded by the German Federal Ministry of Education and Research, the project also involves the CAT Catalytic Center, RWTH Aachen University, the Leibniz Institute for Catalysis and the Fraunhofer Institute for Chemical Technology.
Carbon dioxide is used twice in the new process. First, the greenhouse gas is incorporated directly into a new kind of precursor (polyoxymethylene polycarbonate polyol), replacing 20 percent of the petroleum. Second, it is also used indirectly, producing a chemical that is also incorporated into the precursor for a further 20 percent saving in petroleum. As a result, the proportion of alternative raw materials is 40 percent.

In addition, the catalyst system and the process design allows for the incorporation of further functionalities that can be exploited for advanced polymer design and properties.
Propylene glycol is a valuable industrial chemical with wide ranging uses including personal care, deicing, heat transfer fluids and polyesters. ADM has commercialized a flexible process to produce propylene glycol from the renewable feedstocks glycerol or sorbitol. Propylene glycol (PG) markets are highly developed and product requirements are well understood. Key to the commercial success of renewable propylene glycol has been understanding the differences and similarities in coproducts from the petrochemical and biobased processes. The end result is USP propylene glycol that is equivalent to PG made from petrochemical sources with identical performance in unsaturated polyester resins (UPR) and the added benefit of certified renewable content. To further the commercial success of biobased PG, ADM is developing a complementary set of renewable diols to expand the opportunities to produce UPR with renewable content.
Aquazol ® (poly(2-ethyl-2-oxazoline)) is produced commercially solely by Polymer Chemistry Innovations. Poly(2-ethyl-2-oxazoline) is a high performance, non-toxic, water soluble, thermally stable, extrudable polymer. These characteristics make it highly attractive for many applications in a wide variety of industries from ceramics to gas and oil, cosmetics and health care. Recent literature and patents exhibit many examples of poly(2-ethyl-2-oxazoline) as a component of di-block, tri-block and multi-block co-polymers. There is great interest in poly(2-ethyl-2-oxazoline) as part of a multiblock copolymer for a number of different applications, especially in the biomedical fields, due to the high biocompatibility of poly(2-ethyl-2-oxazoline). A survey of literature, customer demand, and additional research showed trends of molecular weights and end group functionality. From this survey of literature we developed a new line of mono and di-functionalized poly(2-ethyl-2-oxazoline). These end-functionalized polymers were prepared, optimized and scaled up to be commercially available for researchers to incorporate into their multi-block copolymers.
Methacrylate functional macromers have been commercialized in pigment dispersion, adhesive release, controlled atmosphere food packaging and contact lens applications. Siloxane macromers with a single functional group synthesized by living polymerizations afford many desirable properties, including, narrow molecular weight distribution, high oxygen permeability and flexible reactive functionality. However, the utilization of siloxane macromers has been limited by economic and compositional considerations. Objectives for commercial siloxane macromer design include increasing their solubility range in organic monomers/solvents, retention of desirable siloxane properties without domain formation and improvement of economics.
POLY 126: Enhanced material properties from new isomer configurations of polyetherimides

Peter M. Johnson, peter.johnson@sabic-ip.com. Innovative Plastics Business Unit, SABIC, Mt. Vernon, Indiana, United States

Polyetherimides are commercially available amorphous thermoplastics (ULTEM™ polyetherimide) with excellent heat stability, mechanical strength and flame performance. However, new applications require enhanced properties difficult to achieve through conventional blending approaches. An alternative to blending is to modify the backbone structure of the resin, changing imide or ether positions to manipulate chain configuration and the resulting resin material properties. Polyetherimides with different isomer locations of imide or ether bonds were synthesized with the same chemical backbone and at equivalent molecular weight. By changing the second imide position on the phenyl ring from meta to para, chemical resistance and glass transition temperature were increased. Radius of gyration was reduced for an average chain with ether bonds at the 3 position on the phthalimide as compared to the 4 position. Polymer resin made with 3 position ether bonds result in higher glass transition temperature and improved flow.
The drilling and completing of a well is a critical step in the process of oil and gas exploration and production. Material science and engineering work together as a borehole is drilled through extreme environments that challenge the upper limits of these material's properties. Throughout drilling procedures, drilling fluids play a critical role in helping to stabilize the borehole, cool and lubricate the drill bit, and carry the cuttings back to the surface. These fluids are weighted to a specific density in order to match the downhole formation pressure and properly stabilize the borehole as it is being drilled; an imbalance of pressure could lead to a blowout event. In order to meet these varied performance requirements, these drilling fluids must have a very specific rheological profile: they must suspend the solid weighting agent and drill cuttings under low to no shear conditions, but then have little resistance to flow under higher shear conditions in order to maximize the rate of penetration of the drill bit. In addition, any chemical additive used to impart such non-Newtonian behavior to the fluid must be stable to high temperatures, pressures, and chemical contaminants that may be encountered in a downhole environment. This talk will focus on the use of styrenic block copolymers as rheology modifiers in drilling and completion fluids, highlighting how the formation of micelles in solution gives structured fluids that lead to formulation options not accessible with non-polymeric additives.
Among polymers, polyethylene is the most important one. It is used across all industries from food packaging to power transmission. Advances in catalysis since the days of Ziegler and Natta have delivered refinements of the structure of polyethylene, and improved control over resin properties. Each major step forward in catalysis has allowed polyethylene to enter application spaces previously inaccessible. For example, precise control of molecular weight and its distribution, control of placement of comonomers, such as hexene or octene, has led to new products with better properties like Dow’s new line of advanced polyethylene resins commercialized as Elite ELITE™ AT, enhanced polyethylene. In addition, recently, The Dow Chemical Company commercialized INFUSE™ Olefin Block Copolymers. Prepared using “chain shuttling” catalysis\(^1\), these products exhibit a new balance of good flexibility and high heat resistance, and can be used in many applications where random copolymers fail. The chain shuttling technology employed to produce INFUSE™ OBCs can be used to produce many other refined polyethylene structures with new and novel combinations of properties\(^2\). The synthesis and properties of several classes of OBCs will be presented, demonstrating, once again, our ability to push the envelope of polyethylene performance.

\(^{TM}\)Trademark of The Dow Chemical Company
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POLY 129: Abundant, low cost U.S. shale gas supply stimulates polyolefins renaissance

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

The abundance and low cost of natural gas (NG) in the U.S. is having a significant positive impact on the U.S. economy. In the case of petrochemicals, NG becomes advantaged as a feedstock over all other feedstocks, particularly naptha (oil) in the U.S., for key molecules. The promise of a reliable, low cost supply of ethane and propane from NG has triggered both significant new investment in the U.S. for ethylene and propylene production from NG, and a divergence from the previously coupled production pathway for manufacturing them. In this talk we will focus, for the most part, on the ethylene pathway. The single greatest use of ethylene is for manufacture of polyolefins. Consequently, the expected long term availability of advantaged ethylene has spawned a new wave of announced U.S.-based investments in polyolefins as well. The net result is a renaissance of the polyolefins industry in the U.S. that is expected to leverage and spur innovations along the value chain from manufacture to fabrication of finished goods in diverse applications from packaging to health care and durable goods. It is anticipated that these investments and the bright outlook for the foreseeable future will also foster continuing innovations in olefin polymerization catalysts, processes and polyolefin design for myriad applications. A review and assessment with examples will be provided for how these benefits can accrue along the value chain and how they contribute as well to sustainability of polyolefins.
POLY 130: Unexpected anomalous diffusion in associating protein hydrogels

Shengchang Tang, tang_sc@mit.edu, Muzhou Wang, Bradley D. Olsen. Chemical Engineering, MIT, Cambridge, Massachusetts, United States

Engineered protein hydrogels are promising candidates in many biomedical applications such as regenerative medicine and tissue engineering. While many studies have focused on controlling their mechanical properties, biofunctionality and stimuli responsiveness, less has been done to elucidate the dynamics of gels on a molecular scale. However, unraveling the diffusion and molecular relaxation of protein gels is critical to gain a better understanding on the self-healing properties and erosion behavior. Here, we report the first systematic experimental measurements on the diffusion behaviors of a model coiled-coil protein in gels by forced Rayleigh scattering (FRS) over different length scales. An unexpected “super-diffusion” is observed where the relation $\tau \sim d^{2\alpha}$ exhibits a pseudo power law in a log-log plot and the scaling exponent $\alpha$ is less than one. When the length scale is large, Fickian diffusion is recovered where an effective diffusion coefficient can be calculated. The anomalous diffusion is found be strongly dependent on temperature as well as the protein concentrations in gels. To quantitatively explain the experimental results, we have developed a “two-state” model, which considers both the diffusion of proteins and the exchange kinetics of the coiled-coil domains. The model is able to capture both diffusion regimes, and it yields estimated association parameters that can be used to obtain a collapsed shear rheology master curve from bulk mechanical measurement.

Anomalous self-diffusion of coiled-coil proteins in hydrogels.
Delivery of therapeutics remains a major challenge in existing cancer therapies despite recent technological advances. Delivery vehicles that enable local and sustained release of therapeutics and allow tailoring of release profiles from patient to patient are needed for improved clinical outcomes. Toward tunable release profiles and patient-specific treatments, we are investigating approaches for degradation-mediated cargo release from injectable hydrogels through the incorporation of novel responsive chemistries. Specifically, poly(ethylene glycol)-based hydrogels were formed by Michael-type reactions for in situ network formation and microenvironment-mediated degradation. Dual degradability of these hydrogels was achieved by incorporation of thioether succinimide linkages that undergo 1) ester hydrolysis and 2) cleavage of the click linkage in reducing microenvironments. Due to abnormal proliferative activities of cancer cells, the concentration of glutathione (GSH), a reducing peptide, is elevated in carcinoma tissues as compared to surrounding healthy tissues. Utilization of reducing-sensitive chemistries thus provides opportunities for microenvironment-responsive degradation and release of cargo molecules over time, with increased rates of release in carcinoma tissues. Due the rapid rate of Michael-type addition, crosslinking was achieved within 20-40 seconds, depending on the identity of thiol groups. Aryl thiol based thioether succinimide (dually degradable, D2ER) linkages exhibited rapid degradation as compared to alkyl thiol based thioether succinimide linkages (solely hydrolytically degradable, D1E), owing to fast click linkage cleavage and thiol exchange reactions. The release of a model cargo protein depended on the rate of degradation of the hydrogel with a 2.5-fold difference in protein release for D2ER as compared to D1E and a non-degradable control. Overall, these results demonstrate the utility of click reactions for the formation and degradation of injectable hydrogels, where the rate of degradation can be tuned through incorporation of select thiol functional groups. This approach presents considerable opportunities for designing hydrogel based drug carriers for triggered therapeutic delivery.
POLY 132: Photodegradable hydrogels for studying axon guidance and the user-directed formation of neural circuits

Tobin Brown, tobin.brown@colorado.edu, Daniel McKinnon, Kristi S. Anseth. Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado, United States

Hydrogels, water swollen polymer networks, can be used to culture cells in a three dimensional environment that mimics the native extracellular matrix. The incorporation of light sensitive chemistries allows researchers to modify the microenvironment of cultured cells with precise spatial and temporal control. Here, we present a step-growth poly(ethylene glycol) (PEG) hydrogel formed by the strain promoted azide alkyne cycloaddition (SPAAC) with the photocleavable nitrobenzyl ether moiety incorporated into the crosslinking units. Two-photon excitation microscopy is then leveraged to erode well-defined three dimensional features within the body of the hydrogel using near IR wavelengths. By creating narrow channels in the vicinity of mouse embryonic stem cell-derived motor neurons (ESMNs), this platform can be used to physically promote and direct axon extension. In a co-culture with muscle cells, the axon’s in vivo synaptic target, the formation of neural networks can be achieved in a user-defined manner.

Two-photon excitation microscopy is used to erode physical channels within a hydrogel. Mouse embryonic stem cell-derived motor neurons extend axons through photodegraded channels. Cells express green fluorescent protein under the motor neuron specific HB9 promoter.
Molecular n-dopants dope conjugated polymers either by reduction of the host material by direct electron transfer or by decomposition of a precursor to an intermediate that is capable of reducing the host. Two examples of molecular n-dopants are the dimethylbenzimidazolium salts (DMBI-X), which release unidentified reactive intermediates during a thermal deposition process, and the 1,3-dimethyl-2,3-dihydro-1H-benzimidazoles (DMBI-H) which dope by hydride transfer. In either case, additional carriers result from the same benzimidazolium cation/host radical anion pair, DMBI+/A•–, reaction product. For DMBI-I dopants, strong n-doping has only been observed for vacuum deposited films, and for DMBI-H dopants, the necessary hydride transfer step will limit the scope of dopable host materials. Here we report on the synthesis, characterization, and doping mechanism of benzimidazoline-radical dimers ((DMBI)2), and their use to form the doped state DMBI+/A•– in conjugated polymers. The distinct properties of the (DMBI)2 dopants relative to the DMBI-H dopants is evident from the reaction rate, polaron intensities, Fermi level shifts, and conductivities achieved using (2-Cyc-DMBI)2 and 2-Cyc-DMBI-H. The distinct reactions by which the dopants function results in greater variability of the doping effect for the DMBI-H compound than for the dimer in the hosts explored in this study. We also report several new n-dopable conjugated polymers that give higher conductivities when doped by (DMBI)2 dopants than what has been reported for solution processed n-doped polymers. The energetic and structural factors that enable the efficient n-doping of these polymers was examined by comparing the doping reaction yield, polaron delocalization length, and thin-film morphology.
Electrochromic devices made from organic polymeric materials have yet to be realized commercially, but show promise due to sub-second switch speeds, color variability, the ability to work in flexible and stretchable devices, open air fabrication, and high optical memory resulting in low power consumption when compared to current display technologies. Neutral colored electrochromic devices are desirable for automotive, aerospace, architectural windows, smart glass/privacy glass, and contrast-enhancement for see-through displays. Herein, the ability to color tune electrochromic polymers will be explored beginning with the use of high-throughput screening in a solid-state device to produce a continuum of copolymers and homopolymers that span the entire visible subtractive spectrum from just two distinct monomers, 2,2-dimethyl-propylenedioxythiophene (ProDOT-Me₂) and 1,3-di-tert-butyl-propylenedioxythiophene (ProDOT-tBu₂). The use of computational modeling of two discrete copolymer systems to tune neutrality and contrast in a large area flexible electrochromic device will also be presented. The two copolymer systems consist of only three monomers, of which ProDOT-tBu₂ was selected due to its absorption on the extreme low end of the subtractive spectrum at 392 nm, ProDOT-Me₂ was chosen due to the high contrast and absorption at 575 nm, and thienothiophene was chosen due to a broad absorption at 850 nm. These studies have significantly reduced the time and synthetic cost associated with traditional methods for color tuning electrochromic devices.
Chemical reactions affected by spin angular momenta of circularly polarized photons are rare and display low enantiomeric excess. Because of high optical and chemical activity, nanoparticles (NPs) signifies the possibility of converting spin angular momenta of absorbed photons into structural changes of nanoscale materials by self-assembling. However, such processes are currently unknown. Here, we demonstrate that circularly polarized light (CPL) strongly affects the nature of self-assembly of racemic CdTe NPs. In particular, illumination of right- and left-handed CPL into NP dispersions induces the formation of right- and left-handed twisted nanoribbons, respectively. Enantiomeric excess of such reactions exceeds 30% which is ~10 times higher than other CPL-induced reactions. In contrast, illumination with linearly polarized light and assembly in the dark led to straight nanoribbons. This observation of imprinting the polarization information of incident photons by NPs opens new pathways for the synthesis of chiral photonic materials and allows for better understanding of the origins of biomolecular homochirality.

POLY 136: Polymer-particle rheological analysis of adsorbed cement additives for improved processing

Lisa R. Murray, lnielse@purdue.edu, Emily G. Soltys, Kendra A. Erk. School of Materials Engineering, Purdue University, West Lafayette, Indiana, United States

Derived from natural sources, cement pastes are essential to repairing and restoring the nation’s infrastructure, which demands good processing capability in order to be mixed and poured efficiently. Polymer additives play a necessary role in cement flow properties due to their ability to stabilize oxide particles for uniform dispersion. However, the molecular-scale physical properties of these plasticizer-particle systems are not well understood. With rheology, we seek to delineate the fluidity of both commercial and custom synthesized polymer additives to improve processing of cementations suspensions. Concentrated magnesium oxide (MgO) suspensions were used as a model for cement pastes in terms of their flow behavior and polymer-particle interactions. Suspensions were tested with a commercial comb-polymer additive of poly(acrylic acid) with poly(ethylene oxide) (PEO) side chains with and without free PEO chains in order to assess both concentration dependency of particle stabilization and the impact of chain overlap and agglomeration under shear. The commercial standard was found to have increased viscosities whereas the free chains promoted lower viscosities. An innovative lignin-based polymer of an acidified lignin core and grafted PAA or poly(methyl methacrylate) (PAm) side chains was also tested for viscosity reduction. This wood-based derivative polymer competes with the commercial additives through the advantages from the stronger steric repulsion and optimization of side chain length. From this work it is demonstrated that alterations to the traditional cement additives are advantageous for improving cement processing.
The COMOFLO algorithm is a dynamic Monte Carlo technique capable of accurately capturing the molecular scale details of polymer melts. Under quiescent conditions the dynamics of the polymer melts are measured through correlation functions. The melts show a crossover from Rouse to reptation-like dynamics with increasing chain length. When the melts are subject to shear flow through a specialized biasing, the proper scaling of the zero shear viscosity with molecular weight is captured. Similarly, when subjected to an extensional flow the extensional viscosity is calculated. The rheological properties are obtained in an \textit{a priori} manner and are in \textit{post facto} agreement with experiments.

Recently, the algorithm has introduced polydispersity. When polydispersity is incorporated its importance is clearly present. Thus the important “missing physics” of incorporating polydispersity into molecular scale simulations has been found. When polydisperse melts are subject to parabolic flow, migration phenomena is observed. The results provide clear evidence of migration in the presence of shear gradients at stress levels far below those needed for chain degradation.

The algorithm is capable of capturing molecular scale details of wall slip. In shear flow, slip is heralded by a disentanglement of chains and shear banding at high shear rates. Entangled polymer melts also exhibit signs of weak slip at moderate shear rates. Polydispersity is found to reduce slip. In the case of parabolic flow, the slip velocity is found to increase with decreasing molecular weight at a constant shear stress, and to increase with increasing polydispersity. These results are all in agreement with experiments and indicate that migration phenomena is fundamentally important in understanding slip phenomena.

This work provides the details behind the development of this algorithm as a tool for understanding the molecular scale behavior of polymers. Results are in \textit{post facto} agreement with experiments and help shed light on the molecular scale details of important polymer phenomena.
Carbon Nanotube (CNT) can introduce electrical and thermal conductivity into polymer. Using dry-jet-wet spin technology, polyacrylonitrile (PAN)/CNT composite fibers with 15 wt% and 20 wt% of CNT content were fabricated. The electrical conductivity of PAN/CNT fibers was enhanced by the annealing process at different temperatures. These fibers could also respond to stretching, and the electrical conductivity decreased by 50 % when the elongation reached 3%. In addition, thermal conductivity of PAN/CNT fibers with Kapitza resistance can be estimated with various CNT concentration and orientation in fibers. Both electrical and thermal conductivity influence Joule heating behavior induced by applying electricity. The temperature of composite fibers can increase from room temperature to higher than hundreds of degree Celsius measured by an infra-red (IR) microscope. Joule heating effect can be estimated according to one-dimensional steady-state heat transfer equation, which reveals that the temperature can be high enough to stabilize or carbonize fibers. With the application of various electrical currents up to 7 mA at a fixed length, electrical conductivity was also enhanced from around 25 S/m to higher than 800 S/m. This research provides a new idea of heating fabrics for thermal regulation, and a new approach for stabilizing and carbonizing PAN – based carbon fibers.
The mechanism of stabilization of MWCNT in water by nanolatex PIL (polymerized ionic liquid) is found to be due to random and irreversible surface saturation. These stabilizing nanolatexes are also found to adsorb conformally to the MWCNT low radius of curvature surfaces. The saturation coverage of nanolatex needed for stabilization is 0.28 to 0.31 weight fraction as MWCNT concentration in water increases from 0.5 to 4% by weight. Mullberry paper and fiberglass tissue nanocomposites with MWCNT produce highly anisotropic thermally conducting materials with thermal conductivities in the 0.5-2 kW/m/K range (low to mid diamond range). It appears close to theoretical transport may be achievable without any vacuum-system processing, as these dispersion and nanocomposite materials are prepared by highly scalable dispersion and coating processes.

FE SEM of sedimented MWCNT. The bright spots are the conformally adsorbed nanolatexes that stabilize these MWCNT in concentrated dispersion.
POLY 140: Thermal and other properties in cellulose nanocrystal composite materials

Jeffrey P. Youngblood¹, jpyoungb@purdue.edu, Jairo A. Diaz², Ashlie Martini³, Robert Moon⁴. (1) School of Materials Engineering, Purdue University, West Lafayette, Indiana, United States (2) Purdue University, Lafayette, Indiana, United States (3) UC-Merced, Merced, California, United States (4) Forest Products Laboratory, Madison, Wisconsin, United States

In this presentation, an overview will be presented of recent research into the thermal and other properties of cellulose nanocrystal nanocomposites. Cellulose nanocrystals (CNCs) are an attractive materials class for possible applications in nanocomposites reinforcement, nanomaterials and biomedicine as they have high strength and stiffness, yet are renewable, biodegradable, non-toxic, cheap, and optically transparent. Here, we will detail efforts to utilize these materials in composites, both as nanoreinforcements and as a neat material for both structural materials and consumer applications with discussion of the resultant mechanical and, in particular, thermal properties. Thus, we provide new elements to understand the interconnection among preparation variables towards an optimal CNC materials design.

Ashby plot of thermal expansion vs. thermal conductivity of cellulose nanocrystal materials.
POLY 141: Thermal and electrical transport in nanoconfined poly(3-hexylthiophene)-multi-walled carbon nanotube composite fibers

Matthew K. Smith\textsuperscript{1}, mksmith@gatech.edu, Virendra Singh\textsuperscript{2}, Kyriaki Kalaitzidou\textsuperscript{2,1}, Baratunde A. Cola\textsuperscript{2,1}. (1) Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States (2) Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States

Due to their astounding electrical and thermal transport properties, carbon nanotubes are often used as filler material in polymer matrixes to create polymer systems with improved conductivity. In general, carbon nanotubes can alter the composite electrical conductivity dramatically with relatively low weight percent loading whereas improvements in the thermal transport properties are much less pronounced due to phonon scattering at polymer-CNT interfaces. However, polymer fibers have recently demonstrated orders of magnitude enhancements in thermal conductivity due to confinement mediated preferential chain orientation and it is well understood that carbon nanotube alignment within a polymer matrix drastically improves transport in the direction of alignment. The focus of the present study is to fabricate nanoconfined conjugated polymer-carbon nanotube nanowire arrays to reduce the interfacial phonon scattering through polymer chain and carbon nanotube co-alignment. We incorporate two unique methods to fabricate nanoconfined poly(3-hexylthiophene)-multiwalled carbon nanotube composites using anodic alumina oxide nanoporous templates. One method involves a sonication induced solution infiltration of composite material into alumina nanopores and the other method entails carbon nanotube growth along the walls of the nanopores and sequential infiltration of polymer. For the first time the impact of nanoconfinement induced co-alignment on the thermal and electrical transport was investigated for each processing technique.

Template fabricated P3HT-MWCNT composite nanowire
Fluorinated polymeric matrices are an attractive class of materials due to their applicability for use in various environments including use as high performance materials. Specifically, perfluoropolyethers (PFPEs) are low molecular weight oligomeric fluoropolymers that have low volatility, minimal shear thinning, and a viscosity that is nearly independent of temperature making them stable in extreme processing conditions. PFPEs are well-known to undergo accelerated thermal degradation in the presence of native metals and Lewis acids. The work presented herein is motivated by the potential of harnessing the energetic behavior as a result of degradation pathways facilitated by exothermic metal-mediated oxidation. Computational modeling/simulation supported by thermal experimental studies showed that micro- and nanometer sized aluminum Fomblin-Y (a PFPE) blended formulations produced a viable energetic material. These formulations serve as an additive in commercial polymeric matrices including epoxy resins, electrospun fibers, and foamed polyurethanes. This work will discuss the preparation, characterization, and thermal transport properties of these composite systems.
Building fully three-dimensional (3D) electronic devices has been a challenge for more than a decade. Most of the efforts so far have relied on advanced processing techniques, which are limited in terms of material compatibility as well as process and device scalability. We propose a new method for building fully 3D interdigitated devices inside a high-surface area aerogel as substrate. The method, based on Layer-by-Layer self-assembly, is rapid (each layer is assembled within seconds), precise (allowing nanometer thickness control) and highly generic (applicable to a wide range of substrates and materials). We demonstrated two types of energy storage devices, a 3D supercapacitor and a 3D hybrid battery with a faradaic cathode. We also demonstrated the preparation of soft, and compressible 3D devices that can operate under extreme bending and extreme compressions up to 75%. The characteristics of the presented method define a new class of energy storage devices that combine softness, shock absorbance and energy storage in a single bulk material.
Thermoelectric systems are very effective in harvesting electricity from waste heat or heat sources with low temperature gradients relative to the environmental temperature - which are inadequate for power generation using conventional systems, but are often present in the environment (like body heat and solar and geothermal energy) or generated from various power generating or consuming systems. Furthermore, it is possible to use them for refrigeration. Their simple leg-type structures, without moving parts, provide enormous advantages over conventional turbines, engines, and compressors. In addition, their high energy density (per unit weight and volume) is ideal for mobile power sources and refrigeration with robustness and silence. This talk includes recent progresses in Yu group for developing new-class of fully organic thermoelectric materials, which can provide light-weight (higher power density), inexpensive, and non-toxic solutions for waste heat recovery or cooling. Polymers are intrinsically poor thermal conductors, which make them ideal for thermoelectrics, but low electrical conductivity and thermopower (or the Seebeck coefficient) have excluded them as feasible candidates in the past. Our recent results demonstrated that electrical properties of organic composites can be brought to degenerate semiconductor or metallic regimes by incorporating carbon nanotubes without significantly changing thermal conductivity. The details of our approach for material synthesis and characterization will be discussed.
POLY 145: Temperature gradient interaction chromatography: Principle and applications

Taihyun Chang, 30019351@acs.org. Chemistry and Advanced Materials Science, Pohang University of Science and Technology (POSTECH), Pohang, Korea (the Republic of)

Overcoming the limitations of the conventional Gel Permeation Chromatography (GPC) separation based on size exclusion principle, Temperature Gradient Interaction Chromatography (TGIC) has been applied to synthetic polymers and pushed the molecular characterization onto a new dimension. TGIC exploits the thermodynamic interactions of polymer molecules with the stationary phase of chromatographic columns, in which the column temperature is controlled during the elution. TGIC exhibits much higher resolution than GPC in the separation according to the molar mass and it allows many useful detectors for polymer characterization to be utilized, which is impossible in the solvent gradient elution.

TGIC have been applied to resolve a number of long-standing problems in polymer characterization such as 1) rigorous determination of molar mass distribution of the anionic-polymerized polymers, 2) effective separation/characterization of polymer mixtures including a purification of block copolymers from their homo-polymer precursors, 3) separation according to chain architectures demonstrating clearly that the branched polymers or ring polymers prepared by the current state-of-art synthesis/purification process are still contaminated by a large amount of byproducts enough to influence their rheological property significantly, 4) characterization/fractionation of individual blocks of block copolymers demonstrating that so-called “monodisperse” block copolymer prepared by anionic polymerization has a block length distribution large enough (more than 10%) to exhibit various morphology from lamellar, HPL, gyroid, to cylinder, 5) separation according to stereoregularity, 6) separation according to functionality or end-groups.

TGIC separation of 14 polystyrene standards, MW range of 2k to 3000k.
Liquid chromatography at critical conditions (LCCC) was first introduced in late 1970s\(^1\) as an isocratic chromatographic technique capable to separate complex polymers by some molecular properties, such as type and number of functional groups or length of individual blocks in polymer chains. More recently we have developed an alternative approach to separation at CPA using a solvent gradient.\(^2\) Such approach, which we called gradient elution at CPA, provides several important benefits for characterization of chemical heterogeneity in polymers compared with the traditional LCCC. They include: a simple way to determine the existence and the composition of CPA, removal of typical LCCC limitations on size/molar mass of macromolecules and geometry of separation media (e.g. pore diameter), and elimination of the adverse effects of variability in chemical structure of stationary phase (e.g. carbon loading in reversed-phase column) on the reliable selection of the chromatographic conditions. These advantages significantly extend the applicability of the method. For example, gradient elution at CPA allows for separation of statistical copolymers by chemical composition and microstructure, which is not possible in LCCC.\(^3,4\)

In this lecture, we illustrate the theoretical predictions on several examples including separation of star-shaped polyethylene glycols by end groups (Cl- or OH-) supported by on-line mass spectrometry (see picture), of poly(dimethylsiloxane) and their copolymers by end groups, characterization of statistical and block-polyacrylates (both linear and star-shaped) by chemical composition heterogeneity and chain microstructure (blockiness), characterization of melt-derived copolyesters with fluorinated side chains.\(^5\)

References

POLY 147: Use of 2-D chromatographic techniques to elucidate macromolecular structures

John A. McConville¹, jmccconville@pss-polymer.com, Peter Kilz², Martina Adler², Wolfgang Radke², Derek Lohmann¹. (1) PSSUSA, Amherst, Massachusetts, United States (2) PSS GmbH, Mainz, Germany

Today’s macromolecules, including synthetic and natural/biological polymers are highly fine-tuned to exhibit their best properties. The molar mass, the chemical composition, the architecture and other parameters are optimized for robust structure-property function relationships.

Size-exclusion chromatography (GPC, SEC, GFC) is often applied to characterize macromolecular species. Since GPC/SEC/GFC separation is not governed by molar mass but hydrodynamic volume, copolymers, polymer architectures and complex macromolecular formulations cannot be characterized easily.

However, the combination of different chromatographic separation methods (HPLC, GPEC, SEC, TGIC, SFC, CE, TREF, etc.) into a 2-dimensional (2D) setup can lead to significantly enhanced information content. Accurate and precise results can be directly derived for each sample component in only one 2D run, e.g. molar mass, chemical composition, endgroup, functionality, degree of branching, architecture, aggregation, etc, depending on the specificity of the selected separation techniques.

This presentation will give application examples from various hyphenations and discuss how the on-line setup can be optimized with respect to easy-to-use and fully automated transfer from the first to the second dimension. Options for data presentation using different plot and evaluation types and access to the final results will also be shown.

Shematic of 2-D system
Complete polymer compositional information of polyolefins is critically valuable in understanding polymer structure-processing-property relationship, thus helping for tailor-designing polymers with desired end-use properties. In this presentation, we will describe an integrated on-line two-dimensional (2-D) technique recently developed in our Lab that can rapidly determine bivariate composition distributions of polyethylenes. Combining analytical TREF (aTREF) and high-throughput SEC (hSEC) via a novel system design, this 2-D aTREF-hSEC system is so powerful that it not only determines the molecular weight distribution as a function of elution temperature (or chemical composition) but also simultaneously determines the chemical composition distribution as a function of molecular weight. Furthermore, this technique is very fast such that a complete polymer compositional determination using this on-line 2-D technique can be done within 24 h while to acquire the similar information via conventional cross-fractionation methods would take weeks or months to finish. Because the aTREF unit and the hSEC unit are controlled relatively independently thanks to the novel system design for this on-line 2-D system, a change of one unit’s experimental conditions does not affect the other’s performance, enabling a large operation window and resulting in a robust and versatile system. What’s more, very high resolution (1 °C) in the TREF dimension has been achieved; even higher resolution, if desired, can also be achieved simply by changing the experimental conditions of the 2-D system. Finally, this 2-D aTREF-hSEC system in principle can be applied equally well to the characterization of other semi-crystalline polymers and amorphous polymers whose solubility is a function of the temperature. Exemplified 3-D chromatograms of some commercial polyethylene resins measured via this novel 2-D aTREF-hSEC system will be discussed in the presentation.
Polyolefin is the most common and chemically simple man-made polymer. One of the key parameters controlling polyolefin microstructure is short chain branching and distribution. Over the last 30 years, several analytical techniques have been developed to analyze the comonomer distribution of polyolefins. The conventional techniques include temperature rising elution fractionation (TREF),[i] crystallization analysis fractionation (CRYSTAF),[ii] and crystallization elution fractionation (CEF).[iii] All of these techniques are based on crystallinity which primarily is a function of the comonomer composition and its distribution. The key disadvantages for crystallization-based techniques are a narrow comonomer range (up to approximately 8 mol%) and co-crystallization. Co-crystallization can pose a challenge for complex multiple-component systems, even with increased analysis time to enhance resolution. Very recently, high temperature liquid chromatography of polyolefins (both at solvent gradient[v] and thermal gradient[vi][vii]) has been developed. These new techniques are able to separate a larger range of comonomer content and eliminate co-crystallization. This paper is focused on the recent advancements, understanding of the separation mechanism, and the application of various techniques to characterize complex polyolefin microstructures.

High temperature gel permeation chromatography (GPC) coupled to refractive index (RI) detection is traditionally used to extract quantitative information such as molar mass averages and distributions of polymers using peak position calibration involving polystyrene standards of known molar mass and chemistry. The repeatability and reproducibility of the molar mass averages obtained by GPC/RI are directly dependent on the baseline stability of the RI detector. Here, we have studied the repeatability, reproducibility, and baseline stability of a dual flow RI detector in the EcoSEC® High Temperature GPC System for the determination of molar mass averages via peak position calibration at temperatures up to 220 °C. The dual flow RI detector design is shown to compensate for any changes in the refractive index of the solvent over time by continuously flowing pure solvent through the reference side of the flow cell, thus significantly increasing baseline stability of the RI detector and the repeatability and reproducibility of the molar mass averages. Additionally, we will demonstrate how single detector high temperature GPC can be used for the characterization of polyolefins, polyethylenes of varying density, and polyphenylene sulfide (PPS) compounds. Finally we will show the coupling of a dual flow refractive index detector to a multi-angle light scattering detector for the determination of absolute molar mass and polymeric size of synthetic polymers.

Figure: GPC elution profile of new and used PPS samples as monitored by RI
Molecularly imprinted polymers (MIPs) are useful in many fields due to their molecular recognition. These uses include separations, sensors, assays, and catalysis. The imprinting is accomplished by polymerizing a monomer with a template molecule. The template can be removed leaving behind a specific binding cavity for that same template. A large focus has been on the crosslinker N,α-bismethacryloyl alanine (NALA) for its chiral selectivity as an OMNiMIP (one monomer molecularly imprinted polymer). NALA was imprinted with L and/or D-Boc Tyrosine to test its binding capabilities with these enantiomers. All of the polymers are tested by high performance liquid chromatography (HPLC) and/or batch rebinding. Batch rebinding and chromatographic techniques allow for the analysis of both thermodynamic and kinetic binding measurements respectively. Different variations of imprints along with different size ranges of the imprinted polymers were evaluated. The information gathered from this MIP was useful to understand NALA’s diastereomeric or enantiomeric effects upon separating enantiomers.
POLY 152: No Abstract
The control over molecular structure enabled by new synthetic techniques has translated to continually improving control over the assembly of molecules and macromolecules, with corresponding improvements in properties of the resulting functional materials. We have designed and synthesized several classes of block and star-block copolymers with stimulus-responsive components and metal-binding sites. These polymers form assemblies with properties that are dependent upon specific conditions. For example, we have investigated a range of synthetic systems that are designed to assemble in water into smaller micellar aggregates at low temperatures and larger vesicles at higher temperatures. A number of factors, including block size and extent of interblock interactions, appear to be important in controlling transformation rate. The design of these and other systems, including metal-functionalized polymers and conjugated polymers for photovoltaic applications, and our efforts to better understand the behavior of the resulting materials will be discussed.
POLY 154: Metal oxide nanoparticle hybrids: New photoresists with extraordinary sensitivity

Jing Jiang, Ben Zhang, Li Li, Emmanuel P. Giannelis, Christopher K. Ober, cko3@cornell.edu. Materials Science & Engineering, Cornell Univ, Ithaca, New York, United States

Lithography, the workhorse technology enabling microelectronics manufacture, has reached astonishing success in producing nanoscale features. Despite this, even higher resolution is needed if plans for next generation electronics are to be achieved. This presentation summarizes approaches to the design of new photoresists that abandon the traditional polymer based strategy and explore the use of nanoparticle imaging materials with dimensions on the order of 5 nm and less. In a recent development, metal oxide nanoparticles based on hafnia or zirconia with ligands of organic acids, are shown to be extremely sensitive to EUV radiation (less than 10 mJ/cm²) and produce high-resolution patterns. It is postulated that these photoresists which incorporate photoactive compounds function via a ligand exchange mechanism that gives the materials their very high sensitivity.
Polymer-grafted nanoparticles interconnected into a network
We are interested in exploiting the readily controlled reversibility of many covalent bonds to access robust materials with dynamic behavior. These dynamic-covalent materials combine the properties of structural integrity with responsiveness and adaptability. A diverse set of reversible covalent bonds has been considered, and while each of these bonds is sufficiently stable to be used for constructing or functionalizing polymers, they can also be readily cleaved by heating, adding water (i.e., hydrolysis), or adding a catalyst or reducing agent that shifts the equilibrium from products to reactants. In addition to discussing new adaptive materials composed of reversible linkages (e.g., boronic esters, oximes, hydrazones), this presentation will also highlight our effort to utilize reversible bonds to “reverse engineer” complex macromolecules. For example, a thermally-reversible inimer was used to confirm the controlled growth of individual branches during self-condensing vinyl atom transfer radical polymerization (ATRP). The resulting hyperbranched polymers contained thermally-reversible branch points that were cleaved quantitatively on heating to yield linear polymers with molecular weights that were similar to the theoretical values that would be expected based on controlled chain growth of individual branches during self-condensing vinyl polymerization (SCVP). In this way, the reversibility of many covalent linkages is exploited to not only prepare new materials but also to provide fundamental insight into basic polymerization mechanisms.
POLY 157: Importance of the intricate linkage of the needs of particular biomedical applications to the design characteristics of functionally-sophisticated nanoscopic macromolecules to achieve efficacy

Karen L. Wooley, wooley@chem.tamu.edu. 3255 TAMU, Texas AM University, College Station, Texas, United States

This presentation will highlight examples that demonstrate the need to align the composition, structure, and properties of polymeric-based nanomaterials to achieve efficacy as biomedical devices. Beyond the standard characteristics of surface chemistry, size, shape, etc., the need to correlate the rates of polymer degradation and drug release profiles to the timeframe of disease progression will be shown to be important in disease treatment efficacy and biological clearance of the devices.

Labeled therapeutic polymer nanoparticles designed for specific biological applications.
ATRP (atom transfer radical polymerization) has been successfully used to synthesize well defined organic-inorganic hybrids and also various bioconjugate materials. Some example of such new polymeric systems and their applications will be presented.
Anion-exchange membrane fuel cells (AMFCs) are of increasingly popular interest as they enable the use of non-Pt fuel cell catalysts, the primary cost limitation of proton exchange membrane fuel cells. Benzyltrimethyl ammonium (BTMA) is the standard cation that has historically been used as hydroxide conductor in anion exchange membranes. Several past studies have focused on the effect of different aromatic ammonium cations on stability in caustic conditions, but few have studied the effects of substituents on the aromatic ring as it applies to caustic stabilities. Herein we study the effects of substitutions on the aromatic ring; namely the effects of methoxy and nitro substituents, on the stability of the cation in a hydroxide solution at elevated temperatures. Our unique method to study cation stability in caustic conditions at elevated temperatures utilizes Teflon Parr reactors suitable for use under various temperatures and cation concentrations. NMR analysis was used to determine remaining cation concentrations at specific time points with GCMS analysis verifying product distribution. We then compare the experimental results with calculated modeling stabilities.

The main pathway of hydroxide based BTMA decomposition is SN2 debenzylation resulting in benzyl alcohol and trimethyl amine. Methoxy and Nitro substituted BTMA degradations also proceed via SN2 reaction resulting in similar products. Our studies show that the electron donating methoxy groups slightly increase stability (compared to that of BTMA), while the electron withdrawing nitro groups greatly decrease stability in base. These results give insight into possible linking strategies to be employed when tethering a BTMA like ammonium cation to a polymeric backbone; thus synthesizing an anion exchange membrane.
Recently, a new family of low-temperature FCs has been proposed, mounting OH−-conducting polymer electrolyte membranes. These systems are known as anion-exchange membrane fuel cells (AEMFCs), and show great promise to address successfully crucial issues affecting conventional low-temperature FCs including proton-conducting electrolytes. In particular, the anion-exchange membranes (AEMs) of AEMFCs generate a strongly alkaline environment at the electrodes. Consequently, the efficient operation of AEMFCs does not require electrocatalysts including platinum-group metals (PGMs), which have a very low abundance in Earth’s crust and are prone to supply bottlenecks. Furthermore, in AEMFCs the OH− charge carriers migrate from the cathode to the anode, thus inhibiting fuel crossover. The implementation of efficient AEMFCs requires the development of AEMs: (a) capable of a facile and selective transport of OH− anions; (b) characterized by good mechanical properties; and (c) showing an acceptable chemical and electrochemical stability. To achieve these objectives it is necessary to obtain a detailed understanding of the complex interplay between the structure and the relaxations of AEMs. The latter membranes are extensively studied by broadband electrical spectroscopy (BES) and thermomechanical methodologies including high-resolution thermogravimetry (HR-TG), modulated differential scanning calorimetry (MDSC) and dynamic mechanical analysis (DMA). The unique synergy of these advanced characterization techniques yields an exhaustive understanding of the various relaxation phenomena taking place in the AEMs. The relaxations play a major role in the mechanism of charge migration, which is elucidated together with its interplay with the chemical features and the hydration degree of the AEMs. The resulting information provides fundamental insights, allowing to improve the synthesis of the materials and to optimize the fabrication process of the AEMs.

![Figure 1](image-url). Three-dimensional $\varepsilon'$, $\varepsilon''$ and tan $\delta$ surfaces of a typical AEM as determined by BES.
New membrane materials are necessary for the development of alkaline fuel cells. Multiblock copolymers with one block that can provide mechanical properties and another block that is highly functionalized with cation functional groups has the potential to provide a design that yields the desired properties necessary for application. A multiblock copolymer composed of the polysulfone of bisphenol A (PSF) and the polyformal of tetramethylbisphenol A (PF) was investigated. The multiblock copolymer was synthesized via interfacial polymerization of hydroxyl-terminated polysulfone, tetramethylbisphenol A, and an excess of dibromomethane. Functionalization was carried out in two steps: bromination of the tetramethylbisphenol A units in the PF segments with N-bromosuccinimide in the presence of Zr(IV)Cl₄, followed by amination with trimethylamine. A high degree of functionality of up to 3.9 bromomethyl groups per PF repeat unit was obtained and is expected to enhance the ionic conductivity of the membranes as a result of the formation of ionic clusters in the ion conducting phase. The resulting benzytrimethyl ammonium functionalized materials remained soluble in DMSO and were readily drop cast into films. The polymers had IECs up to 1.92 meq g⁻¹, with hydroxide conductivity at room temperature water determined to be 38 mS cm⁻¹. The phase morphology was studied with tapping mode atomic force microscopy and the materials exhibited a two-phase morphology with a bicontinuous morphology detected in films containing 31 mol% of the polyformal.
Perfluoro-sulfonic acid (PFSA) polymers are used as the electrolyte in most solid-state energy-conversion and storage devices including fuel cells, flow batteries, and solar-fuel generators. Of great importance is their role in electrodes or catalyst layers where there is a need for ion conduction and mechanical stability. Recently, we have shown that the properties of Nafion ionomer in catalyst layers is thought to be different than in bulk Nafion, causing high transport resistances. In addition, we have shown how confinement and substrate interactions can alter the morphology and thus transport properties of the ionomer when it exits as a thin-film, which is the case in catalyst layers. In this talk, we will revisit these issues by examining morphology of thin-films of Nafion and other lower equivalent-weight PFSA ionomers, on metallic substrates, mainly through GISAXS as shown in the Figure, where the GISAXS profiles suggest anisotropy and a possible alignment of domains with Nafion on a gold substrate. Also, the transport properties of thin-films will be examined with an aim of relating these observations with fuel-cell performance data and catalyst-layer-ionomer water-uptake data. In addition, we will also examine the impact of hygrothermal ageing on the structure and swelling of the thin-films to initially probe lifetime concerns. Such studies as mentioned above show that there is alignment and ordering of the domains after ageing and as a function of thickness, especially on a platinum substrate.
POLY 163: Diffusion NMR as a tool for understanding ion and solvent transport in anion exchange membranes

Himanshu Sarode¹, hsarode@mymail.mines.edu, Yuan Yang², Andrew M. Herring¹.
(¹) Chemical and Biological Engineering, Colorado School of Mines, Golden, Colorado, United States (²) Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado, United States

Solid state NMR has been used as a tool for understanding many chemical and biological systems in science. Here we report the use of Diffusion NMR as a way to characterize transport properties of anion exchange membranes for applications in low temperature fuel cells.

We have studied the transport properties in a block copolymer membrane of Polyethylene and Polyvinyl benzyl trimethyl ammonium Bromide with a moderate IEC of 1.8 meq/gm using diffusion NMR technique. The membrane has a moderate water uptake of 13 to 15% and Bromide form conductivity of 14 mS/cm under saturated humidity conditions at 60°C. We studied the ion transport of fluoride and bicarbonate ions in the membrane to probe effects of ion- polymer interactions on their self diffusion coefficients. We also correlate the self diffusion coefficients with inplane conductivity of the membrane using the Nernst-Einstein Equation. We also studied the transport of water and methanol in this membrane. This solvents study gives us idea about potential fuel crossover in a working fuel cell. We found lower methanol transport in this membrane, making them as one of the possible candidates for barrier layers in protective clothing applications.

We also found that water has a highly restricted self diffusion telling us that the path of water transport is highly tortuous in the membrane. Water self diffusion coefficient was found to be 0.1 x 10^-5 cm^2/sec at 30°C.

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Ionic Conductivity of PE-b-PVBTMA[F⁻] membrane under 95% relative humidity condition
Anion exchange membranes (AEM) serve as the basis for alkaline membrane fuel cells by allowing facile conduction of hydroxide between electrodes. The major advantage of this type of fuel cell is the enablement of using cheaper, non-precious catalysts, as reaction kinetics is greatly improved under basic conditions. In order to allow OH⁻ to transport across the AEM, organic cations are tethered to the polymer backbone. These cations are found to be susceptible to the hydroxide attack, and will degrade over time. This greatly limits the lifetime of the fuel cell. In the search for high stability cations, a detailed understanding of the degradation pathways and reaction barriers for hydroxide attacking reaction is required. In this research, we performed density functional theory calculations to investigate the hydroxide degradation pathways of different types of cations. For cations with charged \( sp^3 \) hybridization atoms, the major degradation mechanism is the Hofmann elimination and SN2 reaction. For cations with charged \( sp^2 \) atoms, nucleophilic addition-elimination becomes the alternative pathway. Based on our calculations, the pathway with the lowest degradation barrier, \( i.e., \) the dominant degradation pathway for the cation, was identified. Based on the comparison of our computational results with experimental measurements, we then were able to use computational method to search for promising cations with higher degradation barrier. Some of the cations identified were predicted to have significantly increased degradation energy barriers, suggesting that they could possess enhanced durability compared to traditional cations and potentially enable new applications.
Porous polymers have been widely studied as proton exchange membranes and as polymeric separators for lithium ion batteries. Porosity reduces the diffusion barriers to both proton transport as well as lithium ion transport and is, therefore, a very useful structural attribute that defines the membrane functions in these applications. Whereas, porosity has been widely examined in polymeric battery separators, this aspect has received less attention in case of proton exchange membranes. Porous olefinic copolymers are in widespread use as battery separators in lithium ion batteries.

Heterocyclic polymers, such as, poly(benzimidazole)s and poly(benzoxazole)s are useful high temperature resistant polymers which have been used as proton exchange membranes, especially at high temperatures. Recently, thermal rearrangement of ortho-hydroxy imides has been extensively explored as a means to prepare poly(benzimidazole)s and poly(benzoxazole)s with intrinsic microporosity. However, there is considerable ambiguity in the literature on the true structure of such polymers. Therefore, it is difficult to understand the relationship between structure and function.

We have examined the thermal rearrangement of several small molecular weight model compounds containing the ortho-hydroximide functionality and have defined optimum conditions for the reaction as well as established the structures unequivocally. Using this knowledge the chemistry has been extended to polymeric structures. The nature of porosity generated during thermal rearrangement has been characterized. Membranes derived from such polymers have been examined for, both, proton exchange properties and as well as lithium ion transport. This study has provided new insights into the relationship between polymer structures and their performance in these applications.
This lecture will discuss recent results on the preparation and study of mesoporous carbon / zirconia / fluoroionomer nanocomposite materials as supports for platinum oxygen reduction reaction (ORR) electrocatalysts, for possible use in polyelectrolyte membrane fuel cell (PEMFC) devices. Carbon materials having high specific surface area and high fractional pore volume were prepared from carbonized silica-templated resorcinol-formaldehyde aerogels in a manner that allowed for inclusion of embedded zirconia nanoparticles in the carbon skeleton. Fluoropolymer ionomer electrolytes were grafted onto the exposed zirconia particles via terminal phosphonate groups on the polymers. Platinum particles were also deposited on the support surface and the resulting materials were studied as ORR catalysts using RDE voltammetry in acid solution. Methods under development for measuring the ionic and electronic contributions to electrical conductivity in the catalysts thin film layers will be discussed, as will the prospects for use of these materials in PEMFC devices.
POLY 167: Hydrolytically stable bio-adaptable thiol-ene network

Daniel A. Zamorano, Daz092020@utdallas.edu, Radu Reit, Dustin Simon, Benjamin R. Lund, Taylor Ware, Walter Voit. University of Texas at Dallas, Lewisville, Texas, United States

Cortical brain probes, used to study the brain and treat disease, often cause damage to the brain during and post implantation. This damage destroys brain tissue and also impedes the brain probe’s response through scarring caused by the stiffness mismatch between the probe and the biological material. One approach to negate these effects has been to use polymers that conform to the ambient environment in the brain lowering their modulus post implantation, minimizing scaring and immune response. Thiol-ene networks, such as Shape Memory Polymer 6 (SMP6) are formed through a “click” reaction that exhibits low cure stress and are compatible with lithographic processing. While this system, SMP 6, conformed well to the brain’s modulus in vivo, it also absorbed a relatively high amount of water (3 %), enabling degradation of the material, through ester bond hydrolysis, over time. With this in mind, new monomers were sought that could have a low rubbery modulus while also being hydrolytically stable. A new monomer, TriCycloDoDecaneThiol (TCDDT), was designed with a very rigid, tricyclic, core while also being completely aliphatic, reducing hydrolytic instability. TCDDT has been successfully synthesized meeting these requirements, producing polymers with a relatively high glass transition, compared to traditional dithiols, and a low rubbery modulus of around 1 KPa. The results of a hydrolytic stability study (1.0 M NaOH at 37°C) showed that these probes handle these extreme conditions much better than previous generations of SMPs, and will survive in vivo indefinitely. In conclusion, this new monomer could be the first generation in flexible electronics that can be used for a wide range of applications that require “high” glass transition temperatures and hydrolytic stability.

Hydrolytic stability test at different timepoints
Polymer-conjugated enzymes could potentially serve as therapeutic agents due to their increased size and accumulation in tumor tissue via the enhanced permeation and retention (EPR) effect. Previous work with protein-p(NIPAM) conjugates have suggested that conjugation improves aggregate stability upon undergoing lower critical solution temperature (LCST) transition. In this work, reversible addition-fragmentation chain transfer polymerization (RAFT) of N-isopropylacrylamide (NIPAM) and N,N-dimethylacrylamide (DMA) using carboxylic acid chain transfer agents (CTAs) was shown to be well-controlled and afforded functionalized, doubly hydrophilic copolymers of p(NIPAM) and p(DMA) of various lengths. Copolymer composition, size, and LCST behavior were analyzed by nuclear magnetic resonance spectroscopy, gel permeation chromatography, and dynamic light scattering. Dynamic light scattering experiments revealed a dependence of aggregate size on heating rate, sample concentration, and copolymer composition. Copolymerization of p(NIPAM) with p(DMA) altered LCSTs. Copolymers were activated for conjugation with N-hydroxysuccinimide and bioconjugation to a model enzyme, trypsin, was attempted.
End-functionalized starch macromolecular reagents were grafted to urethane-linked polyesters via copper-catalyzed azide alkyne cycloaddition chemistry to provide amphiphilic hybrid polymers. The starch concentration in the final graft copolymers was varied from 28-79 weight percent and the impact of starch concentration on protein repellency was studied. Quartz crystal microbalance with dissipation (QCM-D) was used to probe the interaction of these polysaccharide-containing copolymers with several proteins in a thin film mode. A general trend correlating higher starch concentrations in the graft copolymer structure with more efficient protein repellency behavior was observed. Details of both the synthesis and the QCM-D study will be presented.
Cellulose is considered the most abundant macromolecules on the planet, and it is found as the structural component of trees and plants in a natural composite. It is well established that controlled acid hydrolysis results in colloidal solutions of cellulose nanocrystals (CNCs). When compared to other traditional nano-fillers such as metallic nanoparticles or carbon nanotubes, CNCs have several distinct advantages such as they are non-toxic, potentially low cost, biodegradable and are decorated with reactive hydroxy groups.

A green-one step methodology encompassing both acid hydrolysis and modification has recently been reported. In this paper we describe the use of different bio-based acids such as citric, malonic, malic, levulinic and acrylic acids in the presence of HCl to simultaneously break down ramie cellulose to CNC’s decorated with functionalities such as carboxylic acid, acryl and keto moieties. The modified CNs were characterized by FTIR, NMR, contact angle, SEM, and XRD.
Cancerous tumor detection through 'smart' imaging agents presents a new method to detect tumors that eliminates the need for invasive methods. This diagnostic technique takes advantage of tumor specific properties, such as pH. The acidic extracellular pH (pHe) of tumors is an important indicator of cancer morbidity and mortality. As such, the ability to measure tumor pHe in vivo using non-invasive and accurate techniques is of great interest to researchers and clinicians. A critical part of this research is developing pH-responsive contrast agents that display transitions at relevant biological pHs. We have prepared a series of pH-responsive block copolymers comprised of a biocompatible block and a pH-responsive block using reversible addition fragment chain transfer (RAFT) polymerization. The pH-responsive blocks were synthesized with different ratios of the two different pH-responsive monomers to control the final pH transition of the block copolymers. Understanding the relationship between the ratio of the monomers and the pH enables for the creation of polymers with a specific, desired pH for use as 'smart' imaging agents.
POLY 172: Antioxidant copolymers in biological applications

Dylan M. Barber, dmb1@williams.edu, Todd A. Brenner, Luxi Qiao, Sarah L. Goh. Williams College, Williamstown, Massachusetts, United States

Reactive oxygen species (ROS) cause irreversible damage to biological macromolecules and act as signaling molecules in pro-inflammatory and proliferative pathways, leading to increasing interest in small molecule antioxidants as models for putative therapeutics. This work builds on existing studies of the antioxidant gallic acid (GA) in the synthesis of antioxidant-conjugated polymers. Using radical polymerization of dimethylacrylamide (DMA) and glycine-functionalized hydroxyethyl methacrylate (Gly-HEMA) we present a post-polymerization synthetic pathway for the preparation of water-soluble p[(GA-Gly-HEMA)\text{-}co\text{-}DMA] (Scheme 1). This work is also extended to block copolymers comprised of hydrophobic p(styrene)- or p(methyl methacrylate)-b-p[(GA-Gly-HEMA)-co-DMA]. Characterization of p[(GA-Gly-HEMA)-co-DMA] consisted of both \textit{in vitro} and \textit{in vivo} techniques. p[(GA-Gly-HEMA)-co-DMA] exhibits radical scavenging activity both \textit{in vitro} and \textit{in vivo}. Using the ABTS radical-scavenging and ferric reducing ability of plasma (FRAP) assays, we determined that the p[(GA-Gly-HEMA)_{0.5}-co-DMA_{0.5}] conjugate, containing an antioxidant loading of 20.7 wt%, retained their antioxidant properties after coupling to the polymer. \textit{In vivo} studies in RAW264.7 murine macrophages revealed that the GA-conjugate is non-toxic at concentrations up to 30 \textmu M and that p[(Gly-HEMA)-co-DMA] polymers are taken up by macrophages in as little as 1 h. Finally, intracellular staining of the pro-inflammatory cytokine TNF-\alpha showed that cells dosed with p[(GA-Gly-HEMA)_{0.5}-co-DMA_{0.5}] are resistant to lipopolysaccharide stimulation.

\textbf{Scheme 1}: Preparation and primary amine deprotection of statistical random copolymer p[(Gly-HEMA)-co-DMA] and subsequent functionalization with gallic acid.
Conductive biomaterials have numerous biomedical applications including biosensors, electrodes for neural stimulation, and substrates for regenerative tissue cultures. Conductive polymers (CP) such as polypyrrole and polythiophene are biocompatible, but have poor mechanical properties for cell and tissue interfacing. Their extended conjugated pi-systems are inflexible, which leads to the bulk materials being stiff and brittle. In addition, very few methods are available to control the nanoscale topology of CP films due to their insolubility and poor processability. To improve CP versatility, we have developed a methodology to create interpenetrating network composites of CPs and silk fibroin. Silk fibroin is a well-studied biomaterial that can be tuned to match the mechanical properties and architecture of a range of biological tissues. Silk structures can be fabricated by electrospinning, casting around sacrificial porogens, and capillary force lithography, which allow fine control of the nanoscale topology and 3D architecture of the material. Here we present a novel methodology to incorporate CPs into silk films that contain patterned nanoscale grooves and demonstrate the creation of flexible, conductive biomaterials that show promise as cell-directing substrates.
Polydimethylsiloxane (PDMS) is a versatile polymer that has many applications, from medical devices and contact lenses, to food and shampoo additives. Despite this versatility, a scalable synthetic method for producing stable, micron-sized, spherical particles (microspheres) of cross-linked PDMS has not been available due to the low surface energy of PDMS and its tendency to aggregate, even during emulsification polymerization. We have demonstrated the use of ultrasonic spray pyrolysis to produce silicone microspheres <5 µm in diameter. In this study, we explore the synthesis and characterization of PDMS microspheres with internal void cavities. We have utilized both sacrificial templating and in-situ gas evolution as methods to produce microstructured PDMS particles. By nebulizing a precursor solution containing both PDMS and polystyrene (PS), we are able to synthesize core-shell microspheres with a non-cross-linked PS core and a cross-linked PDMS shell. The resulting spheres can be washed with acetone to dissolve the polystyrene, leaving hollow PDMS microspheres. Changing the PDMS:PS ratio in the precursor solution affects particle morphology, especially the resultant hollow core size. We have also utilized the chemistry employed in the formation of bulk “foamed” silicones to produce microspheres with internal cavities caused by in-situ hydrogen evolution. These materials have been characterized by SEM, TEM and FTIR.

PDMS core-shell microspheres produced via ultrasonic spray pyrolysis (USP). The precursor solution contained a 5:1 ratio of PDMS:polystyrene (PS). (a,b) SEM and TEM of PDMS-PS core-shell microspheres obtained using 35,000 MW PS. TEM shows light gray PS core surrounded by darker gray PDMS shell. (c,d) SEM and TEM of hollow PDMS microspheres obtained via sacrificial templating using 800 MW PS. Indented regions, caused by the collapse of the hollow elastomeric microsphere under vacuum, evident in both SEM and TEM.
The convergent syntheses of star block copolymers via polymer coupling reactions have inherent difficulties such as steric impediments. Along with the inherent error in the reacting polymers’ molecular weights, these impediments often result in long reaction times and the use of a coupling partner in excess. Due to this, a quick and direct method is needed to monitor and optimize polymer coupling reactions. Our research has focused on the synthesis of resorcinarene-core polylactide (PLA)/polyethylene glycol (PEG) star block copolymers, which have the potential to self-organize into micelles for use in drug-delivery applications. The method that has been investigated for preparing these new star block copolymers involves a convergent synthesis beginning with a macrocyclic core that then has PLA chains grown from it. In this synthesis, the end groups of star PLAs have been modified with alkyne functional groups and, subsequently, coupled to an azide-functionalized PEG via a Huisgen dipolar cycloaddition reaction. In the process of synthesizing the star block copolymers, No-D (no-deuterium) NMR spectroscopy has proven invaluable for optimizing the polymer coupling conditions. Through a series of No-D NMR studies, the correct ratio of reactants was determined in order to minimize residual PEG azide and to make the purification of the desired product easier. The ratio of copper catalyst was also optimized to minimize residual amounts in the product, while still allowing for completion of the reaction in a reasonable amount of time. In this presentation, the synthesis of four- and eight-armed resorcinarene-core PLA/PEG star block copolymers will be described. The general utility of No-D NMR spectroscopy in optimizing polymer coupling conditions will also be illustrated.
In this work two-stage polymeric systems of orthogonal crosslinking reactions were used to create polymer networks with distinct physical properties. The first stage occurs via a self-limiting step growth mechanism using the Thiol-Michael addition reaction. First stage networks are malleable and easily inserted for biomedical uses. The second stage of polymerization occurs via radical homopolymerization of excess acrylates in the network increasing crosslink density in the network, resulting in a more rigid material with higher storage modulus.

Additionally, shrinkage stress associated with each reaction pathway is important to determine its viability for use in biomedical devices. High shrinkage stress may result in cracking which compromises the effectiveness of the medical device. This study involved the development of a novel method for shrinkage stress measurement in two-stage polymer systems. Specific innovations included the use of a triphenyl phosphate and methanesulfonic acid (TPP/MsOH) initiating system to delay the polymerization, allowing application into a cantilever beam tensometer to measure shrinkage stress. In addition, the correlation between tethered acrylates in a polymer system and its overall effect on mechanical properties was determined. In this case, two-stage systems exhibited lower shrinkage stress in comparison to acrylate homopolymerization. Decreasing acrylate tethering in the network also lowered shrinkage stress in the material. Future applications of this research involve the development of polymer systems with reduced shrinkage stress and a reliable means of quantifying that reduction.
Organogels are an interesting class of soft materials where an organic fluid is immobilized by the addition of a suitable organogelator. A variety of organogelators, ranging from small molecules to polymers, have been researched and developed for novel applications ranging from drug delivery to consumer products such as deodorant and shampoo. In this study, the ability of trans-1,4-polyisoprene (TPI) to act as an organogelator is examined. TPI is the geometric isomer of cis-1,4-polyisoprene (CPI). While CPI is a viscoelastic liquid at room temperature, TPI is semi-crystalline with a melting temperature of ca. 60 °C. TPI's crystallinity provides high mechanical strength, cut abrasion and electrical insulation, and it is used as a processing additive, such as improving the green strength of synthetic polyisoprene. It was hypothesized that TPI would act as a good organogelator if it was able to crystallize in organic solution and form a three-dimensional percolating network. Gelation of TPI/organic solvent was tested by dissolving TPI (10 wt%) at elevated temperature and then cooling. Gelation was qualitatively confirmed by inversion, where a gelled solution did not flow over long time scales. TPI was observed to gel n-alkanes, anisole and butyl acetate. TPI failed to gel phthalates (insoluble) and aromatic solvents (soluble at RT), THF (soluble at RT) and ethyl acetate (insoluble). The gels were further characterized to determine the minimum gelation concentration, gel transition temperatures as a function of composition, and gel morphology. The gel transition temperature vs. concentration curve was consistent with the melting point depression of a solute in solution expected for gelation driven by the crystallization of TPI. Finally, efforts to dry the TPI gels to generate functional xerogels will be presented.
Several covalently crosslinked imidazolium and 1,2,4-triazolium-containing polyester networks were prepared by Michael addition polymerization to probe how ionic functionality affects thermal and mechanical properties. As part of this study, variations in acrylate:acetoacetate ratio as well as counteranion were investigated and the results will be discussed. An increase in acrylate concentration was found to increase the glass transition temperature $T_g$ (determined by Differential Scanning Calorimetry), the thermal stability (determined by Thermogravimetric Analysis) and storage modulus (determined by Dynamic Mechanical Analysis) of the networks, presumably due to an increase in crosslink density. Swelling studies were also conducted and supported this hypothesis. Use of larger, non-coordinating counteranions such as bis(trifluoromethylsulfonyl)imide [NTf$_2$] resulted in lower $T_g$ values, but improved thermal stabilities. A comparative analysis of the thermal and mechanical properties of imidazolium versus 1,2,4-triazolium systems will also be discussed. In general, the 1,2,4-triazolium networks were found to be less thermally stable than the analogous imidazolium systems.
Polyurethanes’ wide property set and tunable cure profile make them the material of choice for applications ranging from soft foams to strong elastomer castings and coatings. However, the high reactivity of isocyanates requires precautions to avoid reaction with water and potential worker exposure during application and curing. Here we discuss a novel polymer produced via the benign reaction of cyclic carbonates with amines which results in a polyurethane/polyhydroxyurethane (PU/PHU) hybrid material with increased adhesion to various substrates as compared to traditional PU controls. The PU/PHU hybrid materials were synthesized by reaction of a cyclic carbonate terminated prepolymer with triethylenetetramine without employing isocyanates in the final curing step. This cured elastomer contains traditional urethane linkages from the initial prepolymer cyclic carbonate capping reaction as well as hydroxyurethane linkages from the final chain extension reaction. The PU/PHU hybrid exhibits elastomeric properties with Young’s modulus of 37 MPa and strain at break of 350% as well as microphase separation made apparent by the presence of two glass transitions. The mechanical and thermal properties of the hybrid material are compared to two PU controls. Both PU controls exhibited multiphase morphologies but possessed mechanical properties inferior to those of the PU/PHU hybrid material. The most important comparison between the PU/PHU hybrid material and the PU controls regards the ability of these materials to adhere to various substrates. The PU/PHU hybrid material exhibits enhanced adhesion to polyimide, poly(vinyl chloride) (PVC), and aluminum substrates when compared to PU controls as well as literature values; the peel forces are also close to those observed in commercial based systems. The adhesive properties of the PU/PHU hybrid were determined using a 180° T-peel test resulting in peel forces of 7.8, 10.5, and 3.4 N/mm on polyimide, PVC, and aluminum, respectively.
Polyurea glycopolymers were synthesized from acetyl protected either mannose- or lactose-containing diamines with four different diisocyanates, namely toluene 2,4-diisocyanate (TDI), isophorone diisocyanate (IPDI), 4,4'-methylenebis(cyclohexyl isocyanate (HMDI) and hexamethylene diisocyanate (HDI), via step-growth polymerization. The obtained acetyl protected glycopolymers were further deprotected and sulfated to obtain sulfated glycopolymers. The influence of the diisocyanates comonomers in terms of the polymers anticoagulant properties was investigated by measuring the activated partial thromboplastin time of the sulfated glycopolymers. The results indicated that IPDI and HMDI-containing sulfated glycopolymers exhibited higher prolongation of the activated partial thromboplastin time than the corresponding TDI and HDI-containing glycopolymers.
POLY 181: Novel poly(borosiloxane)s and their properties

Puhup Puneet, rupakagain2008@gmail.com, Raman Vedaranaj, Noriyoshi Matsumi. (1) JAIST Schl of Matl Science, Ishikara, Japan (2) Dept of Materials Science, Japan Adv Institute of Science Technology, Nomi Ishikawa, Japan (3) Material Science, Japan Advanced Institute of Science and Technologies, Nomi, Ishikawa, Japan

Polysiloxane compounds are extensively studied for its flexibility and thermal stability. In spite of common availability of borosilicate glass, linear poly(borosiloxane) has not been reported to date. In this study, we have prepared poly(borosiloxane) via dehydrocoupling polymerization of bifunctional silanol and mesitylborane. Their structures were supported by NMR and IR spectra. After adding ionic liquid, the obtained non-flammable ion gels showed relatively high ionic conductivity.

The synthesis of poly(borosiloxane) was carried out by dehydrocoupling polymerization of bifunctional silanol and mesitylborane in the presence of rhodium or palladium catalyst (Scheme 1). Polymerization was successful under various reaction conditions (Table 1). $^{11}$B-NMR spectrum showing boron atom with one chemical environment indicated highly alternating unit sequence structure of 1. A model reaction was set to analyze the nature of arrangement in copolymers by replacing diphenylsilanediol with triphenylsilanol. The obtained high yields of 2 infers highly alternating nature of the polymerization (Scheme 2).

Gel permeation chromatographic (GPC) analysis showed the number average molecular weight reached higher than 10000 g/mole. Further characterizations and studies of these polymers are underway. From TGA measurements, these polymers shows more than 40% of ceramic yield at 500°C, demonstrating non-flammability of the polymers. The fluoride ions sensitivity test was also done by impedance measurements. These polymers could detect nM concentrations of fluoride ion. The impedance of the polymer film on GC electrode decreased with increase in the concentration of fluoride ion. The ionic conductivity was found to be in the range of $10^{-4}$-10$^{-3}$S/cm after mixing it with various ratios of ionic liquid and lithium salt.

Reference:
Due to their excellent biodegradability and biocompatibility, polysaccharides are ideal candidates for a variety of biomedical applications. However, the access of polysaccharides in pure form is limited. Herein, we report for the first time a reverse anomeric effect (RAE)-mediated polymerization to synthesize high molecular weight sugar poly(orthoesters). When RAE-enabled promoters, including 4-dimethylaminopyridine (DMAP), triphenyl phosphine (TPP) and imidazole were employed, sugar poly(orthoesters) with molecular weights up to 18.1 kDa were achieved. In comparison, when a RAE-unenabled catalyst, such as tetrabutylammonium bromide (TBABr) or tetrabutylammonium iodide (TBAI) was used, only a small molecular weight polymer in the range of 3-6 kDa was obtained. The sugar poly(orthoesters) were then subjected to construct nanoparticles by emulsion/evaporation procedure. With the orthoester linkages, the NPs were highly pH-responsive and demonstrated a quick decompose to release of the drug payloads at low pH values. The cell viability studies demonstrated that the drug-loaded NPs exhibit significantly higher killing effect at lower pH values.
The preparation of technologically important polyurethanes while avoiding the use of toxic isocyanates is an emerging field of study. One of the more promising routes involves the reaction between cyclic carbonates and amines to form polyhydroxyurethanes. Depending on the ring size of the cyclic carbonate, this synthetic approach is limited by slow reactivity and/or availability of diverse monomer structures. Here we report approaches to increases the rate of reaction between cyclic carbonates and amines using different classes of organocatalysts. Synthetic routes to new cyclic carbonate monomers and physical properties of their corresponding polymers are also detailed. In addition, we prepared polyhydroxyurethane structural equivalents to polyurethanes to determine how the presence of hydroxyl groups on the backbone impact polymer properties.
Aromatic π-electron conjugated polyelectrolytes (CPEs) are synthetic organic materials exhibiting intrinsic fluorescence and unique structural properties that have been used for various biological applications including sensing, imaging, and delivery of biologically active substances. Introduction of flexibility and biodegradability to the fluorescent conjugated backbone promises increased control of self-assembly behaviors with polyanions and modulation of sub-cellular localization patterns of these materials. We report a novel synthetic technique to control the flexibility in the backbone of poly-p-(phenyleneethynylene)s (PPEs) by employing a ternary monomer coupling approach with careful design and varied ratio of monomers under Sonogashira reaction conditions. While an increased amount of flexible linkers in the conjugated PPE backbone results in the formation of conjugated segments with shorter average conjugation length, retention of fluorescence properties comparable to those of a fully conjugated PPE backbone can be achieved in materials with less than 50% of flexible linker content. The resulting series of polymers allows for the systematic investigation of the effect of polymer backbone flexibility on aggregation, self-assembly and cellular uptake mechanisms of this class of materials.
The Baylis-Hillman reaction provides densely functionalized substrates which are very useful scaffolds in organic synthesis. However such useful starting materials are underutilized in polymer chemistry. We recently showed that such Baylis-Hillman adducts are versatile starting materials for both chain growth and step growth polymerizations. Under RAFT conditions, alkyl hydroxymethyl acrylates efficiently provide functionalized homopolymers or block copolymers. In addition, alkene functionalized diols from the Baylis-Hillman reaction undergo step growth polymerization to yield poly(ester urethane)s or polyesters. The alkene group which can be functionalized either pre- or post-polymerization using the thiol-ene reaction provides a further synthetic handle to modulate the polymer properties. Hence the availability of dual functional groups at every repeat unit enables tailoring the properties of such polymers pre- and post-polymerization. We are currently demonstrating the use of such densely functionalized polymers in engineering and biomedical applications and results in these directions will be presented.
Recently, iron(II) complexes bearing bis(imino)pyridine ligands have been shown to be active catalysts for the living ring opening polymerization of lactide to form poly(lactic acid). An interesting feature of this chemistry is that the catalysts can be reversibly deactivated and activated with the addition of chemical oxidants and reductants, respectively. Extension of the redox-control demonstrated in these reactions to copolymerization reactions is described so that a redox-switchable block copolymerization is achieved starting with both monomers in solution. Since epoxide polymerization reactions demonstrates complementary reactivity compared to lactide polymerization (i.e. active for iron(III) complexes but inactive for iron(II) complexes), copoly(ester-b-ether) are synthesized starting with a mixture of lactide and epoxide. Due to the exquisite chemoselectivity demonstrated by the catalyst, the composition and length of blocks are dictated by the oxidation state of the catalyst and the time when redox reagents are added to the reaction. Synthesis of block copolymers is discussed along with their potential application as new thermoplastic elastomers or amphiphilic copolymers useful in drug delivery.
In this paper, we report the materials design, synthesis and characterization of a class of new multicomponent polymeric membranes where some larger molecules can permeate faster than smaller ones, or so-called reverse-selective gas separation membranes. Reverse-selective gas separation membranes have attracted much attention owing to their advantages for certain commercial gas separation applications, for example CO$_2$ removal from H$_2$. These newly designed and synthesized copolymers consist of alternating PEO sequences and rigid iptycene-containing polyimide segments, wherein the bulky iptycene-containing imide sequences provide high gas permeability and mechanical strength via the unique chain “threading” and “interlocking” mechanism, while the CO$_2$-philic characteristic of PEO sequences provides high solubility selectivity towards CO$_2$. The copolymers are systematically varied in their chemical structure in terms of PEO sequence length (from 600 to 2,000 g/mol), PEO weight fraction (20% - 60% wt), and iptycene structure (triptycene vs. pentiptycene). FTIR and $^1$H NMR confirmed the desired macromolecular structure of the copolymers as well as the target PEO content. Physical properties such as glass transition temperature, mechanical properties, and thermal stability were shown to strongly depend on the chemical structure/composition of the multicomponent copolymers. Similarly gas transport properties were very sensitive to the detailed phase morphologies in these membranes. Relating the permselectivity with the copolymer composition suggested that there might be a competing effect between the reduced size-sieving diffusion due to minimization of free volume by chain “threading” and the preferential sorption of larger condensable CO$_2$ by increasing PEO content, which led to a “turnover” trend producing reverse-selective membranes.
Very narrow band gap donor-acceptor (DA) conjugated polymers demonstrate complex and unique electronic properties. Developing an understanding of the interplay between chemical and electronic structure in these systems will require control of the frontier orbital energetics (separation, position, and alignment), ground state configurations, interchain arrangements, solid-state properties, and many other molecular features with synthetic precision that has yet to be demonstrated. Cross-conjugated 4H-cyclopenta[2,1-b:3,4-b']dithiophene (CPDT) structural units, in combination with strong acceptors with progressively delocalized π-systems, afford modular DA copolymers with broad and long wavelength light absorption that spans technologically relevant wavelength (λ) ranges from 0.7 < λ < 3.2 μm (E_{gap} < 0.5 eV). These solution-processable materials possess some of the narrowest band gaps reported to date and illustrate how incorporation of peripheral cross-conjugated substituents within a π-conjugated system provides a much more complex, versatile, and highly valuable tool for the tuning of material properties. Such control has also resulted in unanticipated physical properties, such as intrinsic electrical conductivity. Quantum chemical calculations indicate that further band gap narrowing is achievable, affording polymers that can interact with a substantially larger portion of the electromagnetic spectrum, and indicated that unique spin, thermoelectric, and magnetic phenomena are present and/or accessible. Of primary significance is that these properties are highly dependent on the functionality, molecular configuration, and building blocks employed, thereby affording new paradigms for the rational generation of materials with novel physical properties.
POLY 189: Polymer separations utilizing 2D liquid chromatography: Inherent limitations and perspectives

Mark R. Schure, mark.schure@gmail.com. R&D, Kroungold Analytical, Inc., Blue Bell, Pennsylvania, United States

Polymer characterization often leads to chemical and physical separations provided by tools such as size-exclusion chromatography (SEC), reversed-phase liquid chromatography (RPLC), liquid chromatography at the critical condition (LCCC) and field-flow fractionation (FFF) among other techniques.

In many cases coupling columns and detectors, for example utilizing two-dimensional liquid chromatography (2DLC) with SEC and RPLC dimensions, increases the discriminating ability. Yet the difficulties often remain - many samples are highly complex and chemical and physical heterogeneity makes these samples extremely difficult to get exacting information for qualitative and quantitative analysis.

This talk will focus on examples of polymer analyses which are difficult and utilize 2DLC. Recent results which show the inherent limitations of this technique in conjunction with mass spectrometry detection will be given based on the statistical description of both 2DLC and mass spectrometry.

A two-dimensional separation
As approaches for polymer synthesis become increasingly sophisticated, polymers that possess more complex chain architecture and chemical composition than linear polymer become readily available. Separation and characterization of polymers that possess multiple distributions in addition to molecular weight distribution has been a challenge. A number of different approaches have been put forward (i.e. multi-detectors and multi-dimensional separations). Among these, separations of polymers other than size exclusion chromatography such as Interactive Chromatography and Liquid Chromatography at the Critical Condition (LCCC) have gained popularity. The experimental development of new separation methods calls for a better understanding of the separation principles behind these experiments. In the past number of years, we have used computational/theoretical approaches to investigate the principles behind LCCC. We have used Monte Carlo simulations and investigated the delicate nature of the critical condition point encountered in the LCCC. We have shown that the critical condition point could depend on the physical size of the pore. We have shown that star polymers do not necessarily co-elute with linear polymers near the critical condition of linear polymers. We will also illustrate how the invisible branches (the branches that is being put under the critical condition) could impact the retention behavior of the grafted copolymers. The talk will present an overview of our computational studies directed toward a better understanding of separation of complex polymers in liquid chromatography at the critical condition.

Lattice Monte Carlo Simulations to investigate the effect of invisible branches on the retention behavior of grafted copolymers. Panel (A): Backbone is in the SEC mode; Panel (B): Backbone is in the LAC mode.
POLY 191: Framework for exploring the effect of physical and chemical heterogeneities on polymer-surface interactions

Chad R. Snyder¹, chad.snyder@nist.gov, Charles M. Guttman¹, Edmund A. Di Marzio¹,². (1) Materials Science and Engineering Division, NIST, Gaithersburg, Maryland, United States (2) Bio-Poly-Phase, Rockville, Maryland, United States

We describe a theoretical framework to calculate the exact thermodynamic and statistical properties of a single polymer chain at or near a surface with monomers of any complexity confined to a lattice of arbitrary dimensions, with boundary conditions and lattice structures not easily dealt with via continuum methods. This theory allows one to study adsorption of polymers onto both surfaces and objects within the lattice of arbitrary shape and roughness, uneven surface energetics, and spatially-varying electrical or chemical gradients. Using this method, we will demonstrate the ability to examine surface adsorption with and without lateral chain confinement effects. With particularly strong relevance to chromatography, we examine the shift in critical condition as a result of surface energy inhomogeneities. Finally, we will show a simple method to create more complex rigid (co)monomers (such as phenyl-like rings), with flexible or semi-flexible linkages, within this matrix formalism.

*Figure: Schematic illustrating some possible surface conformations of a poly(p-phenylene)-like polymer built in a lattice framework. Blue and red blocks indicate surface sites that are attractive and repulsive, respectively, and the green and purple spheres of the polymer show how an edge-on or face-on adsorption preference could be incorporated into the polymer.*
The basis of polymer adsorption chromatography is the relative surface interaction energy. However in practice the quantity itself remains unknown, and appropriate chromatographic conditions are frequently found by extensive trial and error or gradient methods. Foreknowledge of this quantity could lead to more efficient development of polymer separation protocols and more precise quantitation of the distributions measured in chromatographic separations. We have developed a concept to measure surface interaction relevant to macromolecular separations via chromatography using a model, low-grafting-density, end-tethered polymer system. Neutron reflectivity data was collected, and compared to physical models of end-tethered polymer behavior, including analytical and numerical self-consistent field theory. The data were fit to the models with the Refl1D package using the DREAM algorithm, which provides Bayesian credible intervals and correlation information on model parameters, resulting in the production of a rigorous estimate of the surface interaction parameter estimates. Ongoing work on this project hopes to demonstrate the utility of this estimate as a generalizable measurement of the surface interaction energy of specific polymer systems.
The macroscopic properties of high-performance bulk polymer composite materials derive from the properties of the microscopic building block component particles, the polymer matrix in which they are placed, and the state of particle dispersion. The rational design of new materials then requires the characterization of the polymer matrix and the individual particles, as well as an understanding of how particle properties change as a function of spatial dispersion, particle size polydispersity, and shape fluctuations. This is a challenging scientific and technical problem, but in principle we can use computer simulations to systematically explore the multi-dimensional parameter space required for designing new composite materials and for characterizing the normally complex-shaped component particles. In the past, the calculation of the composite properties has normally been restricted to rather idealized descriptions of particle shape for mathematical expediency (e.g., ellipsoids or spheres) since the real treatment involves the numerical solution of complicated differential equations, but this approach has limitations in terms of adequacy of physical description. To overcome this issue, we combine molecular dynamic simulations, numerical path-integrations (ZENO) and finite element calculations (COMSOL). As a specific illustration of this computational path, we calculate the electric and magnetic polarizability tensor of carbon nanotubes and graphene sheets having complex morphologies. Knowing these basic particle properties, one then can estimate electromagnetic properties of nanocomposites made with these particles, i.e., conductivity.
Hydrophilic macroions represent a transition stage between small ions (following Deby-Huckel theory) and large colloids (DLVO theory). We found that such macroions show completely different solution behavior than either of previously known systems. Study on their behavior is of a great interest to understand the missing region in between. Dendrimers like PAMAM and PPI with the ability of being charged at different levels in solution can be a good candidate to fit this model.

PPI dendrimer’s surface amines can be protonated and become charged, which will induce electrostatic repulsion between dendrimers and makes them stay individual in solution. Initiation of assembly process needs the overcoming of this electrostatic repulsion. Presence of oppositely charged counterions and reduction of solvent polarity were both necessary to induce enough screening effect to overcome the repulsive force.

We suggested that the electrostatic interaction between PPI dendrimer and oppositely charged counter-anions can be considered as a major driving force yielding dendrimer molecules to form hollow spherical nanoparticles with known structure and controllable size. Nanoparticles’ sizes -measured using light scattering techniques- can be controlled based on dielectric constant and pH of the solution. It was shown that decreasing solution polarity will increase the size of nanoparticles. We also investigated the effect of changing pH on formed spheres. It was observed that changing pH at the same time will alter the dendrimer surface charge and ionic strength of solution which each have opposite effect on the size of spheres. At different pH and solution polarity either of above factors can be dominant and affect more on the nanoparticle’s sizes. This resulted in creation of a transition between “low polarity, high pH” and “higher polarity and lower pH” conditions in solutions.
In fouling experiments, it is common to conduct studies in either of two modes: (1) fixing the transmembrane pressure (TMP) difference across the membrane and allowing permeate flux to vary in time or (2) fixing the permeate flux and allowing the TMP to vary in time. Many literature studies report data from constant TMP experiments, and industrial filtration systems often operate at constant flux. To explore the similarities and differences between operation at constant flux and constant TMP, a comparison is presented of constant-flux and constant-TMP operation of flat-sheet polysulfone ultrafiltration membranes during oil/water emulsion filtration. For a given set of experimental conditions, the threshold/critical flux was determined using a flux-stepping method in constant flux crossflow filtration. The membrane performance during fouling tests in both constant flux and constant TMP experiments was investigated at fluxes above and below the critical flux. Membrane resistance evolution during the experiments was compared for constant flux and constant TMP operation. At fluxes below the critical/threshold flux, the membrane resistance measured in constant flux and constant TMP fouling experiments was similar. At fluxes above the critical/threshold flux, the membrane resistances differed for the two operating modes, in some cases by more than an order of magnitude.

Surface modification has been widely studied as a mean to reduce membrane fouling. Membrane surface coating using dopamine solution, which undergoes polymerization under alkaline, aerobic conditions to form polydopamine, has previously been shown to significantly improve membrane fouling resistance to oil/water emulsions. However, the studies using crossflow filtration test were mostly conducted under constant TMP operational mode. Here, we present a comparison of constant flux and constant TMP fouling results on membranes that were surface treated using polydopamine and those that were not. These studies are also extended to other advanced concepts, pioneered in the Emrick laboratories, for surface modification of membranes to improve fouling resistance.
Although chemical synthesis has evolved to a relatively advanced state, the ability to prepare well-defined self-assembled materials of controlled shape, size, and structural hierarchy is still in its relative infancy and currently remains the virtually exclusive domain of biology. In this talk the development of a promising new route to such materials, termed “crystallization-driven living self-assembly” (CDSA), will be described. This approach was discovered as a result of an investigation of the solution self-assembly behavior of block copolymers with crystallizable polyferrocenylsilane metallolblocks. It offers an interesting and potentially powerful new route to well-defined micelles and hierarchical materials with controlled dimensions and a variety of potential applications. Moreover CDSA appears to be extendable to a wide range of different crystalline core-forming blocks, including bio-relevant and p-conjugated materials.
POLY 197: Tuning dispersion of nanoparticles in polymer matrices

Ryan C. Hayward, rhayward@mail.pse.umass.edu. University of Massachusetts, Amherst, Massachusetts, United States

We seek to use well-defined interactions between polymers and nanoparticles to precisely control the self-assembled morphologies, and resulting properties, of polymer nanocomposites. In one example, we take advantage of hydrogen bonding interactions between ligand and matrix polymer chains to tailor dispersion of grafted nanoparticles in polymer matrices. Favorable interactions yield dispersion even when entropic considerations would lead to aggregation of athermal systems, and the temperature-sensitivity of hydrogen bonds provides opportunities for the design of materials with tailored and switchable dispersion states. In a second example, we study how the introduction of randomly grafted polymers influences the dispersion state of nanoparticles in polymer matrices. A newly designed ligand that allows for efficient photo-chemical coupling with benzophenone grafting agents incorporated into random copolymer chains provides a new approach to fine-tune the level of particle aggregation, without the need to synthesize polymer grafts with well-defined molecular weight distributions or chain-end functionalities.
POLY 198: Getting dopey with polymers and nanoparticles

Jeffrey Pyun, jpyun@email.arizona.edu. University of Arizona, Tucson, Arizona, United States

We will review advances in field of polymer-nanoparticle composite materials along with our own advances in using functional inorganic nanoparticles as monomers to form colloidal polymers. At the heart of these efforts is the development of new synthetic methods to prepare functional polymer ligands to enable the synthesis and stabilization of nanoparticle materials. We will discuss seminal systems from the Emrick and UMASS group on the colloidal polymerization of semiconductor nanocrystals and metal nanoparticles as well as the recent developments in the field on the polymerization of quantum dots, dipolar magnetic nanoparticles and heterostructured semiconductor nanorods. These types of colloidal polymeric materials have been demonstrated exhibit synergistic optical, electrical, electrochemical and catalytic properties. [Figure 1]
POLY 199: New approaches to designer polymers

Craig J. Hawker, hawker@chem.ucsb.edu. Univ of California, Santa Barbara, California, United States

A variety of new strategies to controlling polymer structure - from organic ATRP to sequence defined macromolecules - will be discussed. The overall objective is to develop simple, yet powerful approaches for preparing functional materials, that can be used by experts and non-experts alike.
Materials will segregate to the interface between two immiscible fluids to reduce the interfacial energy. Per particle, the reduction in the interfacial energy will depend upon the size and shape of the particle and, to a first approximation, the cross-sectional area of the particle at the interface. So, for example, nanosheets, like graphene or clays, will occupy a large interfacial area and result in a significant reduction in the interfacial energy per particle or sheet. Nanorods, like carbon nanotubes or tobacco mosaic virus, will orient parallel to the interface to maximize the reduction in the interfacial energy and, in fact, can form two-dimensional liquid crystalline phase at the interface to optimize packing coverage of the interface. Nanoparticles, with the smallest cross-sectional area, are only weakly held at the interface where the reduction in interfacial energy competes against thermal energy, resulting in liquid like assemblies at the interface. One route to enhance the interfacial activity is to generate Janus-type particles, where one part is soluble in one fluid, while the second is soluble in the other. This increase in the interfacial activity leads to an unusual jamming behavior of the nanoparticles at the interface and a route to generate structured liquids (see Figure).

Figure: A droplet of water containing carboxy-functionalized PS nanoparticles in PDMS containing an amine-functionalized PDMS after deformation by an electric field in two orthogonal directions.
This presentation will describe the integration of polar, hydrophilic organic functionality into polymers, starting with the synthesis of novel monomers and working through the development of polymerization chemistry that affords well-defined, functional macromolecular materials. In particular, the synthesis of zwitterionic polymers will be highlighted, including their use to alter the electronic properties of metal and semiconductor surfaces and the associated improvement in device properties including organic solar cells.
We have used an alternate crosslinking approach to prepare low EW, water insoluble perfluorosulfonimide (PFSI) ionomers with the structural motif shown in Figure 1. These ionomers display significantly greater conductivity at low relative humidity (10-20%) than Nafion® membranes of comparable thickness [1]. The process used to prepare these novel PFSI ionomers includes the following steps: (1) prepare a low EW PFSA resin from either TFE and PSEPVE or TFE and Dow vinyl ether, (2) convert the PFSA resin to its corresponding sulfonamide resin by reaction with ammonia, (3) treat the sulfonamide resin with a sulfonimide (SI) oligomer with sulfonyl fluoride end groups, and (4) retreat the resulting resin with either the same SI oligomer or another difunctional sulfonyl fluoride to convert all sulfonamide groups to sulfonimide linkages. Reaction work-up generally includes hydrolysis, acidification, and purification.

POLY 203: Highly conductive alkaline poly(phenylene oxide) poly(vinyl benzyl trimethyl ammonium) diblock membrane for anion exchange membrane fuel cell applications

Tara P. Pandey, taarapp@gmail.com, Matthew W. Liberatore, Andrew M. Herring. (1) Chemical and Biological Engineering, Colorado School of Mines, Golden, Colorado, United States (2) Colorado School of Mines, Golden, Colorado, United States

A necessity to develop a well forming anion exchange membrane (AEM) is evidenced by the recent increased in the number of publications on AEM for fuel cells applications. The higher cathode reaction kinetics at AEM fuel cell opens the possibility of using inexpensive metal catalysts. Poly(phenylene oxide) poly(vinyl benzyl trimethyl ammonium) hydroxide membrane with titrated IEC of 3.2 meq/gm of dry membrane was studied as an AEM for fuel cell applications.

Environmentally controlled electrochemical impedance spectroscopy measurements were performed as function of temperature and humidity (%RH) under N2 environment. The membrane ionic conductivities of 0.137 ± 0.015 and 0.024 ± 0.006 S/cm at 95%RH and 40%RH; respectively were observed at 60 ºC in CO2 free alkaline form. This is the first AEM reported to have a measureable conductivity at as dry as 40%RH. But ionic conductivity suffered tremendously when the AEM was exposed to ambient air. Properties of air controlled vs air exposed AEM will be discussed along with the difference in liquid and vapor water uptake behavior of these membranes under similar conditions of temperature and %RH. A complete set of electrochemical and morphological study of the membrane will be discussed in the presentation.

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Air controlled (Blue) vs air exposed (Red) in-plane OH⁻ conductivity measurements of the membrane at 60ºC. The Cl⁻ conductivity (Black) represents the value in native counter-ions form of the membrane.
Nitroxide mediated polymerization was used to make poly(vinylbenzylchloride) (PVBC) blocks from the terminal end of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). A series of block copolymers with different length of PVBC block was synthesized for examination as anion exchange membranes (AEMs). Menshutkin reaction was conducted to convert PVBC blocks to ion-conducting poly(vinylbenzyltrimethylammonium chloride) [PVBTMA(Cl)] blocks. The block copolymers were found to be phase-separated as determined by the observation of two glass transition temperatures using differential scanning calorimetry. PPO-b-PVBTMA membranes were prepared through melt pressing and were found to be crosslinked after the thermal treatment, providing mechanical stability and suppressed water uptake. Hydroxide conductivity of PPO-b-PVBTMA increased with an increase in the amount of PVBTMA block lengths. A sample with an ion exchange capacity of 2.9 meq/g was found to have a water uptake of 95 % and a hydroxide conductivity of 132 ± 3.8 mS/cm at 60 °C under fully hydrated conditions.
New highly hydroxide-conductive anion exchange membranes (AEMs) are required in order to achieve long-lasting low-cost solid-state alkaline fuel cells (AFCs). In this study, we synthesized and investigated the ion transport properties and morphology of polymerized ionic liquid (PIL) diblock copolymers comprised of various covalently attached cations: butylimidazolium, butylmethylimidazolium, trimethylammonium, pentamethylguanidinium, butylpyrrolidinium, trimethylphosphonium. Diblock copolymers consisting of a non-ionic component, methyl methacrylate (MMA), and a functional component, 2-bromoethyl methacrylate (BrEMA), were synthesized via the sequential reversible addition-fragmentation chain-transfer (RAFT) polymerization technique and subsequently quaternized with various functional cations. The nanoscale morphology of the block copolymers was characterized using small-angle X-ray scattering and transmission electron microscopy. Transport of bromide and hydroxide ions was measured with electrochemical impedance spectroscopy and water uptake was measured with dynamic vapor sorption. The transport-morphology relationships at various humidities and temperatures were investigated as function of cation type.
POLY 206: High-modulus, high-conductivity nanostructured polymer electrolyte membranes via polymerization-induced phase separation

Morgan W. Schulze¹, schu2704@umn.edu, Lucas D. McIntosh¹, Marc A. Hillmyer², Timothy P. Lodge¹,². (1) Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota, United States (2) Chemistry, University of Minnesota, Minneapolis, Minnesota, United States

Solid-state polymer electrolyte membranes (PEMs) must achieve high modulus, toughness, and temperature stability without sacrificing ionic conductivity. Herein we report a simple, one-pot synthetic strategy utilizing polymerization-induced phase separation via the copolymerization of multifunctional monomer in a mixture of ionic liquid and macro chain transfer agent. Simultaneous in situ block polymer formation and chemical crosslinking produces nanostructured PEMs that achieve an unprecedented combination of high conductivity (ca. 1 mS/cm) and high modulus (ca. 1 GPa), owing to the long-range, co-continuity of poly(ethylene oxide)/ionic liquid and highly crosslinked polystyrene domains. These mechanically robust, high conductivity PEMs hold great potential for use in lithium-ion batteries and high-temperature fuel cells.
POLY 207: Morphology and transport in a tris(2,4,6-trimethoxyphenyl) phosphonium functionalized PPO for alkaline fuel cells

Ye Liu\textsuperscript{1}, yeliu@mines.edu, Bingzi Zhang\textsuperscript{4}, Yuan Yang\textsuperscript{3}, Söenke Seifert\textsuperscript{5}, Yushan Yan\textsuperscript{2}, Matthew W. Liberatore\textsuperscript{3}, Andrew M. Herring\textsuperscript{3}. (1) Chemical Engineering, Colorado School of Mines, Golden, Colorado, United States (2) Dept of Chemical Engineering, University of Delaware, Newark, Delaware, United States (3) Colorado School of Mines, Golden, Colorado, United States (4) Department of Chemical & Biomolecular Engineering, University of Delaware, Newark, Delaware, United States (5) Argonne National Lab, Lemont, Illinois, United States

Anion exchange membranes (AEMs), used as the solid electrolyte, play an important role in the alkaline fuel cell (AFC) performance. Long-life operation and high conductivity are two requirements of a good AEM. We previously proved that modification of the imidazolium cation by attaching 2,4,6-trimethoxyphenyl groups provide an efficient way to improve the cation stability.\textsuperscript{1} Our current work focuses on a bulky tris(2,4,6-trimethoxyphenyl) phosphonium, whose structure is shown in Figure 1. Besides contribution for the duration enhancement, we are more interested in the bulky cation’s influence on the transportation behavior.

Ion transport in the AEM derives from a combination of several membrane properties. The transportation directly relates to the local morphology that whether there are unimpeded channels for anions pass through.\textsuperscript{2} Water molecules located in the membrane facilitates anionic groups transfer by providing sufficient anion hopping sites.\textsuperscript{3} In our study, the water transportation is measured by using of pulsed field gradient NMR, and the anion transport property is quantified by the conductivity measurements. Insight on the anionic groups movement based on the number of water molecules per cation is investigated. A new understanding of the interplay of transport and morphology is being developed. Since ambient carbon dioxide will react with the OH\textsuperscript{−} to form a mixture of CO$_3^{2−}$ and HCO$_3^{−}$ in the film, conductivity OH\textsuperscript{−} form is studied using an airtight BekkTech conductivity cell. All the other measurements are performed with Br\textsuperscript{−} anions, as synthesized.

Reference

Figure 1. Structure of tris(2,4,6-trimethoxyphenyl) phosphonium
POLY 208: New family of base-stable, anion-conductive block copolymer membranes

**Pepa Cotanda**¹², **mjcotanda@lbl.gov**, **Nitash P. Balsara**¹. (1) UC Berkeley, Berkeley, California, United States (2) Berkeley Lab, Berkeley, California, United States

Anion-conducting membranes are used in a variety of energy and separations applications that need to operate under basic conditions like fuel cells and artificial photosynthesis. Alkaline fuel cells have received significant interest in recent years relative to acidic fuel cells because of advantages when operating under alkaline conditions, which include the possibility to use inexpensive non-noble metals as catalysts to greatly reduce the cost of the device. While many reports have demonstrated the high potential of these systems, conductivity improvement and alkaline stability enhancement are still a big challenge.

Amphiphilic diblock copolymers containing diallyldimethylammonium have been synthesized for the first time by reversible addition fragmentation chain transfer polymerization (RAFT). Membranes of these block copolymers have been made by drop casting from dimethylformamide and their stability and ion conductivity in strong basic conditions has been studied. The microphase separation of these materials in dry conditions and hydrated state have been investigated using small angle X-ray scattering (SAXS). Initial evaluation of these new membranes revealed very unique properties in terms of conductivity and stability in basic conditions.
Electrochemical energy conversion devices, based on polymer electrolytes have the potential for high system power densities, using relatively in-expensive components, at much higher efficiencies, than can be achieved with heat engines, at their relatively moderate temperature of operation. Proton exchange membrane (PEM) based devices are mostly being considered for hydrogen applications due to their realized very high power densities. Here the need is to develop PEMs that operate with less water and at elevated temperatures. Anion exchange membrane (AEM) based devices have the potential for use with multiple fuels as fuel cells, and to electrolyze not only water but also electrolytically reduce a range of substrates. AEMs can be operated with a large variety of anions depending on the application. Here the need is to use water efficiently for anion transport and as a reactant for hydrocarbons or for hydroxide conducting systems. Next generation ionomers must be designed for water management and utilization and gas permeation or transport without compromising the mechanical properties of the material through excessive swelling or softening.

As we move away from water saturated, state of the art PEM materials such as the perfluorosulfonic acids the ions in the newer materials are typically less dissociated and the transport pathways more tortuous depending on the properties of the material. The consequence of this is that ion transport shows higher activation energy barriers, and becomes more coupled with the thermal properties of the polymer, through both side chain motion and backbone relaxation. In this talk we will provide examples of all of these defects to ion transport in a variety of AEM and PEM materials. We will relate morphology via SAXS and microscopy to transport from electrochemical impedance spectrsocpy and NMR diffusion measurements. Importantly we will discuss design rules for the fabrication of practical ion conducting polymers for modern applications.
POLY 210: Rheological and morphological characterization of fractionated rigid-rod sulfone polymers

Joshua Tropp², troppj@jay.washjeff.edu, Katrina M. Knauer¹, Sarah E. Morgan¹. (1) School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, Mississippi, United States (2) Chemistry, Washington & Jefferson College, Pittsburgh, Pennsylvania, United States

Polysulfone (PSU) and Polyethersulfone (PESU) are rigid rod polymers with high thermal, chemical and hydrolytic stability. These properties have led to applications such as filtration membranes, medical devices, and high performance composites where surface and interfacial properties are critical to performance. Current studies focus on the surface modifications of these polymers, while the structural basis of the macroscopic properties of unmodified sulfone polymers is not fully understood. Additionally, there is still a lack of establish models to explain the effect of solvent on the surface properties of semi-rigid/rigid rod polymer films. A fundamental understanding of the relationship between the surface properties of the polymer films and the solutions from which they are cast could allow for easier processing and more cost effective procedures. This work investigates the effect of chemical structure and chain rigidity of PSU and PESU on the rheological data, surface tension parameters and surface morphology. Commercial polymers were fractionated into systems of varying molecular weight and narrowed molecular weight distribution and characterized via gel permeation chromatography. Solution rheology experiments were carried out in order to characterize the viscoelastic properties of the polymer solutions of varying concentration, molecular weight, and chemical structure. Surface morphology and surface energy of solution cast films was measured via atomic force microscopy and contact angle measurements. Results indicate that slight changes in chain rigidity and molecular weight have a significant effect on the rheological behavior of the polymer solutions and that these properties can be manipulated to control surface properties of the cast films.
Layer-by-layer (LbL) assembly is a promising alternative to current textile flame retardant treatments, which frequently use expensive or hazardous halogenated chemicals. Novel flame retardant nanocoatings composed of environmentally benign chitosan (CH) and poly(sodium phosphate) (PSP) were deposited onto cotton fabric using layer-by-layer (LbL) assembly. The cotton fabric is rendered self-extinguishing due to the charring promoted by the CH-PSP thin film. To improve the feel (i.e. hand) of the cotton fabric, it was rinsed in an ultrasonication bath between each polyelectrolyte deposition step. Weakly adhered polyelectrolytes are believed to be removed by ultrasonication, thus preventing the fabric from becoming stiff due to bridges between fibers. The cotton fabric consistently passed the vertical flame test after a 17-bilayer coating added only 9.1 wt%. Evidence of more uniform deposition of the coating due to ultrasonication and evidence of intumescence was provided through electron microscopy. Microcombustion calorimetry (MCC) revealed that peak heat release rate and total heat release were reduced by 73% and 81%, respectively. Ultrasonication rinsing greatly improved the hand of the coated fabric, reducing shear stiffness, geometric roughness, and bending rigidity. The ability to render cotton fabric, with a soft hand, self-extinguishing marks a major milestone in the development of these environmentally-benign, flame retardant nanocoatings.
The removal of residual oil, or sheen, remains a major barrier to efficient environmental remediation. Recently, our group has reported on a hybrid inorganic-organic magnetic shell crosslinked knead-like (MSCK) nanoparticle system for the entrapment and recovery of sheen. These MSCKs were achieved by the co-assembly of amphiphilic diblock copolymers and iron oxide nanoparticles, which produced spherical micelles with magnetically active cores exhibiting oil uptake capacities that reached ten times their mass. In order to probe the effect of morphological changes on the efficiency of oil sequestration, we have begun investigations into the development of hybrid cylindrical analogs. Web-like networks of cylindrical micelles ca. 30 nm in diameter were constructed through the co-assembly of amphiphilic diblock copolymers of poly(acrylic acid)90–block-polystyrene120 (PAA90–b-PS120) and oleic acid stabilized iron oxide nanoparticles. This network architecture was characterized through transmission electron microscopy (TEM) and atomic force microscopy (AFM). Ongoing studies include the intramicellar crosslinking of their hydrophilic shells and determination of their oil loading capabilities against a complex crude oil.

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 was incorporated within various polymer matrices to integrate dynamic topology changes. DA functional groups were incorporated via initiators, crosslinkers and an inimer to integrate DA linkages. Upon the application of a thermal stimulus, the retro-DA was induced and topological changes were induced upon the polymer backbone. [figure1]
The nanomaterial graphene has been shown to have a number of unique properties that could be useful for many different applications. It is a strong oxygen and water barrier; for this reason, it has been proposed as an anticorrosive additive for coatings. Previous work has been conducted involving the fabrication of polyurethane-graphene nanocomposites for corrosion resistant coatings. Unfortunately, the solubility of graphene in polyurethane was found to be poor even in the presence of dispersing aids; as a result, the anticorrosive properties of graphene failed to be incorporated into the nanocomposites. Current work includes the synthesis and testing of a novel compatibilizer for stabilizing graphene in polyurethanes. The compatibilizer contains a group that participates in π-π interactions with graphene and a group that has favorable, non-covalent interactions with polyurethane. Here, we report the resulting anticorrosive properties of the nanocomposites, as well as the compatibilizer’s effectiveness in producing uniform graphene dispersion throughout the polymer matrix.
Ruthenium (Ru)-catalyzed carbon-carbon double bond metathesis is an important reaction both for small molecule synthesis and for synthesis of polymers by reactions like Ring Closing Metathesis (RCM) or Ring Opening Metathesis Polymerization (ROMP). However, in some cases where Ru catalyst loadings are 0.1 mol % or greater, Ru leaching may contaminate the products. Such contamination can be undesirable either esthetically or in terms of potential toxicity. Here is an introduction to different strategies based for removal of Ru residues using polyolefins are described. The first process uses polyolefins as phase tags and/or as solvents for removing N-heterocyclic carbene complexes in a thermomorphic manner. This efficiently separates Ru from polymer products leading to Ru residues that are <1% of the starting Ru catalyst loading. The second process uses a polyolefin quenching agent to remove the Ru. In this case, a polyisobutylene (PIB)-bound isocyanide was prepared. This reagent colorimetrically phase separated all of a dark green Hoveyda-Grubbs complex from a polar phase into a nonpolar phase. The resulting gravity based liquid/liquid separation of a heptane and polar phase then separated the Ru residues from products.
Block copolymers (BCPs) can self-assemble into periodic nanostructures which make them attractive for a multitude of applications. For lithographic patterning, the ability to selectively remove one block is remarkably beneficial. This process often requires harsh conditions and usually damages the other block, diminishing the fidelity of subsequent pattern transfer steps. To solve this problem, a BCP was synthesized that contained a polymer block that undergoes rapid depolymerization when exposed to strong acids. Poly(dihydroxy-tetrahydro naphthalene) (poly(DHTN)) was synthesized under high mechanical stirring from DHTN and dibromomethane in a two-phase reaction mixture. The poly(DHTN) homopolymer was coupled to azide-terminated poly(trimethylsilyl styrene) by the copper-catalyzed azide-alkyne click reaction to form the block copolymer. Selective depolymerization of the poly(DHTN) block was demonstrated in an acid vapor chamber.
Recent research in the field of structure-property relationships for high-performance polycyanurate networks (also known as cyanate ester networks) has demonstrated a strong connection between the development of structures incorporating increased free volume during cure at high conversions and the uptake of moisture. This connection facilitates the use of new strategies to decrease the uptake of water and thereby improve the performance of these networks. In one example, we show that the moisture uptake of polycyanurate networks is reduced by up to 50% when a methyl group ortho to the cyanurate oxygen is introduced into the network structure. In this case, although the free volume in the network increases at high conversions, the presence of the methyl group blocks access to favored binding sites used in moisture uptake. In another example, we explore the effect of the molecular architecture of bridging groups between aromatic rings on the development of free volume during the thermal cure at high conversions, and the resultant impacts on water uptake.
Utilizing thiol-ene ‘click’ reactions, it is possible to produce thermoset networks that are highly homogeneous and thus exhibit enhanced energy damping capabilities. Such networks are prevalent in the coatings industry due to their facile preparation under ambient conditions. This talk will present some recent results in the 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. In addition, we present results in the high-impact compression testing to demonstrate the energy damping capabilities of these materials.

The glass transition temperature for thiol-ene thermosets can be tuned by varying the composition of mixed thiols in the composite. The Tg can be reliably predicted using the Fox equation.
Ablative thermal protection systems are commonly used as protection from the intense heat during re-entry of a space vehicle and have been used successfully on many missions including Stardust and Mars Science Laboratory both of which used PICA – a phenolic-based ablator. Historically, phenolic resin has served as the ablative polymer for many TPS systems. However, it has limitations in both processing and properties such as char yield, glass transition temperature and char stability. Therefore alternative high performance polymers are being considered including cyanate ester resin, polyimide, and polybenzoxazine. Thermal and mechanical properties of these resin systems were characterized and compared with phenolic resin.
POLY 220: Versatile conjugated polymer/di-ureasil hybrid materials: From enhanced emission quantum yields to white light emission

Niamh Willis-Fox¹, willisfn@tcd.ie, Ana-Teresa Marques²,³, Mario Kraft³, Ullrich Scherf³, Hugh Burrows², Rachel C. Evans¹. (1) School of Chemistry, Trinity College Dublin, Dublin, Ireland (2) Departamento de Quimica, Universidade de Coimbra, Coimbra, Portugal (3) Makromolekulare Chemie, Bergische Universität Wuppertal, Wuppertal, Germany

Incorporation of conjugated polymers (CPs) into an inorganic host allows modulation of the optical properties and aggregation state of the CP¹, whilst simultaneously improving the environmental stability.² However, due to the chemical incompatibility of the two components, inhibiting phase separation across all length scales can be challenging.¹ Here, we investigate the potential of di-ureasil hybrids, comprised of an organic polyether grafted onto a siliceous network via urea linkages,³ as host materials for CPs. Blue-emitting CPs (Fig. 1a) were incorporated into the di-ureasil, resulting in a dramatic enhancement in the photoluminescence quantum yield to ~60%. Subsequent inclusion of red-emitting CPs (Fig. 1c) enabled the emission color to be tuned across the blue-white-yellow spectral region via Förster resonance energy transfer. Results for the structural and optical characterization of these materials will be presented and provide insight into the mechanisms responsible for the observed photophysical behaviour. CP-di-ureasils can be cast as thin films from solution, retaining their emission properties, making them intriguing prospects for light-emitting devices and optical sensors.

In this talk we will present recent results from our laboratory relating to the application of intra-chain radical chemistry to the synthesis of polymeric nanostructures. Specifically, we'll report on the formation of nanoparticles from single polymer chains (single-chain nanoparticles or SCNP) using a variety of intramolecular radical coupling and polymerization reactions. We will also present our characterization methods for these materials including spectroscopic methods, triple detection size exclusion chromatography, and electron microscopy.

Figure 1: Schematic representation of this chemistry and TEM image of the resulting nanostructures.
Thermal degradation of composites and thermoset materials under oxidative conditions depends on oxygen permeation behavior and local oxidation rates. Both parameters are required to predict spatially dependent polymer degradation with diffusion limited oxidation models. This presentation will review the acquisition of oxidation rates for epoxy materials and then focus on the optimization of experimental approaches and data extraction approaches, which are applied to characterize thin films of low permeable polymers to derive the required permeability data. The competition between oxygen permeation and reactive loss determines the evolution of degradation depth profiles with temperature. Two different epoxy thermosets are compared in their degradation features, in terms of the temperature dependence of oxidation rates, permeability, oxidative depth based on DLO models, experimentally observed discoloration, carbonyl profiles by IR spectroscopy, and the thickness of Total Oxidized Layer (TOL) based on theoretical degradation kinetic models. Evidence has been obtained that the ingress of thermo-oxidative damage is material specific for behavior linked to Tg, and that any TOL evaluation of composites under high temperature may not necessarily reflect a single oxidative equilibrium process.

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POLY 223: Improving mechanical properties of highly branched perfluorinated polymer membranes

Matthew J. Quast\textsuperscript{1}, quast1mj@cmich.edu, Aaron D. Argall\textsuperscript{2}, Cassandra J. Hager\textsuperscript{2}, Anja Mueller\textsuperscript{2}. (1) Science of Advanced Materials, Central Michigan University, Mount Pleasant, Michigan, United States (2) Dept of Chemistry, Central Michigan University, Mt Pleasant, Michigan, United States

In polymer membranes branching leads to desirable film forming characteristics, although in fluorinated hyperbranched systems the resulting material lacks any chain entanglement or crystallinity - which becomes problematic for systems where mechanical robustness is required. Techniques to mitigate the mechanical deficiencies of perfluorinated hyperbranched systems will be reported here. A variety of AB\textsubscript{2} monomers were prepared with varying lengths of linear, alkyl spacers. The AB\textsubscript{2} monomers were copolymerized with a variety of linear AB perfluorinated monomers and the resulting mechanical properties were examined. For materials lacking any mechanical resilience a poly(ether ether ketone) (PEEK) was used as a strengthening agent. These techniques have shown to create robust and creasable polymer membranes from highly branched systems.
Aerogels are highly porous solids having low density, high surface area, low dielectric constant, and low thermal conductivity. In the past few years, cross-linked polyimide aerogels have been extensively studied. Depending on the structure of the polyimide backbone, flexible, foldable, non-flaking thin films can be cast, or stiffer thick parts can be mold with good mechanical properties. Their unique features have made them good candidates for various aeronautic and aerospace fields including lightweight substrate for antenna, or multi-layer insulating films recently tested for inflatable decelerators used in entry, decent and landing operations. However, high material cost still remains an issue. The cross-linkers used to make these aerogels such as octa (aminophenyl)-silsesquioxane (OAPS) are quite expensive, or like 1,3,5-tris(4-aminophenoxy) benzene (TAB), are custom made. The main approach of this study is to use a triisocyanate, N3300A, as a cross-linker to improve the flexibility of the polyimide aerogels by inserting urethane/urea linkages into the network. In addition, N3300A is a low cost, commercially available material. Moreover, with the isocyanate reactive groups, a more stable polyimide solution with amine or hydroxyl end-groups can potentially be preserved for an extended period before being cured.
Asymmetric flow field flow fractionation: An effective separation technique for polymers for which SEC/GPC fails

Stepan Podzimek, stepan.podzimek@synpo.cz. (1) Analytical and Physical Chemistry, SYNPO, Pardubice, Czech Republic (2) Institute of Chemistry and Technology of Macromolecular Materials, University of Pardubice, Pardubice, Czech Republic

From its dawn in the sixties of the last century size exclusion chromatography (SEC/GPC) has developed in a well-established and the most powerful method for the determination of molar mass distribution and, in combination with a multi-angle light scattering detector (MALS), also for the characterization of polymer conformation, aggregation and branching. However, the method often fails to completely separate branched polymers, polymers containing ultra-high molar mass fractions and/or swollen supermolecular structures, and polymers interacting with SEC column packing. These polymers can be effectively separated by asymmetric flow field flow fractionation (AF4). Acrylic copolymers prepared by emulsion polymerization are typical example of polymers for which SEC separation often fails. The presentation gives a brief overview of the AF4 principles as well as several examples of the AF4-MALS characterization of polymers that cannot be correctly characterized by SEC-MALS. An example of AF4-MALS analysis of polymer containing ultra-high molar mass species is shown in Figure 1.

Figure 1 Example of AF4-MALS analysis of polymer containing ultra-high molar mass fractions: molar mass versus retention time plot overlaid on the signal of refractive index detector.
POLY 226: Root causes of molecular weight loss of poly(cyclic butylene terephthalate) in pCBT/clay nanocomposites during processing

John W. Lyons, JQLyons@chartermi.net, Joe J. Kiefer. Dow Chemical Co., Midland, Michigan, United States

The pCBT component of pCBT/clay nano-composites can undergo significant molecular weight reduction during processing. This can be problematic because the toughness of such composites becomes unacceptable if the Mw becomes too low. A size exclusion chromatography (SEC) scheme was developed to measure molecular weight distributions of pCBT. From SEC before and after processing the net extent of chain scission during processing could be estimated. The net extent of chain scission was correlated with several process variables in a designed experiment to understand the chain scission process better. Correlation of torque and temperature with molecular weight in a Haake mixing bowl allowed on-line continuous estimation of molecular weight during processing under a variety of conditions.
POLY 227: Leveraging polymer separation science to design new materials

Stephan Moyses, stephan.moyses@sabic-ip.com, Robert W. Allen, Nancy Jestel. T&I, SABIC, Selkirk, New York, United States

In the engineering plastics industry, the battle for competitiveness is also fought in the analytical lab. Behind every new material technology advancement there is often a great deal of effort advancing analytical science. This presentation will provide an insight how polymer separation science contributes to this effort. Examples will include elucidating the reaction pathways that took place during a chemical reaction (ex: reactive extrusion, see figure below) and explaining a material’s performance during critical moments in its life cycle. By providing these clues to the product developer or process engineer, the reaction parameters or resin formulation can be adjusted yielding materials with improved properties. This information has become paramount in an environment where IP landscape is often crowded. To meet the ever increasing demand for more pertinent information, a combination of skills are necessary that cover such diverse fields as chromatography, spectroscopy, chemometrics and modeling. Examples will be provided that illustrate how polymer separation science is contributing to the advancement of new materials in an industrial analytical lab.

![Two-dimensional chromatograms evidencing the block copolymer formed by coupling a polyamide polymer with a poly(phenylene ether) polymer via reactive extrusion.](image)

Two-dimensional chromatograms evidencing the block copolymer formed by coupling a polyamide polymer with a poly(phenylene ether) polymer via reactive extrusion.
POLY 228: Monitoring kinetics of polymeric processes

Michael F. Drenski3, Colin A. McFaul1, Alina M. Alb2,1, Frederick Twigg1,2, Curtis Jarand2,1, Wayne F. Reed2, wreed@tulane.edu. (1) Tulane University, New Orleans, Louisiana, United States (2) Physics Dept, 2001 Stern Hall, Tulane University, New Orleans, Louisiana, United States (3) Advanced Polymer Monitoring Technologies, Inc, New Orleans, Louisiana, United States

Recent advances in monitoring kinetics of polymeric processes by this group will be surveyed. These include kinetics of monoclonal antibody (mAb) aggregation using simultaneous multiple sample light scattering (SMSLS) and monitoring polymerization reactions with Automatic Continuous Online Monitoring of Polymerization reactions (ACOMP). For mAb aggregation a quantitative aggregation rate, the AR, is defined in terms of fractional increase of aggregate mass per second (1AR=1s⁻¹) and AR for several mAb are determined for different stressors, including temperature, stirring, exposure to gas/liquid interfaces, and formulation conditions. mAb instability kinetics are dependent upon the type of stressor(s). Progress in using light scattering spikes (LSS) to monitor the onset and evolution of particulates within a background of soluble aggregates is presented.

Three new ACOMP directions are highlighted; ‘Second generation ACOMP’ (SGA) is being developed to monitor the onset and evolution of polymer stimuli responsive behavior during synthesis, by using multiple, independent light scattering and viscosity detector stages, with ability to change both T and solution conditions between detection stages. Early SGA results on monitoring LCST in copolymers with NIPAM of automatically varying comonomer composition are presented. Progress on development of a more versatile SGA prototype is discussed with respect to experiments planned for several stimuli responsive polymers from various synthetic polymer groups.

First steps in using ACOMP to both monitor and control polymerization reactions are being taken. Ideal reaction trajectories are posited for polymerization reactions in order to produce endproducts of desired properties, then providing active control to steer reaction trajectories towards the ideal ones.

Finally, ACOMP has now been installed, for the first time, in the full scale industrial reactor milieu. Some features of this technology transfer program are highlighted.
Homogeneous catalysis is widely used to prepare polymers, intermediates, and pharmaceuticals. However, methodologies to separate such catalysts and/or their ligands from products are needed. Our group has explored a variety of greener, more efficient liquid/liquid and liquid/solid separation strategies that use phase selectively soluble polymeric materials. While these separations are efficient, some leaching of the catalyst into the product phase of a two-phase solvent system occurs. Here studies that use dyes as surrogate catalysts show how the use of oligomeric hydrocarbon polymers as additives or solvents minimizes leaching of polyisobutylene-bound catalysts. In these studies, low dispersity unfunctionalized and functionalized polyolefin oligomers are used to replace volatile hydrocarbon solvents in mixed solvent systems that form a biphasic mixture after a catalytic reaction. By using polyisobutylene-bound azo dyes as catalyst surrogates, we have been able to show that leaching of a polyisobutylene-bound material into the polar phase can be reduced with added hydrocarbon oligomers as cosolvents.

Effect of adding polymer cosolvents on leaching into the polar phase
Recent research on superoleophobic yet hygroscopic materials has led to the development of new technology for the separation of multi-phase liquid mixtures via preferential coalescence of one phase at solid surfaces with engineered liquid repellence. When integrated into liquid-liquid extraction operations, the coalescence provided by the liquid-repellent surfaces enables the development of a new method for treating fuels. For example, if a kerosene-based hydrocarbon fuel is mixed with an extraction medium (such as an ethanol/water mixture), undesirable compounds such as benzothiophenes will be extracted into the ethanol/water mixture, which may be separated from the fuel by passage through an oleophobic hygroscopic membrane, leaving behind refined fuel. We present initial work on the determination of partition coefficients of benzothiophene in a variety of extraction media and dodecane, diffusion coefficient measurements for determination of needed residence times for extraction, and initial separation results using superoleophobic hygroscopic membranes.
POLY 231: Surface patterning of Ultrafiltration membranes to mitigate particulate and protein fouling

Sajjad Maruf, sajjad.maruf@colorado.edu, Yifu Ding, Alan R. Greenberg, John Pellegrino. Dept. Mechanical Engineering, UCB427, Univ. of Colorado, Boulder, Colorado, United States

Flux decline due to fouling is a common phenomenon in most liquid-based filtration processes. Non-chemical approaches that can minimize or delay fouling during filtration are highly desirable. Recently, we have developed a methodology to impart sub-micron scale patterns directly onto the surface of ultrafiltration (UF) membranes. With careful control of the processing variables, patterns can be directly imprinted without sacrificing membrane permselectivity. Model suspensions (containing either silica particles or proteins) were filtered using patterned and non-patterned (control) membranes. For each suspension, there was a significant improvement in the overall filtration productivity and regeneration characteristics for the patterned membranes relative to those of the control. These experiments revealed that the patterned membranes evidenced an appreciable reduction in both surface deposition rates and adsorption. For silica suspensions the surface patterning evidently increased the critical flux over the full range of particle sizes employed. This effect increased with higher crossflow velocity and increased angle between the flow direction and the pattern lines. For protein suspensions, surface patterning also significantly reduced the degree of fouling at all combinations of ionic strength and pH. These effects were attributed to the enhanced diffusion of foulant induced by the surface patterning.

Figure 1: a) Schematic representation demonstrating the relationship between the feed flow direction (arrows) and the surface pattern orientation imprinting and its influence on particulate deposition. b) and c) protein deposition on patterned and non-patterned membrane.
Polymeric films with coextruded multilayer architectures of alternating layers of particulate filled nanocomposites were investigated for improvements in gas/fire barrier properties and electrical conductivity. Gas transport models demonstrate a need for higher aspect ratio platelets for maximum barrier enhancement. Therefore, high aspect ratio graphene nanoplatelets (xGnP®) melt-blended into linear low density polyethylene (LLDPE) layers were alternated with layers of un-filled low density polyethylene (LDPE) to produce films with properties typical of high loading nanocomposites. Improvements in material properties are possible through a boundary movement phenomenon that occurs when a system of alternating layers of miscible polymers with highly different mobilities are allowed to interdiffuse in the melt. The greater mobility of the more linear LLDPE chains as compared to the more branched LDPE chains cause a layer movement in the direction of the more slowly diffusing LDPE chains. The high aspect ratio platelets remain in the shrunken LLDPE layers resulting in an increase in concentration in the nanocomposite layers. The property improvements in the nanocomposite layers are reflected in the overall film properties. The effects of particle size, loading, and melt processing conditions on composite morphology and properties were analyzed. Multilayer layer thicknesses and annealing conditions of the films were also studied. Bulk composites were utilized for comparison with the multilayer films through various stages of particle concentration where the annealed multilayer systems demonstrated properties indicative of high loading composites.

(Top) Moving boundary phenomenon in multilayer system of alternating LDPE and LLDPE nanocomposite layers. (Bottom) Relative oxygen permeabilities of (■) graphene/LLDPE composites and (Δ) multilayer system before and after annealing.
Aluminum (Al) based thermites are of great interest because of their high energy density and potential for a wide array of energy generation applications. These thermites are composed of a metal fuel (Al) and an oxidizing agent (i.e. molybdenum trioxide (MoO₃) or copper oxide (CuO)). Many studies have shown improved reactivity with these composites when the particles are on the nano-scale. This study focuses on investigating how the use of a fluorinated additive, specifically perfluoropolyether (PFPE), alters reactivity. Energetic blends of Al and fluorinated oxidizers such as PFPE are interesting reactive composites due to the high surface exothermic chemistry between fluorine (F) and Al that promotes Al reactivity. Using PFPE as an additive introduces a competitive reaction path resulting in the formation of either aluminum fluoride (AlF₃) or aluminum oxide (Al₂O₃). Semi-confined burns, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed for varying percent of PFPE in Al/MoO₃ and Al/CuO composites in order to examine the reaction kinetics for each blend as well as Fourier transform infrared (FTIR) to examine the products. Results show that the performance of the thermite-PFPE blends is highly dependent on the oxidizing agent used. The blends with MoO₃ show an increase in reactivity while the blends with CuO show a decline in reactivity when increasing the PFPE additive. This behavior may be linked to the bond dissociation energy of the reactants and the overall reaction kinetics.
This study examines the effect reinforcement fabrics have on the combustion behavior of thin film energetics. Nano-metric aluminum and molybdenum trioxide composites were mixed into a silicon binder and blade cast around a reinforcement fabric to form a flexible free standing film. Plain weave 5 to 6 oz fiberglass, carbon fiber, and arimid clothes were studied. In order to understand the effect these cloths have on the combustion and mechanical properties of the thermite film, one film composition was used to generate all samples with the type of cloth being the only variable. All films were cast at a thickness of 2.5mm with constant volume percent solids to ensure mixtures cast consistently. The films were ignited in a non-confined test apparatus and the flame propagation was recorded with a high speed camera. Additional samples were subjected to tensile and puncture testing to characterize the mechanical properties of the film. The results show that the presence of the reinforcement fabrics reduce the flame speed of the films. This is likely caused by the fabric having negligible participation in the reaction, thus acting as a heat sink creating less energy release and slowing the flame speeds. The mechanical properties of these films exhibit behavior that would be expected when comparing the relative strengths of the different reinforcement fabrics.
Polyketone (PK) nanocomposites containing non-covalently modified graphene nano platelets (GNP) were prepared by solution casting. The GNP with high aspect ratio largely reduces moisture or gas permeability by increasing the tortuosity when the GNP was homogeneously dispersed in the polymer matrix. To prevent GNP aggregation in the matrix, pyrene derivatives that non-covalently functionalize the GNP through π-π interaction were added. The pyrene derivatives on the GNP surface not only facilitate a homogeneous dispersion of GNP but also improve the interaction between GNP and PK matrix, which provides a low permeability and results in an efficient load transfer across the matrix. Each type of functional group on the pyrene basal plane has different effect on the graphene dispersion in the matrix, and further affects the final barrier property of PK nanocomposite film. For example, 1-aminopyrene (APy) which is a bifunctional molecule with a pyrenyl group and an amino group exhibited a remarkable improvement in graphene dispersion. This could be ascribed to the hydrogen bonding interaction between a polar amino group of APy and a carbonyl group of PK. A small shift of absorption peak for the carbonyl group was observed in FT-IR spectra. Consequently, water vapor transmission rate (WVTR) of 1 wt% GNP-APy/PK was about 12% lower than that of GNP-Py/PK and 30% lower than pristine GNP/PK.
In this work we present our findings on some inter and intra molecular interactions and revealed by x-ray single crystal structural analyses on a series of structurally related oligothiophenes. Br…Br intermolecular interactions and N…S intramolecular interactions being the most pronounced in driving the crystal packing. Implications on solid state properties including solid state polymerizations will be presented. The molecules included in this study include oligothiophene and ethylenedioxythiophene (EDOT) substituted with a variety of groups. In particular we were interested in structures of molecules endowed with strong electron accepting groups including: halogens, nitro, cyano, dicyanovinyl and tricyanovinyl groups. The focus of the presentation will be on how these structural modifications impact planarity and packing of molecules with emphasis on the role of inter- and intra- molecular interactions in the observed crystal structures of these materials. In addition some aspects of the synthesis, electrochemistry and optical properties of these closely related molecules will be presented.
Interfaces play a crucial role in electrical and thermal transport related structure-property relationships in many different areas of scientific interests, including composites and electronics reliability. Within the specialized field of nanoelectronics, fabrication of carbon nanotube (CNT) based devices has attained consistent attention, partly due to their excellent electrical and thermal transport properties. However, the use of CNT devices has still been limited because of their unknown performance reliability and variability. Often, CNT junction interfaces act as limiting factor in achieving optimal transport properties. In this context, we will describe non-equilibrium molecular dynamics simulations to characterize the cross-contact thermal transport for CNTs and graphene nanoribbons (GNRs). We find that length, diameter, number of walls (in MWCNTs), and degree of CNT deformation, all play important roles towards determination of contact conductance. For GNRs, the aspect ratio of the nanoribbons best characterizes the lateral thermal conductance. The observations will be discussed using several vibrational features associated with out of plane phonon modes observed in thermally anisotropic materials, such as CNTs and GNRs. We will also briefly discuss the electronic transmission features of metallic nanotubes as calculated using non-equilibrium Green’s function method within the framework of tight binding density functional theory for different inter-CNT lateral distances. Using estimated contact conductance, a multi-scale approach, based on statistical distribution of effective contact resistances (based on CNT distance) that originates from thermal fluctuations of intermolecular distances, is employed to predict effective electrical conductivity in polymeric matrix materials as a function of temperature.
Electrical percolation in a system of conductive filler mixed into resistive polymer takes place within narrow particle concentration range as a sharp transition from high resistivity of polymer to low resistivity of particles’ conductive network. Volume concentration of particles percolating in polymer matrix depends mostly on their space filling properties. Therefore, conductive grades of carbon black (CB) have high structure to allow percolation under 10 percent by volume. These rules work well for random dispersions of CB melt-mixed with polymers in extruder or a stationary mixer. What happened if CB is surface treated? Would self-assembly of particles effect the percolation behavior? The presentation attempts to answer these questions.

VULCAN® XC72 high structure carbon black was treated with diazonium salts of 4-fluoroaniline (4-FA) and butyl ester of p-aminobenzoic acid (BAB). Melt-mix of BAB-CB with low density polyethylene has smoothened electrical percolation curve versus step-wise percolation of non-treated CB dispersion. Change of percolation behavior of surface-treated CB can be explained by higher inter-particle junction resistance in dispersion. We also found distinctive difference in percolation behavior of 4-FA and BAB surface treated and untreated VULCAN® XC72 carbon black in various polymers melt-mixed and cast from solvents.

When polyurethane (PU) films are cast from solvent (as shown on the left image with 1% BAB-CB), BAB-treated CB particles are organized in PU in a way, that no signs of percolation are observed. When plotted, log of volume resistivity for composite film is a linear function of CB concentration within the whole range, up to 35 weight percent of CB. In comparison, not treated CB percolates at about 3% w/w (right image). We are able to rationalize the electrical properties of treated CB dispersions in polymers within the framework of surface modification of CB particles that screens particle-particle direct contact to form conductive network. Rheological experiments confirm proposed model.
Nanodielectrics, or dielectric polymer nanocomposites, can exhibit significant improvements in voltage endurance and dielectric breakdown strength compared to unfilled polymer. This work takes advantage of the large interfacial area between the matrix and the filler as a means to introduce chemistry that can further tailor the dielectric properties of the composite. The large surface to volume ratio of the filler can be detrimental to dispersion as it can promote agglomeration. This obstacle is overcome by grafting polymer chains to the surface of the filler. Reversible addition fragmentation chain transfer, or RAFT polymerization, is utilized to graft polymer chains to the filler surface and control the molecular weight of the grafted polymer. Our studies show that surface group chemistry can contribute significantly to property optimization. In addition to polymer chains, polarizable surface ligands are added to the filler that are believed to act as electron traps, preventing percolation across the composite. It was found that adding surface functionalized nanoparticles to the matrix can improve the overall dielectric breakdown strength by as much as 30% over the unmodified matrix with only 2% loading.
Intramolecular energy transport mechanisms were studied by relaxation-assisted two-dimensional infrared (RA 2DIR) spectroscopy method. Vibrational energy propagation in materials is governed by two limiting regimes, diffusive and ballistic. While the diffusive transport is associated with random walk hopping and observed in many molecular systems, the discovery of ballistic energy transport remains relatively new. It involves vibrational states delocalized over the transport region leading to high efficiency constant speed wavepacket propagation. Oligomers of PEG, perfluoroalkane and alkane chains of various lengths were used in this study. We have discovered that the efficient ballistic regime is common to molecules with repeating units and thus it has to be taken into account as fundamental part of any energy dissipation process in molecules. Present study sheds light on the contributions of both ballistic and diffusive mechanisms into the energy dissipation within molecules. Switching between two regimes and limiting factors for the transport speed in molecules are discussed. The highest speed of 1320 m/s is detected in linear alkanes.

Ballistic and diffusive regimes of energy transport are identified within a molecule using 2DIR spectroscopy method.
Our laboratory has recently demonstrated that wedge-type block copolymers, synthesized by ruthenium-mediated ring-opening metathesis polymerization (ROMP) of exo-norbornene functionalized monomers, self-assembled to visible light reflecting dielectric mirrors. Polymers with molecular weights greater than 1250 kDa failed to self-assemble to well-defined nanostructured materials due to a heightened propensity for chain entanglement. Thus, a new dendritic-like monomer system was designed to increase the rigidity of the block copolymers and minimize the capability for chain entanglement. The synthesis of the dendronized monomers, their polymerization via ROMP to block copolymers, and the self-assembly of these rigid block copolymers will be discussed in this presentation.
Sub-nanoliter volumes of Perfluorosulphonic acid (PFSA) polymer were confined within the zeolite-cladded pores of micro-porated stainless steel substrate. There is a large interfacial contact area between the PFSA polymer and the zeolite surface, perturbing the polymer chain conformation and distribution of the functional groups within the narrow volume. This resulted in improved proton conductivity, thermal stability, and water retention. Ion beam dissection of the samples was carried out to study the local interfacial structure and chemistry at high resolution. High resolution microscopy shows possible anchorage of PFSA within intercrystalline gaps between the zeolite crystals. This could explain the increased stability of the material. A perturbation in chemical composition appears to propagate from the interface into the bulk PFSA and could have contributing factor on the proton conduction.
Synthesis and characterization of thiophene containing angular polycyclic aromatic hydrocarbons (PAHs) are studied. Bis(benzothieno) naphthalene 1 (BBTN-1) is synthesized by the coupling of methyl 3-bromothiophene-2-carboxylate with 1,5-bis(naphthaleny1)boronic acid through Suzuki coupling, followed by the hydrolysis of the methyl esters. Ring closing step will proceed by formation of acid chlorides and Friedel-Crafts chemistry. Isomer, BBTN-2, is synthesized in the likewise manner. Alkylsilyl acetylene substituents are attached via organolithium chemistry for solution processability. This structure-property relationship study aims to enhance the stability and performance of angular PAHs in electronic devices by the presence of additional Clar structures, relative to bistetracene. Results of this investigation may open new opportunities to explore these materials in mainstream applications such as bulk heterojunction solar cells and large-area, roll to roll solution processable transistors. Synthetic steps are confirmed via NMR and FTIR. Molecular packing motifs and crystal orientation is characterized via x-ray crystallography and x-ray diffraction, respectively. UV-vis spectroscopy, circular voltammetry, and ultraviolet photoelectron spectroscopy are utilized to investigate electronic structure. Target molecules are implemented into OFETs and OPVs to analyze device performance as well. Thermal properties are determined using TGA and DSC.

Scheme 1. Synthesis of BBTN-1

Figure 1. BBTN-1 (left), BBTN-2 (middle), bistetracene (right)
We described the synthesis of a series of well-defined polystyrene based light harvesting materials, in which the polystyrene backbone was prepared through nitroxide-mediated living radical polymerization (NMP), with degree of polymerization (DP) varying from 35 to 170. The chromophores in these polymers, polypyridyl Ru (II), were fully attached to the polystyrene backbone by the alkylene-azide click chemistry. The polymer structures were confirmed by nuclear magnetic resonance and infrared spectroscopy.

We evaluated the photophysical and electrochemical properties of the Ru-polypyridine polymers in MeOH and acetonitrile. The polymeric chromophores exhibited similar absorption and emission spectra compared to monomeric chromophore, while the polymers showed distinct life time and quantum yield versus different counter ions or solvents. Molecular dynamics simulation of the polypyridylruthenium derivatized polystyrene in different solvents support the energy transfer and experimental photophysic studies.

Based on the similar strategy, the first chromophore-water oxidation catalysts (WOC) polymer assembly was synthesized, with Ru(II)-H2O(bpy)(terpy)(water oxidation catalyst) and Ru(II)(bpy)3(chromophore) units assembled to well-defined polystyrenes with ratio of 1:4. The preliminary data from emission and life time studies revealed the fast intra-chain electron transfer process in the WOC polymer assembly. Upon light excitation, the electrons would transfer from water oxidation catalyst centers to adjacent chromophore units in 15 ns. This effect was expected to enhance the TOF of water oxidation reactions. Our research involving the water oxidation catalysts (WOC) polymer assembly supplies an alternative way to make efficient catalyst-chromophore assemblies.
POLY 245: Development and characterization of layer-by-layer assembled ferrocene polymer/enzyme films for usage as biofuel cell anodes

Nicholas P. Godman¹, nichopg@ou.edu, Jared DeLuca³, David Schmidtke⁴, Daniel T. Glatzhofer². (1) Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma, United States (3) University of Oklahoma, Norman, Oklahoma, United States

Previous work has shown that ferrocene tethered to the nitrogen of linear polyethylenimine (Fc-Cₙ-LPEI) is an effective electron mediator for chemically crosslinked, solution cast glucose bioanodes. Layer-by-layer assembly of redox polymer/enzyme films provides a fast and efficient means to decrease the fabrication processing time. Films constructed from Fc-Cₙ-LPEI and periodate modified glucose oxidase (p-GOX) were characterized by varying the mediator tether length (three or six carbons) and the washing time between polymer/enzyme layers. The physical processes by which films are fabricated was elucidated by looking at the change in the electrochemical and steady-state enzymatic response of films assembled with various numbers of bilayers. Once the tether length and wash time were selected, Fc-Cₙ-LPEI/p-GOX films were used as the anode in a glucose/O₂ biofuel cells using a commercially available air-breathing platinum cathode. The electrochemical approximation of film thickness, distribution of ferrocene throughout the films, and the effect of pH on the biofuel cell will all be discussed.
A series of semi-fluorinated Diels–Alder polyarylene copolymers were synthesized by copolymerization of 1,4-bis(2,4,5-triphenylcyclopentadienone)benzene with 1,4-diethynyl-2,3,5,6-tetrafluorobenzene and 1,4-diethynylbenzene as co-monomers. The feed ratio of the fluorinated and non-fluorinated diethynylbenzene co-monomers was varied to allow systematic variation in the level of fluorination in the resulting polyarylene copolymers from 0 to 100 mol%. The semi-fluorinated polyarylene copolymers were characterized by $^1$H and $^{19}$F NMR, ATR–FTIR, elemental analysis, TGA, DSC, DMA, GPC, water contact angle analysis, and refractive index measurements. $^{19}$F NMR spectroscopy confirmed the addition of fluorine into the copolymers, while FTIR spectroscopy and elemental analysis established a linear correlation with increasing fluorine content as the feed ratio of the fluorinated monomer increased. Thermal analysis showed little change in the series of copolymers for onset of decomposition ($T_d = 550 \, ^\circ\text{C}$), however, the char yield increased dramatically as more fluorine content was added to the polymer (55 to 75%). Water contact angle analysis showed minimal surface effects; 100 mol% fluorinated monomer compared to 0 mol% fluorinated monomer ($90^\circ$ versus $88^\circ$, respectively). The refractive index (RI) results nicely showed the lowering of the RI as more fluorine content was added to the copolymer.
In recent years quantum dot materials have become the subject of intense research interest in a number of areas including photovoltaics\(^1\), optoelectronics\(^2\), and biological sensing\(^3\). Quantum dots have been synthesized from a number of materials, but those of silicon (SiQDs) are of special interest due to silicon’s natural abundance, relatively low cost, ease of processing, and biological compatibility.

While hydride-terminated SiQDs are luminescent, their usefulness can be greatly increased by surface modifications that can modify their bandgap, increase their stability in ambient conditions\(^4\), change their solubility\(^4\), increase their quantum yield\(^5\), and make them suitable for biological applications\(^3\).

In this work, we present two novel methods for the passivation and functionalization of hydride-terminated SiQDs. First, we show that passivation with certain conjugated organic ligands produces SiQDs that exhibit a modified bandgap (as shown by red-shifts in the photoluminescent (PL) spectra), and that the extent of ligand-dot energy transfer can be controlled by changing the diameter of the SiQDs. Several ligand-dot systems are presented, showing that the extent of bandgap modification and location of HOMO and LUMO can be controlled. In addition, we show passivation with siloxane moieties (applied for a number of years on bulk silicon\(^6\), and, more recently, on SiQDs\(^4\)) with silanols by a new catalytic process, utilizing relatively mild conditions\(^4\), which show blue-shifted PL spectra.

Trifluorovinyl aryl ether (TFVE) functionalized silicotungstic acid has been copolymerized with other TFVE monomers, resulting in a water stable film. Polymerization occurs via thermally induced cyclo-polymerization, forming perfluorocyclobutyl groups. Perfluorocyclobutyl polymers have been shown to have several properties that are ideal for high temperature fuel cell operation including high Tg, high dielectric constant, and chemical stability [1]. Silicotungstic acid, an inorganic super acid, is able to retain tightly bound water and conduct protons above 100 °C [2]. Both the acid functional group and the backbone of this novel polymer are suitable for high temperature and low humidity proton exchange membrane fuel cell (PEMFC) operation. The disappearance of the IR peak at 1833 cm⁻¹ and appearance at 961 cm⁻¹ are indicative of depletion TFVE groups and the formation of perfluorocyclobutyl groups, respectively [3]. 19F NMR has also been used to confirm polymerization has occurred, by disappearance of peaks at -120, -127, and -134 ppm, corresponding to the three fluorines of the TFVE group [4]. Preliminary proton conductivity over 0.40 S/cm at 80 °C and 95% RH has been achieved with an unoptimized membrane.

A series of novel poly(fluorene), poly(3-hexylthiophene), and poly(p-phenlyne) derivatives bearing alternating cyclopentadienyl-based repeat units were synthesized using Suzuki-Miyaura cross-coupling methods. The spectroscopic and (spectro)electrochemical properties of this novel class of π-conjugated systems will be presented and compared against their aromatic congeners.
POLY 250: Modifying the bandgap of ITO and ZnO by 2eV using novel conjugated aromatic phosphonic and carboxylic acid ligands

Brett W. McNichols¹, bmcnicho@mymail.mines.edu, Unsal Koldemir³, Jennifer L. Braid³, Amanda Morgenstern³, Mark E. Eberhart¹, Reuben T. Collins³, Dana C. Olson⁴, Alan Sellinger². (1) Chemistry, Colorado School of Mines, Castle Rock, Colorado, United States (2) Dept Chemistry Geochemistry, Colorado School of Mines, Golden, Colorado, United States (3) Colorado School of Mines, Golden, Colorado, United States (4) National Renewable Energy Laboratory, Chemistry and Nanoscience Center, Golden, Colorado, United States

We report on the synthesis and characterization of conjugated aromatic phosphonic and carboxylic acids, that when attached to the surface of quantum dots and electrode surfaces, can have a profound effect on the resultant optoelectronic properties such as bandgaps and workfunctions(1). It was determined that the direction and magnitude of the molecular dipole moments of the acids can be related to the eventual changes in the quantum dot and electrode properties. For example, we are able to demonstrate the tuning of ZnO and ITO electrodes by 1eV in either direction (2eV range) depending on the acid attached to the surface (2,3). Similar effects will be reported on other electrodes and quantum dots.


POLY 251: Fluorescence conjugated microporous polymers with amino receptors as metal cation chemosensor

Anting Chen², achen47@binghamton.edu, Jetty L. Duffy-Matzner¹, William E. Bernier², Wayne E. Jones². (1) Chemistry Department, Augustana College, Sioux Falls, South Dakota, United States (2) Department of Chemistry, State University of New York at Binghamton, Binghamton, New York, United States

Fluorescence Conjugated Polymers (FCPs) have drawn interest for more than two decades because of their ability of sensitively and selectively detecting metal cations in environmental and biological systems. In contrast to solution based FCPs, solid state sensing materials would provide for a more practical device approach to applications. Recently, Conjugated Microporous Polymers (CMPs) which have permanent microporosity in the solid state and extended π-conjugation have been designed and used in ultrasensitive gas sensing device. By combining FCPs and CMPs, a solid state Fluorescence Conjugated Microporous Polymer (FCMP) with a N,N,N'-trimethylethyleneamino receptor was designed and synthesized using Sonogashira cross-coupling reaction [Figure 1]. Different polymerization solvents, and different activation procedures were evaluated to optimize the sensitivity of the sensor. The surface area of the resulting polymer film/powder was evaluated using the Brunauer-Emmett-Teller (BET) method. Photophysical studies including UV-vis absorption and fluorescent emission, fluorescent quantum yield and fluorescent quenching with different metal cations were carried out to establish a relationship between the porosity of the polymer and sensor sensitivity.

Figure 1: Sonogashira cross-coupling reaction between 1,3,5-triethynylbenzene and N-(2,5-dibromothiophene-3-ylmethyl)-N,N,N'-trimethylethane-1,2-diamine
POLY 252: Roles of quinoidal character, regioregularity, and polydispersity in determining the photovoltaic performance of conjugated copolymers

Tianyue Zheng¹, tyzheng@uchicago.edu, Luping Yu². (1) University of Chicago, Chicago, Illinois, United States (2) The University of Chicago, Chicago, Illinois, United States

This work covers the research about the structure, property, performance relationship about polymer solar cells (PSCs). First, an efficient synthetic method is developed for creating ladder-type, oligomeric donor monomers with fused benzodithiophene structures. These monomers are copolymerized with fluorinated thieno[3,4-b]thiophene ester to form a series of polymers which were investigated as donor materials in polymer/fullerene solar cells. Photophysical and electrochemical characterizations are used in conjunction with quantum-chemical calculations to identify the interplay of quinoidal and charge transfer character of conjugated copolymers, providing broadly applicable design rules for tuning the excitation character of conjugated copolymers. X-ray diffraction, mobility measurements, and solar cell device characterization are used to analyze neat films and bulk heterojunctions of these copolymers, demonstrating the importance of the spatial symmetry of the structure unit in determining the charge transport characteristics of conjugated copolymers. Second, the influence of polymer polydispersity on the performance of PSCs composed of PTB7 and PC₇₁BM as the active layer materials was studied to reveal that polymers exhibiting large polydispersity index (PDI) may contain structural defects that play the role of energy transfer and charge trapping/recombination centers. The results highlighted the importance of controlling PDI of donor polymers for polymer solar cells.

Effect of structure and polydispersity on photovoltaic properties of polymers
Core-shell hybrid nanostructures have attracted broad research efforts because of the wide range of their potential applications. The composite particles possess unique properties that neither the core nor shell alone can display. Recently, we developed a method to prepare covalently immobilized layers of conjugated block copolymers on the surface of superparamagnetic (SPM) nanoparticles via surface-initiated chain-growth polycondensation. We chose iron oxide nanoparticles, in particular superparamagnetic magnetite, as it has been used as contrast agent for MRI applications. Conjugated polymers such as polythiophenes, poly-p-phenylenes and polyselenophenes were chosen as the organic shell. In the case of multilayered shells (consisting of block copolymers), the efficiency of energy transfer between the shell sublayers (and therefore the emissive properties of the particles) were found to be dependent on the sequence of the sublayers. Choosing which polymer would be the first sublayer grafted to the core surface was an important factor in controlling the energy transfer. Depending upon the type and proximity of the polymer shell to the core, we observed different extent of fluorescent efficiency and excitation quenching. Control experiments were also carried out on hybrid particles having silica cores without the magnetic component.
Organic π-conjugated polymers have applications in electronic devices, including photovoltaics and light-emitting diodes. Gradient and block copolymer additives have been shown to stabilize the morphology of organic photovoltaic devices over time. These copolymers can be synthesized via a chain-growth cross-coupling polymerization using nickel-based catalysts with chelating phosphine ligands. However, a slow initiation rate (relative to the propagation rate) leads to some loss of sequence control and broader dispersities. Because the turnover-limiting step for both initiation and propagation is the same (reductive elimination), the only way to selectively accelerate the initiation rate is to modify the precatalyst. Our approach has involved using reactive ligands that undergo fast reductive elimination with the monomer. We have prepared a series of precatalysts with aromatic and heteroaromatic reactive ligands with the goal of accelerating precatalyst initiation. The initiation rates for each precatalyst were measured using both $^{19}$F NMR and IR spectroscopies. Consistent with our hypothesis, precatalysts with fast initiation rates were shown to generate polymers with narrower dispersities and presumably, better sequence control.
POLY 255: Growing green polymers using the sun: Organocatalyzed photoredox mediated polymerization

Jordan C. Theriot, JCTHERIOT@GMAIL.COM, Garret Miyake. Chemistry and Biochemistry, University of Colorado, Boulder, Denver, Colorado, United States

Polymers are undeniably one of the most important and useful materials to ever be produced. Over half of the 200 million tons of polymers produced annually are synthesized through radical polymerizations, which typically require energetically demanding conditions (e.g. elevated temperatures or UV light). Here, we present a greener alternative to produce well-defined polymers: a controlled radical polymerization (CRP) that uses a photoredox organocatalyst and visible light to initiate and reversibly deactivate a polymerization. This presentation will discuss our research in the development of this photoorganocatalyzed variant of atom transfer radical polymerization (ATRP). Effects of catalyst structure on the scope of polymerization as well as mechanistic insights will be discussed.
The presence of a dynamic bond in a polymeric assembly, by virtue of its reversible nature, enables the system to reconfigure its molecular architecture and provides a mechanism for controlled release of small molecules such as dyes, drugs, and fragrances. We demonstrate the formation of oxime-functional macromolecular stars that are able to dissociate and reconstruct themselves upon application of a stimulus. The reversible nature of the oxime bond in the presence of externally added alkoxyamines or carbonyl compounds enables reconfiguration via competitive exchange. Reversible addition-fragmentation chain transfer (RAFT) polymerization was utilized to prepare well-defined amphiphilic block copolymers in which a hydrophobic keto-functional block allowed self-assembly into micelles in water. Adding a difunctional alkoxyamine small molecule to these solutions resulted in crosslinking of the micelles to yield macromolecular stars. The reversible nature of the O–alkyl oxime linkages was demonstrated via competitive exchange with excess of carbonyl compounds or monofunctional alkoxyamine under acidic conditions and at elevated temperatures to result in dissociation of the stars to unimolecular oxime-functional polymer chains.
The exquisite nanostructure control of block copolymers covers a wide range of different morphologies having 0D-3D continuity. There is much promise with the recent development of optical metamaterials from block copolymers with chiral morphologies, yet the predictable control of nanoscale chirality in 3D morphologies has remained largely elusive. Others have recently demonstrated precise control over 1D-continuous helical morphologies by employing a unique chiral-crystallization phenomena with enantiopure poly(lactide)s. Here we probe how this additional energetic parameter can be applied to new systems with addition constraints. We have prepared a range of poly(hexyl acrylate-b-styrene-b-L-lactide)s (HSL) as model ABC triblock terpolymer systems where the enantiopure poly(L-lactide) has a tunable crystalline character. We explore how new parameters including the degree of crystallinity and crystallite size balance with the typical enthalpic and entropic processes governing polymer self-assembly. The insights provide a new degree of control over the chirality transfer from the molecular backbone to the nanoscale morphology. We anticipate that further studies will enable the extension of these concepts to the facile fabrication of a range of advanced chiral nanomaterial based devices.
Nanoscale science and technologies has been developed tremendously during the last two decades, introducing a variety of nanomaterials with unique properties. However, incorporation of the properties into macroscale functional applications has been limited. An essential challenge is the integration of such unique properties into assemblies for micro- and macroscale devices and discovering appropriate conditions under which this can be accomplished. Here we explore the self-assembly of nanoparticles (NPs) in solid-state under external stress for discovering fundamental understandings of mechanisms and various engineering applications. 1. Yoonseob Kim et al. *Nature*, 2013, 500, 59-63 first demonstrated an example of excellent stretchable conductors from self-assembly of spherical NPs in solid-state. Free-standing stretchable conductors were assembled by layer-by-layer assembly. High conductivity and stretchability were observed and the properties originated from dynamic self-organization of NPs under stress. Modified percolation theory to incorporate the self-assembly of NPs gave excellent match with experimental data. 2. The current study demonstrated the chiroptical activities of NPs in solid-state for the applications of biosensing devices and optoelectronics. Unconventional transfer of macroscale stresses shaped nanoscale assemblies with handedness. Chiroptical responses were reversibly tunable by controlled stresses. Computational simulation supported the chiroptical properties originated from self-assembly of NPs in solid-state.
The objective of this research is to understand how to effectively use cellulose nanocrystals (CNCs) produced at pilot scale as additives to thermosetting polymer matrices. CNCs were incorporated into a waterborne epoxy resin following two processing protocols. These processing strategies varied only by order of addition and adhered to a stoichiometric ratio of epoxy prepolymer to amine hardener. Nanocomposites made by first premixing an aqueous CNC suspension with the epoxy prepolymer followed by addition of the amine hardener (2-step mixing) showed enhanced dispersion compared to composites made by mixing all components at once (1-step mixing). The degree of dispersion was qualitatively assessed with polarized light microscopy. The dispersion mechanism was probed with zeta potential analysis and scanning electron microscopy (SEM). The zeta potential of an epoxy/CNC/water mixture indicated a dependence on CNC concentration. This result revealed an electrostatic association between the epoxy prepolymer and CNC. SEM visually confirmed an epoxy/CNC association. The improved dispersion resulted in a 49 and 30% increase in the glassy storage modulus ($E'$) of a 5 and 10 wt.% composite, respectively. While the glass transition temperature increased with CNC concentration for both processing strategies, the increase was greater for 1-step mixed composites with a decrease in $T_g$ of approximately 5 °C across all concentrations tested for the 2-step mixed composites. The processing method did not impact thermal degradation patterns or the moisture content of the samples. Although the CNC concentration did impact the onset of thermal degradation, the extent to which it did was not as great as expected as predicted by the rule of mixtures. The model correctly predicted onset of thermal degradation for a 2 and 5 wt.% composite and under predicted for the 10 and 15 wt.% case. Overall, these results highlight the importance of understanding processing-structure-property relationships in these nanocomposites as they are considered for higher volume applications and provide a path forward for further materials design opportunities.
Two complementary reactions have been developed to facilitate post-functionalization of poly(methionine) (poly(Met)). These reactions can be utilized to introduce a wide range of functionality and to control polymer conformation. We have found that numerous alkylation reagents react with poly(Met), allowing access to sulfonium derivatives functionalized with oligoethylene glycol (OEG), sugars, and other functional groups. Subsequently, these conjugates can be further derivatized into S-alkyl homocysteine derivatives. Using these complimentary processes, we synthesized a library of thermo-responsive OEGylated homocysteine derivatives from poly(Met). These polymers display a range of tunable cloud points, allowing us to establish structure-property relationships for the series.
POLY 261: Understanding and improving protein loading in PLGA-PEG nanoparticles

Sunandini Chopra¹, schopra@mit.edu, Jong-Min Lim¹, Omid Farokhzad², Rohit Karnik¹. (1) Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (2) Anaesthesiology, Brigham and Women’s Hospital, Boston, Massachusetts, United States

Polymeric nanoparticles (NPs) are emerging as promising protein drug delivery carriers for both oral and parenteral methods of administration. However, the process of protein loading and the location of the protein drug within the polymeric NPs remains unclear. A good understanding of the mechanism of protein loading is imperative for designing more efficient drug delivery systems. In this study, insulin and Poly (lactic-co-glycolic acid) –Poly (ethylene glycol) (PLGA-PEG) NPs are used as model protein and polymeric drug delivery carriers respectively. Here, we show that electrostatic interactions play a key role in mediating the formation of these NPs. It is also observed that most of the protein molecules interact with the corona of the NPs instead of the core. The application of anionic polymers and chelating ions helped to achieve up to 11-fold increased loading. These results provide a deeper insight into the formation of protein loaded polymeric NPs synthesized by nanoprecipitation method, which can lead to improvement and development of future protein drug delivery systems.

Insulin loading is the same when it is added after NP synthesis but its hydrodynamic radius changes and is similar to the size of an empty PLGA-PEG NP (** p < 0.05).

Insulin loading increases 20 fold on washing the NPs with only water and not PBS but the hydrodynamic radius remains unchanged (** p < 0.05).
Amphiphilic block copolymers are of considerable interest due to their applications as emulsifier, dispersant, stabilizers, compatibilizers, etc. In the present study, a range of poly(2-oxazoline) (POx)-based amphiphilic block copolymers were synthesized using 4-cyano-4-(dodecylthiocarbonothioylthio)penty1-4-methylbenzenesulfonate (CDPS) as a dual initiator for reversible addition-fragmentation chain transfer (RAFT) polymerization and cationic ring-opening polymerization (CROP) in a one-step procedure. Methyl (meth)acrylate, butyl (meth)acrylate, tert-butyl (meth)acrylate, and N-isopropylacrylamide were polymerized for the hydrophobic block, and 2-methyl-2-oxazoline and 2-ethyl-2-oxazoline were used as the hydrophilic block. RAFT polymerization and CROP proceeded independently in a controlled manner and resulted in amphiphilic block copolymers with a narrow molecular weight distribution. CDPS was found to be a useful dual initiator for the one-step synthesis of POx-based amphiphilic block copolymers via a combination of RAFT polymerization and CROP.
POLY 263: New binuclear α–diimine nickel catalysts for ethylene polymerization

Abdulhamid A. Alsaygh, asaygh@gmail.com. National center for Petrochemical Technology, King Abdulaziz City for Science & Technology, Riyadh, Saudi Arabia

Bi-nickel centered catalyst [Py$_2$C=N-C$_6$(CH$_3$)$_4$-N=CPy$_2$ Ni$_2$Br$_4$] was prepared by Schiff-base condensation of dipyridylketone with 2,3,5,6-tetramethylphenyleneamine, and subsequent metathesis reaction with (DME)NiBr$_2$. Comparing with mono-nickel-center catalysts, the new catalyst demonstrated much higher catalytic activity. The catalytic activity and the properties of the obtained polymer were dependent on the reaction condition. The resultant polyethylene possesses high branching, low molecular weight and polydispersity ranging from 2.64 to 4.33. The catalyst activity reached up to 6.26×10$^2$ KgPE/h.Ni.bar, at 24°C, with Al (MAO)/Ni ratio at 800. These nickel precatalysts are of potential industrial interest for the production of polyethylene waxes and lubrications.
Star polymers are an interesting class of macromolecules possessing polymeric arms extending radially from a core center. In our growth from strategy, the core can be synthesized by incorporating multiple initiating sites for the polymerization of carbodiimides taking advantage of the recently reported Ni(II) mediated living polymerization. When incorporating chiral side chains, these star polymers are produced possessing single-handed helical, rod-like polycarbodiimide arms. The star architecture imparts a new set of intriguing properties that include self-assembly in different solvents and liquid crystallinity. Here, we report synthesis of a star polymer by using core-first method. The initiating core can be synthesized via trimerization of 3-methyl-4-bromobenzonitrile to yield a triazine ring with three aryl bromide initiating groups. In the presence of triphenylphosphine, the nickel(0) center of bis(1,5-cyclooctadiene) nickel(0) (Ni(COD)2) will undergo oxidative addition into aryl bromide bond to yield a core with three [bis(triphenylphosphino)aryl]nickel(II)bromide complex in its periphery. Exposed to carbodiimides, the tris-Ni initiators grow helical arms in a controlled fashion. The preparation of these helical stars and their solution and solid-state characterization by tapping-mode atomic force microscopy (TM-AFM), powder X-ray diffraction (XRD), electronic circular dichroism (ECD), vibrational circular dichroism (VCD), differential scanning calorimetry (DSC) and dynamic light scattering (DLS) will be discussed.

Fig. Synthesis route and AFM images for star polymer
Sodium p-styrene sulfonate (NaSS) is an industrially important anionic monomer manufactured from organic bromine compound. NaSS and its (co)polymer are widely used in many applications, such as emulsion, dyeing improver, finishing agent for clothes, dispersant, antistatics, ion exchange membrane, scale inhibitor, and oil field chemicals, etc.

Water-soluble copolymers of NaSS with water-soluble monomers, such as acrylic acid, methacrylic acid, acrylonitrile, and acrylamide, are well known. In contrast, copolymers with water-insoluble monomers have been scarcely reported.

We report the copolymerization of Sodium p-styrene sulfonate (NaSS) with N-substituted maleimide, their properties, and application.

Homogeneous radical copolymerization was conducted in water-based solution at 60°C. Copolymerization of equimolar NaSS with N-phenylmaleimide (N-PMI) proceeded smoothly in a homogeneous system and generated water-soluble polymer (PM-5005). It was assumed that the copolymerization reaction progressed in an alternative manner, similar to styrene with N-PMI.

PM-5005 showed higher surface activity than the equimolar styrene copolymer (ST-5005) due to the higher weight content of hydrophobic component in PM-5005 (45 wt%) compared to ST-5005 (34 wt%). Moreover, PM-5005 showed markedly higher viscosity than ST-5005 and NaSS homopolymer. This specific viscosity was not observed when N-benzylmaleimide (N-BMI) or N-cyclohexylmaleimide (N-CHMI) were used instead of N-PMI. This result suggested that this specific viscosity was attributed to the difference of polymer conformation as well as the monomer sequences and the content of hydrophobic component.

PM-5005 can be expected as a heat-resistant thickener and a dispersant for CNT, etc. We will report more detail about the properties and application of these NaSS/N-substituted maleimide copolymers on the day.
POLY 266: Synthesis, morphological behavior, and ODT of poly(cyclohexadiene)-based copolymers

Konstantinos Misichronis, kmisichro@gmail.com, Jihua Chen, Keum J. Kahk, Adam Imel, Mark D. Dadmun, Justin G. Kennemur, Frank S. Bates, Jimmy W. Mays, Kunlun Hong, Apostolos T. Avgeropoulos. (1) Bldg 8610 MS 6494, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States (2) Univ of Ioannina MAT SCI Eng, Ioannina, Greece (3) Univ of Minnesota, Minneapolis, Minnesota, United States (4) Center for Nanophase Materials Science, Oak Ridge National Lab, Oak Ridge, Tennessee, United States (5) Neutron Science Directorate, Oak Ridge National Lab, Oak Ridge, Tennessee, United States (6) Chemistry, University of Tennessee, Knoxville, Tennessee, United States (7) Chemistry & Biochemistry, Florida State University, Tallahassee, Florida, United States

The synthesis, via anionic polymerization, and characterization of a series of linear diblock copolymers of the PS-PCHD [PS: polystyrene and PCHD: poly(cyclohexadiene)] type was performed. A wide range of volume fractions was chosen (0.25 < φ_PS < 0.94) in order to study the morphological behavior of this system in great extent. The results indicated that all samples exhibited low molecular weight distribution and molecular as well as compositional homogeneity. The morphological characterization of the BCP’s was performed via TEM, SAXS and rheology was used for the first time in this kind of system in order to determine the interaction parameter χ. Unique morphologies, like the core-shell cylinders and the 4-layer, 3-phase lamellae are exhibited providing new information concerning the self-assembly of the PS-PCHD copolymers and their potential use in nanopatterning applications.

Figure 1: Hexagonally closed pack cylinders of a PS-PCHD copolymer after annealing above Tg.
Functionalized PEG derivatives are finding ever-increasing applications in the areas of pharmaceuticals and targeted drug delivery by their judicious incorporation into nanoparticle-forming polymeric systems. We are investigating a range of novel bifunctional azido-PEG derivatives that possess terminal hydroxyl-, carboxylate-, methoxy-, amino- and alkynyl-moieties and sought to identify a simple, rapid, and robust method to quantitatively determine the level of azide substitution in our intermediates.

In this poster, we describe the synthesis of a range of novel bifunctional azido-PEGs (I), their uncatalyzed click reactions with a range of dipolarophiles, and identification of optimal conditions to afford triazoles (II), which may be utilized to quantitate their level of azide substitution.

Figure 1. Click reactions of PEG azides with dipolarophiles
In this study, glycidol was polymerized by cationic ring-opening polymerization (initiated by BF$_3$) in dichloromethane in the presence of a variety of ethers. The ethers chosen were: diethyl ether, diglyme, MTBE and THF. In some cases, the polymerization was carried out in neat ether. The ethers were examined for their ability to emulsify the reaction mixture, with the goal of obtaining high molecular weight hyperbranched polyglycidol. Glycidol was also polymerized in the absence of emulsifier, as a control. All polymerizations were monitored by gas chromatography, and were quenched upon completion by addition of water. The polymer was recovered by evaporation of the solvent and subsequent drying on a lyophilizer and tested for solubility in various solvents. The polyglycidols thus obtained were also analyzed by differential scanning calorimetry (DSC), FTIR, gel permeation chromatography (GPC) and NMR (1H and 13C). These analyses revealed that glycidol copolymerized with THF under these reaction conditions. There was, however, no noticeable effect of the other emulsifying agents on the polymerization or on the molecular weight of the polyglycidol obtained.
Electrophilic trisubstituted ethylenes, alkoxy ring-substituted butyl 2-cyano-3-phenyl-2-propenoates, RPhCH=\(\text{C(CN)CO}_2\text{C}_4\text{H}_9\) were prepared and copolymerized with styrene. The monomers were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-substituted benzaldehydes and butyl cyanoacetate, and characterized by CHN analysis, IR, \(^1\)H and \(^{13}\)C-NMR. All the ethylenes were copolymerized with styrene in solution with radical initiation (ABCN) at 70°C. The compositions of the copolymers were calculated from nitrogen analysis and the structures were analyzed by IR, \(^1\)H and \(^{13}\)C-NMR.
Polymer brushes have been studied extensively and continue to be a topic of interest due to their unique properties that result from the structure that is imposed on the covalently surface-attached polymer chains. Until recently, research focus has only investigated the surface polymerizations of conventional vinyl monomers using well-understood living polymerization techniques such as RAFT and ATRP, which produce brushes of random coil polymers. In contrast, the understanding of rigid rod polymer brushes is in its infancy and our work aims to understand the underlying structure and properties of such systems. We have adopted a chain-growth condensation rigid rod polyaramid from literature, designed a functional initiator that can be grafted to a silicon substrate, and successfully grew polyaramid brushes from a monomer solution, demonstrating the first examples of rigid-rod polyaramid brushes in literature. Lessons learned from these studies can be applied to the design and development of new chain-growth condensation brushes that would have the potential to demonstrate some very impressive properties due to molecular ordering.
One of the most widely employed families of hyperbranched polymers (HBPs) utilizes 2,2-bis(methylol) propionic acid (bis-MPA) as a branching monomer. HBPs of this type contain numerous hydroxyl end-groups. The location of the hydroxyl end-groups within the dendritic structure is still rather elusive. Furthermore, as the generation number, or number of layers of repeat units varies, the distribution of the hydroxyl end-groups within the structure changes. Thus, determining the chemical reactivity of the hydroxyl groups, as well as determining the reactivity as a function of generation number, will aid in better synthesis, modification, and application of these bis-MPA HBPs. The second (H20) and fourth (H40) generation bis-MPA HBPs were functionalized with hexyl isocyanate and the reaction kinetics were monitored via $^1$H nuclear magnetic resonance (NMR) spectroscopy. In addition to the linear and terminal hydroxyl groups, the formation of a third-type of hydroxyl group, called ‘pseudo-linear’, was observed in the NMR spectra.
Poly(N,N-(dimethylamino) ethyl methacrylate-b-poly(ethylene glycol) methyl ether methacrylate-b-lauryl methacrylate) triblock copolymers were synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization, and characterized by GPC and $^1$H NMR spectroscopy. They exhibited high interfacial activity which could be tuned by simply adjusting the solution pH, and remarkably reduced the interfacial tension of dodecane/water as well as heavy crude oils. With a low copolymer concentration of 0.05 w/v %, the apparent viscosity of Shengli crude oil was reduced from 34000 to 350 mPa·s after emulsification with the help of the obtained copolymers at 20 °C, and the formed emulsion exhibited long-term stability for more than 3 months.
Poly(ether ether ketone)s (PEEK) have unique thermal stability, solvent resistance and mechanical properties. Since the original synthesis of PEEK, many modifications have been made to enhance their properties. Previously, PEEK monomers having oxyalkylene linkages were synthesized and polymerized in typical AA + BB polymerization reactions using NAS conditions. Two AB versions of these monomers (4-fluorophenyl)(4-(2-(4-hydroxyphenoxy)ethoxy)phenyl)methanone and 4-(2-(4-phenoxyphenoxy)ethoxy)benzoic acid have been synthesized and polymerized by typical NAS (Potassium Carbonate, Toluene, NMP) and Friedel-Crafts (MSA, Phosphorous Pentoxide) procedures, respectively.
POLY 274: Synthesis of eumelanin-inspired polyindoles

K. A. Niradha Sachinthani, niradha@okstate.edu, Toby L. Nelson. Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma, United States

Melanins are naturally occurring pigmentary polymeric networks found in skin, hair, eye and brain of mammals. Eumelanin, a brown-black biopolymer, is the most common form of melanin, which is composed of 5,6-dihydroxyindole and 5,6-dihydroxyindole-2-carboxylic acids. It is known as photoprotective agent due to its high degree of conjugation, and extremely higher absorption of ultraviolet and visible radiation. Eumelanin biopolymers have also been proposed for optoelectronic and photovoltaic applications but isolation of natural eumelanin is a difficult task. Therefore, it is beneficial to synthesize synthetic eumelanin materials, which mimics the natural pigment. Currently, we have synthesized an eumelanin-inspired indole core, methyl 4,7-dibromo-5,6-dimethoxy-N-methyl-1H-indole-2-carboxylate which can serve as a new building block for organic semiconductors. Here, we present our efforts toward the synthesis and characterization of eumelanin-inspired polyindoles using different cross coupling methods such as Suzuki Miyaura and Grignard Metathesis.
POLY 275: Synthesis of fluorescently labelled sodium polystyrenesulfonate via atom transfer radical polymerization

Paul Balding¹, pbalding3@gatech.edu, Alyssa M. Blake¹, Paul S. Russo², Wayne Huberty³, Rafael Cueto⁴. (1) Georgia Institute of Technology, Atlanta, Georgia, United States (2) Chemistry, University of Minnesota, Baton Rouge, Louisiana, United States (3) Louisiana State University, Baton Rouge, Louisiana, United States (4) 101 LSU Union Bldg, Louisiana State University, Baton Rouge, Louisiana, United States

The efficacy of an atom transfer radical polymerization (ATRP) approach in the synthesis of optically tagged poly(styrenesulfonate) sodium salt (NaPSS) was analyzed using gel permeation chromatography coupled with multiple-angle light scattering (GPC/MALS). Completely sulfonated NaPSS was achieved by direct synthesis of monomeric 4-styrenesulfonic sodium salt with a fluorescein isothiocyanate (FITC) labelled 4-vinylaniline monomer incorporated as the optical tag. The concentration of FITC conjugated to the 4-vinylaniline monomer was varied to control the degree of fluorescence intensity of the final polymer. UV-VIS analysis confirmed the ability to tune the degree of tagging NaPSS with FITC. Extensive dialysis was conducted to remove unreacted FITC from the polymer solution to ensure that the optical properties were solely accounted for by tagged polymer. The addition of sodium chloride salt to the aqueous reaction system suppressed the deactivator hydrolysis from the Cu(I) metal to allow for a slower and more controlled polymerization. The realization of high molecular weight (Mₚ), up to 900 000 g/mol, and a polydispersity index (PDI) as low as 1.02 indicate the efficacy of this synthetic approach.

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A ruthenium-based solid-supported metathesis catalyst system was investigated for its propensity to form cyclic poly(alkenamer)s over linear poly(alkenamer)s. This system was used in the ROMP of a variety of cycloalkene monomers and produced the resulting poly(alkenamer)s in good yield; additionally, linear polymers of these cycloalkenes were synthesized via ROMP using traditional Grubbs-type metathesis catalysts. The presumed cyclo poly(alkenamer)s and linear poly(alkenamer)s were envisioned to possess sufficiently disparate physical properties to discriminate them from one another. This hypothesis was tested using both melt- and solution-state samples of cyclic and linear poly(alkenamer)s in conjunction with physical blends thereof; this general process was predicted to provide a means to quantitate the cyclic:linear poly(alkenamer) ratio and thus provide the information necessary to optimize the cyclo polymerizations to maximize this ratio. Additionally, novel ionophore-functionalized cyclooctene derivatives were synthesized to enhance the solubility properties of the resulting polymers in polar media and thus enable methods of analysis which are incompatible with traditional poly(alkenamer)s.

The synthetic scheme for cyclic polyoctenamers and polypentenamers via ring-expansion metathesis polymerization.
POLY 277: Synthesis and characterization of eumelanin-inspired ethynylene-linked polymers

Santosh Adhikari, santoshpeace@yahoo.com, Subhashini Selvaraju, Toby L. Nelson. Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma, United States

Melanins are naturally occurring pigment found in hair, eye, skin and brain of mammals. Eumelanin is a type of melanin which is responsible for the brown and black coloration and it has extremely high light absorption ranging from 200 to 600 nm in the electromagnetic spectrum. It is known to be a heterogeneous network, formed by two monomers 5,6-dihydroxyindole and 5,6-dihydroxyindole-2-carboxylic acid. In 1974, Eumelanin was established as an amorphous organic semiconductor with the work of Proctor and McGinness. Currently, we have synthesized a eumelanin-inspired indole core, methyl 4,7-dibromo-5,6-dimethoxy-N-methyl-1H-indole-2-carboxylate which can serve as a new building block for organic semiconductors. From this indole core, a series of small molecules have been synthesized with different alkynyl substituent at the 4, 7 - positions that alter the optoelectronic properties. Here, we will present the synthesis and characterization of eumelanin-inspired ethynylene-linked polymers.
POLY 278: Synthesis and characterization of alkoxy-functionalized polyselenophenes

Devang Khambhati, dev.khambhati@okstate.edu, Toby L. Nelson. Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma, United States

Regioregular poly(3-alkylthiophenes) (rr-P3ATs) have shown to be one of the most promising conjugated polymers (CPs) for organic electronics. Researchers have demonstrated that optoelectronic properties can be altered by substituting thiophenes with selenophenes to produce poly(3-alkylselenophene)s. The incorporation of electron rich side chain e.g. alkoxy groups at the 3-position on the thiophene ring yields poly(3-alkoxythiophenes) (P3AoT) with reduced bandgaps compared to rr-P3AT. Herein, we report the synthesis and characterization of alkoxy-functionalized polyselenophenes (PAoSe), which have lower bandgap compared to P3AT and P3AoT. These materials are promising candidates for organic electronic devices.
Melanins are the primary determinant of pigment in mammals and plants. 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. Currently, we have synthesized several eumelanin-inspired molecules that display interesting optoelectronic properties. Our efforts toward the synthesis and characterization of eumelanin-inspired copolymers with different phenylenevinylene moieties will be presented.
Naturally occurring antimicrobial peptides (AMPs) are amphipathic molecules that eliminate a wide range of bacteria and are found in a variety of eukaryotic organisms. Unlike current synthetic antibiotics, bacteria do not appear to develop resistance to AMPs, and these peptides are highly selective. Synthetic mimics of AMPs are of interest for their potential cost effectiveness and ability to target specific bacteria. Statistical copolymers of aminopropyl methacrylamide (APMA) (lysine mimic) and guanadinopropyl methacrylamide (GPMA) (arginine mimic) were synthesized via aqueous RAFT polymerization. Antimicrobial activity against E. coli, S. aureus, and P. aeruginosa was evaluated. Specific compositions provided high activity and selectivity. Attempts to determine mechanism of activity will be described.
POLY 281: PEGylated O₂-riched enzyme conjugatable polymer for long-term high performance electrochemical glucose sensors

Zhe Li\textsuperscript{1}, lizhe.jerry@gmail.com, Sagar Vaddiraju\textsuperscript{2}, Fotios Papadimitrakopoulos\textsuperscript{3}. (1) Institute of Material Science, Polymer Science, Storrs, Connecticut, United States (2) UCONN, Storrs, Connecticut, United States (3) University of Connecticut, Storrs Mansfield, Connecticut, United States

The function and lifetime of an implantable CGM device are intimately linked with the stability of the glucose oxidase (GO\textsubscript{x}) enzyme, responsible for glucose detection. Biofouling, co-substrate inefficiency and enzyme denaturation are major concerns for long-lived implantable devices. Poly(ethylene glycol) (PEG)-ylated polymer offer an opportune venue to minimize biofouling, while retaining their highly hydrated state to prevent enzyme denaturation. In this contribution, to provide extra co-substrate supply while allowing for minimizing protein absorption and enzyme leaching, we report the synthesis and characterization of a random copolymer based on PEGylated side chains together with cinnamyl ethyl methacrylate (CEMA) and glycidyl methacrylate (GMA) (namely poly(PEGMEM-CEMA-GMA)) and utilized for redox enzyme-based devices. The mixture of this polymer and GO\textsubscript{x} enzyme was incubated for 24 hour to realize the reaction between the GO\textsubscript{x}-amine and GMA-epoxide group. The glucose sensor was made by simply dip-coating into above mentioned mixture followed by being exposed to ammonia vapor overnight. This dip-coated enzyme-polymer layer affords improved stability and activity for the immobilized GO\textsubscript{x} enzyme, while reducing non-specific protein fouling by an order of magnitude. The sensors showed improved sensitivity (150 nA·mM\textsuperscript{-1}·mm\textsuperscript{-2}) as well as significant better linearity ($k_m$ of 50 mM). Continuous \textit{in vitro} sensor testing in phosphate buffer saline (PBS) shows enhanced stability with only 15% in gradual loss of sensitivity over 90 days. These results indicate the potential importance of this type of amphiphilic random copolymer as host matrices in various enzyme based device platforms.
Recent advancements in 3-D printing technology have highlighted the need to develop new polymeric inks for advanced biomedical and industrial applications. The scientific community has made remarkable advancements so far in building customized printers, but few reports are focused on development of polymers that can be used in commercially available 3-D printers. Research done, with commercially available 3-D printers in the biomaterials field, has been so far focused on use of polymer inks such as polylactide and polycaprolactone. The limiting factor of available polymers could be due to the fact that polymeric inks for fused deposition modeling (FDM) need to satisfy the stringent requirements of appropriate melting temperatures and liquid-phase viscosity. To this effect we report the synthesis and characterization of a new family of polyesters that can be printed by commercially available FDM instrument. The printed scaffolds can be functionalized by bioactive small molecules or proteins to elicit desired biological response. The polyester microstructure and molecular weight are characterized by nuclear magnetic resonance and gel permeation chromatography respectively. The thermal characteristics are studied by differential scanning calorimetry, thermogravimetric analysis and rotational rheometry. The functionalization of surface is achieved by two distinct strategies: (i) direct reaction of surfaces with linker molecule in aqueous media followed by conjugation of protein (ii) reaction of polymer-biotin surfaces with avidin and functionalization by biotinylated proteins.
Regulation of protein activity by conjugation to polymers is important in bioengineering and biomedical applications. The stability of protein-polymer conjugates may be improved by minimizing the number of polymer chains in the conjugate, as well as by choosing the optimal site on the protein for conjugation. In this work site-directed mutagenesis was used to prepare two pyrophosphatase (PPase) mutants with reactive thiol groups near to and far from the active center, respectively. Poly (2-hydroxyethyl methacrylate) (pHEMA) and poly(2-(dimethylamino) ethyl methacrylate) (pDMAEMA) were modified by introducing a pyridyl disulfide group at the polymer chain end, which was further reacted with the thiol group on the protein surface. Conjugation of pHEMA near the active center resulted in a clear and reversible decrease (or complete loss) of protein activity due to a conformational change in the tertiary structure of the protein. In contrast, conjugation of pDMAEMA to a specific site on the PPase surface far from the active center led to a significant increase in activity and stability at acidic pH because of the prevention of protein aggregation. In summary, our results provided a general approach for efficient on-demand control of protein activity and stability based on site-specific conjugation of polymers.

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Microdialysis (MD) sampling is a diffusion-based separation method that has the ability to sample any analyte that can diffuse across the membrane. However, one challenge for MD is that for soluble proteins greater than 10 kDa, the relative recovery (RR) using 100 kDa MWCO PES membranes is between 1 and 5% at flow rates of 0.5 and 1.0 μL/min. There are two major barriers that lead to these low recovery values: nonspecific adsorption (NSA) and poor solute mass transport. To overcome these two barriers, the modification of polyethersulfone-based (PES) MD membranes has been initiated by Laccase, an oxidase enzyme that catalyzes the oxidation of phenols, polyphenols, and anilines by one-electron abstraction. Laccase has been used to modify flat sheet PES membranes using 4-hydroxybenzoic acid (4-HBA) to create a hydrophilic polymer brush network. By functionalizing the MD membranes with carboxylic acid functional groups, one can envision adding different agents to different sides of the membrane, which may increase mass transport by selectively attaching targeted affinity agents. To confirm the laccase chemistry with the MD PES membrane, XPS was used to confirm covalent attachment of 3-chloro-4-hydroxybenzoic acid. To confirm that mass transport of large molecular weight solutes was not affected by the NSA of laccase, and the addition of the polymer brush, FITC-labeled dextrans (4 and 10 kDa) were used in microdialysis recovery experiments.

This study focuses on reducing the NSA on the membrane by making the PES membrane more hydrophilic using a laccase catalyzed reaction to add 4HBA polymers onto the membrane surface. By obtaining a more hydrophilic membrane surface, irreversible protein adsorption will be reduced. Here we have shown using XPS that the attachment of 3-chloro-4-hydroxybenzoic acid is confirmed by the presence of a carbon-chlorine peak, and an increase in the carboxylic acid functional group and the ether linkage. This study also shows that laccase does not adsorb onto the membrane in a way that alters the RR of FITC-4/10, and that the optimal reaction time to attach 4HBA to a CMA 20 microdialysis probe is 2 hours for the outside and 1 hour for the luminal side of the probe.
A series of functionalized poly(arylene ether)s, PAEs, based on 3,5-difluorobenzene sulfonamides with varying groups on the sulfonamide moiety were investigated. The main goal of the project was to tune the thermal and, potentially, electronic properties of the PAEs by altering the organic groups present on the sulfonamide nitrogen atom, including combinations of alkyl, allyl, aryl, and benzyl moieties. Furthermore, the benzyl and aryl groups provide sites for the introduction of aryl bromides and iodides, which can undergo further modification via post polymerization modification chemistry. Using 3,5-difluorobenzenesulfonyl chloride as a starting material, \( N \)-phenyl-\( N \)-R-3,5-difluorobenzene sulfonamides were prepared, followed by conversion to the corresponding PAEs by reaction of 3,5-difluorobenzene sulfonamides with bisphenol A. The polymers were characterized by size exclusion chromatography, NMR spectroscopy, thermogravimetric analysis and differential scanning calorimetry. The polymers displayed moderate thermal stability in air, glass transition temperatures depending on the R group.

\[ \text{Scheme 1. Synthesis of functionalized PAEs} \]
Polymer based triplet-triplet annihilation upconversion (TTA-UC) emitters with tunable inter-chromophore distances were investigated. 9-anthrylmethyl methacrylate was chosen as the chromophore monomer and methyl methacrylate as chain extender. Poly(AnMMA-co-MMA) with different percentages of AnMMA monomer ratio were synthesized using reversible addition-fragmentation chain transfer (RAFT) polymerization. Platinum octaethylporphyrin was used as sensitizer to form TTA-UC systems. It is observed that TTA-UC intensity first increases with increasing AnMMA percentage in the polymers then decreases, and ultimately disappears even though increasing the AnMMA percentage. The results reveal the key aspects affecting TTA-UC in polymeric system, and hopefully give implication to the design of polymer-based TTA-UC systems.
POLY 287: Investigating the effects of a low refractive index counter-diffusive component in two-chemistry holographic photopolymer

Marvin Alim\textsuperscript{3}, marvin.alim@colorado.edu, Benjamin Kowalski\textsuperscript{2}, Christopher Bowman\textsuperscript{1}, Robert McLeod\textsuperscript{2}. (1) UCB 596, Univ of Colorado, Chemical Biological Eng, Boulder, Colorado, United States (2) Electrical, Computer and Energy Engineering, University of Colorado Boulder, Boulder, Colorado, United States (3) Materials Science and Engineering, University of Colorado Boulder, Boulder, Colorado, United States

A previously proposed quantitative reaction/diffusion kinetics model for two-chemistry holographic photopolymers is expanded upon to include the effects of a counter-diffusing binder component in predicting refractive index contrast (\(\Delta n\)). During holographic recording, while writing monomer diffuses from the dark fringe to the bright fringe regions as photopolymerization occurs, the more mobile non-photopolymerizable low refractive index component will diffuse in the opposing direction due to mass transport. This spatial redistribution enhances the final refractive index modulation of the recorded holographic material. Candidate low refractive index components used in commercial holographic media, poly(vinyl acetate) (PVA) and cellulose acetate butyrate (CAB), were investigated.

![Image showing the process stages: Initiation, Reaction/diffusion, Flood cure, Index profile, n]
Recent advances in polymer chemistry and material sciences have led to movements in academia and industry. Over time, progress in the field will be taught in university classrooms. As scientific discoveries are made and the field changed, the methods by which educators are teaching about such advances need to transform to keep up with the increased knowledge. A challenge with current methods of polymer chemistry education is the sheer span of intelligence, much of which is often taught through memorization and a minute amount of engagement with the materials—a daunting task for many students who learn kinesthetically. Now using a 3D-block building video game, a virtual hands-on method is described for use as a tool to teach polymer chemistry to individuals and groups of all ages, specifically targeting K-12 students. Many students from elementary school to college engage in the world of MineCraft (~17,000,000 copies sold worldwide). This sandbox game starts a player in a pixelated environment and allows them to chop, mine, and build to shape their world. Though the developers have limited the “vanilla” version to trees, rocks, farm animals and some resources, they invite the community to modify the basic platform. This presents an excellent opportunity to incorporate the concepts of chemistry into this world and to use it to teach students. To this end we have developed a mod for MineCraft called Polycraft.

Polycraft incorporates the ideas of organic and polymer chemistry into the world of MineCraft, enabling players to gather minerals and other materials, e.g. crude oil, and to traverse from raw resources into monomers, polymers, and items via realistic processing methods. In this system, individuals begin to quickly understand the underlying techniques and chemistries that go into creating plastics, such as distillation, injection molding, machining, and hydraulic fracting. This mod shows promise as a viable method for education in classrooms over polymer chemistry, which can allow for advanced science integration at a younger age.

Figure 1: A screenshot showing distillation columns, a chemical processor, and a steam cracker in Polycraft.
Functional polymers bearing a pendant vinyl group in every repeating unit have attracted great interest for their ability to be subsequently modified or crosslinked to design new polymeric materials with desirable properties tailored for certain applications. However, although the chemoselective polymerization of polar divinyl monomers has recently been achieved, a simultaneous control over chemoselectivity and stereoselectivity has been a challenge. Accordingly, this presentation will describe the first chemoselective and stereoselective, as well as controlled and efficient, polymerization of methacrylate-based bifunctional monomers by chiral, single-site ansa-metallocenium catalysts. Whereas the methacrylic double bond is isospecifically polymerized in a controlled fashion (via conjugate-addition coordination polymerization by the cationic metal center), the non-conjugated vinyl group within the monomer is left intact. The resulting highly isotactic polymers carrying the side-chain vinyl groups can be readily further functionalized, for example, through thio-ene click reactions.
Protein adsorption to biomaterial represents a key first step in many material-solution interactions. Quartz Crystal Microbalance with Dissipation (QCM-D) has emerged as a sensitive and rapid tool to study these interfacial phenomena. Herein we report the synthesis, characterization and protein adsorption profiles for several starch-containing hybrid polymers. The starch-based hybrids were synthesized by both graft-to and graft-through approach. A series of starch containing hybrid were synthesized (28%, 36%, 53% and 79%) and their protein adsorption characteristics were measured. Additionally, protein adsorption profiles of these amphiphilic graft copolymers were compared to relevant controls including polycaprolactone, PEG-g-polyurethane and urethane linked polyester (base polymer). In general, starch based hybrid polymers showed considerably lower protein adsorption compared to that of polycaprolactone acting as a control. At the same time, as the starch concentration in the hybrid increased from 28% to 53%, protein adsorption decreased significantly. These results show the versatility of starch as a biocompatible protein repellent surface modifier and advocate well for the future of polymeric material design.
POLY 291: Synthesis and characterization of new low band gap polymers containing ethyl and phenyl ester functionalized polythiophene derivatives

Devon M. Shircliff, shircldm@dukes.jmu.edu, Brycelyn M. Boardman. Chemistry and Biochemistry, James Madison University, Harrisonburg, Virginia, United States

Two new monomers 3-ethyl-2-(2,5-dibromothiophene)-3-ylacetate (1) and 3-phenylethyl-2-(2,5-dibromothiophene)-3-ylacetate (2) containing ester functionalities were synthesized to develop novel low band gap polymers. These monomers 1 and 2 were copolymerized with 2,5-bis(trimethylstannyl)thiophene to yield poly [3-ethyl 2-(thiophene-3-yl)acetate-2,2'-thiophene (PETAT) and poly [3-phenylethyl 2-(thiophene-3-yl)acetate-2,2'-thiophene (PPTAT). Additionally, these electron donating monomers 1 and 2 as well as 2,5-bis(trimethylstannyl)thiophene were incorporated with the electron withdrawing monomer, 4,7-dibromobenzo[c]-1,2,5-thiadiazole, to develop two new push-pull conducting polymeric systems; poly [3-ethyl 2-(thiophene-3-yl)acetate-2,2'-thiophene-2,6-diyl-alt-2,1,3-benzothiadiazole-4,7-diyl] (PETATBT) and poly [3-phenylethyl 2-(thiophene-3-yl)acetate-2,2'-thiophene-2,6-diyl-alt-2,1,3-benzothiadiazole-4,7-diyl] (PPTATBT). PETAT and PPTAT show a slight reduction in band gap at 1.9 and 2.0 eV as opposed to the standard poly-3-hexylthiophene (P3HT) at 2.3 eV, whereas PPTATBT and PETATBT show a dramatic reduction in the band gap as low as 1.6 and 1.7 eV respectively. UV-Visible spectroscopy of films of PETAT and PETATBT show minimal changes in the λ<sub>max</sub> versus the polymers in solution. Alternatively, films of PPTAT and PPTATBT show significant bathochromic shifts as a result of the pendant phenyl moiety of 2. The impact of the phenyl moiety was further investigated using atomic force microscopy (AFM).

UV-Visible spectra and polymeric structures of PETAT (blue), PETATBT (red), PPTAT (green) and PPTATBT (purple). UV-Visible spectrum of P3HT (dark purple) for reference.
Renewable $\alpha,\omega$-diene monomers have been prepared from ferulic acid, biosourced diols (isosorbide and butanediol) and bromo-alkenes using a chemo-enzymatic synthetic pathway then studied as monomers in ADMET polymerization. All monomers and polymers have been thoroughly characterized using NMR, GPC, DSC and TGA. ADMET polymerization was optimized with regard to the catalyst loading (Hoveyda-Grubbs II), the reaction medium (in mass vs. in solvent), and the temperature, and led to polymers with molecular weight up to 25 kDa. Thermal analysis of these new poly(ester-olefin)s showed excellent thermal stabilities (283-370 °C) and tunable $T_g$ depending on the nature of the biobased diol and the chain length of the alkene in the $\alpha,\omega$-diene monomer.
POLY 293: Electrochemical redox-unlocked smart polymeric ring

Anchao Feng¹, fac11@mails.tsinghua.edu.cn, Liao Peng², Jinying Yuan². (1) Tsinghua University, Beijing, China (2) Department of Chemistry, Tsinghua University, Beijing, Beijing, China

The precise synthesis of well-defined macromolecular structure with delicate topological architectures, such as star-, brush-, and dendritic-shaped, have attracted extensive interest in recent decade due to their broad applications in nanomaterials and bioscience. Among them, cyclic polymers, possessing an enclosed and endless structure, have become a hotspot more than 50 years. Nowadays, the dominated methods of preparation of cyclic polymers could be classified into three main categories: (i) ring-expansion polymerization, (ii) ring-closing metathesis (RCM), and (iii) head-to-end “click” cyclization. In view of the covalent linkage in preceding methods, we wonder if noncovalent bond is capable of serving as a form of connection for a polymeric ring. In present study, we exploit a smart polymeric vesicle based on the active assembly of β-cyclodextrin (β-CD) and ferrocene (Fc) into a host-guest pair. Normally, β-CD can form an exact 1:1 inclusion complex with Fc, and uncharged Fc species is strongly bound in the cavity of β-CD, whereas the charged species (Fc⁺) dissociate rapidly from the cavity. This process can be reversibly switched under external voltage. Herein, an electrochemical redox-switchable polymeric ring based on noncovalently head-to-end host-guest recognition is developed. It involves a class of telechelic linear poly(L-lactide) (PLLA) bearing β-cyclodextrin (β-CD) and ferrocene (Fc) peripheries. This linear β-CD-PLLA-Fc precursor can form supramolecular ring through terminal cyclization between β-CD and Fc species, and the noncovalently active connection has an unexpected electrochemical redox-responsiveness, that is, voltage can manipulate the polymeric ring to reversibly switch at open or closure states. It is anticipated that this supramolecular head-to-end linking would open a new methodology for “smart” ring polymers.

Schematic of linear β-CD-PLLA-Fc precursor head-to-end self-assembly into ring polymer and its reversibly voltage-switching between linear and ring macromolecules through host-guest terminal recognition.
POLY 294: Study of polymer dynamics in linear low density polyethylene by solid state NMR

Lucas Caire da Silva¹, cairelucas@gmail.com, Robert Graf², Clifford Bowers¹, Kenneth B. Wagener³. (1) University of Florida, Gainesville, Florida, United States (2) Max Planck Institute for Polymer Research, Mainz, Germany

ADMET (Acyclic Diene Metathesis) polymerization of specific α,ω-dienes has provided us with four deuterium-labeled precision linear low density polyethylene (ADMET-LLDPE) samples with a methyl branch placed at every 15th and 21st backbone carbons. The control over the polymer primary structure and deuterium position along the chain introduced by ADMET-LLDPE afforded models for Solid State NMR spectroscopy studies. Details of molecular dynamics in the crystalline structure of ADMET-LLDPE can be gained by the combined use of echo ²H NMR and CP/MAS ¹³C techniques. It has been shown that introduction of methyl groups into the crystal lattice creates defect sites which determine the local oscillation motion around the branching points (Y. Wei, R. Graf, J. C. Sworen, et al., 2009). The new four deuterium-labeled structures presented [figure 1] will give us a chance to directly detect and measure how the oscillatory motion propagates along the backbone as a function of methylene spacing between the methyl branches. Such study will provide direct observation of local dynamic in LLDPE which can be used to further extent the knowledge over the mechanical relaxation in linear polymers as a function of defects distribution along the chain. Control over the primary structure by ADMET and detailed analysis by Solid State NMR has been proven a powerful combination to study the molecular dynamics of macromolecules.

![Figure 1 - Structures of the deuterium-labeled model ADMET-LLDPE studied by solid state NMR.](image-url)
Polythiophene (PEDOT) attracts much attention because of its high electrical conductivity, good environmental stability and high transparency etc. Generally, it applies in the photochromic material of antistatic coating, organic thin film solar cell material, OLED materials, transparent electrode. However, its application is limited for the insoluble and infusible make processing difficult problem, which limits its application. This paper focuses on PEDOT improve processing performance, by chemical oxidation polymerization successfully prepared PEDOT / PSS dispersion liquid conductivity, and thus the production of the adhesion and good transparency of the antistatic coating is a main component. In this paper, ammonium persulfate was used as the oxidant, PEDOT / PSS were synthesized by chemical oxidation. During the experiment to study the PSS, influence the amount of ammonium persulfate, and the size of the theoretical solids content of PEDOT / PSS conductivity and particle size. Found that the preferred reaction conditions: the molar ratio of the acid group with a PSS in the yellow monomer is 2: 1; ammonium persulfate and monomer molar ratio of 1.5: 1 theoretical solids content in the range from 2.5% to 4.0%. With homemade PEDOT / PSS formulated into anti-static coating, applied to the PET sheet, the surface resistance of $10^5 \Omega \sim 10^8 \Omega$, which reached the antistatic coating requirements.
Because of their inherent biocompatibility and biodegradability, polysaccharides are ideal polymers for a variety of biomedical applications, such as serving as nanoparticles for controlled drug delivery. However, the syntheses and construction of sugar-containing nanoparticles are very challenging. Herein we report the synthesis of a novel sugar amphiphilic copolymer polyhydroxysaccharides-block-polylactides and a successful construction of nanoparticles.

2,3,4-tri-O-allyl-1,6-anhydro-a-D-glucopyranose (2) was synthesized as the monomer, and efficient polymerization was achieved when using BF₃·OEt₂ as a catalyst, which gave α-1,6-glycosylated polysaccharides (3) with molecular weight of 21 kDa. The co-polymerization with lactide via ring-opening polymerization (ROP) was efficient, giving co-polymers (4) with molecular weight of 24 kDa. The subsequent oxidation of the allyl groups using OsO₄ gave amphiphilic copolymer (5), which was used to construct sugar-coated nanoparticles with TEM sizes of 10 ± 2 nm.
In the present work, we have developed a graphene based polyurea composites of enhanced mechanical properties for structural applications. Graphene having the unique properties of high mechanical strength, electrical conductivity and thermal conductivity has become a center of nanomaterials research. Having strong Vander walls force between the graphene sheets makes the dispersion of graphene unstable in solvents. One of the recent methods coming from Dr. Green’s group is to stabilize graphene by pyrene derivatives which can later be dispersed into water and also can be used in nanocomposites while preserving its characteristic conductivity and mechanical properties. In the present work, we stabilized graphene using Polybutyric acid (PBA) which is also a pyrene based acid. To prepare pure polyurea (PU) sheets, we mixed Versalink P-1000 oligomeric diamine (VP1000) and Isonate 143 L at a weight ratio of 4:1 and subsequently cure the PU at 80 °C for 4 h. We varied graphene content in polyurea/graphene composites from 0 to 2wt%. The optimum enhancement of mechanical properties was achieved for 0.6 wt% graphene. Currently, we are working on graphene stabilization using the admiceller polymerization through formation of thin polymer film on graphene. The functionalization work using admiceller polymerization is certainly a novel idea which will be explored in my work using pristine graphene. In my project, I would explore the pristine graphene formation using admiceller polymerization and use of that graphene in polymer to form nanocomposites.

REFERENCES
Recently, more attentions have been paid to natural polymer-based flocculants in wastewater treatment, since they are believed to be low-cost, biodegradable, and environmentally friendly. In this study, a cationic and amphiphilic monomer, dimethyl acryloyloxyethyl benzyl ammonium chloride (DBC), has been successfully grafted onto chitosan (CS) with ceric ammonium nitrate (CAN) as the initiator. The prepared graft copolymer (denoted as CS-g-PDBC) was then characterized in detail by using Fourier-transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD), field emission scanning electron microscope (FESEM) and thermogravimetric analysis (TGA). Subsequently, this graft copolymer was applied to treat the emulsified oil wastewater and the results indicated that CS-g-PDBC was much more efficient than those of CS and two other commonly used flocculants, i.e. cationic polyacrylamide (CPAM) and polyaluminum chloride (PAC). Moreover, the effects of various flocculation parameters, including droplet charge density, pH value and CS-g-PDBC dosage, on the flocculation efficiency were systematically investigated. Based on these investigations in combination with Zeta potential measurements, a flocculation mechanism of CS-g-PDBC in emulsified oil wastewater treatment has been proposed.
We studied the dynamical properties of a series of mono-dispersed polyisoprenepolymers whose twochain ends wereend-capped with fullerene (C$_{60}$). These mono-dispersed polymers were synthesized through anionic polymerization of isoprene in hexane solution using a special technique. Forpure polyisoprene without C$_{60}$, the storage modulus $G'$ and the loss modulus $G''$ displayed an entanglement plateau at high frequencies and a Newtonian-fluid behavior at low frequencies. For C$_{60}$-end-capped polyisoprene, although italso displayed an entanglement plateau at high frequencies, at low frequencies it was not Newtonian and itsterminal relaxation time was slightly larger than that of pure polymerwith similar molecular weight. In addition, there was significant difference in their tackiness properties. When one piece of polymer was placed on the top of another piece, after ten hours the C$_{60}$-end-capped polyisoprene was relatively easy to separate, whilethe pure polyisopreneof the same molecular weight would completely stick together. These results suggested that the traditional reptation process of polymer chains in melts as well as in interfaceshad been considerably interrupted by the presence of C$_{60}$-chain-end structure.
POLY 300: Large molecule incorporation into polyimide aerogel matrix for enhanced aerospace application

Stephanie L. Vivod, stephanie.l.vivod@nasa.gov, Mary Ann B. Meador, Coleen R. Pugh. (1) NASA Glenn Research Center, Cleveland, Ohio, United States (3) Department of Polymer Science, The University of Akron, Akron, Ohio, United States

Polyimides are desirable materials for space applications due to their ability to retain their physical and mechanical properties over a wide range of temperatures. The use of triptycene or triptycene derivatives in the polyimide backbone has been shown to enhance thermal stability as well as decrease density and increase free volume. Polyimide aerogels have been fabricated to maintain the same high temperature use with increased porosity, lighter weight and extremely low densities. It is expected that these characteristics will be enhanced by incorporation of large three-dimensional rigid triptycene monomers into the backbone of the polyimide chain. Augmented characteristics may include greater thermal stability, higher glass transitions, increased tensile strength, and lower refractive indices and dielectric constants. These multifunctional materials may find use in aerospace applications as ultra-lightweight structures for habitats, inflatable decelerators, and insulation for rovers or EVA suits for astronauts.

A new kind of chlorine-containing hyper-cross-linked polymers (HCPs) were prepared, which exhibit a high surface area, large pore volume, controllable average pore size and hydrophobicity. The synthesized HCP-0.5 sample, which has the biggest BET specific surface area (1394 m²/g) and pore volume (1.55 m³/g), was used as a novel adsorbent for removing benzene, a typical volatile organic compound. The results of the static adsorption/desorption experiments at three different temperatures (298, 308 and 318 K) showed that HCP-0.5 had a very large adsorption capability for benzene. Dynamic adsorption experiments of benzene on HCP-0.5 under dry and humid condition (RH=80%) were carried out to investigate the effect of water vapor on the adsorption capacity for benzene. It was revealed that the existence of water vapor had little effect on dynamic adsorption capacity of benzene on HCP-0.5 and almost does not change the breakthrough time. Therefore, these synthesized chlorine-containing polymers can be efficient and competitive adsorbents for removing VOCs, especially under humid conditions.
POLY 302: Control of kinetics and stress development in polymer networks with acrylated vs. methacrylated polymer nanoparticles

Parag K. Shah², parag.shah@colorado.edu, Jeffrey W. Stansbury²,¹. (1) Craniofacial Biology, University of Colorado Denver, School of Dental Medicine, Aurora, Colorado, United States (2) Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado, United States

Polymer network structure can be controlled using nanostructured materials for achieving desired physical and chemical properties. We have prepared polymeric nanoparticles (nanogels) that can be swollen by monomer in order to tune network structure and bulk properties while influencing overall polymerization kinetics. The hypothesis is that these nanogels, which are functionalized with (meth)acrylate reactive groups, can control local rates of polymerization in (meth)acrylate matrices at the nano scale due to relative differences in the local environment and differential copolymerization reactivity.

Nanogels were made using thermal solution polymerization of isobornyl methacrylate and ethoxylated bisphenol-A-diglycidyl dimethacrylate (80:20 mol). Mercaptoethanol was used as a chain transfer agent to maintain short primary chains and prevent macrogelation as well as to provide chain-end functionality for further modification with isocyanatoethyl acrylate (IEA) and isocyanatoethyl methacrylate (IEM) to give acrylate or methacrylate-functionalized nanogels. These nanoparticles (~5 nm; ~20k molecular weight) were dispersed in triethylene glycol dimethacrylate (TEGDMA) at loading levels of 5, 25 and 50 wt%.

The nanogel loaded solutions had progressively lower shrinkage stress as compared to the TEGDMA control. The nanogels behave as swollen pre-polymerized particles and reduce the volume fraction of polymerizable monomer, thereby reducing shrinkage and consequently, shrinkage stress. The addition of nanogels leads to proportionally faster overall reaction rates, regardless of whether acrylate or methacrylate reactive groups are present, which indicates the local reaction rate in and around the nanogels is enhanced with respect to the TEGDMA homopolymerization rate. This can be attributed to the increased viscosity due to the addition of the highly branched multifunctional nanogels leading to autoacceleration behavior. At the same loading levels, nanogels with IEM exhibit faster reaction kinetics as compared to analogous IEA functionalized nanogels.

![Polymerization kinetics and shrinkage stress as a function of nanogel loading and functional groups compared with TEGDMA](image)
POLY 303: Light controlled thiol-Michael addition initiated by photocaged superbases

Xinpeng Zhang², xizh5879@colorado.edu, Weixian Xi², Shunsuke Chatani², Maciej Podgorski¹, Christopher Bowman³. (1) Chemical and Biological Engineering, University of Colorado, Boulder, Colorado, United States (2) University of Colorado Boulder, Boulder, Colorado, United States (3) UCB 596, Univ of Colorado, Chemical Biological Eng, Boulder, Colorado, United States

The thiol-Michael addition reaction is a powerful and widely used tool due to its “click” nature, which allows for high reaction efficiency, “green” chemistry and high yield. It has been widely employed in various applications, such as dendrimer synthesis, polymerization, biological modification and surface functionalization. Unfortunately, not too many efficient, photo-sensitive catalysts have been designed to photo initiate these “click” reactions. To achieve higher efficiency and better light sensitivity, two types of photo catalysts have been made to accelerate the photo-triggered thiol-Michael addition reaction. As a “superbase”, guanidine and its derivatives can catalyze thiol-Michael reaction efficiently and have been protected by different photocages in the study.

We have designed and synthesized two different photo-base catalysts, NPPOC-TMG (UV sensitive) and Coumarin-TMG (visible light sensitive). The properties of the photobases, such as UV absorption and cleavage efficiency mainly depend on the protecting photocages. A variety of methods have been used to study the properties of these photobases, for example, UV absorption, quantum yield, model reaction test and polymerization kinetics behavior of the catalysts. Also, different types of experiments including FT-IR, NMR, DMA, UV-Vis absorption test etc. were performed to characterize and evaluate the performance of the photo-base catalysts. Both photo-catalysts exhibit excellent catalytic activity and achieve over 90% conversion in short time in a model reaction. The polymerization kinetics also showed the efficiency of these catalysts in the crosslinking networks. In summary, these new initiating photocaged superbases efficiently catalyze the thiol-Michael addition and also enable temporal and spatial control over this reaction.

Mechanism of photo-caged TMG release which can be controlled by UV or visible light
POLY 304: Synthesis of a biocompatible hydrogel platform for drug delivery using oxime click chemistry

**Kelly A. Gilmore**, kelly.a.gilmore@vanderbilt.edu, **Dain B. Beezer**, **David M. Stevens**, **Elizabeth A. Delesky**, **Eva M. Harth**. (1) Department of Chemistry, Vanderbilt University, Nashville, Tennessee, United States (2) Department of Pharmacology, Vanderbilt University, Nashville, Tennessee, United States (3) Department of Materials Science and Engineering, University of Florida, Gainesville, Florida, United States

We present a degradable hydrogel system for drug delivery using oxime click chemistry by employing a ketone-functionalized polyester and an amino-oxy functionalized polyglycidol. The biocompatibility and orthogonal nature of this chemistry makes these gels an attractive option for the delivery of both synthetic and biological therapeutics. Additionally, the synthesis method for these materials allows for control over the properties of the resulting gel based upon the ratio between the polyester precursor and the polyglycidol crosslinker. The potential of these gels to serve as a successful delivery platform was assessed by studying the swelling and degradation profiles, as well as the *in vitro* release rate of a model drug. Biocompatibility and cytotoxicity of the gels were studied using NIH 3T3 cells.

Because of the orthogonal nature of this crosslinking chemistry, these gels also have the potential to be utilized as a platform for a more complex delivery system, and could be used to encapsulate an additional delivery vehicle. Polyester nanosponges formed using amine-epoxide chemistry have been successfully synthesized in our lab and have been shown to be an effective delivery vehicle for a number of hydrophobic drugs, both *in vitro* and *in vivo*. These particles can be entrapped within the gel matrix and serve as an ancillary boundary to the release of a therapeutic, which lends an additional degree of tailoring to the release rate.
The objective of this work was to develop tough and glassy thiol-X network materials through the elimination of interchain ester linkages from their structures and by that extend the scope of thiol-X reaction implementations. To achieve the goal ester-free multifunctional thiols such as tetra(2-mercaptoethylene)-silane and 1,2,3-tris(3-mercaptopropylene)-1,3,5-triazine-2,4,6-trion were synthesized and used in stoichiometric reactions with divinyl sulfone and/or hexamethylene diisocyanate. Further, thermomechanical properties of neat phosphine-catalyzed thiol-vinyl sulfone and thiol-vinyl sulfone-isocyanate networks fabricated in a controlled manner were reported, and a comparison with ester-containing thiol-acrylate step-growth networks was performed.

It was shown that neat thiol-vinyl sulfone networks containing high weight fractions of sulfone groups exhibit significantly higher glass transitions temperatures ($T_g$) than structurally similar but ester-containing thiol-acrylate networks. $T_g$s as high as 112°C were achieved for ester-free thiol-Michael polymers (Fig. 1).

It was also shown that the combination of sulfone and thiocarbamate structural effects generally shifted the $T_g$ toward higher values and improved the materials' toughness.

Figure 1. Dynamic mechanical analysis curves for a neat thiol-vinyl sulfone network with no interchain ester linkages
The radical-mediated reaction between a multifunctional thiol and a multifunctional alkyne has emerged as a powerful approach for the synthesis of functional polymer networks. In this presentation, we report thiol-alkyne photopolymerization in miniemulsion as a route to functional polymer nanoparticles. Thiol-yn e miniemulsions are prepared via ultrasonication of a thiol/alkyne oil phase in an aqueous continuous phase containing surfactant. Thiol-yn e systems typically result in a higher crosslink density, which could lead to better performance properties for applications in the coatings, cosmetics, and biomedical industries. By adjusting the alkyne functionality from monofunctional to tetrafunctional, the crosslink density, and thus the thermomechanical properties of the resulting nanoparticles can be tuned over a wide range. By exploiting nonstoichiometric reaction conditions, we synthesize polymer nanoparticles with excess alkyne functional groups on the surface. These excess alkynes serve as reactive handles for facile postpolymerization modification using sequential thiol-click reactions, or orthogonal azide-alkyne reactions yield highly functional polymer nanoparticles.
In photopolymer-based composites systems, light attenuation due to absorption and scattering from fillers induce variation in the light available throughout a composite. This typically leads to ‘top-down’ curing, creating stress concentration gradients within the composite and at substrate interfaces. This study examines the reaction kinetics of dimethacrylate-based filled materials using a unique visible-light free-radical photoinitiator in an effort to create more uniform cure in thick specimens.

Initiation with either a single component titanocene photoinitiator [bis(cyclopentadienyl)bis[2,6-difluoro-3-(1-pyrryl)phenyl]titanium (Irgacure 784, 1 wt%) or camphorquinone/ethyl 4-dimethylaminobenzoate (CQ/EDMAB, 0.2/0.6 wt%, respectively) was compared in triethylene glycol dimethacrylate (TEGDMA) and BisGMA/TEGDMA (70/30 wt%) resins. Silane-treated barium glass (0.4 µm) was used at various loading levels. Measurements included resin viscosity (viscometer) and reaction kinetics (FT-IR).

Introduction of the titanocene initiator resulted in dramatically different kinetic profiles depending on the resin viscosity. At 10 mW/cm² in BisGMA/TEGDMA resin (viscosity = 1.6 Pa*s), conversion of 64.4(±0.3)% was achieved, compared to 61.5(±0.2)% for the CQ/EDMAB control. At the same intensity, TEGDMA (viscosity = 0.05 Pa*s) reached a conversion of only 3.9(±0.4)%), compared to 72.8(±0.3)% for the CQ/EDMAB control. Incorporation of inorganic particulate filler into TEGDMA from 50-80 wt% resulted in minimal conversion at 50-60 wt% levels and moderate to high levels of conversion obtained at the more viscous 70-80 wt% filler levels.

With the appreciable increase in performance at intermediate light intensities, which may indicate a critical interaction between excited state and ground state species, this initiating system has the potential to be used effectively in highly viscous materials with significant levels of organic or inorganic filler, where the light attenuation profile may offer a unique prospect for bottom-to-top rather than top-down photocuring.
Thermosets exhibit desirable temperature and solvent resistance but generally have limited possibilities for reuse and biodegradability. In an effort to prepare readily degradable thermosetting polymers, work in our group has focused on the synthesis of aliphatic polyesters containing disulfide crosslinking groups. These “green” thermosets can be made from renewable monomers and are expected to degrade to low toxicity, environmentally acceptable products after use. This affords the possibility of both advanced resorbable materials for biomedical applications and gives the possibility of unique “green” thermosetting materials for non-medical applications. We report here characterization of a series of oligomers and polymers of poly(alkylene mercaptosuccinates) with varying crosslink densities. Characterization by 2D COSY 1H-1H NMR showed good agreement between starting monomer concentrations and monomer ratios in the polymer. GPC showed successful chain extension of the oligomers which were then crosslinked to give flexible, high quality thermoset films. The crosslink density was controlled by modifying the mercaptosuccinic acid : succinic acid ratio. The molecular weight of the oligomers was controlled by overbalancing with diol and the resultant oligomers were later chain extended by transesterification. The polymers were cured in air at 110°C to effect crosslinking and afforded high quality films. The cured films exhibited desirable degradation under standard compost conditions.

Figure 1. 400 MHz HNMR of oligo-(hexylene mercaptosuccinate)-co-(hexylene succinate) with varying incorporation of pendant thiols.
Porous covalent-organic materials (COMs) are a class of porous materials with high surface area and diverse pore dimensions, topologies and chemical functionalities. Fascinated by their applications in gas storage/separation, catalysis, and electronics, more and more efforts have been devoted to this field. Different methodologies based on irreversible or reversible reactions have been adopted to construct those versatile networks. Boron chemistry, such as borate ester, boroxine, borosilicate, borazine forming reactions, has been intensively studied and applied in the synthesis of porous COMs during the past ten years. However, other than those sp2-hybridized boron formation reactions, the use of the charged, sp3-hybridized boron as the linkage to synthesize the porous networks has not been explored. In this work, we will discuss the synthesis and ion conductivities of the sp3-hybridized boron-linked network.
Immune activation and the effectiveness of vaccine adjuvants are modulated by the detection of specific molecular activators via pattern recognition receptors (PRRs). The cytosolic PRR nucleotide-binding and oligomerization domain 1 (NOD1) has been shown to play distinct roles in both inflammation and vaccine adjuvants. Despite the implications of NOD1 in disease, the spatial and temporal aspects of the molecular activators of NOD1 have not been determined. Here, we present remote activation of NOD1 via photocaged NOD1 agonist. Based on established SAR for the molecular activator of NOD1, D-glutamyl-meso-diaminopimelic acid (iE-DAP), we have strategically protected the agonist with a photolabile protecting group, 6-nitroveratryloxycarbonyl carbamate (NVOC). With this photocaged agonist, NOD1 activity is suppressed and then regained upon exposure to light. We confirmed NF-κB production upon exposure to light in a model cell line, as well as activity in primary cells by examining cytokine production in bone marrow derived dendritic cells (BMDCs). This will allow us to better explore the spatial and temporal mechanism of NOD1 activation, leading to a better understanding of immune signaling.
POLY 311: Effect of spatially predetermined agonist presentation on immune response via polymeric systems

Keun Ah Ryu¹, karyu@uci.edu, Katarzyna Slowinska², Rock Mancini¹, Aaron P. Esser-Kahn¹. (1) Chem Dept, UC-Irvine, Irvine, California, United States (2) Chemistry and Biochemistry, California State University, Long Beach, California, United States

Many vaccines present agonists in a spatially organized manner to immune cell receptors. Though the effect of such synergistic stimulation of immune cell receptors are well known, the specific relationship of spatial orientation of agonists and the consequent immune response is unknown. To study the importance of spatial organization in agonist presentation, we report the synthesis of covalently coupled agonists of Toll-like receptors (TLR) with established synergistic profiles, at predetermined molecular distances. In particular, immunostimulants including imidazoquinolines, pyrimido[5,4 b]-indoles, lipoteichoic acids, and CpG DNA, are linked with PEG polymers of varying lengths. The activation of immune cells with the immunostimulant heterodimers are also reported herein.
Photo-caged agonists of pattern recognition receptors, such as TLRs and NLRs, have been used to provide useful insight into the spatial-temporal aspect of innate immune stimulation. NOD2 is a highly conserved NLR found in eukaryotes, which recognizes muramyl dipeptide (MDP), a component of bacterial cell walls. Mutations in NOD2 are implicated in inflammatory bowel diseases such as Crohn’s disease and Blau Syndrome and MDP is known to be an active component of Freund’s complete adjuvant. Despite this significance, there is currently no known crystal or NMR structure for NOD2, so little is known about how it recognizes MDP. A recent in silico study of zebrafish NOD2 (zNOD2) suggests the importance of hydrogen bonds between the Arg845 of zNOD2 and the carbonyl groups of MDP. We synthesized a photo-caged NOD2 agonist using 4-methoxy-2-nitrobenzyl to cage an individual amide linkage on the backbone of MDP. The photo-labile protecting group should provide sufficient steric interactions to block this imperative hydrogen bonding. The photo-caged agonist will then be used to examine the spatial-temporal aspect of NOD2 activation as well as provide experimental evidence for the proposed mechanism of binding.
CpG is a well-known immune stimulant that has been studied in both cancer immunotherapy and vaccines. A previous clinical trial evaluating CpG for glioblastoma immunotherapy showed limited efficacy. However, we hypothesize that this efficacy could be enhanced by improving CpG delivery to immune cells. To improve delivery to phagocytic immune cells, we modified the CpG sequence with a lipid-PEG tail and coated this modified oligo onto single-walled carbon nanotubes (SWCNT-CpG). We evaluated the efficacy \textit{in vitro} and \textit{in vivo} of both the modified CpG alone and SWCNT-CpG.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{diagram.png}
\caption{Diagram of improved CpG immunotherapy in brain cancer through enhanced delivery.}
\end{figure}
POLY 314: Use of high speed/high resolution size based chromatographic separation of polymeric materials with micro viscometric detection

Michael J. O'Leary, michaeloleary80@gmail.com. Waters Corp, Boxborough, Massachusetts, United States

Recent developments in polymerization processes have utilized a wide array of strategies. The development has evolved from simple polymer chains to complex polymers capable of performing multiple functions within a single molecular chains. As these new materials evolve their control and understanding has come under intense scrutiny utilizing a wide range of analytical technology ranging from chromatographic separation to advance mass spectrometry.

Addressing the challenges of material characterization has often been focused on hyphenated detection techniques such as so called triple detection. This approach utilizes a concentration detector such as a refractive index (RI) detector as well as a viscosity detector and a multi angle light scattering detector.

With the introduction of the Waters Advanced Polymer Chromatography system (APC) a break though was achieved in high speed high resolution size based separation. This approach delivered a novel approach to the separation equipment including the separation column as well as the entire flow path to yield a high speed / resolution separation maintained from injection to detection with traditional detector options such as RI and UV detection. The use of conventional viscometer detectors and multi angle detectors with APC has been limited due to the optical path and associated band broadening of the viscometer and light scattering detectors available to the polymer scientist.

In this study the expansion of the APC approach is presented. A new high resolution micro viscometer is evaluated and shown to match the optical requirements and chromatographic dispersion control needs enabling high speed high resolution multi detector analysis.
POLY 315: Online coupling of specialty detectors in GPC for chemical and molar mass detection

John A. McConville², Derek Lohmann², dlohmann@pss-polymer.com, Thorsten Hofe¹, Markus Cudaj³, Gisela Guthausen³, Manfred Wilhelm³. (1) PSS GmbH, Mainz, Germany (2) PSSUSA, Amherst, Massachusetts, United States (3) KIT, Karlsruhe, Germany

For macromolecular materials in liquid chromatography, challenges exist when both molar mass distribution and chemical composition information is required. One solution to solving the problem is the use of size exclusion chromatography hyphenated with medium resolution nuclear magnetic resonance (SEC-MR-NMR). Through digital and mechanical improvements of a specially designed 20 MHz table-top NMR, a substantial increase in sensitivity and chemical selectivity could be achieved. ¹H NMR spectra of PMMA and PS homo-polymers as well as PS-PMMMA block-copolymers were of sufficient quality to enable detection and formulation of unknown polymer compounds. ¹H NMR spectra of acceptable resolution and S/N ratio were collected online during the chromatography.

In addition, coupling GPC to ESI-MS enables generation of absolute molar mass and distribution data for polymers up to 10 kDa. Deconvolution via a sophisticated software algorithm enables direct access to calibration curves and molar mass distribution data, allowing for the reconstruction of the molar mass distribution of polymer mixtures.

We will present methods and challenges, as well as data generated utilizing the coupling techniques.

Schematics for GPC-MS and GPC-NMR
Recently, microporous organic polymers, especially synthesized by hyper cross-linking from functionalized aromatic monomers, have shown to be effective for carbon capture and storage with considerable capacity and selectivity. Herein, a class of novel hyper cross-linking polymers (HCPs), based on green and renewable carbohydrates functionalized by various hydroxyl groups, was synthesized by Friedel–Crafts alkylation. These carbohydrate polymer, which have BET surface area around 800 m²g⁻¹ can absorb about 4.3-6.9 wt% of CO₂ with the CO₂/N₂ selectivity up to 64 at room temperature (298 K) by hydrogen bonding and dipole-quadrupole interaction. Furthermore, we experimentally and computationally studied the structures of carbohydrate backbones and determined several features, including quantity and reactivity of hydroxyl groups, and configurations of carbohydrate monomers, that governing their CO₂ absorption ability, which sheds light on understanding the structure/function relationship and designing better CO₂ separation materials.
We propose a room-temperature and ambient-pressure fabrication process of SiO$_2$ nanofilms on flexible poly(ethylene terephthalate) (PET) substrates. Langmuir–Blodgett (LB) films containing silsesquioxane units (pDDA/SQ22) are successfully photo-oxidized into SiO$_2$ nanofilms without PET degradation by UV–ozone treatment. Thicknesses of the obtained SiO$_2$ nanofilms are tuned by 0.4 nm per monolayer, indicating that this method affords SiO$_2$ nanofilms with precisely controlled thickness. Photo-oxidized SiO$_2$ nanofilms have good transparency and high electric resistance even on flexible PET substrates. The resulting SiO$_2$ nanofilms also serve as a protecting layer for PET substrates against photo-oxidizing degradation. Thereby PET films retain optical transparency even after UV–ozone treatment. Results of an investigation of the photo-oxidization mechanism reveal that UV–ozone induced conversion from silsesquioxane to SiO$_2$ comprises two photochemical reaction processes: (1) decomposition of organic moieties in LB films and (2) subsequent photo-oxidation of residual silsesquioxane units. The time constant of the second reaction depends strongly on the initial film thickness. This sequential and thickness-dependent conversion indicates that the conversion is controlled by the diffusion of extrinsic oxygen sources into films. Results show that this method is promising for the coating of transparent insulating SiO$_2$ layers for flexible optoelectronic device applications.

**Figure 1.** (a) Photograph of pDDA/SQ22 LB films with 20 layers on PET substrate after 1000 min UV–ozone treatment. The hazed region corresponds to the bare PET substrate without coating. (b) Transmission spectra of pDDA/SQ22 LB films on the PET film after UV–ozone treatment for 1000 min (red) and PET film before (black) and after UV–ozone treatment (blue). (c) Log plots of conductivity in photo-oxidized LB films fabricated on PET/ITO substrates.
A new water soluble polyester (PIOT) with fluorescent property was synthesized and characterized, and further formed PIOT-HA NPs with anionic hyaluronic acid (HA) by electrostatic interactions in aqueous solution. Through specific interactions between HA locating on the surfaces of PIOT-HA NPs and CD44 protein expressed on the cancer cell line MDA-MB-231, PIOT-HA NPs could selectively bind to cancer cells and be use to image. Upon white light irradiation, the PIOT-HA NPs sensitized oxygen to generate reactive oxygen species (ROS). The ROS could inactivate the neighboring CD44 protein, which inhibits invasion of MDA-MB-231. In addition, the PIOT-HA NPs showed degradability towards treatments of alkali and/or hyaluronidase, which could reduce accumulating of the PIOT-HA NPs in vivo. These findings demonstrated that the PIOT-HA NPs could be developed as a multi-functional and safety material for cancer diagnosis and treatment.
We describe the preparation of mechanoresponsive 3D-printed structures using an entry level fused filament fabrication printer. Using a dual extrusion setup, filament comprised of poly(ε-caprolactone) containing a spiropyran mechanophore was used to prepare tensile test specimens containing various spiropyran concentrations, spiropyran control molecules, multiple materials, or mechanoresponsive regions embedded within the specimen. Upon tensile elongation, the materials exhibited distinct color changes that are attributed to mechanochemical isomerization of the spiropyran mechanophore. By taking advantage of the unique capabilities of 3D printing, materials were produced that would be difficult, if not impossible, to prepare using traditional manufacturing techniques. Additionally, the combination of 3D printing and mechanoresponsive materials enabled the fabrication of a prototype force sensor that can be used for quantitative force determination by simply counting activated mechanoresponsive regions within the sensor.
While the development of light-responsive nanosystems for biological applications is a burgeoning area of research, our triggered degradation approach is distinct as it allows for stable formulations. Following on our recent work introducing intramolecular cyclization as an efficient mechanism for on-demand depolymerization, we hypothesized that ornithine, which forms a 6-membered lactam ring upon deprotection, may be introduced as a crosslinker to create light-degradable nanogels to allow delivery of hydrophilic cargo. As these materials also degrade in response to NIR, they hold promise for spatiotemporally precise control over protein delivery in cultured and engineered tissues.

Our short crosslinker yields nanogels with a tight enough mesh to retain payload in the absence of irradiation. In this work we use coumarin-based crosslinkers to allow two-photon NIR triggered degradation. Both the crosslinker and resulting gels are stable in PBS in the absence of irradiation and fall apart through intramolecular cyclization when irradiated with UV and NIR light. Crosslinker controlled degradation was investigated by NMR and LCMS ($t_{1/2} = 10$ h (irradiated) vs 20 days (control) at 37 °C). Light-responsive nanogels (200 nm) formulated from the crosslinker are stable in the absence of irradiation for at least a week at 37 °C, while brief UV or NIR irradiation triggers disassembly within a few hours of incubation.
POLY 321: Supramolecular polymers synthesized by thiol-ene click polymerization from supramonomer

Qiao Song, songqiaothu@gmail.com, Fei Li, Liulin Yang, Zhiqiang Wang, Xi Zhang. Department of Chemistry, Tsinghua University, The Key Lab of Organic Optoelectronics & Molecular Engineering, Beijing, China

Supramolecular polymer has gained a significant development, but it remains a challenge to fabricate supramolecular polymers with controlled compositions and structures. We have proposed a method for fabricating supramolecular polymers through polymerization of supramonomers. Compared to typical monomers, supramonomers are monomers constructed by noncovalent synthesis, which are able to further polymerize through conventional polymerization process. Here we describe the fabrication of supramonomers based on supramolecular complexation between cucurbit[8]uril and the tetrapeptide Phe-Gly-Gly-Cys. Then the supramolecular polymers are obtained by thiol-ene click polymerization of the supramonomers with maleimide-terminated poly (ethylene glycol). Benefiting from pH dependent nature of thiol-ene click reaction, we're able to control the polymerization rate in a wide range through pH control. Therefore, we have successfully converted the spontaneous process of supramolecular polymerization into easy-controllable covalent polymerization, which may provide a new perspective on the fabrication of supramolecular polymers with controlled compositions and structures.

This study is aimed to develop responsive polymer materials especially responding to biochemical signals in a concentration relative to physiological environment. Reactive oxygen species (ROS) include hydrogen peroxide and oxygen radicals et al., which are biochemical signals in a concentration as low as around 50-100 μM in inflammatory regions. Since selenium-containing polymers exhibit outstanding ROS responsiveness and Te has a lower electronegativity than Se, we are wondering if tellurium-containing polymers can be used as ROS responsive materials with extraordinary sensitivity. Herein, we will discuss the synthesis of two tellurium-containing hyperbranched polymers and their ROS responsiveness. One polymer with lower cross-linking degree was dispersed in water to form particles and swelled when 100 μM H$_2$O$_2$ was added, indicating that this polymer has ROS responsiveness in a biologically relevant ROS concentration. The other one with higher cross-linking degree showed no ROS responsiveness, indicating that cross-linking degree of polymer has an effect on ROS responsiveness. It is anticipated that such a highly sensitive ROS responsive tellurium-containing hyperbranched polymer can be applied to eliminate excess ROS in physiological environment and release drugs in a controlled manner.
Although surface interactions between polymers and cells have shown significant promise in enhancing medical device functionality, little work has been performed to evaluate similar techniques for thermosensitive shape memory polymers (SMPs). Over the last 10 years, we have developed a variety of minimally invasive medical devices using SMPs; however, these devices are used in areas that do not require barrier membrane coverage to be useful. Facilitating endothelial attachment to SMP surfaces should help expand the range of cardiovascular applications for these promising materials.

In this work, we evaluate the effect of varying chemical makeup of these shape memory polymers on endothelial cell attachment, while maintaining the shape memory functionality. This is accomplished mainly by altering percent composition of the monomer components and molecular weight of the crosslinking agent. Extensive work has been performed to assess the thermomechanical and bulk consequences of manipulating chemical composition of SMPs due to the marked effects on the shape memory capabilities of the material; few studies, however, investigate the result of varying chemical makeup on the surface properties and cell compatibility of these materials. A greater understanding of the material surface properties and the material-cell interface will facilitate the expansion of these materials to more realms of biomedical devices.

Endothelial cells attached to the surface of a shape memory polymer.
We will discuss how to combine supramolecular polymers with layer-by-layer technique, leading to fabrication of supramolecular polymeric networks with function of photocatalysis. To this end, we have employed host-enhanced pi-pi interaction to fabricate supramolecular polymeric networks by alternating deposition of porphyrin bearing four naphthalene groups and cucurbit[8]uril at the liquid-solid interface. The fabricating progress of supramolecular polymeric networks can be efficiently controlled, simply by adjusting the number of layer pairs of LbL films. Moreover, upon irradiation of visible light, these supramolecular networks exhibit good catalytic features for the oxidation of various phenols. Considering that various building blocks with different functional groups can be employed to fabricate different kinds of functional surfaces, it is anticipated that this strategy for fabricating supramolecular polymeric networks at the interface has potential applications in the fields of sewage disposal, biocatalysis, to name a few.

Reference

POLY 325: Cooperative effect of cucurbit[8]uril-based π-π interaction

Zehuan Huang, huangzh13@mails.tsinghua.edu.cn, Ke Qin, Liulin Yang, Zhiqiang Wang, wangzhiqiang@mail.tsinghua.edu.cn, Xi Zhang, xi@mail.tsinghua.edu.cn. Tsinghua University, Beijing, China

We have established a new method of supramolecular polymerization promoted and controlled by self-sorting recently. Although cucurbit[8]uril(CB[8])-based π-π interaction has been successfully introduced to drive supramolecular polymerization, it remains unclear if there exists cooperative effect and how it is influenced and adjusted by structural variations.

This research is aimed to investigate the cooperative effect of CB[8]-based π-π interaction. For this purpose, we design and synthesize a series of model compounds containing the benzyl moiety with various positive charged side groups. In this way, hydrophobicity and steric factor of positive charged moieties can influence the cooperative effect of CB[8]-based π-π interaction and then result in relative changes of stepwise affinities (corresponding to K1 and K2), thus making binding modes divided into three types.

For the first mode (K2 >> K1), strong cooperative effect can lead to the direct formation of ternary complexes; for the second mode (K2 ≈ K1), weak cooperative effect can allow the coexistence of binary and ternary complexes during the binding process; for the third mode (K2 << K1), a stable binary complex can be formed due to the absence of this effect and even suppress the second step binding.

This line of research reveals the fundamental influence of cooperative effect in the complexation between CB[8] and guest molecules, which provides guidance for tuning CB[8]-based π-π interactions as driving forces for supramolecular polymerization.
POLY 326: Chloride concentration trigged drug delivery system based on imidazolium-containing conjugated polymer nanoparticles

Zhuo Chen²,¹, zhuochen016@gmail.com, Kirk S. Schanze¹, Niveen M. Khashab². (1) Department of Chemistry, University of Florida, Gainesville, Florida, United States (2) Advanced Membrane and Porous Materials Center, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia

Nanoscale stimuli-responsive drug delivery systems have received tremendous attention in the medical field and have shown promising results in preclinical animal models. In this work we prepared chloride concentration trigged drug delivery nanoparticles which are fabricated with a conjugated polyelectrolyte (CPE) with polyfluorene backbone and imidazolium side groups (PF-Im). The PF-Im polymer combines the emissive nature of conjugated polymers and the property of poly(ionic liquid), whose solubility changes along with different counter ions. The polymer with Br⁻ and Cl⁻ counter ion (PF-Im-Br or PF-Im-Cl) is water-soluble; but PF-Im with PF₆⁻ counter ion (PF-Im-PF6) is acetone-soluble but water-insoluble. Using this property, PF-Im-PF6 and hydrophobic drugs (neutralized dextrin, Dox, as a model drug) can be fabricated into nanoparticles via nanoprecipitation method. The PF-Im-PF6/Dox nanoparticles are stable in deionized water for weeks; however, when treating the nanoparticle with Cl⁻, ion exchange will happen and the PF-Im polymer will become water-soluble PF-Im-Cl and the nanoparticle will destruct, along with drug releasing. The drug releasing rate can be regulated by chloride concentration. In the solution with Cl⁻ concentration of 0.1 M, Dox slowly releases and reaches plateau after 15 hours. The drug releasing behavior can be tracked by monitoring the fluorescence of PF-Im polymer. When embedded in the nanoparticle, Dox can quench the PF-Im fluorescence efficiently, as it’s a good electron transfer quencher. After nanoparticles are destructed and Dox is released, the fluorescence of PF-Im will “turn on”. This chloride concentration trigged drug delivery system has the potential in the application of slow-releasing drug carrier and chloride-related disease treatment.
We have established a novel photodynamic therapy (PDT) system in which the photosensitizer is activated by chemical molecules instead of outer light source. To the best of our knowledge, this is the first reported PDT system for treating cancer and microbial infections that is independent of light irradiation.

The system is aimed to address the major bottle neck of PDT is for the requirement of outer light source, which always limits effective therapeutic of PDT to the lesions in deeper tissue. In this system, luminol, hydrogen peroxide and horseradish peroxidase (HRP) were used as bioluminescent molecules and a cationic oligo(p-phenylene vinylene) (OPV) that acts as the photosensitizer. They meet the spectra overlap requirement for bioluminescence resonance energy transfer (BRET) as the donor-acceptor pair. The excited OPV sensitizes oxygen molecule in the surrounding to produce reactive oxygen species (ROS) that kill the adjacent cancer cells in vitro and in vivo and pathogenic microbes.

By avoiding the use of light irradiation, the new strategy for treating cancer and microbial infections opens a new therapy modality to tumor and pathogen infections.
In block copolymers, microphase separation allows for the formation of long range ordered phases. This behavior can be directed by templating microscale features on a surface followed by back filling with an appropriate block copolymer. The polymer then phase separates, providing a way to create nanoscale features using microscale lithography.

Mixed polymer brushes can accomplish similar results. In this system two polymers, polystyrene and poly(methyl methacrylate), are grafted from the surface utilizing free radical initiators covalently bound to the substrate. We demonstrate that mixed polymer brushes also microphase separate similar to that seen with block copolymers, so the composition of the brush determines the phase behavior of the system. Lithography could also be employed to direct long range ordering in mixed polymer brush systems.

Polymer brushes offer several distinct advantages over spin-coated block copolymers systems. Since the polymers are attached to the surface, they are more robust towards both mechanical and chemical processes. The substrate also does not need to be planar; brushes can be grown from a wide variety of surface geometries such as spheres or cylinders. Finally, features such as right angles, which are traditionally difficult to replicate with block copolymers, should be more readily accessible using a mixed polymer brush system.

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Figure 1. Phase behavior of polystyrene and poly(methyl methacrylate) mixed polymer brushes
The aim of this work is to examine the shape memory properties of polymer networks derived from photo-mediated copper-catalyzed azide-alkyne cycloaddition (photo-CuAAC). Photo-CuAAC has advantages over other polymerization reactions by being photopolymerizable, using accessible functional groups, and containing a stiff triazole linkage. Azides and alkynes can be made from a variety of readily available starting materials including multifunctional halides, alcohols, isocyanates, epoxides, among others in less than two steps with high yield. Due to the versatility in monomer design, These CuAAC derived polymers possess narrow glass transition temperatures ranging from 55°C to 120°C, and the triazole linkages increases the glass transition compared to similar polymer networks polymerized with thiol-ene chemistry. The step-growth nature of this reaction creates a uniform network with a narrow, well-defined glass transition desirable for shape memory polymers. We test the shape memory properties of two photo-CuAAC networks that have 99% shape fixity and 99% shape recovery with a more narrow recovery than comparable step growth shape memory polymers. These results demonstrate a new polymerization chemistry to build shape memory polymer networks with tunable properties.
POLY 330: Bioderived polymers prepared from $N$-(acryloyl-2-pyrrolidone)s with ether and thio-ether-based residues

Rajani Bhat, 88rajani@gmail.com, Agostino Pietrangelo. (1) Chemistry, Rutgers University, Cranford, New Jersey, United States (2) Chemistry, Rutgers-Newark, Newark, New Jersey, United States

A series of substituted $N$-(acryloyl-2-pyrrolidone)s were synthesized from pyroglutamic acid, a bio-derived resource. The monomers were tailored to bear a number of structurally diverse residues that are tethered to the pyrrolidone scaffold via ether or thio-ether moieties. Structure/property correlations and the application of these systems as drug delivery agents will be discussed.
Embolic materials have been commonly used to treat various vascular diseases such as arteriovenous malformation (AVM) and cerebral aneurysms. Pt coil is considered as the best material among many embolic materials because of its safety, stability, and easy handling. It, however, could not always achieve complete treatment; often causes reflow of blood into the target lesion and it requires repeated embolization. This phenomenon is due to its low occlusion efficiency that is determined by packing density and formation of a thrombus by an embolic material. Many attempts to improve the occlusion efficiency have been conducted using polymer particle materials, viscous liquid materials, and liquid-to-solid gelling system. Some materials showed better embolization efficiency than Pt coil but their toxicity, instability, and hard handling limited their use in treatment.

In this work, we suggest a novel embolic material using polymer hydrogel containing radiopaque organic compound. The basic concept of this work is to make a ‘bilayer’ hydrogel composed of two hydrogels that have different swelling ratio each other. Acrylic acid (AA) was copolymerized with triidobenzoyloxoethyl methacrylate (TIBOM), a radiopaque compound, and poly(ethyleneglycol dimethacrylate) (PEGDM), a crosslinker, to form a hydrogel. The degree of crosslinking was determined by the ratio of AA to PEGDM, and it also affected to swelling ratio of a hydrogel. A ‘bilayer’ hydrogel was fabricated by forming one hydrogel onto another hydrogel using photo-lithography. It would be bent in water and finally rolled up like a ‘coil’ by different swelling ratio if two hydrogels have different degree of crosslinking (Figure). The coils were fabricated in various diameters (0.5 – 2.3 mm) by controlling the difference of swelling ratios of bilayered hydrogels. The packing density obtained from experiment using glass aneurysm model (67 – 72%) was higher than average value of Pt coils (32%). The radiopacity of the hydrogel coil was similar with human bone, and it was considered to be enough to use as an embolic material.

![Figure](image)
POLY 332: Novel hydrogelator for the creation of supramolecular structures for biomedical applications

Yuan Gao³, yuan.gao@nih.gov, Cristina Berciu⁴, Daniela Nicastro¹, Bing Xu¹, Ferenc Horkay². (1) Brandeis University, Waltham, Massachusetts, United States (2) Section on Tissue Biophysics and Biomimetics, National Institutes of Health, North Potomac, Maryland, United States (3) Section on Tissue Biophysics and Biomimetics, NIH, Bethesda, Maryland, United States (4) Biology, Brandeis University, Waltham, Massachusetts, United States

Supramolecular structures constructed from small molecules such as peptides could be used to develop smart materials for future applications in tissue engineering, regenerative medicine, and drug delivery. In these systems the sol-gel transition is initiated by physical or chemical stimuli. In the present work we use an enzymatic hydrogelation strategy to develop a novel molecule that self-assembles in the biological environment in the presence of phosphatase. First, we verify that self-assembly process occurs inside living mammalian cells using various techniques such as fluorescent microscopy and transmission electron microscopy. Supramolecular self-assembly occurs on the surface of the endoplasmic reticulum, where the dephosphorylation activity is most pronounced. Second, we demonstrate that the small molecules can also self-assemble in living mice bearing HeLa tumor in which the phosphatase is over-expressed. Since self-assembly can also incorporate guest molecules into nanofibers, fluorescent imaging was made to reveal that supramolecular assemblies prolong the retention of a photo thermal therapy agent (ICG) within the tumor site. The in situ formation of supramolecular structures not only shows its spatiotemporal specificity but also minimizes the accumulation of therapeutic agents in the healthy part of the body, which is important for potential biomedical applications.
Recently, interest of electrochemical redox stimuli have grown tremendously because of its easy
trigger mode and the significance of the change of potential in biological systems. β-
cyclodextrin-ferrocene(β-CD-Fc) linker has been widely investigated in these systems, with
applications as molecule machines and drug delivery vehicles. Star amphiphilic copolymers with
well-defined and flexible structures are considered to be excellent choices for drug delivery
systems, for their unique properties such as lower intrinsic viscosity and high surface reactivity
compared with linear analogues.
Driven by the idea that to use star polymers to improve the biocompability and efficiency of the
β-CD-Fc-based drug delivery systems, we designed and synthesized star polymer 4-arm-poly(ε-
caprolactone)- β-CD(4A PCL-β-CD) and linear polymer polyethylene glycol-Fc (PEG-Fc). They
can form non-covalent supramolecular block copolymer 4A PCL-β-CD/Fc-PEG and self-
assemble to form micelles (Figure 1).
For the polymer synthesis, PEG-Fc was get from the EDC reaction of methoxy PEG and
ferrocenecarboxylic acid, while 4A PCL-β-CD was get from the click reaction of 4A PCL with
alkynyl group and β-CD with azide group. As the results of differential scanning calorimetry
(DSC) and thermal gravity analysis (TGA) shown, 4A PCL has lower melting temperature and
degree of crystallinity compared with the linear analogues, thus can make the drug vehicles more
biocompatible. Besides, we characterized the micelles by dynamic light scattering (DLS) and
transmission electron microscopy (TEM). Because the electrochemical activity of the β-CD-Fc
linker, the 4A PCL-β-CD/Fc-PEG micelles have potential to be electrochemical responsive and
can be applied as potential controlled drug released carriers.
POLY 334: Production of polymeric composites with self-healing functionality by multi-axial electrospinning

Jamal Seyyed Monfared Zanjani¹, jamals@sabanciuniv.edu, Burcu Saner Okan², Mehmet Yildiz¹, Yusuf Z. Menceloglu¹. (1) Faculty of Engineering and Natural Sciences, Sabanci University, Istanbul, Turkey (2) Sabanci University Nanotechnology Research and Application Center, SUNUM, Istanbul, Turkey

Thermoset polymeric materials have brittle behavior and suffer from poor resistance to crack initiation and growth while subjecting to external loads, resulting in gradually degradation of properties as a function of time. Thus, the production of polymeric composites with self-healing functionality is highly desirable and has started to gain a great attention in the recent years.

In the present study, a novel architecture of self-healing electrospun fibers with encapsulated dicyclopentadiene (DCPD) as healing agent is fabricated through multi-axial electrospinning process (Figure 1). In contrast to the most of the encapsulation methods, electrospinning is based on physical forces to form the core/sheath structure, and it provides uniform morphology and prevents the leakage of healing agent through the fibers. In order to obtain fibers with healing functionality, DCPD is encapsulated inside of fiber covered by two different polymeric layer with different polarities which are polyacrylamide (PAAm) as an intermediate layer and polymethyl methacrylate with dispersed catalyst particles as an outer layer. Electrospinning of PAAm as an intermediate layer of fiber provides an inert media for DCPD monomers inside the fibers. The low affinity of middle wall polymer and healing agent encapsulated in the core of fibers provides minimum interaction of healing agent with surrounding media as well as decreases the diffusion rate of healing agent through the wall of fiber resulting in extending the efficiency and lifetime of healing functionality of fibers.

Figure 1. Schematic of self-healing concept, (A) healing fibers is embedded in a structural composite matrix, (B) Crack formation in the matrix because of external load and rupture of healing fibers, (C) Release of healing agent from broken healing fibers, (D) healing of initiated micro-cracks.
POLY 335: Detecting early metal corrosion via “turn-on” fluorescence in smart epoxy coatings

DEBANJANA GHOSH, dghosh@georgiasouthern.edu, Weihua Ming. Department of Chemistry, Georgia Southern University, Statesboro, Georgia, United States

Metal corrosion has been a perennial issue that has enormous economic impact if not detected timely and treated properly. The decision on when to perform maintenance on existing steel and other metallic structures is unfortunately delayed until extensive corrosion has occurred. We have developed a “turn-on” fluorescence strategy by embedding spirolactam molecules in coatings to successfully detect early metal (steel and aluminum) corrosion, which is capable of “reporting” early stages of metal corrosion. This strategy has the potential to save tremendous cost related to metal maintenance.
POLY 336: Glucose sensitive hydrogels with embedded ferromagnetic particles for continuous glucose monitoring

Seung-Hei Cho\textsuperscript{1,2}, cho.seunghei@utah.edu, Jules J. Magda\textsuperscript{1}, Prashant Tathireddy\textsuperscript{3,2}.\textsuperspace
(1) Chemical Engin Dept Rm 3290, University of Utah, Salt Lake City, Utah, United States (2) Applied Biosensors, Salt Lake City, Utah, United States (3) Electrical and Computer Engineering, University of Utah, Salt Lake City, Utah, United States

Biomolecular sensors have received attention in the biomedical field because they can potentially be used to simplify complicated, time-consuming, and site-limited medical procedures. The accuracy and efficiency of a biomolecular sensor depends on the analyte recognition element, as well as the method used to transduce analyte recognition events into electrical signals. In the current research, the material used as the analyte recognition element was a glucose sensitive hydrogel (GSH), which is a cross-linked polymer network that reversibly swells and absorbs water in response to changes in external glucose concentration changes. This material was chosen due to its properties such as good biocompatibility, nontoxicity, and easy modification of chemical structure. We developed a GSH using 3-acrylamidophenylboronic acid as a glucose-binding monomer, and N-3-dimethylaminopropyl acrylamide as a monomer for enhancing glucose-binding selectivity. This GSH shrinks in response to increase of environmental glucose concentration while the hydrogel swells in response to increases of environmental fructose concentration. In situ synthesis of ferromagnetic nanoparticles within the GSH was performed, so that a magnetometer could be used to transduce GSH swelling changes into an electrical signal. Use of a magnetometer has many advantages, such as non-invasiveness, high sensitivity, small size, low price, and low power usage. The ferromagnetic particle alignment within the GSH was optimized with guidance from computer simulation results (Comsol 4.3, Comsol Multiphysics®). Glucose response of the GSH was measured with a commercial magnetometer (HMC 5883L, Honeywell). The GSH with ferromagnetic particles aligned parallel to the magnetometer surface showed good sensitivity in the physiological glucose range (0 to 10 mM).

Figure 1. Computer simulation of magnetic flux with x-direction aligned magnetic particles within a hydrogel. Figure 2. Glucose responses of a magnetic particle embedded glucose responsive hydrogel measured by a magnetometer.
Highly efficient, reproducible and scalable approaches for the exfoliation, processing and assembly of MoS$_2$ are critical for emerging electronic and energy applications. Additive free techniques, such as solvent assisted exfoliation, offer numerous advantages, including the potential to minimize chemical modification of the layer and the resultant introduction of opto-electronic defects. The mechanism of exfoliation and the role of the organic solvent, such as N-Methyl-2-pyrrolidone (NMP), however is not well understood. Based on systematic variation of solvent moisture content, environment (N$_2$/Air) and processing conditions (sonication time and centrifugation speed), we confirm that MoS$_2$ exfoliation in NMP is substantially enhanced by the in-situ formation of organic reductants during the sonication process. Oxidative by-products (5-hydroxy-N-methyl-2-pyrrolidone / N-methylsuccinimide) of NMP are redox active to transition metals, resulting in the formation of negatively charged MoS$_2$ layers and their subsequent electrostatic stability in solution. Higher NMP moisture content corresponds to more efficient exfoliation. Likewise, inert atmosphere (N$_2$) and no moisture are not suitable for exfoliation. The underlying exfoliation mechanism and reactivity of the solvent were confirmed by multiple characterization techniques, including GC-Mass, XPS, UV-Vis, Raman, and PL spectra as well as HR-TEM and AFM images. The identification of the role of organic reductants in the solvent-assisted exfoliation of MoS$_2$, and the recognition that MoS$_2$ exfoliation in NMP is more complex than surface energy equivalence, provides new routes to tailor transition metal chalcogenide exfoliation and control the layer defect structure for organic solvent-based opto-electronic inks.
Molecular gels contain nanofibrillar networks which are formed by self-assembly of low molecular weight species. The intrinsic non-covalent nature of these gels makes them especially sensitive to environmental variables such as temperature, pH, chemicals or ultrasounds among others. Controlling the assembly/disassembly process of gels allows for the preparation smart materials with biomedical applications such as controlled release or tissue engineering.

Following our previous work on molecular gels,¹ here we report on a novel approach to prepare smart molecular gels which is based on the simultaneous use of two low molecular weight gelators. Choosing the appropriate stimulus, selective disruption of full disruption of the two-component fibrillar network can be achieved.

In one case, the use of mixtures of organogelators 1 and 2, which contain respectively naphthalimide and acridine fluorescent groups, affords a photonic material with tunable properties. The presence of both gelators in the fibres of the gel allows for energy transfer between both fluorophores. The addition of acetic acid selectively disassembles one of the fibrillar networks, blocking the energy transfer process.

In another example, two gelators derived respectively from pyridine and L-proline, afford two-component hydrogels with pH tunable properties. Upon going from basic to acidic pH four different stages are seen: two component gel, solution, one component gel and solution again. The chameleonic nature of this gel can be exploited for pH-controlled release of entrapped species.

POLY 339: Preparation of neutral color polymeric electrochromic devices using an commercial organic dye

Yumin Zhu¹,², YUMZHU11@GMAIL.COM, Michael T. Otley¹,², Xiaozheng Zhang², Mengfang Li², Gregory A. Sotzing¹,². (1) Department of Chemistry, University of Connecticut, Storrs, Connecticut, United States (2) Polymer Program, University of Connecticut, Storrs, Connecticut, United States

Electrochromics that exhibit neutral color transitions are of special interests in the current display industry for the fabrication of lighter, thinner and lower-power devices. A neutral color is a color not associated with any single hue. Among the eyewear market for military and consumer use, neutral grey sunglasses have dominated a large portion as they don’t distort human eye perception of colors or affect the contrast and their low brightness minimizes eye fatigue and develops a calm, non-distractive atmosphere. As opposed to the traditional synthetic approach to create derivatized conducting polymers for achieving a specific color, we introduce a facile, one-step method to color tune electrochromic devices (ECDs) that switch between two neutral colors via in situ electrochemical polymerization of 3,4-Ethylenedioxythiophene (EDOT) in the presence of a commercially available solvent yellow dye. By optimizing polymer and yellow dye absorption intensities, neutral grey color ECDs were yielded with 30% photopic contrast (without background correction) and switching speeds as low as 1.5 seconds on flexible PET-ITO substrates. In addition, these devices demonstrated defect free color uniformity and stability over 1000 switching cycles. Large ECDs of 100 cm² active area were assembled, surpassing the switching area required for sunglasses, lenses, and small display applications. The in situ approach could be adapted to tune optical and colorimetric properties of other EC polymers in combination with the use of commercially available dyes.

(a) Percent transmittance and (b) images of a 100 cm² neutral color ECD prepared via the in situ method in its neutral (-2 V) and oxidized (+2 V) states, respectively.
POLY 340: Rationally engineering phototherapy modules of eosin-conjugated responsive polymeric nanocarriers via intracellular endocytic pH gradients


Spatiotemporal switching of respective phototherapy modes at the cellular level with minimum side effects and high therapeutic efficacy is a major challenge for cancer phototherapy. Herein we demonstrate how to address this issue by employing photosensitizer-conjugated pH-responsive block copolymers in combination with intracellular endocytic pH gradients. At neutral pH corresponding to extracellular and cytosol milieu, the copolymers self-assemble into micelles with prominently quenched fluorescence emission and low $^{1}$O$_{2}$ generation capability, favoring highly efficient photothermal module. Under mildly acidic pH associated with endolysosomes, protonation-triggered micelle-to-unimer transition results in recovered emission and enhanced photodynamic $^{1}$O$_{2}$ efficiency, which synergistically actuates release of encapsulated drugs, endosomal escape, and photochemical internalization processes.
Thermal and dynamic mechanical analysis of films prepared from treated diatomaceous earth (DE), untreated diatomaceous earth (DE), silica and epoxy have been studied. Epoxy films with different amounts of untreated and silane-treated DE were prepared. The storage modulus of the films was found to increase with the incorporation of treated and untreated DE particles in an epoxy matrix. A broad tan-delta peak was observed for the films with treated DE as compared to that of untreated DE particles. Similar mechanical properties were observed for epoxy-untreated DE and epoxy-silica films. The thermal properties of the epoxy-DE films have also been studied using differential scanning calorimetry (DSC).

Figure 1: Preparation of epoxy and treated DE films; A - treated DE powder, B - epoxy in THF, C - epoxy-treated DE films, D - scanning electron micrograph of treated DE.
In this study, a novel polymer assembly is utilized to create ionic polymer composite actuators. Ionic polymer-metal composites (IPMCs) have been demonstrated in several instances and are pursued for their potential application as artificial muscles. These IPMCs utilize expensive and brittle layers of precious metal to operate. Here, we demonstrate the creation of ionic polymer-carbon composites (IPCCs), which demonstrate similar actuation properties as IPMCs without using any precious metals. These composites contain carbon fiber electrodes that are synthesized via electrospinning of a polyacrylonitrile/dimethylformamide solution and a subsequent heat treatment. The resulting electrode material is flexible, conductive (6 S/cm), and highly porous (96% porous by surface area). Following the synthesis of the electrodes, a Nafion® ionomer solution is impregnated into the electrodes and a Nafion® membrane is placed between the two electrodes. In operation, an applied voltage creates an ion concentration gradient in the Nafion® membrane, which also establishes a water concentration gradient. This effect, confirmed through neutron imaging, causes asymmetric membrane swelling and deformation. Upon application of a +/- 5 V electric field, the IPCCs demonstrate noticeable actuation. Similarly, upon application of mechanical deformation a voltage of 1.3 mV/mm is generated across the device. Potential applications for these IPCCs include artificial muscles or flexible energy harvesting for use in clothing.

A schematic of the IPCC device. The electrospun carbon electrodes are impregnated with Nafion and are layered on either side of a Nafion membrane. Application of a voltage causes ion transport between electrodes, resulting in device actuation.

An image demonstrating the electro-mechanical response of an IPCC actuator. The voltage generated by the device changes sign based on the direction of the actuation.
Cyanate ester (CE resins), also known as polycyanurate networks, are thermoset polymers that offer an outstanding combination of physical properties that have made them highly desirable for applications ranging from printed circuit boards and radomes to magnet casings for thermonuclear fusion reactors and aerospace components. Since many of the desired properties of CE resins are shared with fluorinated polymers, a logical approach to further optimize polycyanurate networks is to impart fluorinated moieties to the polymer backbone. In previous accounts, we introduced the first of a new class of fluorinated cyanate ester resins that exhibited extremely low moisture uptake at full cure which was among the lowest values measured for any polycyanurate network. Herein we present the synthesis and characterization of a new perfluorocyclic-functionalized polycyanurate derived from bisphenol A and perfluorocyclopentene.
Graphene oxide (GO) was prepared from natural flaked graphite by using a modified Hummers method. The ultrasonication process was added to exfoliate Graphene oxide sheet and cut them into smaller pieces. Then, the aniline monomer was added into the system and the in situ polymerization of polyaniline was occurred after adding the oxidant, (NH₄)₂S₂O₈ (APS). The open cycle potential (OCP) curve was recorded during the in-situ polymerization. It was found that there is a significant reaction time delay on OCP, which indicated a delay in polymerization by using different counter ions such as HCl, HClO₄, and H₂SO₄, as indicated in Figure 1. The resulting GO/Polyaniline composite was fully characterized by transmission electron microscopy (TEM), Atomic force microscope (AFM), Fourier transform infrared spectroscopy (FTIR), Raman spectra, Thermo Gravimetric Analyze (TGA) and fluorescence spectrometer. The corresponding industrial applications would be reported during the presentation.
Graphene / polyaniline nanocomposite was successfully produced by using aniline monomer react with expendable Graphite in the assistance of supercritical carbon dioxide (SC CO₂). The graphite was intercalated by the aniline monomer and exfoliated during the aniline polymerization. The resulting graphene / polyaniline nanocomposite was fully characterized by transmission electron microscopy (TEM), Atomic force microscope (AFM), Fourier transform infrared spectroscopy (FTIR), Raman spectra, Thermo Gravimetric Analyze (TGA) and fluorescence spectrometer. We had demonstrated a single-step process to achieve the aniline intercalation and polymerization to make the Graphene / Polyaniline composite. The polyaniline was firmly attached at on the surface of graphene to form a uniform “comb” network structure, which had the benefit to leverage the functional performance from polyaniline and nano features from Graphene structure. The functionalized Graphene / polyaniline nanocomposite would have potential applications in supercapacitor, transparent electrodes and catalysis, and nano devices.
The described coatings include the group A components which can cure into film and the group B components which contain curing agent. The group A components include modification of graphene oxide, zinc powder, waterborne resins, fillers, hydroxyl dispersing agents, auxiliaries. In group B are divided into aqueous polymer isocyanate. To join the modification of graphene oxide to anti-corrosion coatings, which has an excellent waterproof and corrosion resistance, alkali resistance, weather resistance, aging resistance and so on. Selecting various components, improving the preservation effect at the same time, greatly reducing the content of zinc powder, overcoming zinc rich coatings by way of sacrifice at the expense of zinc power coating, smartly reduces zinc oxide fog in welding. Meanwhile, anti-corrosive coatings are waterborne and green environmental protection, volatilizing organic solvent-free.
As a probe of the critical driving forces for polymer adhesion, temperature-modulated differential scanning calorimetry (TMDSC) on adsorbed poly(vinyl acetate) (PVAc) on silica has been performed. Three different regions of thermal activity were observed. At low adsorbed amounts, the onset of segmental motion occurred at temperatures significantly higher than glass-transition temperature ($T_g$) of the bulk polymer. With increasing the adsorbed amount, two other regions were found at temperatures slightly higher and slightly lower than the $T_g$ of bulk PVAc. Molecular dynamics simulations were performed to provide insight on the structure of adsorbed PVAc on silica and explain the experimental results. The effect of adsorbed amount and temperature on the structure of PVAc near the silica surface, in the bulk-like polymer region and the polymer/air interface has been analyzed. These effects have been quantified as the number density of carbonyl groups of PVAc as a function of the radial distance from the oxygen atoms on the silica surface and also the orientation of chemical groups at interface. The silica surface modified the polymer structure at the interface and polymer chains formed three different layers evidenced by changes in the number density profile and the orientation of carbonyl groups.
The synthesis and preliminary characterization of nanocomposites obtained by loading polyethylene oxide with TiO$_2$ nanoparticles are reported. Almost cubic TiO$_2$ nanoparticles (anatase) of about 15 nm have been purchased from Nanostructured and Amorphous Materials, Inc. PEO has been purchased from Sigma Aldrich. PEO-TiO$_2$ nanocomposites were obtained by high pressure homogenization by using a Nano DeBee equipment, at room temperature. Differential Scanning Calorimetry measurements have been performed by TA Instruments equipment. Raman spectroscopy spectra have been recorded by Bruker Sentera confocal microscope with a laser diode operating at 785 nm. Raman spectra of some samples (pristine PEO, TiO$_2$, and some PEO-TiO$_2$ nanocomposites) are collected in Fig. 1. The typical Raman lines of anatase and of PEO have been observed. Upon loading with TiO$_2$, the lines due to the polymeric matrix are becoming weaker and broader. The dependence of the Raman line position, shape, and width on the concentration of TiO$_2$ is analyzed in detail. Additional information obtained by DSC are discussed. The dependence of the melting, crystallization, and glass transition temperature on the content of TiO$_2$ and heating/cooling rates are discussed. The DSC dependencies for the second heating-cooling cycle, showing the glass, crystallization, and melting transitions are shown in Fig. 2.
Certain materials properties are viewed as contradictory. High electrical and thermal conductivity are associated with hard, crystalline materials such as metals or graphite. Conversely, softness is associated with biological materials, polymers, colloids, and disordered structures, which are also thermally and electrically insulating. We have essentially accepted that certain contradictions cannot be resolved. For example, we have no material that is electrically conductive like a metal and can be sutured or sewn, despite the obvious need in medical devices and wearable electronics. Nanoscale carbon—including Carbon Nanotubes (CNTs) and graphene—has remarkable electrical, thermal, and mechanical properties; thus, it is uniquely suited as building block for novel conductors. Yet, broad applications of nanoscale carbon to real-world problems have largely gone unfulfilled because of difficult synthesis and laborious processing. This hurdle can be overcome by treating CNTs and graphene as hybrids between polymer molecules and colloidal particles and designing fluid-phase directed assembly routes for soft conductors. Even at minute concentrations, CNTs form complex fluid phases with intriguing properties. In crowded environments (e.g., gels), CNTs reptate like stiff polymers; surprisingly, the small bending flexibility of CNTs strongly enhances their motion. CNTs and graphene can be solution-processed in strong acids, their sole true solvents. At low concentration, these fluids can be used for making transparent, conducting, flexible films and coatings, as well as highly porous, soft three-dimensional structures (foams). At high concentration, CNTs and graphene form liquid crystals that can be scalably spun into high-performance multi-functional fibers. These CNT fibers combine the high conductivity, strength, and the emergent property of softness; they are already finding high-value applications in aerospace electronics, Hi-Fi cables, and field emission. As soft conductors, CNT fibers provide a natural interface to the electrical function of the body as restorative sutures for electrically damaged heart tissue as well as electrodes for stimulating and sensing the activity of the brain. Fluid processing allows the direct coating of shielding conductors in coaxial cables.
As the second most abundant natural polymer after cellulose[1], lignin provides an ideal platform for the development of novel polymeric and composite materials. Lignin is a hydrophobic, cross-linked polymer comprised of varying quantities of three phenylpropanoid monomers known collectively as monolignols. Easily isolated from plant materials during the industrial processing of biomass, lignin is abundant in industrial waste streams[2]. While the structure of monolignols serves as a useful scaffold in monomer design, lignin is considered a low value product and has little commercial use. In 2011, the worldwide pulp and paper industry produced 50 million tons of lignin but only 2% was used commercially and the rest was burned as a low value fuel[3]. To utilize this underused material as a feedstock, a series of monomers and polymers based on the monolignol scaffold were developed for the incorporation of lignin-based monomers into polymeric materials. The resulting copolymeric materials were characterized by both material and chemical properties. Preliminary results from these new monolignol-based copolymers are suggestive that lignocellulose may be useful as a new feedstock for commodity polymeric materials.


Standard lignin monomers (monolignols)
To address the dual problems of the depletion of natural resources and the environmental impact of a growing volume of wastes, effective recycling of various products and materials has become an important challenge. Especially, the amount of plastic waste is extremely large, and thus it is very important to establish effective process of recycling them as soon as possible.

However, the mechanical properties and durability properties of the products made from waste plastics are believed to be inferior to those of products molded from virgin plastics, and thus their application area is presently limited. Usually, the reason of above phenomena has been thought to be caused by chemical degradation. However, we recently found that recycled pre-consumer polypropylene (Pre-RPP) was not chemically degraded and had almost same molecular properties of virgin polypropylene (VPP), the inner structure and mechanical properties were very different. And by choosing suitable molding temperature, molding time, and cooling condition, the mechanical properties of Pre-RPP had changed very much and some of them became almost same properties of VPP. These results suggest that the main factor of the degradation of wasted plastics is physical degradation and we can establish new recycling process to establish environmentally benign material cycle. We extended the investigation to recycled packaging plastics. We also found that tensile properties of these plastics also much depend on temperature of molding and cooling conditions.
Sustainable polymers derived from renewable resources have recently been gaining attention. The current study details the ring-opening polymerization of gluconolactone, a cyclic ester derived from glucose, initiated by an aluminum alkoxide, Al(Oi-Pr)$_3$. Experiments were performed under an inert N$_2$ atmosphere with 1.0 mol% catalyst loading in DMF. Analysis of the product was carried out via $^1$H NMR, $^{13}$C NMR and LC/MS. To investigate the mechanism, density functional calculations were performed with Gaussian 09 using the M06L functional and the 6-31G(d) basis set. Thermodynamic calculations suggest a coordination-insertion mechanism, as opposed to an anionic pathway. Additionally, structure and reactivity of proposed aggregates of the Al(Oi-Pr)$_3$ initiator were investigated.
Polyarylamines are valued for their hole-transporting ability and high degree structural stability. However, due to the highly conjugated nature of the molecular structure, solution processing of these materials is severely limited. In order to increase solubility, perfluorocyclopentene (PFCP) functional units were installed in the backbone of arylamine polymers. The incorporation of fluorine in polymeric systems is known to improve solubility resulting in better processability to afford bulk materials. This work will focus on the synthesis, thermal characterization, and optical properties of PFCP-functionalized \(N,N'\)-diphenylbenzidine bisphenol A step-growth copolymers. The successful synthesis of these new partially fluorinated polyarylamines and their properties demonstrate great potential in the evolving area of organic electronics.
Polymer photovoltaic cells have the potential to be more cost-effective on the large scale compared to their inorganic counterparts, due to their ease of processing through solution casting and inkjet printing onto flexible substrates. Unfortunately, polymer photovoltaic cells only achieve low efficiencies when compared to inorganics. Conventional polymer photovoltaic devices utilize fullerene derivatives as the electron accepting and transport material, giving high performance, but come with drawbacks, like narrow visible light absorbance, environmental instability, and poor processability. This project aims to synthesize and use tri(perylene bisimides) (tri-PBIs) as a novel electron accepting material in polymer solar cells, with the potential to increase the efficiency of polymer solar cells through increased light absorbance and morphology and phase control, and bring greater photochemical stability and increased device lifetime to the cells. Tri-PBIs were synthesized according to literature procedure, and characterized with 1H NMR, MALDI-TOF mass spectrometry, and UV-Vis spectroscopy. Morphologies of the P3HT:tri-PBI blends were characterized using atomic force microscopy.
POLY 355: Incorporation of Diels-Alder chemistry into polymer matrices via an inimer approach

Erik D. Crenshaw, ecrensha@calpoly.edu, Miles Markmann, Tristan Kleine, Alex E. London, Philip J. Costanzo. Chemistry, California Polytechnic State U, 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 was employed to prepare an inimer compound to integrate DA linkages at branching points within a branched polymer backbone. Upon the application of a thermal stimulus, the retro-DA was induced and subsequent branch points were reduced to transform a highly branch architecture into a linear topology. [figure1]
Fluorinated compounds have been readily integrated into polymers, composites, and other functional materials for use in hydrophobic applications due to their low surface energy. Fluorinated silsesquioxanes (F-POSS) in particular have drawn attention for their robust structure and industrial scalability. However, previous endeavors to obtain these specialized materials have relied heavily on incorporating perfluorinated carbon chains into the periphery of the materials’ structure. Due to a heightened concern for the environmental impacts of perfluorinated carbon chains, there is growing need for alternatives that mitigate these fears whilst maintaining the desired properties. This work will discuss current research efforts on the preparation, properties, and characterization of functional F-POSS materials, with a focus on the development of new monomers with latent reactivity.
Due to being excellent activators, sulfonamide groups were used to synthesize polyarylene ethers (PAEs) through meta-activated nucleophilic aromatic substitution (NAS). A series of \(N\)-alkyl-\(N\)-phenyl-3,5-difluorobenzene sulfonamides was synthesized, with alkyl groups ranging from methyl to dodecyl, along with \(N\)-allyl-\(N\)-phenyl-3,5-difluorobenzene sulfonamide. These sulfonamides were then polymerized with bisphenol-A and the molecular weights of the polymers were determined using gel permeation chromatography (GPC). Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to determine the glass transition temperatures (\(T_g\)) of the polymers. \(T_g\) values were inversely proportional to the alkyl length chain of the polymer with the methyl version possessing a \(T_g\) of 122 °C while the dodecyl group exhibited a \(T_g\) of only 46 °C. Introduction of the allyl group provides potential access to “post” polymerization modification reactions through thiol-ene chemistry as well as a site for cross-linking to afford elastomers.

Figure 1. \(T_g\) values of the synthesized PAEs vs. the alkyl chain length.
Conducting polymers (CPs) have been a prime topic in materials research in recent years due to their remarkable electrical and optical properties. In addition to their demonstrated use in solar cells, diodes, and transistors, CPs have become a popular substitute for metals in devices that electronically interface with biological tissues. Unfortunately these polymers tend to be brittle and inelastic due to their inherent conjugated backbone, limiting these prospective applications. To combat this issue, we are investigating the effects of crosslinking on the mechanical and electrical properties of polypyrrole and polythiophene-based films. To synthesize such materials, the two ends of a flexible polyether were functionalized with either pyrrole or thiophene-based monomers. By controlling the stoichiometry, differing amounts of these bi-functional crosslinking groups were then incorporated into conducting polymer films via electropolymerization. Here we report the mechanical, physical, and electrical properties of films containing different proportions of crosslinker as characterized using FTIR, CV, SEM, DMA, TGA, DSC, and conductivity measurements.
POLY 359: Optimization silk-polypyrrole composite films for use as electromechanical actuators

Jesse Larson¹, jesselarson10@gmail.com, Nathan Bradshaw¹, Carly Klemke², Sean Severt¹, Janelle Leger², Amanda Murphy¹. (1) Chemistry, Western Washington University, Bellingham, Washington, United States (2) Physics and Astronomy, Western Washington University, Bellingham, Washington, United States

Conductive polymers have been shown to expand and contract in response to electrical stimuli, allowing them to be used as actuators that can emulate the function of muscle tissue. Therefore, devices made from these polymers are highly sought after for a variety of biomedical applications. We have recently developed single component, metal-free actuators based on composites of silk fibroin and poly(pyrrole) (PPy). The incorporation of silk gives these devices enhanced mechanical strength, flexibility, and biocompatibility over PPy films alone. Here we present the fabrication and characterization of optimized silk-PPy composite films, and evaluate the electrochemical stability, free-end bending actuation performance, and strain and force generation of devices in a biologically-relevant environment.

reduce ↔ oxidize
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 was employed to prepare an DA-initiator compound to integrate DA linkages within the main chain of the polymer backbone. Upon the application of a thermal stimulus, the retro-DA was induced and the molecular weight of polymer was reduced. [figure1]
Our group explores thiol-ene / acrylate thermoset polymers for desired thermomechanical properties (especially shape change / shape memory and modulus change at certain conditions) for application in neural interface devices and flexible electronics [Ware et al., Polymer Reviews 53, p.108 (2013)]. During the fabrication process of such devices, thin films need to be created from the liquid monomer mixture before curing. Here, we present our investigations of the spin coating of SMP-6, a shape memory polymer, that is created by mixing a tri-ene (TATATO), an acrylate (TCMDA), a tri-thiol (TMICN), and a photo initiator (DMPA), then curing the mixture under UV irradiation for 1 hour at 365 nanometer, and then post curing for 24 hrs at 120 °C. The SMP-6 monomer mixture is a relatively viscous fluid (approximately 900 cP) that thins relatively slowly (several minutes) during the spin coating process, and this allows for the coating of a relatively wide selection of thicknesses (2 to 80 µm). Figure 1 a) and b) shows the spin curves recorded using various spin times (residence times). Average film thickness and the variation across samples were measured after curing using a stylus profiler tip scanned relative to the original substrate surface at severed sections. Thickness variation was found to be below 0.5 micrometer for 4 and 6 min spin times, but up to 5 micrometer for 0.5 min spin time. Thickness variations can also be observed and monitored through visual inspection, as seen in the photographs of Figure 1 c and d. Other film defects include particles and their comets, and bubbles. In order to reduce thickness variations and to be able to filter the monomer mixture from particles, dilution with solvents was investigated. We present preliminary results from acetone-diluted samples.
POLY 362: Investigation of thermally induced microphase separation in dicarboximide functionalized oxanorbornyl diblock copolymers by atomic force microscopy

**Tom Kolibaba, kolibatj@plu.edu, Dean A. Waldow. Department of Chemistry, Pacific Lutheran University, Tacoma, Washington, United States**

Solid polymer electrolytes (SPEs) offer a route to safer and potentially more efficient lithium-ion batteries by eliminating the use of flammable electrolyte supports. However, current SPEs are limited by the fact that their lithium-ion conductivity is tied the local segmental dynamics of the polymer backbone and that many do little to prevent the dendritic growth that can cause short-circuits and fires in lithium ion and lithium metal batteries. Polymers with a bulky, sterically hindered backbone and an ion-conductive tail may offer a solution to the first issue, by working to decouple ionic conductivity from local segmental dynamics. The addition of a high-modulus block to this polymer generates nanomorphologies leading to conductive ion “paths” and structural regions to prevent lithium dendrites from growing. Consequentially, the nanomorphologies of dicarboximide functionalized oxanorbornyl diblock copolymers synthesized via ring opening metathesis polymerization were investigated through the use of atomic force microscopy and thermal annealing to determine the phase diagram of this diblock system.
The creation of bisphenol-A (BPA) replacements is an important task for the chemical industry, as concerns have been raised due to its potential as a disruptor to the endocrine system. BPA is the most widely used platform for epoxy resins, which accounts for a large amount of the thermoset polymer market. Levulinic acid has been praised as one of the “Top Value Added Chemicals from Biomass” by the US Department of Energy. Derived from the degradation of cellulose, levulinic acid is a biobased platform chemical which has proven to be relatively non-toxic, easily producible and can be converted into a range of chemicals. The reaction of levulinic acid with phenol yields diphenolic acid which has displayed promise as a replacement of BPA in polycarbonates, but has relatively been unexplored in epoxy resins.

We report the synthesis of epoxy monomers from esters of diphenolic acid. The diglycidal ethers of diphenolate esters (DGEDPE) were cured using isophorone diamine (IPDA), a widely used hardener for epoxy resins. Results were compared to the diglycidal ether of bisphenol-A (DGEBA) under similar curing conditions. Thermal and mechanical properties were tested using dynamic mechanical analysis and tensile testing. We saw that DGEDPE has similar mechanical and physical properties of DGEBA. The thermal properties of DGEDPE can be controlled through manipulation of the ester, with a near linear relationship between number of carbons in the side chain and the glass transition temperature. Further investigations are being carried out to examine this monomer’s applicability for the replacement of DGEBA for structural applications.
POLY 364: Investigation of self-assembled nanomorphologies of functionalized dicarboxide oxanorbornyl diblock copolymers via small angle X-ray scattering and optical birefringence

Jesus Rosales, rosaleja@plu.edu, Dean A. Waldow. Department of Chemistry, Pacific Lutheran University, Tacoma, Washington, United States

Solid polymer electrolytes (SPE’s) may offer a solution to safer lithium-ion batteries by replacing more flammable electrolyte supports. However, these SPE’s have shown to be less efficient in terms of ionic conductivity in comparison to traditional battery electrolytes. A solution to this problem could be to use a diblock copolymer electrolyte that is composed of a conductive block that could address the polymer’s conductivity and a rigid block that could address dendritic growth on the battery’s electrodes. Diblocks can form self-assembled nanomorphologies, which could allow lithium ion conductivity in the diblock electrolyte. In our exploration of these diblock materials, we were able to synthesize functionalized dicarboxide oxanorbornyl diblocks with a monomer using an ethylene oxide side chain and another monomer using a phenyl side chain via ring opening metathesis polymerization (ROMP). We explored the nanomorphologies of the diblocks using small angle X-ray scattering (SAXS) and optical birefringence on annealed polymer films. Data from a variety of diblock copolymers will be presented with the graph below being for a diblock copolymer (0.45 wt. fraction of the structural block) after annealing at 180°C for 45 minutes and slowly cooling at a rate of 0.5°C/minute.
Epilepsy is a neurodegenerative disease that affects more than 3 million people within the United States. Epilepsy is characterized by the continued presence of seizures, which occurs when there is an imbalance between the neurotransmission mediated by the central nervous system neurotransmitters, glutamate and γ-amino butyric acid (GABA). Cationic, polymeric nanoparticles have been hypothesized to be a potential transporter for negatively charged, small interfering ribonucleic acid (siRNA), which can be used for selective gene silencing of the GABAergic genes, in the potential neurological model organism, *D. tigrinia*, a species of planarian flatworm. In this study, polymeric nanoparticles where fabricated from alanine-based polymers p(H$_2$N-Ala-EMA), p(H$_2$N-Ala-EMA)-b-PMMA and py-p(H$_2$N-Ala-EMA)-b-PMMA, through the use of dialysis and then characterized using Scanning Electron Microscopy (SEM). Biological toxicity tests were carried out for both varying concentrations of polymeric nanoparticle solutions in whole and regenerating *D. tigrina* worms. Conformation and structural characterization of si-RNA and polymeric nanoparticle complexes were done using gel retardation assay, SEM and Atomic Force Microscopy (AFM). Future investigations will include characterizing siRNA-polymeric nanoparticle complexes with dynamic light scattering and utilizing such complexes to selectively silence the GABAergic genes of interest in *D. tigrina*.
The safety and dependability of current lithium-ion battery’s electrolyte support is under criticism due to flammability and dendrite issues. A potential method to address this issue is the development of solid polymer electrolyte supports. By synthesizing polymers that containing a rigid, bulky backbone coupled with an ion-conducting ethylene oxide region, our aim is to potentially decouple ionic conductivity from the segmental motion of the polymer. We report the syntheses and characterization of novel ethylene oxide functionalized dicarboxide oxanorbornyl monomers and polymers working towards the understanding side chain length. Dicarboxide oxanorbornyl monomers with varying oligomeric ethylene oxide side-chain lengths were synthesized and subsequently polymerized via ring-opening metathesis polymerization. The synthesized materials were characterized with $^1$H NMR, GPC and DSC. Ionic conductivity and dielectric spectroscopy measurements will be performed to analyze the relationship of the ionic conductivity relative to the polymer segmental motion.
There are two methods for introducing functional groups to poly(arylene ether)s, PAEs, in particular poly(arylene ether ketone)s, which are typically prepared via nucleophilic aromatic substitution, NAS. The first method involves the synthesis of functionalized monomers “pre” to the polymerization process. The second method installs the functional groups “post” to the formation of the polymer. It is of interest to design a single monomer that allows either the preparation of functional monomers in situ, followed by subsequent polymerization or preparation of the polymer followed by modification. This presentation describes our efforts to utilize reactivity differences in 3,5,4'-trifluorobenzophenone (1), to prepare functional poly(arylene ether ketone)s via a one-pot procedure. Kinetic studies afforded the activation energies for the three different fluoride reactive sites. The kinetic parameters were then applied to the polymerization of 1, acting as a B₂-type monomer, with Bisphenol-A to provide a polymer carrying the third fluorine site for “post” modification.
POLY 368: Energy efficient, closed-loop, water-free protocol for processing of cellulosics with quantitative recovery of an ionic liquid solvent

Darren Smith¹, Ryan Carrazzone¹, rjc9908@rit.edu, Mason Schloder², Thomas W. Smith¹. (1) School of Chemistry and Materials Science, Rochester Institute of Technology, Webster, New York, United States (2) College of Health Sciences and Technology, Rochester Institute of Technology, Rochester, New York, United States

About 200 million tons of cellulose are used annually as pulp in the manufacture and processing of textile fibers and packaging materials. The two industrial methods most often used to process cellulosic materials are the viscose method and the NMMO (N-methylmorpholine-N-oxide) process. Although the dissolution in NMMO has many advantages, the majority, 95%, of the cellulose fiber derivatives are still manufactured in the viscose process with intermediacy of the xanthate ester. Given concerns relating to environmental impact, particularly in regards to the viscose process, the chemicals used in processing cellulose have come under greater scrutiny; and, more cost effective and ecologically benign, alternatives are continually being sought. In recent years, numerous studies have been published on the dissolution of cellulose and the dissolution and deconstruction of lignocellulosic materials in ionic liquids. As is the case with NMMO, ionic liquids provide a solvent-based protocol for processing cellulosic materials. Hydrophilic ionic liquids, specifically alkylimidazolium chlorides, acetates and alkylphosphonates, have been reported to be excellent solvents for dissolution and processing of cellulose. In these reports, cellulose has typically been regenerated by dilution of the cellulose/ionic liquid solution with water. Due to their high cost it is necessary that ionic liquid solvents be recovered and reused. This being said, recovery of the hydrophilic ionic liquid in a water-free state is energy intensive. In the present research, a low-energy, water-free, process for dissolution and processing of cellulose in an ionic liquid, 1-ethyl-3-methylimidazolium chloride (EMImCl), with quantitative recovery of EMImCl in a water-free state has been demonstrated.
Incorporation of high aspect ratio nanoplatelets has been widely investigated in efforts to increase the barrier properties of commercial polymer films. In this study we pursued the creation of high barrier systems that outperform typical nanocomposites though the use of unique microlayer film architectures. Short stacks of high aspect ratio graphene nanoplatelets (xGnP®) were melt blended into Linear Low Density Polyethylene (LLDPE). The nanocomposites were further coextruded with pure Low Density Polyethylene (LDPE) in an alternating multilayer system to further enhance the barrier properties. It has been shown that when microlayers of LLDPE and LDPE are taken into the melt and allowed to interdiffuse, that the greater mobility of the more linear LLDPE chains as compared to the more branched LDPE chains cause a layer boundary movement in the direction of the more slowly diffusing polymer chains. This results in a thickening of the LDPE layers and a shrinkage of the LLLLDE nanocomposite layers where particle concentration can be increased to loadings that would otherwise be difficult to melt process. In this investigation we looked into the effects of particle size (5μm and 25μm diameter xGnP®), particle loading (0.25-15 wt/wt%), and melt processing conditions (number of extrusion passes) on barrier and melt flow properties. Oxygen gas transport, nanocomposite morphology, and melt flow properties were all monitored to optimize the nanocomposite systems before multilayer coextrusion.
Acrylonitrile is a monomer found to be easily polymerized into PAN fibers that has been used extensively in the textile industry. This PAN fiber was subsequently utilized as a carbon fiber precursor with high processing costs that limited its application. Several studies have been concluded showing the acility to co-polymerize acrylonitrile with several different monomers including methyl acrylate, vinyl acetate, styrene, vinyl imidazole, etc. Currently, acrylonitrile-co-1-vinyl imidazole polymer has been applied as a precursor for carbon fiber with its unique melt processability which can lower cost of production. Due to this, other applications have been made available which includes nitric oxide loading for enhanced wound healing via external bandages along with applications in supercapacitors. Here we have synthesized several different vinyl nitrogen containing ring monomers such as vinyl triazole and vinyl pyrrole and compared the properties exhibited by the copolymer post polymerization with acrylonitrile. These variable polymers are characterized using several different analytical techniques. With the unique characteristics of each polymer we will further investigate the ability to load and release NO along with its effects on stabilization of carbon fiber precursors.
In this project we seek to analyze the Shape Memory Polymers (SMP) developed in the Advanced Polymer Research Lab (APRL) at the University of Texas at Dallas for their comparative characterization and applications in subsequent uses. Shape memory polymers have a wide range of applications, with a significant focus here on biocompatible devices for use in vivo. The cross-linking of the thiolene networks allows novel compositions resulting in higher glass transition temperatures and low rubber modulus, as well as increased thermal stability. Due to the unique properties of these materials, thiol-ene SMPs show excellent promise for substrates in the flexible electronics industry.

To better understand how these polymer systems behave and to characterize them more completely for comparison to both other novel SMPs and current market available alternatives, it is necessary to perform rigorous testing as well as chemical analysis to ascertain performance across all possible situations for potential application. This includes the various chemical compatibilities proposed for testing here. To complete this project, it is intended that various cure methods and developments be compared across possible SMP compositions established in the lab, with particular emphasis on SMP 6, as well as commercially available alternatives for equivalent biocompatible usage. This will include exposure testing to ambient environments by means of degradation and stability testing at lengths commensurate to those expected in vivo. Analysis will then be performed to ascertain overall performance of the SMPs.

While an ultimate goal of basic chemical compatibility may be the desired outcome here, it is merely the first step in the performance analysis necessary to transition these shape memory polymers from laboratory to industry. Taken in aggregate, this research allows a more complete picture to be developed of not only SMPs, but the field of polymer research that is currently lacking in thermoplastics in general.

Figure 1. Curing of SMP 6 under UV and UV + heat
High-χ block copolymers are attractive for lithography due to their ability to self-assemble in the sub-10 nm regime. Unfortunately, surface energy minutiae often hinder the formation of useful orientations. For lithographic applications, this is particularly important, as orientation must be reproducible and defect-free across the entirety of the substrate. To facilitate the orientation process, an algebraic model has been developed to predict orientation conditions that confer perpendicular and parallel lamellar orientation. This model compares the free energy of perpendicular lamellae versus that of parallel lamellae at different film thicknesses with different top and bottom interfaces. Preliminary results show that with one neutral interface, the thickness window favoring vertical orientation shrinks as the other interface becomes more preferential. Furthermore, several unique circumstances exist when both interfaces are equally preferential toward the block copolymer, with the model predicting a wide processing window in which perpendicular orientation is preferred. Additionally, the thicknesses that can produce perpendicular orientation vary wildly depending on the preferences of the top and bottom interfaces. To test the validity of the model, rigorous experimental orientation studies were performed. These experiments largely corroborated the model's predictions. The results of this study will prove valuable for understanding thin film orientation control and for selecting processing conditions for block copolymer directed self-assembly.
Triblock copolymer brushes were created using ring opening metathesis polymerization, ROMP. Norbornenyl N-hydroxysuccinimidyl ester (N-NHS) was synthesized as the reactive monomer that will allow an amine modified DNA linker to be attached to the first and third block, while the central block will consist of polyethylene glycol, or PEG, of varying chain lengths and repeating units. These varying PEG chain lengths will allow us to have a size tag that is resolvable via transition electron microscopy, TEM. This will be important to verify that our DNA functionalized triblock polymers are in fact assembling in the pre-programmed fashion, namely an A-B alternating linear structure. Using a palindromic DNA sequence on macromonomer-A that will only hybridize to the sequence on either side of macromolecule-B we expect to form nanoworms or nano sausages.

(A) Gel image of the hairpin DNA-polymer conjugate and free DNA-1 (fluorescein filters were applied). (B) DLS data of the conjugate before (top) and after (bottom) annealing. (C) TEM image of the free DNA-polymer conjugate, showing a sphere-like morphology. (D–F) Condensed brushes following annealing. The inset in D shows the worm-like structure as it is being formed; the scale bar is 100 nm. Arrows point to branching (E) and displacement. (F) defects.
Polyurethanes represent a broad class of polymers widely applied in everyday-life. Although polyurethanes are easy to produce and have a broad range of adjustable properties, only a few polyurethane-based nanomaterials have been realized so far. Here we designed a novel class of water-soluble polyurethanes that combine multiple functionalities relevant for biomedical nano-applications. They can change their chemical and mechanical properties triggered by both changes in pH inside the body and intracellular redoxosomes. Crosslinking water-soluble polyurethanes leads to hydrogels, which are materials with soft mechanical properties useful for applications like drug delivery or tissue engineering. However, previously reported methods to create polyurethane-based hydrogels are limited for biomedical use, since they are based on toxic isocyanate-terminated prepolymers. Our novel gelation mechanism is based on physical interactions and does not require any free isocyanate groups, rendering our hydrogels non-toxic and applicable as drug delivery systems or injectable gels for in-situ tissue engineering.

Instant gelation of the polymer solution initiated by addition of acid
A series of novel, polypropylene oxide (PPO) based organogels have been synthesized and their moduli measured by cavitation rheometry (CR). Various molecular weights of amine terminated PPO were reacted with hexamethylene diisocyanate to yield PPO with urea functionality and isocyanate termini. Dissolution of the isocyanate terminated PPO into a variety of organic media and subsequent reaction with a primary amine yielded gels with moduli up to 50 kPa at weight percents as low as 2% for some solvents tested. The effect of size of primary amine “capper” was investigated but little effect on final moduli was observed. Solvent polarity was found to have a significant effect on the strength of the gels with non-polar solvents such as toluene and dichloromethane resulting in much stronger gels than those formed in more polar solvents such as THF and ethyl acetate. Additionally, the length of the PPO chain was investigated, where shorter PPO chain lengths were found to result in stronger gels at identical weight percent due to higher density of hydrogen bonding urea groups per mass of gel.
The effects of excess polyethylene oxide (PEO) chains on cementitious magnesium oxide (MgO) suspensions were examined through shear start up and creep tests along with viscosity calculations. Previous experiments involving MgO suspensions used samples with different amounts of ADVA, a superplasticizer found in commercial cements. During these past experiments, it was found that suspensions with the greatest magnitude of jamming could be due to extra ADVA comb-polymer that did not adsorb to MgO particles in the suspension. Because the side chains of ADVA are composed of PEO, excess PEO chains were introduced into new samples with constant ADVA content to investigate the entanglement between particles and particle aggregation. Suspensions with an increased concentration of PEO had broader overshoot peaks and thus longer periods of jamming. These suspensions were also more resistant to flow according to creep tests, which supports aggregation. After calculating viscosities of plateaus from shear start up data, it was discovered that there was not a linear trend in viscosity. However, samples with low PEO concentration and samples with high PEO concentration followed different trendlines. Experiments involving a different rheometer fixture, and a different ratio of MgO to water are underway.
Well-defined diblock methylcellulose self-assembled thermoresponsively into ribbonlike nanostructures in water. A cryogenic transmission electron microscopy (cryo-TEM) technique was used to detect the ribbon-like nanostructures formed by the diblock copolymers consisting of hydrophilic celllobiosyl and hydrophobic 2,3,6-tri-O-methyl-cellulosyl blocks, methyl β-D-glucopyranosyl- (1→4)-β-D-glucopyranosyl-(1→4)-2,3,6-tri-O-methyl-celluloside (GG-236MC). Moreover, 2 wt. % aqueous solution of GG-236MC exhibited thermo-reversible gelation behavior at approx. 25 °C. Mechanism of gelation and structure-gelation relationships will be discussed in detail.
A main challenge in colloid science is the development of smart delivery systems that store and protect actives from degradation and allow release in response to an external stimulus like temperature. Hollow nanogels made of temperature-sensitive polymers are particularly promising materials. The stimuli-sensitive void size, shell thickness and permeability determine cargo storage and its release behavior. Thus, determination and control of these morphological parameters are of outmost relevance for the design of new, functional drug delivery vehicles.

Here we investigate quantitatively void size and shell thickness of hollow nanogels at different states of swelling by means of Small Angle Neutron Scattering (SANS) employing contrast variation. We demonstrate the structure-sensitivity dilemma: hollow nanogels with a slightly cross-linked shell reveal distinct temperature-sensitivity but possess nearly no void and are thus hardly “hollow”. Nanogels with a stiff shell are indeed hollow (albeit with smaller void as compared to the core size of the template) but less temperature-sensitive.

This concept was extended to develop unique doubly temperature responsive hollow microgels. These consist of two concentric thermoresponsive polymer shells made of poly(N-isopropylacrylamide) (PNIPAM) and poly(N-isopropylmethacrylamide) (PNIPMAM), respectively. This versatile approach allows preparing hollow particles with individually tunable properties on the particle inside and outside, respectively, for various applications as multifunctional smart materials.
Poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) is a known “smart” polymer that reversibly aggregates in aqueous solution in response to external stimuli such as temperature, pH, or ionic strength. Smart polymers have wide ranging applications from encapsulation and release to smart surfactants for the oil and gas industry. Atom transfer radical polymerization was used to synthesize a series of polyethylene glycol-block-PDMAEMA diblock copolymers. Molecular weight and molecular weight distribution of the PEG-PDMAEMA diblock copolymers were characterized using gel permeation chromatography and $^1$H-NMR spectroscopy. The cloud point, or the temperature at which the polymer visibly aggregates in solution, was determined for each polymer in buffered aqueous solution using UV-Visible spectroscopy. Cloud point varied with polymer molecular weight, polymer concentration, pH, and salt concentration. Additional characterization was conducted using fluorescence spectroscopy with pyrene to study changes in hydrophilic and hydrophobic microdomains in aggregating copolymers, and dynamic light scattering to determine aggregate size as a function of temperature. Aggregation behavior varied with polymer molecular weight, polymer concentration, pH, and ionic strength.
POLY 380: Shape memory polymer foams through emulsion-templating

Inna Gurevitch, Christine Warwar, Michael S. Silverstein, michaels@tx.technion.ac.il.
Department of Materials Science and Engineering, Technion – Israel Institute of Technology, Haifa, Israel

PolyHIPEs are porous emulsion-templated polymers that are usually synthesized within surfactant-stabilized water-in-oil high internal phase emulsions (HIPEs). Typical polyHIPEs have highly interconnected porous structures and low bulk densities. Surfactant-free polyHIPEs can be synthesized through the formation of nanoparticle-stabilized Pickering HIPEs. Temperature-responsive shape memory polymer (SMP) foams based on acrylates and methacrylates with crystallizable side-chains exhibited fixity ratios of 1.0 for compressive strains of 70 % and relatively high recovery ratios. In these SMP foams, the recovered structure is identical to the original structure seen in Figure 1a following quite extensive deformation, as seen for a compressive strain of 65 % in Figure 1b. Changing the type of stabilization, crosslinking strategy, locus of initiation, or polymerization mechanism produced profound differences in the porous microstructure and in the SMP properties. While the methacrylate-based SMP exhibited a single-stage recovery, the acrylate-based SMP, with identical side-chains, exhibited a two-stage recovery associated with the individual thermal transitions of two different crystalline phases. The recovery behavior was described using Kelvin-Voigt units in series with the dependence of viscosity on temperature described using a WLF-like relationship. SMP foams that respond rapidly in aqueous environments were produced by simultaneously polymerizing a hydrogel (HG) in the HIPE’s aqueous internal phase and forming HG-coated polyHIPEs.

Figure 1. SMP foam (scanning electron microscope micrographs): (a) as-synthesized; (b) at 65 % compression.
A series of poly(N-acryloyl-2-pyrrolidone)s were prepared from pyroglutamic acid, a bio-derived resource. Their physicochemical properties (including stimuli-responsivity) were found to be highly dependent on the structure of the residue tethered to the pyrrolidone scaffold. Structure/property correlation studies on these materials including their performance as thermo-responsive drug delivering micelles will be presented.
The detection of anions with organoborane-based receptors and related polyfunctional organometallic compounds has received tremendous attention over the past several years. The underlying principle is that tricoordinate organoborane moieties are inherently electron-deficient, featuring an empty p-orbital that may either show π overlap with pendant substituents or, most relevant to sensory applications, reversibly bind Lewis basic substrates.[1]

Our group is pursuing the modification of oligomeric and polymeric materials with photoactive organoborane moieties. One of the potential advantages of polymeric sensory systems is that signal amplification effects may be observed.[2] Moreover, dual detection mechanisms become possible upon incorporation of the fluorophores into amphiphilic block copolymer structures.[3] Recent results by our group will be discussed.

A new class of surface has recently been presented in the literature; porous materials infused with liquids. These surfaces have properties of both liquids and solids, and can be used to create surfaces with superior wetting and adhesion compared to solid surfaces. When the liquid is imbibed into the porous solid a thermodynamically determined amount remains in the film, actually following the surface features. This perfectly smooth liquid layer has lower adhesion than the solid, and creates surfaces with extremely low roll off angles. Our group has develop a version of this new class of surfaces using polyelectrolyte multilayers. We also use a nanoparticle based porous material as the subtrate. Our film is both hydrophobic and oleophobic, which extremely low contact angle and hysteresis. These surfaces have interesting properties with respect to inhibition of ice nucleation, heat transfer, drag reduction, and so on. However, they do suffer from one specific mode of failure - the loss of lubricant with use. We have examined this failure mode and used different strategies to reduce it; including changing the viscosity of the imbibed liquid, feature size, and by gelling the infused liquid.
Fuel cells are highly efficient, environmentally friendly, and quiet devices that can convert the chemical energy of a fuel to electricity or heat through a chemical reaction. As one type of fuel cell, the proton exchange membrane fuel cell (PEMFC) is a good candidate for application in automobile transportation and portable devices. The proton exchange membrane functions as a solid electrolyte in a fuel cell and greatly affects the performance of the fuel cell device. This research focuses on investigating the synthesis of sulfonated poly(m-phenylene isophthalamide) (MPDA-SIPA\_x) as a membrane material. The excellent thermal and chemical stability and mechanical properties of polyamides were the original motivation for this project. A series of polyamides with different percentage of ionic repeat units (x) was successfully synthesized in this project using Yamazaki reaction conditions (Scheme 1). The synthesis involves directly using sulfonic acid functionalized monomer without post modification to accurately design the ion exchange capacity (IEC) of the target polymer. The protonated form of the polymer was characterized by NMR spectroscopy, electrochemical impedance spectroscopy, thermal gravimetric analysis, dynamic vapor sorption, small angle X-ray scattering, water uptake, and ion exchange capacity. The proton conductivities of MPDA-SIPA\_40 and MPDA-SIPA\_45 achieved 116mS/cm and 145mS/cm at 80°C under 95% relative humidity, higher than that of Nafion 117, which is 114mS/cm under the same conditions.
Anion exchange membranes (AEM) facilitate ion transport in polymer electrolyte membrane fuel cells. An AEM must have a high ionic conductivity, low gas/fuel crossover, and be chemically and mechanically stable over the lifetime of the fuel cell. Development of thin polymer films is critical to reduce membrane resistance, but maintaining membrane integrity becomes increasingly difficult. Additionally, humidity changes during fuel cell operation causes water content changes in the polymer. Repeated swelling and contraction puts significant stresses on the membrane. Water taken up by the polymers at high humidity acts as a plasticizer increasing elasticity of the films. However, previously tested AEMs displayed low elasticity and elongation under dry conditions, which could lead to pinholes and cracks during humidity cycles. A new polyethylene-b-poly(vinylbenzyl trimethylammonium) diblock AEM has been synthesized with improved elongation and elasticity. This polymer can be solution processed into thin (10 micron) films. Extensional tests of the polyethylene diblock showed that at dry conditions the polyethylene diblock has a good Young’s modulus (210 ± 30 MPa) and elongation to break (150 ± 20 %), and reasonable strength (28 ± 4 MPa). When hydrated, water in the membrane acts as a plasticizer reducing the modulus by 95% and increasing elongation by 47%, but only reducing strength by 29%. While the changes in strength and elongation are acceptable, the dramatic reduction in modulus from dry to hydrated states requires improvement and warranted further investigation. Dynamic mechanical analysis was utilized to investigate moduli changes while ramping humidity. The moduli go through a dramatic reduction when humidity is ramped and shows signs of hysteresis during dehumidification. Continued study will further investigate the effect of hydration on the mechanical performance of the polyethylene diblock and relate this effect to ionic transport through the membrane. Advanced knowledge of AEM mechanical properties will aid in design of robust membranes to improve fuel cell lifetime.
Original proton conducting fluorocopolymers grafted by azole functions (imidazole, benzimidazole, 1H-1,2,4-triazole) were synthesized through grafting poly(iodoethy vinyl ether–alt–chlorotrifluoroethylene) copolymers by 4(5)-hydroxymethylimidazole, 2-mercaptobenzimidazole or 1H-1,2,4-triazole-3-thiol. Imidazole, benzimidazole and 1,2,4-triazole functionalized copolymers were characterized by $^1$H and $^{19}$F NMR spectroscopy and by thermal analyses (DSC and TGA), and were used in the preparation of blend membranes with sulfonated PEEK (sPEEK). Properties of the three series of membranes were comprehensively studied to evidence the influence of the nature of the azole group on membrane microstructure, thermal properties, and water uptake. Proton conductivities of blend membranes comprising a fluorinated polymer component functionalized with triazole is significantly higher than those with imidazole or benzimidazole moieties, and detailed characterizations have identified an optimal composition in terms of the basic (-NH):acidic (-SO$_3$H) groups ratio of 1.7 in this system, where the proton conductivity at 140 °C and at low relative humidity (< 25 %) reached 7 mS.cm$^{-1}$ for a blend membrane containing 60 %-wt of s-PEEK and 40 %-wt of poly(IEVE-alt-CTFE)-g-1H-1,2,4-triazole-3-thiol$_{95\%}$ copolymer (Figure 1). The proton mobility of these PEMFC blend membranes was studied by infrared spectroscopy and particularly by $^1$H Magic Angle Spinning Solid State NMR spectroscopy. Following acidification of a suspension of this copolymer leading to acidified (II') copolymer, the $^1$D $^1$H MAS spectrum displayed two populations corresponding to triazole and triazolium groups, respectively. The 2D $^1$H EXchange SpectroscopY spectrum of (II’) showed faster proton dynamics of the triazolium protonated form than in the copolymer containing only non protonated triazole groups.

Figure 1: AC proton conductivities of M1: III-62 (35) / s-PEEK (65) (n = 0.9), M2: IV-64 (35) / s-PEEK (65) (n = 0.9), M3: V-95 (40) / s-PEEK (60) (n = 1.69), and s-PEEK membranes vs. reciprocal temperature and RH < 25 %.
We report foldable supercapacitor electrodes using a macroporous cellulose fiber network, Kimwipes, as the scaffold through a simple “dip-absorption-polymerization” method. Single-walled carbon nanotubes (SWCNTs) wrapped around the cellulose fibers as the conductive skin, while ultrathin (~50 nm) and ultralong (tens of microns) polyaniline (PANI) nanoribbons were synthesized in situ between macroporous cellulose fibers and interpenetrated within the SWCNT network. The hybrid material showed good volumetric (40.5 F/cm³) and areal capacitance (0.33 F/cm²), which could be attributed to the synergistic effect between electron transport within the SWCNTs network and fast charge transfer of the PANI nanoribbons. The paper-based hybrid electrode was highly flexible and compliant; it could be folded back and forth as an origami crane up to 1000 times without mechanical failure or loss of capacitance. We believe that the combination of triple networks and the unique morphology of PANI nanoribbons played critical roles to the repeated foldability. Finally, we assembled six all-solid-state supercapacitors based on the SWCNT/PANI nanoribbon paper electrodes connected in series, which lighted LED before, during and after folding for 500 cycles.
Porous polymers have been widely employed in materials useful in energy applications. Porosity can reduce the diffusion barriers to both proton transport as well as lithium ion transport and, thus, define membrane functions. Whereas, porosity has been widely examined in polymeric battery separators, this aspect has received relatively less attention in case of proton exchange membranes. Heterocyclic polymers are useful high temperature resistant polymers which have been used as proton exchange membranes. Recently, thermal rearrangement of o- amino and o-hydroxyl imides has been used to prepare poly (benzimidazole) s and poly (benzoxazole) s with intrinsic microporosity. However, there is considerable ambiguity in the literature on the true structure of such polymers, making it difficult to understand the relationship between structure and function. We have examined the thermal rearrangement of several small molecular weight imide derivatives containing ortho-hydroxyl and ortho- amino groups with the purpose of defining optimum conditions for this reaction and establish the resulting rearranged structures. The chemistry has also been extended to polymeric analogs. Additionally, a new class of poly (benzimidazoles) s which contain cyclophane groups in the main chain have been synthesized with instrinsic porosities.
Large-scale rechargeable batteries are expected to play a key role in today’s emerging sustainable energy landscape. State-of-the-art lithium-ion batteries are not only widely used in electric vehicles, but they are currently gaining traction as backup power in aircraft and smart grid applications. In all of these cases, safety is a challenging limitation: the low flash points of currently used small molecule organic alkyl carbonates impose a high risk of ignition under most operating conditions. For this reason, extensive efforts are being made to develop viable nonflammable electrolytes to replace these organic solvents.

Herein, we will describe a new class of nonflammable liquid and solid-state electrolytes based on low molecular weight fluorinated polyethers, which exhibit low glass transition temperatures, high chemical stability, and compatibility with various polymers and electrodes, making them promising electrolyte alternatives. These polymers are being developed as an intrinsically fireproof platform that can be chemically tailored to achieve the desired thermal, mechanical, and conductive properties for specific battery applications. We will report synthetic modifications used to introduce a range of functional groups to expand the available materials for optimization of this class of materials in the Li ion battery electrolyte application. Mesoscale ion transport and the relationship between fluoropolyether chemical structure and electrochemical property elucidated via advanced nuclear magnetic resonance (NMR) spectroscopy and galvanostatic polarization techniques will also be discussed.

In conducting redox polymers (CRPs) the diverse and unique set of properties of conducting polymers (CPs) is further expanded by the ones given by the functional redox group. For electrical energy storage purposes the individual properties of the CP, i.e. high electronic conduction, and the redox moiety, i.e. high charge storage capacity and well defined redox characteristics, are desirable. Conceptually CRPs based on a CP backbone and a redox active pendant group (PG) includes three principal units, the CP backbone, the PG and the link between them, which all need to operate in synergy. As CPs are only conducting in their charged state the pendant group needs, for instance, to have a redox potential within the conducting region of the CP backbone to benefit from CP conductivity, as exemplified by polyphenylthiophene in figure 1 (left panel).

The requirements for the link are less apparent, and to a large extent overlooked, and are the main focus of the presented work. We show that the link can communicate significant interaction between the PG and the CP backbone even to the extent that the charge carriers in the CP are lost during redox conversion of the PG and hence that the conductivity is reversibly lost due to the polymer-PG interaction (Figure 1, right panel). With correct design of the link such undesirable interactions can be avoided. In this work the design principles, including energy matching between PG and CP and the nature of the link, will be outlined specifically for electrical energy storage in CRPs.

Figure 1: The left panel shows the cyclic voltammetry of polyphenylthiophene, with the conducting region for this polymer indicated, together with the redox potential of known possible PGs. The right panel shows the cyclic voltammetry of an energy matched CRP together with in-situ conductivity data showing that the polymer conductivity is lost during PG oxidation.
Organic matter based battery materials have attracted large interest due to their inherent ability to provide an environmentally benign alternative to inorganic batteries because such materials can be produced from renewable resources via eco-efficient processes. One class of organic compounds that have been used as electrode materials or as component in composite materials in secondary batteries is conducting polymers. To be able to use conducting polymers in electrical energy storage applications the relatively rapid self-discharge (SD) needs to be overcome. We have therefore undertaken an investigation of the SD behavior of polypyrrole (PPy) in a PPy/cellulose composite material. In the present work we study the dependence of potential, temperature, and pH on the SD rate in oxidized PPy in water solution.

Based on the results we present a model for SD in PPy where an initial and polymer intrinsic faradaic reaction leads to an unstable intermediate that reacts further to form various polymer degradation products (figure 1). From activation parameters we further estimate the redox potential of the intermediate state and conclude that SD is in fact the same process that leads to overoxidation, a general feature of p-doped conducting polymers. At elevated pH the faradaic SD reaction is out-competed by a potential independent reaction with a rate that depends linearly on hydroxide ion concentration.

Figure 1: The left panel shows the proposed mechanism of self-discharge in polypyrrole. An endergonic and polymer intrinsic redox reaction leads to an unstable intermediate that reacts further in a reaction that causes polymer degradation. The right panel shows the redox potential of the intermediate (filled circles) evaluated from the activation energy of self-discharge together with the polymer Fermi level (open circles) as function of applied potential. The colored area corresponds to the activation energy required to reach the intermediate state.
Securing this nation’s energy future will require the development of new materials for energy storage applications as well as for energy conversion. Here, nanostructured – specifically nanoporous – solids have the potential to lead to many technological breakthroughs. Their high surface area, electrical conductivity, environmental compatibility and chemical inertness make them very promising materials for use as electrode materials in supercapacitors and rechargeable batteries. At Lawrence Livermore National Laboratory research on nanoporous materials is driven by their use in targets for high energy physics experiments. Ironically, understanding how the pore structure and materials strength evolve as the surface environment is manipulated is a common theme in designing new porous materials for both these two diverse applications. The ability to measure changes in morphology and chemistry of the nanoporous materials in-situ and in-operando with x-ray spectroscopies has provided the needed feedback to develop nanoporous materials with optimized microstructures for these applications. In many cases unique properties are observed in nanoporous materials as the surface environment and density are manipulated. The two thrusts of this talk will cover (1) recent in-operando x-ray absorption spectroscopy experiments that demonstrate that nanostructured carbon electrodes undergo profound bias- and time-dependent evolution of the electronic structure under applied bias. Complementary ab-initio modeling suggest that both surface distortion and specific adsorption are responsible for these changes in the electronic structure (2) the development of carbon aerogels able to wick cryogenic hydrogen needed for laser fusion targets and development of super strong nanoporous carbons able to withstand volume changes associated with charge-discharge. This work was performed under the auspices of the US DOE by LLNL under Contract DE-AC52-07NA27344
POLY 393: Mechanochemical degradation of three-arm star polymers: Kinetics and modeling

Gregory I. Peterson, petersgi@uw.edu, Derek Church, Andrew J. Boydston. Chemistry, University of Washington, Seattle, Washington, United States

The effect of star versus linear polymer architecture on the rates of mechanochemically induced bond scission has been explored. We determined rate constants for chain scission of linear and star polymers and confirmed the mechanistic interpretation of star polymer chain scission that is governed by the spanning rather than total molecular weight. We further demonstrate that these results hold true when a mechanophore is incorporated near the core of the star polymer. As an extension of this work, a model for predicting the molecular weight distributions of mechanochemically degraded star polymers has been developed. The model was shown to be in good agreement with experimental distributions and average total molecular weights obtained during degradation experiments. Generalization of the model to four- and n-arm star polymers was also achieved.

Depiction of the mechanochemical activation of mechanophores in linear and star polymers.
The morphology and ion conductivity of two polymerized ionic liquid (PIL) diblock copolymers of similar chemistry, but differing alkyl side chain lengths, were investigated. The two PIL diblock copolymers in this study consist of a non-ionic component (MMA) and an ionic liquid (IL) component (1-[(2-methacryloyl)X)-3-butylimidazolium bromide) (MXBIm-Br), where X represents ethyl (E) or undecyl (U), i.e., poly(MMA-b-MEBIm-Br) and poly(MMA-b-MUBIm-Br) for short and long alkyl side chain lengths, respectively. These two copolymers were compared at a similar ion exchange capacity (IEC = 1.4 meq/g) and similar MXBIm-Br volume fraction (~40 vol%). Transmission electron microscopy, small and intermediate-angle X-ray scattering, and small-angle neutron scattering were used to examine differences in morphology between the two polymers under dry, humidified, and fully hydrated conditions. The impact of these morphological differences on bromide ion conductivity was explored. Specifically, the block copolymer with a longer alkyl side chain length has a higher conductivity with lower water uptake at similar IEC and MXBIm-Br volume fraction, which correlates to differences in morphology. Only in the longer alkyl side chain length copolymer was an additional scattering peak observed in both X-ray and neutron scattering under fully saturated conditions. These results suggest the formation of an ionomer/water channel within the MUBIm-Br microdomain under saturated conditions, which results in accelerated ion transport. This study suggests that the location of the imidazolium moiety within the PIL block copolymer can play a role in the morphology and subsequently the ion conductivity, which may have an impact on various energy and separations applications.
POLY 395: Investigating the crystallinity of polytetrafluoroethylene (PTFE) by using terahertz time-domain spectroscopy (THz-TDS)

Francisco Senna Vieira, franciscosennavieira@gmail.com, Celio Pasquini. Univ Estadual De Campinas, Campinas Sp, Brazil

Terahertz-time domain spectroscopy (THz-TDS) has the ability to probe the crystallinity of several materials, mainly due to the interaction of THz radiation with optical phonons in crystal lattices. Crystallinity of polymers is a particularly important parameter, as it affects many properties of the material, such as yield stress, modulus elasticity, among others. In this work, THz-TDS has been applied to investigate the crystallinity of polytetrafluoroethylene (PTFE) samples. PTFE samples with variable crystallinities were prepared by means of ball-milling in a planetary ball mill. THz spectra of PTFE pellets (thickness = 1.72 mm) were acquired using a THz-TDS spectrometer operating with the asynchronous optical sampling (ASOPS) principle. The acquisition time for each spectrum was around 4 minutes. The THz spectra of PTFE showed an absorption peak at 3.73 THz which could be directly correlated with the crystallinity, as shown in Figure 1. As the milling time increases, it is clear that the 3.73 THz peak becomes less intense. Preliminary differential scanning calorimetry (DSC) measurements showed that the heat of fusion correlates well with the 3.73 THz peak intensity ($R^2 = 0.90$), indicating that THz spectroscopy can be a useful tool to probe the crystallinity of PTFE in a shorter time.

Figure 1: THz spectra of PTFE with different crystallinities.
POLY 396: Application of single-chain polymer nanoparticles from consecutive ROMP-RCM process

Yugang Bai\textsuperscript{1}, baiyugang@outlook.com, Hang Xing\textsuperscript{4}, Xin Yi Phang\textsuperscript{1}, Yi Lu\textsuperscript{2}, Steven C. Zimmerman\textsuperscript{3}. (1) University of Illinois at Urbana-Champaign, Urbana, Illinois, United States (2) Dept of Chemistry, Univ of Illinois, Urbana, Illinois, United States (3) Chemistry, University of Illinois, Urbana, Illinois, United States (4) Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States

Linear polymer from ring-opening metathesis polymerization can be intramolecularly crosslinked and dihydroxylated to yield water-soluble, single-chain polymer particles controllably. The strategy allows excellent valence control, and the particles serve as excellent carriers as functionalities of interest can be loaded in any stage during synthesis. The particles were used as a powerful tool to study the influence of polymer particle surface properties on their cellular endocytosis process. A general trend of endocytosis efficiency and monomer structure could be observed, and the particles' behavior could be qualitatively predicted by LC-MS analysis of their respective monomers. In addition, the hydroxyl-rich particles with controlled valency were used as templates for metal nanoparticle synthesis, yielding metal particles with retained valency. The resulting metal particles could thus do self-assembly according in a pre-designed manner. This bottom-up strategy allows larger scale synthesis of monovalent metal nanoparticles with higher yield and less size restrictions.

Monomer-derived particle lipophilicity control can be used to tune the particles' cell-uptake behavior.
POLY 397: High stiffness in aromatic-aliphatic poly(tyrosol carbonate) by hierarchical control over isomer sequence, phase behavior, and chain orientation

Sven D. Sommerfeld\textsuperscript{1}, sd.sommerfeld@gmail.com, Sanjeeva N. Murthy\textsuperscript{3}, Zheng Zhang\textsuperscript{3}, Murat Guvendiren\textsuperscript{5}, Koustubh Dube\textsuperscript{2}, Joachim B. Kohn\textsuperscript{1}, kohn@rutgers.edu. (1) Rutgers Univ, Piscataway, New Jersey, United States (2) Rutgers University, Piscataway, New Jersey, United States (3) New Jersey Center for Biomaterials, Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States (4) Chemistry, Rutgers/ NJCBM, Piscataway, New Jersey, United States (5) Life Sciences, Rutgers/ NJCBM, Piscataway, New Jersey, United States

One of the challenges in biomaterials is to design a functional, synthetic polymer that is also stiff and strong at physiological conditions. In natural materials, these features are brought about by the synergy of emergent features at different hierarchical levels: Small repeating backbone sequences lead to supramolecular arrangements. Here, we applied a biomimetic approach to design synthetic polymers with sequence control and then by optimally processing the polymer to exploit the synergy arising from hierarchical structures.

We developed a new class of degradable, aromatic-aliphatic polycarbonates based on tyrosol, a small (hydroxy)alkyphenol. Poly(tyrosol carbonate) with a strictly alternating sequence (\textit{alt}) of diaryl (head-to-head, HH) and dialkyl (tail-to-tail, TT) carbonate isomers was obtained by a pre-programmed dimer approach: First, the diaryl carbonate diol of tyrosol was formed by biphasic phosgenation and subsequently polymerized. A scrambled sequence (\textit{scr}) of HH, TT and the aryl alkyl (head-to-tail, HT) carbonate isomers was obtained by direct polymerization of tyrosol. Comparing \textit{alt} to \textit{scr}, the sequence had a large effect on the thermal behavior: \textit{Alt} rapidly transitioned from the amorphous phase into a 1-dimensional mesophase at 90 °C and further into a 3-dimensional crystalline order at 150 °C. \textit{Scr} only attained a 1-dimensional mesophase after extensive annealing at 100 °C for 20 h and melted at 149 °C. By using a combination of thermal and mechanical treatments, polymer films of practical utility were produced. Oriented, semi-crystalline \textit{alt} films showed superior stiffness over similarly processed \textit{scr} with moduli of \(E_T = 5.4 \pm 0.3\) GPa and \(E_T = 3.8 \pm 0.2\) GPa, respectively. In conclusion, the combination of sequence control in aromatic-aliphatic polycarbonates and processing methods delivered a promising platform for a new generation of biomedical polymers.
Unlike alkane thiols that can readily self-assemble into vertically standing monolayers (SAMs) on conductive substrates (e.g., gold thin films) large molecules pose a significant challenge to form similar structures. A greater challenge is to incorporate these structures into functioning molecular electronic devices. Moreover, few reports have studied molecules beyond 1 ~ 3 nm in length, thus most reports of molecular devices are constrained to studying tunneling effects. Recently we employed a “bottom-up” approach to synthesize conjugated polymers that are covalently tethered to conductive substrates and integrate them into electronic devices. We grow conjugated polymers with considerable length (up to 90 nm) using a surface initiated Kumada catalyst-transfer polycondensation (SI-KCTP) in a “grafting from” method from the conductive oxides ITO and LSMO. Linear growth of the polymer with respect to time is observed, allowing systematic control over polymer brush length. Spectroscopic measurements suggest a high degree of orientation of the polymer perpendicular to the substrate. Gold electrodes are deposited on the polymer film surface and IV curves are measured using conducting AFM. A distinctive change in length-dependent conductance is observed in devices with polymer film thickness greater than ~5nm corresponding to a change in electron transport mechanism from tunneling to charge injection. SCLC mobility measurements demonstrate a significant increase in hole mobility over typically deposited polymer thin films. Spintronic measurements are ongoing, but preliminary evidence shows that spin-valve-like devices can be made and tested.
**POLY 399: Middle and end labelled PMMA-d3: The effect of chain ends on polymer dynamics**

**Ugo N. Arua, ugnarua@yahoo.com, Frank D. Blum. Chemistry, Oklahoma State University, Stillwater, Oklahoma, United States**

Poly(methyl methacrylate) (PMMA) block copolymers with deuterated segments were synthesized using atom-transfer radical polymerization with activators generated by electron transfer (AGET-ATRP) mediated by an iron catalyst. The polymer samples prepared had deuterated middle or end segments. These polymers were used to observe differences between the dynamics of the different segments of PMMA, in bulk, using solid state deuterium NMR. The implications to the behavior of these polymers when adsorbed will also be presented.
Colloidal Unimolecular Polymer particles (CUPs) were prepared by the process of water-reduction on copolymers with a hydrophobic backbone and hydrophilic pendant groups. CUP systems are composed of solid, spherical polymer particles as the dispersed phase suspended in the continuous aqueous phase. Copolymers of methyl methacrylate (MMA) with either methacrylic acid (MAA), 2-acrylamido-2-methylpropane sulfonic acid (AMPS) and [2-(methacryloyloxy)ethyl]trimethylammonium chloride (MADQUAT) were prepared by free radical polymerization technique with a 9:1 ratio of hydrophobic:hydrophilic monomer ratio. Three different molecular weights for each type of copolymer were synthesized to study the effect of molecular weight/particle size of CUPs on the surface tension. Dynamic surface tension studies performed using the maximum bubble pressure tensiometer revealed that the rate of change of surface tension was highest for sulfonates followed by QUATs and lowest for carboxylates at similar molecular weight. The effects of concentration and molecular weight were investigated.
POLY 401: Modified ABS for fused filament fabrication 3D printing with improved interlayer adhesion

Kejia Yang¹, kejia.yang@utdallas.edu, Benjamin Lund¹, David Sydney¹, Christina Thompson¹, Ronald Smaldone¹, Walter Voit¹,². (1) Chemistry, The University of Texas at Dallas, Richardson, Texas, United States (2) Materials Science and Engineering, The University of Texas at Dallas, Richardson, Texas, United States

Fused filament fabrication (FFF) 3D printing is increasingly becoming a vital tool in many industries for its ability to produce a wide range of physical parts quickly. Acrylonitrile butadiene styrene (ABS) is one of the most popular materials for FFF process. In FFF, ABS is melted then extruded through the print head and deposited to a substrate layer by layer. However, the quality of FFF printed parts lack the strength, toughness and reliability of parts manufactured traditionally because of their poor interlayer adhesion. The fact that the materials need to be melt processed during printing make it difficult to use crosslinked polymers directly for FFF 3D printing. This presentation will discuss modifications on ABS, by employing thiol-ene and dynamic covalent chemistry, for improved adhesion between interlayers without compromising the melting processibility as well as the strategies on FFF printing modified ABS with consequently lower Tₙ and modulus.

Scheme 1. Modification on ABS
Because of their potential utility as electrolyte membranes in capacitive devices ranging from batteries and supercapacitors to fuel cells and actuators, interest in poly(ionic liquids), PILs, continues to increase. Advantages that may be garnered by virtue of the use of PILs include the realization of single-ion conducting systems in which only target ions are mobile, a greatly expanded use-temperature range, and, design latitude in fabrication of thin film devices and devices having non-planar geometries. Our studies have been focused on poly(ionic liquids) derived from 4-vinylimidazolium salts. As compared to 1-vinylimidazolium polymers, attachment at the 4(5)-position of the imidazole ring affords increased rotational and translational degrees of freedom for the imidazolium moiety that may result in greater free volume and greater ability for the imidazolium moiety to interact cooperatively in the transport of target ions. In this presentation, the synthesis of 1-butyl-2,3-dimethyl-4-vinylimidazolium triflate, its polymerization, and, ion exchange to yield a trio of polymer salts is described. The thermal characteristics of tetrasubstituted poly(4-vinylimidazolium salts) and corresponding trisubstituted poly(4-vinylimidazolium salts) were evaluated. While the mid-point glass transition temperatures, $T_{g\text{-mid}}$, for the trisubstituted 4-vinylimidazolium polymers with $\text{CF}_3\text{SO}_3^-$, TFSI$^-$ and $\text{PF}_6^-$ counterions were found to be 153 °C, 88 °C and 200 °C, respectively, the $T_{g\text{-mid}}$ for the tetrasubstituted 4vinylimidazolium polymers with corresponding counter-ions was tightly clustered at 98 °C, 99 °C and 84 °C, respectively. This dramatically reduced influence of anion type on the glass transition temperature was attributed to the increased distance between the center of anions and cations in the poly(1-butyl-2,3-dimethyl-4-vinylimidazolium) polymer set.

![Poly(1-butyl-2,3-dimethyl-4-vinylimidazolium triflate)](image-url)
Precision synthesis and neutron reflectivity experiments coupled with self-consistent field theory (SCFT) can provide unparalleled insights into the physics of polymers near interfaces. In this work, we studied the effects of polydispersity on the microphase separation lamellar forming diblock copolymer thin films. A dually reactive block copolymer containing a polydisperse block of poly(glycidylmethacrylate) (PGMA) connected to a near-monodisperse block of poly(4,4-dimethyl-d6-2-vinylazlactone) (PVDMAd6), PGMA\textsubscript{142}-b-PVDMAd\textsubscript{6148}, was synthesized. SCFT predicted that the symmetric di-block copolymer has a lamellar morphology in the bulk. The morphology was confirmed by transmission electron microscopy (TEM) and small angle neutron scattering (SANS) experiments. In order to study the microphase separation in thin films, dilute solutions of the block copolymer were deposited onto silicon substrates and annealed above the polymer’s glass transition temperature resulting in films with thicknesses of 12.3 nm, 28.6 nm, and 41.2 nm. Specular neutron reflectivity experiments were done to probe the number of strata in the films along with the spatial distribution of each block. SCFT was used to predict the structure of the thin films and to construct the models used to fit the neutron reflectivity data. A relatively good agreement between the experimental and theoretical results was observed providing useful physical insights into the thin film structure of PGMA\textsubscript{142}-b-PVDMAd\textsubscript{6148}. In particular, it was found that the polydispersity causes entropic segregation resulting in the polydisperse block (i.e., PGMA) residing in the middle of the film despite favorable interactions with the silicon substrate. The entropic effects were found to be the driving force for assembly in ultra-thin films with thicknesses of 4-5 times the radius of gyration. Furthermore, the coordinated experimental and theoretical study has led to the development of a facile and robust framework that can easily be tailored to study other polymeric systems near interfaces.
Dendronized polymers (DPs) are macromolecules that carry dendrons at every backbone repeat unit. Dendrons can be developed to higher generations $g$. Due to the branched architecture and steric demand of the dendrons, DPs will adopt a cylindrical shape and internally be densely packed at higher $g$, particularly when $g$ approaches $g_{\text{max}}$. Beyond $g_{\text{max}}$ the attachment of a defectless next $g$ is not possible anymore.\[1\]

The goal of this work is to gain $g$-dependent information about the interior of DPs such as local polarity and accessible volume for guests and solvents. Our method is based on a new series of DPs with $g=1-4$ which carry a solvatochromic probe ($p$-nitroaniline) covalently fixed at the branch point of $g=1$. The $\lambda_{\text{max}}$ values of these samples are determined by UV/Vis spectroscopy for solvents with $2<\epsilon_r<47$ and most of them show clear $g$-dependence. While in all other solvents $\lambda_{\text{max}}$ with increasing $g$ seems to converge near 395 nm,\[2\] in toluene (at 65 °C) a much stronger $g$-dependence is observed resulting in $\lambda_{\text{max}}=410$ nm for $g=4$. Thus, in all solvents the branches are in fact increasingly shielding the probe but except for in toluene the probe remains somewhat solvent accessible. Toluene is a poor solvent for our DPs\[3\] and our results suggest that the branches collapse, with the toluene molecules being largely squeezed out of the interior resulting in a $\lambda_{\text{max}}$ which reflects the intrinsic polarity of the branches. Our studies are flanked by MD-simulations performed by Prof. C. Alemán, Barcelona, which provide numbers for how many solvent molecules are incorporated into the various $g$ DPs.

Biofilms are made of communities of microbial cells that grow on living or inert surfaces. The formation of biofilms presents a fundamental problem in water technology, environmental biology, food hygiene and in many medical and technical systems. It is therefore necessary to investigate methods to prevent the growth of biofilms. This study will examine the inhibition of the growth of Pseudomonas Aureginosa on a glass slide by modifying a glass surface using hydrophobic liquid-infused nano-porous poly(butyl methacrylate-co-ethylene dimethacrylate) polymers (slippery BMA-EDMA). As a mimic to bacterial adhesion, Texas red-conjugated BSA will be adsorbed to plain; liquid-infused and non-liquid-infused nano-porous polymer covered glass surfaces. Analysis of simulated samples using fluorescence microscopy showed that BSA adhered at a higher level to the plain glass surface than to the polymer coated glass surface. Studies are underway to determine if the novel surfaces prevent adhesion of biofilms generated by Pseudomonas Aeruginosa.
Composites made from polar polymers such as poly(vinyl pyrrolidone) or poly(vinyl acetate) (PVAc) and graphene oxide (GO) have yielded large increases in fracture toughness when used in carbon fiber-epoxy laminates. A combination of differential scanning calorimetry (DSC) and deuterium ($^2$H) solid-state NMR has been used to understand the behavior of composites of PVAc and GO. From calorimetry, no glass transition was observed, but deuterium NMR spectra identified the onset of rapid segmental motions over a very broad temperature range. Some segments had a transition at temperatures lower than the bulk polymer, and some had transitions that were higher than bulk. These differences were deemed to be due to the interaction of the polymer with different surface functionalities of the GO. This heterogeneity lead to a glass transition that was too broad to be observed by calorimetry, but was clearly evident by NMR.

An idealized PVAc chain interacting with different regions of the GO surface.
POLY 407: Covalent functionalization of graphene-based platelets for tailored solubility and assembly

Brendan McGrail, Bradly Rodier, Emily Pentzer, ebp24@case.edu. Chemistry, Case Western Reserve University, Cleveland, Ohio, United States

Two-dimensional platelets have garnered much attention for use as fillers in polymer matrices, improving the mechanical, thermal, and electronic properties of the polymer in various ways. Graphene and its oxidized analogues are one such class of nanoplatelet fillers that have found widespread use in a variety of polymer applications. Unfortunately, one limitation to the preparation of graphene (oxide) polymer composites is the poor dispersability of the platelets in solvents and polymers due to their tendency to aggregate and stack. We will report the controlled covalent modification of graphene oxide and reduced graphene oxide in an acidic aqueous environment in high yield and on the large scale, and the incorporation of these materials into a variety of polymers. The chemistries used for these modifications are robust and scalable, allowing for functionalization with a variety of small molecules and polymers, giving materials of tunable solubility. We will also report on the selective functionalization the platelet as a route to control dispersability and dictate platelet assembly into higher order structures and at interfaces.
There has been continuing interest in the fundamental concepts underlying the assembly of polymer grafted nanoparticles in polymer based hybrid materials, and the consequences of this assembly on end-use properties. Here we focus on two applications: (i) the use of these grafted systems as membranes for gas separations and (ii) the competition of the self-assembly of these nanoparticles with the crystallization of the matrix polymer into which they are embedded. The consequences of these ideas on the biomimetic assembly of hydroxyapatite nanoparticles will be discussed.
The assembling behavior of four thiophene-containing conjugated polymers (CPs): poly(3-hexylthiophene) (P3HT), poly(3,3-didodecylquaterthiophene) (PQT-12), poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b] thiophene) (PBTTT-14), and poly(2,5-bis(3-tetradecylthiophen-2-yl)thiophen-2-yl)thiophen-2-yltiazolo[5,4-d]thiazole) (PTzQT-14), on CNTs was investigated through the microscopic studies of the nanowires formation. It is found that the formation of CP crystals from CNT surfaces is influenced by factors such as polymer backbone spatial structure, backbone rigidity and CNT size or surface curvature. The crystallization behavior of CPs from CNTs reveals the attachment modes on CNTs. P3HT and PQT-12 have a zigzag backbone structure that allows a thermodynamic stable co-axial attachment on CNTs, providing an ordered growth front for the further crystallization. In contrast, fused rings in PTzQT-14 and PBTTT-14 create a stair-step like backbone structure that causes a kinetics controlled wrapping conformation on CNTs, generating a twisted growth front that hinders the crystallization. When the polymer warps CNTs, the rigidity of polymer backbone influences the wrapping mode. Polymers with more flexible backbones (i.e. PBTTT-14) would take a denser wrapping mode on CNTs. The CNT diameter plays an important role in the nanowire formation when CPs attach the CNT in the wrapping mode. Larger nanotubes with smaller surface curvature will create less twisted polymer growth front, allowing the crystallization of CPs. P3HT and PQT-12 can crystallize from both SWCNT and MWCNT attributed to co-axial attachment of the polymer along CNT, but PTzQT-14 can only crystallize from MWCNT due to the wrapping of CNT. The smaller curvature of MWCNT allows the crystallization of PTzQT-14. In addition, P3HTs with molecular weight less than 10KDa form nanoribbons from MWCNTs. It is believed that P3HT chains can take a transversal orientation on MWCNT. The alkyl chain and π-π interactions between P3HT molecules lead to the formation of nanoribbons.
POLY 410: Improved carbon nanotube fibers through crosslinking and surface modification

R. Benjamin Ripy, rripy@utk.edu, Xinyi Lu, Namgoo Kang, Jimmy W. Mays.
Chemistry, The University of Tennessee, Knoxville, Tennessee, United States

There is a need in the aerospace industry to increase the strength and modulus of current carbon fiber. Carbon nanotubes offer a route to improve these properties, but as of yet they have not been properly utilized due to their graphitic, lubricant like properties. The first route is a grafting from method that attaches benzocyclobutene derivatives to the surface of the CNTs and converts these to initiators. Then polyacrylonitrile is grown from the surface using ARGET ATRP. These grafted CNTs are dispersed at different loading levels in a PAN doped solution and spun. The second route to achieve the goal is to crosslink the CNT yarns and threads via a grafting-to method. Crosslinkers of different lengths with BCB groups have been synthesized and cycloaddition to CNT bundles has been performed. The first approach has been successful in attaching 60% (by weight) of PAN. This was verified using TGA-MS, TEM, and SEM. The second approach has shown 20% grafting of the polymer crosslinks to the CNT bundles. This was verified using TGA, TEM, and XPS. Both of these methods have accomplished their initial grafting goals. The next step is to mechanically test the carbonized fiber; then, reaction conditions will be optimized to determine proper grafting levels and molecular weights to increase the fiber’s strength and modulus.

Pristine CNTs

PAN grafted CNTs
POLY 411: Lignin expanded acrylonitrile-butadiene-styrene (ABS) thermoplastic for composite applications

Amit K. Naskar, NASKARAK@ORNL.GOV, Sam K. Akato, Don L. Erdman. Materials Science Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States

Lignin, a biomass-derived macromolecular material, was used as an extender of Acrylonitrile-Butadiene-Styrene (ABS), a common industrial thermoplastic resin. Solvent fractionated Kraft lignin was incorporated in ABS matrix by melt-blending technique. The effects of lignin incorporation on thermal stability, morphological, mechanical and rheological properties of the ABS matrix were investigated. Small amounts of lignin increase ABS tensile modulus, while higher amounts diminish overall mechanical strength. However, addition of polyethylene oxide (PEO) as compatibilizer at 10% loading of lignin content improves the performance of high-lignin content ABS. In fact, 30% lignin-loaded ABS exhibits tensile properties nearly equivalent to that of neat ABS. Such an approach can be used to lower ABS cost while reducing the carbon footprint of this petroleum-derived resin. The resin was used for manufacturing chopped carbon fiber thermoplastic composite. Nearly 25 volume % chopped carbon fiber reinforced composite prepared by compression molding, exhibited 90 MPa tensile strength and 0.70 % ultimate elongation.

SEM micrograph of carbon fiber compsoites of lignin-modified ABS resin
HIGH molecular weight polyacrylonitrile with low polydispersity has been successfully synthesized utilizing reversible addition fragmentation chain-transfer (RAFT) polymerization. Herein, a comprehensive study was performed to understand the effects of reaction temperature, RAFT agent selection, concentration of solvent, concentration of monomer, the molar ratio of RAFT agent to initiator, and the molar ratio of monomer to RAFT agent on the polymerization kinetics and the molecular weight as well as the polydispersity. The key to success is attributed to the combination of reducing the number of side reactions by low reaction temperatures, and also improving the interchange reaction between active and dormant states through deliberate selection of RAFT agents. Gel permeation chromatography (GPC) equipped with a multi angle laser light scattering (MALLS) detector was used to measure the absolute weight average molecular weight and polydispersity of the resulting polymers.

Lowering the temperature for RAFT polymerization of acrylonitrile yields higher molecular weight, lower polydispersity, and higher conversions at long reaction times.
Carbon nanotubes (CNT) are of great interest as reinforcement materials in polymer matrix composites (PMCs) due to their exceptional tensile properties. However, the tensile properties of bulk CNT materials, such as yarns or sheets, are significantly poorer than those of the individual nanotubes due to weak inter-CNT interactions. Our group has examined covalent modification and crosslinking as a method to increase the tensile properties of bulk CNT materials. For example, CNT sheet functionalized with 3 mol % amine groups exhibited a specific tensile strength of 205 ± 22 MPa/(g/cc); approximately a 65% improvement over the 127 ± 11 MPa/(g/cc) value for the non-functionalized sheet. The specific modulus of the amine functional sheet was 2.59 GPa/(g/cc), compared to 0.78 GPa/(g/cc) for the non-functionalized.

This trend was not retained in our initial experiments using these functionalized CNT sheets to prepare 50/50 wt% composites with epoxy thermoset resins. PMCs prepared with the amine functionalized sheet had a specific tensile strength of 141 ± 37 MPa/(g/cc) and specific tensile modulus of 3.22 ± 0.62 GPa/(g/cc), versus 198± 49 MPa/(g/cc) and 6.81 ± 1.03 GPa/(g/cc) for composites prepared using the non-functionalized sheet.

This presentation will examine our efforts to improve the tensile properties of PMCs prepared using these functionalized CNT sheet materials. The purpose of the functional groups is to enhance both the CNT-CNT interactions as well as the CNT-matrix interactions. PMCs from sheets bearing different densities of amine or epoxide functionalities are being prepared to determine the optimal degree of functionalization. Two different commercially available matrix polymers, epoxy and polybenzoxazine, are being tested.
POLY 414: Application of multi-agonist scaffolds to modulate antigen presentation and adaptive immunity

Janine Tom, jktom3@gmail.com, Aaron Esser-Kahn. Chemistry, University of California, Irvine, Los Angeles, California, United States

The development of immunotherapies has resulted in a dramatic decrease in the number of cases of several diseases, including measles and polio, demonstrating the need to continue vaccine research to eliminate prevalent diseases, such as malaria and ebola. Some of the most successful vaccines have been empirically determined, leaving the mode of action unknown. Consequently, vaccine development can be slow and the available formulations are not as effective as they should be. We are working on understanding how the immune system functions and battles pathogens on a fundamental level in order to design more successful and safer vaccines. Recently, the use of multiple immune agonists, especially Toll-like receptor (TLR) agonists, has been used to enhance specific immune responses. Thus, indicating that multiple agonists will be needed, instead of one agonist, to design vaccines that can eliminate promiscuous diseases. Using synthetic chemistry, we have probed immune system responses by conjugating multiple TLR agonists together. Incubating our constructs with immune cells, we have shown modulation of innate immune responses, suggesting downstream changes in adaptive immune activation. Here, we are applying our multi-agonist compounds to antigen presentation via conjugation to a peptide antigen. Consequently, we can determine how different combinations of agonists affect antigen presentation and subsequently T cell and antibody responses. Ultimately, these multi-agonist scaffolds can mechanistically inform us about immune system signaling and activation, allowing us to design more effective vaccines.
The National Institute of Allergy and Infectious Diseases at NIH supports research projects that explore innate immune mechanisms, their impact on adaptive immunity, and the discovery and development of novel adjuvants triggering these mechanisms. One of them, the Adjuvant Discovery Program, is designed to generate novel compounds capable of safely enhancing the efficacy of vaccines for the general population as well as for special populations. A major challenge for the identification of novel candidates is the lack of robust, validated and widely applicable in vitro assays to predict in vivo adjuvanticity. This is, in part, due to the wide range of cellular and molecular targets of vaccine adjuvants, but also to the lack of understanding what in vitro responses correlate with adjuvanticity and/or reactogenicity in vivo. The NIAID discovery program involves HTS of compounds for adjuvant activity and has yielded valuable insights into the usefulness of different in vitro screening assays for novel adjuvants. A commonly used approach for identifying novel candidates is the use of NF-kB reporter cells. Numerous cellular processes, including engagement of innate immune receptors involve NF-kB signaling. Nevertheless, many “hits” from NF-kB-based screens do not stimulate cytokine production in confirmatory screens. Cytokine-secretion is a more biologically relevant readout, but more expensive and limited by our understanding of what cytokines correlate with in vivo adjuvanticity. A frequently used exclusion criterion for adjuvant candidates is cytotoxicity. However, cell death is associated with the efficacy of many immunostimulatory compounds and, thus, it is advisable to study the extent as well as the type of cell death induced rather than to simply dismiss such compounds. Systematic adjuvant discovery is a multidisciplinary effort and greatly benefits from the close collaboration between medicinal chemists, immunologists and formulation experts.

Targets of vaccine adjuvants and molecular/cellular consequences of receptor engagement.
Toll-like receptors (TLRs) are a family of conserved pattern recognition receptors that recognize pathogen associated molecular patterns and serve as primary sensors of the innate immune system. Engagement of toll-like receptors serve to link innate immune responses with adaptive immunity and can be exploited as powerful vaccine adjuvants for eliciting both primary and anamnestic immune responses. Toll like receptor-7 that recognizes single stranded RNA from viruses is also activated by small-molecule imidazoquinolines. We identified in our structure-activity relationship studies, a highly potent, Th-1 biased, immunostimulatory TLR-7 agonistic imidazoquinoline compound 1. We hypothesized that imidazoquinolines are small, polar, and may diffuse away from the site of injection and cause systemic immune activation. This hypothesis led us to synthesize and evaluate several macromolecular constructs of imidazoquinolines such as a model self-adjuvanting α-lactalbumin construct, a hexameric dendrimer molecule bearing six units of compound 1 and several TLR-2/7 dual agonistic lipopeptide conjugates. All these macromolecular constructs were evaluated for adjuvanticity in murine and rabbit models of vaccination and they induced robust, high-affinity immunoglobulin (IgG) titers to the model antigen. Additionally, epitope mapping experiments showed that these macromolecular constructs induced immunoreactivity to more contiguous peptide epitopes along the amino acid sequence of the antigen. Of the several TLR-2/7 dual agonistic molecules synthesized and evaluated for adjuvanticity, we identified a thiourea-linked compound that not only showed very strong humoral immune response in terms of rapid induction of high affinity antibodies but was also found to be highly potent in exhibiting T-cell immune responses in murine model of *M. tuberculosis* vaccination and challenge. These TLR-7 agonistic macromolecules were consistently found to be superior compared to a small-molecule TLR-7 agonistic imidazoquinoline.
Immune potentiators represent a chemically diverse class of materials that can be used as direct immunotherapies or as adjuvants for vaccines. Synthetic small molecule Toll-like receptor agonists (TLRas) are some of the most promising immune potentiators for clinical application but are often limited by suboptimal pharmacokinetic characteristics. In this study, linear biocompatible polymers were used as chemically tunable scaffolds for controlling pharmacokinetics and modulating activity of TLRas. Combinatorial synthesis and in vivo structure-activity studies were used to evaluate how properties of Polymer-TLRa conjugates (Poly-TLRas) influence the magnitude and spatiotemporal characteristics of innate immune activation in mice. These studies identified that high densities of agonists attached to particle-forming polymers through hydrophilic linker groups are optimal for the capacity of Poly-TLRa to induce high magnitude and persistent innate immune activation in lymph nodes. Mechanistic studies using whole animal imaging and cellular level tracking identified that particle formation by Poly-TLRa strongly enhances the magnitude and duration (>14 days) of innate immune activation in lymph nodes by restricting agonist distribution and promoting uptake by antigen presenting cells. Optimized particle-forming Poly-TLRa formulated with protein antigen were found to be effective for eliciting protective CD4 and CD8 T cell responses in two different infectious challenge models. In conclusion, polymer carriers of TLRas represent a versatile and effective platform for modulating both innate and adaptive immunity and warrant further investigation as direct immunotherapies and / or as a class of adjuvants for vaccines.
Recent research into the immune system has revealed that foreign pathogens are detected through a series of receptors on antigen presenting cells. These receptors are synergistically activated by multiple pathogen associated molecular patterns. Materials scientists have a large role to play in the coordinated design of vaccines and synthetic activators of the immune system. We report on our development of chemical and polymeric tools for interacting with the immune system. Our methods involve the controlled presentation of TLR agonists to their receptor through light-mediated uncaging. These light-activated TLR agonists have been tested against dendritic cells and we will report on the results. Additionally, we will report on our work using these TLR agonists to probe synergistic interactions between different TLRs.
POLY 419: New opportunities in viral nanoparticle protein:polymer conjugates

Jaqueline D. Wallat\textsuperscript{2}, Sergey Isarov\textsuperscript{1}, Jun Zhang\textsuperscript{1}, Jonathan K. Pokorski\textsuperscript{2}, jon.pokorski@case.edu. (1) Case Western Reserve University, Cleveland, Ohio, United States (2) Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio, United States

The synthesis of polymeric nanoparticles with precisely controlled shapes, sizes and surface chemistry is critical to enable many advances in biomedical fields, especially those of drug delivery and molecular imaging. The bottom-up synthesis of precise structures, in particular those of high aspect ratio, is a challenging task using the self-assembly of block copolymers. In contrast, nature has evolved pathways for the precise and reproducible assembly of myriad particulate shapes and sizes, with structures known to atomic resolution. The most commonly used biological templates for chemical modification are viral nanoparticles. They are typically stable to chemical modification, organic co-solvents, and thermal denaturation. Combined with their precise assemblies and diverse range of architectures, viruses represent excellent scaffolds for the templated synthesis of precision nanoparticles. New strategies to graft polymers directly from tobacco mosaic virus (TMV), a 300 x 18 nm rigid protein tube, will be presented. TMV is unique, in that chemistry can be differentially performed on the inside and outside of its viral capsid, which could lead to complex composite polymer nanoparticles. Graft-from ATRP from both the interior and exterior surface of TMV will be described. Additionally, a new type of aqueous graft-from chemistry, ring-opening metathesis polymerization (ROMP), will be described from the surface of monomeric proteins and TMV.
Our research has focused on the unique properties that can be accessed when functionality is strategically placed in a biomaterial structure. The present research focuses on material properties such as shape memory and x-ray contrast. Since Langer and Lendlein first demonstrated the tremendous potential of shape memory polymers in biomedical applications, there has been a continuing interest in utilizing these materials as intelligent medical devices. Our research focuses on several areas: micro- and nanotopography, and reactive functionality. We have developed thermally responsive micro-patterned poly(ε-caprolactone) (PCL) to examine the interaction of human mesenchymal stem cells (hMSCs) with dynamic surface patterns using PRINT™. We have also begun research on novel polymer structures containing functionality capable of micro- or nanoscopic shape memory and post-functionalization. While this application is accessed by the introduction of functionalization that allows for click chemistry, the second major application of interest relies on the incorporation of stable halogens along the polymer backbone for computed tomography contrast agents. Our research efforts towards a processable system based on non-aromatic iodinated polyesters and the resulting shape memory and radiopaque properties will be presented. In addition, our work with macro and micro reversibility with also be described.
Herein we report the synthesis of single-chain nanoparticles (SCNPs) via the acid-catalyzed formation of acetal crosslinks. These SCNPs, which are converted back to their linear counterparts by exposure to aqueous acid, represent an example of a crosslinking strategy that is stimulus responsive and reversible. The formation of crosslinks is characterized by $^1$H-NMR spectroscopy, and triple-detection GPC is used to characterize the molecular weight and size of the nanoparticles and parent polymers. Due to their dynamic nature, these nanoparticles have potential applications in drug delivery and next generation smart and responsive materials.
Optically healable polymers are of great interest because the stimulus can be applied locally. Most healable polymers exhibit relatively weak mechanical properties and exclude a large range of opportunities for applications such as high performance coatings. We introduce supramolecular polymer glasses based on low-molecular weight monomers as a new class of healable materials. The monomer consists of three ureidopyrimidone (UPy) units linked together, and the molecule can via dimerization of the UPy moieties assemble into a supramolecular network which behaves like a glassy polymer. Rheological studies of the UPy-based supramolecular glass showed that upon heating above \( T_g \) the material shows frequency-dependent storage and loss moduli, indicating polymer like properties. It was found that material properties, in particular above \( T_g \), can be easily modified by incorporation of a competitive hydrogen bonding guest molecule (e.g. DMF or a mono-functional UPy compound) that acts as a ‘supramolecular plasticizer’. Furthermore, upon irradiation with ultraviolet light, rapid optical healing of damaged surfaces was observed without a change in the material properties. Our work demonstrates that supramolecular glasses are a promising new class of stimuli responsive materials. This approach can be extended to a broad range of new materials based on supramolecular monomers with other core groups and binding motifs to tune the materials properties.
Azo moieties have been widely studied as radical polymerization initiators, but interestingly only a few studies have demonstrated their usefulness as stimuli-responsive motifs that are covalently incorporated in macromolecular constructs. The azo motif is known to be activated by heat, which results in the cleavage of its C-N bonds inducing the release of N₂ and producing C-centered tertiary radicals that can further react. These systems were also proven to cleave under mechanical activation in solution by sonochemistry. However, the solid-state behavior of azo-containing polymers has remained unexplored. Here we present the synthesis of azo-containing polyamides and polyurethanes, and report on the thermally induced response of these materials in solution and the solid state. We show that the thermally triggered responses, quite surprisingly, depend strongly on the nature of the polymer backbone, the state of matter, and in solution also on the nature of the solvent. The solid-state properties of the azo-containing polyurethanes may be particularly useful. In this case, a thermally induced molecular weight decrease is observed, leading to a significant reduction of the extension at break and the tensile strength (see Figure).

**Figure.** A) Stress-strain curves of neat (black line) and heated (red) samples of azo-containing polyurethanes, and top left a sketch representing the azo moiety. B) Scheme illustrating the molecular weight decrease detected between the neat and heated samples.
POLY 424: Synthesis and phase behavior of alkyne-functionalized di- and triblock copolymers and their cobalt carbonyl adducts

Bingyin Jiang\textsuperscript{1}, jiangbingyin@gmail.com, Bin Qian\textsuperscript{1}, Pengqing Yu\textsuperscript{1}, Robert B. Grubbs\textsuperscript{1,2}, robert.grubbs@stonybrook.edu. (1) Chemistry, Stony Brook University, Stony Brook, New York, United States (2) Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, United States

Stabilizing and controlling the spatial arrangement of metallic nanoparticles with polymers has been of great research interest. Multi-block copolymers can phase separate at nanometer scale to adopt a series of morphologies from spherical to cylindrical to gyroid to lamellar. Incorporation of appropriate functional groups within specific blocks of block copolymers can enable the localization of metallic species to specific nanometer-scale domains. We have synthesized alkyne functional polystyrene-\textit{block}-poly(4-(phenylethynyl)styrene) (PS-\textit{b}-PPES) diblock copolymers and poly[4-(phenylethynyl)styrene]-\textit{block}-polyethylene oxide-\textit{block}-poly[4-(phenylethynyl)styrene] (PPES-\textit{b}-PEO-\textit{b}-PPES) A-B-A triblock copolymers over a range of molecular weights and compositions by reversible addition-fragmentation chain transfer (RAFT) polymerization. Reaction of dicobalt octacarbonyl with these block copolymers proceeded with selective incorporation of cobalt species (Co\textsubscript{2}(CO)\textsubscript{6}) to the alkyne-functionalized blocks. The phase behavior of these block copolymer-cobalt adducts was studied by transmission electron microscopy (TEM). The observed morphologies of the cobalt-containing copolymers shift from PPES/Co minority domains to PPES/Co majority domains as the weight fraction of the PPES/Co blocks increases. Heating these composites leads to loss of CO groups and formation of cobalt nanomaterials. Both PS-\textit{b}-PPES and PPES-\textit{b}-PEO-\textit{b}-PPES cobalt nanocomposites exhibited magnetism after thermolysis. This study provides a method to localize metallic species in an organic matrix at nanometer scale, in which the morphology and size of the metal-containing regions is tunable by altering the polymer composition. Such an approach shows potential in nanopatterning, catalyst preparation, and many other areas.

Phase separated morphology observed for sample: PS\textsubscript{89}-PPES\textsubscript{41}[Co\textsubscript{2}(CO)\textsubscript{6}]\textsubscript{36}
The growth of cells in culture is essential to a wide range of biological and biomedical research, from stem cell studies to high throughput screening, as well as the production of all manner of biotherapeutics and other bio-derived compounds. At the same time, bench-scale cell culture can be quite tedious due to the need to repeatedly passage cells. This process results in variations in pH and nutrient levels as well, not to mention the risks of contamination.

In order to address these issues, we have for some time now pursued the synthesis of synthetic, non-toxic, biocompatible hydrogels designed to absorb acidic metabolites (e.g. lactic acid) and release nutrients (e.g. glucose) in mammalian cell culture applications. We have previously published on the success of these efforts through the use of a specialized polyurea network prepared via organic sol-gel chemistry. Here, we report on our next-generation materials, representing a far broader palette of swelling and release behavior. These new networks, based on epoxy resin chemistry, are simple to produce and display a broad range of performance characteristics, enabling for the design and selection of materials to match the needs of disparate cell culture applications.

Following an overview of our synthetic efforts, the swelling and release behavior of these networks are described, both in aqueous buffer and cell culture media, as well as the results of our efforts to develop quantitative performance metrics for these materials that are meant to aid in the rapid identification of those most suited to meet a given need. In addition, we demonstrate a novel approach to the study of hydrogel swelling at the microscale via confocal fluorescence microscopy. Finally, we report on the outcome of cell culture studies carried out using selected polymer networks. The result of these efforts as a whole is a description of a novel family of responsive hydrogels with the potential to regulate the pH and nutrient levels in cell culture, as well as the presentation of a new means of characterizing the swelling behavior of hydrogels in general.
POLY 426: Helical polypeptides mediated nonviral gene and siRNA delivery

Lichen Yin³, Nan Zheng⁴, Hua Lu², Nathan Gbrielson¹, Kyung Hoon Kim¹, Xiaojian Deng¹, Rujing Zhang⁵, Jianjun Cheng¹, jianjunc@illinois.edu. (1) Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States (2) The Scripps Research Institute, La Jolla, California, United States (3) Department of Materials Science and Engineering, University of Illinois, Urbana, Illinois, United States (4) University of Illinois, Urbana, Illinois, United States (5) University of Illinois at Urbana-Champaign, Urbana, Illinois, United States

We designed a class of helical, cationic charged polypeptides via the ring-opening polymerization of vinyl benzyl glutamic acid N-carboxyanhydrides. These materials have unusual helical stability and display excellent cell penetrating property, outperforming TAT peptide. By controlling the chemical, morphological and self-assembly structures of these side chain charged, helical polypeptides, we identified a few materials that showed excellent gene and siRNA delivery efficiency in vitro and in vivo.
POLY 427: Organic photovoltaics: Materials microstructure and its effects on device parameters

Alberto Salleo, asalleo@stanford.edu. Stanford Univ Geballe Lab For, Stanford, California, United States

In organic solar cells, the power generation process is usually divided into basic steps: light absorption, exciton migration, exciton splitting and charge migration to the contacts. Thanks to fundamental and engineering advances, the performance of organic solar cells, as measured by their power conversion efficiency has been steadily increasing, up to ~10% for single junctions and >12% for tandems. There is a broad consensus in the organic photovoltaic community that all the steps involved in generating photocurrent are dependent on the microstructure of the materials. Ultimately then the microstructure is directly coupled to the typical device parameters used to measure power conversion efficiency: $J_{SC}$, $V_{OC}$ and FF.

In this presentation I will discuss a few examples of such coupling. In particular, I will show that all charge generation proceeds via a ground-state charge-transfer (CT) state at the donor-acceptor interface. The energy of this CT state is directly related to the $V_{OC}$ and is affected by molecular conformations and aggregation at the interface. Finally, I will discuss how crystalline disorder in the pure phases induces electronic traps, which are responsible for poor transport and a degradation of FF.

Ultimately, the promise of organic electronics is the ability to design materials to perform predetermined functions. The example of organic photovoltaics demonstrates that this promise can be fulfilled only if we understand how the microstructure of these materials, as analyzed at several length-scales, affects their function.
POLY 428: High efficiency BODIPY lamellar organic photovoltaics

John Chen¹, chenjj@usc.edu, Sarah M. Conron¹, Patrick Erwin¹, Michael Dimitriou², Kyle McAlahney¹, Mark E. Thompson¹. (1) Department of Chemistry, University of Southern California, Los Angeles, California, United States (2) National Institute of Standards and Technology, Gaithersburg, Maryland, United States

Recent advances in organic photovoltaics (OPVs) have shown promising alternatives to green energy, enabling cost-effective and lightweight substitutes to traditional silicon solar cells. The synthetic versatility of organic small molecules has driven small-molecule based OPVs to reach power conversion efficiency surpassing 8%. Boron dipyrromethene (BODIPY) dyes are a class of highly absorptive materials suitable for OPVs. A benzannulated BODIPY (bDIP) molecule exhibiting strong absorption at 640 nm is used as an electron donor with C⁶₀ as the acceptor. The BODIPY dye demonstrated the best performance in lamellar architecture (ITO/bDIP/C⁶₀/bathocuproine/Al), giving power conversion efficiency up to 4.5 %. The insensitivity of short-circuit current to bDIP thickness was probed by neutron reflectivity experiment. The analysis on reflectivity measurements suggests the presence of a mixed layer at the D/A interface in the bilayer device. bDIP and C⁶₀ exhibit a substantial amount of mixing, forming a 13 nm mixed layer when C⁶₀ was deposited onto a room temperature bDIP film. Planar-mixed heterojunction (PMHJ) devices were fabricated to understand the extent of spontaneous mixing between the donor and acceptor material. The native mixed region in the bilayer device was shown to most resemble a blended 1:3 bDIP:C⁶₀ layer in the structure:(ITO/bDIP/bDIP:C⁶₀ blend/C⁶₀/bathocuproine/Al). Our results show a discrete interface in lamellar devices cannot always be assumed to be present. A PMHJ-like picture may be a more realistic representation of our lamellar devices.
POLY 429: Role of linking chemistry on charge separation and photovoltaic performance of all-conjugated block copolymers

Jorge Mok, Yen-Hao Lin, Kendall Smith, Kevin Yager, Seth B. Darling, David J. Gosztola, Youngmin Lee, Richard Schaller, Enrique Gomez, Rafael Verduzco, rafaelv@rice.edu. (1) Argonne National Laboratory, Lemont, Illinois, United States (2) Brookhaven National Laboratory, Upton, New York, United States (3) Penn State University, University Park, Pennsylvania, United States (4) Rice University, Houston, Texas, United States (5) Dept of Chemical and Biomolecular Eng, Rice University, Houston, Texas, United States (6) Chemistry, Northwestern University, Evanston, Illinois, United States (7) Center for Integrated Nanotechnologies, Los Alamos, New Mexico, United States (8) Institute for Molecular Engineering, University of Chicago, Chicago, Illinois, United States

All-conjugated block copolymers bring together distinct pi-conjugated polymers and represent promising materials for the development of organic photovoltaic devices. Recent work from our group has demonstrated all-conjugated block copolymer OPVs with nearly 3% power conversion efficiencies. Here, we explore the role of linking chemistry on performance and charge separation by studying two all-conjugated block copolymers with identical composition and molecular weights but which differ only in the linking group between donor and acceptor polymer blocks. We analyze the same system that has shown near 3% power conversion efficiencies, comprised of a poly(3-hexylthiophene) (P3HT) donor polymer and poly(2,7-(9',9'',dioctylfluorene)-alt-5,5-(4',7'-di-2-thienyl-2'-1',3',-benzothiadiazole) (PFTBT) polymeric acceptor. The linking group is comprised of a fully conjugated push-pull monomer, oriented with the electron rich segment either adjacent to P3HT or the PFTBT block. Photovoltaic device studies, X-ray scattering, and transient absorption measurements provide information on the microstructure and electronic properties of donor-acceptor all-conjugated block copolymer films. We show that changing the orientation of the linking group can decrease power conversion efficiencies and photocurrents by more than an order of magnitude. In the optimal configuration of the linking group, transient absorption measurements reveal charge separated states (free charges) in block copolymers with fully conjugated linking groups. These measurements also reveal ultrafast charge recombination (< 1 ns) for even the most efficient block copolymer OPVs, with power conversion efficiencies greater than 2%. This suggests that further optimization of all-conjugated block copolymer may be available through tailoring the linking group to increase charge-separation while suppressing charge recombination. All-conjugated block copolymers may also serve as a useful model system for studying charge separation and charge-transfer states at organic donor-acceptor interfaces.
In order to develop cost effective and efficient polymer based photovoltaic solar energy conversion systems, a novel DBfA type of conjugated block copolymer system was designed, synthesized, and preliminarily studied, where D is a donor type conjugated block, B is a non-conjugated and flexible aliphatic hydrocarbon bridge chain (containing two, four, and six methylene units), and fA is a fluorinated acceptor type conjugated block (See Figure 1). Preliminary characterizations revealed, the UV-Vis absorption of the DBfA is an overlap of individual absorptions of D and fA, while the solution steady state photoluminescence (PL) emission of D was quenched between 10-60% in DBfA depending on measuring conditions such as concentration. Thin film morphology studies revealed more uniform and nanoscale phase domains of DBfA as compared to D/fA blend. Preliminary solar cell device studies revealed two orders of magnitude increase of photoelectric power conversion efficiency of DBfA versus simple D/fA blends. These results exhibit a viability of potential cost effective polymer based approaches toward photovoltaic.

Figure 1. Chemical structure of a DBfA type block copolymer.
POLY 431: All-polymer solar cells

Zhenan Bao, zbao@stanford.edu. Chemical Engr Dept MC 5025, Stanford University, Stanford, California, United States

The performance of organic solar cells consisting of a donor/acceptor bulk heterojunction has rapidly improved over the past few years. Major efforts have been focused on developing a variety of donor materials to gain access to different regions of the solar spectrum as well as to improve carrier transport properties. On the other hand, the most utilized acceptors are still restricted to the fullerene family, which includes PC$_{61}$BM, PC$_{71}$BM and ICBA. The high cost of fullerenes hinders the potential commercialization of organic solar cells at industrial scale. In comparison to the existing high performing donor materials, the molecule pool of acceptors is still extremely limited, thus inhibiting the further development of organic solar cell in fundamental research and practical application. To that end, the design of new classes of cost-competitive acceptor materials is crucial.

However, despite intensive research focused on creating an efficient all polymeric solar cells for the past decade, only three different recipes with PCE only reaching 2% have been reported. In recent months, there have been further improvements to the PCE which were up to 3.6%. The fundamental understanding of all-polymer solar cells is still in its inceptive stage regarding both the materials chemistry and structure physics. Thus, rational design rules must be utilized to enable fundamental materials understanding of the all polymer solar cells.

We report high performance all-polymer solar cells employing polymeric donors and acceptor. Phase separation of the two polymers were fine-tuned by changing backbone of polymeric donors. In fact, we observed a direct correlation between the short circuit current ($J_{SC}$) and the phase separation size. Additionally, with side chain engineering of the polymeric donor, the phase separation size of the all polymer blends was further reduced. We obtained a record PCE of 4.8% (average from 20 devices), with an average $J_{SC}$ of 9.8 mA cm$^{-2}$. The highest PCE is above 5.0%, with $J_{SC}$ as high as 10.2 mA cm$^{-2}$, and $V_{OC}$ of 1.02 V. Further improve is underway.
A novel method of precisely constructing stable and controllable conjugated polymer (CP)/fullerene nanostructures is presented. By building in non-covalent interactions between CP nanofibers (NFs) and fullerene derivatives, supramolecular polymer/fullerene composite NFs are obtained in solution for the first time. Specifically, a conjugated block copolymer having poly(3-hexylthiophene) (P3HT) backbone selectively functionalized with polar isoorotic acid (IOA) moieties, P1, is used as the building block. Self-assembly of P1 in mixed solvents leads to well-defined NFs decorated with IOA groups on the periphery, onto which phenyl-C61-butyric acid methyl ester (PCBM) and modified PCBM molecules are subsequently attached non-covalently via complementary hydrogen bonding interactions. Formation of such complex structures are studied in detail and confirmed by NMR, UV-Vis absorption spectroscopy, transmission electron microscopy (TEM), atomic force microscopy (AFM), and X-ray scattering measurements. Thin films of such composite NFs displayed controlled morphologies at both macroscopic (long-range ordering) and microscopic (polymer packing orientation) levels. Application of these composite NFs in organic photovoltaic (OPV) devices leads to not only superior performance but also much improved thermal stability, when compared with conventional bulk heterojunction (BHJ) devices.

References
Conjugated polymers possess many exceptional electronic, optical, and thermal properties and thus are well suited for organic semiconducting applications, such as photovoltaic cells, thin film transistors, and light-emitting diodes. However, there are several issues that have to be addressed for commercial development of products based on these materials. Of particular interest is the development of efficient conjugated polymer photovoltaic cells from low-cost materials as this is beneficial for large-scale synthesis. To this end, our group has begun making conjugated polymer building blocks from low-cost starting materials such as hydroquinone, and furfural. Specifically, we have developed novel conjugated polymers based on the electron-deficient 3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DFDPP) and electron-rich benzo[1,2-b:4,5-b']difuran (BDF) moieties (Figure 1). We have selected DFDPP and BDF as building blocks because conjugated polymers comprising it have exhibited excellent performance in bulk heterojunction photovoltaic cells. Additionally, we can prepare monomers based on these heterocycles from readily available starting materials in a few short steps. Novel donor-acceptor copolymers can be synthesized by combining the DFDPP and BDF monomers with various co-monomers. Our recent work on these materials will be presented.

Figure 1. Generic structures of DFPPD and BDF polymers.
Semi-random copolymers represent an emerging class of materials for which the optoelectronic and photophysical properties of these “push-pull”, donor-acceptor (D-A) materials can be fine-tuned with exquisite control. Here, we present our recent work on a number of systematic studies. (1) A series of semi-random D-A copolymers were synthesized with varying amounts of benzodithiophene (BDT) donor and thienoisindoledione (TID) acceptor. With BDT:TID ratios between 1:1 and 7:1, the LUMO of these materials can be systematically tuned over a range of 0.4 eV, allowing us to probe the optimal energetic driving force for charge separation in polymer:fullerene organic photovoltaic (OPV) devices. (2) The synthesis and characterization of bis- and tris-BDT monomers is reported; these monomers were used to create well-defined alternating polymer structures with repeating (D-D-A) and (D-D-D-A) units, which are compared to semi-random materials with analogous D-A content. OPV device efficiencies of these materials demonstrate that the semi-random copolymers consistently outperform the alternating ones. (3) Finally, we report how a combination of side-chain engineering on the BDT core and the incorporation of various BDT units into semi-random D-A copolymers and terpolymers can be used to tune photophysical properties of the materials, including lifetimes of photoconductance transients of copolymer:fullerene films as measured by time-resolved microwave conductivity.

Absorptivity of semi-random copolymers in chloroform solution.
One focus of our research program involves the study of sensitized triplet-triplet annihilation (TTA) or triplet fusion (TF) in solution and soft materials using highly photostable metal-organic chromophores in conjunction with energetically appropriate organic molecules with large singlet-triplet gaps. Selective excitation of the long-wavelength absorbing sensitizer efficiently generates long-lived triplet states that serve as energy transfer donors. In the presence of appropriate molecular acceptors, diffusion controlled triplet-triplet energy transfer takes place, producing the excited triplet state of the acceptor while regenerating the ground state of the sensitizer. When sufficient numbers of the sensitized triplets are produced, TTA takes place which results in either frequency upconverted light or the formation of desired chemical products. Various combinations of donor and acceptor have been explored and data will be presented on a number of these systems spanning light conversions ranging from the near-visible to the near-IR. This presentation will describe many examples of upconversion phenomena realized in solid-state polymeric materials along with emerging classes of acceptor/annihilator chromophores. TF processes will be shown to operate at high efficiencies with concomitant linear incident power density response, demonstrated in both theory and experiment using non-coherent photons.
We have demonstrated the formation of oxime-functional hydrogels that are able to disassemble and reassemble upon application of a stimulus. Keto-functional copolymers were prepared by conventional radical polymerization of \( N,N \)-dimethyl acrylamide (DMA) and diacetone acrylamide (DAA) to prepare the hydrogels. The water soluble copolymers (P(DMA-stat-DAA)) were chemically crosslinked with difunctional alkoxyamines to obtain hydrogels via oxime formation. Gel to sol transitions were induced by the addition of excess monofunctional alkoxyamines to promote competitive oxime exchange under acidic conditions at 25 °C. UV-Vis spectroscopy was employed to characterize the release behavior of an encapsulated dye in the oxime-functional hydrogel in the presence of excess monofunctional alkoxyamine and catalytic acid. In addition to their chemo-responsive behavior, the P(DMA-stat-DAA) copolymers possess lower critical solution temperatures (LCST) which varies with the DAA content in the copolymers. This thermo-responsive behavior of the P(DMA-stat-DAA) was utilized to form physical hydrogels above their LCST. The hydrogel formation and its mechanical properties were studied by rheology. The tunable degradation properties of these oxime-functional soft hydrogels and the thermo-responsiveness of the physical hydrogels showed potential for a variety of applications, such as coatings for medical devices, sensors, scaffolds for biomolecules (e.g., proteins and dyes), and network scaffolds for tissue engineering purposes.
Polymers bearing dynamic covalent bonds may exhibit dynamic properties, such as self-healing, shape memory and environmental adaptation. However, most dynamic covalent chemistries developed so far require either catalyst or change of environmental conditions to facilitate bond reversion and dynamic property change in bulk materials. Here we present the rational design of hindered urea bonds (HUBs) (urea with bulky substituent attached to its nitrogen) and the use of HUBs to make polyureas and poly(urethane-ureas) capable of catalyst-free dynamic property change and autonomous repairing at low temperature. Given the simplicity of the HUB chemistry (reaction of a bulky amine with an isocyanate), incorporation of the catalyst-free dynamic covalent urea bonds to conventional polyurea or urea-containing polymers that typically have stable bulk properties may further broaden the scope of applications of these widely used materials.
POLY 438: Supramolecular motifs in dynamic covalent PEG-hemiaminal organogel networks

Jeannette M. Garcia, jmgarcia@us.ibm.com. Chemistry and Materials, IBM Almaden Research Center, San Jose, California, United States

A unique concept in material design was explored in the synthesis of macromolecular networks that incorporate dynamic covalent and supramolecular cross-links to produce two distinct networks. A kinetic approach to the synthesis of a suite of PEG-based hemiaminal compositions to afford covalently cross-linked PEG-hemiaminal dynamic covalent network (HDCN) organogels were shown to exhibit temperature-dependent dynamic covalent behavior. Self-healing and mechanical properties of HDCN organogels were dependent on concentration and temperature during synthesis; gels synthesized at lower temperatures behaved as elastomeric materials, while gels synthesized at higher temperatures with superstoichiometric amounts of paraformaldehyde exhibited self-healing behavior. Detailed NMR studies indicate the formation of two distinct networks (a dynamic covalent and supramolecular based network) the dynamic behavior of each can be triggered by different temperature and kinetic windows. Under specific conditions the dynamic behavior of both these networks can be triggered to access unique material properties from the combination of these two distinct types of dynamic bonds that include self-healing and network rearrangement. Nuclear magnetic resonance spectroscopy (NMR) studies showed a temperature-dependent equilibrium between NMP-soluble formaldehyde and hemiaminal covalent cross-link junctions, creating a unique dynamic system that can be trapped under the right conditions. The mechanical properties of self-healing HDCNs and elastomeric HDCNs were characterized by compressive mechanical testing and oscillatory shear rheology as a function of temperature. Optimization of conditions towards an elegant self-healing, dynamic system is presented in this work, demonstrating the capabilities of HDCNs as elastomeric organogel materials with potential applications in printable materials, cargo delivery, and adhesives.
Materials were designed based on cross-linked dynamic covalent bonds’ inherent self-healing ability. A dynamic network of imine-primary amine bonds prepared by PEO diamine and benzyl-trialdehyde shows malleability under stress by dynamic mechanical analysis (DMA). The disappearance of aldehyde C=O peak and appearance of imine C=N peak in IR spectrum have further confirmed the cross-linked network. H-NMR kinetics demonstrate the driving force of the self-healing process is due to imine and primary amine bond exchange. Solvent polarity affects the rate of bond exchange shown in both H-NMR and DMA. Samples made with polar aprotic solvents show fastest dynamic bond exchange compared to polar protic and non-polar solvents. Through the dynamic bonds, the damaged sample was able to be reattached and healed over time. Organic gels have been shown to successfully exhibit malleability and are capable of self-healing based on dynamic exchange of imine and primary amine bonds.
Evolving mission criteria and cost-driven requirements for aerospace systems are motivating Air Force investment in the development of multifunctional materials. Environmental and occupational health concerns are also driving the development of non-toxic, “green” materials. However, because the industrial aerospace community is extremely risk-averse, the responsibility to achieve significant advances in materials technology falls largely to the government laboratories. This presentation will discuss on-going chemical and materials research performed at the Air Force Research Laboratory, Rocket Propulsion Division. Recent activities include fundamental research on the development of new polymer cure systems using non-toxic reactive compounds.

Current solid rocket propellant systems commonly use multifunctional isocyanates to cross-link a hydroxyl-terminated polybutadiene (HTPB) binder. Because this approach has resulted in many environmental and occupational health concerns, a more environmentally friendly chemical approach to the cure reaction is desired. Methods utilizing compounds and/or reactions commonly found in nature are, therefore, less likely to be subject to severe regulatory restrictions, but these approaches also often involve a trade-off between performance and environmental benefit. Thiol-ene “click” chemistry is somewhat similar to the current cross-linking method and is, therefore, likely to deliver the required performance without creating the environmental and health risks associated with isocyanates. The technical approach includes chemical synthesis of environmentally benign candidate polymers, as well as identification of cross-linking agents suitable for propellant binder systems. Examination of cure chemistry options, formulation of propellant samples, and characterization of the crosslinking chemistry will be examined.
Order in purely organic network polymers is hard to achieve, as reversible, dynamic covalent bond formation is required. Strategies focused on thermodynamic controlled transformations, as kinetics would not seemingly favour reversibility. Herein, we report formation of crystalline network polymers under kinetically favoured conditions by using quaternary ammonium salt linked networks. Charged bulky bridges align, even under fast reaction times (20 minutes) if the rotational freedom is granted. Adding vicinal methyl substituents block the ordering, hence form amorphous networks. Raman experiments and SEM images reveal stacking of 2D layers.
A new initiation method that will allow polymeric systems to be polymerized without the use of heat or application or radiation was introduced. Radicals will be produced by means of a magnetic macro-initiator (MI) upon application of an external alternating current magnetic field (AC MF). The magnetic MI was prepared by coating a magnetic nanoparticle core with molecules containing a weak bond capable of cleaving and forming free radicals. Magnetically induced polymerization via the decomposition of a magnetic MI under the influence of an externally applied AC MF was shown to be possible through the use of molecular dynamics (MD) simulations. A minimum force of 62 kcal/molÅ applied to the core of the MI is required in order to decompose the C-N bond of the azo group, producing free radicals. Three different magnetic core (Fe₃O₄, FeCo, and Co) MIs were tested to initiate free radical polymerization of different acrylics with minor increases in temperature as compared to the thermal decomposition temperature of the azo group. The minimum magnetic field to break the C-N bond of the azo group, Fe₃O₄ > FeCo > Co. In order to have safe and effective magnetically induced polymerization, both the concentration of the MIs used and the duration of the AC MF need to be carefully controlled.
Magnetic induction represents a highly useful means of achieving rapid heat transfer without the need for physical connections. In polymer nanocomposites with magnetic nanoparticles, exposure to high-frequency alternating current may be utilized to induce a significant amount of heating, with the spatial distribution of heating controlled by the distribution of nanoparticles. Although these methods have proven useful for initiating chemical cure reactions in thermally polymerized networks, the introduction of metals such as iron and cobalt in magnetic nanoparticles often results in significant decreases in the thermo-chemical stability of the networks. We present a method for overcoming these difficulties by first coating the magnetic nanoparticles with a nanoscopic layer of silica. The surface functionality of the silica may then be controlled to provide compatibility with the polymer network, while isolating it from the damaging effects of undesirable metals. The method has been used successfully to prepare polycyanurate networks reinforced with silica-coated nanoparticles.
In this presentation, an overview will be presented of recent research into structural materials made from cellulose nanocrystal (CNC) composite laminates and nanocomposite fibers. CNCs are an attractive materials class for possible applications in nanocomposites reinforcement, nanomaterials and biomedicine as they have high strength and stiffness, yet are renewable, biodegradable, non-toxic, cheap, and optically transparent. Here, we will detail efforts to utilize these materials in composites, both as films utilizing their high strength and stiffness in laminates to control toughness and as a nanoreinforcements in fibers for composite applications. Discussion of the resultant mechanical behavior will be presented.

Scanning electron microscopy (SEM) image of cellulose nanocrystal (CNC) reinforced polymer fiber fracture surface at different contents.
POLY 445: Sustainable, high-performance fiber composites

Christopher Kuncho², Johannes Möller², Wenhao Liu², Emmanuelle Reynaud¹, Daniel F. Schmidt², Daniel_Schmidt@uml.edu. (1) Mechanical Engineering, U. Mass. Lowell, Lowell, Massachusetts, United States (2) Plastics Engineering, U. Mass. Lowell, Lowell, Massachusetts, United States

Continuous fiber reinforced thermosets serve a range of industries, from transportation to sporting goods to wind energy. Petroleum derived resins form the basis for the majority of these materials, and such composites are effectively impossible to recycle without substantially degrading the performance of their constituent elements. We report on work designed to directly address these issues.

First, we describe investigations to better understand and optimize the properties of bio-derived thermosets based on epoxidized linseed oil (ELO), and demonstrate the creation of high performance bio-derived thermosets and glass-reinforced composites from inexpensive components via this approach. We find that the mechanical properties of these materials rival those of conventional resins and composites. Furthermore, we see evidence of a higher level of damage tolerance vs. conventional systems, highlighting potential performance advantages via this approach as well.

Second, we detail our efforts to introduce reworkability into commercially available high performance epoxy resins used in wind energy applications. Inspired by the work of Liebler et al (2011), our efforts focus on the combination of epoxy / anhydride chemistry with transesterification catalysts, and emphasize screening for improved catalyst activity. Catalysts are assessed both for the degree of high temperature creep they enable and also the strength of the materials under the reworking conditions. Discussions of our efforts to realize reworkability in practice will also be presented, as well as the applicability of the same catalysts in the context of our optimized bioepoxy networks.

Finally, we report on our attempts to combine these two approaches both in order to better understand their generality and realize a high performance, bio-derived, reworkable fiber composite with significant practical utility.

A unidirectional glass fiber reinforced anhydride cured bioepoxy resin composite
Cellulose nanocrystals (CNCs) are attracting growing interest as a bio-based, inexpensive, high-stiffness filler and are potentially useful for the reinforcement of a broad range of polymers. Processing of these materials is, however, quite intricate, especially with processes that are useful for technological exploitation. Hurdles include the facts that (i) CNCs have a strong tendency for aggregation, (ii) suffer from mechanical degradation when processed under high shear (ii), and display limited thermal stability. This presentation will summarize our recent efforts to overcome these problems. Processing-structure-property relationships will be discussed on the basis of several selected materials systems and processes. Examples that will be presented include template-made nanocomposites of low-density polyethylene and CNCs, solution-cast poly(vinyl acetate)/CNC nanocomposites that were post-processed by different melt-processing schemes, and poly(amide 12)/CNC nanocomposites that were prepared by direct mixing in a roller blade mixer.
Sustainable composites can be produced through ecologically responsible conversion of renewable and fossil resources using industrial biotechnology and enhanced by nanotechnology. This approach represents a triple technological convergence that results in an emerging class of materials that can be referred to as ecobionanocomposites. Similarly, the recent rapid developments in Industrial Biotechnology are making the conversion of biomass into useful monomers, polymer matrices, and natural fibers increasingly feasible.

This talk will provide an overview of recent developments in developing hierarchically structured composites materials. In particular, the phenomena of stereocomplexation is exploited to produce materials with an additional degree of supramolecular ordering. One example of these composites consists of biobased polylactides (PLA) grafted to cellulosic nanowhiskers (CNW) embedded in a stereocomplexing matrix. The approach has also been utilized to graft polymer onto inorganic particles including fumed silica which can then be embedded in the stereocomplexing matrix. More recently, the approach has been extended to blended matrices. This leads to nanocomposite materials with six phases being simultaneously present thus providing an elegant hierarchically structured material. Finally, we report on reactive systems in which the nanocomposite materials may be utilized in conventional vacuum infused resin transfer molding (VRTM). Implications for property changes associated with this new paradigm in polymer composites are discussed.

**Figure 1. Films of the ecobionanocomposites are transparent.**
Cellulose nanocrystals (CNCs) are one of nature’s most abundant structural building blocks and possess outstanding mechanical properties such as a tensile modulus comparable to Kevlar. It remains challenging to upscale these properties in CNC neat films and nanocomposites due to the difficulty of characterizing interfacial bonding between CNCs that govern stress transfer under deformation. Here we present new analyses based on atomistic simulations of shear and tensile failure of the interfaces between Iβ CNCs in elementary fibrils, providing new insight into factors governing the mechanical behavior of hierarchical nanocellulose materials. We compare the two most relevant crystal surfaces and find that hydrogen bonded surfaces have greater tensile strength compared to the surfaces governed by weaker interactions. On the contrary, shearing simulations show that friction between the atomic interfaces depends not only on surface energy but also the energy landscape along the shear direction. While being a weaker interface, the intersheet plane exhibits greater energy barriers to shear. Analytical models to describe the stick-slip energy landscapes are developed, accounting for size-effects. Our simulations combined with simple theoretical predictions explain experimental observations on the mechanical properties of cellulose nanocomposites and their variation with environmental factors as moisture. Our results pave the way for tailoring hierarchical CNC materials by taking a materials-by-design approach as commonly done for metals, where mechanical properties can be tuned through a deeper understanding of grain boundary physics and nanoscale interfaces.
Ionic liquids (IL) have been the focus of materials research for some time due to their unique physical and chemical properties. Of significant interest is their ability to solubilize biopolymers such as cellulose, chitin, keratin, and silk. However, full dissolution and regeneration using IL solvents often results in biomaterials with inferior properties compared to the native material. When natural substrates are only partially dissolved and regenerated through a process called Natural Fiber Welding (NFW), much of the native biomaterial structure can be maintained while still allowing for significant material modification. If functional materials (e.g. magnetic, conductive, antimicrobial) are present in the IL-welding solution, these materials will be entrained in and on the surface of the substrate.

Several lignin-cellulosic-based composite materials, containing either two or more biopolymers or biopolymer and functional materials, have been prepared and characterized. The degree of welding was characterized through XRD and the distribution of materials was quantified through fluorescent imagery and SEM. The material properties of the composites were also determined via tensile testing. Overall, the resulting composites maintained the desirable properties of the biopolymer substrate while also exhibiting the attractive properties of the added material, showing that NFW offers a viable route to create composites from traditionally difficult to process biomaterials.

Figure. NFW of cotton yarn.
Hydrogels are highly hydrated three-dimensional polymeric network that mimics native tissue microenvironment. However, the utility of hydrogels is severely hampered by its limited mechanical stiffness and toughness. Ranges of chemical and physical mechanisms are proposed to engineer mechanically stiff and tough polymeric network; for example a covalent crosslinking gelatin hydrogel have stiffness between 3-30kPa. A range of nanoparticles is incorporated within the hydrogel network to enhance to mechanical stiffness by 2-5 folds. But most of these modifications render the formation of brittle hydrogels. Here, we report covalently reinforced elastomeric hydrogels from methacrylated gelatin (GelMA) and (poly-ethylene glycol)-diacid functionalized magnetic nanoparticles (MNPs) (Fig 1a). The addition of small amount of MNPs (0.0005%) to GelMA (5%) results in more than a 10-fold increase in mechanical stiffness and a 20-fold increase in toughness. The increase in mechanical stiffness of nanocomposites indicates a strong covalent interaction between the free amine groups available on GelMA backbone with the PEG-diacid group available on MNPs (size approx. 8 nm) as determined by infrared, nuclear magnetic resonance and X-ray photoelectron spectroscopy. The mechanical stiffness of nanoengineered hydrogel can be easily tailored to 1MPa by fine-tuning the size of MNPs (4, 8 and 12 nm) and GelMA concentration (2.5, 5, 10 and 15%) (Fig 1b). Moreover the nanoengineered hydrogels are highly elastomeric and can sustain more than 90% compressive strain without any plastic deformation. These nanoengineered hydrogel can be used to engineer mechanically stiff network for biomedical applications including tissue-engineered scaffolds, drug delivery vehicles, bioactuators and sensors.

Fig 1: (a) Surface functionalized MNPs are combined with GelMA to obtain highly porous and interconnect hydrogel network. (b) The modulus of nanocomposite hydrogel can be controlled by varying the nanoparticles loading (0-0.5 ug) and polymer concentration (2.5-15wt%).
POLY 451: NMR and kinetic studies of nitric oxide loading of poly(acrylonitrile-co-1-vinylimidazole) for advanced wound healing

Benjamin Batchelor¹, ben.batchelor@utdallas.edu, Alysia Lowe¹, Samsuddin Mahmood¹, Kenneth J. Balkus², Bruce M. Novak³. (1) Chemistry, University of Texas at Dallas, Richardson, Texas, United States (2) Dept of Chemistry BE26, Univ of Texas, Richardson, Texas, United States (3) School of Natural Sciences Mathematics, University of Texas at Dallas, Richardson, Texas, United States

Nitric oxide (NO) plays an important role in physiological functions in the body, naturally synthesized by nitric oxide synthase. NO has been shown to enhance wound healing, generating research interest in the incorporation of NO into thromboresistant polymers for medical devices. Such polymers can be processed by melt-spinning to create surgical suture type materials. These melt-spun sutures can have the high tensile strength and durability necessary for wound closure. The polymers of interest are based off copolymerization of acrylonitrile with 1-vinylimidazole. It has been disputed in previous works that polyacrylonitrile (PAN) will load nitric oxide via carbon-bound diazeniumdiolates, thus it was rightfully assumed that the copolymerization of PAN with another monomer will be also be a carbon bound diazeniumdiolate specials. Through studies utilizing 1-D and 2-D NMR techniques along with kinetic studies, the location of nitric oxide loading has been ascertained. Along with binding locations of diazeniumdiolates on the polymers, the release profiles have been evaluated for their structural changes to the base polymer while also allowing for advanced wound healing.
Strategies capable of specifically abrogating autoimmune responses in an antigen-specific manner would revolutionize the treatment of autoimmune diseases. The liver is continuously exposed to non-pathogenic food, self, and microbial antigens and thus has acquired specialized mechanisms that induce immune tolerance to antigens. In the liver, antigens taken up by hepatic antigen presenting cells (HAPCs), are presented to T cells in the presence of anti-inflammatory mediators, which induces T cell deletion and anergy. For this reason, we hypothesized that a biomaterial-based strategy that targets antigens to HAPCs would induce antigen-specific tolerance. In order to target antigens to HAPCs, we identified receptors for N-acetylgalactosamine, which are enriched on HAPCs, as suitable targets for antigen delivery.

Here, we present a synthetic N-acetylgalactosamine glyco-polymer, termed pGal, that when conjugated to protein antigens targets these antigens to HAPCs and thus induces antigen-specific tolerance. Conjugates of pGal and the fluorescent protein phycoerythrin (PE) were synthesized and administered to mice via tail vein injection. Flow cytometry analysis of the liver cells revealed that liver sinusoidal endothelial cells, hepatocytes, and stellate cells from mice treated with pGal-PE had a multi-fold increase in the percentage of PE+ cells as compared to mice treated with free PE. To demonstrate the ability of pGal-antigen conjugates to prevent the development of autoimmunity, we treated non-obese diabetic (NOD) mice with pGal-insulin conjugates via weekly tail vein injection. After 30 weeks, only 45% of the animals treated with pGal-insulin developed diabetes, whereas 93% of the mice treated with appropriate controls developed diabetes (Figure 1). Given the ability to tether pGal to virtually any protein antigen, we anticipate that pGal conjugates can be used to treat and prevent a variety of autoimmune disorders as well as host versus graft diseases.

Figure 1. pGal-Insulin reduces the number of NOD mice that develop diabetes.
POLY 453: Biomaterials for recruitment and differentiation of endogenous regulatory T cells

Steven Little, add47@gmail.com. Chemical Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania, United States

Next generation biomaterials will be capable of communicating with the biological microenvironment in ways that are similar to real cells and tissues. A primary way that this is accomplished in situ through secretion and spatiotemporal organization of soluble proteins that can lead to the homing and/or differentiation of specialized endogenous cells. Only recently has the technology been made available to program biomaterials to produce such spatiotemporal control over release. This talk will present several examples of the programming of biomaterials to mimic the release and organization of natural proteins to achieve site-specific homing and control over the behavior of endogenous regulatory cells toward treatment of disease and even regeneration of tissues.
Polymeric nanocarriers constitute a rapidly developing field for various biomedical applications ranging from chemotherapeutics to contrast agents. Here we report on the application of multifunctional polypeptoid-conjugates to activate the immune system against a model tumor antigen fragment. In order to achieve specific cell targeting via various receptors for antibodies the polypeptoid itself should not be taken up by any of the very many different cells in the body and needs many functional groups prone to clean conjugation chemistry, in order to derive chemically well defined structures with a high biological specificity. Towards these goals, a new nanocarrier is introduced which consists of a cylindrical brush polymer with polypeptoid side chains carrying an azide functional group on each of the many side chain ends. After efficient “click” conjugation of dye and an anti-DEC205 antibody to the periphery of the cylindrical brush polymer, antibody mediated specific binding and uptake into DEC205+ positive mouse bone marrow derived dendritic cells (BMDC) was observed whereas binding and uptake by DEC205- negative BMDC and non DC was essentially absent. Additional conjugation of the model OVA-antigen fragment SIINFEKL yielded a multifunctional polymer structure that conferred a much stronger antigen-specific T cell stimulatory capacity of pretreated BMDC than application of antigen or polymer-antigen conjugate. First in vivo results on the biodistribution and on the antigen specific activation of the immune system in mice will also be presented.
Abstract:
Research in the Spiegel Laboratory utilizes techniques and insights from organic chemistry to modulate and/or create immunological function, an area termed “Synthetic Immunology.” This talk will describe our lab’s recent efforts in this field, which range from complex molecule synthesis to the creation of novel paradigms in immunotherapy. Specific topics to be discussed will include: (1) investigations into advanced glycation end-products (AGEs) – a class of complex, non-enzymatic post-translational modifications of proteins with effects on immune function; (2) rational design and biological characterization of immunomodulatory small molecules, called antibody-recruiting molecules (ARMs) and small-molecule antibody mimics (SyAMs); and (3) development of technologies for rapid identification of selective ligands for cell surface targets.
Safe and effective next generation vaccines require the development of pathogen-mimicking formulations that facilitate the delivery of antigens/adjuvants to lymph nodes. However, the current design of materials for vaccine delivery is largely empirical and is limited to characteristics such as size, shape, surface geometry and molecular patterns. Rational design of materials for vaccine delivery requires a thorough understanding and control of the structure-property relationship at the molecular level. Here we discuss two types of molecular conjugations that efficiently target antigens/adjuvants to lymph nodes. Structurally optimized molecular vaccines can dramatically enhance lymph node accumulation follow s.c. injection, leading to 30 fold augmenting the antigen-specific CD8 T cell priming and enhanced anti-tumor efficacy. This new materials have broader implications for future works in therapeutic immunomodulation in other contexts such as autoimmunity and vaccination.
POLY 457: Celebration of the award winners

Karen L. Wooley, wooley@chem.tamu.edu. 3255 TAMU, Texas AM University, College Station, Texas, United States

This presentation will highlight the award winners and their accomplishments.
Studies of spherical nanoengineered drug delivery systems have suggested that particle size and mechanical properties are key determinants of in vivo behavior; however, for more complex structures, detailed analysis of correlations between in vitro characterization and in vivo disposition are lacking. Anisotropic materials in particular bear unknowns in terms of size tolerances for in vivo clearance and the impact of shape and rigidity. Herein, we employed cylindrical polymer brushes (CPBs) to answer questions related to the impact of size, length and rigidity on the in vivo behavior of PEGylated anisotropic structures, in particular their pharmacokinetics and biodistribution. The modular grafting assembly of CPBs allowed for the systematic tailoring of parameters such as aspect ratio or rigidity while keeping the overall chemical composition the same. CPBs with altered length were produced from polyinitiator backbones with different degrees of polymerization. The side chain grafts consisted of a random copolymer of poly[(ethylene glycol) methyl ether methacrylate] (PEGMA) and poly(glycidyl methacrylate) (PGMA), and rendered the CPBs water-soluble. The epoxy groups of PGMA were subsequently reacted with propargylamine to introduce alkyne groups, which in turn were used to attach radiolabels via copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC). Radiolabeling allowed the pharmacokinetics of intravenously injected CPBs to be followed as well as their deposition into major organs post dosing to rats. To alter the rigidity of the CPBs, core-shell-structured CPBs with polycaprolactone (PCL) as a hydrophobic core and PEGMA-co-PGMA as the hydrophilic shell were synthesized. This modular build-up of CPBs allowed their shape and rigidity to be altered, which in turn could be used to influence the in vivo circulation behavior of these anisotropic polymer particles. Increasing the aspect ratio or rigidity of the CPBs led to reduced bioavailability, higher clearance rates and, increased mononuclear phagocytic system (MPS) organ deposition.
Harvesting ambient energy from humidity gradients is an attractive approach to design remote devices and regulators. Embedding logic and feedback within the component materials and geometry simplifies design, reduces sensor demand and ultimately points toward autonomic material systems (i.e. smart composites). The challenge however is to understand the interdependent correlation between geometry (i.e. boundary conditions), material composition (i.e. mechanical properties, absorption rate), and external energy gradient (i.e. humidity gradient profile, rate). To address this challenge, a polyimide – sulfonated poly(amic acid) copolymer system was developed, where mechanical responsivity in a humidity gradient can be tuned via composition and spatial patterning. Oscillatory (~1 Hz) motion of monolithic films in inhomogeneous gradients can be understood via conventional bilayer swelling and predicted via mechanical analysis. More complex actuation and location can be designed by prescribing sample geometry, and “printing” an absorption rate pattern across the film by local laser anneals to control the conversion ratio of PI-(ester-sulfonyl) to PI-(carboxylic acid). The excellent thermal stability, fatigue behavior and chemical resistance of polyimides provide materials with outstanding mechanical integrity, demonstrating >100 oscillatory and locomotion cycles without performance degradation. The combination of co-polymer synthesis, local patterning and mechanical design provides a novel platform to combine mechanical responsibility and feedback control within a single material system.
stimuli responsiveness in polymer design is burgeoning and is providing basis for diversely new and advanced materials. These advanced materials include switchable porosity in membranes and coatings, switchable particle formation and thermodynamically stable nanoparticle dispersions, mechanicochemically-coupling polymers that provide directed mechanical stress in response to intensive fields, colloidal crystallization, and switchable stabilization and compatibility of nanomaterials in changing environments, among others. The growth of ionic liquid applications and the concomitant incorporation of ionic liquids into polymeric materials have resulted in a plethora of new polymers based on the imidazolium group. We discuss particular cases exemplifying the above behaviors that highlight important phase change processes that are thermodynamically controlled.

Mechanicochemical coupling driven dewetting following anion exchange in the wetting homopolymer on quartz.
Rational design of dual-emissive luminescent materials plays an important role in ratiometric oxygen sensing. Fluorescent difluoroboron β-diketonates (BF$_2$bdks) show two-photon absorption, strong emission, good photostability, and demonstrated utility for bioimaging applications. When coupled with biocompatible poly(lactic acid) (PLA), BF$_2$bdks exhibit intense fluorescence and room temperature phosphorescence (RTP) in the solid state. These single component, biodegradable materials minimize dye heterogeneity and dye-matrix leaching and can be easily fabricated into nanoparticles suitable for cellular uptake and oxygen-sensing applications. For increased tissue penetration of light and multiplexing applications, red-shifted dyes with different emission wavelengths are desirable. To this end, a new series of thiophene-substituted model complexes were synthesized and luminescence was investigated in methylene chloride solution and dye/PLA blends. Under UV irradiation, all materials showed blue light absorbance and intense emission in air and under nitrogen. Also RTP (afterglow) was observed when UV excitation had ceased. By varying bdk donor ability (Me, Ph, PhOMe) and heavy atom substitution (Br, I) on the thiophene ring, red shifted RTP was achieved (RTP > 600 nm). Promising model candidates inspired synthesis of dye-polymer conjugates made from hydroxyl-functionalized dye initiators via ring opening polymerization of DL-lactide. Additionally, nanoparticles were fabricated from these polymers to calibrate oxygen sensitivity. Synthesis, characterization and potential applications of these materials will be discussed.
The formation of sub-10 nm structures from block copolymer (BCP) self-assembly is being investigated for high-resolution patterning. For nanofabrication applications, the orientation and alignment of BCP domains that have high etch contrast are critical. Silicon-containing BCPs are capable of forming sub-10 nm features and have inherent etch resistance. Lamella-forming poly(styrene-block-trimethylsilylstyrene) (PS-PTMSS) was synthesized and oriented via thermal annealing between neutral surface treatments and polarity-switching top coats. A process flow for integrating orientation control with e-beam defined pre-patterns has been established. Both chemo- and grapho-epitaxy were demonstrated using chemically and topographically patterned substrates resulting in density multiplications up to 6x and trench subdivisions up to 7x, respectively. This work demonstrates the compatibility of DSA with BCPs that require top interface functionalization to control orientation.
POLY 463: Switchable ultrahydrophobic and superhydrophilic polymer surfaces: Synthesis, characterization, and application

Thorsten Hofe\textsuperscript{1,2}, thofe@pss-polymer.com. (1) PSS GmbH, Mainz, Germany (2) Polymer Chemistry, HS Fresenius University of Applied Science, Idstein, Germany

Multifunctional polymer surfaces based on the hierarchal surface structure, show Ultrahydrophobic and Superhydrophilic behavior. To achieve this multifunctionality it is necessary, to combine different functionalities in one material or in this case in one polymer molecule. This implies the production of core-shell-nanoparticle layers on a variety of substrates as polymers and metals with easy-to-clean (anti-soil and anti stain behavior) and self-cleaning properties.

The Ultrahydrophobic properties of a lotus leaf are based on a hierarchal surface structure in the μm and nm range. The lotus leaf surface can be copied by the use of a polymer particle in the μm range and a polymer coating in the nm range.

The synthesis of tri block copolymers using controlled living polymerization techniques and the preparation of the core-shell-nanoparticles will be presented.

The superior advantages and possibilities of 2-dimensional separation techniques including FT-IR identification will be discussed to determine the molar mass and the composition of the polymers.

The discussed polymers consist of a block responsible for the anchoring to the substrate, a “hydrophilic” and a “hydrophobic” block. This offers the possibility to combine responsive switching of the wettability behaviour and the anchoring to a substrate in one molecule. The wetting behaviour of the prepared polymer brushes can be switched by external stimuli: temperature, pH-value, solvent atmosphere, salt concentration etc.

The surface properties will be discussed as a function of the polymer composition and the molar mass.

Superhydrophilic and Ultrahydrophobic surface behavior was achieved using μm based hierarchical silica particles and nm scaled polymer surface structure.

Applications for the possible industrial use of these new surface properties will be shown.

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Fig.1 shows a Water drop on a ultrahydrophobic modified PVC surface.
Single-chain technology has had a major impact on the field of precision polymer design over the last few years. One of its aims is the emulation of naturally occurring single-chain architectures (e.g., the three-dimensional structure of a protein) with synthetic polymers. With this goal in mind, it is mandatory to move synthetic single-chain architectures into the environment in which these bio-macromolecules work – water. In the current contribution, we present the reversible folding of single polymer chains in aqueous environment on the basis of cyclodextrin (CD) host/guest chemistry. Therefore, a water-soluble polymer, namely poly(N,N-dimethylacrylamide), was prepared via the RAFT polymerization technique, carrying the host (β-CD) and guest (adamantyl) moieties at the chain ends (see Scheme 1). The single-chain folding of adamantyl-β-CD α-ω-functionalized poly(N,N-dimethylacrylamide) and its reversion at elevated temperatures were monitored by dynamic light scattering (DLS) and nuclear Overhauser enhancement spectroscopy (NOESY) (see Figure 1).
The main advantages of organic semiconductors are their ease of processing and more importantly their mechanical flexibility. Whereas most silicon based semiconductors are restricted to solid substrates, semiconducting polymers can easily be adapted to flexible substrates, opening up new application routes. However with the introduction of flexible and potentially wearable electronics, the susceptibility to externally induced physical damage to the organic semiconductor has to be taken into account.

To circumvent the issue of material disintegration, our focus shifted to self-healing polymers, which exhibit the ability to repair induced damages or defects in their structure in order to restore the polymers initial mechanical and physical properties. To date the most common self-healing approaches are based on reversible Diels-Alder reactions, photo-induced healing or the incorporation of reactive components into the material matrix. These approaches are certainly appropriate for the healing of “traditional” polymers, but are not entirely compatible with the specificities of \( \pi \)-conjugated semiconducting polymers.

In this paper we will lay out our design approach to combine the unique properties of semiconducting polymers with the advantages of self-healing materials. We will discuss our unique approach and elucidate the employed chemistry to synthesize self-healing semiconducting polymers. We will highlight how lowering the glass transition temperature of the semiconducting polymer lead to improved flow properties allowing the physical healing of damaged material, thus restoring the physical integrity and semiconducting character of the polymer.

Schematic representation of self-healing semiconducting polymers.
POLY 466: Light harvesting using colloidal quantum dots and hybrid organic-inorganic materials

Edward Sargent, ted.sargent@invisageinc.com. University of Toronto, Toronto, Ontario, Canada

Colloidal quantum dots are inorganic semiconductors whose small size determines their bandgap via quantum confinement. Traditionally they have relied on the use of long aliphatic ligands in synthesis, and this has necessitated required exchange to shorter, more conduction-compatible, ligands to produce thin semiconducting films. I will summarize progress in advancing the performance and processing of colloidal quantum dot solids and their utilization in energy-harvesting devices.
Selective incorporation of inorganic nanocrystals into a block copolymer matrix capable of forming phase separated film structures is an approach that is particularly interesting for hybrid photovoltaic applications, in which control over nanostructure of the film is essential for device performance. One effective strategy for preparing such hybrid nanocomposites is the direct synthesis of semi-conducting nanocrystals in the block copolymer matrix, with at least one conducting polymer block. In-situ synthesis of semi-conducting nanoparticles in a block copolymer matrix eliminates the need for rigorous post-synthesis functionalization of the nanoparticles prior to incorporation in the polymer matrix. Herein, the described strategy was utilized to prepare hybrid nanocomposites via in-situ growth of CdS nanoparticles in amphiphilic poly(3-hexylthiophene) (P3HT) block copolymers with poly(acrylic acid) (PAA) and poly(2-vinylpyridie) (P2VP). The preferred complexation of the Cd precursor with the PAA or the P2VP followed by bubbling with H₂S gas allowed for the CdS to be incorporated exclusively into the amphiphilic domain of the block copolymer. FT-IR, TEM, and DLS were utilized to characterize the resulting nanocomposites.
The performance of polymer and hybrid solar cells is strongly dependent on their efficiency in harvesting light, exciton dissociation, charge transport, and charge collection at the metal/organic/metal oxide or the metal/perovskite/metal oxide interfaces. In this talk, the integrated approach of combining material design, interface, and device engineering to significantly improve the performance of polymer (PCE of ~11%) and hybrid perovskite (PCE of >17%) photovoltaic cells will be discussed. Specific emphasis will be placed on the development of low band-gap polymers with reduced reorganizational energy and proper energy levels, formation of optimized morphology of bulk-heterojunction layer, and minimized interfacial energy barriers using functional surfactants and graphene oxide. At the end, several new device architectures and optical engineering strategies to make tandem cells and semitransparent solar cells will be discussed to explore the full promise of polymer and perovskite hybrid solar cells.

Scheme 1. Schematic illustration of a solution-processible FPI-PEIE hybrid ETL in an inverted polymer solar cell.
Design and study of new conjugated polymers has been an active field of research for the past 20 years. More recently, in the last 5 years, both low bandgap polymers and fluorinated polymers have become of increasing interest. Low bandgap polymers have the ability to absorb a larger portion of the visible light spectrum, increasing the efficiencies of organic photovoltaics (OPVs). Selective fluorination of conjugated polymers has, in many cases, been shown to improve device efficiencies by 1-2%.

We report the design and synthesis of new fluorinated conjugated materials by direct arylation polymerization as well as their properties and function in OPV type devices. Using a set of materials based on poly(thieno[3,4-b]thiophene-alt-benzodithiophene) with different alkyl, aryl, perfluoroalkyl and perfluoroaryl pendant functionalities, we have studied the correlation between absorbance, morphology, crystallinity, charge mobility and the OPV performance in an effort to identify structure-performance relationships in these highly fluorinated materials.
POLY 470: Novel hierarchical composites of inorganic carbon and polysiloxanes for next-generation energy applications

James P. Lewicki\textsuperscript{2}, lewicki1@llnl.gov, Marcus A. Worsley\textsuperscript{2}, Theodore Baumann\textsuperscript{1}, Eric B. Duoss\textsuperscript{1}, Robert S. Maxwell\textsuperscript{3}. (1) Lawrence Livermore Nat L Labs, Livermore, California, United States (2) Material Sciences Division, Lawrence Livermore National Laboratory, Livermore, California, United States (3) Lawrence Livermore National Laboratory, Livermore, California, United States

Polysiloxanes and Graphene: Two very different, yet uniquely versatile families of materials which, when combined can be utilized to design a vast range of complex and hierarchal 3-dimensional, flexible network architectures. At LLNL we have been making extensive use of these diverse and fascinating materials to design and synthesize some truly novel composites - with the potential for applications ranging from; flexible ultra-low ‘k’ dielectric coatings, negative temperature coefficient electronic switching materials, ultra-capacitors, electro-active materials, highly thermally resistant ablative materials and patterned media capable of large-scale isotropic dimensional change. Here we present a review of some of our recent efforts in this exciting and technologically relevant area of advanced materials science. The results of the synthesis and characterization (via a range of analytical methodologies including solid state NMR, degradative thermal analysis and broadband dielectric spectroscopy) of unique polysiloxane/carbon aerogel/carbon nanotube & graphene architectures will be presented. We will also present an overview of our ‘materials by design’ approach for the formation of 3-dimensional composite structures of sub-micron pattern resolution which can be triggered to undergo large-scale (fully reversible) isotropic changes in volume in response to external stimuli. Emphasis will be given to the relationship between the underlying (dynamic) network structure and the macro-scale physical properties of complex polysiloxane composites. And to the importance of combining a range of interrogative analytical methodologies with a ground up synthetic approach, in order to build well-defined & well understood materials at all size scales. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.
Organic photovoltaics (OPV) is a promising candidate technology for the low-cost fabrication of modules to harvest solar energy. Although OPV technology has significantly matured over the past few years, there remain significant challenges in addressing the gap between lab-scale devices and real manufacturing. Structure-property-performance relationships for OPV devices are still underdeveloped, and relationships based on one system are not necessarily transferrable to new, higher-performance systems. This talk will describe our efforts to develop measurements that support OPV manufacturing. Using a blade coating process as a prototype for slot-die coating, we have developed several techniques to observe the structure of OPV films in-situ as they dry. Our measurements include synchrotron-based X-ray scattering and a variety of optical methods. We use these techniques to identify the mechanisms by which formulation and processing choices influence the nanoscale structure of the films. Several OPV systems will be described including polymer/fullerene, small-molecule/fullerene, and polymer/polymer. Throughout solidification, we can follow the number of phases, their composition, and the extent of order within them. In-situ techniques provide far more information about the solidification process than can be obtained by measuring already-dried films, providing a valuable tool to guide the selection of formulation and processing parameters.
POLY 472: Photoinduced charge transfer and thermal recombination dynamics of a ternary cascade heterojunction composed of poly(3-hexylthiophene), titanyl phthalocyanine, and Buckminsterfullerene

Jaehong Park¹, chem.jaehong.park@gmail.com, Obadiah Reid¹², Garry Rumbles¹².
(1) Chemical and Materials Science, National Renewable Energy Laboratory, Littleton, Colorado, United States (2) Department of Chemistry, University of Colorado at Boulder, Boulder, Colorado, United States

Photoinduced electron and hole transfer (PIET and PIHT) and thermal charge recombination dynamics (CR) of trilayer thin-films comprising titanyl phthalocyanine (TiOPc), regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT) and C₆₀ are studied using flash-photolysis time-resolved microwave conductivity (fp-TRMC) and time-resolved fs-ms transient absorption spectroscopy. Carrier generation following photoexcitation on TiOPc is independently observed at both the P3HT/TiOPc and TiOPc/C₆₀ interfaces, and the trilayer P3HT/TiOPc/C₆₀ structure exhibits enhanced photoconductance signal and longer charge-recombination lifetime relative to the bilayer controls. From pump-probe transient absorption spectroscopy, more detailed carrier generation dynamics was studied. Each bilayer P3HT/TiOPc and TiOPc/C₆₀ exhibited ultrafast electron/hole transfer as well as exciton-diffusion limited processes. Our pump-probe transient absorption results also indicates that following initial charge generation processes to produce P3HT⁺/TiOPc⁻ and TiOPc⁺/C₆₀⁻ at each interface from (P3HT/TiOPc*/C₆₀) via electron transfer and hole transfer processes, the final charge separated product of (P3HT⁺/TiOPc/C₆₀⁻) is responsible for the long-lived photoconductance signals at fp-TRMC. In this study, we demonstrated that the combination of fp-TRMC and classic pump-probe transient absorption spectroscopy can serve to complement to each other and can be utilized to elaborate charge-generation and recombination dynamics for more complicated ternary cascade heterojunction system.
Decentralized, off-grid power could be used to bring modern conveniences to the underdeveloped world potentially freeing hours of labor currently used to access energy in crude forms, chiefly through burning wood. Arguably, the greatest potential for impact on humanity for alternative energy lies in Sub-Saharan Africa (SSA) with its large, dispersed, and impoverished population and with the highest solar irradiance for populated areas on earth, particularly in east and central Africa. The opportunity involves building, from virtually ground zero, an energy supply that could be based on zero carbon footprint with low operating costs. Currently the impact of photovoltaics in SSA is limited to powering cell phone towers, a very few examples where donated PVs have been installed by non-governmental organizations (NGOs), and a few cases where centralized governments have purchased solar powered street lamps and the like. For example, in a country like Ethiopia with the second highest population in Africa (roughly 100M), there are approximately 20K solar systems. The chief obstacle to the use of solar power is the cost of PV panels, batteries, control electronics and wiring. Through two projects, partly funded by the US Department of State and the Agency for International Development, we have collaborated with African universities in the development of technology to manufacture photovoltaics and sensors in Africa for use in the African market taking advantage of low labor costs. In the NanoPower Africa Project (NPA) we were able to develop manufacturing capabilities for printed electronics technology to produce silicon based solar cells intended to charge cell phones. Funding for the NPA project ended in 2013. Some of the partners in the project have decided to target short-term manufacturing development in Ethiopia that has lead to plans for solar panel and battery assembly facilities on several university campuses in the Tigray and Oromo regions of Ethiopia. This presentation will give a brief overview of the potential for the use of technology to address development issues using these examples from SSA.
POLY 474: Application of ambipolar units to nontraditional donor-acceptor polymers: A potential new paradigm for the design of low band gap materials

Trent Anderson, Michael E. Mulholland, Ryan Schwiderski, Seth C. Rasmussen, seth.rasmussen@ndsu.edu. Department of Chemistry and Biochemistry, North Dakota State University, Fargo, North Dakota, United States

Low band gap materials play a critical role in organic photovoltaics and organic photosensors. The most commonly applied approach to the production of low band gap conjugated materials is through the utilization of a 'donor-acceptor' (D-A) framework. This D-A approach to low band gap materials was first introduced in 1992 by Havinga and coworkers, in which it was proposed that materials with alternating electron-rich (donor) and electron-deficient (acceptor) moieties along the same backbone could result in a hybrid material with HOMO levels characteristic of the donor and LUMO levels characteristic of the acceptor. This approach has since become a critical design factor in the generation of low and reduced band gap materials. A class of such materials have utilized thieno[3,4-b]pyrazines (TPs) and its analogues as 'acceptors' in D-A frameworks for the successful generation of low band gap materials. Recent reports, however, have revealed that TPs act simultaneously as both strong 'acceptors' and strong 'donors', with donor abilities comparable with 3,4-ethylenedioxythiophene. As such, the TP unit contains an internal D-A interaction that dominate the electronics of TP-based materials. Effects of the ambipolar nature of TP on its materials will be presented along with the potential of utilizing TP as a donor in D-A frameworks to produce nontraditional materials.
POLY 475: Polymeric strategies for the encapsulation of cell lysates in view of anticancer immunotherapy

Lien Lybaert, lien.lybaert@ugent.be, Bruno De Geest. Ghent University, Ghent, Belgium

Anti-cancer immune-therapy is recognized as one of the most promising strategies for treatment of metastatic cancer. It practices the patient's own defense mechanism by activating it in such a way that it recognizes and eliminates malignant cells. Here we report an innovative generic strategy for the encapsulation of patient-specific cancer antigens into particles. This approach covers a broad range of tumor-associated antigens and enables the induction of specific routes of cell-death potentially leading to more specific, more efficient and more potent immune activation of the patient. First, we demonstrate in situ encapsulation of live whole cancer cells into polymeric microcapsules followed by killing of the cancer cells and release of the cancer cell lysate into the hollow void of the capsules. Live B16 melanoma cells were used as a cancer model and were coated in a Layer-by-Layer (LbL) fashion with alternating layers of poly(vinylpyrrolidone) (PVP) and tannic acid (TA) using hydrogen bonding as driving force for multilayer assembly. Fine-tuning of the assembly conditions was assessed by real-time flow cytometry, fluorescence microscopy, SDS-PAGE and TEM and allowed us to obtain cell-templated bio-hybrid capsules containing a high amount of encapsulated proteins. Second, contrary to the in situ encapsulation of cancer cells, we explore the conjugation of cell lysate to polymers. A copolymer composed of hydroxypropyl methacrylamide and aminopropyl methacrylamide (HPMA-co-APMA) via RAFT polymerization was synthesized. Disulfide or maleimide groups were introduced to allow interaction with cancer cell lysate respectively via reversible thiol-disulfide exchange or Michael addition. High encapsulation efficiencies were visualized and the (ir)reversible binding properties were confirmed by SDS-PAGE.
Tannic acid (TA) is a natural polyphenolic known for its antioxidant, antibacterial and anticarcinogenic properties were used in this investigation to prepare bulk hydrogel and microgels. The poly(Tannic acid) (p(TA)) hydrogels in bulk were synthesized by using trimethylolpropane triglycidyl ether (TMPGDE) as crosslinker, and microgels were prepared in water-in-oil micro emulsion. Furthermore, p(TA) materials were chemically modified using different modifying agents such as 3-chloro-2-hydroxypropyl ammonium chloride (CHPACl), thioglicolic acid (TGA), chlorosulfonic acid (CSA), glycidyl methacrylate (GMA). The chemical modification of p(TA) particles with (CHPACl) is given in Figure 1. The details of morphological and physicochemical characterization were done via SEM, TGA, FT-IR, DLS and zeta potential measurements. The bulk hydrogels of p(TA) as potential wound dressing materials were tested for in vitro degradability in physiological and chronic wound healing conditions (pH 7.4, 37.5 °C), or acidic/basic conditions. The antioxidant properties of bare and modified p(TA) based materials were also investigated by employing FC, ABTS and DPPH scavenging assays. As TA molecule is known for strong antimicrobial properties against various bacteria, fungi, yeasts, and viruses; we also tested the p(TA) based materials for their antimicrobial susceptibility against Escherichia coli ATCC 8739, Staphylococcus aureus ATCC 6538, and Bacillus subtilis ATCC 6633, Pseudomonas aeruginosa ATCC 10145, and Candida albicans ATCC 10231. Furthermore, bulk and micron sized p(TA) hydrogels and their modified forms for potential drug delivery devices are tested by the release of TA itself from p(TA) materials at pH 7.4 and 37.5 °C. Furthermore, biocompatibility of TA and p(TA) materials for apoptotic and necrotic effects against L929 fibroblast cells and A549 cancerous cells were examined to further illustrate their biomedical applications.
POLY 477: Multiresponsive polymer-protein conjugates as immuno-modulating strategy

Nane Vanparijs, nane.vanparijs@ugent.be, Ruben De Coen, Bruno De Geest. Ghent University, Ghent, Belgium

Relative to soluble antigen, particulate antigen is much better recognized by the immune system as being foreign and leads to an altered way of uptake, processing and presentation by antigen presenting cells. However, a general strategy to formulate protein antigens into nanoparticles that are sufficiently small to efficiently drain to the lymph nodes is still lacking. Here we present a bio-conjugation approach involving covalent coupling of stimuli (i.e. temperature and pH) responsive polymers to a protein antigen. These stimuli responsive properties affords straightforward polymer-protein conjugation below in aqueous medium below the polymer phase transition temperature, whereas above this phase transition temperature nanoparticles are formed. We report on an interesting class of pH-degradable temperature-responsive polymers that at fixed temperature undergo an irreversible hydrophobic to hydrophilic transition. This unique property causes disassembly of the nanoparticles, liberating the protein for further processing. We report on how the polymer-protein nanoparticles interact with dendritic cells (i.e. the most potent class of antigen presenting cells) and how they alter the antigen-specific immune response.
Over the last five years, our group has been exploring synthetic approaches to gel network formation that allow direct control over key performance properties, including porosity, mesh-size, swelling, elasticity, toughness, and chemical functionality. By focusing on a generalized framework in which each of these properties can be tuned independently, we have been building the foundation for a versatile class of gel networks applicable throughout a range of applications, including size- and affinity-based separations, catalytic supports, and implant and tissue scaffold technologies. This presentation will focus on the utility of our approach, in which spherical domains formed during melt-state self-assembly of block copolymers are used as the primary building blocks for network formation. Chemical and processing specific manipulation of tethering strategies allows one to produce an incredible range of swollen network materials, with applications from gas separation membranes to biological tissue mimics. Importantly, this motif lends itself to complete preservation of shape, elasticity and mechanical performance following repeated cycling, with tunable compressive and tensile properties that can compete with some of the best double network and slip-link gels to date.
A novel method for the formation of monodisperse microsphere hydrogels has been developed. This technique allows for the creation of microgels tailored for individual applications with minimal variation to the formation procedure, facilitating a robust yet facile production process. Allyl functionalized polymers are crosslinked with difunctional thiol species, in the presence of the desired cargo, to form the hydrogel products in the range of 10-30 microns. This process has been implemented to create hydrophobic, hydrophilic, and amphiphilic structures which can be loaded with a range of cargo including, but not limited to, small molecule drugs and biological therapeutics. Model release data has been obtained and indicates a linear release profile sustained over an extended period. The release rate of the cargo can be tailored by either the choice of crosslinking species or doping of the system with poly(glycidol). Gels formed from crosslinked poly(glycidol)s have shown intriguing physical characteristics and will be investigated for their application in inhalants and vaccines.
POLY 480: Cyclic defects in tetrafunctional poly(ethylene glycol) networks and networks with mixed junction functionality

Ken Kawamoto², ken_k@mit.edu, Mingjiang Zhong²¹, Bradley D. Olsen¹, Jeremiah A. Johnson².
(1) Chemical Engineering, MIT, Cambridge, Massachusetts, United States (2) Chemistry, MIT, Cambridge, Massachusetts, United States

Polymer networks contain defects that necessarily affect their mechanical properties. Understanding these defects is important to applications such as the study of cellular interactions with their environment, adhesives, and other commodity products. For example, poly(ethylene glycol) (PEG) networks are one type of hydrogels that have utility as cell culture and tissue regeneration scaffolds. The mechanical properties of the culture platform on which cells grow can affect their growth and morphology, but the topologies underlying these mechanical differences and those that may not be rheologically measurable are unknown at present. We present the synthesis of PEG networks and quantification of topological imperfections therein that can be applied to PEG networks used for cell culture scaffolds.

Primary loops are one topological defect that, until recently, could not be independently quantified. We previously reported the Isotopic Labeling Disassembly Spectrometry (ILDaS) paradigm that allows for the direct measurement of first order network defects in trifunctional (f=3) networks. For the first time, we measure the fraction of primary loops in tetrafunctional (f=4) networks and mixtures of tri- and tetrafunctional networks (f=3,4) using macromonomers with molecular weight dispersity. Furthermore, we have extended the application of this methodology to polymer systems that do not have isotopic labels, which lowers the cost and convenience of this type of analysis. The quantification of loops in these polymer networks has been corroborated by Monte-Carlo simulations and rate theory calculations. Finally, this work is the first step toward quantifying primary loops in polymer networks more similar to commercial products, which use polymers and crosslinkers with molecular weight dispersity.

A schematic representation of the methodology for quantifying first-order network imperfections.
POLY 481: Synthesis and characterization of thermoreversible hydrogels based on ABC triblock copolypeptoids

sunting xuan¹, sxuan1@tigers.lsu.edu, Donghui Zhang², Chang-Uk Lee³. (1) louisiana state university, Baton Rouge, Louisiana, United States (2) 437 Chemistry Materials Building, Louisiana State University, Baton Rouge, Louisiana, United States (3) chemistry, Louisiana State University, Baton Rouge, Louisiana, United States

ABC triblock copolypeptoid [i.e., poly(N-allyl-glycine)-b-poly(N-methyl-glycine)-b-poly(N-decyl-glycine) (PNAG-b-PNMG-b-PNDG)] with varying composition were synthesized by sequential primary amine-initiated ring-opening polymerization of the corresponding N-substituted N-carboxyanhydride monomers (i.e., Al-NCA, Me-NCA and De-NCA). The triblock copolypeptoids with specific compositions (e.g., PNAG⁸⁶-b-PNMG⁹⁷-b-PNDG₁₃, PNAG⁸⁶-b-PNMG⁹⁷-b-PNDG₁₃, and PNAG₂₃-b-PNMG₂₆-b-PNDG₁₀) were shown to undergo thermo-reversible sol-gel transitions in aqueous solutions (5-10 wt%) with increasing gelation temperature respectively. The PNAG₄₆-b-PNMG₅₂-b-PNDG₁₀ based hydrogel showed higher storage modulus (G’) than PNAG₈₆-b-PNMG⁹₇-b-PNDG₁₃ and PNAG₂₃-b-PNMG₂₆-b-PNDG₁₀ hydrogels. The gelation is very fast and the formed gel is injectable through 24G needles. The TEM and DLS analysis revealed the formation of spherical micelles. The sol-gel transition is considered to be triggered by the association of the thermo-responsive corona segment (i.e., PNAG) above the lower critical solution temperature (LCST), resulting in a physically cross-linked micelle network. The alamarBlue cytotoxicity study indicated that the hydrogel is non-toxic to the human adipose-derived stem cells (hASCs). The enzyme encapsulation study of the horseradish peroxidase with hydrogel indicated that no deactivation of the enzyme was caused within the hydrogel even after 24h. All the attractive properties made the hydrogel a potentially biological material such as tissue-engineering scaffold for hASCs.
POLY 482: Development of hydrogels and functionalized silica surfaces utilizing novel fluorocyclic precursors

Abby R. Jennings\textsuperscript{2}, abbyroth@yahoo.com, Carl Thrasher\textsuperscript{1}, Scott T. Iacono\textsuperscript{3}. (1) Chemistry, United States Air Force Academy, USAF Academy, Colorado, United States (2) Chemistry Research Center, United States Air Force Academy, Colorado springs, Colorado, United States (3) Department of Chemistry, United States Air Force Academy, Colorado Springs, Colorado, United States

We recently developed a library of new fluorocyclic monomers that contain functional groups which provide for a straightforward means of incorporating them into a wide variety of highly functional materials. Such materials include, but are not limited to, polymers and copolymers, blended composites, hydrogels, and functionalized surfaces. Furthermore, some of the precursors contain latent reactive groups, allowing for post-synthetic modifications and the ability to tune properties. This work will discuss the design and synthesis of the fluorocyclic monomers, as well as, employing the monomers for the preparation of hydrogels and for functionalizing silica surfaces. The properties of the resulting functional materials will also be discussed in detail.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fluorocyclic_monomers.png}
\caption{Fluorocyclic monomers with \textit{X} = \text{(EtO)}_3\text{Si}, \text{R} = \text{H or \text{CH}}_3, \text{O} = \text{Si(OEt)}_3.}
\end{figure}
POLY 483: Hyperbranched epoxy with POSS modification for enhanced toughness polymer composites

Sarah E. Morgan\(^2\), sarah.morgan@usm.edu, Qifeng Jin\(^2\), John Misasi\(^2\), Jeffrey S. Wiggins\(^1\). (1) School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, Mississippi, United States (2) School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, Mississippi, United States

Epoxy-amine glassy networks are widely used as matrix materials in high performance polymer composites because of their combination of thermal and mechanical properties, processability, and solvent resistance. Because of their innate brittleness, a great deal of effort has been focused on improving the toughness of these materials. General approaches to reduce brittleness involve incorporation of dispersed tougheners, such as rubbers, engineering thermoplastics, and rigid nanoparticles. Hyperbranched polymers provide an alternate route for toughening the glassy matrix with minimal increase in viscosity, due to their highly branched and functional structure, high molecular weights, and low processing viscosity. This paper reports the synthesis of hyperbranched epoxies (HBE) for incorporation into epoxy-amine matrices, which were modified with polyhedral oligomeric silsesquioxane (POSS) nanostructured chemicals. The hyperbranched epoxide and monoamine POSS modified hyperbranched epoxide were characterized through FTIR, 1H NMR, dynamic and static light scattering, MALLS, and rheological experiments. The thermal and mechanical behavior of the epoxy matrices was examined with DMA and uniaxial compression. Fracture toughness was evaluated by single-edge-notch-bending test method following ASTM D5045 and the modified epoxy matrices morphologies were investigated by SEM. POSS modification was found to enhance mechanical performance.
Established layer-by-layer (LbL) flame retardant mechanisms have been combined to produce a ‘stacked’ nanocoating for flame retarding polyurethane foam. A bilayer system of chitosan (CH) and vermiculite (VMT) clay provides a base layer, protecting the polyurethane long enough for a charring system of CH and ammonium polyphosphate (APP) to activate and form an enhanced char layer via intumescence. Stacking these two recipes allows the foam to self-extinguish when exposed to a butane torch without flame spread or shrinking of the foam. Cone calorimetry showed a peak heat release rate reduction of 66% relative to uncoated foam. Combining these two layer-by-layer systems produces a stacked coating that eliminates melt dripping and reduces the overall flammability of the polyurethane foam, which is commonly used in furniture. This coating acts as an environmentally benign template for flame retarding various complex substrates, especially those found in household furnishings.
Inspiration for the current study is derived from the fact that despite significant studies on polybenzimidazole (PBI) nanocomposite based proton exchange membrane (PEM) for fuel cells, the importance of understanding the nanocomposite interface has been inadequately addressed in literature till date. Since the interphase structure is closely related to the surface functionalization of the nanoparticles (NPs), there is a need to explore the surface chemistry in order to develop materials with desired properties. In my presentation, I would like to share our findings on the effect of aliphatic chain length of the surface modifier of silica NPs on important properties of PBI nanocomposite membranes for use as PEM and to underline the quantitative links between dispersion pattern of NPs in the polymer matrix with proton conductivity and different kinds of stability. Silica NPs decorated with long chain amine silane coupling agent (LAMS) was used to induce the compatibility with oxy-polybenzimidazole (OPBI) matrix. Structure and morphology analysis of nanocomposites by WAXD and TEM, respectively, showed the formation of self-assembled networks of the modified NPs in the (OPBI/LAMS) matrix, whereas a completely dispersed structure was observed for the unmodified NPs (UMS) in the (OPBI/UMS) matrix. The self-assembly of LAMS NPs helped in increasing proton conductivity by creating more proton hopping sites. Large mechanical reinforcements were obtained with OPBI/LAMS membranes. The presence of LAMS’ assembly safe-guards the polymer chains from thermal and oxidative degradation thus enhancing the membranes’ stability and durability in fuel cell operating conditions. Water uptake and dimensional stability studies of the membranes showed promising results.

Reference
POLY 486: Improvement of mechanical properties of methacrylate based composites by latex particles

Benedict Sandmann¹, sandmannb@gmx.de, Bobby Happ¹, Igor Perevyazko¹, Stephanie Hoeppener¹, Tobias Rudolph², Felix H. Schacher³, Martin D. Hager³, Urs Fischer⁶, Peter Burtscher⁶, Norbert Moszner⁶, Ulrich S. Schubert⁴. (1) Organic- and Macromolecular Chemistry, Friedrich Schiller University Jena, Jena, Germany (2) Friedrich-Schiller University Jena, Jena, Germany (3) Laboratory of Org. Macromol. Chemistry, Friedrich Schiller University of Jena, Jena, Germany (4) Laboratory for Organic and Macromolecular Chemistry, Friedrich-Schiller-University Jena, Jena, Germany (5) IOMC, Friedrich-Schiller-University Jena, Jena, Germany (6) Ivoclar Vivadent AG, Schaan, Liechtenstein

The fracture toughness of polymeric materials and composites can be enhanced by the incorporation of polymer nanoparticles. The combination of a soft core and a hard shell leads to an improvement of the fracture toughness of the polymeric nanocomposites. Thereby the mechanical resistance of the materials is commonly decreased.

In our approach core–shell nanoparticles consisting of a ethyleneglycoldimethacrylate (EGDMA) crosslinked poly(butylacrylate) (PBA) core and a poly(methylmethacrylate) (PMMA) shell were synthesized. The polymer particles were implemented in triethylene glycol dimethacrylate (TEGDMA)/urethane dimethacrylate(UDMA) based composites in order to enhance the mechanical properties. Different core–shell ratios were applied to study its influence on the fracture toughness and E-modulus. An examination of shell-crosslinking with TEGDMA up to 8% was performed to improve particle stability and redispersing ability. The particle morphologies were characterized by dynamic light scattering (DLS), cryogenic transmission electron microscopy (cryo-TEM) and analytical ultracentrifuge (AUC). Latex sizes of 70 to 220 nm were achieved. The mechanical properties (fracture toughness, E-modulus and Kmax) of polymer composites were investigated in a three-point bending test. Core/shell ratios of 50/50 showed a decreasing effect to fracture toughness, E-modulus and Kmax. Polymer particles with core/shell ratios of 30/70 lead to a significant increase of mechanical properties which make them interesting in particular for hard tissue applications like bone cements or dental replacement material.
Reversible addition-fragmentation chain transfer (RAFT) polymerization has been widely used for the synthesis of varying polymer architectures, including polymer brushes on nanoparticles for incorporation into polymer nanocomposites. Surface modification via RAFT allows for control of the surface properties and therefore the interface between the nanoparticle and polymer matrix. Adverse interactions between the nanoparticles, grafted polymer, and polymer matrix can lead to aggregation and autophobic de-wetting. This can be suppressed while the entropic and enthalpic effects are decoupled for their independent study, using a bimodal system containing a small number of long, matrix compatible chains on a surface that primarily consists of a short dense brush. RAFT allows for the control of brush parameters such as composition, graft density, and molecular weight for both populations separately and independently. Bimodal brush grafted silica nanoparticles show superior dispersion and thermomechanical properties over monomodal brush grafted particles in polymer nanocomposites. Furthermore with a mixed bimodal system, short brushes offer an added enhancement in properties while keeping nanoparticles dispersed, as the long brushes remain matrix compatible for entanglement. Analogous to block copolymers, the addition of a polymer chain population with different chemical composition can lead to materials with added and differing properties compared to a bimodal system with a single chemical composition. The synthesis of these bimodal systems via grafting-from and grafting-to methods will be discussed as well as the above-mentioned enhancement in properties.
POLY 488: Development of nanosilica thermoset resins for filament winding and prepreg applications

James M. Nelson, jnelson1@mmm.com. CComposites, 3M, Saint Paul, Minnesota, United States

The use of nanosilica to modify neat resin and carbon fiber composite properties for use in composite fabrication processes will be discussed. The use of these materials in sporting goods, compressed natural gas cylinders, automotive (composite driveshaft) and composite tooling applications will be discussed.
The level of dispersion within polymer nanocomposites has been a widely explored topic. Nanofillers have been shown to greatly improve and/or add a multitude of mechanical, optical, transport and other properties to polymers. To achieve such desired properties in a predictable manner, random dispersion of nanoparticles throughout the material is often preferred. In general, it is energetically favorable for inorganic particles to aggregate in a polymer matrix, unless interactions are screened by polymeric ligands coating the nanoparticle surface. Currently, the dominant methods of grafting— to or –from the surface of nanoparticles require chain end modification or specific polymerization methods that may not be suitable for all particles or polymerization methods.

Here, we present a simple method to achieve dispersion of gold nanoparticles within polymer matrices by solution state photografting of benzophenone (BP)-containing random copolymers. A benzyl ether ligand that stabilizes gold nanoparticles (AuNPs) in solution while possessing selectivity towards hydrogen abstraction and subsequent coupling with BP was designed. This method of graft introduction by ultra-violet (UV) light exposure allows for control over the dispersion state in the resulting polymer films, as illustrated by transmission electron microscopy (TEM) and ultraviolet-visible spectroscopy (UV-Vis). Additionally, we provide insight into the rather efficient mechanism by examination of hydrodynamic size with UV exposure. This general method may be a key starting point for the fabrication of intricately designed nanocomposite systems previously unobtainable.
Multilayer polymer composites containing alternating layers of polycarbonate (PC) and polyvinylidene fluoride (PVDF) show great promise as the active dielectric material in high energy density capacitors. The dielectric strength of these films is increased relative to monolithic PC or PVDF because the interfaces serve as barriers to the propagation of an electrical breakdown. The energy density of the film is proportional to the square of the applied field. First generation PC/PVDF multilayer films show breakdown strength ($E_B$) greater than 750 V/μm under divergent field conditions and energy densities ($U_d$) as high as 13 J/cm³. To further increase the dielectric strength and energy density, we have prepared two new types of interface-modified structures: graded permittivity multilayer composites and enhanced adhesion multilayer composites. Both types of composites contain thin interfacial layers positioned between the discrete layers of PC and PVDF, designed to take advantage of subsequent changes in the dielectric or mechanical properties of the film. These composites show increased dielectric strength ($E_B = 900$ V/μm under divergent field conditions and $E_B = 760$ V/μm under homogeneous field conditions) and energy density ($U_d = 16$ J/cm³) relative to standard multilayer films without interface modification. The talk will also focus on structure and failure analysis on interface-modified films using advanced imaging techniques such as AFM, TEM, and FIB/SEM.

Figure 1. Dielectric strength as a function of composition for 32-layer PC/PVDF-HFP films (red circles) and 65-layer PC/PMMA/PVDF films (blue circles) as measured under homogeneous field conditions using an electrostatic pulldown breakdown technique.
Oral vaccination is painless, convenient, and has potential to induce both systemic immunity, and mucosal immunity locally in the gut. Since mucosal surfaces represent a major portal of pathogen entry into the human body, a first line of defense at these surfaces could help neutralize pathogens before they can cause infection. However, the longstanding barriers to a successful oral vaccination have been the degradation of vaccine antigens in the acidic and enzyme-rich environment of the stomach, and the poor transport of the large vaccine molecules across the tightly-packed epithelial cells lining the intestines. In this presentation I will describe a novel concept, that pollen grains, the bane of allergies for some, can be engineered for use as a simple modular system for oral vaccination by helping to carry the vaccine antigens across the intestinal epithelium. Using spores of *Lycopodium clavatum* (clubmoss) (LSs), we show that LSs can be chemically cleaned to remove native proteins to create intact clean hollow LS shells, which can then be filled with molecules of different sizes demonstrating their potential to be broadly applicable as an oral vaccination system. We further show that when LSs formulated with ovalbumin (OVA) were orally fed to mice, a significantly higher anti-OVA serum IgG and fecal IgA antibodies were stimulated compared to those induced by the use of cholera toxin as a control adjuvant. Cholera toxin is a potent experimental mucosal adjuvant, however, due to its toxicity it cannot be used in humans. The antibody response was not affected by pre-neutralization of the stomach acid, and persisted for up to seven months, demonstrating durability of response. Confocal microscopy revealed that LSs can translocate in to mouse intestinal wall. Overall, this suggests that LSs have potential to be used as a novel approach for oral vaccination.
mRNA-lipoplexes are capable of inducing cytotoxic T cells (CTL) following subcutaneous immunization. Transfection of dendritic cells with mRNA-lipoplexes is accompanied by a strong induction of type I IFNs. Remarkably, these type I IFNs decrease the strength of the evoked response, as evidenced by an over tenfold increase in CTL numbers in IFNaR/- mice. Although type I IFN have positive effects on the quality of the immune response following immunization with protein antigens, they negatively interfere with the strength of mRNA based vaccination by imposing an antiviral status upon the dendritic cell, resulting in inhibition of antigen translation and diminished antigen presentation.
Even when treated with aggressive current therapies, most patients with primary or metastatic malignant brain tumors survive less than two years. Although immunotherapy is being studied as a potential treatment, the blood-brain barrier and local tumor immunosuppressive milieu may prevent penetration of cytotoxic antibodies or immune cells into the brain. Local delivery of immunostimulatory molecules such as CpG can overcome this suppressive environment, but at high doses may also cause toxic brain inflammation. Thus, there is a pressing need for a safer, more effective targeted strategy to enhance CNS immune responses to malignant brain tumors. We recently demonstrated that carbon-nanotubes (CNTs) are efficient nontoxic carriers of macromolecules into tumor inflammatory cells, and when conjugated with CpG (CNT-CpG), result in robust activation of inflammatory cells. Remarkably, even a single low-dose injection of CNT-CpG (but not free CpG) eradicated brain tumors in animal models and protected surviving animals from tumor rechallenge. These findings suggest that enhanced delivery of immunostimulatory molecules into the brain can induce a strong local and systemic anti-tumor response.
POLY 494: Modulating adaptive immunity with “carrier-free” polyelectrolyte multilayer films

Yu-Chieh Chiu¹, Lisa Tostanoski¹, Christopher Jewell¹², cmjewell@umd.edu. (1) Fischell Department of Bioengineering, University of Maryland, College Park, Maryland, United States (2) Microbiology and Immunology, University of Maryland Medical School, Baltimore, Maryland, United States

Despite the tremendous benefits that vaccines and immunotherapies have provided, treatments for infectious disease, cancer, and autoimmunity would benefit from strategies that provide greater control over the specific characteristics of immune responses that are induced. Biomaterials offer great potential in this area because these agents allow spatial and temporal control over the delivery of drugs and vaccines. However, many biomaterials intrinsically stimulate the immune system without the addition of other signals, leading to lack of definition in the function and contributions of each vaccine component (e.g., antigen, adjuvant, carrier). Macromolecule-based vaccines and immunotherapies with highly-defined compositions could improve treatment effectiveness and selectivity by allowing a more rational approach to selection of antigens, adjuvants, or immune-modulatory signals. Toward this goal, we have developed polyelectrolyte multilayers (PEMs) assembled entirely from immune signals. These “carrier-free” vaccines are composed of peptide antigens and molecular adjuvants modified with oppositely-charged peptide blocks serving as “anchors” (Fig. 1A,B). These films can be coated onto template particle cores for injection, or following core dissolution, prepared as hollow capsules comprised of peptides, adjuvants, or other immune signals (Fig. 1C). During this talk we will describe the use of these PEMs to modulate dendritic cell and T cell function ex vivo and in vivo. This approach could provide more sophisticated control of immune function without contributions from innate immune characteristics exhibited by synthetic polymers widely-used in drug delivery and PEMs.

Fig. 1: A and B) Assembly strategy for preparing PEMs from immune signals. C) Confocal microscopy images depicting each signal type.
Efficient co-delivery of subunit antigens and immunomodulatory agents to antigen-presenting cells in lymphoid tissues is required for effective modulation of antigen-specific immune responses. Here we present two distinct lipid-based nanoparticle systems that generate cytotoxic CD8+ T lymphocyte (CTL) responses. The first vaccine platform system is termed interbilayer-crosslinked multilamellar vesicles (ICMVs) that were formed by fusing liposomes into multilamellar vesicles and subsequent crosslinking of adjacent lipid headgroups across lipid bilayers within multilamellar vesicles. To compare ICMVs to other conventional nanoparticle vaccines, we immunized C57Bl/6 mice with a model antigen, ovalbumin, formulated into ICMVs, rehydration vesicles, and poly(lactide-co-glycolide) acid nanoparticles (NPs). ICMVs elicited a significantly enhanced CTL response, compared with other two vaccine NPs. We also compared OVA-loaded ICMVs to conventional DC-based vaccines and OVA + CpG emulsified in Montanide. OVA-ICMV vaccination increased the frequency of OVA-specific CD8+ T cells by ~31-fold by d 7, compared with OVA-DC and OVA-CpG-Montanide (Fig. 1), demonstrating superiority of ICMVs to conventional DC-based vaccines and a strong experimental adjuvant system. The second vaccine delivery platform is based on synthetic high-density lipoprotein nanodiscs (sHDLs). We have used an ApoA-I mimetic peptide (ESP22) to formulate phospholipids into homogenous nanodiscs with the average diameter of 10 ± 2.3 nm. These nanodiscs effectively delivered MHC-I minimal epitope peptides and CpG to dLNs and mediated anti-tumoral CTL responses against established tumors. These results suggest that lipid-based nanoparticles are promising vaccine delivery systems.

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POLY 496: Concurrent block copolymer polymersome stabilization and bilayer permeabilization by stimuli-regulated “traceless” crosslinking


The fabrication of block copolymer (BCP) vesicles (polymersomes) exhibiting synchronized covalent crosslinking and bilayer permeabilization remains a considerable challenge as crosslinking typically leads to compromised membrane permeability. Herein it is demonstrated how to solve this dilemma by employing a stimuli-triggered crosslinking strategy with amphiphilic BCPs containing photolabile carbamate-caged primary amines. Upon self-assembling into polymersomes, light-triggered self-immolative decaging reactions release primary amine moieties and extensive amidation reactions then occur due to suppressed amine pKa within hydrophobic milieu. This leads to serendipitous vesicle cross-linking and the process is associated with bilayer hydrophobicity-to-hydrophilicity transition and membrane perme-abilization.
Cooperative polymerization, aided by the nucleation-elongation mechanism, has the promise of providing polymers and nanostructures that are otherwise inaccessible. The molecular origin of the cooperative growth of polymers is driven by a secondary interaction, often based on polarization, electrostatics, or steric-driven secondary structure. However, for the first time, we demonstrate that covalent dative interactions between the nitrogen in the imine building blocks and the boron in the boronate ester can be used to achieve cooperative polymerization. Our results suggest that the initial polymer formation through sequential boronate esterification of boronic acids and bifunctional catechols under ambient conditions serves as the nucleus for monodisperse nanoparticle assembly. The dynamic nature of the dative interaction in this equilibrium self-assembly has been shown to endow these nanoparticles with thermal responsive characteristics. Further, we show that a metal ion-induced change in the particle morphology was observed by TEM. Our results suggest that the formation of these hollow metal-organic nanoparticles can be attributed to the Kirkendall effect. We expect that these findings will not only have a considerable impact on the development of supramolecular systems based on cooperative polymerization and dynamic covalent bonds, but also on the development of metal-organic materials.
The development of ‘smart’ biomaterials capable of responding to external stimuli such as pH, light, and temperature have become increasingly popular due to their possible applications including controlled release of therapeutics. The most widely used thermoresponsive biomaterials are based on acrylamides that undergo a reversible hydrophilicity change at a specific lower critical solution temperature (LCST). However, the nondegradable backbone of poly(acrylamides) limits their use in vivo. On the other hand, thermoresponsive biopolymers such as elastin-like peptides (ELPs) have been gaining interest due to decreased toxicity and self-assembly abilities but require complex synthetic methods. Recently our lab has developed a library of novel thermoresponsive polyesters inspired by polyacrylamides prepared by simple room temperature carbodiimide coupling. The resulting thermoresponsive polyesters exhibit a range of LCSTs dependent on polymer structure and environment similar to that of ELPs and show inherent hydrolytic degradability. These materials have a multitude of potential applications such as degradable scaffolds and protein and drug delivery.
Polycarbodiimides are an interesting class of polymers that have a wide range of potential applications. These include optical sensory, data devices, and liquid crystals which are continuing being explored. One interesting feature of polycarbodiimides are their relatively low ceiling temperature, Tc, and complete decomposition back to carbodiimide monomers is believed to be governed by a radical mechanism. With the application of thermogravimetric analysis (TGA), mass spectroscopy (MS), Fourier Transform infrared spectroscopy (FTIR), full profiles of the decomposition products of polymers can be determined. By incorporating the multiple analyses in tandem, the weight loss can be directly correlated to specific masses or functional groups that either the MS or FTIR can analyze. While investigating the depolymerization of the polycarbodiimides, a new phenomenon occurred with a specific subset of the polymer class. During heating, masses and functional groups began to appear before monomer depolymerization could occur. It was determined that the polymers began to absorb gasses at room temperature and will begin to release during heating of the polymer system.
Injuries on the battlefield are often of a penetrating, traumatic nature and are likely to result in massive hemorrhage. Current technologies are limited in their ability to prevent infection and are difficult to remove from the wound at later stages of treatment, often causing further tissue damage. Therefore, a need exists for new wound-contact materials that incorporate hemostatic, antibiotic drug releasing, and absorptive elements to reduce wound-related mortality and morbidity. A novel block-copolymer hydrogel consisting of a stimuli-responsive poly(N-isopropylacrylamide) block covalently linked to a PEG-crosslinked poly(acrylic acid) portion was designed to provide these elements. Through RAFT polymerization, the relative lengths of the PNIPAM and PAA-PEG segments were easily altered to regulate response to thermal and pH stimuli, as well as moderate drug release and exudate absorption kinetics. Microporous materials have been prepared by the high internal phase emulsion polymerization method to aid in rate of absorption and drug release. The rates of absorption, drug release, and hemostasis are presented herein.
POLY 501: Enhanced dry adhesion from tapered nanorods and their shape effect

Younghyun Cho¹, younghc@seas.upenn.edu, Gyuseok Kim¹, Yigil Cho¹, Su Yeon Lee¹, Helen Minsky², Kevin Turner², Dan Gianola¹, Shu Yang¹. (¹) Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States (²) Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, Pennsylvania, United States

High-aspect-ratio polymer pillars have been of great interest in wetting and dry adhesion due to their unique surface topography. Specifically, tunable dry adhesion as manifested in gecko foot hairs has been attributed to millions of hierarchical fibrillar structures on gecko toe pads, allowing for adhesive attachment and rapid detachment. So far, most gecko-like adhesives are fabricated from polymer pillars with cylindrical cross-section with relatively low adhesive strength (10-30 N/cm²), which often is not tunable. Here, we report on the preparation of tapered nanorods from epoxy and temperature-responsive shape memory polymers (SMPs) with various cross-sections and study the shape effect on adhesion strength. In order to realize those various tapered nanostructures, we fabricated anodized aluminum oxide templates (AAO) with tapered pores by a combination of hard- and mild anodization, and pore etching process. The pore depth (a few tens of nanometers to a few micrometer) and diameters (80-300 nm) of AAO templates were precisely controlled, and cone, pencil, and stepwise structures were realized. We then created various tapered nanorods from epoxy and SMPs. The adhesion force was measured by nanoindentation. It showed that depending on the shapes of the nanorods, the adhesion force gradually increased up to 48 N/cm² with the indentation depth for triangular shaped nanorods, but decreased for stepwise or pencil shaped nanorods to 24 N/cm² after indentation depth reached 150 nm. To understand the deformation mechanism of the tapered nanorods and the resulting adhesion behaviors, we performed in-situ indentation experiments in SEM. We confirmed that different nanorods deformed differently depending on the load applied in the normal direction. The results from in-situ imaging corroborated well with finite element analysis and nanoindentation measurements, suggesting that the shape of the nanorods played a key role in mechanical response, thus, dry adhesion strength. Furthermore, we prepared SMP tapered nanorods, demonstrating tunable and strong adhesion via an interlocking mechanism.

FE-SEM images of various tapered AAO templates and epoxy structures; Pencil, Stepwise, Long triangular, and Short triangular Structures.
POLY 502: To randomize or not to randomize: An investigation into the cell-uptake of polymers

John Moraes¹, john.moraes@outlook.com, Sébastien Recalcati¹, Guillaume Gody², Raoul Peltier¹, Sebastien Perrier², Harm A. Klok¹. (1) STI-IMX-LP, EPFL, Lausanne, Switzerland (2) University of Warwick, Coventry, United Kingdom

We investigate the effect of monomer sequence on the uptake of polymeric chains by cells. Four configurations of the monomers $N$-acryloylmorpholine, 2-hydroxyethylacrylamide, $N,N$-dimethylacrylamide were investigated to determine if uptake could be promoted or hindered by an appropriate selection of polymeric architecture. Our findings show that re-arrangement of the monomer sequences results in a significant difference in uptake behaviour depending on individual block sequence or randomness. The insights gained will prove useful in the rational design of effective polymeric drug delivery systems.

Cartoon depicting the assessment of cell uptake behaviour for four isomeric polymer samples.
POLY 503: Polyelectrolyte exceeding ITO capabilities in flexible electrochromics

Yumin Zhu\textsuperscript{1,2}, YUMZHU11@GMAIL.COM, Michael T. Otley\textsuperscript{1,2}, Xiaozheng Zhang\textsuperscript{2}, Mengfang Li\textsuperscript{2}, Gregory A. Sotzing\textsuperscript{1,2}. (1) Department of Chemistry, University of Connecticut, Storrs, Connecticut, United States (2) Polymer Program, University of Connecticut, Storrs, Connecticut, United States

Electrochromics, a color change controlled by an electrical stimulus, is one technology being explored for numerous applications and has already been successfully commercialized in areas such as eyewear, smart windows and transportation glasses. As opposed to traditional displays built on rigid substrates, flexible displays have recently attracted significant growing interests due to their conformability and light weight and are considered as the next generation of electronics. Herein, we report the in situ fabrication of flexible electrochromic (EC) displays in a one-step lamination procedure utilizing a new polyelectrolyte material based on poly(ethylene glycol) dimethacrylate and poly(ethylene glycol) methyl ether acrylate as host polymer, containing lithium trifluoromethanesulfonate as the salt and propylene carbonate as plasticizer. The polyelectrolyte composition parameters were thoroughly investigated and optimized for enhancing the EC device (ECD) performance. Optimized electrolyte systems exhibit an ionic conductivity up to $1.36 \times 10^{-3}$ S/cm, and yield flexible electrochromic devices of switching speed as low as 1 second, photopic contrast as high as 53% (non-baseline corrected) with less than 6% loss after 2000 switching cycles using poly(2,2 dimethyl-3,4-propylenedioxythiophene) as the electrochromic material. In addition, a systematic mechanical flexibility test indicated that optimized systems exceeded the commercial indium tin oxide coated polyethylene terephthalate substrates in sustainable minimum bending radius of curvature, ensuring that ECDs will function under extreme stresses even if the substrate is damaged. Under these results, 110 cm$^2$ defect free flexible EC displays with high resolution patterns were assembled and tested to demonstrate their real world applications.

110 cm$^2$ in situ ECDs patterned (a) UCONN (b) HUSKIES employing PEDOT and a copolymer formed by 99 wt% pyrrole and 1 wt% EDOT respectively in their neutral and oxidized states in (1) flat and (2) bent configuration.
Conjugated polymers and oligomers provide a unique encompassing set of structurally tunable optical, electronic transport, and redox properties that allows their present and potential use in a host of applications which span, field effect transistors, light emitting diodes, solar cells and photodetectors, electrochromism, along with batteries and supercapacitors. Their properties are controlled by repeat unit, macromolecular, and solid-state structures, all of which are dependent on the chemical identity of each system. In this presentation, we will examine how chemistry enables the creation of new conjugated polymers where a specific property is pushed towards its limit. We will discuss the control of morphology via a combination of structure and processing method (focusing on spray, blade and slot-die coating), and use organic photovoltaic (OPV), electrochromic polymer (ECP), and charge storing supercapacitor platforms for materials characterization. The flexible synthetic chemistry of dioxythiophene-based polymers has allowed us to complete the color palette of vibrantly colored to transmissive, and near infrared, switching electrochromes of any color. By properly controlling the electronic states in DA polymers via introduction of new donors (dithienogermole) and acceptors (isoindigo), in conjunction with fullerene blend morphology and solar cell device architecture, AM1.5 power conversion efficiencies in excess of 8% have been attained.
POLY 505: Synthesis and characterization of conjugated fulvene chromophores and polymers

Stephen M. Budy¹, stephen.budy@gmail.com, Kristian J. Knuths², Adaobi Davidson¹, Gary J. Balaich², David W. Ball¹, Scott T. Iacono³. (1) Department of Chemistry, Cleveland State Univ, Cleveland, Ohio, United States (2) Department of Chemistry, United States Air Force Academy, Colorado Springs, Colorado, United States (3) Department of Chemistry and Chemistry Research Center, United States Air Force Academy, Colorado Springs, Colorado, United States

In the pursuit of alternative energy sources, organic electronics are making significant progress in terms of efficiency and reliability. The design of new conjugated polymers for these applications often relies on combining donor and acceptor groups in an alternating polymer backbone chain. A series of conjugated fulvene chromophores and polymers were synthesized via Suzuki and Sonogashira palladium-catalyzed coupling condensation reactions. The chromophores and polymers were characterized by NMR, ATR–FTIR, TGA, DSC, GPC, X-ray crystallography, UV-vis and fluorescence measurements, and DFT calculations. Organic electronic applications will be discussed as well.
We have demonstrated that the piezoelectric performance of polyvinylidene fluoride (PVDF) can be doubled through the controlled incorporation of carbon nanomaterials. Specifically, PVDF composites containing carbon fullerenes ($C_{60}$) and single walled nanotubes (SWNT) are fabricated over a range of compositions and optimized for their Young’s modulus, dielectric constant, and $d_{31}$ piezoelectric coefficient. Thermally stimulated current measurements show a large increase in internal charge and polarization in the composites over pure PVDF. The electromechanical coupling coefficients ($k_{31}$) at optimal loading levels are found to be 1.84 and 2 times greater than pure PVDF for the PVDF-$C_{60}$ and PVDF-SWNT composites, respectively. Such property-enhanced nanocomposites bring significant advances to electromechanical systems employed for structural sensing, energy scavenging, sonar, and biomedical devices.

In this work, we employ PVDF-$C_{60}$ composites (the highest piezoelectric value of any polymer composite) in a yarn structure to produce large-displacement, electrically driven artificial muscles. Polymer composite fibers of 1 mm in diameter are drawn through core shell extrusion, with a soft metal conductive core that acts as an inner electrode. Fibers are gold coated and twisted into a yarn-like structure. Through extensive twisting, tight coils are formed in the structure which, upon applying a voltage between the inner and outer electrodes of the yarn, expands and contracts across the length and the width of the structure. Torsional strain allows for the coils to be “unravelled” which greatly increases the elongation of the muscles. Alternately, the application of long strains enable this material to be a long-stroke energy harvesting device. Many piezoelectric energy harvesting material are only able to endure small strains before undergoing catastrophic degradation. The development of large strain energy harvesters presents manifold applications where large deformations/movements are anticipated.

![Figure 1. Side (A) and cross-sectional (B) view of core-shell piezoelectric composite fibers with conductive metal core.](image)
The long-term goal of this line of research is to develop a disruptive printed memory resistor or “memristor” in the form of multi-functional colloidal particles that can be printed into devices using additive manufacturing tools. The central hypothesis is that sub-100 nm particles can be formed from non-conjugated polymers that exhibit inherent path-dependent conductive (PDC) characteristics and printed into memristors. Specifically, the effect of chemical structure on the conformationally induced switching properties of a range of non-conjugated polymers with pendant carbazole and oxadiazole moieties was investigated with a specific goal to create a polymer that exhibits a tailorable multi-state conductance appropriate for being employed as a synaptic substitute. Figure 1 presents the I-V curves of a memristor based on the 70/30 copolymer (PKN) of 2-(9H-carbazol-9-yl)ethyl methacrylate and 4-[5-(1-naphthyl)-1,3,4-oxadiazol-2-yl]-1-naphthyl methacrylate after bistable switching and indicates that the conductive nature of the device is improved with subsequent voltage cycles. With each subsequent cycle, the memristor exhibits a diminishing improvement in conductivity; between the first and second cycles, the current at 2 VDC has increased 1.9 times while is 1.2 times greater between the second and third cycles. This enhancement may be attributed to a combination of an improvement in ring-ring correlation and trap filling. Surprisingly, after the third cycle, a reversed voltage scan was performed along the positive voltage domain (not shown) and then a fourth cycle was taken. This fourth scan exhibited a current at 2 VDC that was 38% lower than the third cycle. This change in conductivity with voltage scans is a basic attribute for building a synaptic substitute.
A recent IPCC report has highlighted the importance and urgency for carbon capture: The atmospheric CO₂ levels have increased to levels unprecedented in at least the last 800,000 years. As a result, there is increasing desire for climate change mitigation, also driven by the need to comply with international legislation. Despite wide research efforts, there are significant challenges facing CCS technologies e.g. carbon capture by absorption will require radically new chemistries, working capacities of solid adsorbents are typically poor and CO₂ utilisation through mineralisation are not practical due to at high operating temperatures, slow rates and low conversions. It is hence clear that extensive future research in novel materials for carbon capture is urgently required into environmentally friendly materials/processes with better performance. We have prepared bioinspired "green" nanosilicas (prepared via aqueous one-step, rapid and pH neutral methods) with embedded amine or enzyme functionalities to allow CO₂ separation and mineralisation respectively. GN exhibit high amine efficiency as high as 0.31 nCO₂/nN (vs. ~0.23-0.3 nCO₂/nN for reported materials), with rapid and stable adsorption-desorption performance over 60+ cycles. For enzymatic sequestration, carbonic anhydrase immobilised on GN was found to be stable even at the enzyme thermal/chemical denaturation conditions (e.g. acidic/basic pH and 60°C). Owing to their green process, GN can be manufactured continuously and when scaled-up to industrial capacities, they can be manufactured at ~$2/kg (significantly lower than $10/kg set for making CCS economically feasible), thus GN provide a significant cost benefit over most other CCS materials.

See www.svplab.com for further details.
Work into synthesizing microvascular materials has recently taken a step forward in the form of a new synthetic process VaSC (Vaporization of a Sacrificial Component) that enables the formation of 3D microstructures that are meters in length. We report on our recent advances in using VaSC to create three-dimensional gas exchange units modeled on the design of avian lungs and vascular systems for heat distribution. We are focused on mass transfer applications for the capture of CO2. We will report on recent research into creating high surface area micro-structures and the use of two phase flow systems to release gas from capture solutions.
A superhydrophobic aluminum alloy surface has been fabricated that is capable of trapping and maintaining a plastron while submerged in flowing water for extended periods of time. Inspired by work from the Kadir group, we confirm that an aluminum alloy surface can be made superhydrophobic by passivation of a hierarchical, micro- and nanoscale, roughened surface. We further explore surface passivation with silanes and fluorosilanes of varying length, comparing them to similar surfaces passivated with fluorinated polymers, POSS and nanoparticles. The resulting water contact and sliding angles of the superhydrophobic aluminum alloy surfaces were measured, showing that low contact angle hysteresis is a key factor towards maintaining a stable plastron. This phenomenon combined with the environmentally responsible application of short-chain fluorosilanes could be utilized to minimize fouling and reduce viscous drag across a heat transfer surface with minimal impact on overall heat transfer efficiency and the environment.
Self-healing of polymers using atmospheric gases is reported for the first time. When methyl-α-D-glucopyranoside (MGP) molecules are reacted with hexamethylene diisocyanate trimer (HDI) and polyethylene glycol (PEG) to form crosslinked MGP-polyurethane (PUR) networks (MGP-PUR), these materials are capable of self-repairing. This process does not occur in the presence of other gases, but requires atmospheric levels of CO₂ and H₂O, thus resembling plant’s behavior during photosynthesis. Molecular processes responsible for this unique self-repair process requires orchestrated physical diffusion of cleaved network segments accompanied by chemical reactions leading the formation of carbonate and urethane linkages. Unlike plants, MGP-PUR networks require no photo-initiated reactions, thus are capable of repairs in darkness under atmospheric conditions. Mechanistic aspects of processes responsible for self-repair will be discussed.
Ethylene glycol, a known poison, is the main ingredient in antifreeze. Ethylene glycol smells and tastes sweet which attracts both children and pets to consume it. Ethylene glycol should not be confused with propylene glycol, a common food additive. Drinking ethylene glycol antifreeze will cause heart and breathing difficulties, kidney failure, brain damage and even death. Two ounces of ethylene glycol antifreeze can kill a dog, one teaspoon can kill a cat and two tablespoons can be lethal to a child. The American Association of Poison Control Centers reported that there were 5,784 poisonings due to ethylene glycols antifreeze in 2012. There were 431 reported cases of children under the age of 5 years old, some of these cases were fatal.

ACTA was funded by the US EPA to develop a safer and greener antifreeze. Their product improves the heat transfer capability of propylene glycol and is 58% better than ethylene glycol antifreeze in a circulating cooling system. Therefore, heat transfer performance and cost should no longer be reasons to use the potential lethal ethylene glycol antifreeze.

ACTA’s additive to propylene glycol antifreeze can reduce our dependence on foreign oil and reduce greenhouse gas emissions because of improved energy efficiency. This safer and greener propylene glycol can improve automobiles’ fuel economy because the car’s radiator could be smaller and less fluid needs to be pumped in the automobiles’ cooling system. ACTA’s product covers a greener and non-toxic chemical.
Polymer nanoparticles with tunable functionality have emerged as a promising and viable technology platform for applications including coatings, cosmetics, nanomedicine, and bio-imaging. The prospects of advancing these and other technologies have provided great impetus for the development of rapid, low-cost methodologies for the synthesis of functional polymer nanoparticles. Nanoemulsions – with droplet sizes typically in the range of 20-200 nm – are particularly well-suited for the synthesis of small polymer nanoparticles. In this presentation, we report the synthesis of small, sub-100 nm polythioether nanoparticles using nanoemulsion thiol-ene photopolymerization. We specifically focus on tailoring the nanoemulsion formulation and processing parameters (ultrasonication time and amplitude) to achieve nanoparticles with diameters in the sub-100 nm range with relatively narrow size distributions. In an effort to demonstrate potential utility of thiol-ene nanoparticles, we exploit the step-growth radical mechanism of thiol-ene photopolymerization under non-stoichiometric conditions to fabricate functional nanoparticles that express excess thiol or alkene at the particle surface. We show that these excess functional groups can be utilized as reactive handles in thiol-Michael and radical-mediated thiol-ene reactions for immobilization of fluorescent moieties via postpolymerization modification.
POLY 514: Raising the glass transition temperature of thiol–ene networks for dental applications

Junting Li, juntingl2014@gmail.com, Timothy F. Scott. (1) Chemical Engineering, University of Michigan, Ann Arbor, Michigan, United States (2) 3074 H.H. Dow Building, University of Michigan, Ann Arbor, Michigan, United States

Polymer networks generated via radical-mediated, step-growth, thiol–ene polymerizations are appealing alternatives to methacrylate-based materials as dental restoratives owing to their reduced polymerization inhibition by oxygen, lower extractable contents, less volume shrinkage and shrinkage stress. Unfortunately, the utility of thiol–ene materials has been hindered by their typically low elastic moduli and glass transition temperatures.

In this work, we designed and synthesized a series of multifunctional thiol- and vinyl-based monomers that incorporated inflexible moieties, such as bisphenol A, tetramethyl cyclobutane and/or norbornene, which were mixed in 1:1 thiol to vinyl stoichiometric ratios, formulated with diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide, and irradiated at 405 nm to effect photopolymerization. Reaction kinetics studies on these polymerizations were performed using FT-IR spectroscopy, exhibiting generally higher conversions compared with equivalent methacrylate-based formulations. The resultant polymers were subject to dynamic mechanical analysis and their respective glass transition temperatures were significantly raised with increased crosslinking density and polymer backbone rigidity. Additionally, pentaerythritol tetra(3-mercaptopropionate) (PETMP), a widely-used tetrathiol incorporating hydrolytically-labile ester functionalities, was replaced with ester-free tetramercaptosilane monomers for resin formulation. The shrinkage stress of each polymer sample was also evaluated by tensometry, exhibiting less shrinkage stress generated during the polymerization than equivalent chain-growth methacrylate polymerizations.

Improvement of the glass transition temperature of thiol–ene networks by increasing the crosslinking density and backbone rigidity with inflexible monomers.
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 definition of co-network structures has not been achieved, largely due to the lack of well-controlled chemistries for their preparation. Here, a thiol-ene end-linking platform enables the systematic investigation of phase-separated poly(ethylene glycol) (PEG) and polystyrene (PS) networks in terms of the molecular weight and relative volume fractions of precursor polymers. The ion conductivity and storage modulus of these materials serve as probes to demonstrate that both phases percolate over a wide range of compositions, spanning PEG volume fractions from ~ 0.3 - 0.65. 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 $d \sim M_n^{0.5}$, for $4.8 \text{ kg/mol} < M_n < 37 \text{ kg/mol}$, where $M_n$ is the molecular weight of the precursor polymers at the same ratio of PEG to PS. Over this range of molecular weights and corresponding $d$-spacings (22-55 nm), the ion conductivity ($10^{-4.7} \text{ S/cm}$ at 60 °C), thermal properties (two glass transitions, low PEG crystallinity), and mechanical properties (storage modulus » 90 MPa at 30 °C) remained similar. These findings demonstrate that this approach to thiol-ene co-networks is a versatile platform to create bicontinuous morphologies.
The development of a novel bone replacement material using in situ polymerization of thiol-acrylate monomers with human adipose tissue derived adult stem cells (HASCs) was studied. Poly(ethylene glycol) diacrylate-co-trimethylolpropane tris (3-mercaptopropionate) (PEGDA-co-TMPTMP) was synthesized with 10% Hydroxyapatite (HA) by an amine-catalyzed thiol-acrylate Michael addition reaction. Initial characterization studies were performed to determine the temperature profile during the exothermic reaction showing a peak temperature of 50°C. To prevent hyperthermic cell damage and support bone regeneration during the exothermic polymerization procedure, the HASCs were encapsulated in alginate particles. The mechanical properties show an improvement over injectable hydrogels with PEGDA-co-TMPTMP exhibiting 9.5MPa in compressive strength. Characterization of the porosity and interconnectivity of pores in the polymeric foam scaffolds were performed using FIB-SEM and Micro-CT. Cell viability experiments within the polymeric scaffold were also studied using AlamarBlue®, as well as fluorescent dyes: Calcein-AM (live) and Ethidium homodimer-1 (dead).
POLY 517: Softening polymer substrates for chronically soft neural interface

Walter Voit, walter.voit@utdallas.edu. UT Dallas, Richardson, Texas, United States

We describe smart engineered shape memory polymer (SMP) substrates, which have been proposed for use in biomedical devices extensively over the past decade. Specifically, the paradigm of softening bioelectronics medicines enables devices such as neural interfaces to be implanted while mechanically rigid and subsequently soften in physiological conditions. Harris et al. have demonstrated softening intracortical electrodes based on the significant swelling of thermally and water sensitive polymer substrates. Building upon this work, we have further demonstrated the fabrication, characterization and demonstration of softening neural interfaces with 5 micron minimum feature sizes patterned using full-photolithography reaching temperature up to 85°C on softening substrates with minimal swelling. SMP substrates are thiol-ene/acrylate copolymers designed to position the glass transition temperature (T_g) to near 55°C, such that after plasticization in fluid, the T_g shifts 20°C triggering softening. This paradigm allows surgeons adequate time for implantation, and maintains sub 3% swelling of the substrate to minimize abiotic device failure and delamination of the patterned Parylene-C barrier coating. We balance mechanical buckling forces, created by modulus mismatches between the device modulus at insertion and that of both agarose gel (in vitro experimental model) and the cortex of a laboratory rat. Other studies have shown how higher modulus materials, such as silicon, tungsten, Parylene-C and polyimides maintain sufficient stiffness to allow implantation into tissue. Our devices match these supra 1 GPa insertion properties, but chronically behave mechanically more similarly to polydimethylsiloxane.

Fig. 1 Intracortical neural interface on softening polymer substrate.
Thiol-X reactions exhibit many desirable properties and are considered click reactions. They have the advantages of being resistant to oxygen inhibition, polymerize rapidly under mild conditions, and exhibit delayed gelation due to their step-growth mechanism. [1] Available multifunctional thiols are often derived from esterification reactions involving mercaptopropionic or mercaptoacetic acid. The thiol-X networks formed from these available substrates suffer from degradation due to ester hydrolysis. This behavior limits their implementation in several potential applications.

In this study a multifunctional thiol tetra(2-mercaptoethylene)-silane (SiTSH) with no degradable moieties is synthesized and used in stoichiometric reactions with 1,3,5-triallyl-1,3,5-triazyne-2,4,6-trion (TTT), divinyl sulfone (DVS) and 2,2 - Bis(acryloxy)methyl]butyl acrylate (TMPTA). The same vinyls are reacted with ester-containing pentaerythritol tetra(3-mercaptopropionate) (PETMP) for comparison (Table 1). Depending on the reaction type they were initiated either by light using 1 wt% bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide-BPO or thermally at 80 °C using 1wt% 2,2,6,6-tetramethyl-1-piperidynyl-N-oxy (TEMPO).

From the tabulated results the following conclusion can be drawn; the novel thiol-X materials with no hydrolitically degradable esters combine all benefits of step-growth reactions such as high conversion and uniform network structure and at the same time eliminate many existing drawbacks including increased Tg and significantly improved solvent resistance and stability.


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<th>Resin Name</th>
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<tbody>
<tr>
<td></td>
<td>Conv. (%)</td>
</tr>
<tr>
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<td>PETMP + TTT</td>
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<tr>
<td>PETMP + DVS</td>
<td>98 ± 1</td>
</tr>
</tbody>
</table>

**The negative values mean wt% loss in weight and the positive values mean wt% gain in weight.

Table 1. Properties of different thiol-X resins
The “Click” chemistry paradigm focuses on highly efficient reactions that achieve quantitative conversion under mild conditions. These reactions in polymer chemistry allow unprecedented control over materials chemical and physical properties. One click reaction of great interest is the Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) where the uniqueness of this reaction arises in the development of properties during polymerization. During the CuAAC the triazole adducts formed possess excellent thermal and chemical stability and the rigid-aromatic linkers should lead to a high glass transition temperature polymer. Furthermore, the step growth nature of the reaction results in the formation of a nearly ideal network structure with a narrow glass transition and few elastically ineffective chains. Lastly, the synergistic combination of the CuAAC with photochemical initiation can be used to afford both spatial and temporal control of polymer formation, structure and patterned assembly.

Herein, we discuss CuAAC photo-polymerized networks by exploring a variety of easily synthesized azide and alkyne monomers. Results show significant enhancements in the mechanical properties by incorporating carbamates and aromatic rings, which are capable of secondary interactions from hydrogen bonding and $\pi-\pi$ interactions respectively. Additionally, the triazole moiety inherent to the CuAAC polymerization process shows a significant contribution to the mechanical properties specifically when compared to an analogous thiol-ene based material. With the growing number of multifunctional azide and alkyne monomers the photo-initiated CuAAC polymerization renders ideal for broad applications within polymer science including coatings, surface modification, and adhesives.
POLY 520: High temperature cyanate ester resins from renewable feedstocks:
Upgrading through deoxygenation or conversion to hybrid resins

Benjamin G. Harvey¹, benjamin.g.harvey@navy.mil, Andrew J. Guenthner², William W. Lai¹, Andrew Chafin¹, Michael Garrison¹, Josiah Reams³, Lee Cambrea¹, Heather A. Meylemans¹, Matthew C. Davis¹. (1) Chemistry Department, Naval Air Warfare Center, Weapons Division, China Lake, California, United States (2) Aerospace Systems Directorate, Air Force Research Laboratory, Lancaster, California, United States (3) AFRL / RQRP, Edwards AFB, California, United States

Lignin is a compelling feedstock for the preparation of bisphenols and thermosetting resins. Phenols derived from lignin and other renewable sources often contain methoxy groups that can impact the properties and cure characteristics of derivative resins. To directly evaluate the effect of methoxy groups on the properties of renewable cyanate esters, a series of "deoxygenated" resins were prepared from renewable bisphenols by conversion to triflates followed by Pd-catalyzed elimination and hydrolysis of the methoxy groups. Reaction with CNBr and base then yielded the cyanate ester resins. The physical properties, cure chemistry, and decomposition pathways of the oxygenated (prepared previously) and deoxygenated resins were then compared. Deoxygenation was found to decrease the melting points of the resins, increase the dry and wet Tgs, decrease the water uptake, and increase the thermo-oxidative stability. The thermal degradation of both sets of resins was monitored by TGA/FTIR. Due to the higher thermal stability of the deoxygenated resins, decomposition proceeded primarily via evolution of small molecules including CO₂ and NH₃. This was in contrast to the lower temperature degradation of the oxygenated resins that resulted in the evolution of phenols and isocyanic acid. A different approach was then explored to take advantage of methoxy-functionalized phenols. New hybrid resins were prepared by allowing a methoxy or alkoxy-functionalized phenol to react with a chlorophosphate. Conversion of the alkoxy-group to a phenol then allowed for the preparation of a series of cyanate ester resins with bridging phosphate groups. Tgs of these materials ranged from 130 to >>300 °C depending on the number of cyanate ester groups per bridging phosphate and the substitution pattern of the aromatic rings. These hybrid resins may have applications in fire resistant composite materials.
POLY 521: Renewable furan-based epoxy-amine thermosets

Giusseppe R. Palmese, palmese@coe.drexel.edu. Drexel University, Philadelphia, Pennsylvania, United States

Renewable alternatives to petroleum-based thermosetting polymers could provide ecological and economic benefits. Such materials should mimic the rigid phenylic structure of incumbent high-performance thermoset monomers. Furans derived from cellulose and hemicellulose, are promising candidates for doing this. Herein the synthesis of furan-based di-epoxies and di-amines is presented. Fully renewable thermosets containing only furanyl rings were prepared for the first time using these monomers. The thermomechanical properties of these polymers were found to be comparable to those prepared using standard phenyl containing monomers. A series of experiments was conducted using phenyl-based analogs to the furanyl monomers and these materials were used to form crosslinked epoxy-amine networks. A structure-property study showed that furan-based polymers possess improved $T_g$ ($\Delta = 8$-$16^\circ C$) and improved glassy modulus ($\Delta = 0.1$-$0.6$ GPa) relative to their phenyl-based analogs. Thus the furan ring has is a viable building block for renewable high-performance epoxy-amine systems and has the potential for being successfully applied to other thermosetting polymers.
The work reported here consists of an investigation of the dynamics of the glass transition and secondary relaxations in terms of possible epoxy network’s molecular structure variations induced by variable cure heating ramp rates or after immersion of cured samples in acetone. A dielectric loss permittivity maximum at frequency ($f_{\text{max}}$) for the sub-Tg δ peak was found to shift to higher values with increasing temperature in Arrhenius fashion. This relaxation was assigned to phenyl ring flipping in the main DGEBF chain facilitated by the presence of adjacent flexible ether linkages. Effect of acetone ingress on the epoxy network’s sub-Tg and Tg motions will be presented. As shown in the enclosed Figure, values of the Tg relaxation peak maximum were found to shift upwards with increased immersion time of the cured samples in acetone. This would reflect faster Tg relaxation motion with increased acetone ingress due to plasticization. Distribution of relaxation times, $G(\tau)$ will be extracted from the fitted spectra and values will then be related to differences in molecular weight between crosslinks ($M_c$) within the epoxy networks.
POLY 523: Aligned CNT composites: Quantitative analysis by TEM tomography

J Alexander Liddle, liddle@nist.gov, Bharath Natarajan, Thomas Lam, Renu Sharma1, Noa Lachman2, Douglas Jacobs3, Brian Wardle2. (1) Center for Nanoscale Science Technology, National Institute of Standards Technology, Gaithersburg, Maryland, United States (2) CNST, Nat’l Inst of Standards and Technology, Gaithersburg, Maryland, United States (3) Aeronautics and Astronautics, MIT, Cambridge, Massachusetts, United States

Aligned CNT nanocomposites exhibit usefully anisotropic mechanical, thermal and electrical properties. We use energy-filtered TEM tomography to generate high-resolution, three-dimensional images suitable for quantitative analysis. We find that CNT morphology – network structure, bundling, alignment and waviness – varies non-linearly with volume fraction. The CNTs exhibit both increased bundling and a much higher degree of alignment uniformity as the volume fraction is increased. We use the data extracted via image analysis to understand the deviation between the observed property enhancements due to the addition of CNTs and those expected from a simple “aligned-fiber” model.

Volume rendered reconstruction of 0.5% vol. aligned-CNT composite. The size of the reconstructed volume is indicated below the figure. The volume is representative since it is orders of magnitude larger than the critical microstructural dimensions (NT diameter and average NT spacing).

Volume rendered reconstructions of 4.5% vol. aligned-CNT composites. The size of the reconstructed volumes is indicated below the figure.
POLY 524: Mapping the lyotropic phase behavior of diblock copolymer iongels

Thomas Bennett, thomas.bennett@uqconnect.edu.au, Idriss Blakey, Kristofer J. Thurecht, kevin Jack. (1) Centre for Advanced Imaging, The University of Queensland, Brisbane, Queensland, Australia (2) Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane, Queensland, Australia (3) Centre for Microscopy and Microanalysis, The University of Queensland, Brisbane, Queensland, Australia

A detailed understanding of the phase behavior of block copolymer/ionic liquid mixtures is an important step towards the eventual implementation of these materials into commercial devices. To this end, the lyotropic phase behavior of five low molecular weight polystyrene-\textit{b}-poly(methyl methacrylate) (PS-\textit{b}-PMMA) block copolymers has been studied in the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfonylelimide (EMIM Tf$_2$N) across an extensive concentration range. The ordered microstructures formed by the mixtures were characterized with small-angle X-ray scattering at 25 °C. As the concentration of EMIM Tf$_2$N was increased, each of the block copolymers, which were disordered (D) when neat, transitioned through a number of well-defined classical block copolymer morphologies, including: lamellar (L), gyroid (G), hexagonally packed cylinders (H) and spheres packed onto a body-centered-cubic lattice (SBCC). The solutions also exhibited several regions of coexisting microstructures, in addition to a wide region which appears to correspond to a disordered network morphology (N). EMIM Tf$_2$N was found to be strongly selective for PMMA, and thus resides almost exclusively in the PMMA domains of the phase separated microstructures. From this data an effective interaction parameter ($\chi_{\text{eff}}$) was calculated between the PS and EMIM Tf$_2$N solvated PMMA domains, which we used to generate an experimental phase diagram for PS-\textit{b}-PMMA in EMIM Tf$_2$N over the weak/intermediate segregation regime (Figure 1). We believe this will prove to be an important tool in future studies of these materials which intend to achieve a particular self-assembled morphology for a specific application.

POLY 525: Spectroscopic Investigations of polyethylene-carbon nanofibers composites

Rogelio Benitez, Ibrahim Elamin, amin@utpa.edu, Brian Jones, Li Jianhua, Dorina Chipara, Karen Lozano, Mircea Chipara, mchipara@utpa.edu. (1) Physics and Geology, THE UNIVERSITY OF TEXAS PAN AMERICAN, Edinburg, Texas, United States (2) Chemistry, The University of Texas Pan American, Edinburg, Texas, United States (3) AXS, Bruker, Madison, Wisconsin, United States (4) Rigaku Americas Corporation, The Woodlands, Texas, United States (5) Mechanical Engineering, The University of Texas Pan American, Edinburg, Texas, United States (6) Mechanical Engineering, Texas A&M University, College Station, Texas, United States (7) Physics and Geology, The University of Texas Pan American, Edinburg, Texas, United States

High Density Polyethylene (PE grade HXM-50100) pellets provided by Chevron Phillips Chemical Company have been loaded with various amounts of carbon nanofibers (Pyrograph III PR-19-from Applied Sciences Inc.) by melt blending using a Haake Rheomex. The mixing was performed at 180 °C and 60 rpm for about 12 min. The nanocomposites were hot pressed at about 150°C for 2 minutes. The as obtained films have been investigated by Wide Angle X-Ray Scattering (Discovery 8, Bruker equipped with the large area detector and heating accessory), Electron Spin Resonance (Elexsys, Bruker X Band spectrometer), and confocal Raman microscope (Senterra, Bruker). X-Ray and Electron Spin Resonance measurements on both as obtained and stretched nanocomposites are reported. The effect of the uniaxial stress on the WAXS spectra and ESR spectra is reported. Additional DSC data were used to analyze the effect of the nanofiller and of mechanical stresses on the melting and crystallization processes. Fig. 1 shows the X-Ray spectra of pressed and stretched nanocomposite containing 20 % wt. nanofibers. Fig. 2 shows the angular dependence of the g-factor (relative to the external magnetic field) for a sample subjected to uniaxial stretching and demonstrates the alignment of carbon nanofibers. Not stretched sample shows no angular dependence.
Innovative new methods are required to accelerate the development time of new aerospace material systems so that material development time is commensurate with the development time of new aircraft. Computational design predicts the effect of changes in the structure and design of materials on the life of full scale components operating in in-service environments. Computational design of material systems would allow selection of material designs that have a high probability of fulfilling their design function and thus would streamline and focus material development efforts that occur on industrial scales. This virtual design approach requires the integration of models from the molecular to the engineering scale. The models integrated in the design environment include: molecular scale models defining surface interactions and transport properties, microkinetic and mesoscale models for failure or damage initiation and propagation, microclimate models defining conditions in and on the exterior of an aircraft, and damage accumulation models that keep track of the advance of damage throughout the structural component of interest until a failure is statistically likely to occur. The present computational design system can estimate the life of a range of polymeric coating systems containing different corrosion inhibitors. The computational design system is constantly evolving, and is currently being used to screen, downselect, and identify novel polymeric coating systems, metallic and alloy materials, and surface finishes for use in future aerospace platforms.

Multiscale models, flight-path pickers, and global climate models are combined with statistical methods to predict service lifetime of material systems.
Using molecular dynamics (MD) we are able to simulate critical distortional and dilatational deformations of crosslinked epoxy thermosets and relate these results to carbon fiber composite performance using finite elemental analysis (FEA) as described by Onset Theory. The MD simulation requires building representative crosslinked polymers, placing these polymers in periodic cells, annealing the periodic structures to an appropriate density, and production MD runs to determine the critical distortional and dilatational deformations. Onset Theory asserts that composites possessing fiber orientations which exploit distortional strain capability of the matrix are more structurally efficient. The effective yield strain as determined from the MD simulation for several amine cured epoxy formulations is shown to be a predictor of matrix distortional critical composite performance. This multiscale modelling approach has been employed to rapidly screen new resin formulations for expected composite performance and target top distortional performers for synthesis, scale-up, prepregging, and composite testing. The ability to virtually assess capability greatly decreases the time and cost of new materials development.

- **Materials fail because they deform too much**
- **There are only two ways to deform a solid body**
  - **Distortion (Change in Shape, No Change in Volume)**
    \[
    \varepsilon_{\text{ym}} = \sqrt{\frac{1}{6} \left[ (\varepsilon_1 - \varepsilon_2)^2 + (\varepsilon_2 - \varepsilon_3)^2 + (\varepsilon_1 - \varepsilon_3)^2 \right]} 
    \]
    * Measured by \( \varepsilon_{\text{ym}} \) (VonMises Strain)
  - **Dilatation (Change in Volume, No Change in Shape)**
    \[
    J_1 = \varepsilon_x + \varepsilon_y + \varepsilon_z = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 
    \]
    * Measured by \( J_1 \) (First Invariant of the Strain Tensor)
Any successful immunologic therapy must not only raise the proper strength of an immune response, but it must also raise the correct phenotype, which can be challenging owing to the complexity of the immune system. Here we will describe self-adjuvanting, modular, supramolecular materials capable of tuning immune phenotype using two models: a vaccine against methicillin-resistant *S. aureus* (MRSA), and an immunotherapy for chronic inflammatory diseases. In both, fibrillizing peptides containing variable B cell and T cell epitopes were designed to co-assemble into nanofibers. In the MRSA vaccine, we found that the ratio between the B cell epitope and the T cell epitope significantly modulated both the strength and the phenotype of the response, with different T cell subsets being favored at different compositions. Only epitope ratios corresponding to the maximal Tfh cell and antibody responses improved the healing of MRSA skin lesions, illustrating the need to target such ratios precisely.

Towards treating chronic inflammatory diseases, we employed a B cell epitope from TNF-alpha and an exogenous T cell epitope. In this model, we found that TNF-reactive antibodies could be raised in mice without T cell responses to the TNF epitope, allowing the accumulation of TNF-neutralizing antibodies in the serum. In both systems, the ability to adjust the strength and phenotype of the immune response was facilitated by the materials’ modular design.
POLY 529: Engineering amphiphiles that target lymphoid tissues and optimally engage immune cells for more effective vaccines

Darrell J. Irvine, djirvine@mit.edu. Massachusetts Inst of Tech, Cambridge, Massachusetts, United States

We have recently focused on the development of engineered synthetic amphiphiles designed to promote both the physical targeting of vaccines to lymph nodes and to enhance triggering of antigen-specific cells in these immune command centers. In cancer patients, visual identification of sentinel lymph nodes (LNs) is achieved by the injection of dyes that bind avidly to endogenous albumin, targeting these compounds to LNs where they are efficiently filtered by resident phagocytes. We translated this “albumin hitchhiking” approach to molecular vaccines, via the synthesis of amphiphiles (amph-vaccines) comprised of an antigen or adjuvant cargo linked to a lipophilic albumin-binding tail by a solubility-promoting polar polymer chain (Fig. 1). Structurally-optimized CpG-DNA/peptide amph-vaccines exhibited dramatic increases in LN accumulation and decreased systemic dissemination relative to their parent compounds in mice, leading to substantially enhanced efficacy of epitope-based vaccines while eliminating systemic toxicity from CpG. Strikingly, CD8+ T-cell responses were strongly correlated with the efficiency of CpG targeting to lymph nodes, leading to 30-fold increases in antigen-specific T-cell expansion relative to traditional peptide vaccines and parallel enhancements in induction of polyfunctional cytotoxic T-lymphocytes. In parallel, we have discovered that multivalent amphiphiles that present nanoclustered antigens can dramatically enhance the engagement of antigen receptors on antigen-specific B-cells. Such antigen nanoclustering enhanced B-cell activation even when antigen was displayed in a highly multivalent manner on the surface of nanoparticles. Altogether, these engineered amph-vaccines provide a simple, broadly-applicable strategy to simultaneously increase the potency and safety of subunit vaccines.

Fig. 1. Structure of amphiphile vaccines and proposed mechanism of "albumin hitchhiking".
A new series of synthetic protein transduction domain mimics (PTDMs) was designed based on key parameters of Pep-1 and TAT. These novel PTDMs were significantly more active than either Pep-1 or TAT alone. To better understand the importance of guanidine and phenyl groups segregation along the backbone both membrane interactions and cellular internalization studies were conducted. The results showed that functional group segregation impacts activity. Their ability to deliver active peptides, proteins, and antibodies into primary T-cells was exploited. This study gives new design guidelines for the development of PTDMs.
POLY 531: Effect of 3D presentation of glycomimetic polymers on lectin interaction

Andrea M. Kasko, akasko@ucla.edu, Walter Liau, Ken Lin. Bioengineering, UCLA, Los Angeles, California, United States

Polysaccharides have historically been recognized as structural materials and as an energy source, and can also play important roles in biological processes such as pathogen recognition, viral entry and immune function, and cell adhesion and signal transduction. However, the lack of tools for the rapid synthesis and characterization of well-defined oligo- and polysaccharides has limited their exploitation for biomedicine. As an alternative, high molecular weight glycomimetic polymers (polymers incorporating sugars, typically not through glycosidic linkages) can be synthesized in large quantities with relative ease. Many structure-property relationships have been established for the interaction between lectins and glycomimetics but the role of 3D presentation of saccharide-containing chains on their interaction with lectins is not well-understood. The carbohydrate binding activity of most lectins is thought to be mediated through multiple carbohydrate recognition domains (CRDs). Lectins from diverse sources lack primary sequence homology but share similarities in their tertiary structure, implying that the 3D presentation of multiple CRDs is crucial for lectin-polysaccharide interactions. We report the synthesis of a glycopolymer-protein conjugate and block copolymers containing a glycomimetic block. These different polymers result in 3D presentation of the glycomimetic chains to lectin, either due to the inherent 3D nature of the protein core or through self-assembly of the block copolymers into nano- and microparticles. This approach allows us to investigate the effect of spatial orientation of multivalent glycomimetic chains on their interaction with lectins.
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