

# *Division of Polymer Chemistry (POLY)*

## Graphical Abstracts



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**Computers in Chemistry**

**March 13-17, 2016 | San Diego, California**

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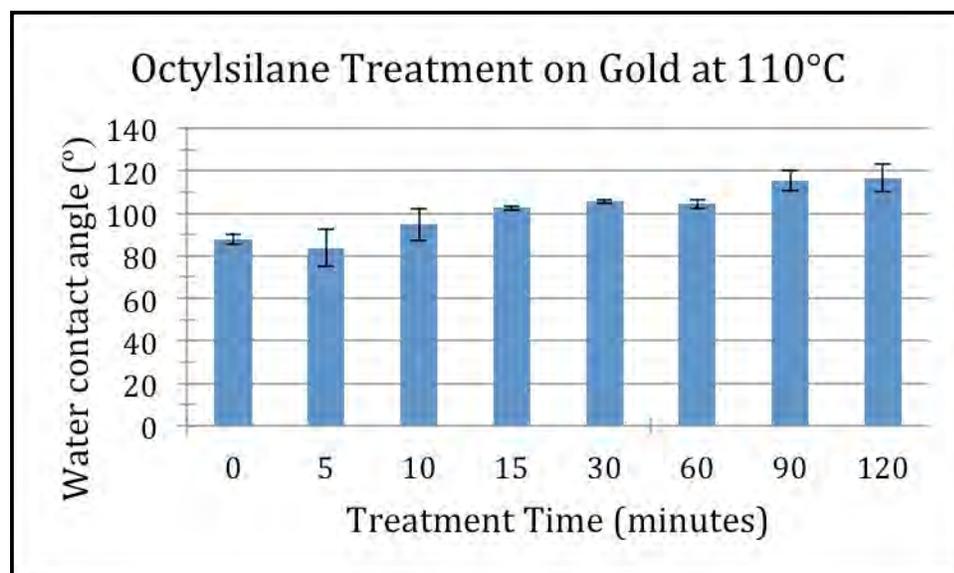
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## POLY 1: Surface modification of oxide-free metal and hydrogenated metal substrates with trihydridosilanes

**Barry Arkles**, *h.c.owheat@gelest.com. Gelest Inc., Pipersville, Pennsylvania, United States*

Trihydridosilanes with a wide range of organic substitution can provide a route for generating self-assembled monolayers on metal substrates by vapour and liquid phase deposition.<sup>1</sup> Under mild conditions, these precursors interact with a variety of clean, hydrogenated and fresh metal and metalloid surfaces, including titanium, silicon and gold. All classes of hydridosilanes have minimal interaction with anhydrous oxide surfaces. Evidence for the change in physical and chemical properties of the surfaces will be presented. After initial deposition, SAMs formed from trihydridosilanes may be converted to monolayers of silicon nitride by pulsing with ammonia or silicon dioxide by pulsing water or oxygen. Alternately, specific reactive functionalities can be incorporated into the trihydridosilanes, allowing them to act as coupling agents. A proposed mechanism for the initial steps of deposition involves the dissociative adsorption of the silanes with the formation of hydrogen, followed by topmost atom layer insertion and concomitant surface reconstruction.

1. B. Arkles, Y. Pan, A.E. Kaloyeros, Thin-Film Deposition of Silicon Nitride and Oxides from Trihydridosilanes, Atomic Layer Deposition 10, ECS Transactions, 2014, 64(9), 243-249.



Trihydridosilane Modification of Gold Surface with Time

## POLY 2: Visible light-driven proton pumps utilizing photoacid molecules and polymeric nanopore scaffolds

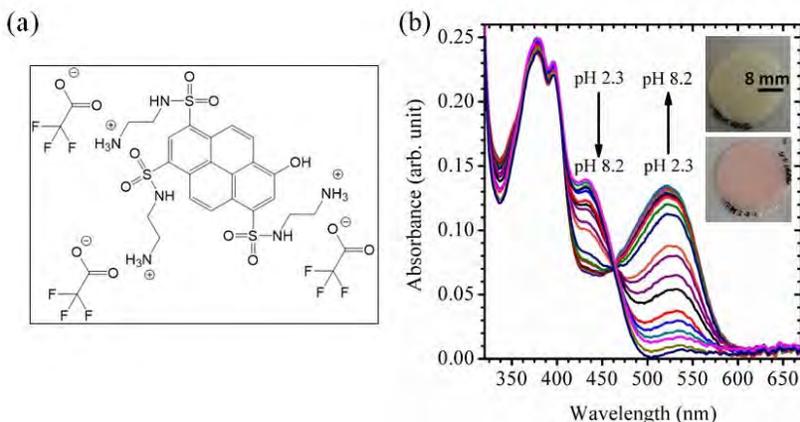
**Christopher Sanborn**<sup>2</sup>, *cdsanborn@smcm.edu*, Shane Ardo<sup>1</sup>. (1) Department of Chemistry, University of California Irvine, Irvine, California, United States (2) Chemistry, University of California, Irvine, Irvine, California, United States

Artificial photosynthesis is potentially a green economic approach for converting sunlight into practical energy. Herein, we report on photo energy conversion into ionic current via solar energy induced endergonic proton transfer across a polymeric membrane.

Water soluble, pyrenol photoacid dye molecules (Fig. 1a) allow for light absorption and proton generation. Spectrophotometric titration curves indicated that the unbound dye in solution had a hydroxyl  $pK_a$  value of 5.8. The photoluminescence measurements indicated that the hydroxyl excited-state  $pK_a$  value,  $pK_a^*$ , was -0.7. Hence, the maximum attainable photovoltage from proton pumps utilizing the dye was estimated to be ~380 mV ( $59 \text{ mV} \times \Delta pK_a$ ).

The initial model system comprised of conical nanopore poly(ethylene terephthalate) scaffolds asymmetrically functionalized with dye molecules. The bound dyes provided a basis for a cationic region adjacent to an unmodified carboxylate region. The tailored regions of fixed charges was intended to mimic a solid-state semiconductor pn-junction and be used to separate photogenerated ions.

Electrochemical and absorption spectroscopy measurements (Fig. 1b) of the bound dye to PET indicated a decrease in the  $pK_a$  value to 5.0, was attached *via* two out of three ammonium groups, and had a binding density of 0.3 dyes/nm<sup>2</sup>. Two-photon fluorescence microscopy of modified films further verified that the dye was covalently attached to the film where it still functioned as a photoacid. Under visible-light illumination and a -100 mV reverse bias, excitation of these photo-acid-sensitized nanopore scaffolds resulted in an ionic photocurrent. This work provides an experimental and theoretical baseline for future work for photovoltaic materials as ion exchange membranes in solar fuel devices.

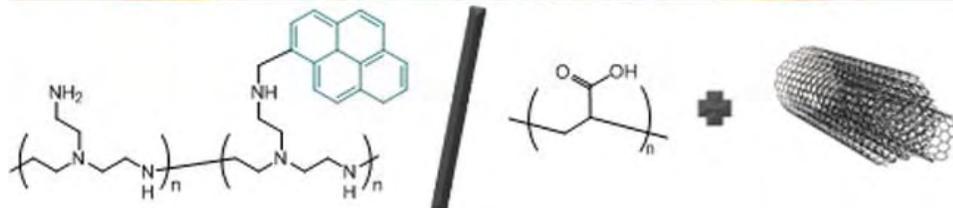


**Fig. 1 (a)** Visible-light absorbing pyrenol photoacid dye. **(b)** UV-Vis absorption spectra of PET nanopours scaffold containing covalently bound dye wetted with aqueous buffer. Insets are digital photographs of the films wetted in acidic (top) and basic (bottom) conditions.

### POLY 3: Pyrene-modified polyelectrolytes/MWNT multilayer thin films extinguish flames on polyurethane foam

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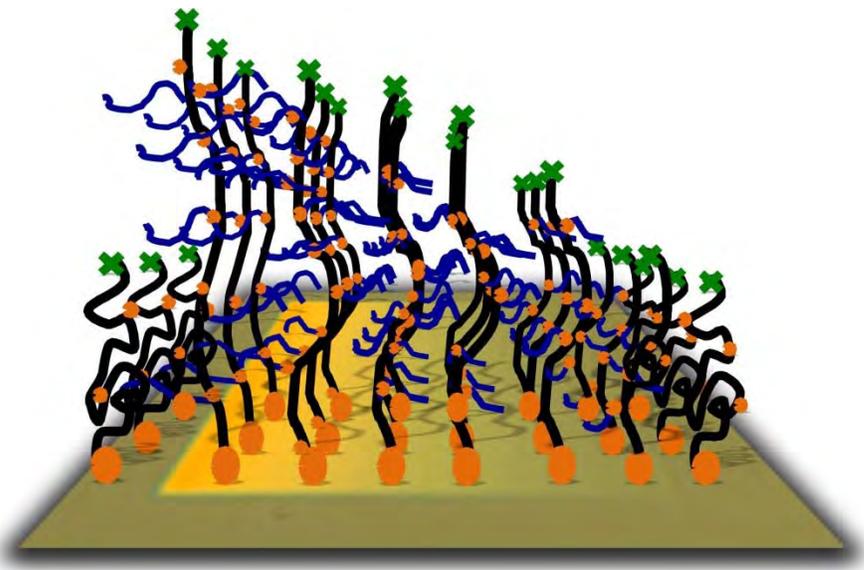
Flame retarding nanocomposite thin films were deposited on polyurethane foam using water-based solutions of cationic and anionic-stabilized multi-walled carbon nanotubes (MWCNT). Layer-by-layer (LbL) assembly was used to coat the open-celled foam to produce uniform protective layers up to 600 nm thick, comprised of cationic polyethylenimine modified with pyrene (PEI-Py), anionic poly(acrylic acid) (PAA), and MWCNT. Coatings of only 6 [PEI-Py/PAA+MWCNT] bilayers (BL) showed tremendous reductions in peak heat release rate (up to 67%) and total smoke release (up to 80%) for the foam. With 9 BL, the foam successfully withstood a vertical burn test, self-extinguishing immediately after removal of the test flame. These dramatic reductions in foam flammability are unprecedented and are attributed to the protective nature of the carbon based char (formed from the coating) that acts as a protective barrier.



## POLY 4: Hierarchical comb brush architectures via sequential light-mediated controlled radical polymerizations

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The synthesis and characterization of branched polymer brushes from a variety of surfaces by sequential light-mediated controlled radical polymerizations was explored. Initially, linear brushes are prepared by surface-initiated copolymerization of methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA). In a subsequent step, the HEMA side chain groups are then functionalized with an initiating group for secondary graft polymerization leading to hierarchical architectures. The increased steric bulk of these polymer side chains results in a dramatic increase in film thickness when compared to the starting linear brushes. This allows chemical gradient and complex three-dimensional (3-D) structures based on comb-brush nanostructures to be obtained using a grayscale photomask.

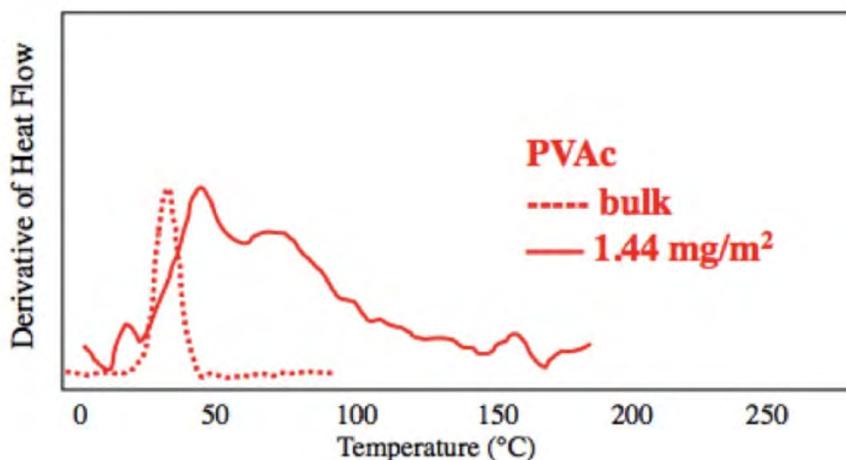


Spatial control over comb-type molecular architectures using light mediated controlled radical polymerization leads to complex 3-D polymer brush structures and tunable surface properties.

## POLY 5: Tightly-bound PVAc on silica: Different from bulk polymer?

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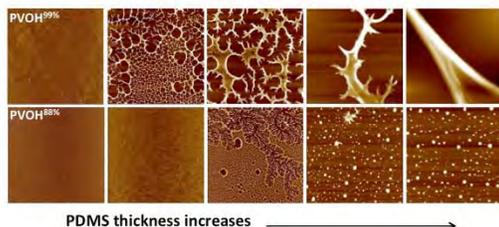
The properties of adsorbed poly(vinyl acetate) (PVAc) are discussed with a specific emphasis on the quantification and behavior of tightly-bound polymer segments. The tightly bound polymer segments are those significantly motionally altered because of their attachment to silica. FTIR revealed that the fundamental interaction was hydrogen bonding between the carbonyl groups and surface silanols. Deuterium NMR identified that some PVAc-d<sub>3</sub> was tightly-bound; rigid well beyond the glass transition temperature of the bulk polymer. The amount of tightly-bound polymer was estimated from modulated differential scanning calorimetry. It was found that a common plasticizer for PVAc also did not penetrate the tightly-bound polymer and was therefore ineffective.



## POLY 6: Unusual morphologies of poly(vinyl alcohol) thin films adsorbed on polydimethylsiloxane substrates

Akchheta Karki, Lien Nguyen, Bhanushee Sharma, Kelly Lim, Yan Yan, **Wei Chen**, *weichen@mtholyoke.edu*. Chemistry Dept, Mount Holyoke College, South Hadley, Massachusetts, United States

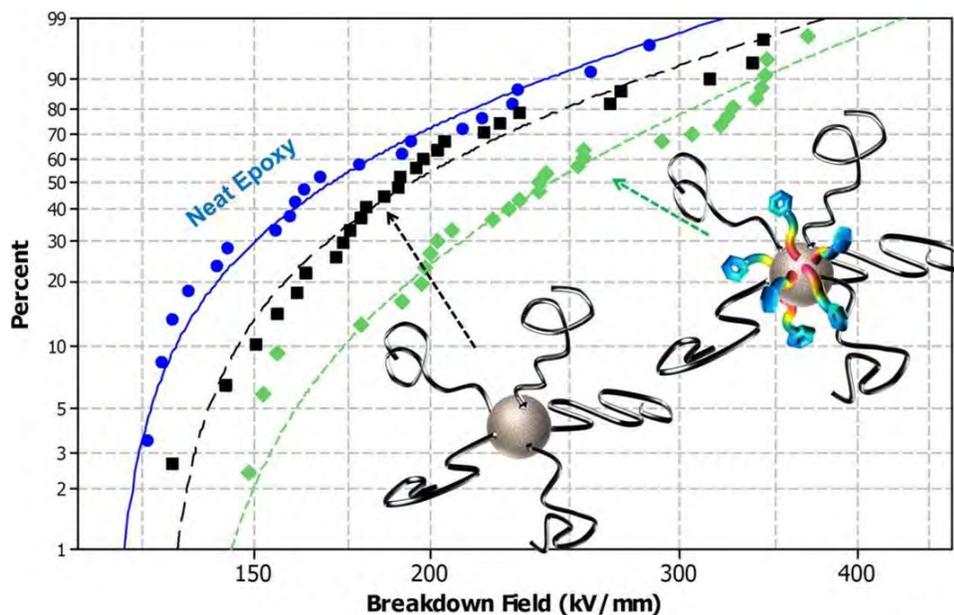
Adsorption of poly(vinyl alcohol) (PVOH), 99% and 88% hydrolyzed, was carried out on polydimethylsiloxane (PDMS) substrates prepared by covalently attaching linear PDMS polymers of 2 kDa, 9 kDa, 17 kDa, 49 kDa, and 116 kDa onto silicon wafers. As the PDMS molecular weight/thickness increases, the adsorbed PVOH thin films transition from continuous to progressively discontinuous morphologies, including honeycomb and fractal/droplet as the result of thin film dewetting upon exposure to air. Since the PVOH film thicknesses obtained under different conditions do not vary significantly, the driving force for dewetting is attributed to the nature of the PDMS substrates – the adsorbed PVOH thin films become less stable and have a stronger tendency to dewet on thicker, more liquid-like PDMS layers. Comparing PVOH<sup>99%</sup> and PVOH<sup>88%</sup> thin films, fractal and droplet morphologies are observed on high molecular weight PDMS substrates, respectively. The formation of the unique fractal features in the PVOH<sup>99%</sup> thin films as well as other crystalline and semi-crystalline thin films is hypothesized to be driven by crystallization force during the dehydration process in a diffusion-limited aggregation fashion. Furthermore, the only significant enhancement in hydrophilicity via PVOH adsorption was obtained on PDMS<sup>2k</sup>, which is completely covered with PVOH thin films. To mimic the lower receding contact angle and less liquid-like character of the PDMS<sup>2k</sup> substrate, light plasma treatment of the higher molecular weight PDMS substrates was carried out. On the treated PDMS substrates, the adsorbed PVOH thin films are in the more continuous honeycomb morphology, giving rise to similarly enhanced wettability. Thus, light plasma oxidation prior to PVOH adsorption can be utilized as a means to effectively hydrophilize conventional PDMS substrates. This study further illustrates that stability and morphology of adsorbed polymer thin films depend on polymer crystallinity as well as substrate physical properties.



## POLY 7: Enhanced dielectric breakdown strength in epoxy based nanodielectrics

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Epoxy based dielectrics are of great interest to the electronics and semiconductor industries. Adding nano-sized fillers to epoxy dielectrics has proven to be an effective method for improving the breakdown strength. The large surface area to volume ratio of the filler can be detrimental to the composite as it can cause agglomeration. This obstacle is overcome by adding polymer chains to the surface of the filler. Reversible addition fragmentation chain transfer or RAFT polymerization is used as a means to attach polymer chains to the filler surface as well as control polymer weight and graft densities. These two parameters are important for controlling the extent of filler dispersion. Previous work has shown that modifying the interface of the composite with conjugated, polarizable surface ligands that act as electron traps is an effective means to improve the dielectric breakdown strength of epoxy nanocomposites. Current work explores new ligand chemistries at the interface as well as the effects of filler dispersion on dielectric breakdown strength. Our studies have shown that well dispersed surface modified silica nanoparticles can increase AC dielectric breakdown strength by as much as 44% with only 2% loading in epoxy based systems.

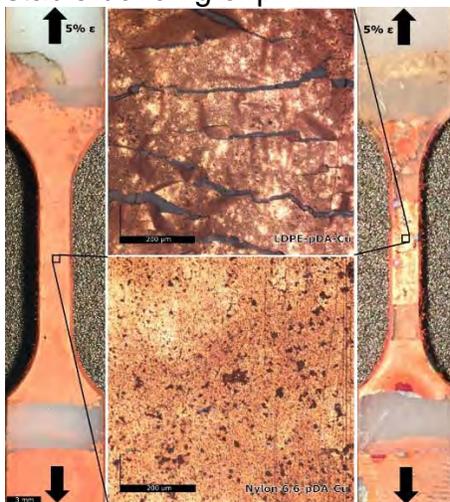


Weibull Plot

## POLY 8: Mechanical characterization of copper thin films on polydopamine-functionalized polymer substrates

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Polydopamine (pDA) is an effective binding mechanism allowing deposition of metal films on to classically inert polymer substrates. However, devices suitable for electronics, biomedical, water treatment, and energy applications have been slow to emerge, in part because the mechanical properties are often poor, inherently dependent on the bond strength of the pDA-substrate interface. pDA is known to form stable bonds with organic species terminated by specific functional groups. This property suggests that wear-resistance of pDA-functionalized devices can be improved by selecting substrates which exhibit stable bonding with pDA. To date, metal-coated pDA systems remain mechanically and tribologically uncharacterized on a substrate-dependent basis. The purpose of this study was to characterize the mechanical and tribological properties of thin metal films bound to a variety of pDA-functionalized polymer substrates. Several commercial polymer substrates were selected on the basis of their surface chemistry. Metallized polymers were fabricated by electroless deposition of copper on pDA-coated substrates. Mechanical and tribological properties of the systems were evaluated by tensile and scratch tests, respectively. Metal coatings were inspected by laser scanning microscopy to characterize wear and failure mechanisms. Robust metal coatings were capable of high strain, thought to be directly related to the inhomogeneous structure. The study suggests that wear properties of pDA-functionalized devices can be improved by appropriate selection of substrate materials exhibiting surface chemistry favorable to stable bonding of pDA.



Copper films deposited on polydopamine-functionalized polymer substrates demonstrate different mechanical characteristics when subjected to tensile loading. After loading to 5% strain, films on LDPE failed and blistered (right/top) while films on nylon 6,6 remained intact (left/bottom).

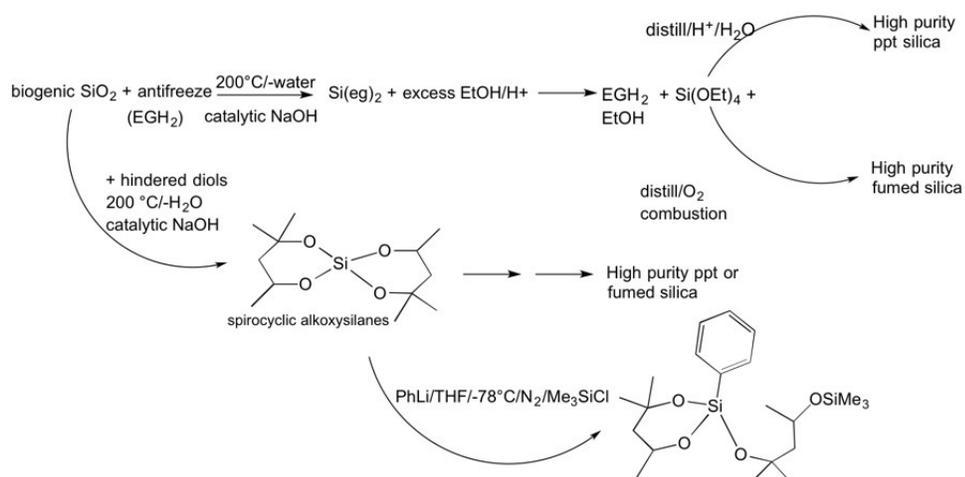
## POLY 9: Escaping the tyranny of carbothermal reduction: Conversion of biowaste silica to alkoxy silanes without using silicon

**Richard M. Laine**<sup>1</sup>, [talsdad@umich.edu](mailto:talsdad@umich.edu), Vera Popova<sup>2</sup>. (1) 2114 Dow, Ann Arbor, Michigan, United States (2) Mayaterials, Ann Arbor, Michigan, United States

Agricultural byproducts used as alternate energy sources generate considerable waste. Harvested rice is milled producing rice hulls that are often burned to generate electricity also producing rice hull ash (RHA). In the U.S. some 100k tons of RHA are produced annually. RHA consists of 70-90 wt % low impurity, high surface area (20-80 m<sup>2</sup>/g) amorphous, porous silica mixed with low impurity, amorphous carbon.

The rice plant does not extract heavy metals from the ground and as such the resulting RHA is relatively pure. Furthermore, it is very easily purified using simple acid extraction to remove small amounts of phosphates and other minor minerals. In this presentation we describe methods of directly depolymerizing RHA SiO<sub>2</sub> to transform it into distillable alkoxy silanes.

\*Michigan Governor's Green Chemistry Award, 2015

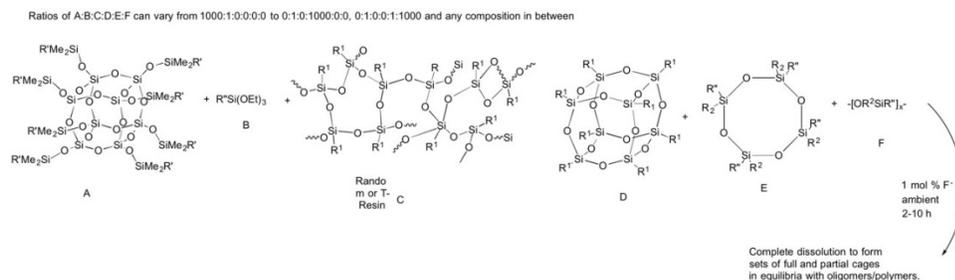


## POLY 10: F<sup>-</sup> catalyzed reactions at silicon as a route to hybrid materials

**Richard M. Laine**<sup>1,2</sup>, [talsdad@umich.edu](mailto:talsdad@umich.edu), Yong Seok Kim<sup>2</sup>, David J. Krug<sup>3</sup>, Joseph C. Fugra<sup>4</sup>, Michael Z. Asuncion<sup>5</sup>. (1) 2114 Dow, Ann Arbor, Michigan, United States (2) Materials Science and Eng, University of Michigan, Ann Arbor, Michigan, United States (3) Macromolecular Science and Eng, University of Michigan, Ann Arbor, Michigan, United States (4) Chemical Eng, University of Michigan, Ann Arbor, Michigan, United States (5) Mayaterials, Ann Arbor, Michigan, United States

We are exploring the use of tBu<sub>4</sub>NF as a means to transform any form of alkoxy silane, Q cage, siloxanes or silsesquioxane (SQ) cages into mixed functional T<sub>10</sub> and T<sub>12</sub> SQs or polymeric solutions as illustrated in the very general scheme shown below.<sup>1</sup> Judicious choice of individual components allows the introduction of a variety of functional groups into SQ cages or the formation of coating systems that provide high temperature stability with control of a wide variety of properties ranging from highly hydrophobic (water contact angles > 120 °C) to materials with controlled refractive indices coupled with thermal stabilities to 350 °C.

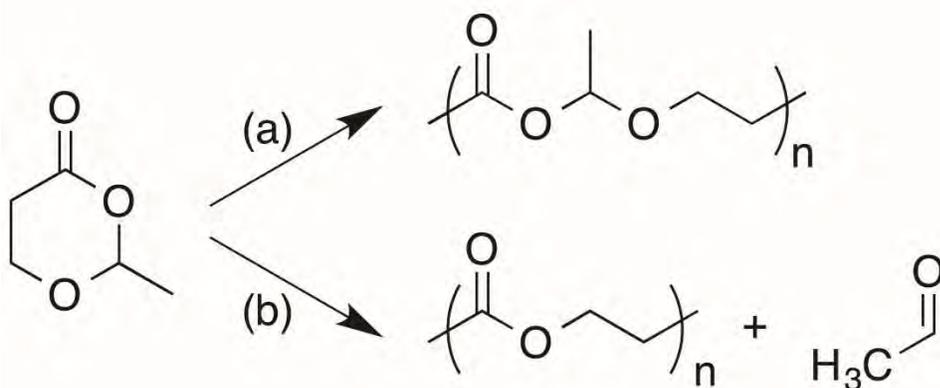
R. M. Laine, C. Soles, D. J. Krug, H. W. Ro, V. Popova, "Silsesquioxane derived hard, hydrophobic and thermally stable thin films and coatings for tailorable protective and multi-structured surfaces and interfaces," U. S. Pat. 8,535,761 Sept. 17, 2014



## POLY 11: Ring-opening polymerization of cyclic hemiacetal esters for the preparation of degradable polymers

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We recently discovered that the ring-opening polymerization of a cyclic hemiacetal ester can lead to polymers containing this acid labile functional group in the backbone of the polymer chain. However, under forcing conditions extrusion of aldehyde competes with this ring-opening process and the cyclic hemiacetal esters can give polyesters that are difficult to otherwise prepare. In this talk I will emphasize our recent work with this class of molecules, discuss mechanistic aspects of the polymerization, and the polymer properties that result.



## POLY 12: Use of cottonseed proteins in adhesive applications

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In this presentation a review is made of the use of cottonseed protein in wood adhesive applications. Both unmodified and modified cottonseed protein isolates were studied and compared to corresponding soy protein isolates for their adhesive properties when bonded to wood composites. Modifications included treatments with alkali, guanidine hydrochloride, sodium dodecyl sulfate (SDS), urea, and others. Wood composites bonded with cottonseed protein exhibited higher shear strength relative to modified or unmodified soy proteins. Cottonseed protein with some modified treatments gave better shear strength than unmodified cottonseed protein. Wood composites bonded with unmodified or SDS-modified cottonseed protein also showed superior retained strengths on a hot water test. Thus, cottonseed protein (with or without modification) seems to be a viable alternative to soy protein for the wood adhesive application.

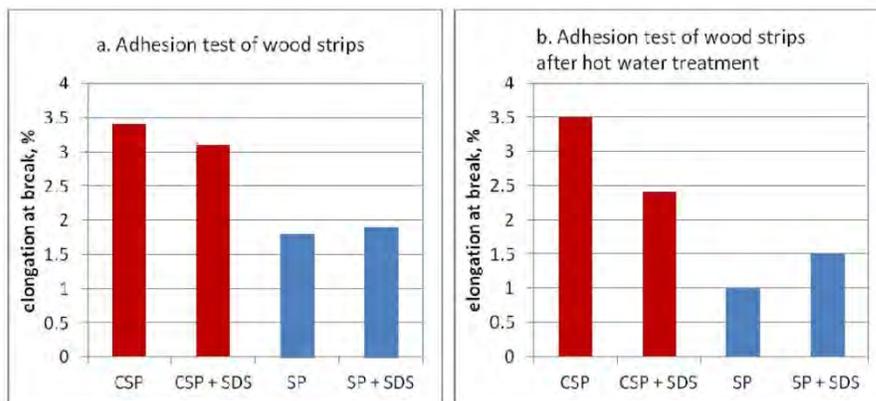


Figure 1. Adhesion test for wood strips bonded with cottonseed protein (CSP) or soy protein (SP), with or without SDS. Strips had 1" x 1" overlap with protein applied, and pressed for 10 minutes at 100°C

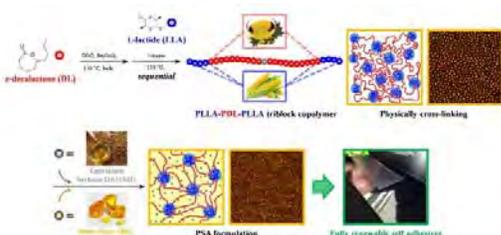
## POLY 13: Fully renewable pressure-sensitive adhesive system

**Sangjun Lee**<sup>1,2</sup>, sangjunlee@ust.ac.kr, Young-Wun Kim<sup>2,1</sup>, Jihoon Shin<sup>2</sup>. (1) Department of Green Chemistry and Environmental Biotechnology, Korea University of Science & Technology (UST), Daejeon, Korea (the Republic of) (2) Center for Biobased Chemistry, Korea Research Institute of Chemical Technology (KRICT), Daejeon, Korea (the Republic of)

Fully Renewable pressure-sensitive adhesive (PSA) systems were established using thermoplastic elastomers (TPEs), tackifier, and plasticizer derived from natural resources such as fatty acid, glucose, rosin, and soybean oil. Through a one-pot, two-step process, controlled bulk ring-opening transesterification polymerization of  $\epsilon$ -decalactone and L-lactide using a dihydroxy initiator and a tin(II) ethylhexanoate catalyst gave ABA type triblock polyesters. We prepared three semi-crystalline poly(L-lactide)-poly( $\epsilon$ -decalactone)-poly(L-lactide) (PLLA-PDL-PLLA) triblocks having molar mass of  $100 \text{ kg mol}^{-1}$  PDL midblock and 10, 20, and  $40 \text{ kg mol}^{-1}$  PLLA end blocks.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy confirmed well defined polymer architectures and molar masses and size exclusion chromatography (SEC) proved precisely controlled molar masses and narrow distributions. Differential scanning calorimetry (DSC) and atomic force microscopy (AFM) were used to infer phase separation between PLLA hard blocks and PDL soft segments. The mechanical behavior of the triblock architectures was investigated by tensile experiments and dynamic mechanical analysis, showing elastomeric behaviors dependent on the molar mass composition and crystallinity of PLLA end blocks in the triblocks. The thermal, viscoelastic, and morphological properties of the elastomers and the adhesive formulations were studied with differential scanning calorimetry, thermal gravimetric analysis, dynamic mechanical analysis, and atomic force microscopy. Probe tack, peel adhesion, and static shear strength tests were performed to evaluate the self-adhesive properties, showing peel strength of  $1.9\text{--}2.6 \text{ N cm}^{-1}$ , probe tack of  $2.2\text{--}3.0 \text{ N}$ , and static shear strength of  $>20 \text{ 000 min}$ . In conclusion, this renewable PSA system could have great potential for sustainability and high adhesive performance.

### References

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2. Ding, K.; John, A.; Shin, J.; Lee, Y.; Quinn, T.; Tolman, W. B.; Hillmyer, M. A. *Biomacromolecules* **2015**, *16*, 2537–2539.
3. Shin J.; Martello, M. T.; Shrestha, M.; Wissinger, J. E.; Tolman, W. B.; Hillmyer, M. A. *Macromolecules* **2011**, *44*, 87–94.



## POLY 14: The PHAome

**Guo-Qiang Chen**, *chengq@biomed.tsinghua.edu.cn*. Tsinghua Univ School of Life Science, Beijing, China

Polyhydroxyalkanoates (PHAs) are a family of polyesters synthesized by bacteria. Similar to the genome, transcriptome or proteome that comprise the entire DNA diverse genetic materials, whole RNA or all proteins expressed at a certain time in one cell or a population of cells, the study of PHAs that exhibit diverse and dynamic arrangements of various monomers is proposed to be called “PHAome”, which is reflected not only by the diverse monomers, homopolymers, random-, block copolymers, functional-, graft polymers, molecular weights and combinations of the above, but also by the whole ranges of PHAs with various molecular weights and monomer ratios at a defined time point in a bacterial cell. Echoing the Materials Genome Initiative launched in 2011 to develop an infrastructure to accelerate advanced materials discovery and deployment, the understanding of the PHAome and the supply of sufficient materials based on it will promote the discovery of new properties and new applications of this family of advanced materials.

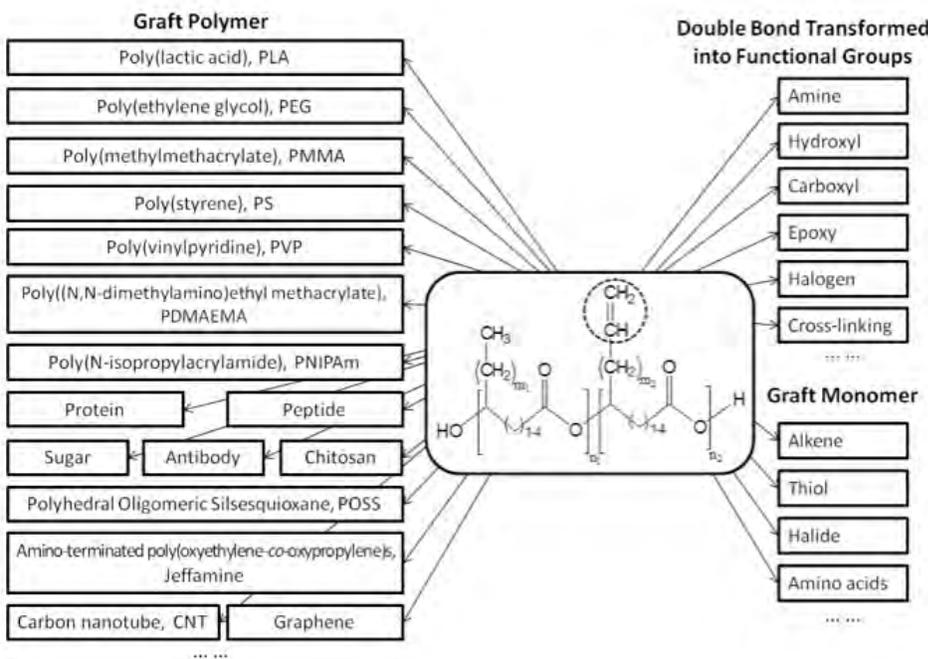
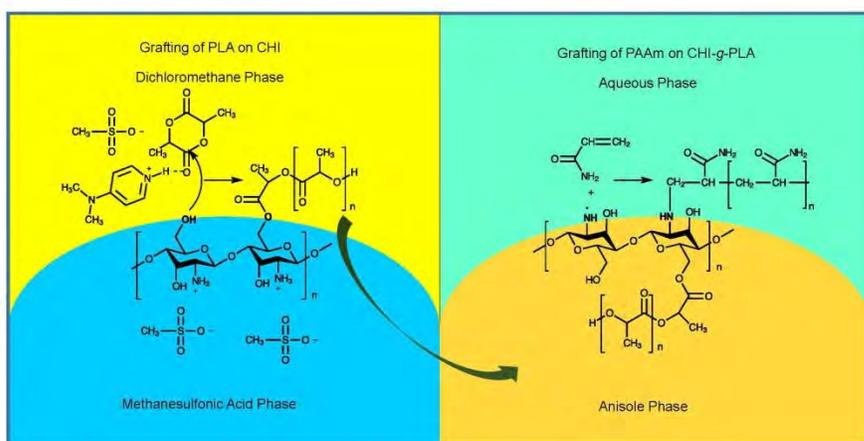


Figure. PHA double bonds on the side chains can be transformed into other functional groups like hydroxyl, carboxyl, epoxy, amides et al. Polymers like proteins, starch, polysaccharides or polystyrene can also be grafted to PHA double bonds. The PHA diversity seems to be limitless.

## POLY 15: Synthesis of hybrid molecular brushes with chitosan backbone in biphasic reaction

**Manasi Chawathe**<sup>1</sup>, *mchawathe@mail.usciences.edu*, **Atithi Pate**<sup>2</sup>, **Sriramakamal Jonnalagadda**<sup>1</sup>, **Alexander Sidorenko**<sup>2</sup>. (1) *Pharmaceutical Sciences, University of the Sciences, Philadelphia, Pennsylvania, United States* (2) *Chemistry and Biochemistry, University of the Sciences, Philadelphia, Pennsylvania, United States*

Hybrid molecular brushes (HMB) are macromolecular constructs consisting of a polymer backbone with side chains with different nature and properties. In this study, HMB composed of polylactide (PLA) and polyacrylamide (PAAm) immobilized on chitosan (CHI) backbone was synthesized. First, grafting of PLA on CHI was performed by ring opening polymerization (ROP) of lactide at room temperature. Methanesulfonic acid and 4-dimethylaminopyridine acted as organocatalysts. Hydroxyl of CHI acted as initiators. ROP was carried out in biphasic system as there is no common solvent for CHI and PLA. This composition allowed us to control the CHI chain degradation. Chemical grafting of PLA on CHI was proven by FTIR and NMR. Chain length and grafting density was estimated by gel permeation chromatography and atomic force microscopy. The product CHI-g-PLA was soluble in polar organic solvents. Grafting of secondary polymer PAAm was done in the course of radical polymerization of acrylamide in emulsion. Amino groups of CHI activated by ammonium persulfate served as initiating sites. The resulting HMB was characterized by atomic force microscopy and dynamic light scattering. HMB may find applications in surface and solubility modifications, as emulsifying agents, wound healing and tissue engineering.



Grafting of PLA and PAAm on CHI backbone in Biphasic Reaction

## POLY 16: Highly porous poly(urethane urea) monoliths from renewable resource polymers through emulsion templating

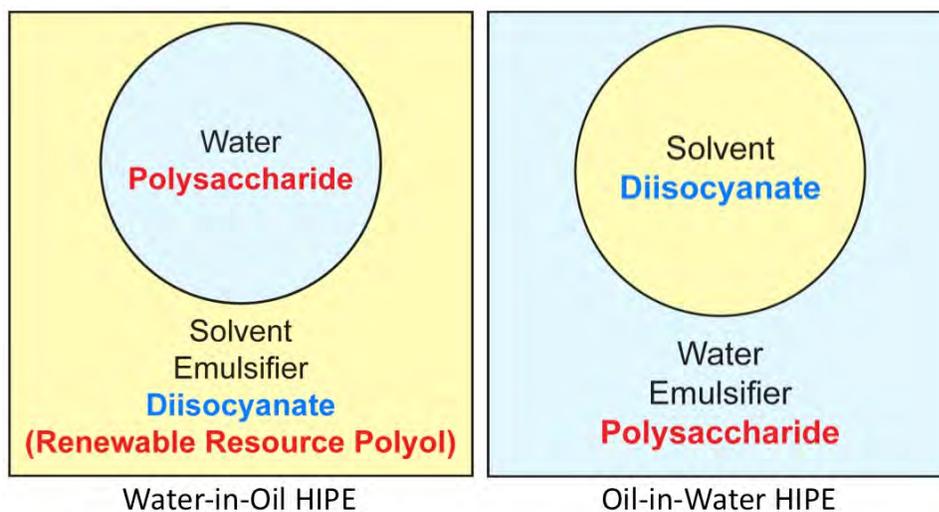
*Tsilil Bialystocki, Liraz Avraham, Inbal Offen, **Michael S. Silverstein**, michael.s@tx.technion.ac.il. Department of Materials Science and Engineering, Technion – Israel Institute of Technology, Haifa, Israel*

PolyHIPEs are highly porous polymers synthesized within high internal phase emulsions (HIPEs). PolyHIPEs are almost always synthesized using free radical polymerization and are almost always crosslinked [1,2]. Biodegradable, crosslinked poly(urethane urea) (PUU) polyHIPEs were synthesized through the step-growth polymerization within water-in-oil (w/o) HIPEs of oligomeric polycaprolactone (PCL) triols [3]. Recent advances in the synthesis of PUU polyHIPEs include non-crosslinked polyHIPEs based upon oligomeric PCL diols, polyHIPEs based on renewable resource polymers (RRPs) (castor oil, polysaccharides), and RRP-based polyHIPEs synthesized within oil-in-water (o/w) HIPEs. Surprisingly, the highly interconnected porous structures of these soluble PUU polyHIPEs were similar to those of typical polyHIPEs. While interfacial polymerization within emulsions is usually used for microencapsulation, here, remarkably, highly porous monoliths were generated. Cell growth studies demonstrated the potential of these polyHIPEs for tissue engineering applications.

[1] Silverstein MS. Prog Polym Sci 2014;39:199-234.

[2] Silverstein MS. Polymer 2014;55:304-320.

[3] David D, Silverstein MS. J Polym Sci A, Polym Chem 2009;47:5806-5814.



Highly porous poly(urethane urea) monoliths containing renewable resource polymers through emulsion templating

## **POLY 17: Biodegradable polymers derived from fatty acids, saccharides and amino acids**

**Abraham (Avi) J. Domb**, *avid@ekmd.huji.ac.il*. School of Pharmacy, The Hebrew University of Jerusalem, Jerusalem, Jeru, Israel

Biodegradable polymers have been used for over five decades as temporary devices and drug carriers to improve human health. These materials should possess specific physical, chemical, biological, functional, biomechanical, and degradation properties that fit the biomedical application at hand.

Biodegradable polymers have been synthesized from natural components: fatty acids, amino acids and saccharides to form compounds with tailored properties that fit the intended application. Injectable pasty polymers were synthesized from castor oil and used for the delivery of agents to diseased sites such as infected bones and solid tumors. Polyesters derived from amino acids have been used as scaffolds for tissue engineering and cationic polysaccharides were used as transfection agents for plasmid DNA and siRNA. Biodegradable balloons have been applied for separation of the prostate from the rectum for irradiation protection and for treating massive rotator cuff tear.

The poster will present the synthesis and characterization of biodegradable polymers and their applications for human wellbeing.

## POLY 18: Biomedical applications of polymers made from natural compounds

Yongguang Jia, Kaojin Wang, Frantz Le Dévédec, Satu Strandman, Marc A. Gauthier, Julien E. Gautrot, **Julian X. Zhu**, [julian.zhu@umontreal.ca](mailto:julian.zhu@umontreal.ca). Chemistry, University of Montreal, Montreal, Quebec, Canada

Natural compounds such as bile acids can be used in the preparation of a variety of new polymers for biomedical and pharmaceutical applications. Bile acids are natural amphiphilic compounds that exist in the gastrointestinal tract. Polymeric biomaterials made of natural compounds are expected to exhibit better biocompatibility and bioacceptance. Medical devices such dental composites and stents can be made of such polymers. Dental monomers have been made from bile acids have shown lower cytotoxicity and lower polymerization shrinkage than the commonly used dental monomers. Homo- and copolymers based on bile acids were found to display tunable mechanical properties and heterogeneous degradation behavior. The main-chain bile acid-based polyesters obtained display typical rubber-like elasticity behaviors with elongation moduli closely matching those of soft tissues such as arteries and cartilage. Multi-shape memory copolymers were prepared through copolymerization. The polymer displayed good shape fixing and recovery in different thermal processing stages over the broad glass transition range, making them useful as functional biomaterials.

### Related Publications:

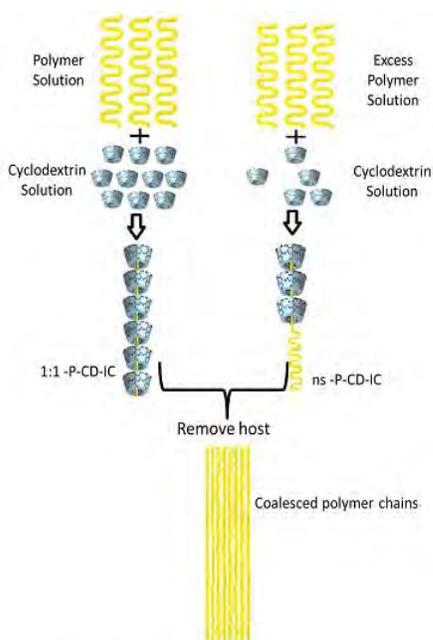
- K. Wang, Y.G. Jia, X. X. Zhu, *ACS Biomater. Sci. Eng.*, **1**, 855, 2015.  
Y.G. Jia, X.X. Zhu, *Chem. Mater.*, **27**, 387, 2015.  
Y.G. Jia, X.X. Zhu, *Langmuir*, **30**, 11770, 2014.  
Y. Shao, Y. Jia, C. Shi, J. Luo, X.X. Zhu, *Biomacromolecules*, **15**, 1837, 2014.  
S. Strandman, I-H. Tsai, R. Lortie, X.X. Zhu, *Polym. Chem.*, **4**, 4312, 2013.  
F. Le Dévédec, S. Strandman, W.E. Baille, X. X. Zhu, *Polymer*, **54**, 3898, 2013.  
F. Le Dévédec, S. Strandman, P. Hildgen, G. Leclair, X. X. Zhu, *Mol. Pharmaceutics*, **10**, 3057, 2013.  
S. Strandman, X. X. Zhu, "Biodegradable shape memory polymers for biomedical applications", Chapter 11 in "Shape Memory Polymers for Biomedical Applications", L. Yahia, Ed., Woodhead Publi, 2015.



## POLY 19: Restructuring polymers for medical devices *via* nano-confinement in and subsequent release from cyclodextrin and urea inclusion compounds

**Alan E. Tonelli**, alan\_tonelli@ncsu.edu. TECS, North Carolina State University, Cary, North Carolina, United States

During the past several years my students and I have been utilizing small-molecule hosts [cyclodextrins and urea] to nanostructure polymers. This is accomplished by first forming non-covalently bonded inclusion complexes (ICs) between these small-molecule hosts and guest polymers, followed by the careful removal of the host molecule crystalline lattice to obtain a coalesced bulk polymer. We have repeatedly observed such coalesced polymer samples to behave distinctly from those produced from their solutions or melts. Coalesced amorphous homopolymers exhibit higher glass-transition temperatures, while crystallizable coalesced homopolymers evidence higher melting and crystallization temperatures, and sometimes different crystalline polymorphs. All the distinct behaviors observed for polymers coalesced from their ICs is a consequence of the structural organization of polymer-host-ICs. Polymer chains in IC crystals are confined to occupy narrow diameter (~0.5 – 1.0nm) channels formed by the crystallization of the small-molecule hosts around the guest polymers. This results in the high extension and separation of guest polymer chains, which leads to unique behaviors for bulk coalesced polymer. In addition, when excess polymer is used to form ICs with CD hosts, non-stoichiometric [(n-s)] ICs, with partially un-included chains, are formed. We will describe several applications of coalescence from their ICs and formation of their (n-s)-ICs for synthetic polymers used in medical devices.

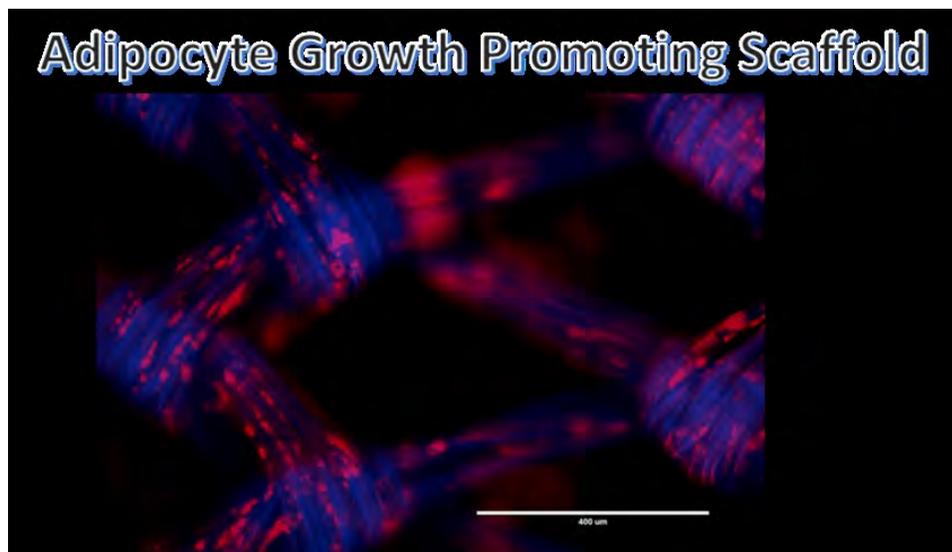


Guest polymers coalesced from their stoichiometric and non-stoichiometric CD-ICs

## POLY 20: Adipomesh a novel adipocyte growth promoting scaffold

Ethan Kallick<sup>1</sup>, Shaohua Li<sup>1</sup>, Ariel Aballay<sup>3</sup>, Howard Edington<sup>2</sup>, **Saadyah Averick<sup>1</sup>**, [saverick@andrew.cmu.edu](mailto:saverick@andrew.cmu.edu). (1) Laboratory for Biomolecular Medicine, Allegheny Health Network, Pittsburgh, Pennsylvania, United States (2) Surgery, Allegheny Health Network, Pittsburgh, Pennsylvania, United States (3) Burn, Allegheny Health Network, Pittsburgh, Pennsylvania, United States

Acute care of third degree burns is challenging due to the extensive damage done to the base layer of skin tissue (i.e. dermal layer). The subcutaneous adipose tissue (i.e. dermal skin layer) has been implicated the burn wound healing cascade and we therefore sought to design a matrix that promoted adipocyte growth and differentiation. Gaining inspiration from the native adipocyte matrix we designed an adipocyte growth promoting coating that can be deployed across a wide variety of substrate and materials to enhance adipocyte growth and differentiation. Initial *in vitro* experiments demonstrate the superiority of our AdipoMesh matrix as a substrate for adipocyte growth and differentiation. Ongoing *in vivo* burn wound healing studies are exploring the potential use of AdipoMesh in acute burn care.

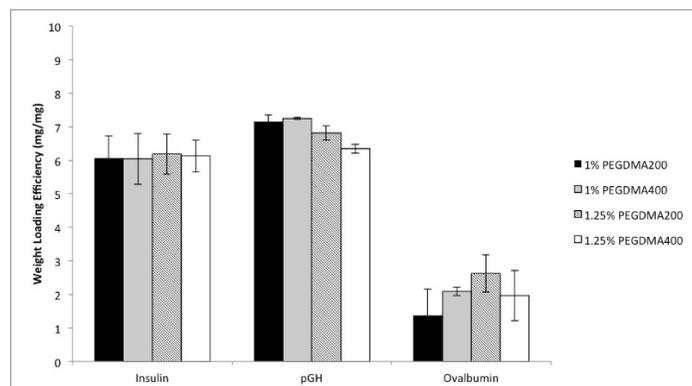


## POLY 21: Optimization of methacrylic acid based pH-responsive hydrogels for the oral delivery of therapeutic proteins

**Stephanie Steichen**, *sdsteichen@utexas.edu*, Colleen O'Connor, Nicholas Peppas.  
The University of Texas at Austin, Austin, Texas, United States

Complexation hydrogels are three-dimensional hydrophilic structures capable of imbibing water and swelling in response to changes in environmental pH. This pH-responsive behavior has been harnessed to develop microparticle carriers for the oral delivery of protein therapeutics. The pH-responsive hydrogel remains collapsed at gastric pH, protecting the protein payload, and only swells to release the protein at intestinal pH, where it can be absorbed. P((MAA-co-NVP)-g-EG), a random copolymer of methacrylic acid (MAA) and N-vinyl pyrrolidone (NVP) with grafted poly(ethylene glycol) tethers, has shown success in the oral delivery of insulin. However, insulin, while still a large biomacromolecule (5.8 kDa), is small relative to other therapeutic proteins such as growth hormone (22 kDa) and ovalbumin (46 kDa). We investigated whether modifying hydrogel properties, such as crosslinking length and density, or optimizing loading conditions, including ionic strength, can improve loading levels of higher molecular weight protein therapeutics.

P((MAA-co-NVP)-g-EG) hydrogel microparticles were synthesized with varying crosslinking lengths (PEGDMA 200 and 400) and densities (1 – 1.25%) and crushed to 30-45  $\mu\text{m}$  microparticles. Protein loading was conducted by swelling the microparticles in a 0.5 mg/mL protein solution for 24 hours at 37°C. Insulin, the smallest protein, loaded at 6% (mg protein/mg particle), whereas pGH, 4 times the size, achieved loading up to 8%. Conversely, ovalbumin, the largest molecule, exhibited loading levels of only 1-2%. Decreasing the ionic strength of the loading buffer maintains the molecular weight trend, but increases overall loading levels by 2-5%. While varying crosslinking length and density can modulate swelling behavior, there was no significant impact on protein loading levels. In addition, these gels show no cytotoxicity and exhibit pH-triggered release of loaded proteins.



Weight loading efficiencies of insulin, pGH, and ovalbumin in P((MAA-co-NVP)-g-EG) hydrogel microparticles (30-45  $\mu\text{m}$ ), calculated as a ratio between the mass of loaded protein and the mass of loaded particles (mg/mg). (N=3)

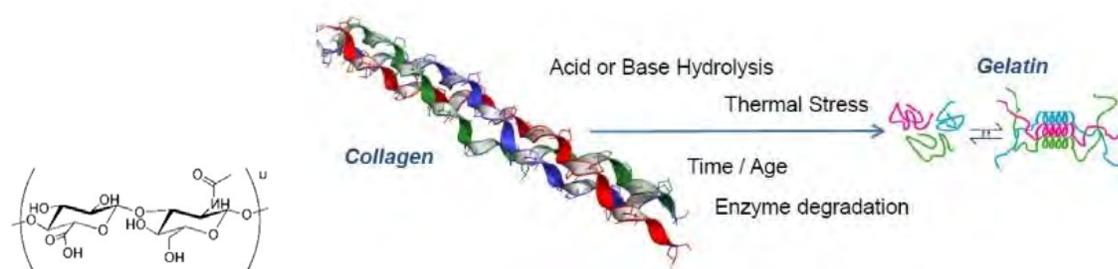
## POLY 22: Characterization of hyaluronic acid and gelatin using asymmetric flow field flow fractionation with advanced detections

**Wei Gao**<sup>2</sup>, [weigao@dow.com](mailto:weigao@dow.com), **Xiaojun M. Liu**<sup>1</sup>, **Xiaodong (David) Lu**<sup>3</sup>. (1) Global R&D, Pfizer, Glen Allen, Virginia, United States (2) The Dow Chemical Company, Collegeville, Pennsylvania, United States (3) Dow, North Wales, Pennsylvania, United States

The physicochemical properties and biocompatibility /biological functions of biopolymers heavily depend on their average molecular weights (MW), molecular weight distributions (MWD), and chain structure in addition to their chemical composition. Detailed understanding of these biopolymers used as medical materials becomes increasingly important in the pharmaceutical, consumer health care and medical device industries.

Hyaluronic acid (HA) or its sodium salt form NaHA, also known as hyaluronan, is an ultrahigh molecular weight naturally occurring polysaccharide. Solutions of intact or degraded forms of HA have been used in ophthalmic surgery, eye care, wound repair, and skin care products. Gelatin is a mixture of peptides and proteins hydrolyzed from collagen, and it has been used in food and pharmaceutical applications. Since the biological or pharmaceutical applications of HA and gelatin are related to their MW and MWD, structure in aqueous solution and in gel form, characterization of these biopolymers has become increasingly critical for product quality and process control in related industries.

In this study, we characterized HA samples from different sources using Asymmetric Flow Field Flow Fractionation (AFFFF) with on-line Multi Angle Light Scattering (MALS), UV spectrometer and differential refractive index detectors. The mass recovery, absolute MW, MWD, radius of gyration, and chain conformation of both HA and gelation were obtained. The results of HA samples used for eye care products are compared with previous results from GPC with advanced detectors. This study concludes that AFFFF is an important complementary separation technique to GPC, especially for biopolymers with ultra large size and /or with strong tendency to interact with GPC columns. The AFFFF also has greater potential to probe polymer conformation difference in different solution and polymer-polymer interactions.

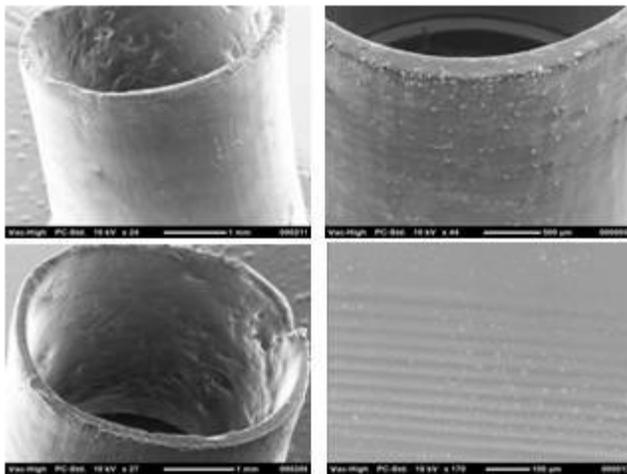


Hyaluronic acid

## POLY 23: 3D printing functional objects with mask projection microstereolithography: Expanding the polymer toolbox

*Justin Serrine, Allison Pekkanen, Nicholas Chartrain, Alison Schultz, Christopher Williams, **Timothy E. Long**, [telong@vt.edu](mailto:telong@vt.edu). Virginia Tech, Blacksburg, Virginia, United States*

Mask projection microstereolithography provides a means to generate a range of polymer structures with tunable surface energies and chemical functionality. Mask projection microstereolithography permits resolution at the dimension of a human cell thus suggesting the opportunity for tunable interactions of scaffolds for tissue regeneration. Our latest efforts involve a focus on the printing of soft networks using ionic liquid monomers in the presence of oligomeric crosslinking agents and photoinitiators. These charged networks offer electrostatic interactions with a range of proteins and nucleic acids. In addition, recent efforts have focused on the 3D printing of poly(ethylene oxide) containing block copolymers and biodegradable polyesters. Polyester design is easily accomplished using melt polycondensation combined with the quantitative introduction of acrylic end groups. This lecture will focus on the design of novel polymers for microstereolithography and a fundamental understanding of the structure-property relationships of the printed objects. Special attention is devoted to a fundamental understanding of the role of the layered 3D printed structure on the tensile and thermomechanical performance of the scaffolds.

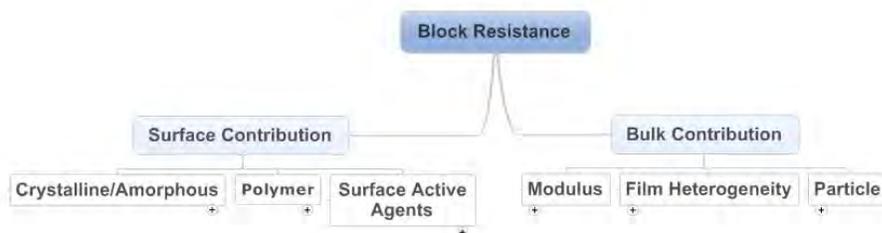


## POLY 24: Additive approach for improving block resistance in coatings

**Partha S. Majumdar**<sup>1</sup>, PSMajumdar@dow.com, Mark R. Winkle<sup>2</sup>, Susan Fitzwater<sup>3</sup>, Michael B. Clark<sup>4</sup>, Arkady Krasovskiy<sup>5</sup>, Scott Ibbitson<sup>1</sup>. (1) Dow Coating Materials, Dow Chemical, Collegeville, Pennsylvania, United States (2) Currently Retired from Dow Chemical, Collegeville, Pennsylvania, United States (3) Currently Retired from Dow Chemical, Ambler, Pennsylvania, United States (4) Core R&D, Dow Chemical, Collegeville, Pennsylvania, United States (5) Core R&D, Dow Chemical, Midland, Michigan, United States

Block resistance, the ability of two coated surfaces to come into contact with each other under pressure and resist sticking, is one of the key performance attributes for waterborne architectural coatings. The reduction in allowable levels of volatile organic compounds in paint has driven the paint formulations to utilize lower  $T_g$  polymers which in turn has further increased the challenge for maintaining or improving block resistance, especially in lower pigment volume concentration coatings which are rich in polymer.

An additive approach for improving block resistance was investigated to address this need. Types of potential block additives explored included fluorocarbon surfactants, hydrocarbon surfactants, crystalline materials, silicone additives, nanoparticles, and water dispersible polymers. High-throughput methodology and conventional bench-top techniques were used to understand the interactions between block additive, polymer, and formulation variables. Surface analyses of selected coatings were carried out using Secondary Ion Mass Spectrometry (SIMS) and X-Ray Photoelectron Spectroscopy (XPS). Migration of the additive to the film-air interface and formation of a uniform layer was critical for improving the block performance. The relative compatibilities between block additives and polymer were determined using molecular modeling since this has a major impact on additive migration. For fluorocarbon and hydrocarbon surfactants, the anionic head group and the chain length of the tail group had a strong influence on migration. However, migration of the additive to the surface was not the only criteria to improve the block resistance of the coating. SIMS and XPS results showed that fluorine substituted silicones and polydimethyl siloxanes investigated in this study could stratify at the surface without enhancing block resistance.



## **POLY 25: New polymer materials for additive manufacturing and understanding failure modes**

**Rigoberto C. Advincula**, [rca41@case.edu](mailto:rca41@case.edu). *Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio, United States*

High value adding is important for industry which focuses on solutions and market needs. In additive manufacturing and 3-D printing, there has been significant advances in fabrication methods and instrumentation over the years, however, the quest for materials with superior properties for actual parts manufacturing and high performance applications is a constant need. It is important to understand the limitation of 3-D printable materials and why they are not able to perform as functional applications which can compromise their thermo-mechanical integrity. Here we focus on methods and materials development for new polymers and nanocomposites that can be used for 3-D printing. This includes FDM and SLA Methods. We demonstrate the use of polyurethane/PC blends and graphene nanocomposites for FDM and crosslinkable functional monomers for SLA.

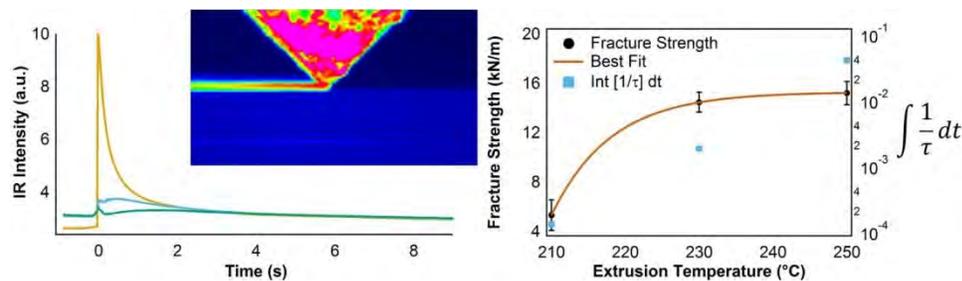


## POLY 26: Fundamental characterization of soft matter 3D printing processes

**Jonathan Seppala**<sup>1</sup>, [jonathan.seppala@nist.gov](mailto:jonathan.seppala@nist.gov), **Kaitlyn E. Hillgartner**<sup>2</sup>, **Chelsea S. Davis**<sup>1</sup>, **Kalman Migler**<sup>1</sup>. (1) Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, Maryland, United States (2) Chemical and Biological Engineering, Colorado School of Mines, Golden, Colorado, United States

3D printing is an important and disruptive production method. In traditional manufacturing techniques customize tooling for a given part requires a large initial investment which is offset by large volume production. In 3D printing no tooling investment is needed and per unit productions costs are flat, which is a huge boon for individualized production. This is especially important in the medical industry where many devices are custom designed for the individual. Although interest in 3D printing seems recent, development has been ongoing for a few decades. 3D printing is now at a point where research and development can focus on understanding and improving the process at a fundamental level.

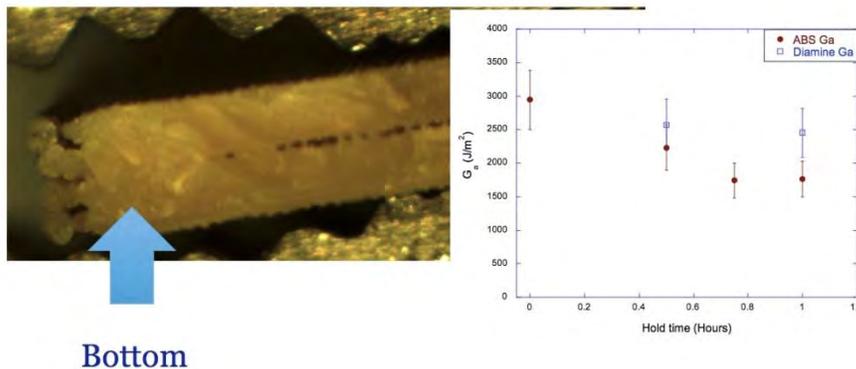
In fused filament fabrication (FFF), a material extrusion 3D printing method, thermoplastic filament is extruded through a rastering nozzle on the previous layer. The resulting strength of the FFF produced part is limited by the strength of the weld between each layer. While numerous factors can affect the weld strength, the temperature of the extrudate and the previous layer dictate the amount of interdiffusion and thus the weld strength. Temperature measurements were performed using forward looking infrared imaging. Interdiffusion estimates were calculated from temperature profiles, normalized using horizontal shift factors from offline rheological measurements of the neat polymer. Weld strength was measured directly by Mode III Fracture using a simplified geometry limiting the measurement to a single weld. Since the processing conditions are known apriori this approach provides the data needed to estimate the final build strength at time of design. The resulting agreement between interdiffusion estimates and weld strength for a range of printing conditions are discussed.



## POLY 27: Improving inter-filament interlayer interfaces in 3-D printing of polymers

Edward Duranty<sup>1</sup>, Neiko Levenhagen<sup>1</sup>, Madeline Stark<sup>1</sup>, **Mark D. Dadmun**<sup>1,2</sup>, dad@utk.edu. (1) Univ of Tennessee, Knoxville, Tennessee, United States (2) Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States

Three-dimensional printing (3DP) of polymer structures is an established platform that has demonstrated the potential to revolutionize the manufacturing of ultra lightweight vehicles and vehicle components. Despite the advances in the field, the performance limitations of 3DP are primarily associated with the formation of interfaces and defects, which in turn result in weak bond strength between the successively deposited polymer layers. This anisotropic behavior dramatically limits the widespread use of 3D printing, thus the amount of interfacial contact and interdiffusion between filaments become important parameters that control the macroscopic physical properties of the printed prototype. Moreover, in the scale-up of 3-D printing, the underlying filaments can cool by the time the printer head returns to deposit the overlaid layer, which dramatically inhibits the inter-filament bonding process between layers. The result is generally a structure with poor inter-layer filament adhesion and integrity. Our current research focuses on developing methods to improve the interfacial bonding between filaments by material design and by post-deposition modification of the underlying filament in large area 3-D printing of polymers. We will also report work in our group that seeks to quantify the interfacial adhesion between filaments and its impact on structural properties, to provide fundamental insight into the effectiveness of various interfacial modification protocols on the 3-D printing process.



## **POLY 28: Patterning methods for flexible electronics: A startup company in a startup industry**

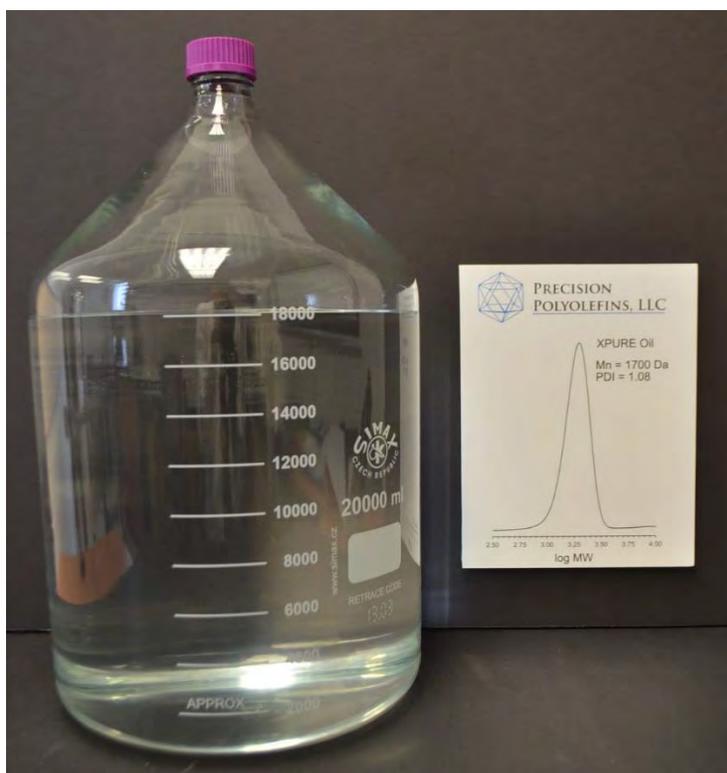
**Christopher K. Ober**, *cko3@cornell.edu. Cornell Univ, Ithaca, New York, United States*

Flexible electronics is a rapidly evolving technology whose goal is to provide low cost printable electronics in a flexible format. It has led to the e-book reader and new display formats and is currently being evaluated as the basis of low cost medical sensors and for smart bandages. Organic semiconductors are an important materials option for flexible electronics, but to date there exist limited lithographic tools for patterning such materials. To solve this problem, Orthogonal, Inc. developed a new type of photoresist based on immiscible fluorinated materials that could be developed in environmentally benign fluorinated solvents. This presentation will describe the invention of orthogonal photoresists and the first stage challenges of taking these concepts to a commercial product.

## POLY 29: PPL (the smallest polyolefins company in the world) - from start-up to scale-up

**Lawrence R. Sita**, *Isita@umd.edu*. Univ of Maryland, College Park, Maryland, United States

With a global production volume of over 140 million metric tons per year, polyolefins are not only one of the most successful classes of commodity polymers ever devised, but civilization and the quality of life as we know it, will be dependent upon these materials far into the future. Not surprisingly, new market opportunities for polyolefins are typically dominated by big business, and accordingly, a fair question to ask is whether a start-up company in this field can be successful. In partial response, this talk will present a progress report on Precision Polyolefins, LLC (PPL) - a university spin-out company that is commercializing a transformational new technology - living coordinative chain transfer polymerization (LCCTP) - that, for the first time, provides access to practical quantities of a large variety of new fundamental forms of polyolefins of tailored molecular structure, tunable molecular weights and very narrow molecular weight distributions from traditional olefin feedstocks. Most notably, PPL has recently validated LCCTP on a pilot-scale within commercial reactors for production of new classes of ultra-low molecular weight 'n-PAO' base stock oils and of high molecular weight polypropylene-based thermoplastic elastomers.



## **POLY 30: Path to an early stage material science start-up company**

**Gabriel G. Rodriguez-Calero**, *ggr@ecolectro.com. Ecolectro , Ithaca, New York, United States*

Ecolectro Inc. was founded in June 2015 to commercialize high performance polymers for sustainable technology applications. In this presentation I will discuss the company's trajectory from pre-incorporation until today. This discussion will include, the idea, securing funding, recruiting personnel and developing technology with limited resources. Furthermore, the presentation will provide some insights into what are the challenging and rewarding aspects of starting a company at the early stages.

## **POLY 31: Performance without permanence: Recyclable thermosets & the future of energy efficient transportation**

**Stefan Pastine**, *stefan@connoratech.com. Connora Technologies, Hayward, California, United States*

In order to meet future efficiency goals, the transportation industry must make vehicles lighter. However, the high-performance thermoset composites needed to meet this goal are simply not recyclable. Environmental implications aside, this is a problem because the cost of carbon fiber composites remains artificially high due to the inability to recycle manufacturing waste.

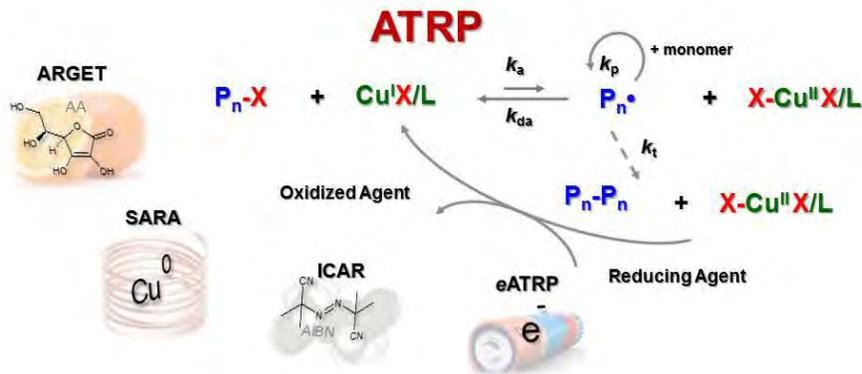
Connora Technologies was founded to solve this problem for OEMs. We supply a molecular technology to manufactures, called Recylcamine®, which gets implemented into the thermoset design. Now, when a composite product is made, all of the production waste can be recycled and implemented back into the manufacturing ecosystem, decreasing the overall cost of the product.

A personal perspective will be provided about the path from scientist to entrepreneur, and innovation in the high-volume chemical industry. Additionally, a general overview of Recyclamine® technology will be presented, including the underlying chemical principals that enable commercially-viable recyclable thermosets.

## POLY 32: Commercial aspects of atom transfer radical polymerization

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

ATRP (atom transfer radical polymerization) is a versatile controlled radical polymerization procedure employed to prepare new block, gradient, graft, star, brush and branched functional copolymers that find applications as various new advanced functional nanostructured materials. Some examples of commercial applications of ATRP in large and small companies will be presented.

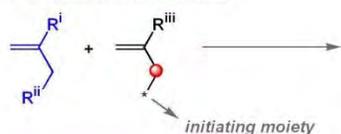


## POLY 33: Synthesis and applications of redox-responsive highly branched polymers

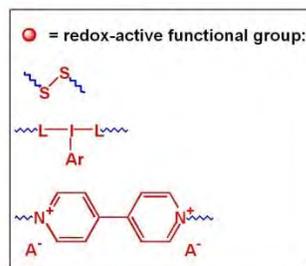
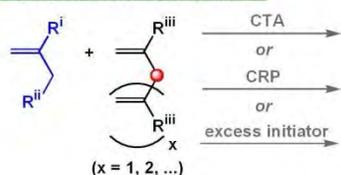
**Nicolay V. Tsarevsky**, [nvt@smu.edu](mailto:nvt@smu.edu), Hongzhang Han, Houliang Tang, Zhaoxu Wang, Shannon R. Woodruff. Department of Chemistry, Southern Methodist University, Dallas, Texas, United States

Highly branched polymers containing multiple branching point redox-active functional groups, including disulfide, viologen, and hypervalent iodine(III) have been successfully synthesized by the homo- and copolymerization of the corresponding functional inimers under controlled/living radical polymerization (CRP) conditions, or by the homo- and copolymerization of functional divinyl monomers (crosslinkers) in the presence of efficient transfer agents (CTAs), excess of radical initiators, or compounds able to reversibly deactivate the propagating chains. All mentioned synthetic techniques as well as applications of the produced materials will be illustrated. For example, viologen-containing branched polymers are useful both as components of electrochromic devices (due to the color change, which accompanies the reduction of viologens to the corresponding radical-cations) and as catalysts of redox reactions; polymers with disulfide groups are degradable upon reduction with phosphines and thiols, and are useful in the drug delivery field; and those with hypervalent iodine(III) groups can exchange their building blocks but can also degrade irreversibly in the presence of reducing agents or monocarboxylic acids.

### (Co)polymerization of inimers



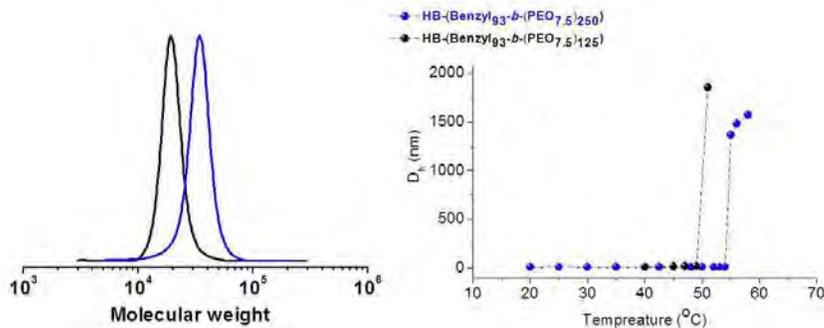
### (Co)polymerization of crosslinkers



## POLY 34: Thermoresponsive hyperbranched polymers with low polydispersity and segmented structure

Yi Shi, **Haifeng Gao**, [gaohaifeng1@gmail.com](mailto:gaohaifeng1@gmail.com). Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana, United States

This talk presents our recent synthesis of hyperbranched polymers with uniform structure and multiple functionalities using one-pot chain-growth CuAAC polymerization of AB<sub>2</sub> monomers. Sequential addition of monomers with various compositions in the one-pot synthesis produced hyperbranched polymers with spherical shape and segmented structure. When hydrophilic monomers that contained water-soluble groups were added in the last step, the produced hyperbranched polymers showed thermo-responsiveness with sharp size transition and flexible tunability of the lower critical solution temperature (LCST).

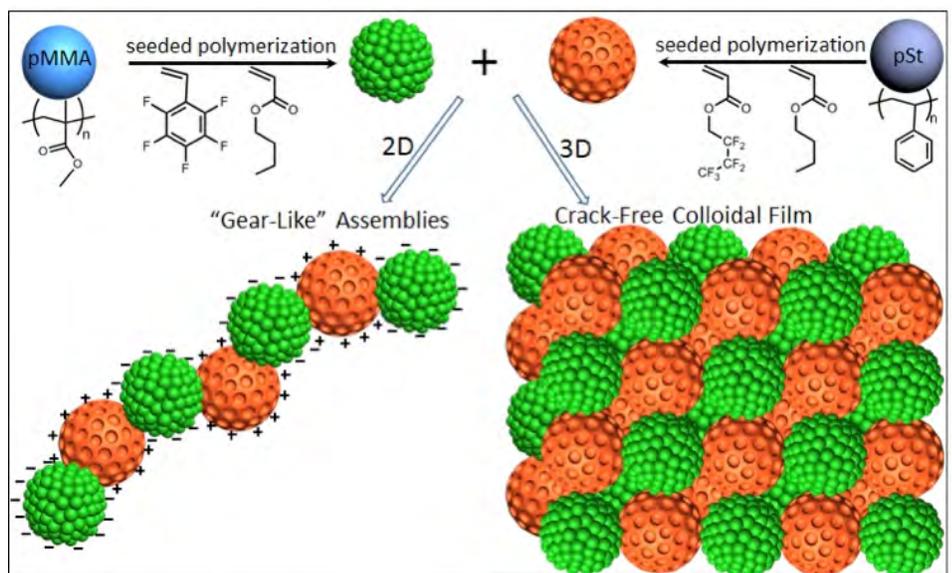


Molecular weight and thermoresponsiveness of hyperbranched polymers with segmented structures

## POLY 35: Stimuli-responsive gibbous and inverse-gibbous colloidal nanoparticles in gear-like assemblies

Chunliang Lu, **Marek W. Urban**, [mareku@clmson.edu](mailto:mareku@clmson.edu). Material Sci Engineering, Clemson University, Clemson, South Carolina, United States

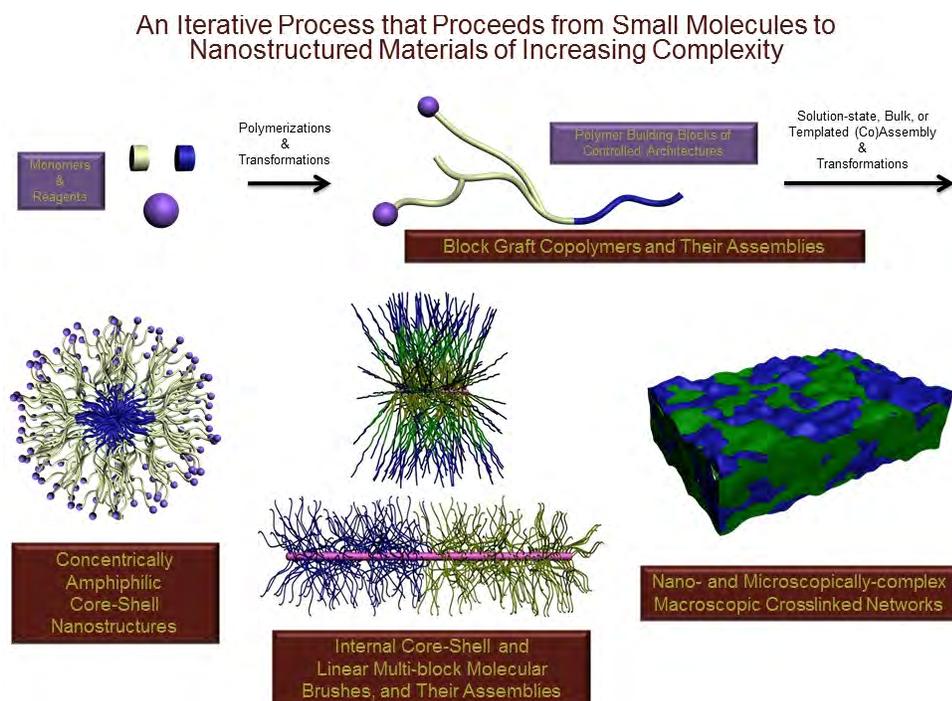
Due to the absence of anisotropic directional bonds, the most challenging and intriguing aspects of nanoparticle assemblies is encoding directionally guided assemblies. Typically, van der Waals, electrostatic, depletion and DNA hybridization, and other forces, were utilized. Other examples are “lock-and-key” shape matching colloids resulting in the higher organized structures. In these studies we took advantage of the localized phase separation and surface tension differences within hydrophobic-hydrophilic environments of colloidal particles and produced water dispersible gibbous and inverse-gibbous colloidal nanoparticles. The topography-matching nanoparticles stabilized by opposite charges are capable of forming “gear-like” directional assemblies due to short-range electrostatic interactions and long-range “gear-like” mechanical interlocking. Guided by surface charges, these stimuli-responsive nanoparticles form 2D directional arrays. Upon surface deposition, 3D colloidal structures develop, resulting in critical for many applications crack-free colloidal films.



## POLY 36: Stimuli-responsive polymers, nanostructures and macroscopic crosslinked networks

**Karen L. Wooley**, [wooley@chem.tamu.edu](mailto:wooley@chem.tamu.edu). 3255 TAMU, Texas AM University, College Station, Texas, United States

We have a keen interest in the development of synthetic methodologies that allow for the preparation of well-defined, reactive polymers and their transformation, *via* combinations of supramolecular and covalent chemistries, into complex functional assemblies on the molecular-to-nanoscale-to-microscopic-to-macroscopic dimensions. This presentation will highlight recent advances.

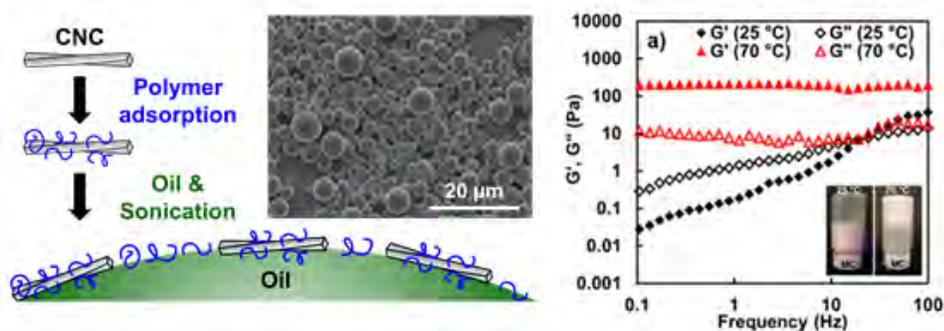


## POLY 37: Responsive and “switchable” cellulose nanocrystal hybrid materials

Zhen Hu, Kevin H. Kan, **Emily D. Cranston**, [ecranst@mcmaster.ca](mailto:ecranst@mcmaster.ca), Robert H. Pelton.  
Chemical Engineering, McMaster University, Hamilton, Ontario, Canada

By learning from nature and using bio-based components, we can engineer sustainable high-performance materials with improved functionality. Cellulose nanocrystals (CNCs) are biocompatible and renewable nanoparticles which have an intermediate hydrophilicity, high mechanical strength and a large aspect ratio. This work explores using responsive CNCs as flocculants, rheological modifiers and emulsion stabilizers. To impart responsive behavior, CNCs were surface-modified using polymer “grafting-from” or polymer adsorption methods; all reactions are one-step and water-based with the goal of developing industrial feasible modification routes and applications.

In the first example, CNCs were functionalized using “grafting-from” free radical polymerization in water with either 4-vinyl pyridine or N-isopropyl acrylamide monomers, using ceric ammonium nitrate as the initiator. The resulting pH and temperature responsive CNCs have potential as flocculants and rheological modifiers in a variety of products. Secondly, the temperature responsive polymer methylcellulose (MC) was physical adsorbed to CNCs which improve the surface activity and wettability of CNCs. MC-coated CNCs can stabilize oil-in-water emulsions and when excess MC is added, thermoresponsive “emulsion gels” arise. The emulsions are extremely stable over long time periods (> 1 year) and multiple heat-cool cycles and the droplet size can be tailored by varying the ratio of polymer to cellulose. These emulsions can further be dried to give “oil powders” which are redispersible and may have applications in food, cosmetic and pharmaceutical formulations.



## POLY 38: Macromolecular structure and aggregate response in block copolymer solution assemblies

**Robert B. Grubbs**, [robert.grubbs@stonybrook.edu](mailto:robert.grubbs@stonybrook.edu), Zhe Sun. State University of New York, Stony Brook, New York, United States

The control over structure facilitated by modern synthetic techniques enables control over the assembly of molecules and macromolecules in functional materials. We have designed and synthesized several classes of block and star-block copolymers with stimulus-responsive components. These polymers form assemblies with shapes and sizes 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. Transitions to and from worm-like micellar assemblies have also been identified. The structural shifts in these systems under specific conditions will be discussed. A number of factors, including block size and extent of interblock interactions, appear to be important in controlling transformation rate (Figure 1). We will describe the design of these and other systems and our efforts to better understand the behavior of the resulting polymer assemblies.

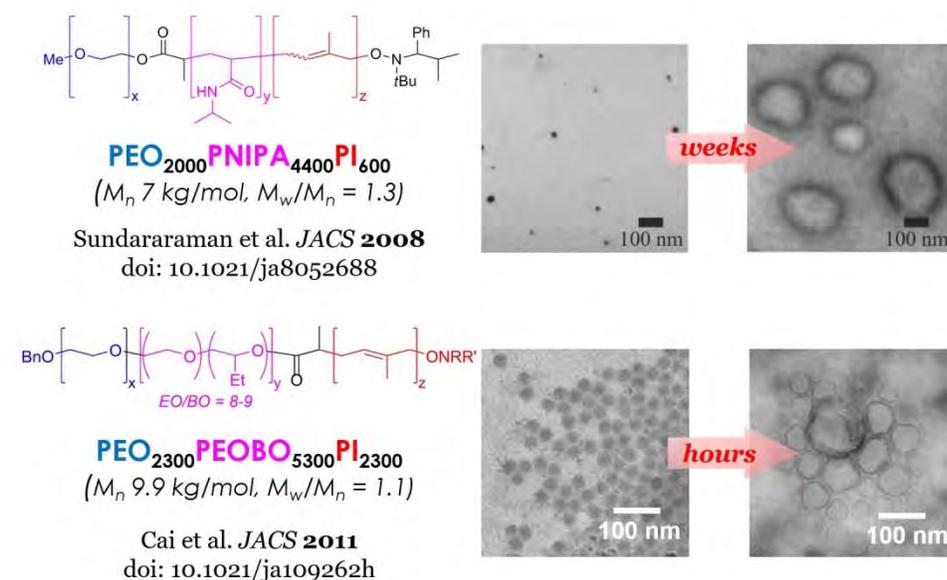


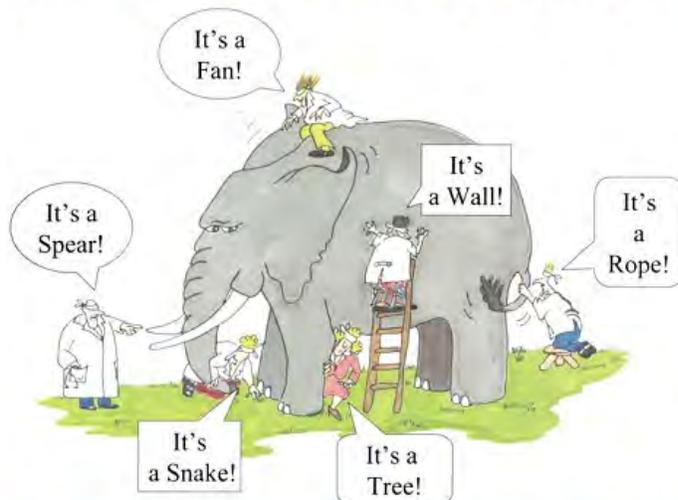
Figure 1. Effect of triblock copolymer structure on micelle-to-vesicle transition rate.

## POLY 39: Macrostructures: How can we characterize the complete chain architectures of polymers?

Rana Gurarslan, **Alan E. Tonelli**, alan\_tonelli@ncsu.edu. TECS, North Carolina State University, Cary, North Carolina, United States

We need only look at the one-to-one correspondence between the primary structures and biological functions of proteins to recognize a similar need to characterize individual chain architectures, *i.e.*, complete macrostructures, of synthetic polymers. Currently the best method for characterizing polymer microstructures is provided by high resolution  $^{13}\text{C}$ -NMR of polymer solutions, which may be sensitive to microstructures encompassing 1 or 2nm of the polymer backbone. However, because of the short-range sensitivity of NMR and other spectroscopic probes, they can only identify and quantify local micro-structures, but are unable to locate them along the polymer chain. This situation is akin to only being able to determine the composition and possibly the amounts of neighboring amino acid pairs or triplets in proteins, rather than their complete primary structures. Any potential experimental probe of synthetic polymer macrostructures must be sensitive to their complete chain architectures, including the types, quantities, and locations of shorter-range microstructures. The Kerr effect, or birefringence electrically induced in dilute polymer solutions, results from the magnitudes and directions of the overall macroscopic dipole moments and anisotropic polarizability tensors of polymer chains and are highly sensitive to their macrostructures. Because potential complete chain macrostructures are virtually innumerable,  $^{13}\text{C}$ -NMR is used to determine the types and amounts of short-range microstructures, and agreement between observed and calculated Kerr effects are used to locate them.

### Cautionary note: tools can bias the perspective



$^{13}\text{C}$ -NMR can identify and quantify body parts, and Kerr-Effect observations can locate them.

## POLY 40: NMR study of the separation mechanism of polyethylene-octene block copolymer by HT-LC with graphite

**Zhe Zhou**, [zzhou@dow.com](mailto:zzhou@dow.com), M. D. Miller, D. Lee, Rongjuan Cong, C. Klinker, T Huang, C. Li Pi Shan, W. Winniford, A. DeGroot, L. Fan, T. Karjala, Kebede Beshah. The Dow Chemical Company, Freeport, Texas, United States

High temperature liquid chromatography (HT-LC) [1][2] and temperature gradient interaction chromatography (TGIC) [3] using a graphite substrate were recently invented to characterize polyolefin microstructures and composition distributions. Their separation mechanisms have been explored by using a series of random copolymers.[4] In addition, the separation mechanism of TGIC for random copolymers was also studied with a high temperature NMR cryoprobe.[3] The proposed separation mechanism for a random copolymer is that the separation is likely based on comonomer content manifested as average ethylene sequence length. Further understanding of HT-LC separation mechanism with polyethylene-octene block copolymers is beneficial in order to extend the use of HT-LC and TGIC to a wider variety of polyolefin materials, and to better characterize more challenging microstructures of new materials. With the high temperature NMR cryoprobe technology,[5][6] it is possible to perform  $^{13}\text{C}$  NMR of polyolefins with a few milligrams of sample. This paper summarizes the NMR study of the materials obtained from preparative scale HT-LC on a polyethylene-octene block copolymer with a high temperature NMR cryoprobe. The results show unambiguously that the HT-LC separation of polyethylene-octene block copolymer is mainly based on the interaction between hard block and the stationary phase, and the strength of the interaction is correlated to the total length of the hard block in the block copolymer.

[1] Miller, M. D. et al., 2011, J. Appl. Polym. Sci., 123, 1238.

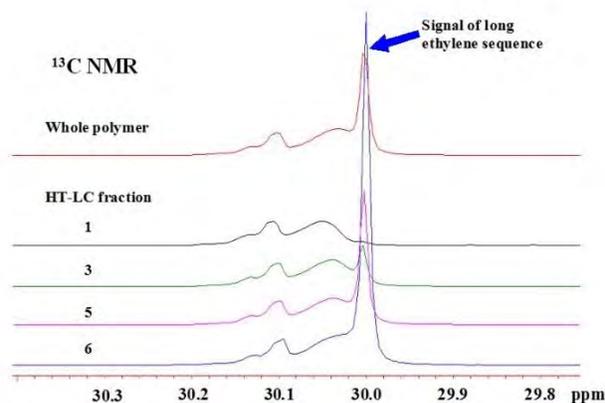
[2] Macko, T. et al., 2011, Anal. Bioanal. Chem., 399, 1547.

[3] Cong, R. et al., 2011, Macromolecules, 44, 3062.

[4] Mekap, D. et al., 2014, Macromolecules, 47, 7939

[5] Zhou, Z. et al., 2009, J. Magn. Resonance, 200, 328.

[6] Zhou, Z. et al., 2009, Macromolecules, 42, 2291.

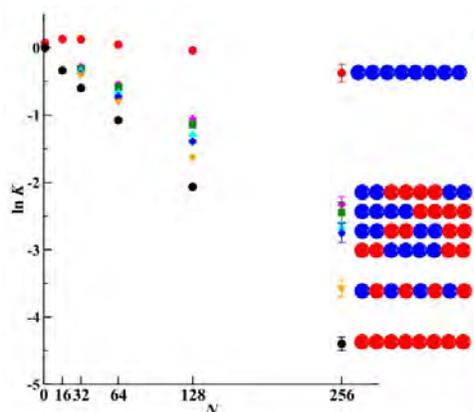


## POLY 41: Monte Carlo simulations of copolymers in liquid chromatography at the critical condition utilizing different pore shapes

**Kimberly N. Struk**<sup>1</sup>, *struk011@umn.edu*, Madeline Hoffmann<sup>1</sup>, Mark R. Schure<sup>2</sup>, Joern I. Siepmann<sup>1,3</sup>. (1) Chemistry and Chemical Theory Center, University of Minnesota, Minneapolis, Minnesota, United States (2) R&D, Kroungold Analytical, Inc., Blue Bell, Pennsylvania, United States (3) Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota, United States

Liquid Chromatography at the Critical Condition (LCCC), is often used for analysis of block copolymers where solvent conditions are chosen to minimize the molecular weight dependence of one of the blocks upon retention ("the critical condition").<sup>1</sup> In this work, Gibbs ensemble Monte Carlo simulations are used to examine the effect of monomer sequence on retention in LCCC. The freely-jointed copolymer chains consist of two monomer types: athermal (A) and critical condition (B). Partitioning between a mobile phase and a spherical or cylindrical pore is examined for linear polymers in five sequences: alternating, diblock, both triblocks, and tetrablock. Furthermore, the partitioning of copolymers with 3, 4, or 5-arm star or H architectures is studied, and the limitations of using LCCC to characterize the molecular weight of copolymers assembled from polydisperse homopolymers are explored. It is shown that a small molecular weight dependence remains at the critical condition which implies that there is no true critical condition where the dependence of retention on molecular weight is zero for any architecture. This suggests that polymer separations can be optimized by finding a near-critical condition, but likely not adhered to over a large molecular weight range found in some polymer samples. The retention order of the copolymers depends on the monomer sequence in both linear and H architectures and multiple B blocks exhibit cooperative adsorption in the nonlinear architectures; hence, the copolymer partition constants all deviate from values determined assuming additive free energies of transfer calculated from the partition constants of the homopolymer chains. The elution order does not differ between spherical and cylindrical pores, but a spherical pore of the same diameter yields greater separation.

<sup>1</sup>Strigel, A. M.; Yau, W. W.; Kirkland, J. J.; Bly, D. D. *Modern Size-Exclusion Liquid Chromatography*, Second Edition; Wiley 2009.



## POLY 42: Structure and properties of crystalline-crystalline block copolymers prepared by living organometallic catalysts

**Rocco Di Girolamo**<sup>4</sup>, [rocco.digirolamo@unina.it](mailto:rocco.digirolamo@unina.it), **Claudio De Rosa**<sup>2</sup>, **Finizia Auriemma**<sup>5</sup>, **Giovanni Talarico**<sup>3</sup>, **Chiara Santillo**<sup>4</sup>, **Ivana Pierro**<sup>4</sup>, **Claudia Ciocce**<sup>4</sup>, **Geoffrey W. Coates**<sup>1</sup>. (1) Cornell Univ, Ithaca, New York, United States (2) Univ of Napoli Dept of Chem, Via Cintia Naples, Italy (3) Dept. of Chemical Sciences, University of Naples Federico II, Naples, Italy (4) Chemical Sciences, Università degli Studi di Napoli Federico II, Naples, Italy (5) Università di Napoli Federico II, Napoli, Italy

The structure, the morphology and mechanical properties of crystalline block copolymers formed by polyethylene (PE) block linked to isotactic polypropylene (iPP) or syndiotactic polypropylene (sPP) blocks are presented. Samples of polyethylene-*block*-syndiotactic polypropylene (PE-*block*-sPP) and polyethylene-*block*-isotactic polypropylene (PE-*block*-iPP) crystalline-crystalline block copolymers with different block lengths have been synthesized by using living, stereoselective polymerization catalysts (Figure 1).

A detailed structural characterization has been performed on both block copolymers for samples crystallized in the bulk, thin films and stretched fibers and stress-induced phase transformations have been analysed.

PE-*block*-sPP samples have been epitaxially crystallized onto crystals of *p*-terphenyl (3Ph) to achieve a control over the crystallization of both blocks and study the dependence of the thin film morphology on the sequential crystallization of the two blocks by cooling from the melt. Ordered nanostructures where the two blocks are organized in separated alternating lamellar domains guided by the orientation of the crystalline lamellae are obtained. We demonstrate that, tuning the block length and using a specific substrate, it is possible to control the crystallization process and obtain large-sized, well-oriented lamellar microstructures with long range order achieved over the area in contact with the crystalline substrate.

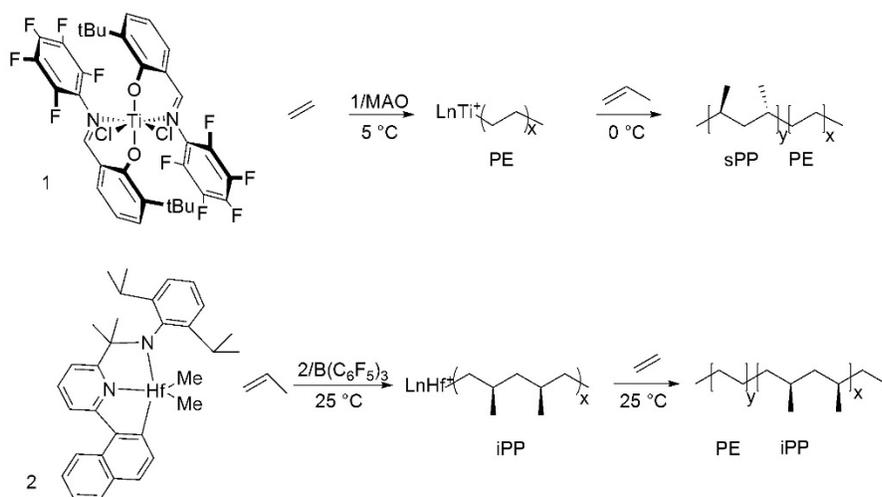
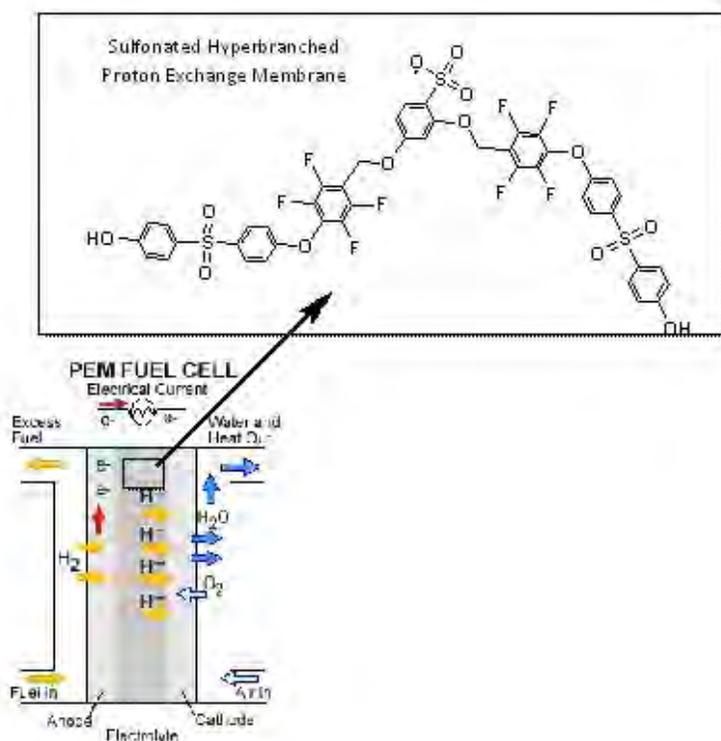


Figure 1. Structure of catalysts used for the preparation of the PE-sPP and PE-iPP block copolymers and sequential polymerization procedure.

## POLY 43: Thermal and mechanical properties of linear ABC polymers for application in proton exchange membranes

**Cassandra Hager**, *cassandrahager@gmail.com*, Matthew Quast, Anja Mueller.  
Chemistry, Central Michigan University, Lake, Michigan, United States

At the forefront of fuel cell research is the design of a hydrogen-powered fuel cell. The problem with this type of fuel cell is the lifetime and performance of the proton exchange membrane (PEM) used in energy conversion. Traditional PEMs require hydration in order for proton transport to occur. With water being present within the system, the catalyst, used for the generation of energy, will degrade faster leading to a lower output of energy and a shorter operating period. A solution is to formulate an anhydrous, tough, yet chemically resistant membrane that would not be restricted by hydration requirements in order to remain operational. The polycondensation of three different monomers were used to produce an ABC polymer to create such a membrane. The polymer was prepared from the polycondensation of the monomers 1,3-bis[(pentafluorobenzyl)oxy]benzene (PFBB), sulfonated-1,3-bis[(pentafluorobenzyl)oxy]benzene (S-PFBB), and Bisphenol-S. Different ratios of PFBB and S-PFBB to bisphenol-S were used to study the hydrophobicity and phase separation effects on thermal and mechanical properties, and proton transport of the resulting polymer membrane. The resulting physical and chemical properties of the membranes will be presented.



## POLY 44: Innovative TG-GC-MS methods for thermal degradation studies of polymers

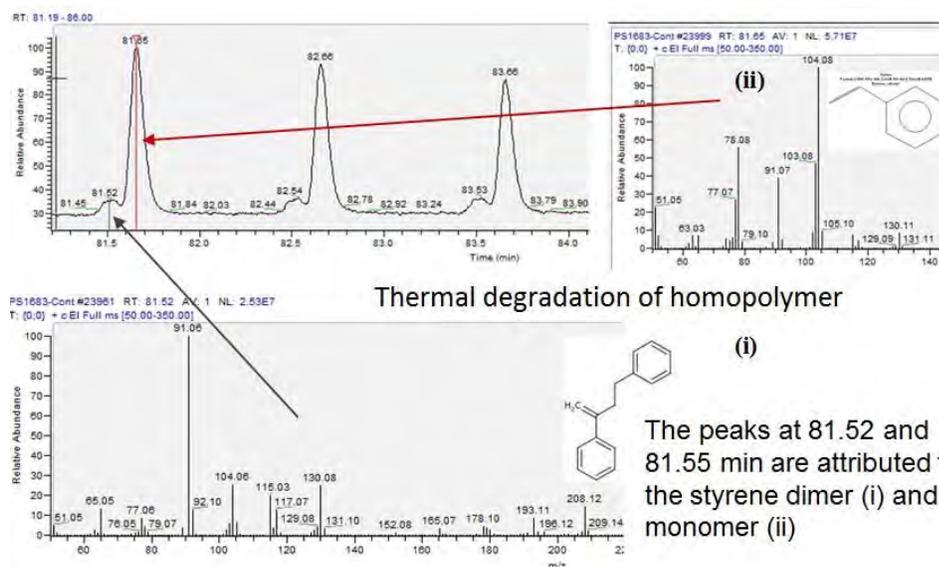
**Kristina Lilova**, *kristina.lilova@setaram.com*. Setaram Inc., Hillsborough, New Jersey, United States

The application of coupled techniques in the field of thermogravimetric analysis is well established, particularly for the investigation of the chemistry of thermal decompositions and identification of the evolved species.

However, these techniques have limitations, especially when a large number of molecules are evolved simultaneously. For that reason a more comprehensive TG-GC-MS technique, which involves a separation of the evolving species by GC and identification by MS, became a necessity.

A new TG-GC-MS line will be presented. The system includes an appropriate automated sampling loop that allows either injection of the gas stream in the GC column or releasing it outside the system. All gases evolving from the TGA furnace also flow through the sample loop so their concentration in the loop reflects the exact gas ratio in the furnace. The whole line, including the sampling loop is designed to withstand high temperatures and can be heated up to 350 °C.

Two examples related to decomposition of polymers will illustrate how this technique that can give more in-depth understanding of the degradation of complex substances. The first example is a study of the thermal degradation of a copolymer of ethylene and 1-octene, which is known to result in a complex mixture of alkanes and alkenes. The second experiment shows the evolved gas analysis of General Purpose PolyStyrene (GPPS) complete degradation. The results demonstrated that a presence of small quantities of heavy molecules with high boiling points (e.g. styrene dimer) can be detected in a gas flow rich in other substances.

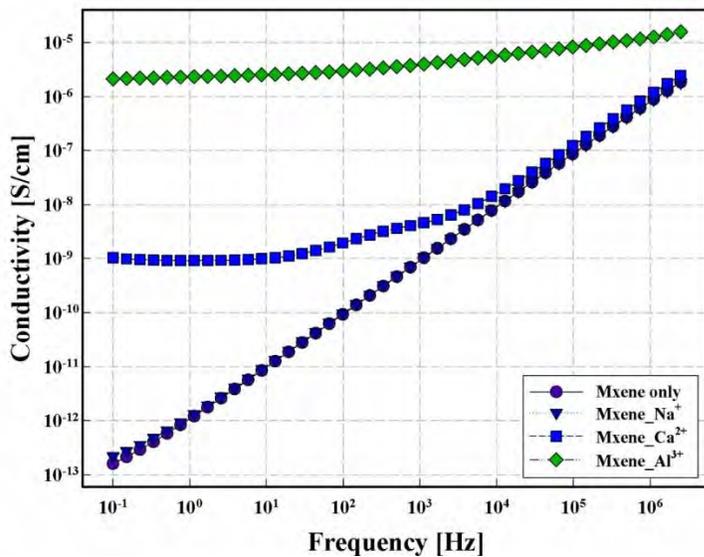


## POLY 45: Ion conduction in polyvinylidene fluoride (PVDF)/MXene nanolayers membrane for water treatment applications

**Mohammad K. Hassan**<sup>1</sup>, mohamed.hassan@qu.edu.qa, Adnan Al<sup>2</sup>, Kashif Rasool<sup>2</sup>, Khaled A. Mahmoud<sup>2</sup>. (1) Center for Advanced Materials, Qatar University, Doha, Qatar (2) Qatar Environment and Energy Research Institute, Hamad Bin Khalifa University, Doha, Qatar

MXenes are a class of 2D inorganic materials consist of few atoms thick layers of titanium carbide ( $\text{Ti}_3\text{C}_2$ ). They combine the characteristics of metallic conductivity of transition metal carbides and hydrophilic nature of their hydroxyl or oxygen terminated surfaces. MXenes are commonly used for Li ion batteries, supercapacitors, composites, photocatalysts, and gas sensors applications.

In this work, broadband dielectric spectroscopy (BDS) technique was used to characterize the ionic conduction in water treatment membranes composed of PVDF and MXene Nanolayers. The membranes were exposed to different doses of water containing the  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , or  $\text{Al}^{3+}$  cations in a cross-flow water treatment set-up. The 2D membranes were able to fully reject  $\text{Al}^{3+}$  cations from water while partially exclude  $\text{Ca}^{2+}$  and completely allow the  $\text{Na}^+$  cations. This result was strongly supported using the broadband dielectric spectroscopy analysis of the membranes' ionic conduction after their exposure to the different cations, as shown in the enclosed Figure. The high rejection rate for  $\text{Al}^{3+}$  cations is evidenced by the very high conductivity of membranes exposed to  $\text{Al}^{3+}$  comparing to  $\text{Ca}^{2+}$  and  $\text{Na}^+$ . Results of this investigation revealed the BDS as a powerful tool to characterize these membranes. This is mainly because valuable information regarding the ion conductance, over broad range of temperature and frequency, was extracted and correlated to polymer chain dynamics.

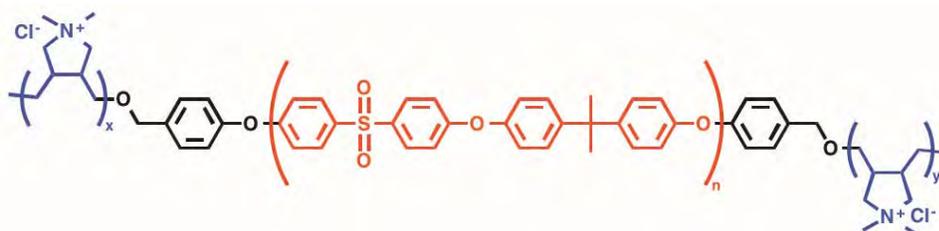


Broadband dielectric spectra at 30 °C showing the ionic conductivity of the Mxene/porous PVDF membranes after exposure to water containing different cations.

## POLY 46: Synthesis and characterization of polysulfone-poly(*N,N*-diallyl ammonium salt) block copolymers for polymer electrolyte membranes

**Derek J. Strasser**<sup>1</sup>, [dstrasse@mines.edu](mailto:dstrasse@mines.edu), **Daniel M. Knauss**<sup>2</sup>. (1) Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado, United States (2) Colorado School of Mines, Golden, Colorado, United States

Polymers of *N,N*-diallyldimethylammonium salts have been commercially important for their use in water treatment, bio-materials, ion exchange resins, and paper additives. Synthesis of *N,N*-diallyl ammonium salt polymers has been shown to proceed smoothly by free radical cyclopolymerization wherein 5 membered ring, cationic repeat units are formed. Herein we report the preparation of hydrophobic-hydrophilic block copolymers containing polysulfone and either poly(*N,N*-diallyldimethylammonium chloride) (PDADMAC) or poly(*N,N*-diallylpiperdinium chloride) (PDApipCl). Polysulfone was terminally functionalized with a radical initiator and block copolymers were then synthesized by the free radical cyclopolymerization of the *N,N*-diallyl ammonium salt in the presence of the polysulfone macroinitiator. The presentation will describe the amphiphilic block copolymer preparation, and the characterization of the membranes produced.

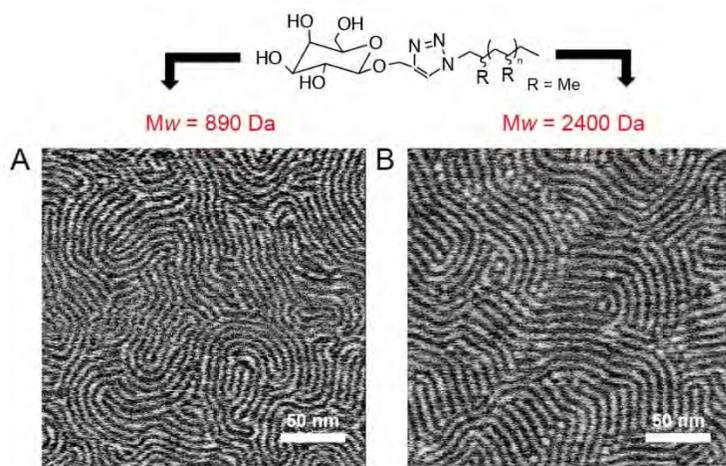


Polysulfone-PDADMAC block copolymer

## POLY 47: Sub-10 nm domain spacing within nanostructured, microphase-separated organic thin films of low molecular weight, *atactic* poly( $\alpha$ -olefin)-sugar hybrid conjugates

**Tessy S. Thomas**, *tthomas1@umd.edu*, Lawrence R. Sita. University of Maryland, College Park, Maryland, United States

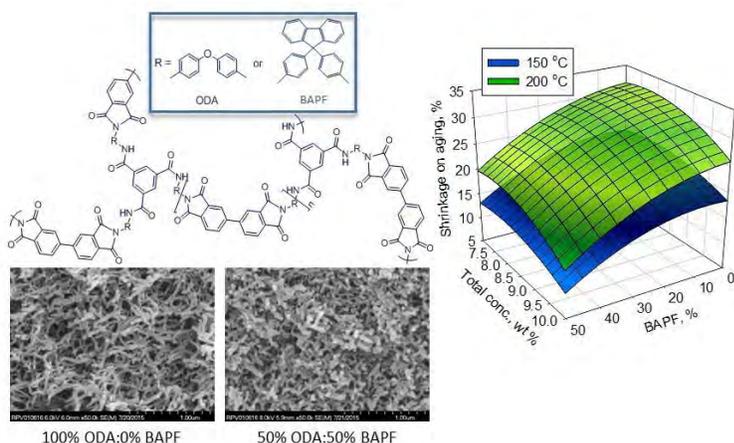
Nanostructured microphase-separated block copolymers with feature sizes  $< 10$  nm are currently of interest as potential alternatives to electron-beam lithography for the nanopatterning of advanced materials for device applications. The principal challenge for achieving this goal is the need to develop low molecular weight block copolymers that possess a high value for the Flory-Huggins interaction parameter,  $\chi$  - which is a measure of the thermodynamic driving force that leads to segregation between dissimilar block domains. This talk will present the results of our investigation of the synthesis and characterization of a novel new class of ultra-low to low molecular weight poly( $\alpha$ -olefin) – sugar hybrid conjugates that display strong microphase-separation within nanostructured organic thin films with sub-10 nm domain spacing. These novel hybrid conjugates are surfactant-like in structure and are comprised of a poly( $\alpha$ -olefin) ‘tail’ that is chemically-tethered to a sugar ‘head’ group. Importantly, a diverse array of the poly( $\alpha$ -olefin) tails with tunable side-chain structures and molecular weights are readily obtained through living coordinative chain transfer polymerization (LCCTP), followed by highly efficient end-group functionalization chemistry. Copper-catalyzed ‘click’ coupling between azido-terminated poly( $\alpha$ -olefins) and alkynyl-derivatized sugar moieties then provide a variety of the desired poly( $\alpha$ -olefin)-sugar hybrid conjugates that have been characterized by GPC, NMR and MALDI-TOF. The self-assembly of these hybrid conjugates in both solution and in organic thin films have been further investigated using DLS, AFM, TEM and XPS. These studies help to elucidate the various roles played by the sugar head group and the poly( $\alpha$ -olefin) tail in controlling self-assembly and potential utility for nanotechnology.



## POLY 48: Synthesis and characterization of cardo-diamine containing polyimide aerogels

**Rocco P. Viggiano**<sup>3</sup>, *rocco.p.viggiano@nasa.gov*, Jarrod Williams<sup>1</sup>, Mary Ann Meador<sup>2</sup>.  
(1) NASA, Lakewood, Ohio, United States (2) NASA Glenn Research Center, Cleveland, Ohio, United States (3) Materials Chemistry and Physics Branch, National Aeronautics and Space Administration, Cleveland, Ohio, United States

Polymer aerogels have become a major research focus in the field of aerogels. With unique advantages over inorganic aerogels including higher strengths and compressive moduli, greater toughness and the ability to be fabricated as a flexible thin film; polymer aerogels have supplanted inorganic aerogels in numerous applications. Of the many polymer aerogels presently available, polyimide aerogels have a distinction for possessing high thermal stability as well as excellent mechanical properties. Research on this class of polymer aerogels has shown that while the onset of thermal decomposition for these materials is typically very high (greater than 500 °C), the aerogels will undergo dramatic thermally induced shrinkage at temperatures below their glass transition temperature ( $T_g$ ) or their decomposition temperature. Attempts to minimize thermal shrinkage were successful when a bulky, space-filling moiety was incorporated into the polymer backbone. An array of 20 polyimide aerogels were synthesized from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and 4,4'-oxydianiline (ODA) and in some cases BPDA and a combination of ODA and 9,9'-bis(4-aminophenyl)fluorene (BAPF). The aerogels were cross-linked with 1,3,5-benzenetricarbonyl trichloride (BTC). The polymer concentration, n-value and molar concentration of ODA and BAPF were varied. The resultant aerogels were subjected to isothermal aging at 150 °C and 200 °C for up to 500 hours. Samples containing BAPF showed a reduction in thermally induced shrinkage by as much as 50% compared to unmodified polyimide aerogels.

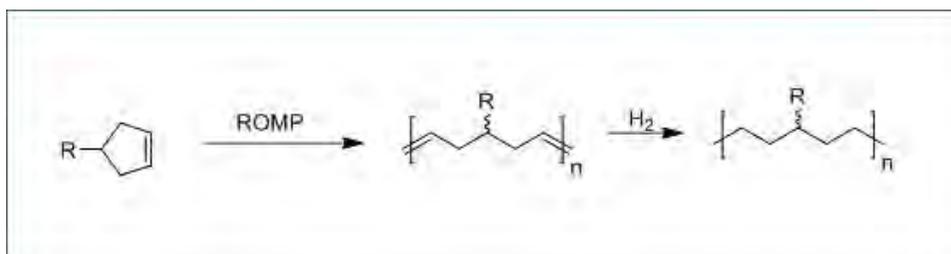


Generalized synthetic route to form a cardo-diamine (BAPF) containing cross-linked polyimide network. Below are SEM images for samples containing 0% cardo-diamine (left) and 50% cardo-diamine (right) in the polymer backbone. A three-dimensional plot shows the dramatic effect that increasing the content of cardo-diamine has on the overall aerogel shrinkage at 150 °C and 200 °C.

## POLY 49: Precision polyolefins from substituted cyclopentenes

William J. Neary, **Justin G. Kennemur**, kennemur@chem.fsu.edu. Chemistry & Biochemistry, Florida State University, Tallahassee, Florida, United States

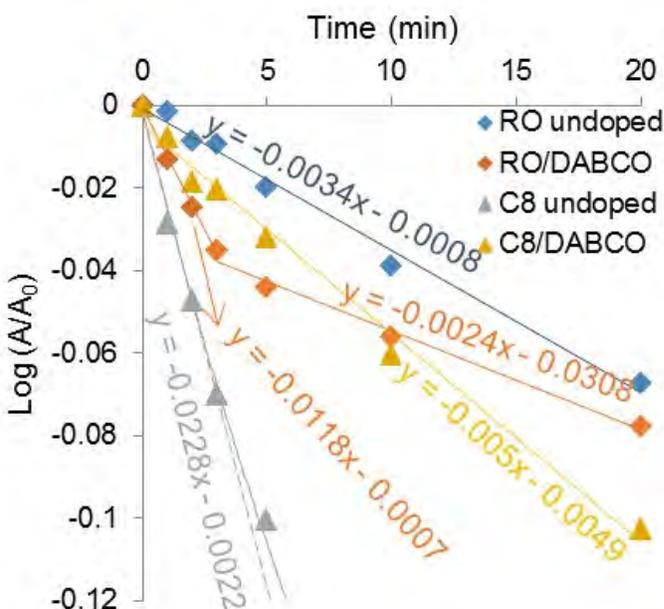
Improved ruthenium-based ring-opening metathesis polymerization (ROMP) catalysts, such as Grubbs third generation (G3) and Hoveyda-Grubbs second generation (HG2), have allowed better initiation kinetics at lower temperatures and with good tolerances to varying reaction conditions. Low ring strain cyclic olefins, such as cyclopentene, that rely on lower temperatures to achieve better conversion, have benefited from the advent of these improved catalysts. This research will discuss new developments in our group aimed at cyclopentene monomers as precursors to new precision copolymer analogs. Synthesis, characterization, and resulting properties of these materials will be discussed.



## POLY 50: Opposite effects of a singlet oxygen quencher on photochemical degradation of dicyano-substituted poly(phenylenevinylenes) with different side chains

**Logan P. Sanow**, *logan.sanow@sdstate.edu*, Jianyuan Sun, cheng zhang. Chemistry and Biochemistry, South Dakota State University, Brookings, South Dakota, United States

DABCO is a popular singlet oxygen quencher and antioxidant used in dye lasers to increase the lifetime of dyes. We doped DABCO into thin-films RO-diCN-PPV and C8-diCN-PPV to increase the photostability of these polymers. DABCO had the intended affect when added to C8-diCN-PPV, but when added to RO-diCN-PPV DABCO decreased the photostability of the polymer. The mechanism of the DABCO initiated photodegradation in RO-diCN-PPV was studied using UV-Vis, GPC, and IR spectroscopy. The initial rate of degradation of DABCO doped RO-diCN-PPV was 3.5 times greater than that of undoped RO-diCN-PPV. This increased rate of photodegradation is due to the initiation of a radical degradation mechanism, facilitated by the transfer of an electron from the HOMO level of DABCO to the HOMO level of singlet excited RO-diCN-PPV. This is possible due to the lower HOMO level of RO-diCN-PPV (-6.04 eV) compared to DABCO(-4.9 eV). C8-diCN-PPV has a HOMO level of -6.68 eV, the energy gap between the HOMO levels of DABCO and C8-diCN-PPV is too large for an electron transfer. DABCO was consumed during the illumination of DABCO doped RO-diCN-PPV, after the consumption of DABCO the rate of degradation decreased. DABCO has been shown to cause an increase in the photodegradation rate depending on the HOMO level of the polymer.



Semilog plot of absorbance vs. illumination time for RO-diCN-PPV and C8-diCN-PPV with and without 15 mol% DABCO

## POLY 51: Recent advances in fluoropolymer chemistry at Clemson University

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With the availability of our improved barricade facility for working safely with tetrafluoroethylene (TFE) on the kilogram scale (see Figure 1) [1], we have undertaken a number of projects in the area of TFE-based co- and ter-polymers. In the area of amorphous fluoropolymers, we have successfully synthesized 2,2,5,5-tetrafluoro-2,5-dihydrofuran and attempted its co-polymerization with TFE, hexafluoropropene (HFP), and SF<sub>5</sub>CF=CF<sub>2</sub>. The preparation and characterization of the polymers formed will be presented, including the crystal structures of several products resulting from the chemistry of this monomer. We continue to prepare sulfonimide ionomers by both the DesMarteau method as well as by the derivatization of co-polymers of TFE and perfluorosulfonyl fluoride-(PFSF)-functionalized trifluorovinyl ethers (TFVE), such as those used in Nafion<sup>®</sup> and Aquivion<sup>®</sup> [2]. The co-polymerization kinetics of TFE with these PFSF-functionalized TFVE monomers as well as with vinylidene difluoride (VDF), chlorotrifluoroethylene (CTFE), and trifluoroethylene (TrFE) have been studied both in the presence and absence of gaseous carbon dioxide (CO<sub>2</sub>). We have also been learning how to prepare perfluoroalkoxy (PFA) resins of commercial quality, so that we might study the incorporation of a ter-monomer aimed at improving the properties of the PFA resin, such as mechanical strength and wearability. The results from these and related studies will be presented.

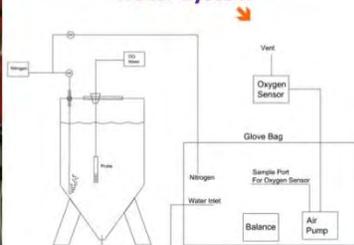
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- D. A. Hercules, D. D. DesMarteau, R. E. Fernandez, J. L. Clark, Jr., J. S. Thrasher, *Evolution of Academic Barricades for the Use of Tetrafluoroethylene (TFE) in the Preparation of Fluoropolymers*, in: *Handbook of Fluoropolymer Science and Technology*, Eds. D. W. Smith, Jr., S. T. Iacono, S. S. Iyer, John Wiley & Sons, Inc., 2014, Hoboken, NJ; Chapter 18.
- Z.-W. Yang, M. Gummalla, Y. Hosokawa, J. S. Thrasher, T. S. Saylor, A. Matsnev, R. E. Fernandez, A. Waterfeld, *Method of Fabricating an Electrolyte Material*, WO Patent 2014098907 A1, June 26, 2014.



Figure 1. (a) 2-Gallon Autoclave with Feed Lines, Etc.

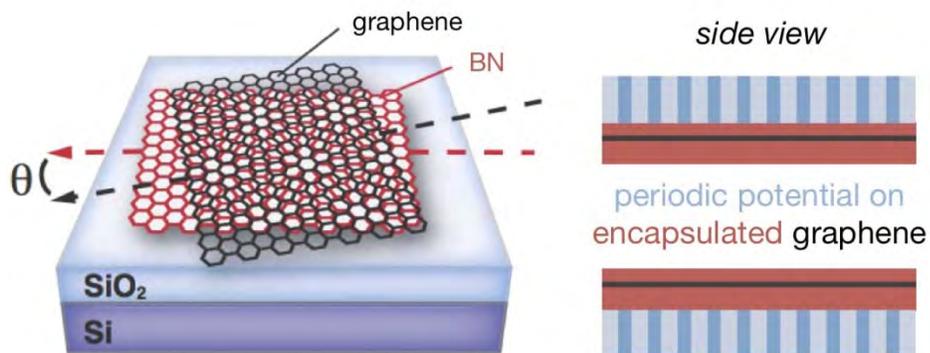
(b) Deionized, Deoxygenated Water System



## POLY 52: Interfacing encapsulated graphene with self-assembled diblock copolymers

**Helen Tran**<sup>1</sup>, ht2321@columbia.edu, **Harrison M. Bergman**<sup>1</sup>, **Cory Dean**<sup>1</sup>, **Luis M. Campos**<sup>2</sup>. (1) Columbia University, New York, New York, United States (2) Chemistry, MC 3124, Columbia University, New York, New York, United States

Nanopatterning two-dimensional materials with long wavelength periodic potentials is a controllable method to modify the intrinsic electronic bandstructure of crystal lattices. Graphene is an ideal material system in which to explore these effects; however, efforts so far have been limited by the difficulty to pattern structures at the necessary length scales (sub-50 nm), while maintaining a high degree of fidelity over micron-scale device channels, using conventional lithographic techniques. Here, the self-assembly of diblock copolymers is employed as the patterning component, where feature sizes may be tuned by varying the polymer composition. We investigate the resulting coupling of interfacing encapsulated graphene devices with self-assembled thin films of diblock copolymers. Self-assembly and post-processing of the diblock copolymer thin films, as well as two-dimensional heterostructures fabrication and device characterization will be discussed.

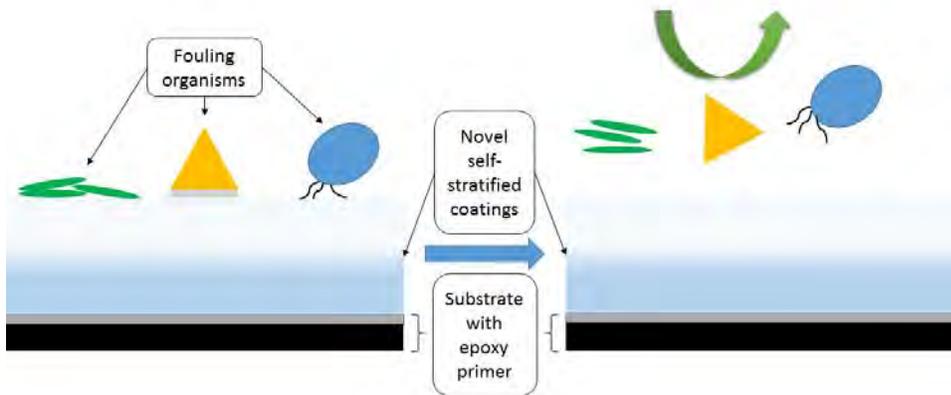


Graphene is encapsulated by insulating boron nitride (BN, top BN not shown for clarity), where the underlying SiO<sub>2</sub> exhibits a periodic potential via nanopatterning with block copolymer self-assembly.

## POLY 53: Non-isocyanate approach for the synthesis of polyurethane fouling release coatings

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A novel non-isocyanate approach was used to synthesize polyurethane fouling release coatings with varying surface chemistries. The novel resin system combines the properties of polyurethanes with the convenient crosslinking chemistry of epoxy. Formulations made using the resins were crosslinked using polyamines and polyamides in varying stoichiometric ratios to make self-stratified coatings. The resins were analyzed using FTIR, NMR and MALDI. Cured coatings were analyzed for solvent resistance, mechanical properties, impact strength and thermal behavior using DSC, DMA and TGA. Contact angles and surface energy experiments were carried out on the crosslinked coatings. Fouling release performance of the cured coatings was analyzed with respect to bacteria, diatoms, barnacles and mussels.

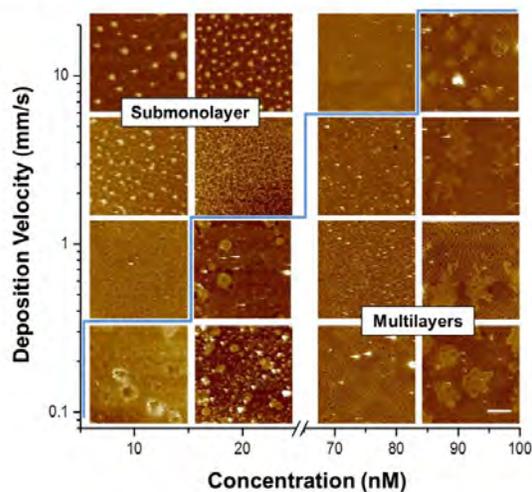


## POLY 54: Impact of architecture and substrate interfacial interactions on the preparation and stability of ordered monolayers of polymer grafted nanoparticle

**Justin Che**, *justinche1@gmail.com*, *Kyoungweon Park, Christopher A. Grabowski, John Kelley, Hilmar Koerner, Richard A. Vaia. Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright Patterson AFB, Ohio, United States*

Rapid, fabrication of stable, large area, ordered assemblies of polymer grafted nanoparticles (PGN) will enable additive manufacturing of novel membrane, electronic, and photonic elements. Due to the single component nature of these hybrids, aggregation and phase separation common in blended polymer nanocomposites are not an issue. Herein, we discuss the relationship between processing conditions, substrate surface energy, and the architecture of the PGN canopy on the hierarchical structure of sub- to mono-layer assemblies. The profile of an isolated gold-polystyrene (PS) PGN depends on substrate-canopy interface energy. At low substrate-PS interface energy, the PS canopy spreads to maximize contact with the surface; whereas at high substrate-PS interface energy the chains attempt to minimize contact area resulting in a more compact, thicker PGN. This behavior is translated up to monolayer assemblies, where rougher, less-ordered assemblies form on substrates with low interface energy (20 mN/m). The process of PGN film formation parallels classic colloidal deposition, and thus large-area (cm<sup>2</sup>), highly ordered monolayer gold-PS assemblies can be fabricated on substrates with high interface energy (80 mN/m) within seconds using flow-coating and a volatile solvent (THF). Using orthogonal gradients of surface energy and temperature, the onset of de-wetting was shown to also depend on the architecture of the PGN, and is more stable than films of linear chains of comparable molecular weight. Overall, this understanding of the correlation between structure-processing conditions of PGNs is the critical step to optimize fabrication of highly-ordered, stable thin films of PGNs with quantized thickness.

Correlation between deposition velocity and concentration on PGN film formation



## POLY 55: Modification of carbon surfaces with hyperbranched polymer for developing novel catalyst materials

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Hyperbranched polymers have a large number of end-groups and a dendritic-like structure. Unlike dendrimers, hyperbranched polymers can be synthesized in one step process from  $AB_x$ -type monomers, where  $x$  is two or more. It means that a large number of catalytically active sites can be introduced if the end-groups are converted into catalytically active functional groups. Our research group has been developing novel hybrid materials of aromatic hyperbranched polymers and carbon and investigating their property as heterogeneous catalysts. This presentation introduce the recent progress of our study on hyperbranched poly(ether sulfone) and its application as a solid acid catalyst. Fig. 1 shows the schematic of the designed material. The polymer studied in this work, hyperbranched sulfonated poly(ether sulfone) (HBPES), is soluble in various conditions, but it can be used as a heterogeneous catalyst by immobilizing HBPES onto carbon black (HBPES/CB). This material can be used as a heterogeneous catalyst at 130 °C owing to the high thermal stability of the aromatic backbone, whereas typical ion exchange resin such as amberlyst cannot be used at over 120 °C (Fig. 2).

### A Novel Solid Acid Catalyst

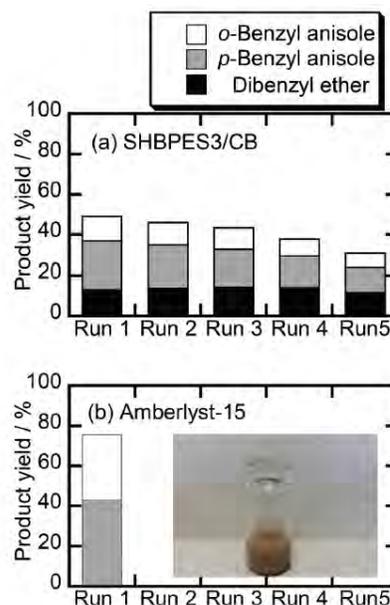
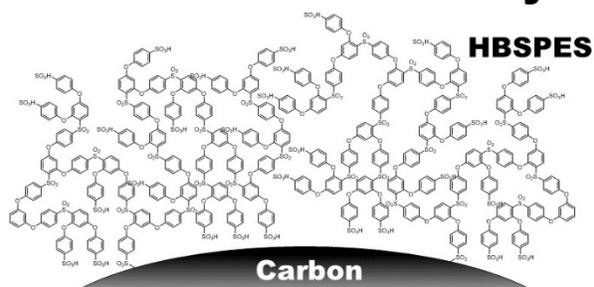


Fig. 1. Schematic of HBPES/CB.

The results of the Friedel-Crafts alkylation over the (a) SHBPES3/CB and (b) Amberlyst-15. Conditions: anisole 18.5 mmol, benzyl alcohol 1.25 mmol, catalyst 75 mg, 130 °C, 20 h. Inset: the reaction mixture after the 1st run with Amberlyst-15.

## POLY 56: Interface-enforced complexation between copolymer blocks

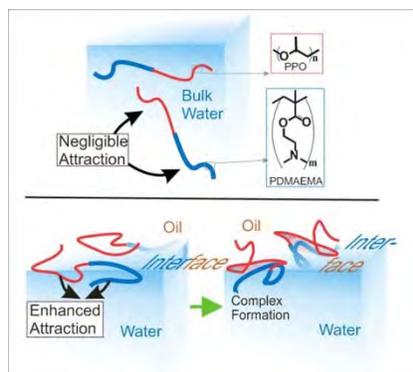
**Alexander Steinschulte**<sup>2</sup>, [Steinschulte@pc.rwth-aachen.de](mailto:Steinschulte@pc.rwth-aachen.de), Weinan Xu<sup>1</sup>, Fabian Draber<sup>2</sup>, Pascal Hebbeker<sup>2</sup>, Andre Jung<sup>2</sup>, Dimitri Bogdanovsk<sup>2</sup>, Stefanie Schneider<sup>2</sup>, Vladimir V. Tsukruk<sup>1</sup>, Felix Plamper<sup>2</sup>. (1) Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States (2) Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany

Amphiphilic copolymers are well known for their self-assembly in solution. At the same time, many amphiphilic block copolymers exhibit surface activity, i.e. polymers can be anchored at interfaces. One important tool to investigate the properties of interfaces is the Langmuir-trough experiment.

Here, the compression isotherms of binary diblock copolymers and corresponding ternary miktoarm stars are compared at oil-water interface. All polymers contain oil-soluble poly(propylene oxide) PPO, water-soluble poly(dimethylaminoethyl methacrylate) PDMAEMA and/or poly(ethylene oxide) PEO. The features of their compression isotherms are well related to the ones of the corresponding homopolymers. Unexpectedly, of all PPO containing copolymers only PEO-*b*-PPO is an effective amphiphile. In contrast, the compression isotherms show a complexation of PPO and PDMAEMA for PPO-*b*-PDMAEMA and the star, reducing their overall amphiphilicity.<sup>1</sup> The weak complex between the blocks of PPO and PDMAEMA in bulk water was only observed for the star, but not for the diblock.<sup>2</sup> However at the interface, the blocks of PPO-*b*-PDMAEMA form a complex due to their enhanced proximity in such a pseudo 2D environment (see Scheme). These results are supported by AFM after Langmuir-Blodgett transfer to a substrate and Monte Carlo simulations with varying confinement.<sup>1</sup>

1) A. A. Steinschulte, W. Xu, F. Draber, P. Hebbeker, A. Jung, D. Bogdanovski, S. Schneider, V. V. Tsukruk and F. A. Plamper, *Soft Matter*, 2015, 11, 3559

2) A. A. Steinschulte, B. Schulte, S. Rütten, T. Eckert, J. Okuda, M. Möller, S. Schneider, O. V. Borisov and F. A. Plamper, *PCCP*, 2014, 16, 4917

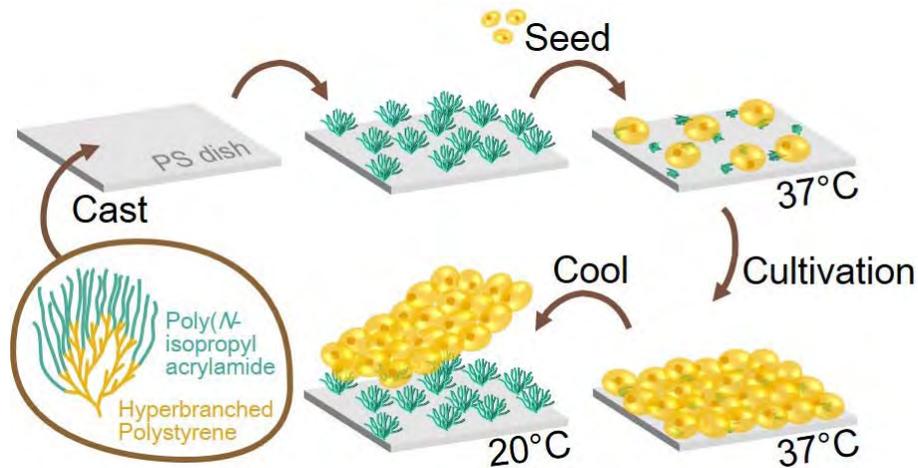


**Interface as "catalyst" for complex formation between the two weakly interacting polymers in PPO-*b*-PDMAEMA; complexation is aided by the close proximity (bottom) while hardly any complexation is seen for PPO-*b*-PDMAEMA in bulk water (top).<sup>1</sup> Reproduced by permission of The Royal Society of Chemistry**

## POLY 57: Copolymer of hyperbranched polystyrene and poly(*N*-isopropylacrylamide) as a thermo-responsive biomaterial for cell sheet recovery

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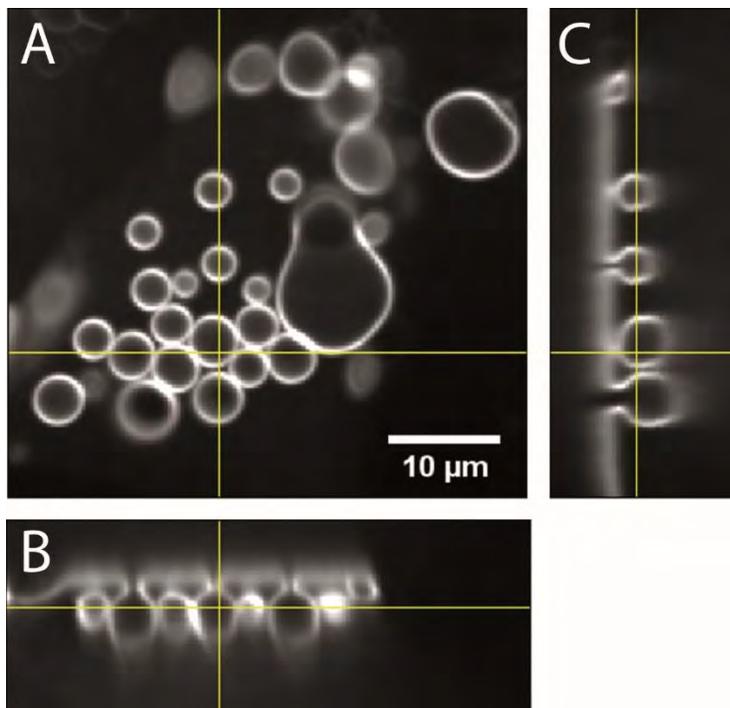
Temperature responsive dishes are promising materials for fabricating a “cell sheet” in tissue engineering. In this study, we have synthesized the copolymers of hyperbranched polystyrene and poly(*N*-isopropylacrylamide) (HBPSt-*g*-PNIPAM), and utilized it as a surface modifier of conventional cell culture dishes (Figure 1). HBPSt-*g*-PNIPAM was synthesized by grafting PNIPAM from the termini of HBPSt via reversible addition fragmentation transfer polymerization. The resulting HBPSt-*g*-PNIPAM was cast from a solution onto a commercial polystyrene (PS) dish to fabricate a thermo-responsive surface (HBP/dish) for cell cultivation. Mouse 3T3 fibroblast cells were seeded on the prepared dish and cultured at 37 °C for four days to achieve high confluent. Fairly large cell sheet was successfully collected by cooling the dish to 20 °C. Linear analogue (LPS-*b*-PNIPAM) was also synthesized and cast onto a PS dish to obtain LPS/dish in a similar manner; however it could not detach a cell sheet in the same condition. To discuss the effect of the dendritic structure on the cell sheet detachment performance, Langmuir-Blodgett (LB) films of HBPSt-*g*-PNIPAM and LPS-*b*-PNIPAM were studied. The results of the LB film accumulation suggest that the hyperbranched structure of the PS segment contribute to the exposure and immobilization of the PS segment onto the PS dish. The current material avoids the use of electron beam polymerization, which requires complicated equipment, for manufacturing a thermo-responsive surface.



## POLY 58: Effect of DexPEG hydrogel cross-link density on the preparation of giant unilamellar vesicles

**Alexander Kros**, *a.kros@chem.leidenuniv.nl*. *Leiden Institute of Chemistry, Leiden University, Leiden, Netherlands*

Giant Unilamellar Vesicles (GUVs) are becoming a popular membrane model system in biophysical studies. Hydrogels consisting of dextran polymers cross-linked by poly(ethylene glycol) are suitable hydrophilic polymer frameworks for the preparation of dense vesicle suspensions at physiologically ionic strength conditions. Herein we perform a systematic study of those polymeric networks with different crosslinks densities and evaluate their performance in the production of GUVs. We characterize various hydrogels in terms of their mechanical and morphological properties. Moreover, the efficiency on the production of GUVs was quantified by flow cytometry and the size distribution was statistically determined by the coulter method. We found that lower mechanical and increased swelling properties promote the production of GUVs, while the size distribution of GUVs is not affected by the physicochemical properties of the DexPEG substrates.



Confocal images GUVs formed from a DexPEG surface. A) A single confocal slice of an image stack of GUVs swollen on DexPEG (2-arm). Lipid composition is POPC : Cholesterol (80 : 20 % mol) fluorescently labelled with ATTO-488-DPPE (0.4 % mol). The yellow lines indicate the orthogonal slices in B and C. B) Horizontal orthogonal slice of GUVs in A reconstructed from confocal image stack. C) Vertical orthogonal slice of GUVs in A. B and C show GUVs that are not yet fully formed closed spheres. Rather, they are still attached by budding necks to the surface of the lipid film.

## **POLY 59: Toward rationally designed, additively manufactured carbon fiber composites with optimized mesostructures**

**James P. Lewicki**, *lewicki1@llnl.gov. Material Sciences Division, Lawrence Livermore National Laboratory, Livermore, California, United States*

High volume fraction carbon fiber (CF)-polymer composites can be extremely strong, stiff and light. CF-polymer composites therefore have the potential to outperform traditional materials (e.g. steel, aluminum) in many demanding applications where extremely high performance to weight ratios are required. However the broad application of CF-polymer composites in such areas is currently limited by manufacturing constraints, a fundamental lack of understanding of CF-polymer composite mesostructure and how it relates to macro-scale materials performance. Here we discuss our efforts in the rational development of a class of next generation high performance CF-polymer composites that are based on a novel ultra-fast curing and rheologically novel epoxy resin/CF system suitable for 3-D printing. With this system and a range of computational design tools, we utilize advanced additive manufacturing technologies to deliver an unprecedented control over fiber alignment in 3-dimensions. We will discuss methods of surface modification of the fiber surfaces and present spatially resolved X-ray scattering and nano-tomography data for the characterization of composite macrostructure. Our results show clearly that with improved rational control of CF-composite mesostructure, it is possible to make materials with truly orthotropic physical properties that significantly outperform equivalent volume fraction CF composites manufactured through conventional means

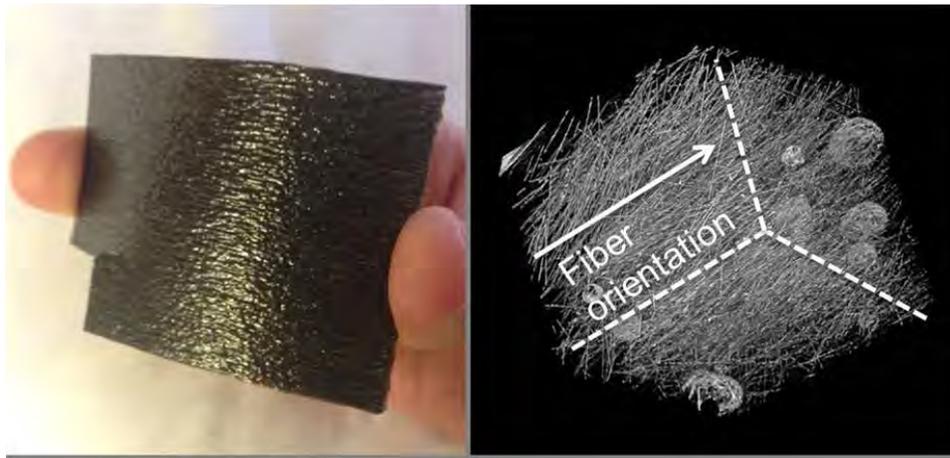
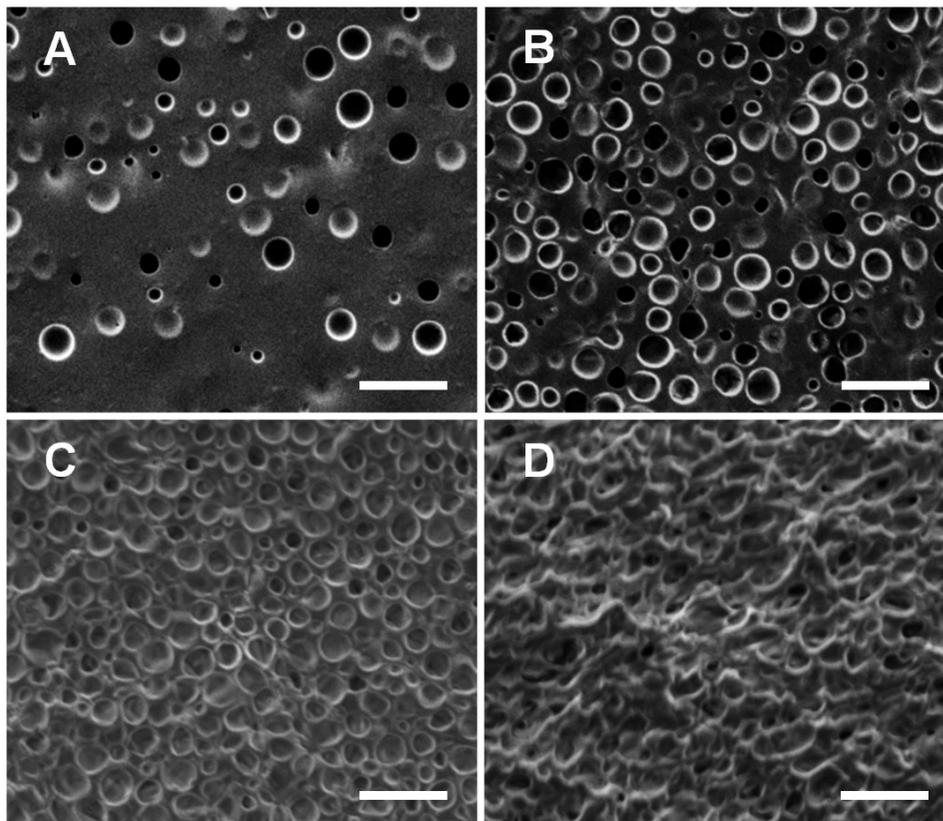


Figure 1. Left - Through a combination of novel resin chemistries and additive manufacture, we can print carbon fiber composites with orthotropic physical properties. Right - these novel physical properties are a result of the unprecedented control we have obtained fiber-phase orientation in 3-dimensions.

## POLY 60: Silicone Elastomers with Discrete Compartments

*Anne Skov, al@kt.dtu.dk, Piotr Mazurek. DTU, Kgs Lyngby, Denmark*

A green and cheap silicone-based elastomer has been developed. Through the simple mixing-in of biodiesel-originating glycerol into commercially available polydimethylsiloxane (PDMS) pre-polymer, a glycerol-in-PDMS emulsion was produced. This counterintuitively stable mixture became a basis for obtaining elastomeric composites with uniformly distributed glycerol droplets. Various compositions, containing from 0 to 140 parts of glycerol per 100 parts of PDMS by weight, were prepared and investigated in terms of ATR-FTIR, broadband dielectric spectroscopy, mechanical properties as well as optical and scanning electron microscopy. The materials were proven additionally to exhibit a strong affinity to water, which was investigated by simple water absorption tests. Incorporating glycerol into PDMS did not compromise the mechanical properties of the elastomer, even in the presence of very high loadings. Also, the swollen elastomers were extremely stable. The elastomer provides a large internal surface area ideal for further functionalization and therefore extra features of the swellable elastomer membrane. Various applications will be discussed.



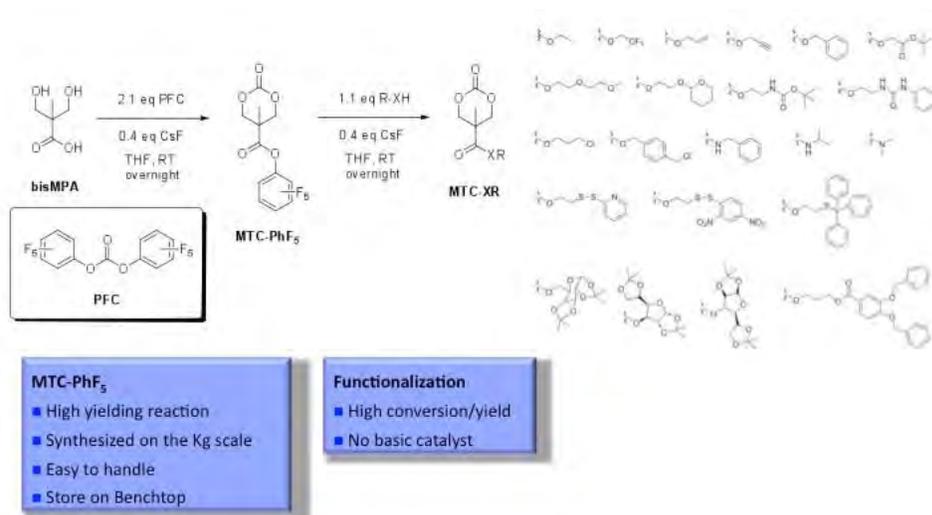
SEM images of cured glycerol-PDMS composite cross-sections. A – 10 phr, B – 50 phr, C – 90 phr, D – 130 phr of glycerol. Scale bars for all images correspond to 10  $\mu\text{m}$ .

## POLY 61: Functional polycarbonates: A broadly useful biodegradable polymer platform

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Functionalized aliphatic polycarbonates have emerged as promising biocompatible materials for use in drug delivery, polymer-based therapeutics, and imaging contrast agents. Much of this research has focused on functionalized cyclic carbonate monomers that can undergo ring-opening polymerization by cationic, anionic, coordination-insertion, organocatalytic, and enzymatic methods. We have developed several new families of organic catalysts that rival or exceed metal-based alternatives for polycarbonate synthesis, both in terms of activity and selectivity. Critically, the successful application of aliphatic polycarbonates in the biomedical field stems from unprecedented ease in which many desired functionalities can be introduced. Significant effort has been devoted to develop facile strategies to incorporate functionality at both the monomer level and post-polymerization by the judicious combination of orthogonal coupling chemistries. In particular, cyclic carbonate monomers and subsequent polymerization having pendant ester, amide, or thioester functional groups based on 2,2-bis(hydroxymethyl)propionic acid have been reported.

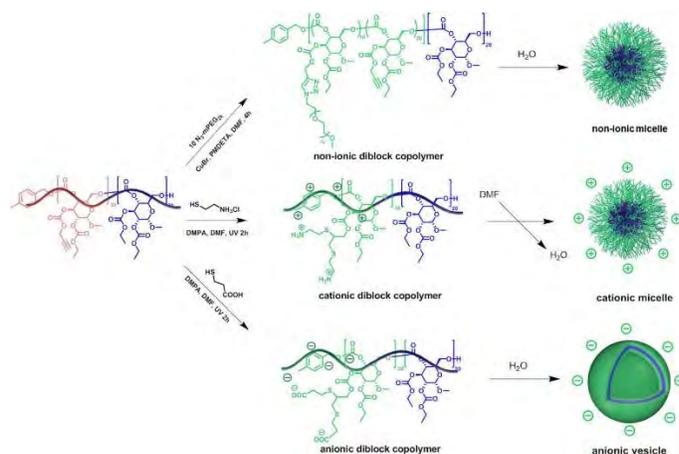
The synthesis of cyclic carbonate monomers having a pendent pentafluorophenyl ester group enabled a diverse library of functional groups, this monomer was synthesized in a single step from commercially available bis(hydroxymethyl)propionic acid. Combining the diol, pentafluorophenyl carbonate and CsF effectively cyclized two hydroxyl groups while concurrently activating the ester with a pendent pentafluorophenyl carbonate. Using nucleophiles such as alcohols, amines and thiols, a library of functional monomers was rapidly generated. These monomers were polymerized using organocatalysis yielding new degradable polymers having many possible pendent groups.



## POLY 62: Development of functionalizable and biodegradable poly(D-glucose carbonate)s as emerging nanomaterials toward biomedical applications

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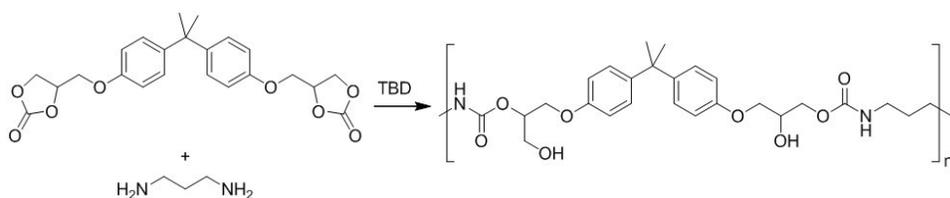
Poly(D-glucose carbonate)s (PGCs) are derived from renewable sources and have the degradation capability into natural byproducts, therefore, they have shown great potential for next-generation biomaterials. However, the lack of functionality that allows for facile and versatile post-polymerization modifications limits the applications of initially-studied PGCs. In this presentation, we report the design, synthesis, and utilization of an alkyne-functionalized D-glucose monomer to construct novel PGC block copolymers. By performing sequential ring-opening polymerizations (ROPs) of D-glucose-based bicyclic carbonate monomers with and without alkynes, well-defined diblock PGCs (PDI < 1.10) bearing pendant alkyne functionalities in a block manner were synthesized and employed for practical and efficient functionalizations through click chemistry. The kinetics of organocatalyzed sequential ROPs were evaluated and both polymerizations exhibited a linear relationship between the monomer conversion and the polymer molecular weight, which confirmed the controlled fashion during each process. Two classic “click” reactions, *i.e.*, azide-alkyne Huisgen cycloaddition and thiol-alkyne addition reactions, were employed to render the alkyne-containing block hydrophilic and provide a variety of amphiphilic diblock PGCs, which could be assembled into a family of nanostructures with different sizes, morphologies, surface charges and functionalities, while maintaining alkynes in the hydrophilic domains for further chemical manipulations, *e.g.*, covalent crosslinking. The micelles and the corresponding shell crosslinked nanoparticles (SCKs) from non-ionic polyethylene glycol (PEG) modified diblock copolymer precursors showed low cytotoxicity toward OVCAR cells, RAW 264.7 mouse macrophage cells, and SJSA cells, making these nanomaterials of interest for biomedical applications. The synthesis, characterization and degradation of these materials will be discussed, with an emphasis toward specific biomedical target applications.



## POLY 63: New monomers and catalysts for sustainable non-isocyanate polyurethanes

**Robert Lambeth**, *bob.lambeth@us.army.mil*. US Army Research Lab, Aberdeen Proving Ground, Maryland, United States

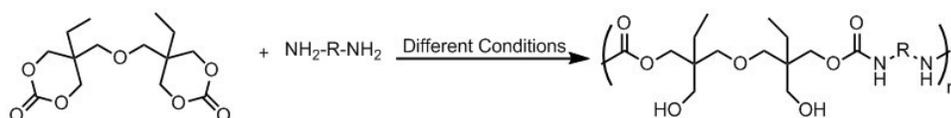
The preparation of technologically important polyurethanes while avoiding the use of toxic isocyanates is an emerging field of study. One of the more promising routes involves the reaction between cyclic carbonates and amines to form polyhydroxyurethanes. Depending on the ring size of the cyclic carbonate, this synthetic approach is limited by slow reactivity and/or availability of diverse monomer structures. Here we report approaches to increase 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.



## POLY 64: Non-isocyanate polyurethanes based on 6-membered cyclic carbonates

**Sanyo Mathew**, *sanyo.mm@gmail.com*, Robert H. Lambeth. Weapons & Materials Research Directorate, U.S. Army Research Laboratory, Aberdeen Proving Ground, Maryland, United States

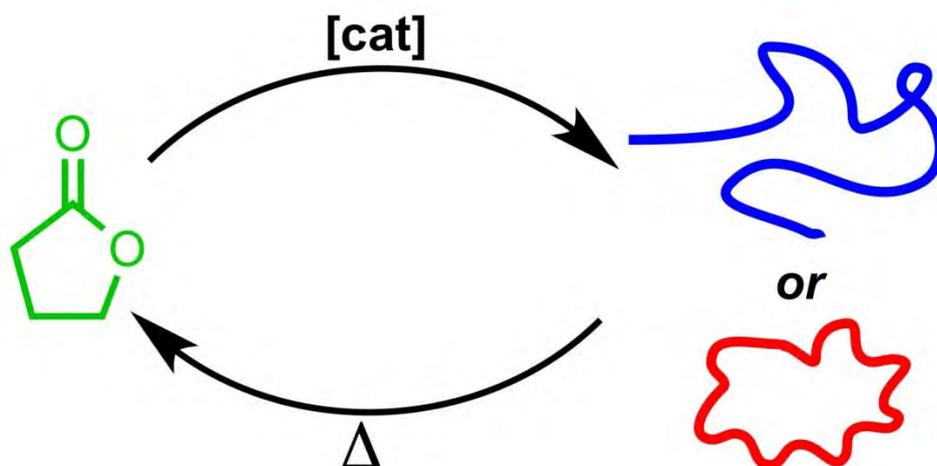
Polyurethanes (PU) are widely used in many modern technologies. In the current manufacturing process, use of toxic isocyanates is highly undesirable. The reaction between cyclic carbonates and amines to form (poly) hydroxyurethanes (PHU) is a green alternative to isocyanate based synthesis. Here we report different synthetic methodologies for the preparation of synthetically challenging bifunctional 6-membered cyclic carbonate (6CC) monomers. It is expected that the rate of polymerization for 6CC monomers will be faster than the more conventional 5-membered cyclic carbonate (5CC) monomers leading to higher molecular weights under ambient conditions. We study this hypothesis and the possibility of side reactions that occur during the polymerization. The effect of different catalysts and reaction conditions on the polymerization will also be discussed.



## POLY 65: Renewable and recyclable polyesters by ring-opening polymerization of bio-derived non-strained lactones

**Eugene Y. Chen**, *eugene.chen@colostate.edu*. Colorado State University, Fort Collins, Colorado, United States

Ring-opening polymerization (ROP) is a powerful synthetic methodology for the chemical synthesis of technologically important biodegradable aliphatic polyesters from cyclic esters or lactones. However, the bio-derived five-membered  $\gamma$ -butyrolactone (GBL) is commonly referred as "non-polymerizable" due to its low strain energy. Recently, we have discovered thermodynamic and catalytic conditions that enabled the effective ROP of GBL, affording high-molecular-weight sustainable poly(GBL). Remarkably, both linear and cyclic poly(GBL)s can be recycled back to the monomer in quantitative yield by simply heating the bulk materials at 220 °C (for the linear polymer) or 300 °C (for the cyclic polymer), thereby demonstrating their complete recyclability. These results revealed a class of truly sustainable (renewable and recyclable) polymers. Other related non-strained lactones have also been investigated for their polymerizability toward the ROP to produce the corresponding polyesters.

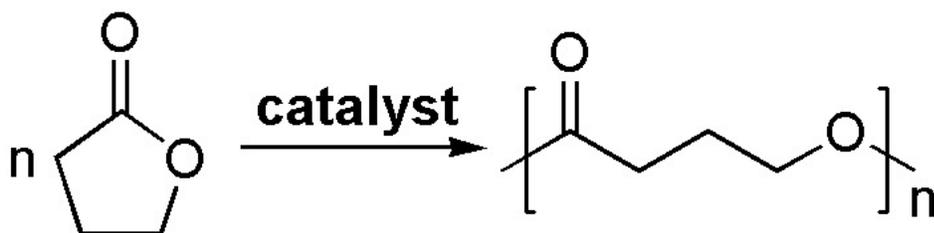


## POLY 66: Completely recyclable biopolymers with linear and cyclic topologies via ring-opening polymerization of $\gamma$ -butyrolactone

**Miao Hong**<sup>2</sup>, hongmiaohm@gmail.com, Eugene Y. Chen<sup>1</sup>. (1) Colorado State University, Fort Collins, Colorado, United States (2) chemistry, Colorado state university, Fort Collins, Colorado, United States

Aliphatic polyesters, which are conveniently prepared by ring-opening polymerization (ROP) of cyclic esters or lactones with relatively high strain energy (such as  $\epsilon$ -caprolactone and  $\beta$ -butyrolactone), have received considerable attention due to their biocompatibility and biodegradability. In contrast, five-membered  $\gamma$ -butyrolactone ( $\gamma$ -BL) is typically referred as “non-polymerizable” due to its low strain energy. Chemical synthesis of poly( $\gamma$ -butyrolactone) (P $\gamma$ BL) through the ROP process can only be realized under an ultra-high pressure of 20,000 atm at 160 degree, producing only low molecular weight oligomers ( $M_n < 3.5$  kg/mol). Poly(4-hydroxybutyrate) (P4HB)—P $\gamma$ BL’s structural equivalent, is produced through a fermentation process, rather than a chemical synthesis.

Recently, we successfully synthesized P $\gamma$ BL materials with relatively high molecular weights (with  $M_n$  up to 30 kg/mol) through catalyzed ROP of  $\gamma$ -BL under ambient pressure. Using the thermodynamic and catalytic conditions we have identified, the efficient ROP has been achieved with monomer conversion up to ~90.0%. The resulting P $\gamma$ BL materials have been analyzed by NMR, MALDI-TOF, GPC, DSC, TGA, and DMA techniques, and the results of these studies pertaining to polymer chain structures, thermal properties, and thermal recyclability will be discussed in this presentation.

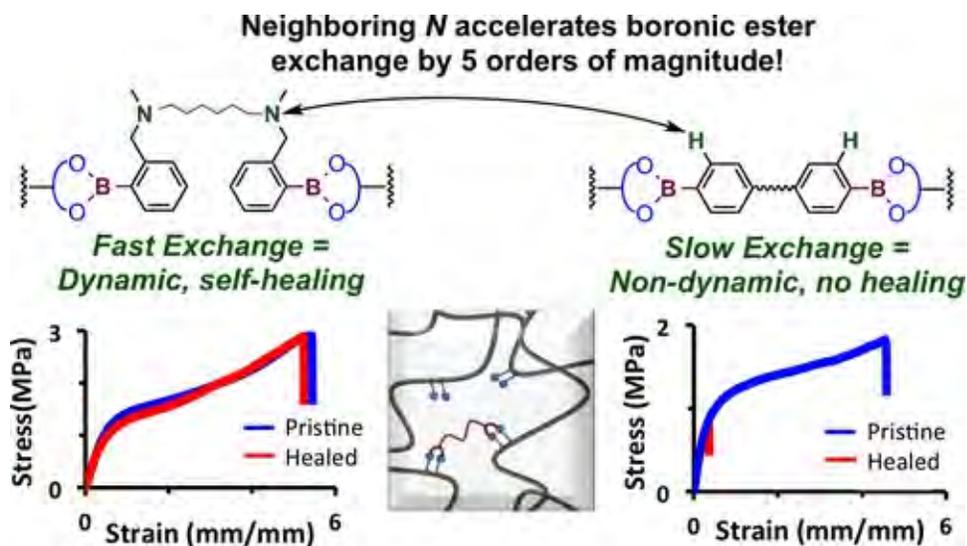


**Ring-opening polymerization of  $\gamma$ -butyrolactone**

## POLY 67: Dynamic bulk materials through tunably dynamic boronic ester bonds

**Jaeyoon Chung**<sup>2</sup>, jaeyooc@uci.edu, Olivia Cromwell<sup>2</sup>, Zhibin Guan<sup>1</sup>. (1) 1102 Nat Sci II, Univ of California, Irvine, California, United States (2) University of California Irvine, Irvine, California, United States

Despite numerous strategies involving dynamic covalent bond exchange for dynamic and self-healing materials, it remains a challenge to be able to tune the malleability and self-healing properties of bulk materials through simple small molecule perturbations. In a recent report in the *Journal of the American Chemical Society*, we successfully demonstrated the use of kinetically tunable rates of boronic ester transesterification to effectively tune the malleability and self-healing efficiencies of bulk materials. Specifically, when we dynamically crosslinked 1,2-diol-containing polymers with two kinetically variable telechelic di-boronic ester crosslinkers, we observed that the sample crosslinked with fast-exchanging di-boronic ester showed enhanced malleability and accelerated healing compared to the slow-exchanging variant under the same conditions. Herein we describe the extension of this concept to a vitrimeric design, in which the pervasive boronic ester bonds form a highly crosslinked network. Compared to our initial report, the much larger mole percentage of boronic ester linkages in the material can offer wider possibilities in tuning the dynamicity of the material. Together, these systems demonstrate the possibility of transferring small molecule exchange kinetics to dynamic and mechanical properties of across multiple types of materials, and may serve as a guide for the bottom-up rational design of tunable dynamic materials.



## **POLY 68: Catalyst development for a HCN-free methyl methacrylate synthesis**

**Takiya Foskey**<sup>2</sup>, *tjahmed@dow.com*, Lauren Huffman<sup>1</sup>, Daniel Arriola<sup>2</sup>, John Briggs<sup>1</sup>.  
(1) *The Dow Chemical Company, Midland, Michigan, United States* (2) *Core R&D, The Dow Chemical Company, Midland, Michigan, United States*

The Dow Chemical Company produces half of the total MMA supply in the USA using the classical ACH process. The desire for acid-free and/or HCN-free routes to MMA has fueled the development of competitive alternatives based on ACH and other feedstocks. This talk will discuss catalyst development for an alternative, ethylene-based route to MMA.

## **POLY 69: Some current microscopy techniques used for characterization of inorganic fillers in tire compounds**

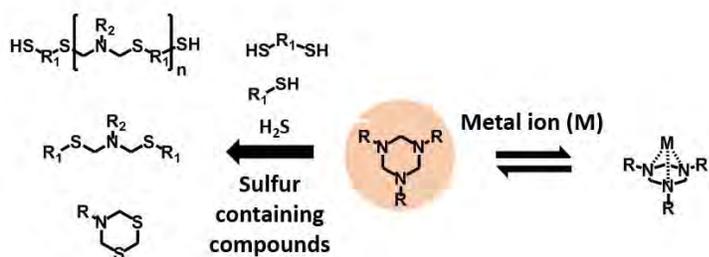
**Bryan D. Korth**, *bkorthy@hotmail.com*. Analytical Science, Goodyear Tire and Rubber, Stow, Ohio, United States

While a ubiquitous object in life, the composition and construction of a tire is highly complex and requires scientists to use a variety of instrumentation to characterize the organic and inorganic components from the human to atomic length scales. Through advances in microscopy, the ability to correlate physical properties, both bulk and local, as well as elemental composition in a given construction allows for continued tire improvement. Advances in technology over the past few decades has shifted the major constraint of characterization from what is possible to what is feasible with the restraints of time, sample preparation, and length scale. Instrumentation that probes mechanical properties, such as Nanoindentation and Atomic Force Microscopy (AFM), provide local modulus information that can be influenced not only by the polymer matrix but also inorganic filler concentration and morphology. In addition, recent advancements in AFM technology has provided access to chemical functionality information at the sub-micron length scale through a number of techniques including photothermal induced resonance (AFM-PTIR). However, these techniques can be restrictive due to sample preparation needs as well as length scale limitations. Beam microscopy techniques, such as scanning electron and scanning transmission electron, can yield useful information on inorganic components as well as chemical functionalities over a wide range of length scales but can still be impacted by varying sample preparation requirements. While powerful, many of the previous techniques lack ready access to three dimensional space, which can be useful for understanding the distribution of filler throughout a compound. For this information, X-ray computed tomography (CT) can be utilized, providing a non-destructive method to visualize the entire volume of a polymer composite. While CT provides greater spatial information, it is only a partial tool due to limitations in both length scale and compositional analysis. While no single method provides full characterization, the combination of techniques can provide a more complete understanding of the inorganic filler and its influence in a tire allowing scientists to drive improvement now and in the future.

## POLY 70: From synthetic developments to applications: Hexahydrotriazines as a materials platform for industrial solutions

**Rudy J. Wojtecki**<sup>3</sup>, *rjwojtec@us.ibm.com*, Gavin O. Jones<sup>2</sup>, Thomas G. Zimmerman<sup>3</sup>, Alexander Y. Yuen<sup>3</sup>, Dylan Boday<sup>1</sup>, J.L. Hedrick<sup>4</sup>, Jeannette M. Garcia<sup>3</sup>. (1) IBM, Tucson, Arizona, United States (2) D2, IBM, San Jose, California, United States (3) Science & Technology, IBM - Almaden Research Center, San Jose, California, United States (4) IBM Research, San Jose, California, United States

Recent synthetic developments have produced a new class of recyclable thermosets based on the formation of Hexahydrotriazine networks – polyhexahydrotriazines (PHTs). From their very recent synthesis, this material platform has garnered significant attention for a spectrum of applications that relies on an overlap between synthetic chemistry, supramolecular interactions with metal ions and their reactivity towards heteroatoms such as sulfur, for instance. Through fundamental studies, which include experimental analytical tools (UV-Vis & NMR titrations) and computational modeling, a variety of metal ions from different groups of elements such as Na<sup>+</sup>, Ca<sup>2+</sup>, Zn<sup>2+</sup> and Ag<sup>2+</sup> were shown to associate with hexahydrotriazines (HTs) in solution. However, their interaction with HTs is not solely a supramolecular association in all cases. Harder Lewis-acid metals lead to irreversible changes in the HTs spectrum, suggesting that some metals lead to chemical changes in the HT. The interaction between HTs and metal ions were exploited in the development of a low cost fluorimeter-based detection system, where changes in the HT's absorption at short wave UV-light (255 nm) are converted into visible light with a fluorescent indicator that enables detection with a silicon photodetector. This device was found sensitive enough to detect trace amounts of heavy metals (<10ppb) in aqueous solutions. Furthermore, understanding the interactions between HTs and metal ions facilitated the development of anti-microbial PHT coatings where Ag<sup>2+</sup> ions are bound to the HT moieties of PHT films and give rise to these properties. In addition to their interactions with metal ions HTs are highly reactive towards inorganic compounds such as thiols. A reactivity that can be exploited for a wide range of applications that includes novel polymer forming reactions and polymer compositions as well as smart coatings for sulfur sequestration and even as a method for the detection of thiols.

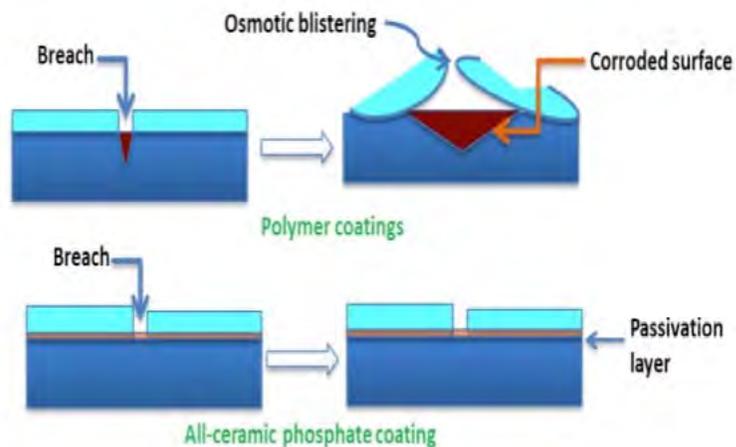


Hexahydrotriazines associate with metal ions and exhibit a unique reactivity towards sulfur containing compounds. Understanding these fundamental properties enables their exploitation for applications and requires an interplay between polymer & inorganic chemistry.

## POLY 71: Inorganic phosphate performance coatings

**Arun S. Wagh**, [arunwaghphd@gmail.com](mailto:arunwaghphd@gmail.com). *Products Development and Research, CeramiCoat Inc., Mount Prospect, Illinois, United States*

Chemically Bonded Phosphate Ceramics are a class of inorganic materials that are formed by acid-base reaction of a suitable oxide with an acid-phosphate at ambient condition. They can be used to produce room-temperature-setting ceramics or cements and have been used as such. This presentation extends their applications as sprayable performance coatings for corrosion and fire protection. The key feature, distinct from the conventional polymer coatings, is that CBPC coating reacts with steel substrate and forms its own passivation layer, which bonds the protective topcoat to the substrate, protects the substrate from osmotic blistering that occurs in conventional coatings, and is stable at  $>600\text{ }^{\circ}\text{F}$ . The coating itself is dense like polymer coatings, but is free of volatile organic compounds (VOC), or hazardous air pollutants (HAP), and additionally, it is heat reflective. Micro-structural studies and phase analyses indicate that the coating is a composite of crystalline particles bonded by inorganic phosphate polymer phases. Detailed performance properties are provided and compared with conventional Epoxy coatings. Based on the phase analysis, archeological evidence justifies long-term durability of these coatings in adverse environment.

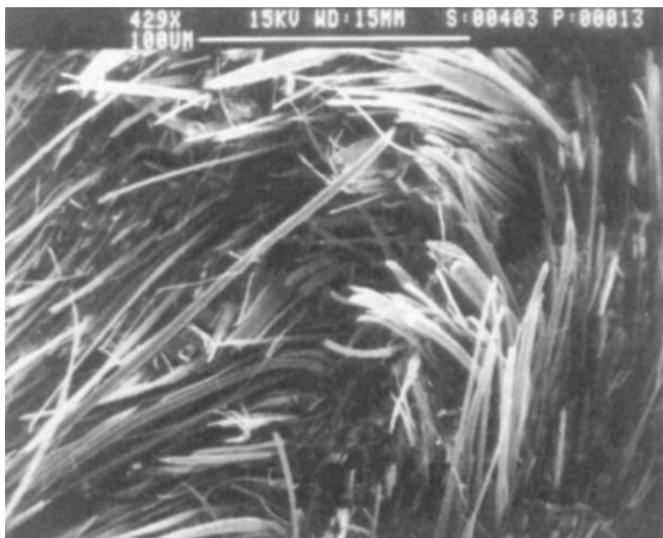


Ceramiccoat is a solution to osmotic blistering problem

## **POLY 72: Generation of thermotropic liquid crystalline polymer thermoplastic composite filaments and their processing in fused filament fabrication**

**Donald G. Baird<sup>1</sup>**, dbaird@vt.edu, **Mubashir Ansari<sup>2</sup>**, **Craig Mansfield<sup>2</sup>**, **Chen Qian<sup>1</sup>**. (1) Virginia Tech, Blacksburg, Virginia, United States (2) Chemical Engineering, Virginia Tech, Blacksburg, Virginia, United States

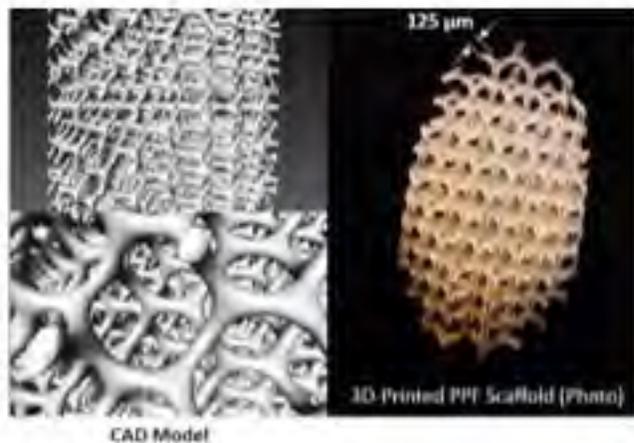
This work is concerned with the generation of thermoplastic filaments (polypropylene initially) reinforced with thermotropic liquid crystalline polymers, TLCP's, of higher melting point than the matrix using a unique dual extrusion technology developed in our laboratory. In this technology, TLCP's and thermoplastic polymers are plasticated in two different extruders at different temperatures producing mechanically stronger filaments than in situ processed filaments in which both the TLCP and matrix are processed in one extruder. TLCP's are plasticated at a higher temperature in the dual extrusion method and then cooled and introduced into the matrix which has usually a degradation temperature lower than the processing temperature of the TLCP's. Because the TLCP's super-cool significantly they can be processed below their melting points. The mixture is then passed through static mixers and a capillary die, producing continuous reinforcement by means of the TLCP phase in the matrix. Initially, polypropylene is used as the matrix with different concentrations (>50%) of a TLCP. The TLCP nearly continuous microfibrils have a modulus and strength which approach those of the lower end of carbon fiber leading to filaments with a modulus approaching 80 GPa and a strength of 700 MPa (60 wt% TLCP/40wt% PP). These filaments are then used in Fused Filament Fabrication (FFF) to generate simple plaques with various layup directions. The advantage of these materials is that they can be severed at the end of the layup process whereas continuous glass and carbon fibers can't. At a later stage, higher performance matrices, such as polyethyleneterephthalate (PET) and polyphenylenesulfide (PPS), will be used. This will address the need for mechanically stronger filaments for FFF which has a major share in the growth of 3D printing technology.



## **POLY 73: Synthesis of well-defined poly(propylene fumarate) oligomers for photocrosslinked 3D printing**

**Matthew Becker**, *becker@uakron.edu. University of Akron, Akron, Ohio, United States*

A ring opening polymerization method for synthesizing oligomeric poly(propylene fumarate) (PPF) provides a rapid, inexpensive, and scalable method of synthesizing PPF. The materials possess a narrow molecular mass distribution, and with highly predictable viscosity. Collectively these features facilitate industrial-scale PPF synthesis and well-defined materials that should enable Good Manufacturing Practice (GMP) certification. The narrow molecular mass distribution and reproducible viscosity characteristics should afford predictable and reliable mechanical performance and resorption profiles for this material. These properties will also reduce the amount of solvent necessary to insure sufficient flow of material during 3D printing. Taken together these accomplishments provide a material that has the potential to fill the resorption time gap in highly accurate, photo-crosslinked, 3D printed materials between the 1-2 months common for many polylactides and 3-5 years often seen in polycaprolactone. A broader resorption window will allow tissue formation to be guided by a scaffold and for remodeling to occur in its absence.

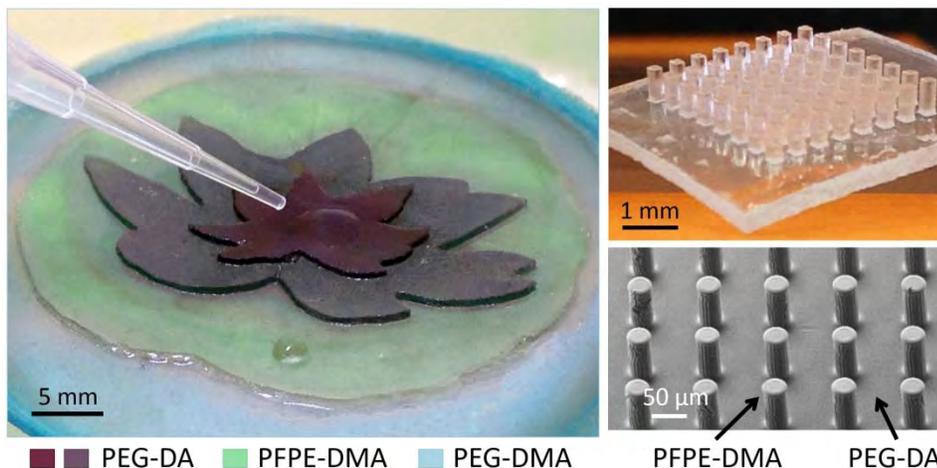


## POLY 74: Oxygen-inhibition lithography for the fabrication of multipolymeric structures and multifunctional devices

**Alessandra Vitale**<sup>1</sup>, *a.vitale@imperial.ac.uk*, **Marzia Quaglio**<sup>2</sup>, **Angelica Chiodoni**<sup>2</sup>, **Katarzyna Bejtka**<sup>2</sup>, **Matteo Cocuzza**<sup>1</sup>, **Candido F. Pirri**<sup>2</sup>, **Roberta M. Bongiovanni**<sup>1</sup>. (1) *Department of Applied Science and Technology, Politecnico di Torino, Torino, Italy* (2) *Center fo Space Human Robotics @PoliTo, Istituto Italiano di Tecnologia, Torino, Italy*

Although current microfabrication technologies, such as standard lithographic and printing techniques, have proved to be very successful in many cases, they still present several limitations. For instance, creating multipolymeric patterned surfaces where different chemistries are involved, and with a good adhesion among the layers, is a very challenging task. Herein, we describe the Oxygen-Inhibition Lithography (OIL), a photolithographic technology that exploits the inhibitory effects of oxygen during UV-curing in air to fabricate multiscale and multimaterial patterns and devices. Exposure time, UV light intensity and material chemistry are selected as critical variables to finely control the formation and the thickness of the inhibition layer; as a result, a simultaneous control over pattern shape, dimensions and composition is achieved. OIL is a general patterning route for a broad range of polymers, and allows the selection of the final properties of the structures on demand, depending on the application. We demonstrate the manufacturing in few minutes of both patterns with varied and complex shapes and closed devices (with embedded structures).

The key feature of OIL is the possibility to combine different properties within the same structure and tune the physico-chemical characteristics of each layer of the device accordingly to the desired application, thus granting a precise and concurrent control over surface topography and pattern functionality. Multifunctional and multipolymeric structures and devices containing different compositions can be easily fabricated with high reproducibility, low cost and very rapidly.



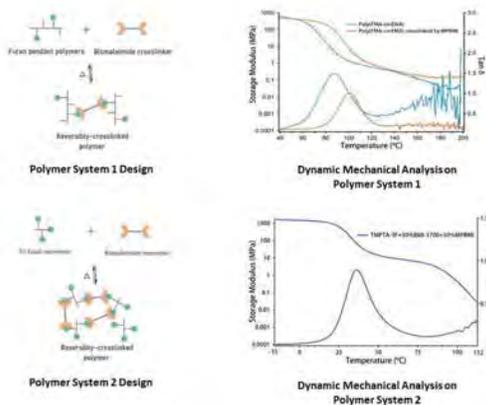
Examples of multipolymeric and multifunctional patterned structures obtained through the OIL technology.

# POLY 75: Novel thermosetting polymers for reducing anisotropy in fused filament fabrication 3D printing

**Kejia Yang**<sup>3</sup>, [kejia.yang@utdallas.edu](mailto:kejia.yang@utdallas.edu), Benjamin R. Lund<sup>4</sup>, Ronald Smaldone<sup>2</sup>, Walter Voit<sup>1,3</sup>. (2) Chemistry, University of Texas, Dallas, Plano, Texas, United States (3) Chemistry, The University of Texas at Dallas, Richardson, Texas, United States (4) Materials Science and Engineering, The University of Texas at Dallas, Richardson, Texas, United States

3D printing technologies have been of growing interest and presented compelling opportunities in various areas. Among them, fused filament fabrication (FFF) 3D printing is dominant in consumer hobbyist arenas since it is a cost-effective process with simple set-up. In FFF, the polymer is melted then extruded through the print head and deposited to a substrate layer by layer. It requires thermoplastic materials, which are melt-processible but poor in mechanical properties (especially when loaded perpendicular to the layer deposition plane), often making FFF unfavored in commercial 3D printing. Crosslinked polymers, also called thermosets, usually have better performance in terms of thermal stability and chemical resistance, as well as better mechanical properties. These qualities make the thermosets desirable for many engineering applications. However, most thermosets are chemically crosslinked and not melt-processible once the crosslinks are introduced into the network. To solve this incompatibility, reversibly-crosslinked polymers present one solution that would improve the interlayer adhesion between layers within FFF printed parts and their mechanical properties while maintaining the melt-processibility of their thermoplastic counterparts.

In this presentation, we will be discussing our work on developing novel melt-processible thermosetting polymers for 3D printing, enabled by reversible Diels-Alder chemistry. Two polymer systems will be covered: 1) a blend of acrylic-based linear polymers with pendant furan groups and bismaleimide crosslinkers, and 2) crosslinked polymers comprising multi-furan monomers and multi-maleimide monomers. We will also discuss our approaches to modify a traditional FFF printer in order enhance printing compatibility with the novel materials shown in this work.



## **POLY 76: Translating basic science into products and the role of diversity in making that happen: The launching of carbon3D**

**Joseph M. Desimone**<sup>1,2</sup>, [desimone@unc.edu](mailto:desimone@unc.edu). (1) UNC at CH Dept of Chem, Chapel Hill, North Carolina, United States (2) Carbon3D, Inc., Redwood City, California, United States

Those of us who participate in convergence science know how extensive and difficult the challenges are to executing it. Beyond pursuing scientific problems through research, we are faced with questions about advocacy, public policy changes, restructuring funding systems, peer review and tenure issues, and other administrative—and crucially important—questions about the structures in which we operate as academic scientists. These questions are vast and aren't associated with any discipline in particular, and I believe the approach to addressing them would be best informed by joining a diverse range of perspectives. These same issues can help fuel the formation of companies that are launched to create a new future.

As scientists, we may be doing ourselves a disservice by not being more deliberate in drawing others who are not scientists into our conversations about convergence. Indeed, when solving scientific problems, I have found in my career that the best, most innovative solutions arise from diverse teams composed of talented individuals with different backgrounds, experiences, and expertise. In this context, I will share my perspective about how diversity should be considered for our ongoing dialogue about convergence science in the 21st century and its essential role in company formation.

**POLY 77: Reflection on my experience to commercialize lab inventions**

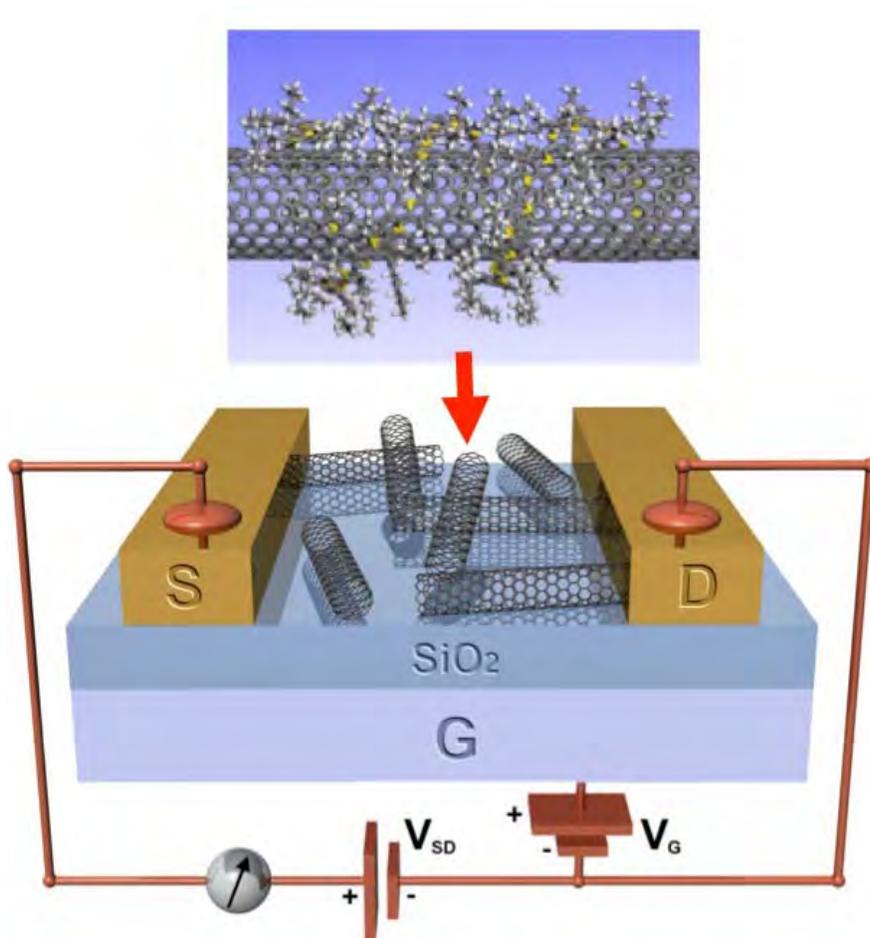
**Zhenan Bao**, [zbao@stanford.edu](mailto:zbao@stanford.edu). *Chemical Engr Dept MC 5025, Stanford University, Stanford, California, United States*

Reflection on my experience to commercialize lab inventions

## POLY 78: Integrated materials systems for chemical sensing

*Timothy M. Swager*, [tswager@mit.edu](mailto:tswager@mit.edu). MIT, Cambridge, Massachusetts, United States

Advanced materials are often defined as materials that have designed properties. However, it is seldom that one single material has all of the properties necessary for creating the desired technological functions. This is particularly true in the design of modern materials for chemical sensing. Some materials may be particularly well suited for carrying a signal, which can be electrical current, and others may provide a means to modulate this property through a complex molecular recognition process. Other materials may be structural to enforce a particular configuration of the materials, and in doing so avoid structural evolution with repeated exposure to chemical signals, humidity, and thermal fluctuations. The latter contributes to what is known as drift in a sensor's response. In this lecture I will discuss some current efforts and thinking from our lab that are directed at producing high performance chemiresistive materials based upon electronic polymers and carbon nanotubes. I will also cover new transduction methods based on chemical reactions and molecular recognition.



**POLY 79: Success stories in commercial functional materials - from haircare to pharmaceuticals**

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

The explosion of interest in developing new synthetic approaches to functional materials has significantly impacted the academic community. However the allure of robust, efficient and orthogonal chemistry is also perfectly suited to addressing emerging challenges in the design and application of new materials and new material applications. This will be illustrated with the emerging development of novel hair care systems and polymer-based therapeutics.

## **POLY 80: Fundamental to commercial chemistry**

**Robert H. Grubbs**, *rhg@caltech.edu. Cal Tech 164-30, Pasadena, California, United States*

Ring opening metathesis polymerization (ROMP) has become a major tool for the synthesis of polymers with well defined structures. The use of ruthenium based systems have allowed the synthesis of extremely high molecular weight brush-block polymers that self assemble into materials with variable length scales. Materials have been prepared that form layered structures that reflect light depending on the molecular weight of the polymers. Multi block polymers are now being prepared to explore the ability to form complex morphologies

**POLY 81: Award Address (Kathryn C. Hach Award for Entrepreneurial Success sponsored by the Kathryn C. Hach Award Fund). Converting pollutants into polymers and specialty chemicals**

**Scott Allen**<sup>3</sup>, *sda@novomer.com*, **Geoffrey W. Coates**<sup>1</sup>, **Anthony Eisenhut**<sup>2</sup>. (1) *Cornell Univ, Ithaca, New York, United States* (2) *KensaGroup LLC, Ithaca, New York, United States* (3) *Novomer, Ithaca, New York, United States*

Novomer is commercializing a family of high performance, cost effective and environmentally responsible polymers and chemicals. Novomer's proprietary catalyst technologies enable traditional chemical feedstocks to be combined with CO<sub>2</sub> and CO to synthesize sustainable chemicals and materials for a wide variety of applications. Novomer co-founders Geoffrey Coates, Tony Eisenhut and Scott Allen identified the potential of a suite of catalysts discovered in Coates' research labs at Cornell University and launched Novomer to develop and commercialize the innovative products and processes. Today, Novomer has two platforms: epoxide/carbon dioxide copolymers and epoxide carbonylation. The CO<sub>2</sub>-based platform uses CO<sub>2</sub> as a raw material to produce a family of polyols for use in polyurethane applications while the CO-based platform uses CO and ethylene oxide to produce chemical intermediates, such as acrylic acid, succinic anhydride, and butanediol. This presentation will focus on the commercial development of the CO<sub>2</sub> and CO platforms and will describe the path an invention takes from the initial university laboratory discovery to a commercial product.

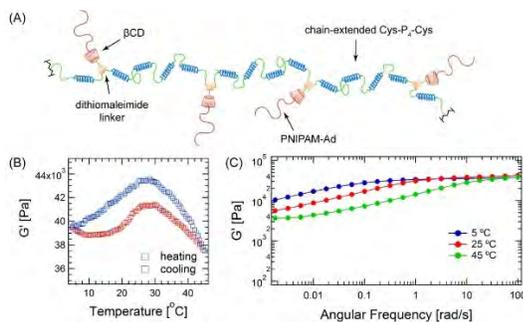
## POLY 82: Selective response and actuation in polymer hydrogels

**Bradley D. Olsen**<sup>1</sup>, [bdolsen@mit.edu](mailto:bdolsen@mit.edu), Manos Gkikas<sup>3</sup>, Shengchang Tang<sup>2</sup>, Chelsea Edwards<sup>3</sup>. (1) Chemical Engineering, MIT, Cambridge, Massachusetts, United States (2) Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (3) Chemical Engineering, Massachusetts Institute of Technology, Brighton, Massachusetts, United States

Hydrogels have attracted a great deal of interest as responsive materials for applications such as controlled release, injectable biomaterials, smart actuators, and sensors. A major challenge in the engineering of these responsive materials is to improve their selectivity, moving towards responses that more closely resemble selective molecular recognition. One area where this presents a particular challenge is the development of porous barrier membranes that can selectively close in response to a specific toxic chemical threat. Not only must the threat be detected, but the membrane must convert the sensing event into a sufficiently large mechanical response to reduce transport rates.

Here, we report the ability to generate such a polymer membrane based on acrylamide hydrogels that can selectively detect and respond to certain organophosphate agents, toxic agents of wide concern. In these materials, oximes are used to selectively degrade an organophosphate compound, producing a thiol degradation product. The acrylamide gel is engineered with disulfide crosslinks, such that thiol exchange leads to a decrease in the total crosslink density and consequently swelling of the gel. This enables simultaneous decontamination, detection, and actuation of the membrane to perform mechanical work such as pore closing. Here, we describe the quantitative response of the materials to model organophosphates and demonstrate the fabrication of the gels into useful structures.

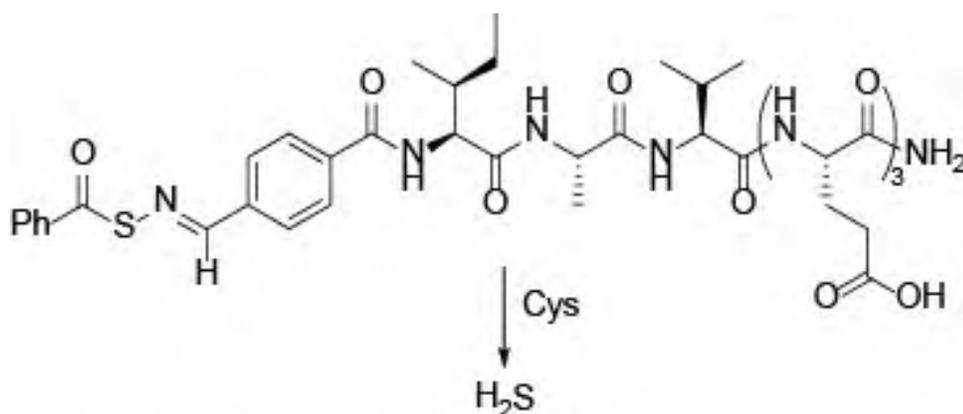
A second example is the response of hydrogels to oxidative stresses, enabling tunable mechanical responses when exposed to air or to selective oxidizing/reducing reagents. When thiols are incorporated at both ends of an associating polymer, mild oxidative conditions can lead to polycondensation of the thiols, resulting in the formation of high molar mass polymers. Such thiol incorporation is easily achieved in artificially engineered protein hydrogels, producing materials that demonstrate remarkable plastic draw to very high strain at break. Stress-optics experiments are used to understand the molecular rearrangements underlying this phenomenon.



## POLY 83: Thiol-triggered hydrogen-sulfide releasing gels

**John B. Matson**<sup>1,2</sup>, [jbmatson@gmail.com](mailto:jbmatson@gmail.com), Yun Qian<sup>2,1</sup>, Jennifer Carter<sup>2,1</sup>. (1) Chemistry, Virginia Tech, Blacksburg, Virginia, United States (2) Macromolecules and Interfaces Institute, Virginia Tech, Blacksburg, Virginia, United States

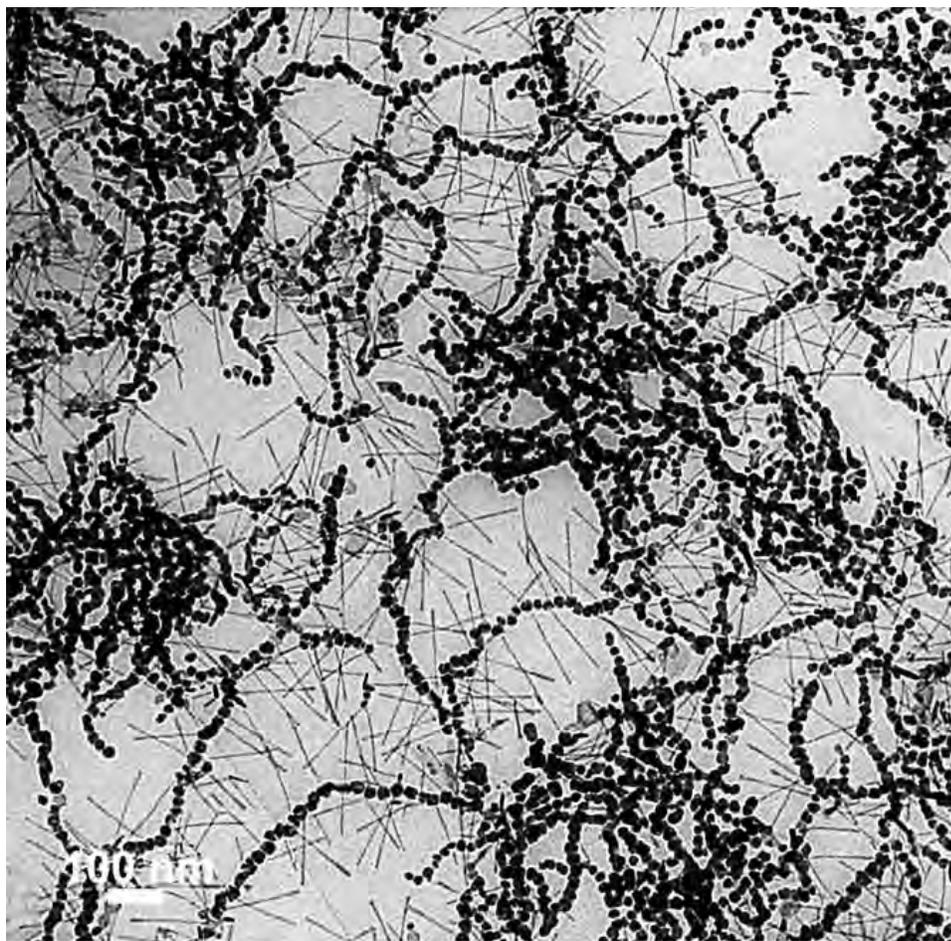
Hydrogen sulfide (H<sub>2</sub>S) is widely recognized as a vital biological signaling gas, and it has significant therapeutic potential. The majority of biological studies on this gasotransmitter have been carried out with systemically administered small molecule H<sub>2</sub>S donors, which have little tissue specificity, fast release, and the potential for off-target effects. For successful therapeutic use of H<sub>2</sub>S that avoids potential off-target effects, efficient delivery to a site of interest must be attained. We address these shortcomings through localized delivery of H<sub>2</sub>S using peptide-based gels. The gels are comprised of peptides derivatized with S-arylothiooximes—a functional group that releases H<sub>2</sub>S in response to thiols. The functionalized peptides self-assemble in aqueous solution to form long cylindrical micelles, and entanglement of these cylindrical micelles leads to gelation in aqueous solution at 1 wt. %. Cysteine-triggered decomposition leads to H<sub>2</sub>S release and disassembly of the gel. We present here the synthesis, mechanical properties, H<sub>2</sub>S release rate, and biological evaluation of these unique gels.



## **POLY 84: Synthesis and blending of magneto-responsive colloidal polymers: Observation of mesoscopic phase separation**

*Jeffrey Pyun, [jpyun@email.arizona.edu](mailto:jpyun@email.arizona.edu). University of Arizona, Tucson, Arizona, United States*

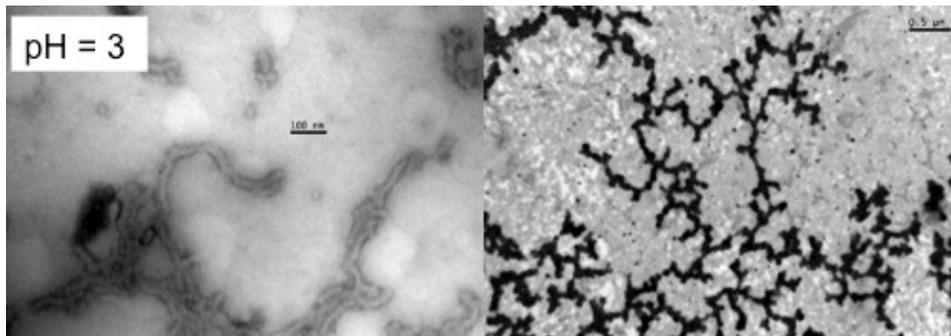
We will discuss our recent efforts the synthesis and dipolar assembly of a polymer stabilized Janus nanoparticle composed of a single dipolar cobalt nanoparticle and side chain moieties composes of semiconductor nanorods or tetrapods. These types of magnetically responsive nanoparticles serve as intriguing nanoscopic monomers to form mesoscopic colloidal polymer like structures. We will discuss our efforts to prepare functional colloidal monomers of these materials and colloidal polymerization of these functional colloids into colloidal polymers Finally, we investigate the phase behavior of these systems by blending experiments with various types of dipolar nanoparticles and nanorods will be discussed to form colloidal copolymers blends of that are mesoscopic manifestations of phase separation of classical immiscible polymers. [figure 1]



## POLY 85: Responsive peptide block polymer assembly: ABA, ABC and star triblocks

Greg Strange, Ian Smith, Craig Machado, **Daniel A. Savin**, dsavin1973@gmail.com.  
Chemistry, University of Florida, Gainesville, Florida, United States

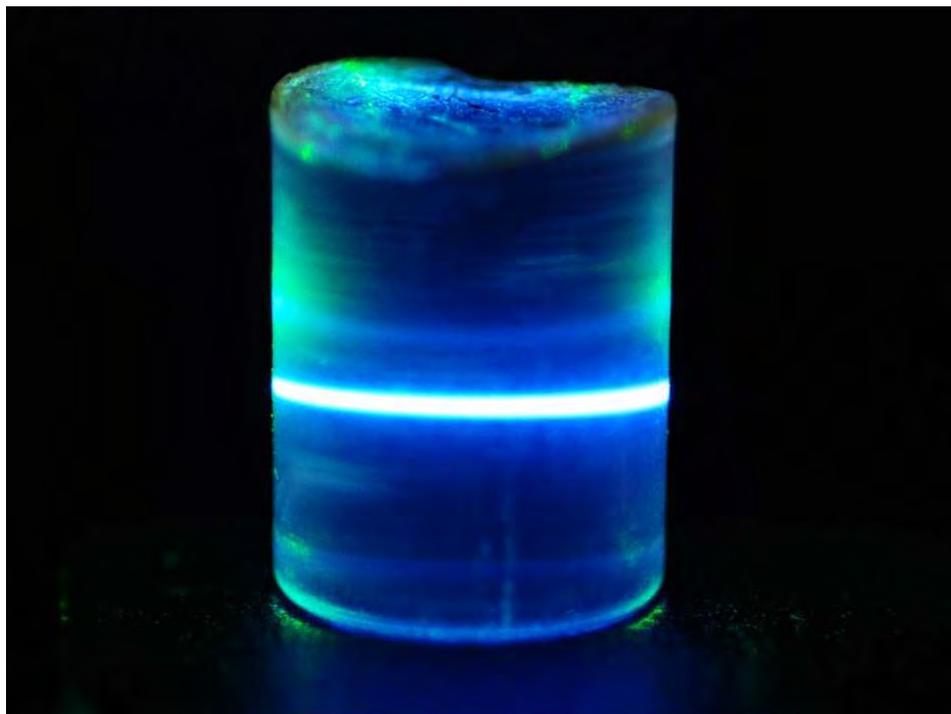
This study involves the bottom-up design and tunability of responsive, peptide-based block polymers. In these studies, amphiphilic triblock (i.e. ABA and ABC) and star polymers containing poly(lysine) (PK) and poly(glutamic acid) (PE) were synthesized and their solution properties studied using dynamic 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 at the interface and interfacial chain density. This talk will present some recent studies 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.



## POLY 86: Low-power photon upconversion through triplet-triplet annihilation in nanostructured polymers

**Christoph Weder**<sup>1</sup>, [christoph.weder@unifr.ch](mailto:christoph.weder@unifr.ch), Roberto Vadruc<sup>2</sup>, Soo-Hyon Lee<sup>2</sup>, David Thevenaz<sup>2</sup>, Yoan C. Simon<sup>3</sup>. (1) University of Fribourg, Adolphe Merkle Institut, Fribourg, Switzerland (2) University of Fribourg, Adolphe Merkle Institute, Marly Fribourg, Switzerland (3) Adolphe Merkle Institute, University of Fribourg, Marly, Switzerland

Optical upconversion (UC) by triplet-triplet annihilation (TTA) is a photophysical process that is useful for a wide range of applications that range from solar harvesting systems to bioimaging. While this effect had been demonstrated in solutions comprising chromophore pairs with appropriately matched electronic levels already over 50 years ago, its adaptation to the solid state is a more recent development. This presentation will provide a summary of our latest efforts regarding the development of polymeric materials that enable efficient TTA-UC. Examples that will be discussed include rubbery and glassy polymer blends and copolymers that comprise suitable chromophore pairs, upconverting nanoparticles, organogels, and nanostructured polymers. The data presented will be used to sketch a picture of the structure-property relationships of upconverting polymeric materials and outline general design rules.



## **POLY 87: Large low temperature thermoelectric power factor, that rivals inorganic semiconductors, from completely organic nanocomposite multilayer thin films**

**Jaime C. Grunlan**<sup>1</sup>, *jgrunlan@tamu.edu*, Choongho Yu<sup>2</sup>. (1) Texas A M Univ, College Station, Texas, United States (2) Texas AM University, College Station, Texas, United States

Low electrical conductivity ( $\sigma$ ) and thermopower ( $S$ ) have long excluded polymers from thermoelectric applications. Combining polyaniline (PANI) with double-walled carbon nanotubes (DWNT) and graphene produces polymer nanocomposites that exhibit excellent thermoelectric behavior (i.e., generate electricity via a thermal gradient). A 470 nm film, deposited using layer-by-layer assembly, exhibits electrical conductivity greater than 100,000 S/m, with a Seebeck coefficient of 130 mV/K. This combination of completely organic materials produces a power factor ( $PF = S^2\sigma$ ) greater than 1800 mW/(m $\bullet$ K<sup>2</sup>), making these nanocomposites competitive with inorganic semiconductors (e.g., bismuth telluride) in terms of conversion efficiency. Sequential layering of PANi, graphene, and double walled carbon nanotubes (DWNT) produces films with increased carrier mobility, originating from strong  $\pi$ - $\pi$  interactions between PANi and DWNT and the higher electrical conductivity of graphene. In this investigation of the thermoelectric behavior of an LbL-assembled film, the resulting multilayer thin films exhibit a remarkable power factor that exceeds lead telluride and is more than half the value of bulk bismuth telluride. Additionally, these water-based systems can be applied like ink or paint, which should further improve their usefulness in harnessing waste heat from a variety of sources (e.g., exhaust manifolds or the human body).

## **POLY 88: Chemistry and ken's way**

**Erik B. Berda**, *erik.berda@unh.edu. Department of Chemistry, University of New Hampshire, Durham, New Hampshire, United States*

Ken Wagener is the consummate educator. This talk will celebrate his contributions, to both our community broadly and more specifically to the people he's taught. I am surely not alone in saying I owe my career to lessons learned from Prof. Wagener, his dedication to teaching and mentoring, and his unwaivering support for his students past and present. Heartfelt congratulations on a well-deserved award.

## **POLY 89: New polymers with functional group containing semi-rigid alternating copolymers**

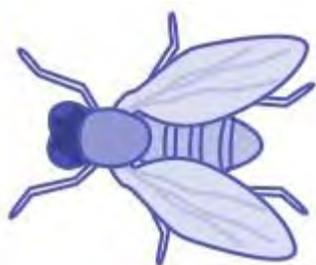
**Sam R. Turner**<sup>2</sup>, [srturmer@vt.edu](mailto:srturmer@vt.edu), *Jing Huang*<sup>1</sup>, *Nadia Nezamabadi*<sup>3</sup>. (1) *Chemistry, Virginia Tech, Blacksburg, Virginia, United States* (2) *Department of Chemistry and Macromolecules and Interfaces Institute, Virginia Tech, Blacksburg, Virginia, United States* (3) *Chemistry, Virginia Tech, Blacksburg, Virginia, United States*

The free radical alternating copolymerization of difficult to homopolymerize comonomers offers a facile technique for synthesizing copolymer backbones with precisely placed functional groups. We have studied the alternating copolymerization of substituted stilbenes with substituted maleimides or maleic anhydride and the results show that these are semi-rigid copolymer structures that possess unique properties in solution and in the solid state arising from the sterically crowded stiffened backbone. We have now enchainned the alternating copolymer sequences in three different polymer structures. We will report our recent results on suspension polymerized nanoporous crosslinked polymer particles containing semi-rigid alternating structures and their carbon dioxide sorbent properties, new microgels containing the same alternating structures prepared via a mini-emulsion technique, and new A-B-A block copolymers with the functional alternating copolymers as the terminal blocks and poly(sulfone) as the center block.

## **POLY 90: Catalysis for monomer and polymer synthesis**

**Robert M. Waymouth**, [waymouth@stanford.edu](mailto:waymouth@stanford.edu). Dept of Chemistry, Stanford University, Stanford, California, United States

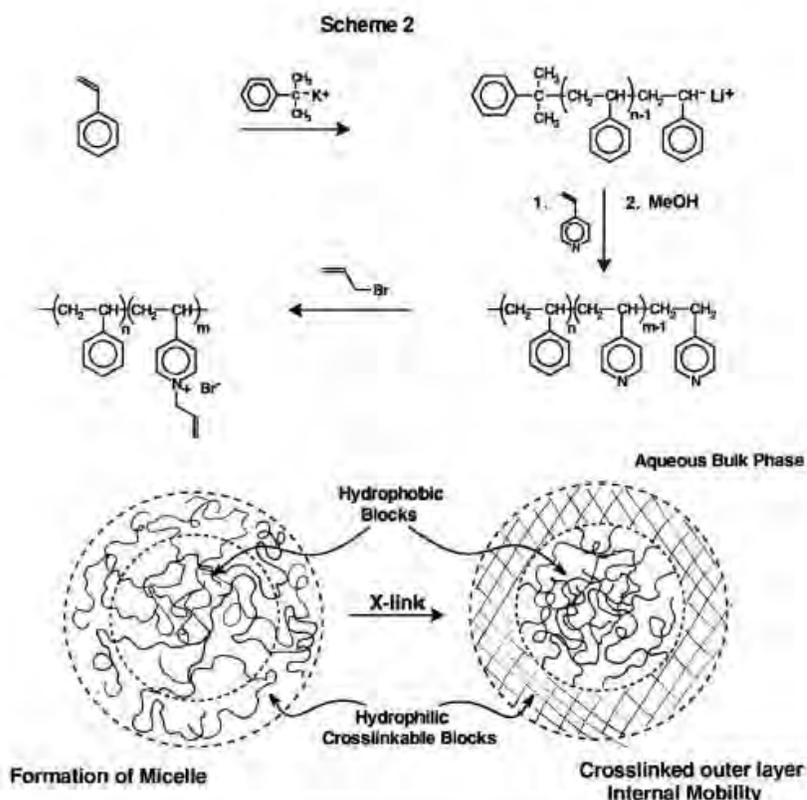
Catalysis is an enabling science for polymer synthesis. We have developed several families of organometallic and organic catalysts for selective polymerization reactions. We have also developed catalytic strategies for generating new monomers for ring-opening polymerization reactions. Mechanistic and kinetic studies have revealed important details of these reactions which illuminate the scope and limitations of these catalytic strategies for monomer and polymer synthesis.



## POLY 91: History of SCKs as an interdisciplinary educational tool, including the Butler Laboratory

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

This presentation will highlight the original conception of the shell crosslinked knedel-like (SCK) nanoparticle design in 1992, and will detail the past twenty years' experimental progression of their synthesis, characterization and optimization toward utility in a variety of applications. Fundamental concepts of polymer chemistry will be emphasized, with attention to retrosynthetic analyses to construct SCKs to possess particular compositions, structures and properties. This retrosynthetic approach was the foundation for a series of Butler Lectures delivered in 2010, and it has continued to be used to advance SCKs to exhibit characteristics that make them capable of applications from drug delivery to crude oil clean-up.



Wooley academic position proposal #1, Fall 1992

## **POLY 92: Deformation mechanisms of block copolymers**

**Edwin L. Thomas**, *elt@rice.edu*. MS 364 1016 Duncan Hall, Rice University Brown Sch of Engr, Houston, Texas, United States

Rubbery - glassy block copolymers provide excellent mechanical toughness due to the combination of deformability and strength. Deformation processes depend on the particular microdomain morphology and for single crystal textures, the orientation of the structure can also exert a strong influence on the behavior. Quasi-static deformation has been relatively well studied with only a few high rate deformation studies. In addition to standard mechanical tests, hypervelocity impact by a spherical projectile is carried out on polystyrene-polydimethylsiloxane diblock copolymers for a series of lamellar samples with different molecular weights to follow how the degree of segregation of the blocks influences energy absorption.

## **POLY 93: Translating university research to the marketplace**

**Joseph M. Desimone**<sup>1,2</sup>, [desimone@unc.edu](mailto:desimone@unc.edu). (1) Department of Chemistry, Department of Pharmacology, Institute for Nanomedicine, Lineberger Comprehensive Cancer Center, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States (2) Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina, United States

From licensing patents to existing companies, to creating entirely new companies, multiple routes exist to enable the translation of academic research to the market. This talk will explore these options and lessons learned from experiences with different approaches, also examining keys to success involving financing, partnerships, company culture, managing conflicts of interest, the role of diversity in team innovation, and the importance of cultural understanding in shaping success both scientifically and in a global marketplace.

## **POLY 94: Synthesis of polymers with controlled structures**

**Robert H. Grubbs**, *rhg@caltech.edu*. Cal Tech 164-30, Pasadena, California, United States

Over the past several decades, a number of methods have been developed that allow the synthesis of polymers with controlled molecular weight and dispersity. ROMP is a tool for the construction of polymers from strained cyclic olefins in a living fashion. This tool combined with other methods such as ATRP have allowed the synthesis of brush polymers of very high molecular weight with controlled dispersity. The living nature can be used to prepare multiblock systems that form well ordered structures such as layered materials that show interesting photophysical properties. Multiblock systems are being explored and their morphologies are now being determined.

## **POLY 95: Teaching and building a polymer laboratory at the University of Florida**

**Kenneth B. Wagener**, [wagener@chem.ufl.edu](mailto:wagener@chem.ufl.edu). Department of Chemistry, the Butler Polymer Research Laboratory, University of Florida, Gainesville, Florida, United States

The University of Florida started work in polymer chemistry in 1946 when Prof. George Butler moved to Gainesville with his wife, Josephine. His research offered leadership to the department for many decades, even after his retirement. In 1995 the university allowed a laboratory to be named in his and Josephine's honor, now widely known as the George and Josephine Butler Polymer Research Laboratory. It consists of numerous synthesis and characterization rooms and houses around 100 people within the Department of Chemistry, including an office to handle the workload of such a large group.

In the mid to late 80s, this polymer effort amounted to ~ 7 people to include one faculty member, four graduate students, a secretary, and Professor Butler as an Emeritus member. The growth to our present size is the result of hiring the right faculty and staff, a bit of good luck, and plenty of opportunity provided by the Department of Chemistry. Professor Butler had an unwavering love for polymers and the people who made it happen; he never left the program, even in retirement, up to his passing in 2007. Josephine felt the same and created a family atmosphere for us all until her passing in 2013.

This story of the creation of the George and Josephine Butler Laboratory forms the basis for how polymer chemistry has been taught at the University of Florida. With so many young faculty on board now, another generation is on its way to advancement in macromolecules, thereby providing an excellent platform for teaching and research for undergraduates, graduates, and postdoctoral scholars, preparing them for their future.

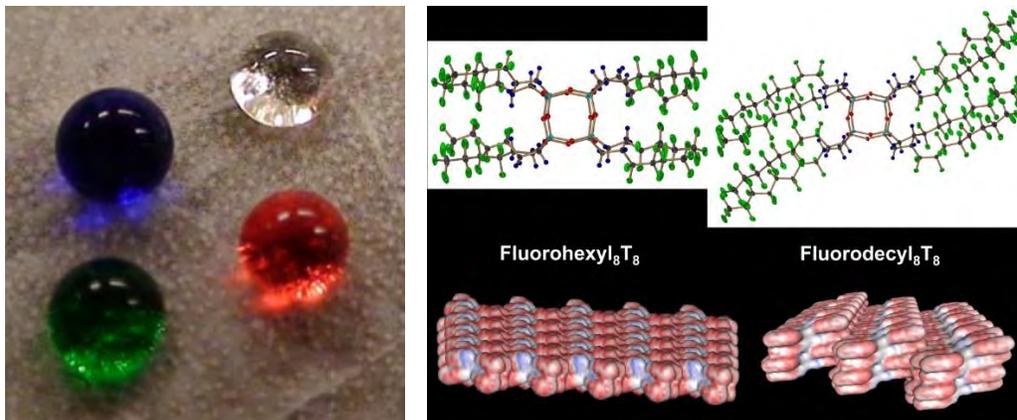


Ken Wagener

## POLY 96: Surface energy, structure, and silicon: Wetting-resistant surfaces from less-familiar compounds

**Joseph M. Mabry**<sup>1</sup>, joseph.mabry@us.af.mil, Andrew J. Guenther<sup>2</sup>, Anish Tuteja<sup>6</sup>, Scott T. Iacono<sup>4</sup>, Arun Kota<sup>2</sup>, Raymond Campos<sup>5</sup>, Sean M. Ramirez<sup>2</sup>, Timothy S. Haddad<sup>2</sup>, Rebecca Stone<sup>2</sup>, Yvonne J. Diaz<sup>3</sup>. (1) AFRL/RZSM, Air Force Research Laboratory, Edwards AFB, California, United States (2) Aerospace Systems Directorate, Air Force Research Laboratory, Lancaster, California, United States (3) ERC Inc., Lancaster, California, United States (4) Department of Chemistry, United States Air Force Academy, Colorado Springs, Colorado, United States (5) University Of Texas At Dallas, Dallas, Texas, United States (6) Mat Sci Eng HH Dow Bldg, University of Michigan, Ann Arbor, Michigan, United States

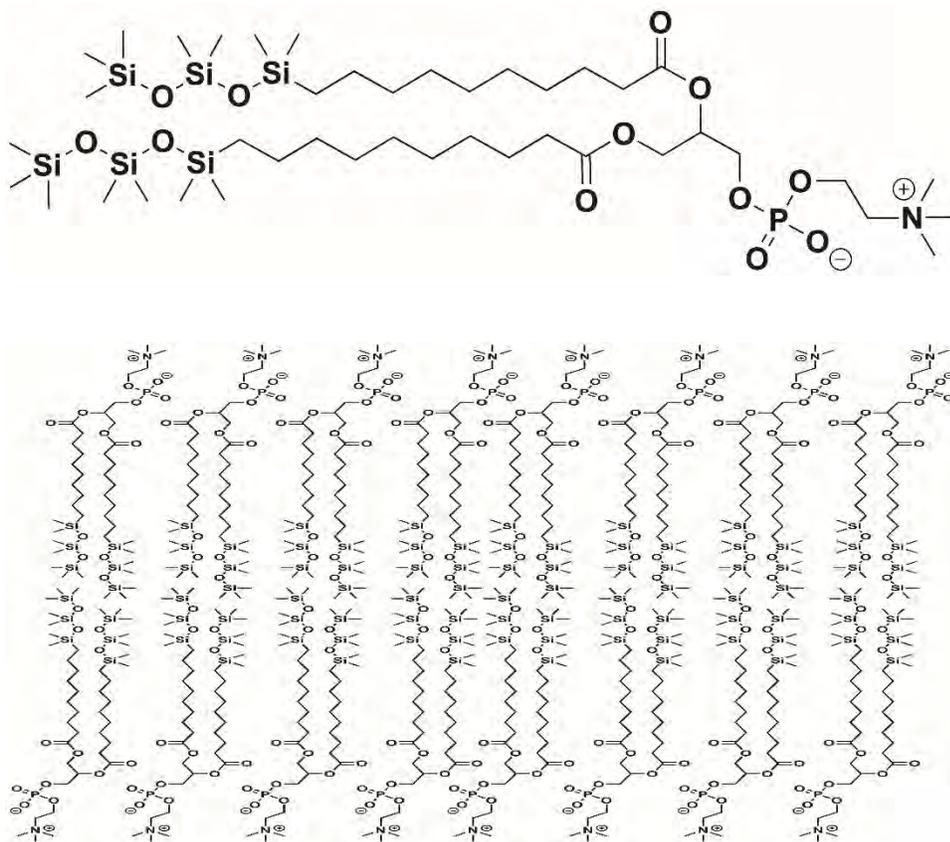
Silicones are well-known for their low glass transition temperatures, which affect dimensional stability, surface energy, and hydrophobicity. However, the properties of many alternative silicon-containing compounds, such as fluorinated polyhedral silsesquioxanes, enable the creation of superoleophobic, or even omniphobic surfaces. The extreme wetting-resistant behavior of these compounds is the result of a combination of factors, including low-surface energy and crystallinity. While low-surface energy values are largely the result of high-degrees of fluorination, allowing these compounds to migrate to the surface in composite materials, the crystallinity enabled by the alignment of flexible silicon-oxygen cores and fluorinated alkyl groups, allows microcrystalline domains, rich in  $-CF_3$  groups, to form on composite surfaces, leading to wetting-resistant surfaces. However, truly remarkable surfaces can be created when an additional level of structure is introduced. Wetting-resistant surfaces have proven useful in many applications, and many different types of compounds and surfaces have been prepared. This presentation will discuss these compounds, as well as the composition and properties necessary to achieve the desired wetting-resistant properties



## POLY 97: Synthesis and properties of siloxane-containing phospholipids

Mark B. Frampton<sup>1</sup>, Drew Marquardt<sup>2,3</sup>, Georg Pabst<sup>2,3</sup>, **Paul M. Zelisko**<sup>1</sup>,  
pzelisko@brocku.ca. (1) Chemistry and Centre for Biotechnology, Brock University, St.  
Catharines, Ontario, Canada (2) Institute of Molecular Biosciences, Biophysics Division,  
University of Graz, Graz, Austria (3) Bio TechMed-Graz, Graz, Austria

Nature provides a broad library of phospholipids that are responsible for providing a barrier between the internal and external cellular environments as well as participating in other biochemical roles. Phospholipids and other lipid-like molecules have the capacity to self-assemble into varying liposomal architectures. Phospholipid-based liposomes are uniquely suited as delivery vehicles and research into liposomal delivery vehicles has been a significant component of pharmaceutical research. To this end we have utilized both traditional chemistry as well as biocatalysis to synthesize trisiloxane-containing phosphocholines (SiPCs). Small angle X-ray scattering (SAXS) data indicated that, unlike their diacyl phosphocholine analogs, SiPCs do not self-assemble into multilamellar vesicles in aqueous solution, instead forming unilamellar vesicles without the need for numerous extrusion sequences. Dynamic light scattering measurements (DLS) revealed that the resulting unilamellar liposomal systems ranged from 100-200 nm in diameter. The synthesis of these systems, their properties, and potential applications will be discussed.

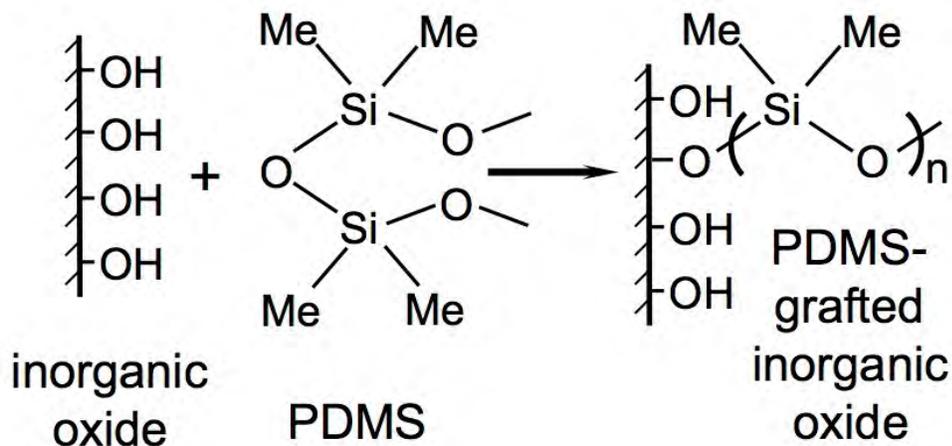


## POLY 98: Silicon and silicone chemistry with an eye toward surfaces

**Thomas J. McCarthy**, [tmccarthy@polysci.umass.edu](mailto:tmccarthy@polysci.umass.edu). Univ of Massachusetts, Amherst, Massachusetts, United States

Over the past two decades our group has developed techniques to introduce specific functional groups onto the surfaces of inorganic substrates (primarily oxidized silicon) with the major goal of understanding dynamic wetting. Tens of thousands of samples were prepared and contact data were recorded. We wrestled with this data and came up with some consistencies that we used in analyzing new data. These approaches led to deep insight into the molecular level events that cause contact angle hysteresis. This chemistry required competent preparative chemists who could reproduce conditions precisely.

More recently we developed some "shortcuts" for preparing hydrophobic surfaces that exhibit little contact angle hysteresis based on co-equilibration of inorganic substrates and reactive silicones. This work will be described and compared with the chemically more elegant methods. This co-equilibration chemistry led us in directions toward silicone synthesis and we are currently developing skills and interests in this arena.



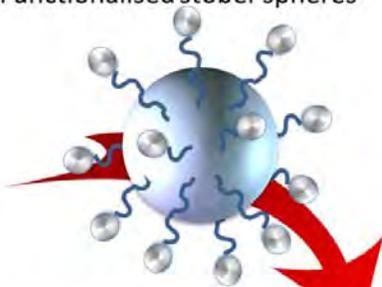
## POLY 99: Functionalised silica nanoparticles: Towards durable super hydrophobic coatings

**Geraldine G. Durand**, *geraldine.durand@twi.co.uk*, Alan Taylor, Nadia Sid, Marta alvarez. TWI Ltd, Cambridge, United Kingdom

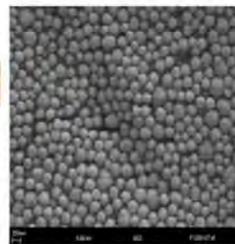
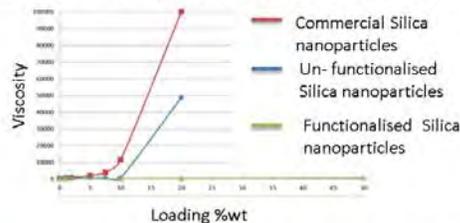
Nanotechnology offers the potential of new functional materials which can be used to address some of the significant challenges facing society. One specific topic which has received much attention is superhydrophobic, easy-clean or self-cleaning coatings. Highly repellent surfaces are expected to improve aerodynamic efficiency, increase safety, reduce maintenance costs and minimise the use of chemicals which foul underground water. Whilst each of these drivers is significant in its own right, the lack of commercial durable highly repellent coatings able to retain their repellency property after exposure to the everyday environment illustrates the need for a new approach.

This presentation illustrates the work that is being carried out by TWI in order to create hybrid coatings that exhibit water repellency and durability by using functionalised nanoparticles. TWI has been investigating silicon chemistry as a route to customise the surface of the nanoparticles before their incorporation into acrylate, epoxy and polyurethane based resin in order to enhance the repellency of the final coatings. The key innovative aspects of the approach are the fabrication of the silica additives and the routes to achieve their specific and tailorable functionalization that allow high loading levels of silica nanoparticles loading (above 50%) into resins without segregation, gelation or the need for diluents. Moreover, the ability to functionalise these particles offers the opportunity to tailor and tune the attributes they display, attributes such as cross-linking, water repellence, oil repellence, reaction rate and environmental response.

Functionalised stöber spheres



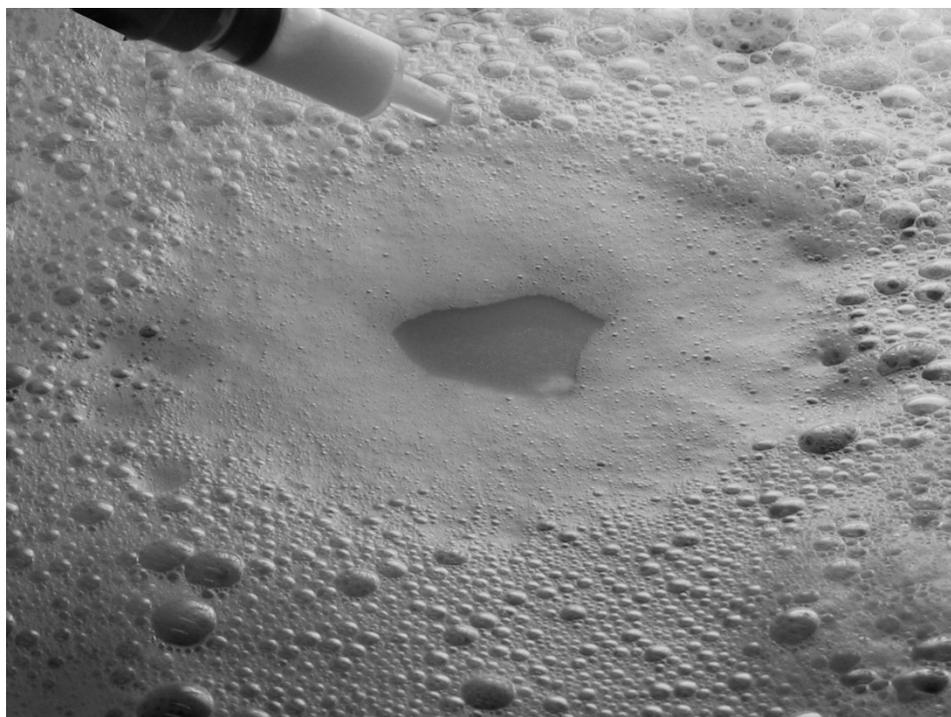
Effect of silica loading on the viscosity of an epoxy resin



## POLY 100: Silicone wettability aspects

**Michael J. Owen**, *michaelowen01@chartermi.net*. Michigan Molecular Institute, Midland, Michigan, United States

Many hydrocarbon-based oils, surfactants and substrates have surface energies in the 20-30 mN/m range. This is a particularly interesting one for silicone materials. The most common silicone is polydimethylsiloxane (PDMS) and its surface tension lies at the lower end of this range (16-21 mN/m depending on molecular weight). Many of the significant applications of PDMS depend on its ability to lower the surface tension of other oils, surfactants and polymers, or to spread over similar low-surface-energy substrates. Examples include antifoams (see photo), personal care products, release coatings and water-repellent coatings. The wetting behavior of PDMS, both wetting by silicones and of silicones, will be briefly reviewed in the light of available surface tension and contact angle data and related to fundamental characteristics such as the low intermolecular forces between methyl groups, the compact size of the methyl group, and the high siloxane backbone flexibility.

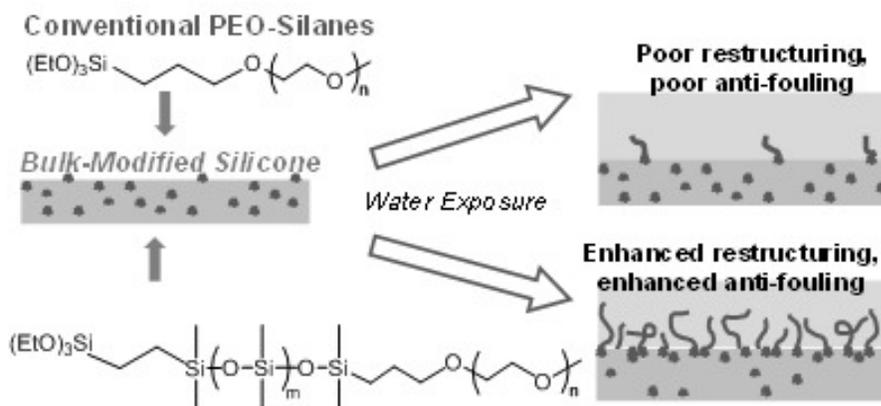


Silicone antifoam in action

## POLY 101: Anti-fouling silicones prepared with PEO-silane amphiphiles

**Melissa Grunlan**, [mgrunlan@tamu.edu](mailto:mgrunlan@tamu.edu), Marc A. Rufin, Melissa Hawkins. 3120 TAMU, Texas AM University, College Sta, Texas, United States

Silicones, particularly silica-reinforced crosslinked polydimethylsiloxane (PDMS), are widely-used for medical, marine and industrial applications. Unfortunately, their extreme hydrophobicity causes poor-antifouling behavior. Although polyethylene oxide (PEO) is known to be exceptionally anti-fouling (e.g. protein resistant), these observations have been largely made when PEO is grafted to a physically stable substrate (e.g. gold and silicon wafer). In this way, migration of the PEO to the water-surface interface, where biological adhesion occurs, is not required. In this work, we sought to enhance the water-driven surface-migration of PEO incorporated into silicones in order to achieve superior anti-fouling behavior. Conventional PEO-silanes consist of a PEO segment separated from the reactive group by a short alkane spacer. In contrast, we prepared PEO-silane amphiphiles with siloxane tethers of varying lengths and as well as variable PEO segment lengths. The resistance of these coatings to proteins, whole blood and biofoulers are related to PEO-silane structure.



## POLY 102: Award Address (Frederic Stanley Kipping Award in Silicon Chemistry sponsored by The Dow Corning Corporation). Designing silicones to control interfaces

**Michael A. Brook**<sup>1</sup>, [mabrook@mcmaster.ca](mailto:mabrook@mcmaster.ca), Yang Chen<sup>2</sup>, Benjamin Macphail<sup>1</sup>, Laura Zepeda-Velasquez<sup>1</sup>, John B. Grande<sup>1</sup>, Ayodele Fatona<sup>1</sup>, Jose Moran-Mirabal<sup>1</sup>, Marlena Whinton<sup>1</sup>, Madiha F. Khan<sup>1</sup>. (1) Chemistry and Chemical Biology, McMaster University, Hamilton, Ontario, Canada (2) EnRoute Interfaces, Hamilton, Ontario, Canada

Silicones are known for the ability to migrate to and control interfaces, leading to their use in applications ranging from foam stabilizers to wound dressings. Hydrophilically-modified silicones, which are particularly interesting at interfaces, typically rely on polyethers, although other hydrophiles can be used. With the exception of superwetters, most silicone surfactants are comprised of complex mixtures. It is our hypothesis that enhanced control of interfaces will arise both from the use of more precise silicone hydrophobe structures and from the use of new hydrophiles.

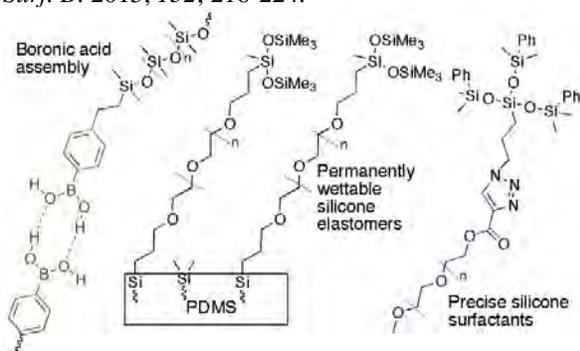
Boronic acids are widely known to complex to saccharides. However, they also form dimer complexes in hydrophobic media, as shown with silicone boronic acids. Once in contact with water, a combination of 1:1 boronic acid dimers and Lewis acid: Lewis base complexes between boron and adjacent oxygen atoms led to resilient thin films or high modulus elastomers without any covalent crosslinks.<sup>1</sup>

Silicone polyethers with small silyl groups exhibit unusual wetting characteristics when tethered to silicone elastomers: permanent contact angles <20° are observed: hydrophobic recovery is suppressed.<sup>2</sup> Such materials are useful in microfluidics applications as they obviate the need to pump aqueous fluids through devices.<sup>3</sup> These surfactants also permit highly stabilized, polymerized microemulsions to be prepared with domain sizes of less than 10 nm.<sup>4</sup>

The head groups of silicone polyether surfactants can dominate surface activity. The Piers-Rubinsztajn reaction was used to create small and medium size dendrons that,<sup>5</sup> once grafted to a polyether using the Huisgen reaction, showed large differences in surface tension<sup>6</sup> and *E. coli* were disinfected.<sup>7</sup>

Unmet needs and strategies to address them will be discussed.

<sup>1</sup>Brook et al. *Chem. Commun.* 2013, 49, 1392-1394; <sup>2</sup>Fatona et al. *Lab Chip* 2015, in press. <sup>3</sup>Brook et al. *Chem. Commun.* 2013, 49, 1392-1394, US Patent 8,648,211. <sup>4</sup>Brook et al. *Chem. Commun.* 2011, 47, 8874-8876. <sup>5</sup>Grande et al. *Polym. Chem.* 2014, 5, 6728-6739. <sup>6</sup>Gonzaga et al. *Chem. Eur. J.* 2012, 18, 1536-1541. <sup>7</sup>Khan et al. *Colloids Surf. B*: 2015, 132, 216-224.



## POLY 103: Progress towards sustainable polyurethanes and polycarbonates built from biobased chemicals

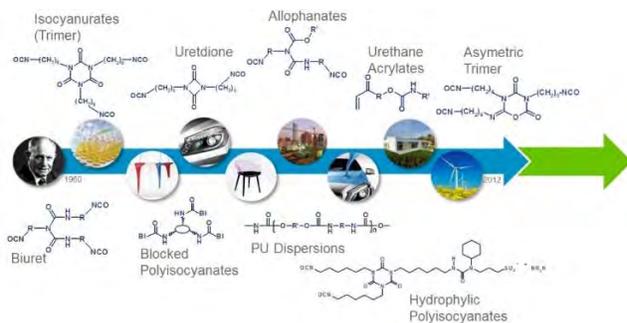
**Don S. Wardius**<sup>1</sup>, *don.wardius@covestro.com*, **Gesa Behnker**<sup>2</sup>, **Frank Buckel**, **B. Vega Sanchez**<sup>2</sup>, **Natalie Rahmen**<sup>2</sup>, **Niklas Meine**<sup>2</sup>, **Jean Pascal Schulte**<sup>2</sup>. (1) Covestro LLC, Pittsburgh, Pennsylvania, United States (2) Covestro AG, Leverkusen, Germany

Polymers from renewable raw materials show the potential to reduce greenhouse gas emissions by saving fossil resources, giving more benign production processes, and using raw materials that took up CO<sub>2</sub> during photosynthesis. Processes like biotechnological fermentations work at low temperatures and produce less waste. Biobased chemicals (e.g., 1,3-propanediol) are being produced cost efficiently at scale. Covestro is interested in chemicals that are more sustainable than their petro-based counterparts, using these to produce high-performance products which can be cost efficient.

Biobased chemicals are produced by biotechnological or catalytic conversion of renewable feedstocks such as saccharides. Covestro is evaluating technologies at an early stage in order to identify the potential of the new process. Covestro is working with leading partners along the value chain to develop production of these chemicals, use them for product developments and ultimately bring high-performance products to the market.

Biobased polyols are known to be useful for polyurethanes suitable for diverse applications including building insulation, cold chain and piping insulation, mattresses or sport shoes. Natural oils like castor and soybean oil, or sugars and glycerol are used to make polyether polyols. Covestro has developed new biobased polyols based on biobased chemicals such as succinic acid.

Now Covestro has developed pentamethylene diisocyanate, a new isocyanate, 70 percent of the carbon content comes from biomass without generating any direct competition for food production. The first biobased polyurethane crosslinker based on this molecule has been launched commercially. This is the first plant-based aliphatic polyurethane hardener to be used for coatings, adhesives and other applications. Covestro has developed fermentation technology for the potential production of biobased phenol. The company is looking at ways to build biobased content into polycarbonate plastics. The pathforward in this endeavor will depend on the economic feasibility of the changeover as well as the benefit that may accrue from having a lower carbon footprint for the production process.

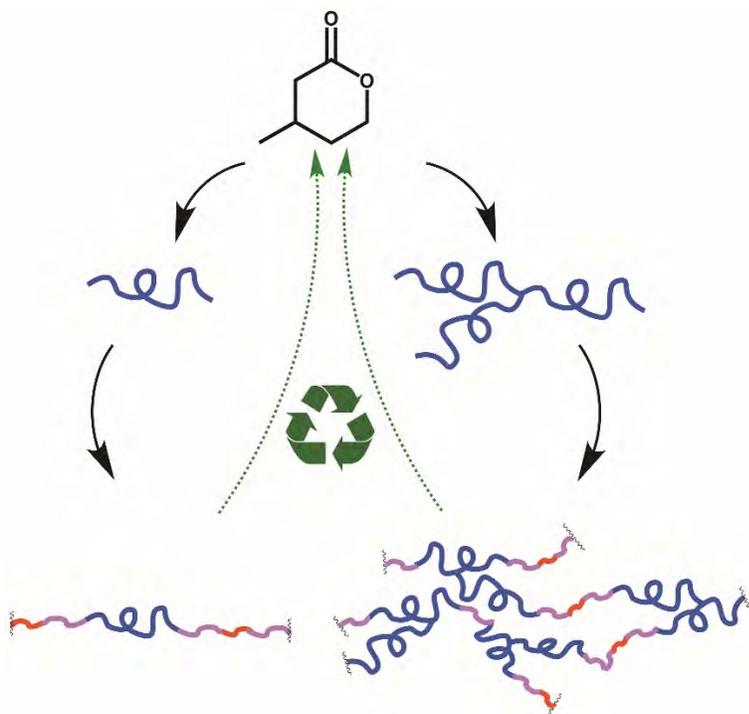


progress in hardeners for polyurethanes

## POLY 104: Sustainable chemically recyclable polyurethanes

**Debbie K. Schneiderman**, *schne643@umn.edu*, Marie Vanderlaan, Derek Batiste, Alexander M. Mannion, Tessie R. Panthani, Marc A. Hillmyer. University of Minnesota, Minneapolis, Minnesota, United States

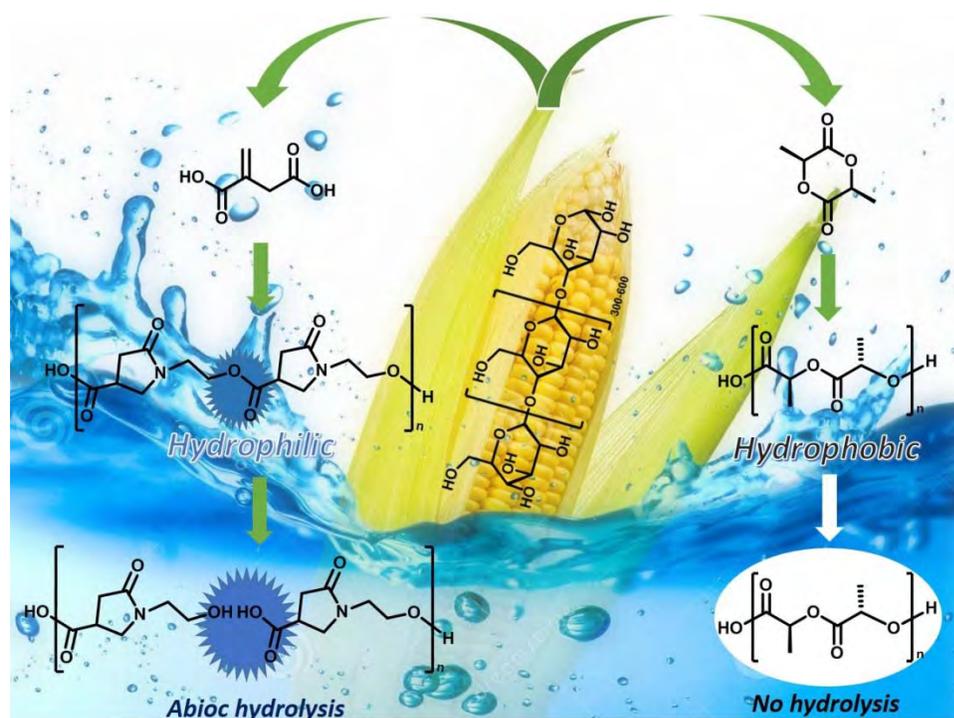
Polyurethanes (PUs), in the form of coatings, adhesives, sealants, elastomers, and foams play a vital role in the consumer goods, automotive, and construction industries. However, because most commercial PUs are petroleum derived and resistant to degradation, there are significant environmental challenges associated with the production and disposal of these materials. We address these challenges with the synthesis of sustainable, chemically recyclable polyurethanes. Our approach employs renewable, degradable hydroxy telechelic poly( $\beta$ -methyl- $\delta$ -valerolactone) (PMVL) as a drop-in replacement for petroleum derived polyols in the synthesis of thermoplastic polyurethanes and flexible foams. We show that PMVL polyols are attractive alternatives to natural oil polyols because they are more reactive and can be synthesized with precise control over molar mass and functionality. We also demonstrate that PMVL polyurethanes can be chemically depolymerized to recover  $\beta$ -methyl- $\delta$ -valerolactone monomer in high purity and yield. This remarkable feature helps to reduce the environmental impact of these materials and bypasses many of the technical challenges that currently preclude chemical recycling of polyurethanes on an industrial scale.



## POLY 105: Synthesis of biorenewable and water degradable polyesters from itaconic acid

**Pengxu Qi<sup>2</sup>**, [pqi@chem.ufl.edu](mailto:pqi@chem.ufl.edu), **Stephen A. Miller<sup>1</sup>**. (1) Chemistry, University of Florida, Gainesville, Florida, United States (2) University of Florida, Gainesville, Florida, United States

Diacid monomer containing N-substituted-2-pyrrolidone (NS2P) ring system have been synthesized from itaconic acid, a biomonomer mass-produced from the fermentation of carbohydrates. By changing the aliphatic diols as the comonomer, the thermal properties of the obtaining polyesters can be tuned, covering the range of Polylactic Acid (PLA), Poly(Ethylene Terephthalate) (PET) and Polystyrene (PS). The high water degradability of these new set of polyesters due to the hydrophilicity of pyrrolidone has been discovered, offering great potential to replace those commodity plastics.



## **POLY 106: High molecular weight sustainable polymers and thermoplastic elastomers from resin acids via living ring-opening metathesis polymerization**

**Mitra S. Ganewatta**<sup>1</sup>, ganewatt@email.sc.edu, Liang Yuan<sup>1</sup>, Md Anisur Rahman<sup>1</sup>, Wenyue Ding<sup>2</sup>, Megan L. Robertson<sup>2</sup>, Chuanbing Tang<sup>1</sup>. (1) Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina, United States (2) Department of Chemical and Biomolecular Engineering, University of Houston, Houston, Texas, United States

Renewable polymers derived from natural biomass have been witnessing an unremitting growth in academia as well as industry. Many natural chemicals including sugars, furans, lignin, plant oils and terpenes are exploited to produce renewable polymeric materials. Resin acids from pine trees are a class of promising biomass for polymer synthesis. However, the bulky tricyclic structure has been problematic in obtaining high molecular weight homopolymers with good mechanical properties. For the first time, we develop a robust method to prepare high molecular weight renewable homopolymers and block copolymers (BCPs) derived from resin acids via “living” Ring-Opening Metathesis Polymerization (ROMP). Using the living ROMP, homopolymer was chain extended with a soybean oil derived norbornene monomer to elaborate BCPs. These BCPs phase separate to produce hard and soft domains that show desirable properties for thermoplastic elastomer applications.

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## POLY 107: Renewable thermoplastic materials from polysaccharides

**Bing Zhou**, [zhoubing.sshy@sinopec.com](mailto:zhoubing.sshy@sinopec.com), James H. Wang, Qin Jia. Sinopec Shanghai Research Institute of Petrochemical Technology, Shanghai, China

Polysaccharides include both structural polysaccharides such as cellulose and chitin, as well as storage polysaccharides (e.g. starch and glycogen). They are not thermoplastic and cannot be processed like a thermoplastic polymer such as polyethylene or polypropylene. There are two approaches to convert polysaccharides into thermoplastic materials, one approach is to maintain the original backbone structures of polysaccharides; the other approach is to convert polysaccharides into polymers having different backbone structures. In this paper, the first approach is used to develop renewable materials from two of the most common polysaccharides: cellulose and starch.

When cellulose is chemically modified into a derivative such as a cellulose ester having sufficient esterification level, the cellulose derivative becomes thermoplastic (i.e. Thermoplastic Cellulose, TPC). Starch can be converted into thermoplastic starch (TPS) through a non-chemical method, i.e. a plasticization process. Thermoplastic starch has the advantages of renewability and low cost; but it has limitations including low tensile strength, low ductility, and high moisture sensitivity. Although thermoplastic cellulose has good tensile strength and low moisture sensitivity, its cost is significantly higher than TPS. The findings in this paper will provide important insights for developing renewable thermoplastic polymer materials from natural polysaccharides.

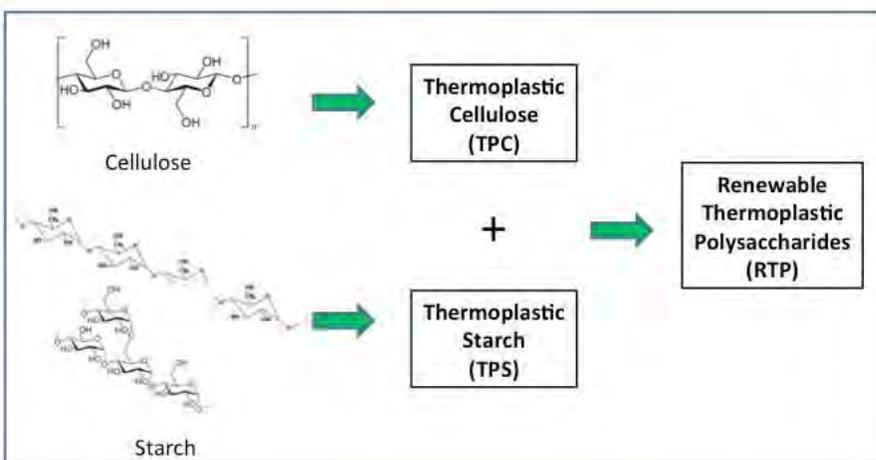


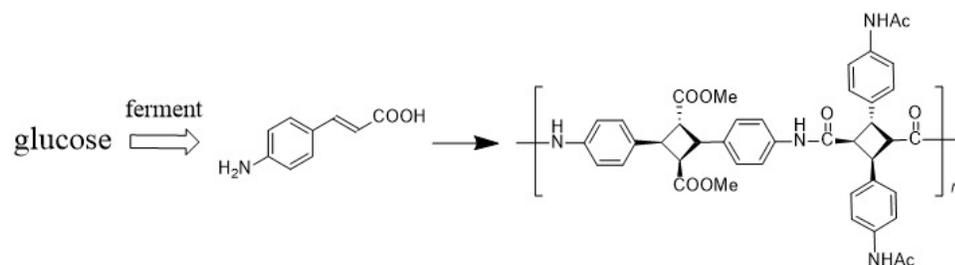
Figure 1, Renewable Thermoplastic Materials from Polysaccharides

## POLY 108: Super-strong, transparent polyamides derived from renewable aromatic amino acid

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(1) Jaist Sch Materials SCI, Nomi, Japan (2) Japan Advanced Institute of Science and Tech, Ishikawa, Japan (3) Japan adv Inst sci and tech, Nomi, Ishikawa, Japan (4) Univ Tsukuba, Tsukuba, Japan

Bio-based polymers obtained by a polymerization of biomolecules are indispensable for establishment of green sustainable society where almost materials should be renewable and recyclable. Conventional bio-based polymers such as poly(lactic acid)s have a worse hand comparing to commodity-type plastics in terms of the balance of cost with performance in materialization. Development of high-performance bioplastics should be effectual on overcoming this problem because advanced plastics circulate in higher price than biological matters such as food additives.

Here we fermented an exotic aromatic amino acid, 4-aminocinnamic acid, from glucose by using metabolically engineered bacterium. Quantitative photodimerization of 4-aminocinnamic acid generated diamino and diacid biomonomers, both of which had functionalized a rigid alpha-truxillate structure and then were used to synthesize series of aromatic polyamides (representative: Figure). These aromatic biopolyamides were processed into highly-transparent plastic films with thermal stability and mechanical performance as high as super engineering plastic films, in spite of amorphous structures. Some of the bio-based polyamide films showed very low thermal expansion coefficient comparable with aluminium, which imply the metal-altnation application. Besides we confirmed mechanical strengths much higher than those of conventional transparent polymeric films and

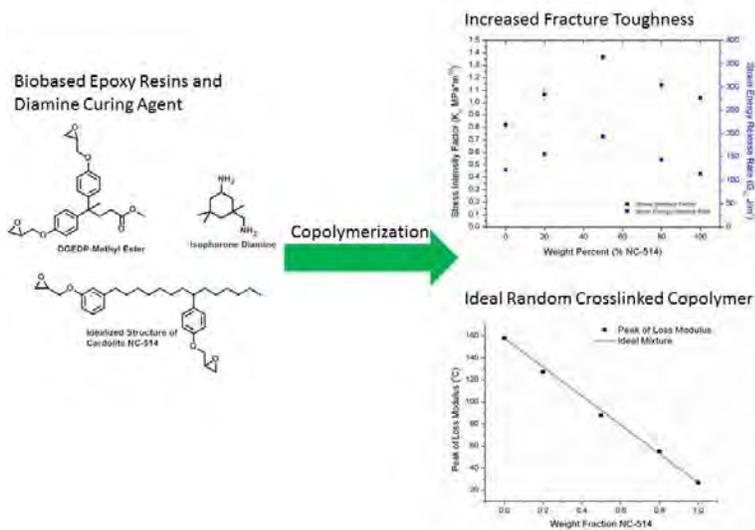


Schematic synthetic route of bio-based aromatic polyamides with high strength

# POLY 109: Improving epoxy resin fracture toughness through biobased cashew nutshell liquid resin for high viscosity applications

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Combinations of diglycidyl ether diphenolate methyl ester (DGEDP-Me), a high viscosity biobased epoxy resin and a flexible lower viscosity epoxy resin from cashew nut shell liquid (NC-514) were prepared to control resin viscosity and realize improvements in cured epoxy resin toughness relative to the neat resins. The viscosities of DGEDP-Me/NC-514 mixtures varied from 660-to-26 Pa.s and curing was performed using stoichiometric amounts of a cycloaliphatic diamine crosslinker. The cured materials were one phase from SEM analysis of fractured surfaces and from x-ray scattering. Furthermore, all resin compositions were transparent and have one alpha transition temperature, confirming resin miscibility. Storage modulus values for cured thermosets range from 3000 MPa to 1000 MPa and alpha transition temperatures varied linearly (158 to 27 °C) as a function of the epoxy resin composition. Oscillatory rheology at different weight percentages of the flexible and rigid epoxy resin components was used to determine the average molecular weight between crosslinks which was correlated to material toughness. Relative to the neat high viscosity resin, 1:1 w/w mixtures of the rigid and flexible epoxy resin components gave increases in the impact strength and mode I fracture toughness of 136% and 66%, respectively. Higher percentages of the flexible epoxy resin resulted in decreased toughness.



## **POLY 110: Probing the morphology, hydration, mechanics and tribology of biomedical coatings with environmental AFM**

**Greg D. Haugstad**, *haugs001@umn.edu. University of Minnesota, Woodbury, Minnesota, United States*

This presentation is an overview of atomic force microscopy (AFM) methodologies applied to crosslinked polyacrylamide and polyvinyl pyrrolidone based lubricious coatings as well as drug-eluting polymeric coatings (block copolymers, blends), under variable humidity and aqueous immersion. (Research was performed in open collaborations with members of an industrial consortium, IPRIME.) Beyond rich surface morphologies and their dependence on hydration, the imaging contrast derived from nanomechanics and/or tip-sample adhesion aids in the identification of components in coatings and thereby assesses phase segregation, local crystallization or other sources of heterogeneity. In the case of drug-eluting coatings, AFM is complemented by confocal Raman imaging to add chemical and crystallinity contrast as well as depth perception.

Defect structures such as craters, pinholes, fissures and wrinkles (for the case of UV-crosslinked, sponge-deposited polyvinyl pyrrolidone coatings) largely disappear at high humidity as well as under aqueous immersion, with the concomitant appearance of crystallites due to the diffusion and aggregation of crosslinking additives.

Nanomechanical probing during complete hydration cycles identifies reversible glass-to-rubber transitions that are further distinguished by degree of crosslinking. Tip-sample adhesion is also strongly sensitive to humidity-controlled glass-rubber transitions (dependent on crosslinking), and reveals significant differences between thin and thick coatings in the case of polyacrylamide. Nanotribological methods further reveal crosslinking-derived differences in coating behavior, especially pertinent to wear. Colloid-probe AFM methodologies are developed and utilized to explore normal and shear response in the gel state under aqueous immersion. In all cases mapped, distance-dependent force measurements ("force spectroscopy") – both slow (force volume) and high-frequency modes (e.g., peak/pulse force) – provide deeper insights into material properties.

The overarching emphasis of this presentation is on (i) commonly available AFM modes to obtain information well beyond simple surface topography; (ii) the enabling "humidity knob", and full aqueous immersion, to study changes in polymeric materials due to hydration as well as small-molecule diffusion within and from polymeric coatings; (iii) the importance of multichannel data acquisition and high data throughput to creative applications of AFM.

## POLY 111: Morphological variations in poly (L-Lactic Acid) (PLLA) vascular scaffolds for the treatment of coronary heart disease (CHD)

**Karthik Ramachandran**<sup>3</sup>, *kramacha@caltech.edu*, **Artemis Ailianou**<sup>3</sup>, **Mary Beth Kossuth**<sup>1</sup>, **James P. Oberhauser**<sup>1</sup>, **Julia A. Kornfield**<sup>2</sup>. (1) Abbott Vascular, Santa Clara, California, United States (2) California Institute of Tech, Pasadena, California, United States (3) Chemical Engineering, California Institute of Technology, Philadelphia, Pennsylvania, United States

Poly (L-lactic Acid) (PLLA) is a semicrystalline and biocompatible polymer that is used in bioresorbable vascular scaffolds for the treatment of Coronary Heart Disease (CHD). To treat CHD, a PLLA scaffold is deployed in the occluded artery to restore blood circulation. Implants made of PLLA undergo hydrolysis to form L-lactic acid that is readily metabolized by the human body, allowing them to harmlessly disappear in two years. The polymer is subjected to tube expansion and laser cutting (Fig. 1A) before it is crimped onto a balloon (Fig. 1D-E). When the crimped scaffold is in position in the diseased artery, the balloon is inflated to deploy the scaffold (Fig. 1F-G). The resulting semicrystalline structure changes over distances of a few microns, requiring X-ray microdiffraction to shed light on the structural changes that occur in PLLA vascular scaffolds which govern their therapeutic function.

Crimping places the outer bend (OB, Fig. 1B) of a U-crest (Fig. 1D-E) under elongation and the inner bend (IB, Fig. 1B) under compression. X-ray diffraction patterns indicate highly oriented PLLA crystallites where elongation was imposed (near the OB) and crystallites tilted out of plane where compression was imposed (at the IB). Between the IB and the OB, there is an unperturbed region with an orientation similar to the expanded tube.

Deployment profoundly alters the structure created during crimping. The tilting of crystallites at the IB during crimping allows them to gracefully separate into diamond shaped voids (Fig. 1G) when the IB is placed under tension during deployment. Consequently, the OB experiences relatively mild compressive stress during deployment and a highly uniform structure is observed. Despite PLLA's reputation as a brittle plastic, the solid state deformation does not fracture the scaffold; rather, the deployed PLLA scaffold has a high degree of orientation, giving the scaffold the radial strength to hold the blood vessel open.

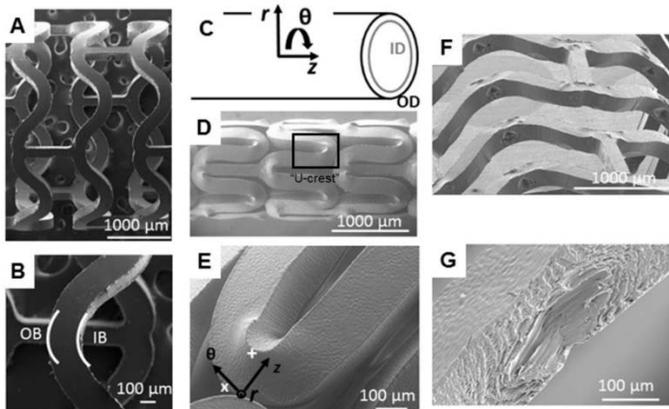


Fig.1. (A-B) Laser Cut Scaffold indicating the inner (IB) and outer bend (OB) (D-E) Crimped Scaffold indicating a U-crest. (F-G) Deployed Scaffold indicating diamond-shaped-voids.

## POLY 112: Molecular weight analysis of implanted polyurethane insulated cardiac leads: Role of allophanate linkages

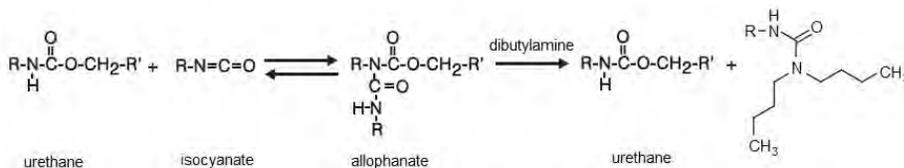
**Emily Chen**, *chene05@sjm.com*, Ajay D. Padsalgikar. R&D, St Jude Medical, Rogers, Minnesota, United States

Allophanate formation is a common side reaction in polyurethane synthesis, where the unreacted isocyanate groups bond with an existing urethane linkage. This results in branching or cross-linking. Depending on the level of cross-linking, allophanates affect the properties of the polyurethane to varying degrees; the melt viscosity, molecular weight and polymer solubility can be significantly affected.

Optim™ insulation is a siloxane based polyurethane that is extremely biologically stable and hence used as insulation on permanently implanted cardiac leads. Due to the differences in the polarity between the segments of Optim™, allophanate linkages may occur. Attempts to characterize allophanates using traditional analytical techniques have not been successful.

The allophanate linkages break down over time when Optim™ is molten, giving Optim™ rheology a time dependent dimension. Concurrent measurements of the molecular weight and allophanate concentration confirm the dissociation of these linkages over time in the molten state.

We used rheometry and gel permeation chromatography (GPC) to confirm the presence of allophanate linkages in our material, and used a titration based technique to quantify the allophanate linkages present in Optim™. We also show that an observed decrease in molecular weight during hydrolytic treatment of Optim™ can be attributed to allophanate hydrolysis, with little to no urethane hydrolysis. Removal of the allophanate linkages from the polymer did not affect the other chemical and mechanical properties of Optim™. This analysis suggests Optim™ insulation has good characteristics for long term biostability in a cardiac lead implementation.



To determine the allophanate concentration, the remaining dibutylamine is titrated with acid, and the results are compared to a blank.

## POLY 113: Use of ion exchange resins in pharmaceutical formulations

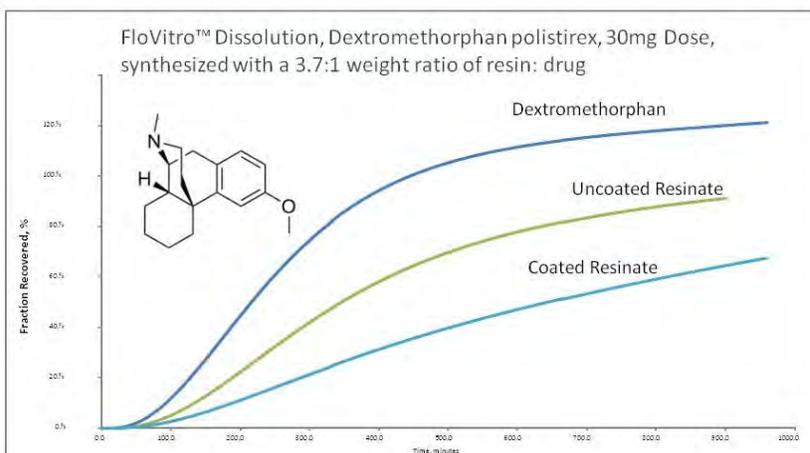
**Amie Gehris**, AGEHRIS@DOW.COM. Dow Pharma and Food Solutions, The Dow Chemical Company, Green Lane, Pennsylvania, United States

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

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

The patented flow through dissolution method used to obtain case study data employed using the Dow's FloVibro™ technology which gives level A IVIVC with no mathematical modeling and is predictive of extended release. This method's concepts and use will be explained during the case studies portion of the presentation. Additionally, a flow through buccal dissolution test was used to obtain data for the taste masking case studies and Dow also holds a patent for the technology which predicts taste masking efficacy using concentration as a proxy for bitter taste.

### Modified Release – Case study #1



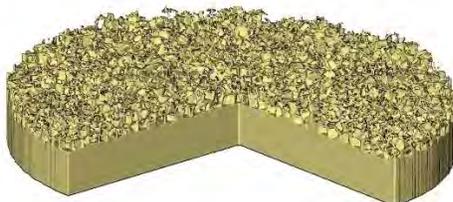
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Controlled Release of Dextromethorphan From an Ion Exchange Resin

## **POLY 114: Mechanical performance of surface porous PEEK for orthopaedic applications**

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Polyetheretherketone (PEEK) is widely used in medical implants because of its high strength, radiolucency, and favorable cytocompatibility. However, it is often linked to fibrous tissue formation instead of osseointegration. In order to overcome this limitation, porous polymers enable bone ingrowth, but inherently lack mechanical properties necessary for orthopaedic applications. Herein, we describe the characterization of an interconnected porous surface and the mechanical performance of surface porous PEEK (PEEK-SP, Scoria™) and PEEK-SP cervical interbody fusion devices. PEEK-SP was created using a patented processing technique. PEEK (Zeniva, Solvay Advanced Polymers) was extruded through a porogen under heat and pressure. The porogen was leached, leaving a porous surface layer of desired thickness. Micro-computed tomography ( $\mu$ CT) was used to quantify the porosity, layer thickness, and pore size of the porous structure. Samples were mechanically tested for tensile, shear, and tensile adhesion strength. Devices underwent further biomechanical tests for expulsion and subsidence.  $\mu$ CT showed that devices had average 63.7% porosity, 220 micron pore size, and 0.69 mm pore thickness. Tensile strength and modulus were unaffected by the porous surface, but elongation to failure decreased. Interfacial shear strength was more than 20 MPa for PEEK-SP, which is greater than trabecular bone (10-15 MPa). PEEK-SP devices had a 70% higher expulsion force and greater subsidence yield force than a predicate device. Tensile adhesion strength was near 25 MPa for PEEK-SP sample, greater than the FDA required 22 MPa. Limiting porosity to the surface enabled the device to maintain its bulk mechanical properties and meet the required performance. The devices were found to have properties substantially equivalent to or greater than predicate devices, leading to FDA 510(k) clearance in September 2015.

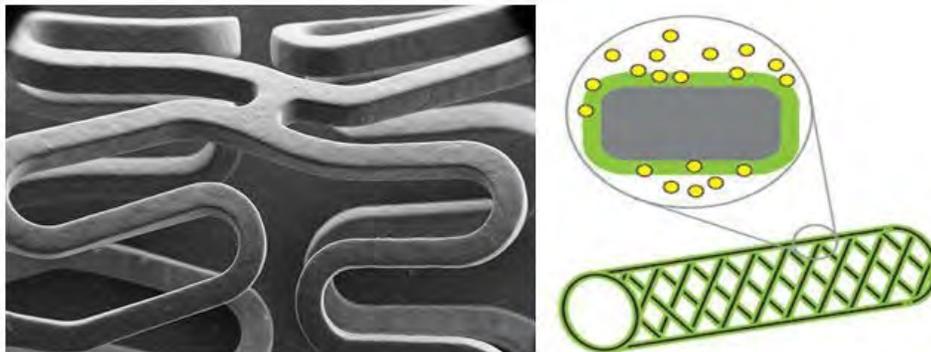


$\mu$ CT section of PEEK-SP sample.

## POLY 115: Characterization of novel degradable polymers for drug delivery applications

**Joram Slager**, [jslager@surmodics.com](mailto:jslager@surmodics.com). SurModics, Inc., Eden Prairie, Minnesota, United States

The degradable polymers commonly used to control the release of therapeutics from medical devices have known limitations. This prompted us to seek degradable polymers with unique properties as matrices for delivering drugs from medical devices. Polymers that we evaluated in this manner include a family of urethane-linked multi-block copolymers comprising blocks of lactide, glycolide,  $\epsilon$ -caprolactone, and/or poly(ethylene glycol); a family of polysaccharides modified with aliphatic sidechains to yield a hydrophobic polymer; and poly(ester amides) and poly(ether ester amides) based on amino acid building blocks. We used physical and chemical assessments to characterize the degradability and the nature of the degradation process of these polymers *in vitro* and *in vivo*. Our results demonstrate the strength of using multiple means of assessment to characterize the biodegradation of polymers. Our evaluation of these materials also illustrates the challenges and unique opportunities that are presented by creating entirely new biodegradable polymers for medical applications.



**POLY 116: Tuning ethylene/1-octene selectivity during olefin polymerization reactions with molecular catalysts**

**Jerzy Klosin**, *jklosin@dow.com*. *The Dow Chemical Company, Midland, Michigan, United States*

The Dow Chemical Company is world's largest practitioner of homogenous catalysis including production of polyolefins. Olefin polymerization with Molecular catalysts allows for unprecedented control over polymer composition and microstructure. This talk will discuss the development of new molecular catalysts within Dow for the production of ethylene-based copolymers. Particular emphasis will be giving to the recent research aimed at modifying structures of catalysts to affect both the polymer molecular weight and the reactivity toward 1-octene during ethylene/1-octene copolymerization reactions.

## POLY 117: FI Catalysts for developing new materials and catalysis

**Haruyuki Makio**, *haruyuki.makio@mitsui-chem.co.jp*. Mitsui Chemicals Singapore R&D Centre Pte. Ltd., Singapore, Singapore

FI Catalyst, a family of highly active and versatile olefin polymerization catalyst having phenoxy-imine ligands, can produce a wide array of olefinic (co)polymers in a controlled manner with high efficiency. Some FI-related materials and technologies have been brought into commercial use.

The design base of FI Catalysts for olefin polymerization can also be extended to a selective olefin trimerization catalyst, consisting of Ti metal center and a tridentate phenoxy-imine-ether ligand. This trimerization catalyst exhibits high activities that exceed any existing catalysts, and has been operated for 1-hexene production on a commercial scale since 2011.

These two examples demonstrate how tunable and modulating properties of the phenoxy-imine ligands can deliver useful applications in both material and catalysis science. In this paper, we will present some of FI Catalyst-derived polymers/materials and their practical applications. We will also report on DFT calculations on the olefin trimerization catalyst and discuss differences and similarities between polymerization and trimerization catalysts.

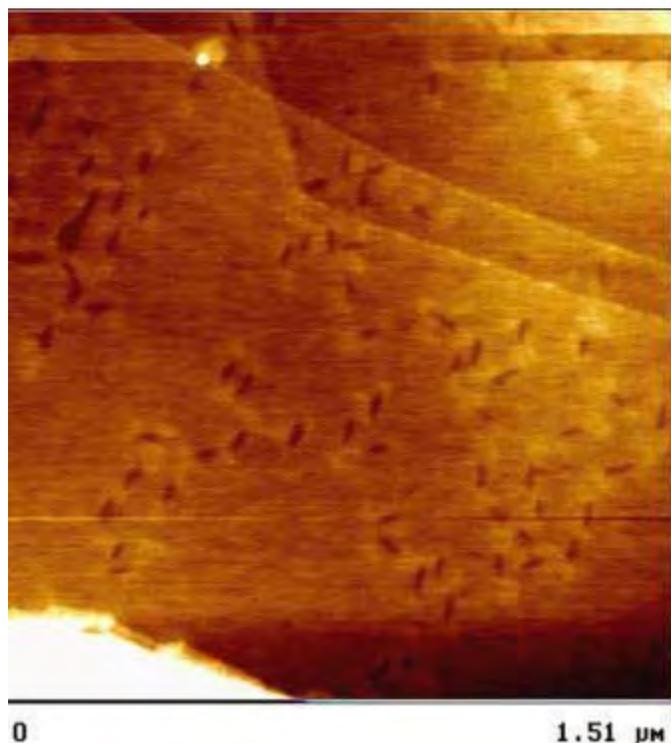


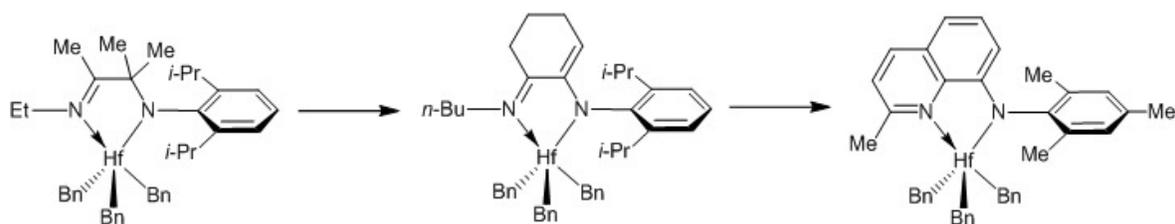
Figure. An AFM image of olefin block copolymer based on FI catalyst

## POLY 118: Group IV polyolefin catalysts supported by bidentate nitrogen-based ligands

**Philip P. Fontaine**, *ppfontaine629@yahoo.com*. Performance Plastics, The Dow Chemical Company, Alvin, Texas, United States

Group IV transition metal complexes supported by bidentate nitrogen-based ligands can give rise to highly active polyolefin catalysts. The core structural motif common to the most active variants is a five-membered metalacycle formed by coordination of the two nitrogen donors to the metal center. Typically, one nitrogen donor is anionic, and the other is neutral. The polyolefin catalysts derived from these complexes are notable for their high activities and their capacities for producing high molecular weight polymers. We have evaluated several variations within this larger class of catalysts, including: imino-amido, imino-enamido, and amidoquinoline complexes.<sup>1</sup> Additionally, we explored derivatization reactions, in which trialkyl precursors ((L)MR<sub>3</sub>) were modified with various protic and unsaturated organic compounds to produce a library of new dialkyl catalyst precursors ((L)M(X)R<sub>2</sub>), which in several instances led to superior catalysts.

[1] J. Klosin, P. P. Fontaine, R. Figueroa, *Acc. Chem. Res.*, 2015, 48, 2004.

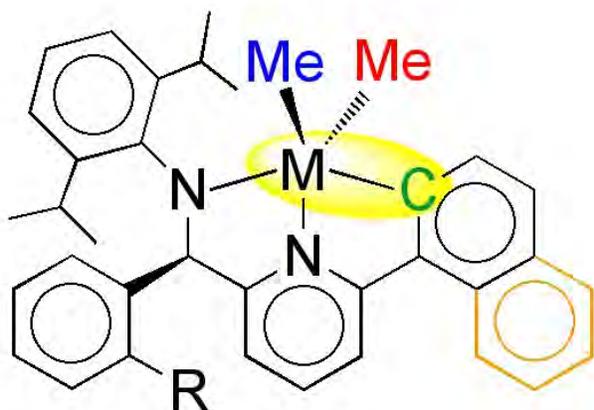


## POLY 119: Activation and reactivity of group(IV) metal-pyridylamido catalysts for olefin polymerization as disclosed by NMR studies

**Alceo Macchioni**<sup>1,2</sup>, [alceo.macchioni@unipg.it](mailto:alceo.macchioni@unipg.it), **Cristiano Zuccaccia**<sup>1,2</sup>. (1) Department of Chemistry, Biology and Biotechnology, University of Perugia, Perugia, Italy (2) CIRCC, Bari, Italy

M(IV)–pyridylamido-based olefin polymerization catalysts (Figure) have several unique features. Initially reported as the first industrially relevant systems to yield highly isotactic polypropylene with solution-process technology, they subsequently attracted even greater attention for their propensity to undergo reversible transalkylation with metal alkyls, thereby opening the door to novel olefin block copolymers through “chain shuttling”, that is, tandem catalysis under coordinative chain-transfer polymerization (CCTP) conditions.

A key feature of the ancillary ligand framework is the ortho-metalation of the aryl moiety bound to the pyridine fragment (highlighted in yellow in Figure). It has been demonstrated that the strained M(IV)–aryl bond is the most reactive site of the cationic catalytic species, resulting from the activation of the neutral precursors by means of Lewis acids such as  $B(C_6F_5)_3$ . In fact, compelling evidence indicates that the first monomer insertion occurs at this site, thereby modifying the ligand *in situ*. Activation with Brønsted acids such as  $[HNMe_2Ph][B(C_6F_5)_4]$ , on the other hand, first leads to the protonation of the M(IV)–aryl bond, which opens the metallacycle and results in a poorly active cation as long as ortho-metalation (with liberation of  $CH_4$ ) is not restored. The M(IV)–aryl bond is also the most reactive site in the presence of  $ER_n$  ( $E=Zn$  and  $Al$ ) moieties, thus leading to the generation of unusual and comparatively stable bimetallic adducts such as  $Hf(\mu-C_{Nph})(\mu-R)ER_{n-1}$ , rather than more typical  $Hf(\mu-R)_2ER_{n-1}$  adducts. Our contribution, mainly based on advanced NMR studies, aimed at clarifying the above-mentioned aspects and other levels of complexity involving bimetallic species will be reviewed.

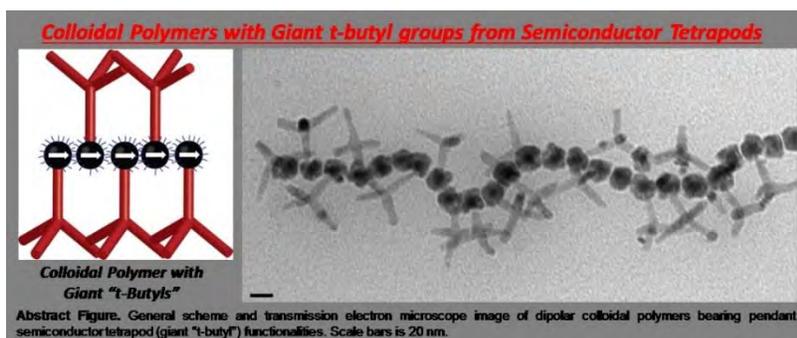


## POLY 120: Synthesis and dipolar assembly of tetrapod functional colloidal monomers: Colloidal polymers with giant T-butyl groups

**Nick G. Pavlopoulos**, *ngpavlopoulos@email.arizona.edu*, Jeffrey Pyun. University of Arizona, Tucson, Arizona, United States

The design of inorganic nanoparticles (NPs) for the purpose of exploiting/studying their inherent properties of self-assembly has garnered much interest in recent years. These assemblies of NPs, or *colloidal polymers*, have been shown to exhibit electronic, magnetic, and catalytic properties distinct from those of the starting *colloidal monomers*. Often, these properties can be tuned by monomer design and degree of polymerization. As such, polymer science provides a useful framework for understanding the assembly of these colloidal species, as well as unique insight into the design of next-generation materials exhibiting more complex architectures or functionalities.

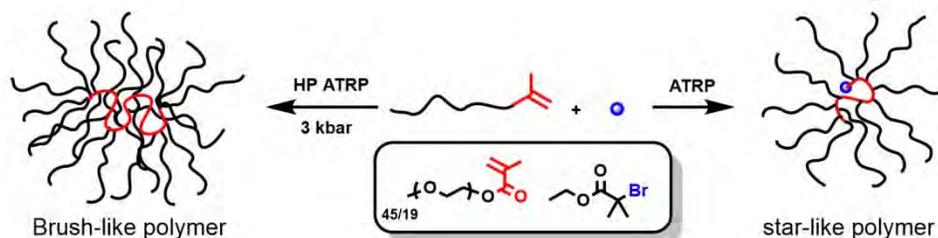
With the concept of applying principles of polymerization to the preparation of new colloidal polymers, we have investigated the synthesis of new colloidal monomer species. These specifically designed monomers allow novel functionalities to be imparted to the final materials. For the first time, we have succeeded in incorporating large, sterically bulky inorganic sidechains into magnetically self-assembled colloidal polymers. Methods were developed to synthesize semiconductor tetrapods (TPs) (40 nm arms) each with a single dipolar tip, which were observed to spontaneously align to form linear assemblies of spherical magnetic NPs (D=20 nm), each with a bulky TP pendant functionality directly attached. The key step to this synthesis was the installation of asymmetry onto the TP framework, which has proven challenging in past research due to the identical nature of the TP arms. Utilizing a novel UV-deposition/ripening process, a single large (~10 nm) Au NP was deposited onto the end of one arm of each TP, providing a site for deposition of dipolar cobalt. These colloidal monomers exhibited spontaneous self-assembly to afford the final polymer with the bulkiest reported semiconductor sidechains. Albeit much larger in overall size, the TP functionalities bear a striking resemblance to traditional “t-butyl” groups. Methods to control the grafting density of TPs in the polymers were established, allowing for random copolymers of modified and unmodified magnetic particles to be prepared, as well as polymers consisting of multiple TP groups per magnetic particle.



## POLY 121: Synthesis of star-like and brush polymers via grafting-through of macromonomers by ATRP

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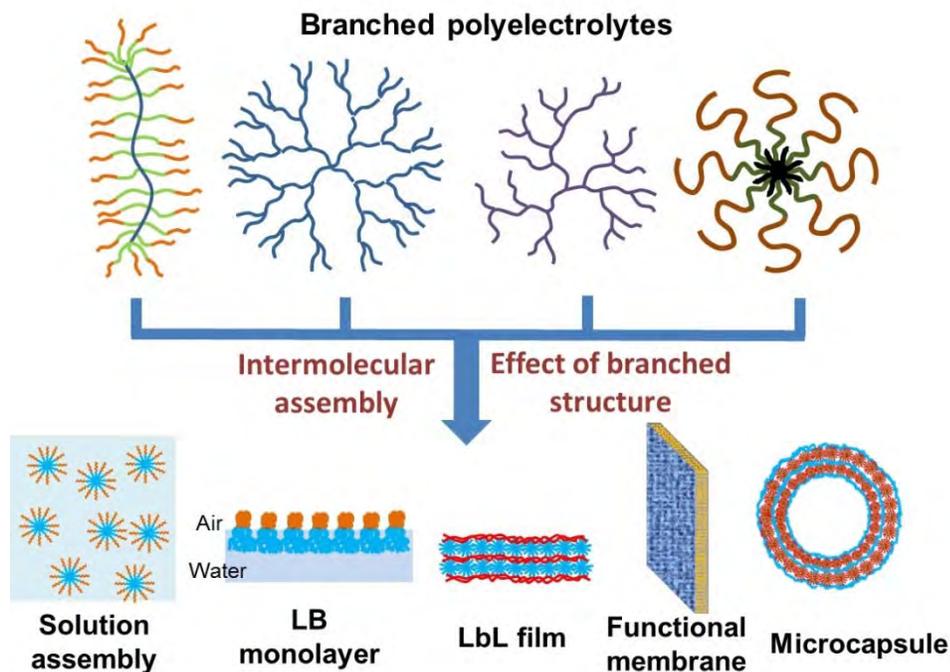
Radical polymerization thermodynamics relies on highly exothermic and entropically disfavored monomer propagation. This implies that at high temperatures and/or low monomer concentrations polymerization of some monomers is inaccessible. A series of poly(ethylene glycol) methyl ether methacrylate (PEGMA,  $M_n = 2080$  or  $950$ ) macromonomer polymerizations were conducted with varied monomer concentration, ranging from  $[\text{PEGMA}]_0 = 50$  to  $300$  mM. ATRP was successful when monomer concentration was above  $75$  mM in organic media whereas polymerization at  $[\text{PEGMA}]_0 = 50$  mM resulted in no monomer conversion. This indicates that the macromonomer concentration was below the equilibrium monomer concentration ( $[M]_e$ ). ATRP under high pressure (HP ATRP,  $p = 3$  or  $4.5$  kbar) allowed to decrease  $[M]_e$  to much lower level, allowing for polymerization up to high monomer conversion ( $>99\%$ ) at low monomer concentration ( $[\text{PEGMA}]_0 = 50$  mM), yielding polymers with narrow molecular weight distribution. Effect of solvent and temperature on equilibrium monomer concentration and maximum attainable degree of polymerization was evaluated. Star-like and bottlebrush polymers were prepared by direct polymerization of PEGMA macromonomer via grafting-through method, using atom transfer radical polymerization (ATRP).



## POLY 122: Assembly of branched polymers into responsive 2D and 3D microstructure

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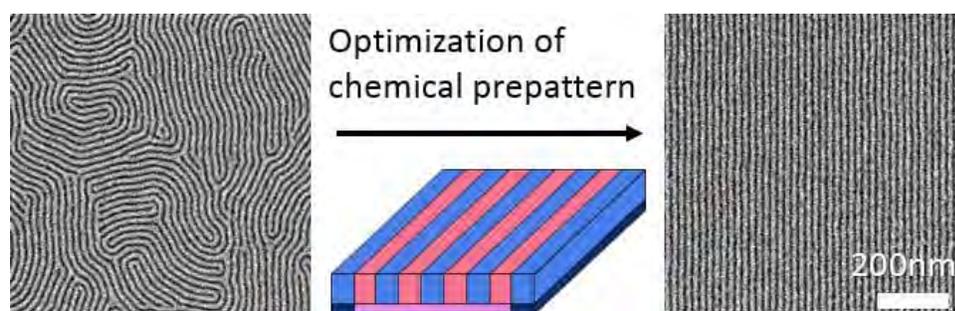
Star polymers with stimuli-responsive arms constitute a unique class of responsive materials, because their responsive properties are quite distinct from their linear counterparts due to the spatial confinement and complex intramolecular interactions of the arms. In order to study the responsive properties of star polymers at the molecular level, and utilize them to fabricate functional microstructures, it is critical to confine them at interfaces and assemble them *via* various intermolecular interactions. This talk will focus on the interfacial assembly of responsive star polymers (to pH, ionic strength, temperature) by using Langmuir-Blodgett technique; as well as the layer-by-layer assembly of star polymers *via* electrostatic interaction or hydrogen bonding. The assembled microstructures include thin films and microcapsules with the ability to reversibly change their structures, encapsulate and release multiple types of cargo molecules, which can lead to applications in smart coating, drug carrier and microreactors.



## POLY 123: Optimizing surface treatments for the directed self-assembly of silicon-containing block copolymers

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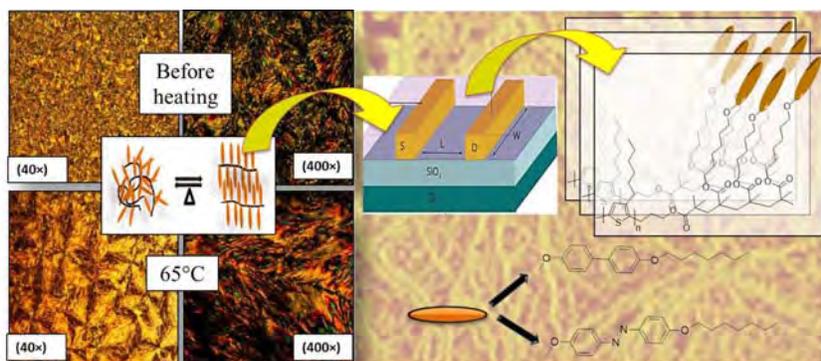
The directed self-assembly [DSA] of a lamellar-forming, silicon-containing block copolymer, poly(4-methoxystyrene)-*b*-poly(4-trimethylsilylstyrene) with a pitch of 20 nm was investigated using a modified version of the process developed to direct the assembly of polystyrene-*b*-poly(methyl methacrylate). The polymer exhibits high plasma etch contrast between the components. The chemical composition and surface energy of the two components of the prepatterned substrate were varied to investigate their effects on the quality of the DSA. Changing the guidestripe from cross-linked polystyrene, which is only weakly preferential to the poly(4-methoxystyrene) component of the block copolymer, to cross-linked poly(4-methoxystyrene) improved the DSA performance, presumably due to the greater affinity of the guidestripe to the block copolymer's guided component. In addition, the background component of the prepattern that produces the optimal DSA results has a surface energy that is not perfectly neutral for the bulk block copolymer but rather closer in surface energy to the non-guided component of the block copolymer. This observation agrees qualitatively with reports about the DSA of polystyrene-*b*-poly(methyl methacrylate) by chemoepitaxy, but the larger overall disparity in the surface energies of the silicon-containing block copolymer components allows a more detailed study of the interfacial energies



## POLY 124: Enhanced supramolecular self-assembly of P3HT by copolymerization with methacrylate attached liquid crystalline mesogens

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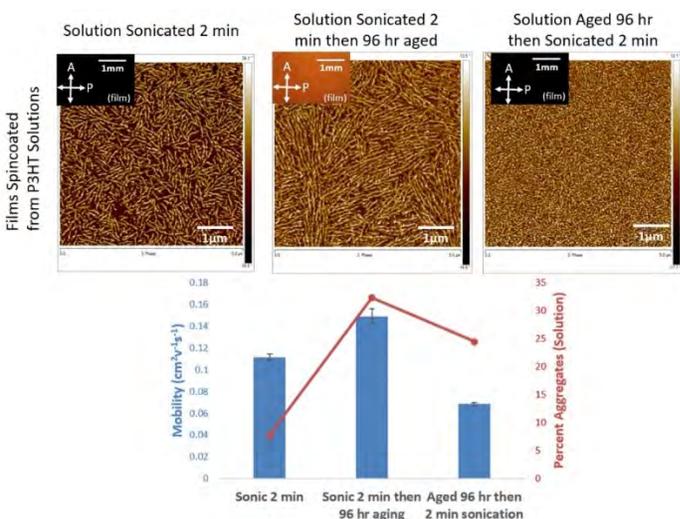
Diblock and triblock copolymers of semiconducting poly(3-hexylthiophene) (P3HT) and side chain liquid crystalline methacrylates were synthesized with the combination of Grignard metathesis polymerization (GRIM) and atom transfer radical polymerization (ATRP). The azobenene (nematic) and biphenyl (smectic) liquid crystalline mesogens were incorporated into the diblock and triblock copolymers with semiconducting P3HT. Both azobenzene and biphenyl have thermotropic properties. In addition azobenzene has photo-responsive properties thus making resulting copolymers potential material for thermal and photo sensors. The effect of the supramolecular assembly on the opto-electronic properties of the resulting block copolymers was investigated. Improved long range ordering of polymer nanowires induce better  $\pi$ - $\pi$  stacking of thiophene units which facilitates charge transport by hopping. This was depicted when the mesogen was switched from nematic to smectic where the hole mobility was increased by one order magnitude with the appearance of  $\pi$ - $\pi$  stacking peak for biphenyl in XRD spectra of the resulted copolymers. The composition of synthesized copolymers was determined by  $^1\text{H-NMR}$ . Characterization of the thermotropic liquid crystalline behavior was done in a combined study with polarizing optical microscopy with heating stage and differential scanning calorimetry. The liquid crystalline mesophases of the copolymers appear above the glass transition of P3HT which helps long range ordering of P3HT by co-crystallization after annealing above the mesophase transitions. Soft and rubbery nature of the P3HT segment at mesophase transitions aid rearranging in to polymer nanowires. The effect on self-assembly and morphological changes of copolymers upon annealing was studied with tapping mode atomic force microscopy (TMAFM), thin film X-ray diffraction studies (XRD), and UV-VIS analysis. The field effect mobilities of the P3HT diblock and triblock copolymers were determined in organic field effect transistors (OFET). Mobilities as high as  $10^{-2} \text{ cm}^2/\text{Vs}$  were measured.



## POLY 125: Long range ordering of poly(3-hexylthiophene) in fluids and films: Effects of self-assembly techniques on liquid crystallinity, material properties and device performance

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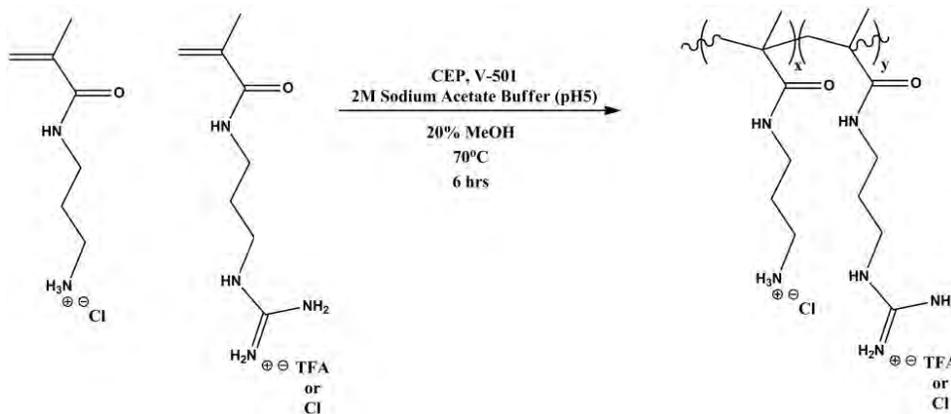
Conjugated polymers have attracted significant interest for organic electronics such as polymer photovoltaics and transistors, due to their potential low cost, light-weight and flexible nature. The charge carrier mobility of these devices can be enhanced with long range macromolecular ordering. Poly(3-hexylthiophene) (P3HT) has recently been shown to exhibit lyotropic liquid crystalline properties after the formation of self-assembled nanowires in solution which can yield long-range alignment. We have shown that the self-assembly and the resulting transition from isotropic to birefringent solutions is time-dependent, requiring a certain percentage of polymer to aggregate (as determined by UV-Vis analysis). Furthermore, we show that not only is the percent of aggregates important, but the length of the nanowires, as controlled by various aggregation techniques is critical to the emergence of a birefringent fluid. P3HT solutions that are sonicated to induce aggregation result in significantly shorter fibers than with aging (as determined by AFM of spincoated films), and as a result, yield isotropic solutions. The relationship between solution-state ordering and the resulting thin film morphological and electrical properties was also explored, through GIWAXS, optical microscopy, AFM, UV-Vis, Raman, and Organic Field-Effect Transistor fabrication and testing. Through various combinations of sonication and aging, high mobility organic field effect transistors were fabricated with an order of magnitude increase in charge-carrier mobility vs. the pristine P3HT solution. These explorations into the evolution of solution-state ordering and the relationship between ordered fluids and resulting ordered thin-films gives further insight into the control of semiconducting polymer ordering for high performance organic electronics applications.



## POLY 126: Effects of copolymer structure and solution properties on antimicrobial activity of RAFT synthesized peptide mimics

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Naturally occurring antimicrobial peptides (AMPs), amphipathic biomacromolecules with high levels of lysine and arginine residues, provide selective toxicity to bacteria without harming eukaryotic cells. A series of water-soluble methacrylamide copolymers with pendant primary amine and guanidine moieties designed to mimic AMP amino acid residues were synthesized via aqueous RAFT polymerization. Molecular weights were targeted to match those of AMPs molecules, and narrow MWDs were obtained. Antimicrobial activity against a range of gram-negative and gram-positive bacteria was evaluated under varying conditions of solution pH, salinity, and nutrients. Toxicity to mammalian cells was evaluated in vitro by MTT assay of MCF-7 cells and hemolysis of red blood cells. Copolymers with high levels of the primary amine demonstrated antimicrobial activity across a broad range of bacteria with low toxicity towards mammalian cells.



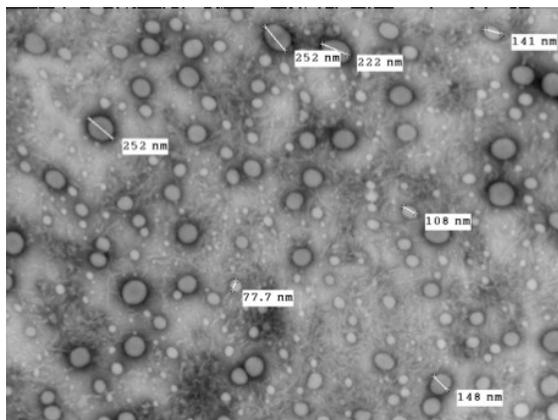
RAFT synthesis of AMPs mimicks

## POLY 127: Polypeptide nanoparticles for ocular drug delivery

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Polypeptides are ideal materials for ocular drug delivery vehicles due to their biocompatibility and biodegradability. Polypeptides of desired molecular weight possessing tunable properties, can be synthesized from amino acid building blocks in a controlled manner using ring-opening polymerization (ROP) of *N*-carboxyanhydrides (NCAs). A series of peptide-based polymers were synthesized *via* ROP of NCAs, namely block copolypeptides, peptide-hybrid copolymers and photocleavable block copolypeptides. Block copolypeptides based on Bn-glutamate and Z-lysine and photocleavable nitrobenzyl-cysteine NCAs were prepared using trimethylsilyl-protected amines (TMS-amines) as initiators. Peptide-hybrid block copolymers based on Bn-glutamate, alanine and leucine were synthesized from commercially available macroinitiators such as Jeffamine and bis(aminopropyl)poly(ethyleneglycol) (BAPPEG). Self-assembly of the polymers was achieved by both direct dissolution and solvent evaporation method. The resultant nanoparticles were characterized using DLS and TEM. Stability of the nanoparticles was determined by measurement of the critical micelle concentrations (CMCs), using both fluorescence spectroscopy and DLS. Crosslinking was carried out in order to enhance the stability of the block copolypeptide nanoparticles for use in biological fluids. The ability to load the nanoparticles with hydrophobic payloads was demonstrated qualitatively with organic dyes. Subsequently, nanoparticles were loaded with the hydrophobic ocular drug dexamethasone and the drug release profile was obtained [1].

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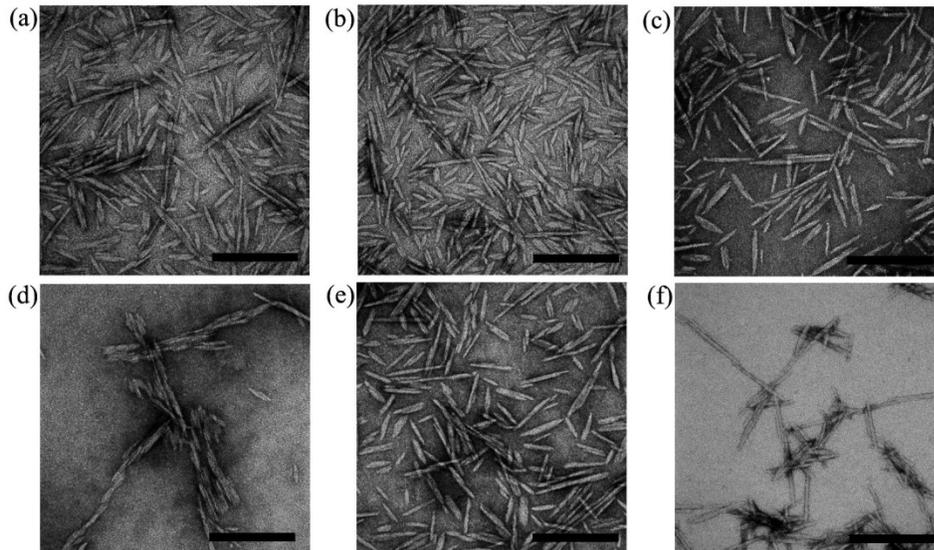


TEM image of self-assembled nanostructures from poly(Leu<sub>10</sub>-b-PEG) copolymer

## POLY 128: Cellulose nanocomposites and the role of surface chemistry

**Jeffrey P. Youngblood<sup>2</sup>**, *jpyoungb@purdue.edu*, Robert Moon<sup>3</sup>, Shane Peng<sup>1</sup>, Youngman Yoo<sup>2</sup>. (1) Purdue University, West Lafayette, Indiana, United States (2) School of Materials Engineering, Purdue University, West Lafayette, Indiana, United States (3) Forest Products Laboratory, Madison, Wisconsin, United States

Cellulose nanomaterials have gained a lot of notice recently owing to their impressive mechanical and thermal properties, environmental benefit, low toxicity and relative low cost. Of these cellulose nanocrystals (CNCs) are semi-commercial and have been used in nanocomposites for a variety of applications. However, CNCs are quite hydrophilic due to the highly hydroxylated and sulfate ester CNC surface and so do not disperse well in hydrophobic resins. Here, we detail our own efforts at preparing CNC nanocomposites and focus on the role of surface chemistry in the behavior by investigating the interplay between chemical modification and properties.



TEM of surface modified CNCs

## POLY 129: Responsive shape-memory porous polymers and hydrogel-filled polymers: Templating within nanoparticle-stabilized emulsions

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PolyHIPEs are porous emulsion-templated polymers that are usually synthesized within surfactant-stabilized water-in-oil high internal phase emulsions (HIPEs) [1,2]. Surfactant-free polyHIPEs can be synthesized through the formation of nanoparticle-stabilized Pickering HIPEs [3,4]. Temperature-responsive porous shape memory polymer (SMP) 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 [5]. Hydrogel-filled SMPs, synthesized by adding hydrogel monomers to the HIPE's internal phase, exhibited more closed-cell-like structures. The nanoscale hydrogel coating was separated from the SMP framework by the stabilizing nanoparticles. The "dual-lock" shape-memory behavior reflected contributions from both the crystalline hydrophobic polymer and the hydrogel. Immersion in water at 80 °C enhanced the recovery rate through rapid capillary-action absorption.

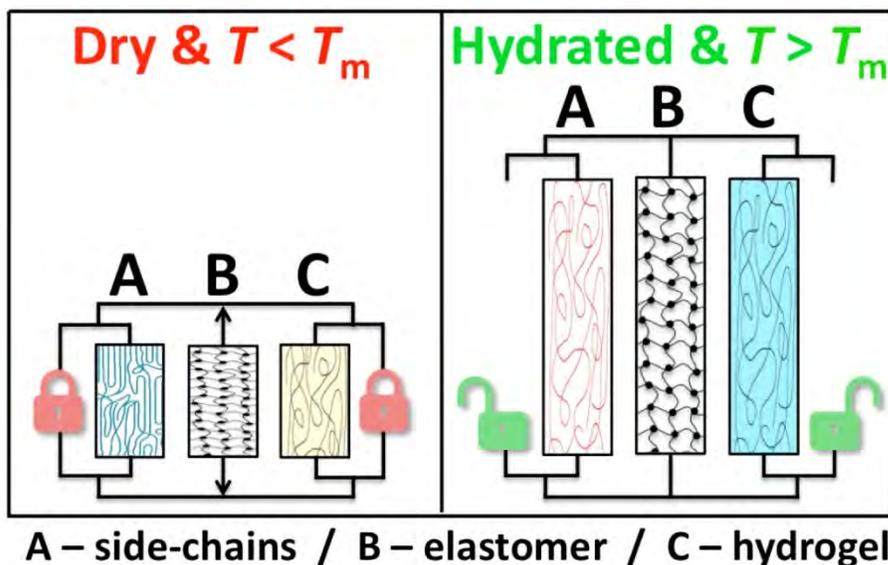
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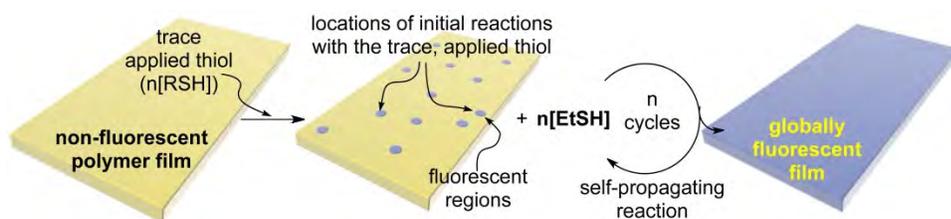


**Dual-lock, hydrogel-filled, shape-memory polymers**

## POLY 130: Stimuli-responsive polymeric materials that transform molecular detection events into autonomous reconfiguration of materials at the nano- and eventually macro-scale

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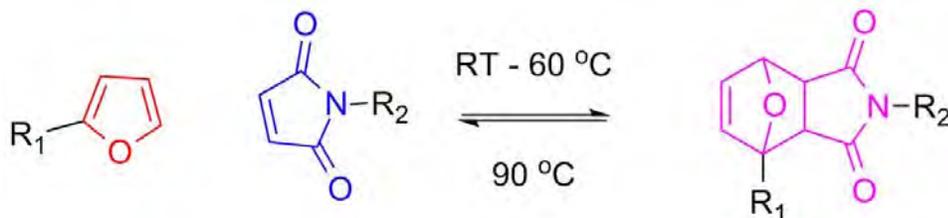
This presentation will illustrate the design of macroscale polymeric materials that autonomously change their properties in response to specific signals. The specific signals initiate changes at the molecular level, but also turn on amplification reactions that, ultimately, give rise to nanoscale followed by macroscale changes in the material. Strategies for realizing such changes across scales include polymers (i) that support self-propagating reactions, or (ii) are designed to depolymerize when triggered. When a new, macroscale function is the goal of the response, then a systems approach is used to integrate more than one polymer into a polymeric material to give rise to (i) selective detection, (ii) amplification, and (iii) specific readouts. This presentation will highlight several examples of these strategies.



## POLY 131: Incorporating Diels-Alder chemistry to prepare thermally-responsive materials

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Diels-Alder (DA) chemistry is becoming increasingly popular due to its simplicity and efficiency. It also imparts a thermo-responsive aspect which can result in the preparation of responsive materials. The versatility of the DA chemistry allows it to be incorporated with a plethora of synthetic strategies for a range of potential applications. This work will describe the development of several different strategies of incorporation of DA chemistry within polymeric materials, including functional prepolymers, initiators, inimers and crosslinkers and post-polymerization modification. Potential applications range from the development of insensitive munitions to rehealable coatings to rheological modifiers to processable matrix resins.[figure1]



## POLY 132: Efficient anticancer polymer prodrug nanoparticles from drug-initiated controlled/living radical polymerization

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In order to overcome the limiting features generally encountered with drug-loaded nanoparticles (NPs) (e.g., burst release, poor drug loading), we aimed at designing a new class of efficient anticancer nanoparticles based on well-defined polymer prodrugs obtained by controlled/living radical polymerization (CLRP). We recently proposed a new approach to prepare well-defined amphiphilic macromolecular prodrugs by nitroxide-mediated polymerization (NMP)<sup>1</sup> of isoprene from an anticancer drug-bearing alkoxyamine initiator (Fig. 1). They self-assembled into narrowly-dispersed nanoparticles and showed remarkable in vitro and in vivo anticancer activities.<sup>2</sup> To further investigate the diversity and universality of this approach, it was adapted to another anticancer drug, cladribine (Cla).

We selected Cla as an anticancer drug due to its demonstrated efficacy in the treatment of hairy cell leukaemia. Our strategy was illustrated by the synthesis of Cla-diglycolic-polyisoprene (Cla-digly-PI) of different molecular weights. NPs of 100–150 nm in diameter with drug content ranging from 6 to 19 wt.% were obtained by nanoprecipitation in water of the desired polymer prodrugs. The use of NMP enabled the preparation of polymer conjugates with variable chain lengths in a facile way. Significant anticancer activities were observed in vitro on L1210 cells (mouse lymphocytic leukemia) with tunable IC<sub>50</sub> ranging from micromolar to nanomolar values.

In summary, a series of cladribine-polyisoprene prodrugs were synthesized by drug-initiated NMP, leading to efficient anticancer NPs. Furthermore, this strategy allowed for fine-tuning the polymer chain length, which is crucial to determine structure-activity relationships and to design optimized drug delivery systems.

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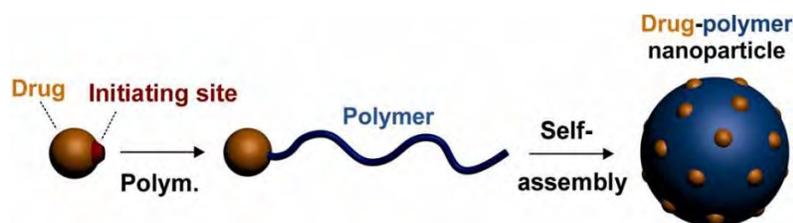
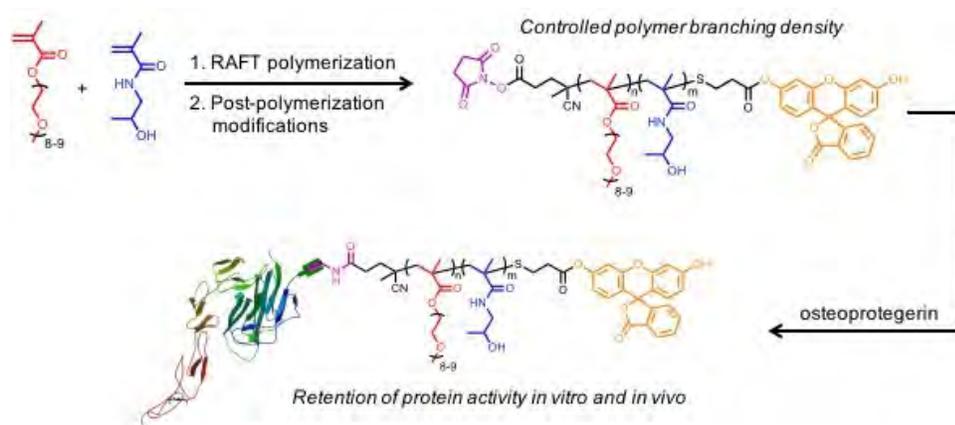


Fig. 1. Strategy to synthesize well-defined polymer prodrug nanoparticles by controlled/living radical polymerization

## POLY 133: Role of polymer architecture on the activity of protein-polymer conjugates for the treatment of disease

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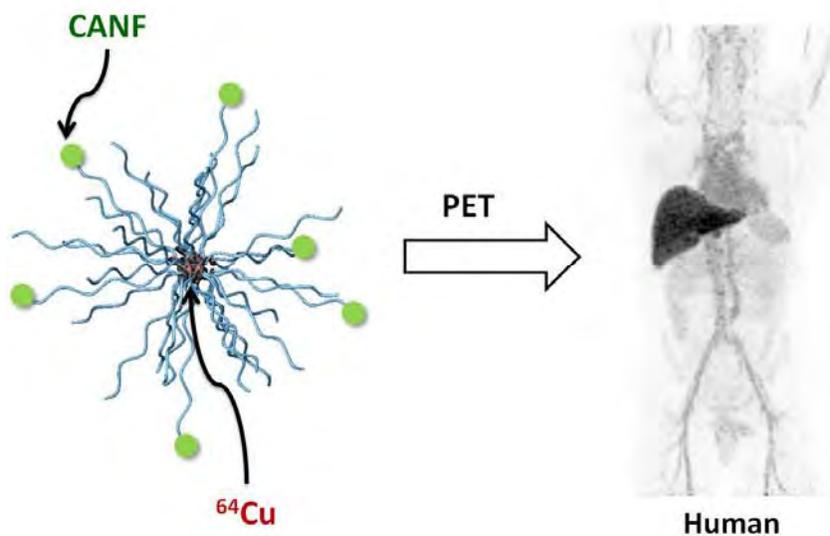
Polymers of similar molecular weights and chemical constitution but varying in their macromolecular architectures were conjugated to osteoprotegerin (OPG) to determine the effect of polymer topology on protein activity in vitro and in vivo. OPG is a protein that inhibits bone resorption by preventing the formation of mature osteoclasts from the osteoclast precursor cell. Accelerated bone loss disorders, such as osteoporosis, rheumatoid arthritis, and metastatic bone disease, occur as a result of increased osteoclastogenesis, leading to the severe weakening of the bone. OPG has shown promise as a treatment in bone disorders; however, it is rapidly cleared from circulation through rapid liver uptake, and frequent, high doses of the protein are necessary to achieve a therapeutic benefit. We aimed to improve the efficacy of OPG by creating OPG-polymer conjugates, employing reversible addition-fragmentation chain transfer (RAFT) polymerization to create well-defined polymers with branching densities varying from linear, loosely branched, to densely branched. Polymers with each of these architectures were conjugated to OPG using a “grafting-to” approach, and the conjugates were characterized by gel electrophoresis. The OPG-polymer conjugates showed retention of activity in vitro, and each conjugate was shown to be nontoxic. Preliminary in vivo studies further supported the nontoxic characteristics of the conjugates, and measurement of the bone mineral density in rats 7 d post-treatment suggested a slight increase in bone mineral density after administration of the loosely branched OPG-polymer conjugate.



## POLY 134: From benchtop to human clinical trials: A successful imaging agent for detecting early-stage atherosclerosis

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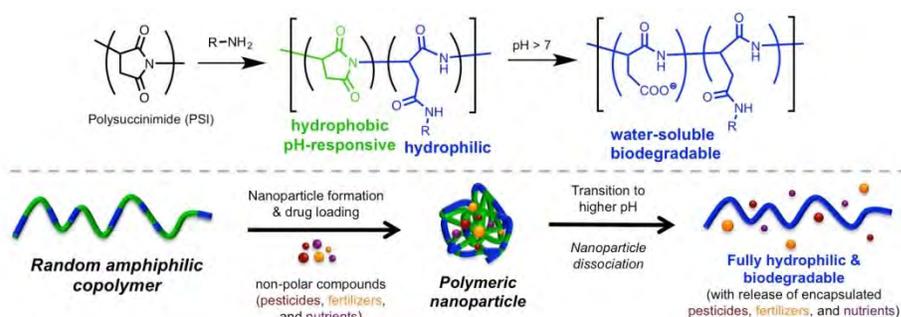
The detection of early-stage atherosclerotic plaque by molecular imaging can enable the early diagnosis of cardiovascular disease in order to greatly increase the likelihood of successful treatment. Currently, atherosclerosis is not diagnosed until the patient suffers an acute cardiovascular event such as a heart attack or stroke. To address this problem, we developed a modular synthetic platform for the preparation of polymeric nanoparticle-based imaging agents that successfully target and image atherosclerotic lesions in mouse models. These imaging agents are composed of carefully designed comb copolymers containing hydrophilic side arms to increase water solubility, a hydrophobic backbone to drive self-assembly of particles, <sup>64</sup>Cu radiolabels for PET imaging and C-type atrial natriuretic factor (CANF) for targeted delivery. A good manufacturing practice-like facility was constructed to scale up the imaging agents for initial human clinical trials and these preliminary in-human studies will be presented.



## POLY 135: Responsive polymeric nanoparticles designed for site-specific delivery in agriculture

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While responsive materials have been extensively studied in the realm of biology and medicine, less attention has been given to the use of such materials in agriculture. Stimuli-responsive nanoparticles have significant potential as vehicles for site-specific delivery of pesticides and nutrients due to variations in pH, ionic strength, and other small molecule triggers within plants. We demonstrate the synthesis of biodegradable and pH-responsive nanoparticles designed to capitalize on the higher pH of the phloem, the tissue in plants that aids with transport of organic nutrients made during photosynthesis, compared to its surrounding environment. Polysuccinimide (PSI) was synthesized from both traditional condensation polymerization of L-aspartic acid, as well as from a novel method utilizing *N*-carboxyanhydride (NCA) ring-opening polymerization (ROP), to serve as a pH-responsive scaffold. Copolymers of PSI were shown to form stable nanoparticles in aqueous medium, encapsulate model hydrophobic molecules, and hydrolyze to release its cargo at increased pH. Lastly, toxicity studies showed little to no toxicity to plant tissue at moderate concentrations.



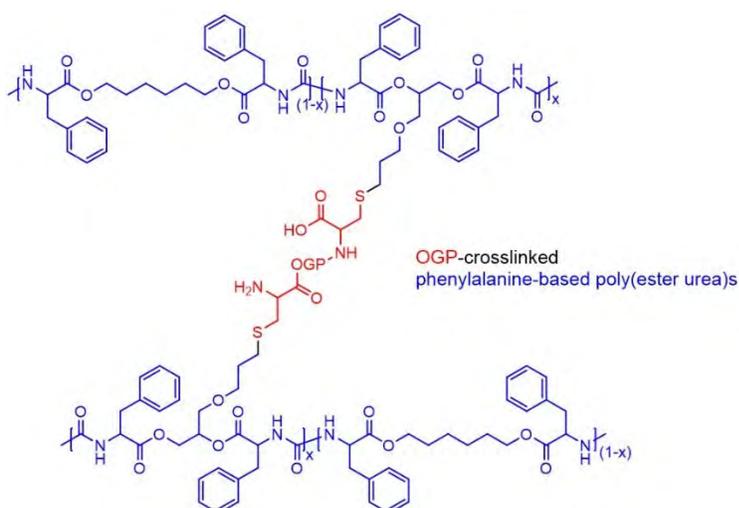
## POLY 136: Peptide crosslinking strategies for increasing mechanical properties in degradable poly(ester ureas)

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Phenylalanine-based poly(ester urea)s (poly(PHE)) are high modulus, resorbable polymers with many potential uses in the surgical repair of bone defects. *In vitro* and *in vivo* studies have shown that poly(PHE)s have non-toxic hydrolysis byproducts, tunable degradation times, and significant synthetic flexibility.<sup>1,2</sup> OGP is a naturally occurring growth factor which aids in proliferation, differentiation, and matrix mineralization of osteoblasts.<sup>3,4</sup> *In vitro* data of OGP-tethered poly(PHE) porous scaffolds showed enhanced signaling for osteogenic differentiation of human mesenchymal stem cells compared to control scaffolds lacking tethered OGP.<sup>5</sup> These results led to the synthesis of the second generation poly(PHE)s crosslinked with OGP peptide for increased stiffness and osteoinductive ability for bone repair. Poly(PHE) copolymers were synthesized with varying degrees of alkene and pendant allyl functionality for efficient radical-induced crosslinking using cysteine and alloc-functionalized-OGP peptides. Poly(PHE) copolymers and OGP-peptides were characterized using NMR (<sup>13</sup>C and <sup>1</sup>H) and mass spectrometry. Tensiometer and preliminary biological testing will be conducted to show the enhanced stiffness and osteoinductive potential of photo-initiated OGP-crosslinked poly(PHE) copolymers.

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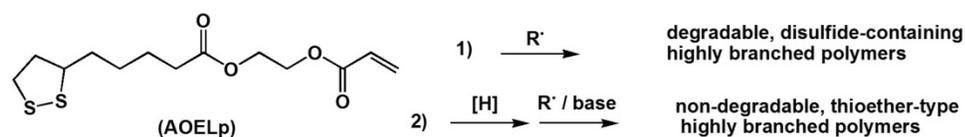
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## POLY 137: Design of degradable and non-degradable highly branched polymers based on lipoic acid

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Lipoic acid was reacted with 2-hydroxyethyl acrylate to yield 2-acryloyloxyethyl lipoate (AOELp). The difunctional monomer, which contained polymerizable cyclic disulfide and vinyl groups, was employed as a building block to prepare sulfur-rich highly branched polymers. Under free radical polymerization conditions, AOELp was converted to a partially reductively degradable (disulfide-containing) highly branched or (at high conversions) network polymers. Alternatively, when AOELp was reduced to the corresponding dithiol compound and then a radical source or a base was added, thiol-ene reactions took place, which yielded thioether-type highly branched polymers, which were not degradable in the presence of reducing agents. Detailed synthetic procedures, polymerization and copolymerization of AOELp, and degradation studies of the obtained branched polymers will be presented.

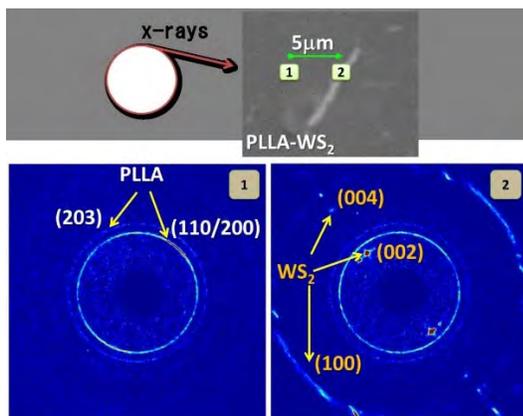


## POLY 138: PLLA-WS<sub>2</sub> nanocomposites for bioresorbable vascular scaffolds

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Coronary Heart Disease (CHD) is a fatal condition which restricts blood supply to the heart due to the buildup of plaque in its arteries. The current standard of care is to restore blood circulation by deploying a metal stent to open the artery. However, metal stents have serious side effects such as Chronic Angina and Late Stent Thrombosis (LST). Bioresorbable Vascular Scaffolds (BVS), made from biocompatible polymers, are a promising new treatment for CHD as they are transient entities in the body. These scaffolds completely dissolve in two years, leaving no foreign matter behind, which eliminates LST. The polymer which has enabled the first clinically approved BVS is poly (L-lactic acid) (PLLA). However, current PLLA scaffolds are much thicker than metal stents (150 $\mu$ m vs 50 $\mu$ m, respectively) for the polymer scaffold to have comparable mechanical properties to a metal stent. A thicker profile is undesirable as it is more difficult to implant and is unable to access small vessels. We propose to enable thinner and stronger BVSs using biocompatible PLLA nanocomposites.

To this purpose we disperse inorganic nanotubes (INTs) of Tungsten Disulfide (WS<sub>2</sub>) (1mm long, 200nm diameter) in a PLLA matrix. Apart from imparting favorable mechanical properties to polymers, biocompatibility assays on WS<sub>2</sub> INTs are very encouraging. We prepared PLLA-WS<sub>2</sub> nanocomposites where several wt% of NTs were dispersed in an amorphous PLLA matrix (SEM image, Fig.1). The PLLA nanocomposites were subjected to varying annealing conditions to examine the impact of thermal history on the final morphology. Using Wide Angle X-Ray Scattering (APS, ANL, 200nm spot size), we were able to probe the morphology in the PLLA matrix and within 5 $\mu$ m of the WS<sub>2</sub> NT (WAXS patterns, Fig. 1). The effect of temperature on the morphology and the concomitant changes in mechanical properties of the nanocomposites will be presented.



Scheme of the experiment, morphology of a PLLA-WS<sub>2</sub> nanocomposite by SEM and WAXS patterns

## POLY 139: Functional macromolecular platforms for sequence-defined polymers and multidrug-loaded nanoparticle chemotherapeutics

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Absolute structural control over polymers – in terms of sequence, length, and stereochemistry – is a Holy Grail of polymer science. Inspired by Nature, polymer chemists over the last century have sought new methods and strategies to control these parameters. An inverse relationship exists, however, between the ability to control the primary structure of a polymer and the ability to scale the production of the same polymer. Our research in the Johnson group aims to address this dilemma by investigating two functional macromolecular platforms that are capable of serving as either a chiral scaffold for the presentation of molecular recognition units in an effort to control polymer self-assembly and interactions at the nano-bio interface, or as multidrug-loaded brush polymers and cross-linked nanoparticles for the treatment of ovarian cancer. The first half of my research involves the development of a controlled step-growth synthetic methodology (Fig. 1A, ref. 1) that is used to prepare unimolecular and sequence-controlled polymers consisting of 32 subunits and variable stereoconfigurations, where some of the reported sequences cannot be made using traditional polymerization techniques. The second half of my research entails the design of drug-conjugated macromonomers and their incorporation into polymeric nanoparticles (Fig. 1B) using ruthenium-mediated ring-opening metathesis polymerization (ROMP), followed by *in vivo* efficacy studies of the multidrug-loaded nanoparticles in a subcutaneous ovarian cancer mouse model.

1. Barnes, J. C.; Ehrlich, D. J.; Gao, A. X.; Leibfarth, F. A.; Jiang, Y.; Zhou, E.; Jamison, T. F.; Johnson, J. A. Iterative Exponential Growth of Stereo- and Sequence-Controlled Polymers. *Nature Chem.* 2015, 7, 810–815.

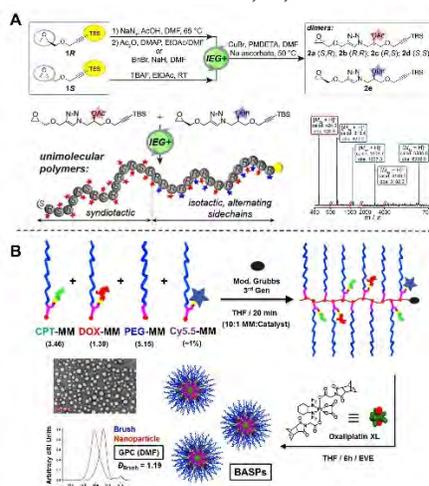
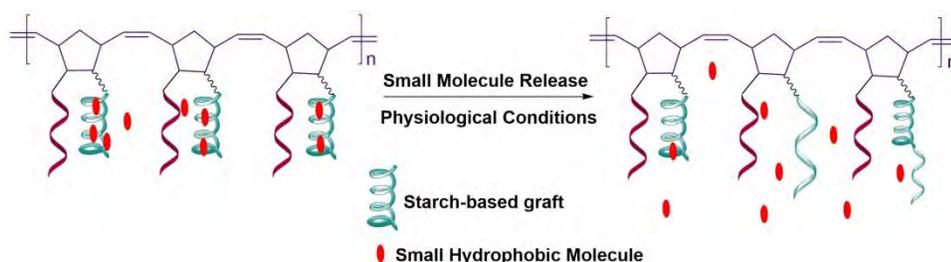


Figure 1. (A) Iterative exponential growth plus (IEG+) of stereo- and sequence-controlled polymers. (B) Ratiometrically loaded combination chemotherapeutics.

## POLY 140: Polynorbornene-*g*-starch copolymers for small hydrophobic molecule encapsulation and release

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Here we report the synthesis and characterization of a novel amphiphilic graft copolymer based on linear starch grafts and polynorbornene (PNB) backbone using ROMP and copper-catalyzed azide alkyne cycloaddition (CuAAC) based click chemistry. We have utilized CuAAC as a secondary tool for grafting alkyne-functionalized linear starch onto azide-functionalized PNB backbone. By varying azide density on the PNB backbone, several starch grafted constructs have been developed with same architecture but different starch loading (weight%). The propensity of starch to form inclusion complexes under suitable conditions has been utilized to load these novel amphiphilic graft copolymers with small hydrophobic molecules. Next, we focused on the release kinetics of these small hydrophobic molecules from these starch grafted polynorbornene systems under physiological conditions.

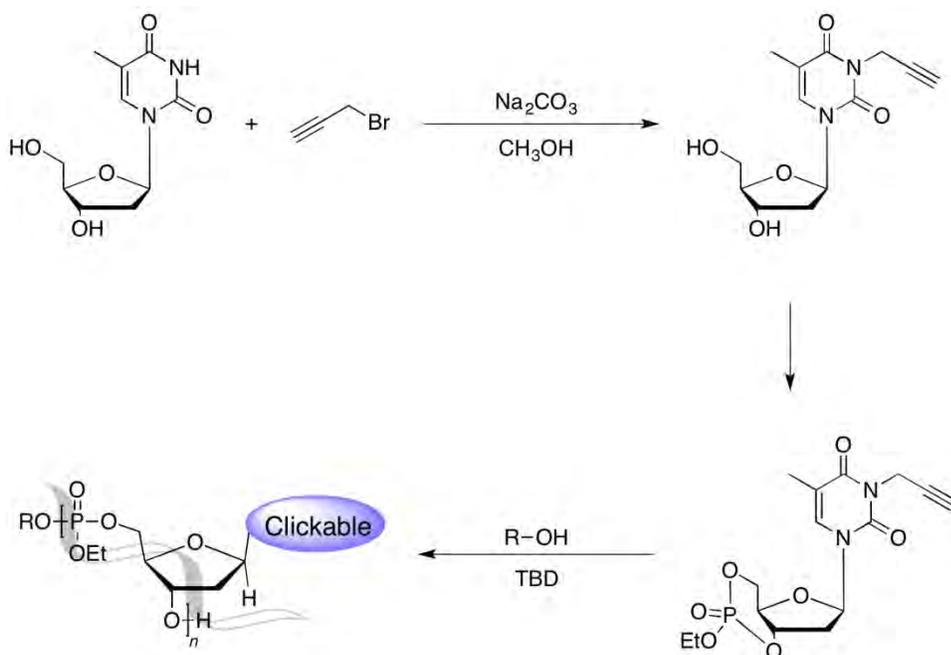


Small hydrophobic molecule release mechanism from polynorbornene-*g*-starch based polymeric construct under physiological conditions

## POLY 141: Deoxyribonucleic acid as a model for the design of functional, degradable polymers

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Deoxyribonucleic acid (DNA) and its derivatives have long been studied by scientists, but an easy route to synthesize it with typical organic reactions remains a challenge. Furthermore, deoxyribonucleic acid itself as a non-toxic material could be designed into a functional and degradable polymer. The monomer of poly(3-propargyl thymidine phosphoester) was synthesized by propargylation of thymidine followed by cyclization to form the 3',5'-cyclic phosphoester with full characterization to show the diastereoselectivity on the cyclization. DFT calculations showed the fused ring exhibits strain energy at least 3.5 kcal/mol higher than unstrained 6-membered phosphoesters which enables the polymerization. The first known example of ring-opening polymerization of 6-membered phosphoesters to achieve clickable poly(3-propargyl thymidine phosphoester) as a DNA derivative – an advanced concept that combines the merits of functional, non-toxic and degradable polymers – has been developed to provide a better solution to future biomedical applications.



## POLY 142: Molecular screws of polycarbodiimides from helix sense selective polymerization and their complexation

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The helix is a ubiquitous motif observed in nature from the molecular to the macroscopic levels. At the molecular level in biological systems, helical motifs include  $\alpha$ -helical secondary structures of enzymes and proteins, double helical structure of DNA and RNA, and super coiled triple helices of collagen. Through complexation, these helical motifs can create super coiled structures. Chemically, when aggregating two complementary helical polymeric chains this complexation is referred to as a stereocomplex. Synthetic polymer examples of stereocomplexes include mixtures of syndiotactic and isotactic PMMA, and mixtures of D- and L-poly lactide. Stereocomplexes when formed can improve mechanical and thermal properties. Herein we report the chiral synthesis of poly (*N*-methyl-*N'*-(2-methyl-6-isopropylphenyl)carbodiimide, left- (*M*) and right-hand (*P*) helices and their self-assembly phenomena upon thermal annealing. These polymerizations are carried out using enantiomerically pure chiral catalysts. The resultant helical polymers show optical activity due to their single-handed structure. Annealing at high temperatures should introduce helix inversions that would racemize the sample. Surprisingly, when heated, their optical rotations never go to zero (racemize). Accompanying the changes in optical rotations, the polymers begin to gel and precipitation can be detected. Likewise, changes to their solid-state morphologies are observed by AFM and SEM imaging. We hypothesize that when racemization begins, stereocomplexation takes place between two complementary strands. To elucidate the properties and structure of this stereocomplex, solid-state  $^{13}\text{C}$  NMR,  $^1\text{H}$ -NMR, DSC, TGA, p-XRD, TM-AFM, SEM, and VCD will be reported.

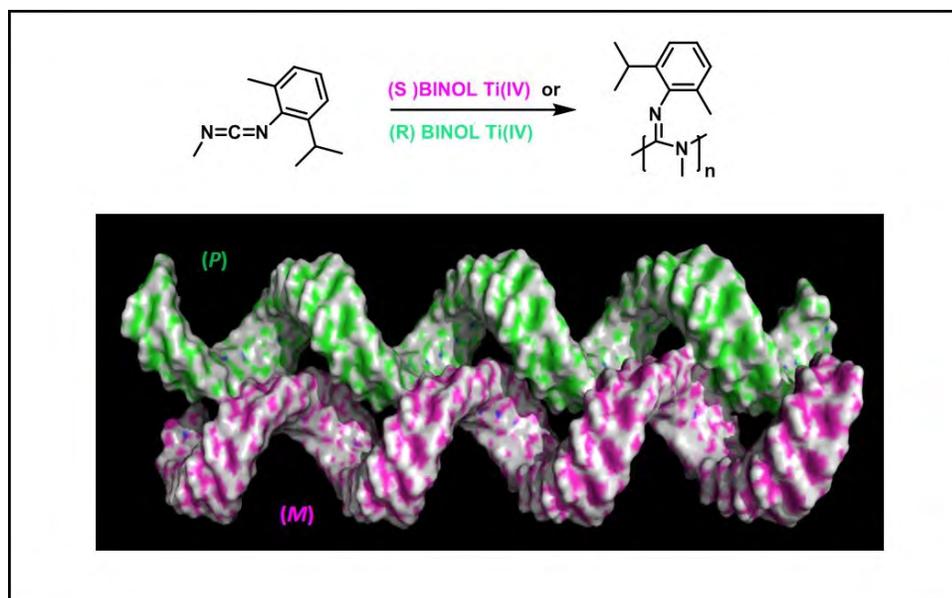
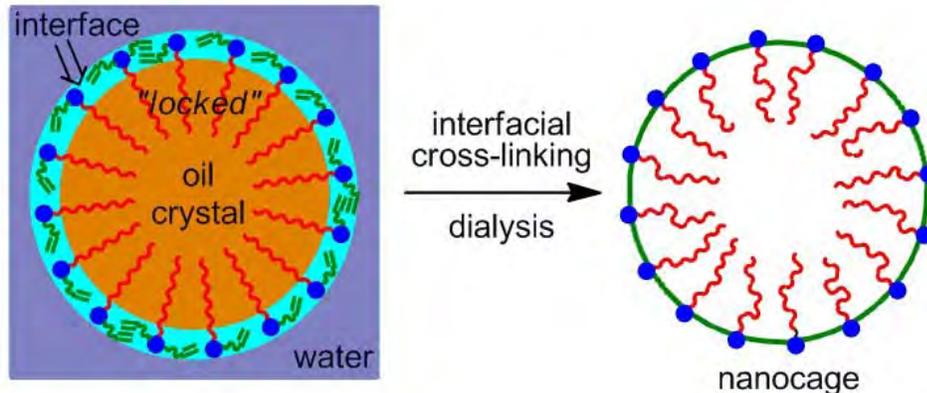


Fig. 1. Space filled model for complexation between two complementary polymeric strands.

## POLY 143: Polyelectrolyte nanocages via crystal-forming miniemulsions

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the State University of New York, Amherst, New York, United States (2) Chemical and  
Biomolecular Engineering, John Hopkins University, Baltimore, Maryland, United States

A variety of quaternary ammonium bromide-based surfactants carrying one or two acrylate groups and having a hydrophobic n-alkyl tail are synthesized, then converted to crosslinked nanocages by interfacial cross-linking of monolayers of surfactant molecules adsorbed by crystallized miniemulsion droplets. These nanocages are characterized by using various instrumental analysis techniques to reveal their structural features. The structural control of these nanocages and the surfactant monolayer stabilization mechanism in the crystal-forming miniemulsion systems are discussed.



Nanocage synthesis using crystallized miniemulsion nanodroplet as template

## **POLY 144: Extremely low friction with hydrophilic brushes in water when segregated from a PDMS matrix**

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Ability to control lubrication is essential to avoid damage of the underlying material and to ensure low energy dissipation in biological and man-made mechanical systems. Initially, our systematic approach to lower the surface friction of wet polymer surfaces employed surface adhesion of various novel short amphiphilic block copolymers prepared by the controlled radical polymerization techniques ATRP and RAFT. Successful syntheses afforded combinations of approx. 5 kDa hydrophilic poly(ethylene glycol) (PEG) (neutral) or poly(acrylic acid) (PAA) (negatively charged) with hydrophobic PS or poly(methoxyethyl acrylate) (PMEA) blocks, where only the neutral diblock copolymers had reasonable adsorption to a PDMS surface and consequently aqueous lubrication. Also amphiphilic graft copolymers: poly(methacrylic acid) (PMAA), P(MEA-co-MAA), or PMEA-co-(2-(dimethylaminoethyl)-ethyl methacrylate) on poly(2-hydroxyethyl methacrylate) (PHEMA) backbones were investigated, where P(MEA-co-MAA)-b-PHEMA showed superior anchoring and stability on the hydrophobic PDMS surface.

We now present a novel “inverted-grafting-to” approach that forms hydrophilic polymer brushes by selective segregation of hydrophilic chains of amphiphilic diblock copolymers, PDMS-*b*-PEG and PMDS-*b*-PAA, from a PDMS matrix. Excellent grafting stability and restoring capabilities are achieved as revealed even under harsh tribological testing since the hydrophilic polymer brushes are generated from an internal source of the material. The film can easily be applied to elastomers, metals and ceramic substrates by spin- or drip-coating. The resulting sliding friction coefficients ( $m$ ) are 0.001 to 0.05 for soft contacts depending on substrate, load, counter surface, pH, and salinity. Here the hydrophilic PAA shows much superior lubricity compared to PEG, which is rationalized by larger reduction of total free energy of the former upon hydration.



Søren Hvilsted

## **POLY 145: Property prediction with molecular dynamics simulations on graphene-epoxy coating materials**

*Lalitha Subramanian, lalitha@aol.com. Scienomics, Danville, California, United States*

Molecular dynamics simulations has become an important tool to capture details such as level of cross-linking, arrangements of polymer chains, functionalization, etc., that influence the macro-scale mechanical, thermal, corrosion resistance properties of coating materials. In this work we will present the mechanical properties of cross linked epoxy polymers on Graphene surfaces. The Build - Simulate - Analyze protocols in MAPS [1] will be presented with molecular dynamics simulations performed using LAMMPS [2]. The complex building step used mimics the curing process of the epoxy resin on top of the activated Graphene surface. We will present the differences between non-activated Graphene versus activated Graphene including the effect of active groups on both sides of the Graphene sheet. Previous simulations [3] have been performed on non-activated Graphene and we see a different behavior of the composite system once the Graphene is activated. Analysis of the mechanical properties is presented using advanced Analyze protocols available in MAPS. After construction of the systems uniaxial elongation is performed in the direction perpendicular to the surface and the effect of different degrees of activation is analyzed.

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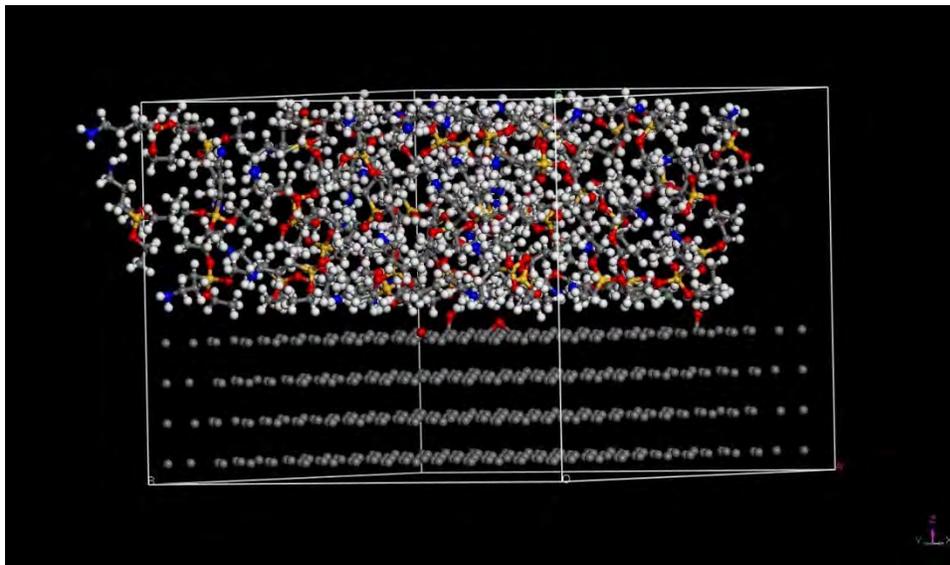
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## POLY 146: Interphase development in thermoset matrix composites

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The fiber/matrix interphase in polymer-matrix composites has an important role in determining bulk stiffness and strength. Atomistic simulations are used to explore the roles of species diffusion and chemical reaction in interphase development. The focus is on two principal interactions: 1) coupling agents and the fiber surface and 2) uncured resin and hardener with the coupling agent. Reactions among resin, hardener, surface-active sites, and coupling agents are based on proximity among reactive sites and have temperature-dependent reaction rates. Once reacted, these regions are investigated for their elastic properties.

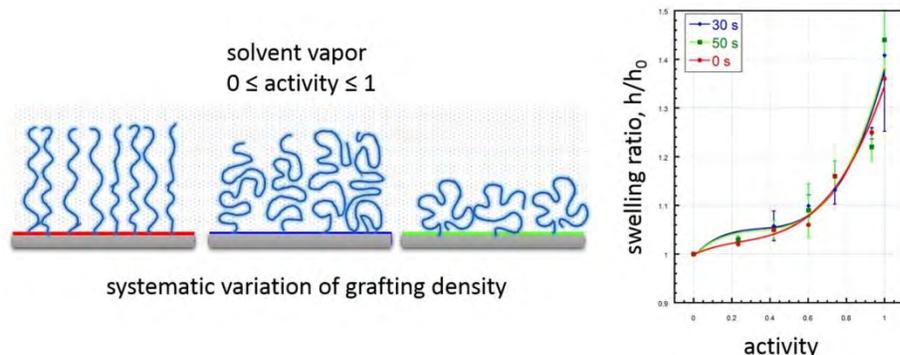


## POLY 147: Comparison of polymer brush solvation across grafting density regimes via vapor absorption measurements

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Tailoring polymer brushes to act as responsive coatings requires knowledge of brush solvation thermodynamics throughout the grafting density continuum, as the extent of chain-chain interactions alters brush sensitivity to its environment. Current brush models each focus on a limited grafting density range; these restricted windows do not compare differences across grafting regimes or quantify where regime transitions occur. Furthermore, these models do not address solvation in the vapor phase, which is desirable for brush applications such as gaseous membranes and sensors. Measurements that provide a quantitative comparison of brushes across grafting densities and solvent phases will yield accurate maps of brush thermodynamics to harness these next-generation thin films.

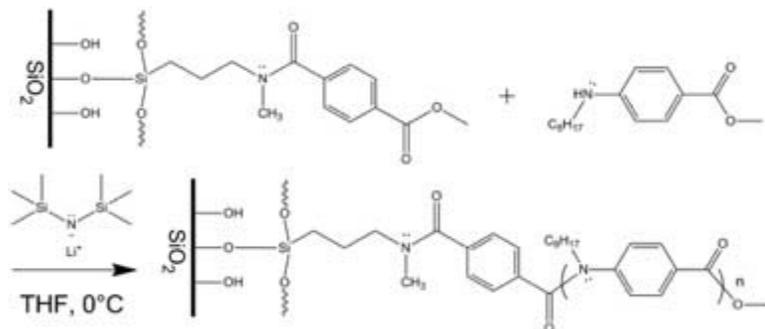
We have previously demonstrated that polymer-solvent interaction parameters ( $\chi$ ) within a dense polymer brush differ greatly from solution, as brush  $\chi$  is dependent on solvent concentration. In this study, polymer brushes with systematically-varied grafting densities were exposed to solvent vapor to compare brush solvation across grafting density regimes. Timed UV irradiation controlled surface initiator concentration. The brushes grafted from those initiators extended into the cross-over regime, which neither of the two primary thermodynamic models accurately capture. In situ x-ray reflectivity measurements were conducted on all brushes to measure film thickness and scattering length density as a function of solvent activity. The polymer-solvent interaction parameter as a function of grafting density,  $\chi(\sigma)$ , was determined using modified mean field theory. At low activity, brushes in the moderate density regimes absorbed more solvent than the high density brushes; this absorption behavior is similar to thin film gels, where chains have a higher degree of mobility.



## POLY 148: Development and application of chain growth aromatic polyamide brushes

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Polymer brushes have been a topic of interest over the past two decades due to their increasing number of applications in areas such as lubrication and protective coatings, tailoring of surface electronic properties, stabilization of colloids, and improving biocompatibility. To date, polymer brush research and applications have been essentially limited to polymers prepared via chain growth polymerization techniques involving vinyl-based monomers. However, recently researchers have established a need to develop polymer brushes based on conjugated polymers for application in areas such as OPV, OLED, and biosensing. We have developed a new surface initiated polymerization technique for the preparation of aromatic polyamide brushes using the substituent effect chain growth polycondensation technique. This presentation will outline the methods used to design and synthesize these novel polymer brushes, in addition, to demonstrating their use as surface coatings for reverse osmosis and nanofiltration membranes in the desalination of water.



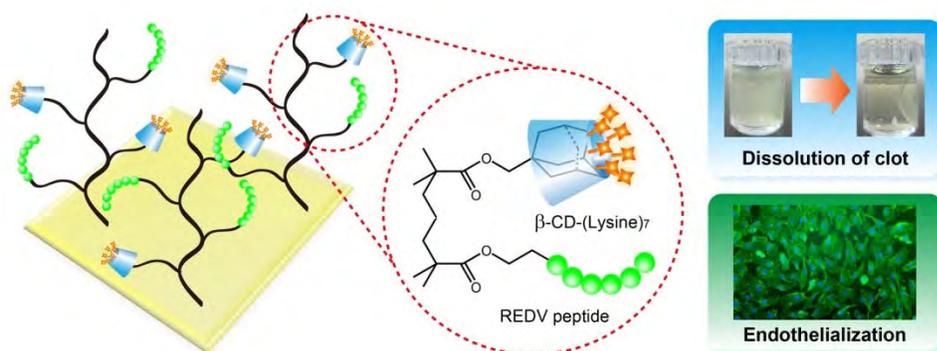
## POLY 149: Fabrication of bioactive surfaces with enhanced blood compatibility via a sequential co-immobilization strategy

**Qian Yu**, [yuqian@suda.edu.cn](mailto:yuqian@suda.edu.cn), Wenjun Zhan, Hong Chen. College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, China

Coagulation and thrombosis on the surfaces of synthetic materials in direct contact with blood cause a variety of serious problems. To improve the blood compatibility, in our previous works, we developed several fibrinolytic surfaces by mimicking the fibrinolysis pathway in the circulatory system to break down blood clots at its early stage of formation. Although effective, these surfaces may suffer problems for long-term use. We have aspired to mimic the vascular endothelium, which is the only known surface that is truly blood compatible. In this work, we developed a dual functional blood compatible surface which can both lyse nascent fibrin clots and promote the adhesion and proliferation of endothelial cells. Polyurethane surfaces were modified with a copolymer, poly(2-hydroxyethyl methacrylate-co-1-adamantan-1-ylmethyl methacrylate), which was served as a spacer for incorporation of two molecules, a peptide with REDV sequence and a modified  $\beta$ -cyclodextrin with 7 lysine ligands, via covalent bonding and host-guest interaction, respectively. The resulting surfaces demonstrated resistance to non-specific protein adsorption, but selectively adsorbed plasminogen from blood plasma, facilitating the fibrinolysis pathway. Meanwhile, this surface was able to promote the adhesion and proliferation of endothelial cells. These results provide a new strategy to engineer dual functional surfaces to enhance material-blood compatibility in all aspects, which will be potentially useful for blood-contacting devices and biomedical applications.

### Acknowledgements

This work was supported by the National Natural Science Foundation of China (21334004, 21404076, and 21125418), the Natural Science Foundation of Jiangsu Province (BK20140316)



Schematic presentation of a blood compatible surface with the capability to both lyse nascent clots and promote endothelialization

## POLY 150: Configurational behavior and charge correlation of zwitterionic brushes at the solid-water interface

**Wei Chen**<sup>1,2</sup>, *wchen@anl.gov*, **Jing Yu**<sup>1,2</sup>, **Jun Mao**<sup>2,1</sup>, **Matthew V. Tirrell**<sup>2,1</sup>. (1) Institute for Molecular Engineering/Materials Science Division, Argonne National Laboratory, Lemont, Illinois, United States (2) Institute for Molecular Engineering, University of Chicago, Chicago, Illinois, United States

Zwitterionic polymers (ZWP), on which each monomer segment bears both a positive and a negative charge, are an understudied class of polyelectrolyte macromolecules, most of which are simple polyelectrolytes (SPE) that bear a single sign of charge on each monomer. As each monomer has no net charge, the chains are not in extended configurations at low salt concentrations. In contrast to SPE, they expand when salt is added since the local attractions between positive and negative ions are screened, thereby producing a rich science base in understanding the configurations, ionic distribution, and in interfacial interactions of ZWP brushes in a variety of relevant and important ionic environments. The technical opportunity stems from observations that ZWP surface layers are particularly resistant to the colonization of microorganisms, with the consequent production of biofilms, on these surfaces. Here we thoroughly characterized the configurational behavior and lateral charge correlation of poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) polymer brushes (Fig. 1a) at interfaces under a variety of ionic (mono- and multivalent) conditions with different concentrations. PMPC polymers only weakly interact with biomembranes *via* van der Waals forces as seen in force and neutron spin echo measurements, indicative of the nonspecific binding nature of PMPC polymers (Fig. 1b and c). In an ionic environment, the ion-induced changes of PMPC chain configurations are not apparent, in contrast to common polyelectrolytes and other ZWPs, such as poly(carboxybetaine) and poly(sulfobetaine) (Fig. 1d). This, in turn, establishes structure-property relationships between surface chemistry and the ability of a thin film to resist foulant adhesion for the design and optimization of antifouling materials.

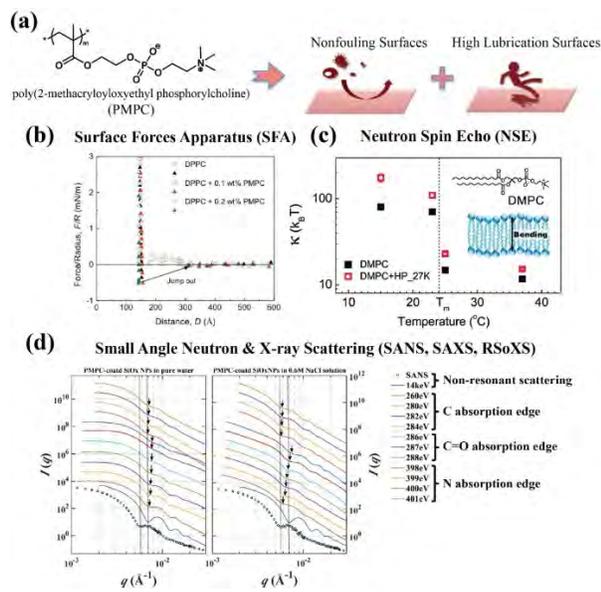


Fig. 1. The chemical structure of PMPC polymers and their corresponding results of SFA, NSE, RSoXS and SANS.

## **POLY 151: Brushing off salt using new polymer brush membranes**

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Tethered polymer chains or brushes have attracted enormous interest for both engineering and biomedical applications such as to stabilize colloids, to reduce friction between surfaces, to design novel fluidic devices, and to fractionate proteins in chromatographic columns. Here we synthesized, characterized and tested a new class of hydrophobic polymer brush membranes.

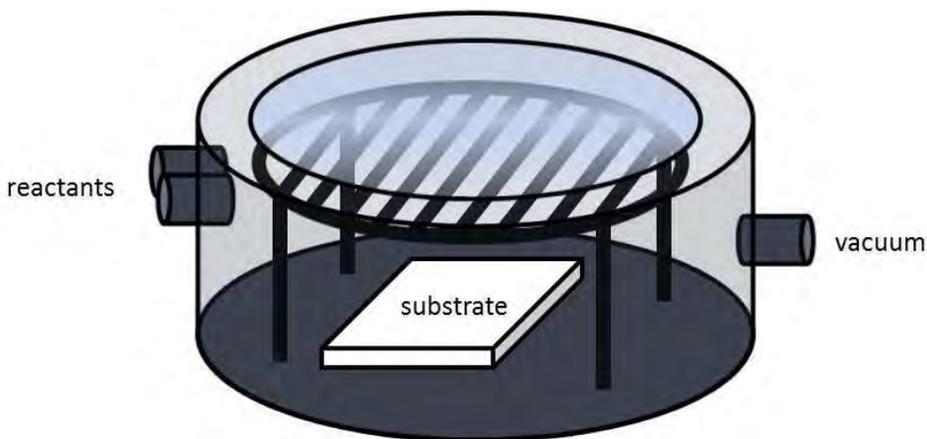
The membranes were *synthesized* by graft-induced polymerization of hydrophobic vinyl monomers onto light sensitive poly(ether sulfone) nanofiltration support membranes, without initiating agents, using atmospheric pressure plasma. Several hydrophobic vinyl monomers were tested to investigate the effect of chain length, the presence of linear versus branched chains, etc. Membranes were *characterized* by using several techniques, such as ATR-FTIR, Atomic Force Microscopy, Ellipsometry and Quartz Crystal Microbalance with Dissipation monitoring to determine brush layer properties such as thickness, graft density, viscoelasticity. The modified membranes were also *tested* for desalination of seawater, which is an urgent challenge and an opportunity to meet future world water demand. Membranes were tested in a high-pressure filtration unit and challenged with 33,000 ppm aqueous sodium chloride solution at 800 psi (55 bar).

The main novelty here is the use of hydrophobic brush-like structures as a selective skin or dense layer attached to a non-selective support membrane. Possible advantages of these new desalination membranes include (i) ease and speed of synthesis as compared with interfacial polymerization and phase inversion, (ii) scalability, (iii) low cost production, and (iv) high fluxes due to a hydrophobic resistance layer. Fouling could be addressed through modification with hydrophilic end-groups. The optimization of these easy-to-synthesize and scale-up membranes could guarantee an alternative to traditional polyamide reverse osmosis membranes, which still remains the major method of choice for desalination of sea water.

## POLY 152: Deposition of functional polymers coatings onto parylene substrates for biomedical applications

**Malancha Gupta**, *malanchg@usc.edu*, Mark De Luna, Christine Cheng. University of Southern California, Los Angeles, California, United States

In this talk, we will discuss methods to covalently attach functional polymer coatings onto parylene substrates for biomedical applications. We use a method called initiated chemical vapor deposition (iCVD) to deposit the polymer coatings. In the iCVD process, we flow monomer and initiator gases into a pancake-shaped reactor. The initiator is broken into free radicals via a hot filament array. The initiator radicals and monomer molecules diffuse to the surface of the substrate and polymerization occurs via a free radical mechanism. Parylene is used as a substrate in many biomedical applications. Since Parylene is inert, it is often necessary to modify the surface with functional polymer coatings. These coatings should be covalently attached to prevent dissolution or delamination. We will discuss two main methods that we have developed to covalently attach the iCVD polymers onto the Parylene substrate. In one method, we use a photo-initiator to create a cross-linked anchoring layer. In the second method, we use a plasma step to create radicals directly on the surface in order to graft the chains.

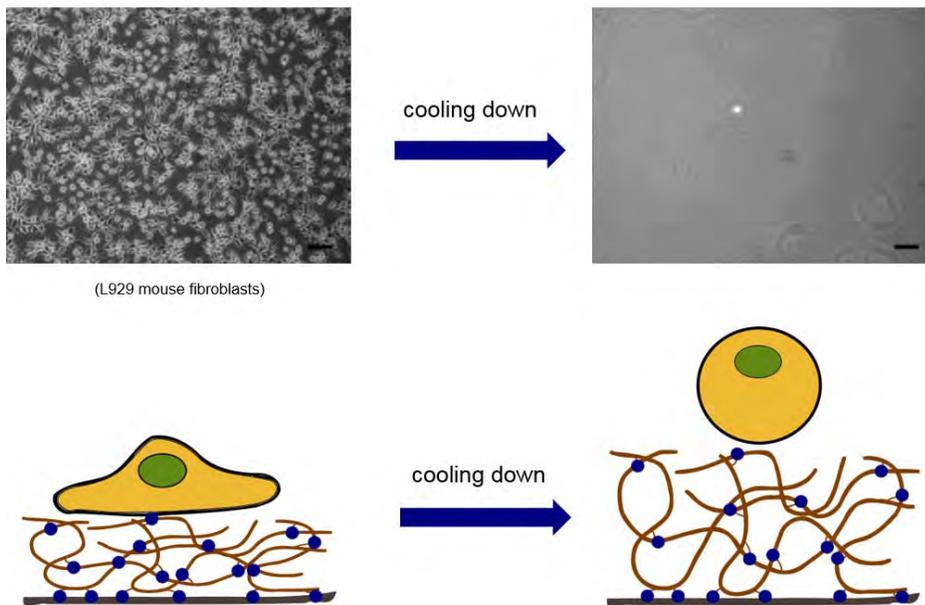


The polymer coatings are deposited via initiated chemical vapor deposition (iCVD).

## POLY 153: Ultrathin polymer coatings for the control of cell-surface interactions

**Michael Henze**, [michael.henze@imtek.uni-freiburg.de](mailto:michael.henze@imtek.uni-freiburg.de), Oswald Prucker, Jürgen Rühle.  
Imtek Univ of Freiburg, Freiburg, Germany

Modern biomedical devices require a subtle control of the interaction pathways of biointerfaces with species in their environment. The precise control of the cell adhesion plays a prominent role among these interactions. Many approaches ask for certain chemical or physical surface properties but also require a spatial control of cell adhesion and special topological features. In our work we concentrate on the development of tailor-made polymeric coatings that can be micro and nanostructured in two or three dimensions. The resulting surface architectures are then used to control cells in many different ways. One example is to generate surfaces which are either cell attractive or cell repellent. The latter situation is achieved if the protein adsorption from the environment is prevented. Such surfaces are bioinert and even blood platelets don't adsorb on them. A combination of such coatings with specific recognition sequences allows for the capture of rare cells in a background of abundant other cells. Such capture devices are interesting tools e.g. for cancer diagnosis. Finally, responsive materials can be used to generate initially cell-attractive surfaces from which cell lawns can be released upon a specific trigger (see Figure).



Thin responsive polymer layers can be used to culture cells and release them on demand.

## **POLY 154: Modified vegetable oil as a styrene replacement in commercial unsaturated polyester resins for fiber-reinforced composites**

*Yili Wu, **Kaichang Li**, kaichang.li@oregonstate.edu. Wood Science and Engineering, Oregon State University, Corvallis, Oregon, United States*

Commercial unsaturated polyester (UPE) resins typically contain a high amount of volatile toxic styrene. A non-volatile modified soybean oil (MSO) was found to be an excellent replacement of styrene in commercially available UPE resins in terms of the mechanical properties of the resulting fiber-reinforced composites. The MSO-UPE resins had low viscosity and long pot life for a typical fiber-reinforced composite application. The MSO and UPE plastic were not able to form a strong polymer matrix individually for fiber-reinforced composites. However, a combination of MSO and UPE plastic had strong synergistic effects between them. The flexural, tensile, and water absorption properties of the kenaf fiber- and fiberglass- reinforced composites made from the MSO-UPE resins were comparable or even superior to those from the styrene-UPE resin. The MSO/UPE weight ratio was investigated for maximizing the mechanical properties of the kenaf fiber-reinforced composites. The curing mechanism of the MSO-UPE resins is discussed in detail.

## **POLY 155: Replacement of styrene with a food additive in commercial unsaturated polyester resins for fiber-reinforced composites**

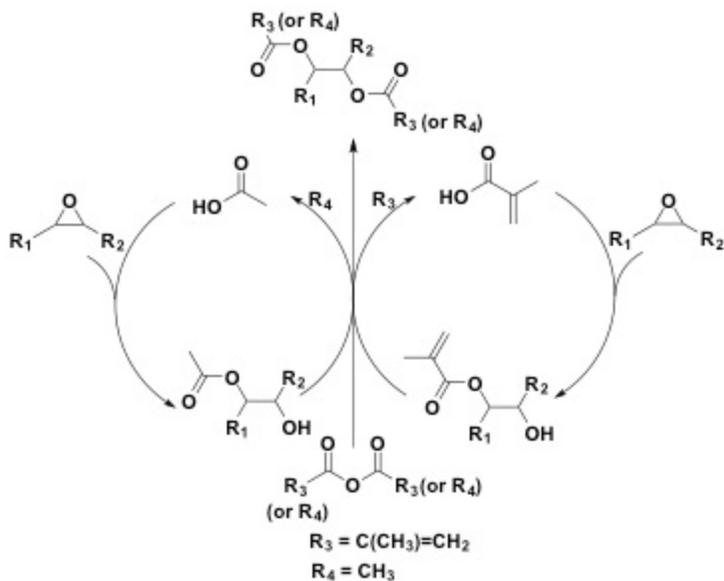
*Yili Wu, yili.wu@oregonstate.edu, Kaichang Li. Wood Science and Engineering, Oregon State University, Corvallis, Oregon, United States*

Styrene is a hazardous air pollutant (HAP) and a volatile, toxic component of most commercially available unsaturated polyester (UPE) resins. A food additive was investigated as a replacement of styrene in commercial UPE resins. The food additive did not homo-polymerize well for forming a strong matrix; but was capable of serving as an excellent crosslinking agent for UPE. It is found that mixtures of the food additive and a UPE plastic at certain weight ratios were superior to the commercial styrene-containing UPE resins in terms of the mechanical properties of the resulting fiber-reinforced composites. The food additive and the UPE plastic were both solid at room temperature. It is unexpected that mixtures of the two were a pourable liquid at room temperature. Effects of temperature on resin viscosity were studied. The food additive/UPE weight ratio was investigated for maximizing the mechanical properties of the fiber-reinforced composites. The curing mechanism of the food additive-UPE resins is discussed in detail.

## POLY 156: Effect of degree of functionality on properties of methacrylated bio-based resins and thermosets

**Arvin Z. Yu**<sup>1</sup>, [arvinzillionyu@yahoo.com](mailto:arvinzillionyu@yahoo.com), **Dean C. Webster**<sup>2</sup>. (1) North Dakota State University, Fargo, North Dakota, United States (2) Dept 2760, North Dakota State University, Fargo, North Dakota, United States

Dual methacrylated epoxidized sucrose soyate (DMESS) have previously been synthesized from epoxidized sucrose soyate (ESS). DMESS showed lowered resin viscosity compared with the single methacrylated product (MESS). However, due to its highly functionalized nature, the resulting thermosets were found to be very brittle. In order to reduce the brittleness, acetate groups were incorporated in the resin synthesis. The synthesis is a one-pot process involving the addition of two anhydrides mixed prior to addition. The resin (MAcetSS) was characterized using Fourier transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H-NMR), gel permeation chromatography (GPC), and viscosity measurements. MAcetSS was mixed with varying amounts of styrene and cured using peroxyesters as initiators. The extent of cure was determined by gel content using Soxhlet extraction and confirmed using FTIR. The thermal and mechanical properties were evaluated using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and tensile testing.



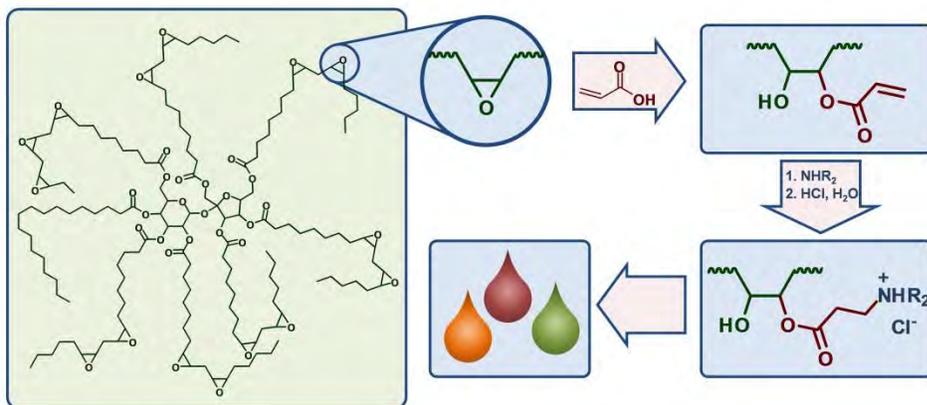
Proposed reaction mechanism

## POLY 157: Highly functional cationic biobased resins for sustainable UV-curable coatings

**Ivan Hevus**, *Ivan.Hevus@ndsu.edu*, Dean C. Webster. *Coatings and Polymeric Materials, North Dakota State University, Fargo, North Dakota, United States*

Vegetable oils and oil based materials are a sustainable alternative to petrochemical based resin components of organic coatings, however, their success depends on their ability to meet the performance requirements to petrochemical materials. With this regard, epoxidized sucrose soyate (ESS), a 100% biobased product made from sucrose and soybean oil, is a very promising raw material for coating resins due to its high functionality and low viscosity. Acrylation of ESS is a promising route to develop biobased UV-curable resins for printing inks due to the excellent wettability of pigments by acrylated epoxidized vegetable oils and the high reactivity of acrylate groups in the UV-induced photopolymerization processes.

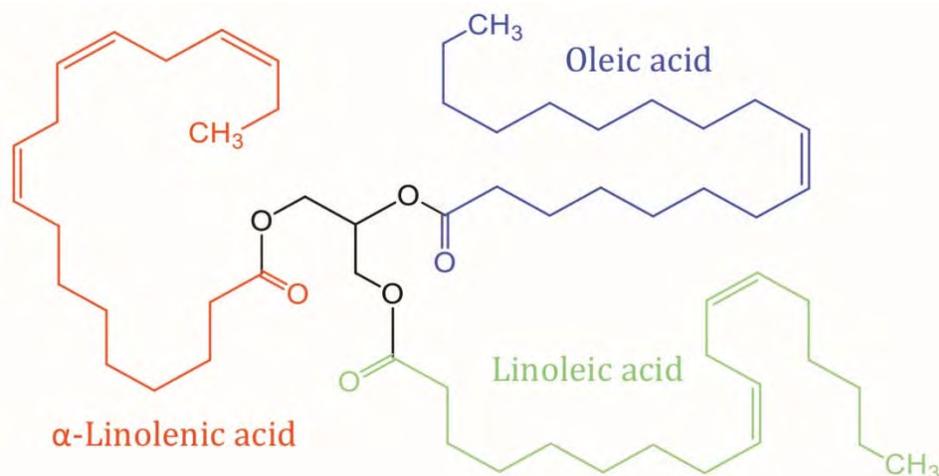
The purpose of this work was to develop a UV-curable ESS based resin system for the use in sustainable printing inks. We modified acrylated ESS with a range of aliphatic amines via Michael reaction to develop biobased acrylate resins with cationic amine groups. The resulting resins were used as a part of a waterborne UV-curable coating system. This way, the sustainability of the ink was further improved by reducing the amount of volatile organic solvents in the formulation. UV cured films made from the developed acrylate resins demonstrated good mechanical and coatings properties which makes the resins suitable for use as components of sustainable waterborne UV-curable printing inks.



## POLY 158: Soy-Based Resins and Fillers for Thermoset Composites

**Coleen R. Pugh**<sup>2</sup>, *cpugh@uakron.edu*, **Brinda Mehta**<sup>2</sup>, **Paula Watt**<sup>1</sup>. (1) Premix Inc, North Kingsville, Ohio, United States (2) Polymer Science, The University of Akron, Akron, Ohio, United States

The development of green polymers for commercial applications such as coatings, adhesives, composites, elastomers, and adhesives has gained momentum in recent years. Converting soybean oil into green resins will reduce our dependence on oil reserves and increase the U.S. market share in the field of biorenewable polymers. Our approaches toward the synthesis of crosslinked polymers include alkene- and alkyne chemistries based on the triglyceride (Scheme 1). This talk will report high-bio content and low toxicity resins derived from functionalized plant oils for various applications via the “ene” chemistry to facilitate commercialization of these green resins. The targeted properties of these green resins are high glass transition temperature of at least 120 °C, Young’s modulus greater than 2000 MPa, and more than 80% bio-content. The bio-content of composites may also be increased using by replacing mineral fillers with renewable biomass fillers. With a density of approximately 1 g/cm<sup>3</sup>, biomass fillers yield compounds at equivalent volume reinforcement with a 20-25% weight reduction compared to mineral filler, which have specific gravities of roughly 2.5 g/cm<sup>3</sup>. This talk will also present a variety of treatments that were studied to reduce the hydrophilic nature of the biomass precursor, especially thermal treatment, which can lead to cure inhibition in the composite systems. Dielectric analysis, squeeze flow rheometry and mechanical testing were employed to evaluate the process and performance of the soy-filler compounds.

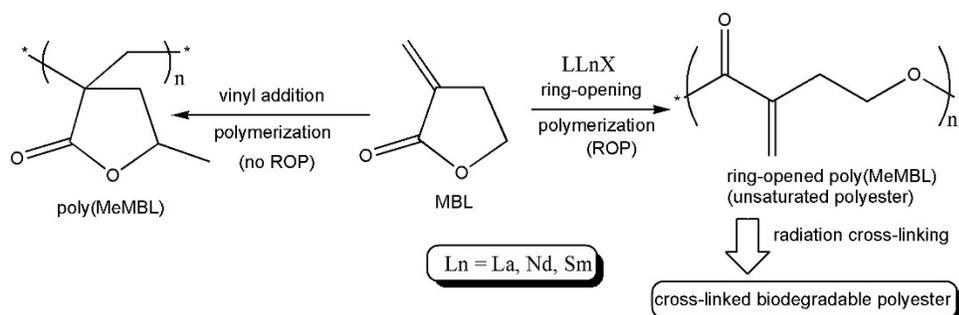


Scheme 1. Triglycerides are the major components of plant oils.

## POLY 159: New lanthanide complexes for the polymerization of $\alpha$ -methylene- $\gamma$ -butyrolactone to obtain biodegradable cross-linkable unsaturated polyesters

**Pascal I. Binda**, *itambibinda@yahoo.com*. Chemistry and Forensic Science, Savannah State University, Savannah, Georgia, United States

Polyesters are commonly applied in bio-medical engineering for drug delivery devices and tissue engineering products because of their biodegradable and biocompatible properties. Cyclic esters containing cross-linkable olefinic pendant arms will be employed for the first time as monomers for cross-linked biodegradable polyesters using new heteroleptic lanthanide complexes (LLnX). The new heteroleptic lanthanide complexes [LLaN{Si(CH<sub>3</sub>)<sub>3</sub>}<sub>2</sub>] (**1**) and [LNdN{Si(CH<sub>3</sub>)<sub>3</sub>}<sub>2</sub>] (**2**) were synthesized from acid-base ligand exchange reactions between chiral ligand and corresponding homoleptic lanthanide compound (La[N{Si(CH<sub>3</sub>)<sub>3</sub>}<sub>2</sub>]<sub>3</sub> or Nd[N{Si(CH<sub>3</sub>)<sub>3</sub>}<sub>2</sub>]<sub>3</sub>, respectively) at -40°C in toluene. Compounds **1** and **2** were subsequently reacted with excess isopropanol to obtain [LLaO<sup>i</sup>Pr] (**3**) and [LNdO<sup>i</sup>Pr] (**4**). The new LLnX complexes will then be used as catalyst for the ring opening polymerization of MBL ( $\alpha$ -methylene- $\gamma$ -butyrolactone).



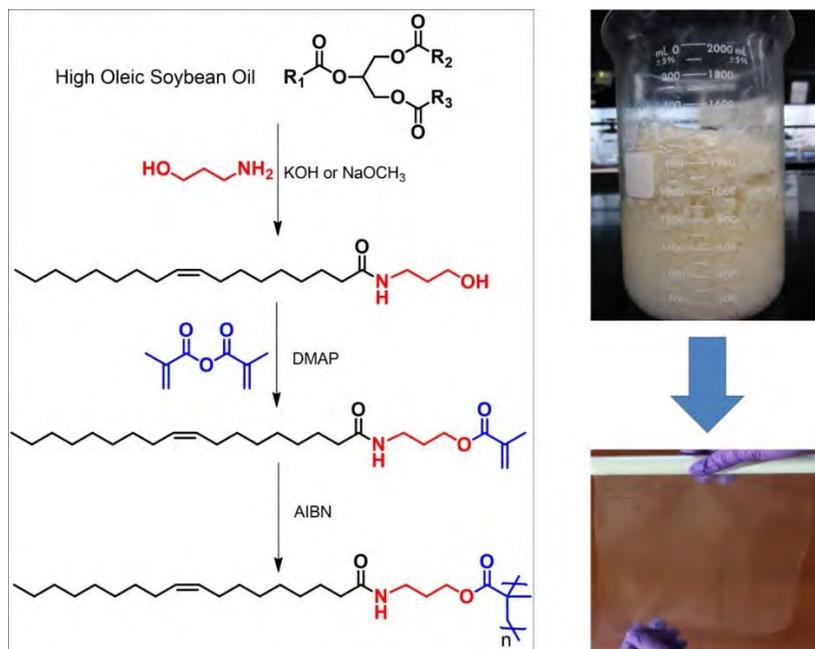
## POLY 160: Monomers, polymers, and nanocomposites derived from plant oil as next-generation sustainable materials

**Zhongkai Wang**, wangzhongkai6@gmail.com, Liang Yuan, Nathan M. Trenor, Chuanbing Tang. Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina, United States

Due to the energy and environmental concerns, sustainable fuels, chemicals, and materials from renewable resources have gained tremendous momentum in a global scale. Plant oils are widely explored as a result of their abundance, low price, and easy modification. We present the design and preparation of novel monomers, thermoplastic polymers, and their nano-composites from soybean oil (SO). Amidation of SO with varied amino alcohols provided a series of mono-hydroxyl terminated derivatives, which were further converted into a variety of methacrylate monomers (SBMAs).<sup>1</sup> Structure-property relationship of the polymers from these SBMAs were elucidated before the first thermoplastics from SO with  $T_g=30^\circ\text{C}$  was prepared in a 2 lbs scale. Thermoset elastomers from random copolymer P(St-co-SBMA) and triblock structured thermal plastic elastomers PSt-b-PSBMA-b-PSt by ATRP were developed.<sup>2</sup> Supramolecular nano-composites with high mechanical stress (30Mpa) were fabricated by introducing cellulose nanocrystals (CNCs) to the modified soybean oil polymers. Finally, multiple shape memory materials with good shape fixity and recovery were prepared by a grafting strategy. Our results demonstrated novel strategies for the design of monomers, polymers, and nanocomposites from plant oil for the next generation of sustainable materials.

### Reference

- (1) Yuan, L.; Wang, Z.; Trenor, N. M.; Tang, C. *Macromolecules* 2015, 48, 1320.
- (2) Wang, Z.; Yuan, L.; Trenor, N. M.; Vlaminc, L.; Billiet, S.; Sarkar, A.; Du Prez, F. E.; Stefik, M.; Tang, C. *Green Chemistry* 2015, 17, 3806-3818.



## POLY 161: Bio based thermoplastic polyurethane

**Guenter Scholz**, *guenter.scholz@basf.com*. Product Development Elastomers, BASF Polyurethanes GmbH, Lemfoerde, Germany

Currently an accepted number of 1% bio based polymers are used in the whole plastics market of expected 350 Mio tons per year. It should be differentiated between compostable and bio based materials although there is a big overlap. There exists an agreement to name a plastic with the supplement 'bio' when at least 20 w%-C of renewable raw materials are used in the formulation. In this lecture either the opportunities for thermoplastic elastomers (TPE) is shown or one example of renewable thermoplastic polyurethane (TPU) is introduced.

What are the main sources of raw material which can be used in TPE respectively TPU?

- castor oil from castor beans
- starch from corn and grain
- lignin from wood
- lysine from bio mass
- palm oil from palm trees

The basic products for polyurethanes are isocyanates, short chain diols and oligomeric polyols. The alcohols are the targeted parts of these products but even isocyanate can be made from such a source.

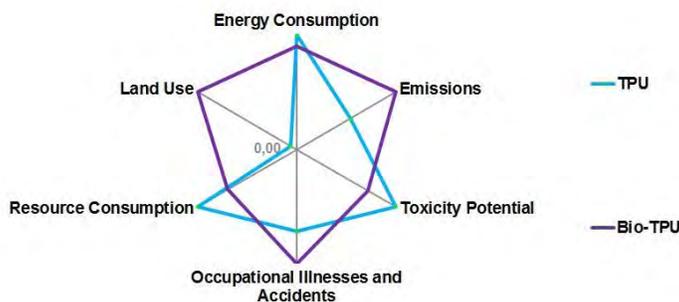
Beside all the discussion about food chain and energy consumption bio based materials should be compared with oil based ones. With the result that there is often no significant difference on an eco-efficiency analysis, it is more a strategic decision or a strong desire using renewable raw materials. The example in the spider chart shows that a bio based TPU has not an overall better ecologic character in his value chain compared to a similar oil based peer. That is also a reason to create bio based plastics with reasonable mechanical properties and price range to have a better acceptance in the market. The earliest interest in renewable TPU came from the consumer market mainly in sport shoes.

The lecture gives an overview on thermoplastic elastomers with the potential of using bio based raw materials and later it will be focused on TPU with a current property profile.

Literature:

Books without editor: G. Holden, H.R. Kricheldorf, R.P. Quirk, *Thermoplastic Elastomers*, Hanser Publishers, Munich, 2004.

Susan L. Bell, *HIS Chemical Process Economic Program, Report 265A*, 2013



## **POLY 162: Industrial applications of medium chain length poly(hydroxy alkanooates): From feedstock to finished article**

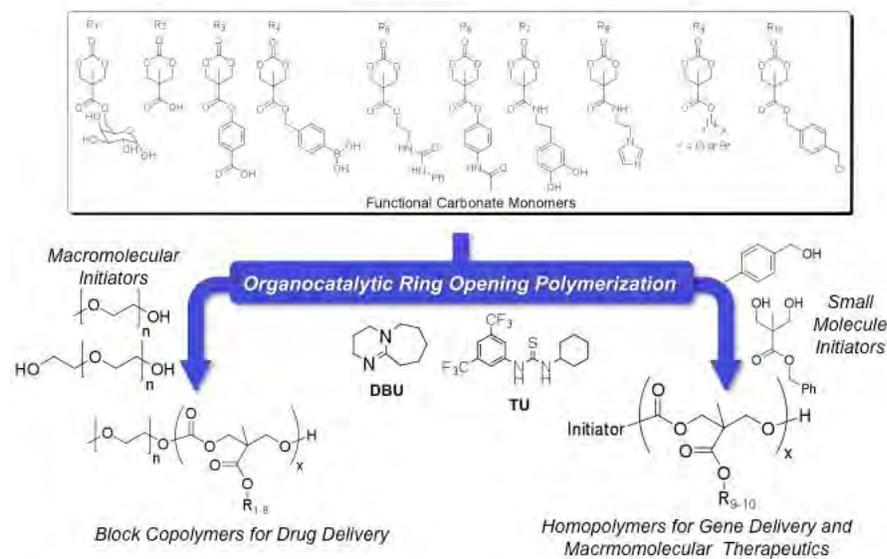
**Michael Mang**, [mmang@mhgbio.com](mailto:mmang@mhgbio.com). Meridian Holdings Group, Bainbridge, Georgia, United States

Medium chain length poly(hydroxyalkanoates) (*mcl*-PHAs) are becoming industrially practical due to a combination of advances in the tools of industrial biotechnology, feedstocks, and manufacturing processes. The polymer structure obtained during fermentation provides thermoplastic polymers with physical properties that are improved compared to conventional PHAs, and the ability to control that structure yields materials that can address performance requirements for a very broad range of final applications. Crystallization kinetics and the development of morphology are determined primarily by side group chain length and composition defined during fermentation, and profoundly and positively affect processing. The use of PHA as a replacement for conventional petroleum based thermoplastics, and the impact of end-of-life considerations will be discussed.

## POLY 163: Supramolecular structures for the precision release of therapeutics

**James L. Hedrick**<sup>1</sup>, [hedrick@us.ibm.com](mailto:hedrick@us.ibm.com), Yi-Yan Yang<sup>2</sup>. (1) IBM Research, San Jose, California, United States (2) Inst Bioengr Nanotech, Singapore, Singapore

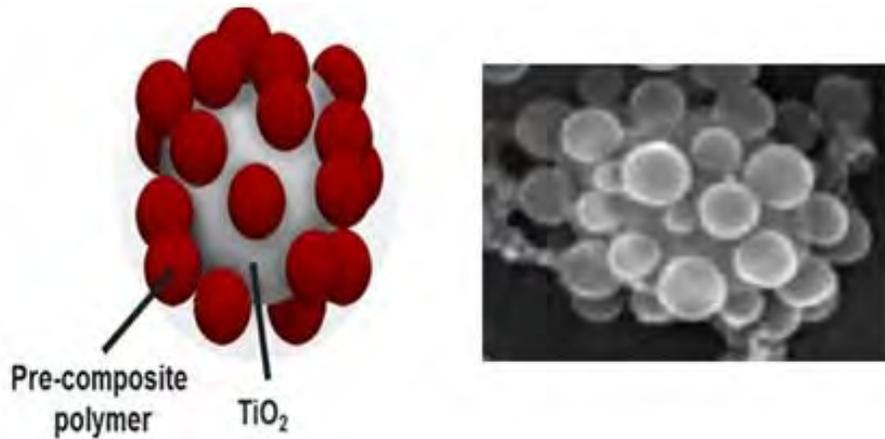
The field of nanomedicine offers significant promise for improving human health by applying the tools of nanotechnology to create and control materials with molecular-level medical effects. The targeting and controlled release of therapeutic agents to specific organs and specific cells in the body is one of the major challenges in developing more effective therapies. This talk will discuss new polymers that have the ability to encapsulate, transport and deliver a variety of cargos. The foundation for this platform is based on our organocatalytic approach to biocompatible/degradable macromolecules with precisely defined molecular weights, end-group fidelity and backbone functionality. These backbones include polylactide, polycarbonate and related degradable polymers with a wide range of backbone functionalities that mimic the rich and diverse functionality of polypeptides. The use of these synthetic methods to generate well-defined macromolecules and their evaluation to test the functional competence of these constructs as drug/gene delivery vehicles will be discussed. An emphasis is placed on the release-rate profiles to mitigate unwanted side reactions.



**POLY 164: Commercial scale self-assembled polymer-pigment composites for waterborne coatings with high performance, improved eco-footprint and lower cost**

**James Bohling**, [jbohling@dow.com](mailto:jbohling@dow.com). The Dow Chemical Company, Collegeville , Pennsylvania, United States

Improved polymer technology has enabled the volatile content of house paints to be dramatically reduced to very low levels over the years. Life cycle assessment has shown that another opportunity for improving the eco-profile of architectural coatings would be to reduce the level of  $\text{TiO}_2$  (opacifier) required.  $\text{TiO}_2$  is typically used inefficiently due to a phenomenon known as “crowding”. Adsorbing latex technology which enables the controlled formation of self assembled polymer-pigment composites has been developed. This is a smarter material which replaces the conventional paint binder and does everything the conventional binder does while additionally helping to improve pigment efficiency. Better film formation and reduced impact of photodegradation can result from this more uniform distribution of  $\text{TiO}_2$ , all while improving its efficiency and improving the eco-profile. Production of this technology is measured by millions of pounds and was awarded a Presidential Green Chemistry Challenge Award by the Environmental Protection Agency.

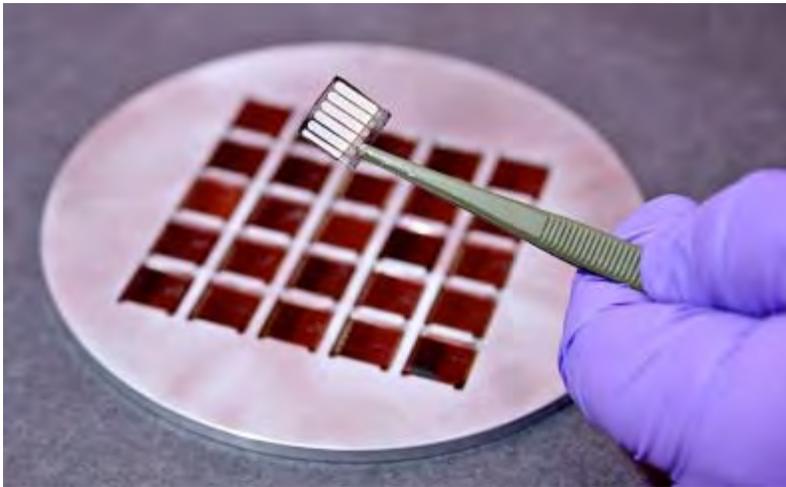


## **POLY 165: Development and life cycle assessment of organic photovoltaics**

**Brian Worfolk**, *brian.j.worfolk@p66.com*, Amit Kapur, Amanda A. Johnston, Kathy B. Woody. Phillips 66, Bartlesville, Oklahoma, United States

The unique features of organic photovoltaics (OPVs), including color variety, flexibility and superior low-light performance, make them well-suited for target applications such as building integrated photovoltaics. To move OPVs from research to a commercial phase, continued improvements are needed in efficiency, lifetime and manufacturing of modules. Phillips 66 has a research group working towards identifying high performing conjugated polymers and photovoltaic device engineering.

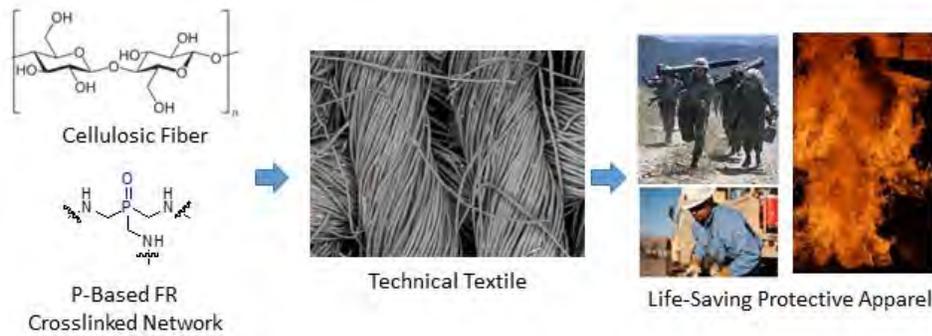
Variables important to efficiency, lifetime and manufacturing of modules can have a significant impact on energy burden; however, energy burden and environmental impact associated with photovoltaic technologies are not widely discussed. One method used to analyze the environmental sustainability of electricity generation technologies is a life cycle assessment (LCA). This presentation will include an overview of the LCA of OPVs produced on a semi-industrial pilot line, using a “cradle-to-grid” approach with a 1 W photovoltaic module as the functional unit. The primary energy demand and energy payback time of high efficiency photoactive polymers will be discussed and benchmarked against other photovoltaic technologies.



# POLY 166: Flame resistant textiles for the 21<sup>st</sup> century: Sustainable solutions from theory to practice

**Jason M. Spruell**<sup>1</sup>, [jspruell@gmail.com](mailto:jspruell@gmail.com), Warren Gerhard<sup>2</sup>. (1) Research Division, Milliken and Company, Spartanburg, South Carolina, United States (2) Research Division, Milliken and Company, Greer, South Carolina, United States

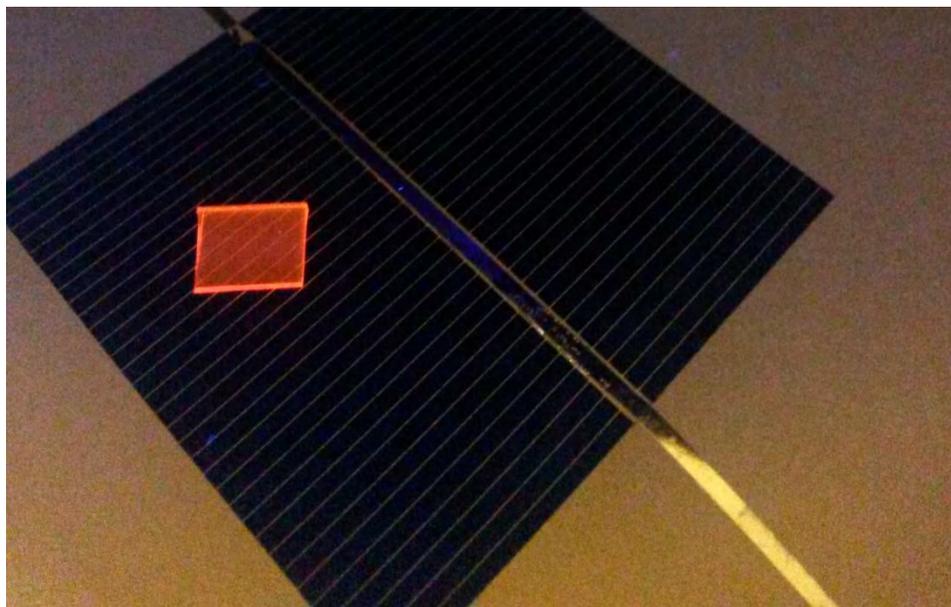
While the demand for flame resistant products has never been greater, the solutions to achieve these properties are under increasing scrutiny. New methods, processes, and chemistries are needed to drive performance of flame resistant products that utilize environmentally benign materials and sustainable processes. We will discuss our efforts to bring innovative and sustainable solutions to market in a maturing field by creating novel chemistries for protective flame resistant fabrics. An overview of the field as well as a deep dive into our modern phosphorus-based flame retardant chemistries and fabric processing will be discussed.



## **POLY 167: Photoluminescent UV curable polymer-quantum dot composite as luminescent down-shifting layer for photovoltaics**

**Guy Draaisma**<sup>1</sup>, [guy.draaisma@dsm.com](mailto:guy.draaisma@dsm.com), **Damien F. Reardon**<sup>2</sup>. (1) DSM, Geleen, Netherlands (2) Materials Sciences RD, DSM Ahead, Geleen, Netherlands

The efficiency of photovoltaics with a poor UV response can be improved by altering the incident light spectrum with luminescent down-shifting. Stable luminescent additives with a large Stokes shift, high photoluminescence quantum yield and a high absorption coefficient in the UV spectral region are required for this purpose. CuInS<sub>2</sub>/ZnS core shell quantum dots were theoretically and experimentally evaluated as down-shifting additive. Enhanced dispersibility of the quantum dots was achieved via a ligand exchange process with a synthesized thiol functional ligand. Raman spectroscopy, liquid state NMR spectroscopy and solid state NMR relaxometry were applied to study the ligand exchange process. Down-shifting films with CuInS<sub>2</sub>/ZnS as additive were successfully prepared, by UV curing, without impairing the luminescent properties. Theoretical simulations predicted that a near unity quantum yield was required to increase the efficiency of current photovoltaics.



Luminescent down-shifting film placed on top of a silicon solar cell. The picture has been taken under 366nm UV illumination. The orange light emission from the down-shifting film is visible.

## **POLY 168: Focusing the HTE approach to polyolefin catalysis**

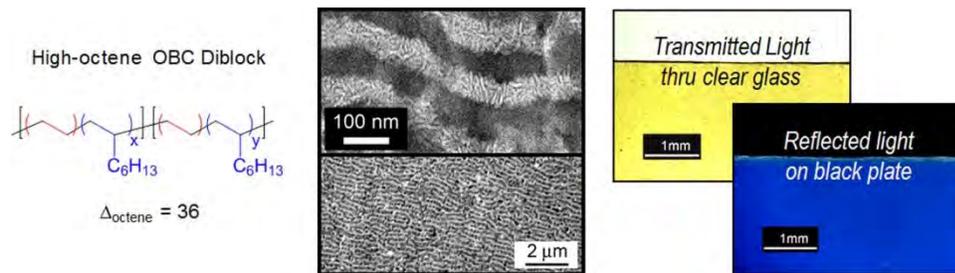
**Vincenzo Busico**, *busico@unina.it*. Dept. Chemical Sciences, Università di Napoli Federico II, Naples, Italy

High Throughput Experimentation (HTE) is often associated with brainless trial-and-error searches, but this is not necessarily the case. This talk will introduce a HTE workflow aimed to the rapid implementation of large and accurate structure-properties databases in polyolefin catalysis, in view of predictive QSAR modelling. A state-of-the-art secondary screening platform operating at high pressure was integrated off-line with advanced polyolefin characterization tools including high temperature cryoprobe  $^{13}\text{C}$  NMR, Rapid Gel Permeation Chromatography and Analytical Crystallization Elution Fractionation. Compared with a conventional approach, a  $10^2$ -fold throughput intensification was achieved without losing in precision and accuracy. Application to classical Ziegler-Natta catalysts for polypropylene production will be used as a case history.

## POLY 169: Polydispersity in block copolymer self-assembly: From photonic polyethylene to advanced lithographic patterning

**Phillip D. Hustad**<sup>1</sup>, pdhustad@dow.com, **Jeffrey D. Weinhold**<sup>2</sup>, **Eddy Garcia-Meitin**<sup>2</sup>, **Gary R. Marchand**<sup>2</sup>, **Jieqian Zhang**<sup>1</sup>, **Valeriy Ginzburg**<sup>3</sup>, **Peter Trefonas**<sup>1</sup>. (1) Dow Electronic Materials, Natick, Massachusetts, United States (2) The Dow Chemical Company, Freeport, Texas, United States (3) The Dow Chemical Company, Midland, Michigan, United States

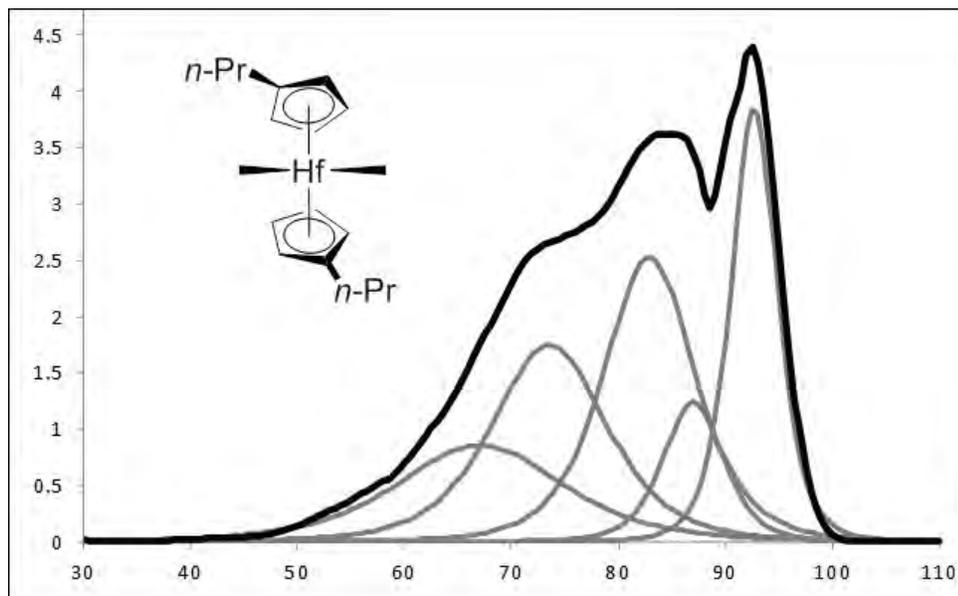
Block copolymer self-assembly has become an important tool for manipulation of properties in soft materials, wherein ordered nanoscale morphologies impart unique properties often unattainable in homogeneous polymer systems. Many applications are now benefitting by incorporation of block copolymer architectures, spanning a range of end uses ranging from adhesives to materials for advanced lithographic patterning. Block composition, chain architecture, molecular weight, and polydispersity all effect order and morphology in these materials. In particular, polydispersity has been found to have a dramatic impact on the length scale of phase separated nanostructures. This presentation will highlight some of the interesting consequences of polydispersity on block copolymer phase behavior and its impact on material properties and applications.



## POLY 170: Mythology of single site polyethylene catalysts

**Roger L. Kuhlman**<sup>1,3</sup>, kuhlmarl@gmail.com, **Cristiano Zuccaccia**<sup>4</sup>, **Alceo Macchioni**<sup>2</sup>, **Anthony Gies**<sup>1</sup>. (1) Dow, Lake Jackson, Texas, United States (2) University of Perugia, Perugia, Italy (3) Univation, Freeport, Texas, United States (4) Università de Perugia, Perugia, Italy

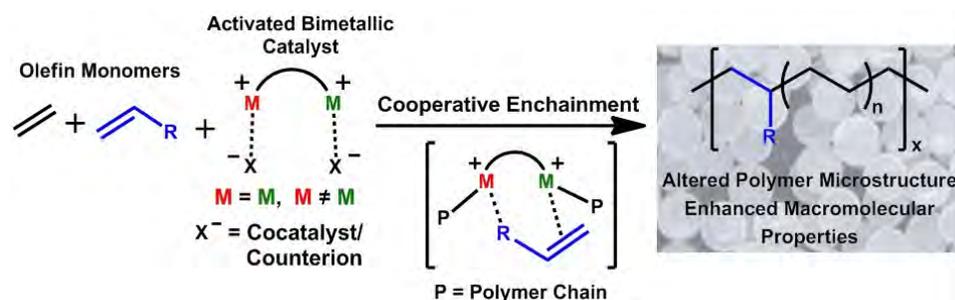
The term “single-site catalyst” is sometimes used to describe a family of olefin polymerization catalysts derived from discrete molecular organometallic precursors. Yet some of these discrete precursors produce polyethylenes with broad and/or multi-modal molecular weight and composition distributions. How can a “single site” catalyst produce multiple polymer components? Perhaps the answer is at least partly explained by complex chemistry involved during the activation processes. Examples are discussed of changes in catalyst molecular structure during the polymerization by in situ ligand modifications, including a conventional metallocene.



## POLY 171: Cooperative catalytic properties of multinuclear electrophilic organometallic ensembles

**Tobin J. Marks**, *t-marks@northwestern.edu*. Northwestern Univ, Evanston, Illinois, United States

This lecture focuses on intricate covalent multi-center interactions as well as non-covalent interactions that modulate catalytic activity and selectivity in olefin polymerization processes. Specific interrelated topics include: 1) Catalytic chemistry and cooperativity effects in homodinuclear group 4 catalysts, 2) Catalytic chemistry and cooperativity effects in heterodinuclear groups 4 + 6 catalysts, 3) Catalytic chemistry and cooperativity effects in homodinuclear group 10 catalysts, 4) Transferring such chemistry to “super-acidic” oxide surfaces. It will be seen that the information obtained from these studies yields design rules for next-generation homogeneous and supported catalysts, and for novel and useful polymerization processes.



Unusual aspects of olefin polymerization mediated by a binuclear catalyst

## **POLY 172: Applications of olefin block copolymers**

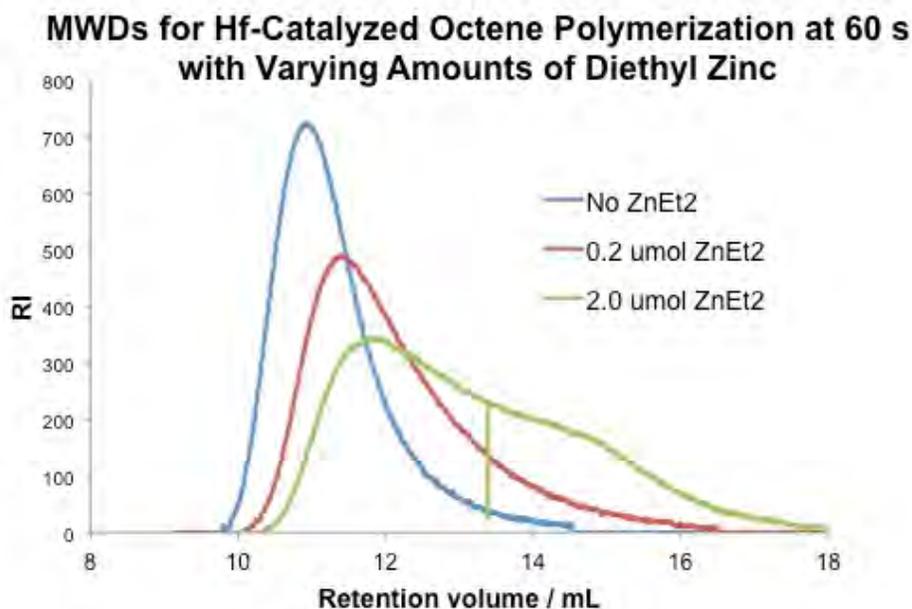
**Gary R. Marchand**, *rmarchand@dow.com*, Russell Barry, Harold Boone, Yushan Hu, Seema Karande, Kyle Kummer, Raymond Laakso, C. Li Pi Shan, Lisa Madenjian, Amaia Montoya-Goni, Jeff Munro, Kim Walton. *The Dow Chemical Company, Freeport, Texas, United States*

The discovery of catalytic chain shuttling chemistry for polyolefins is driving the creation of entirely new polymeric materials. These materials are being used as unique alternatives to more complex and costly polymers. They are also enabling entirely new applications for polymer blends and multi-layer engineered structures. First, a multiblock polyolefin thermoplastic elastomer was made by combining a high melting polyethylene homopolymer block with a flexible, low Tg ethylene copolymer elastomer block. This thermoplastic elastomer was commercialized in 2008. A subsequent olefin block copolymer with a crystalline polyethylene copolymer segment and a crystalline isotactic polypropylene segment (EP-iPP) was commercialized in 2014. The polyethylene-polypropylene block copolymer is the ideal compatibilizer for the two largest volume polymers manufactured in the world. Applications for olefin block copolymers include polymer toughening agents, smart packaging, adhesives, fashion fibers, medical products, building & construction uses, footwear, and automotive materials.

## POLY 173: Chromophore-labeled gel permeation chromatography applied to the study of hafnium pyridylamide catalyzed polymerization of 1-octene in the presence of diethyl zinc

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Ultimately, the composition and block lengths of the Dow "Chain-Shuttling" process for catalytic synthesis of olefin block copolymers are determined by the rates of propagation and transalkylation with chain transfer reagents. Are there practical methods for studying these kinetics? The time-evolution of polymer molecular weight distributions are accessible by gel permeation chromatography and rich in kinetic information. Chromophore-labeling reagents and UV detection enable detailed information to be extracted from a single gel permeation chromatogram. Specifically, active site counts, the rates and reversibility of chain-transfer between Hf-polymeryls and diethyl zinc, and the extent to which catalysis conforms to living behavior are revealed by quantitative gel permeation chromatography with pyrene labels. These studies suggest a practical route to elucidating the kinetics of chain-shuttling catalysis under conditions used commercially.



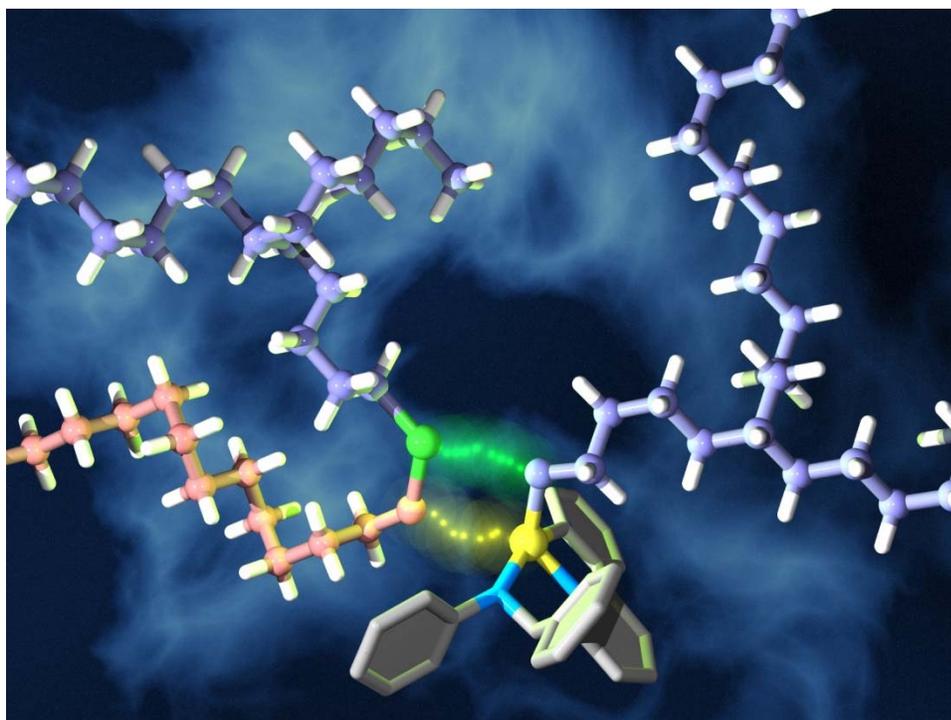
**POLY 174: Award Address (ACS Award in Polymer Chemistry sponsored by ExxonMobil Chemical Company). Advances in olefin block copolymers**

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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, narrow molecular weight distribution metallocene polymers can be used in applications where extractible oligomers are unacceptable, and high comonomer content ULDPE can be extremely effective for impact modification of some thermoplastics. Continuing this trend, The Dow Chemical Company commercialized INFUSE™ Olefin Block Copolymers. Prepared using “chain shuttling” catalysis, 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. The synthesis and properties of several classes of OBCs will be presented, demonstrating once again our ability to push the envelope of polyethylene performance.

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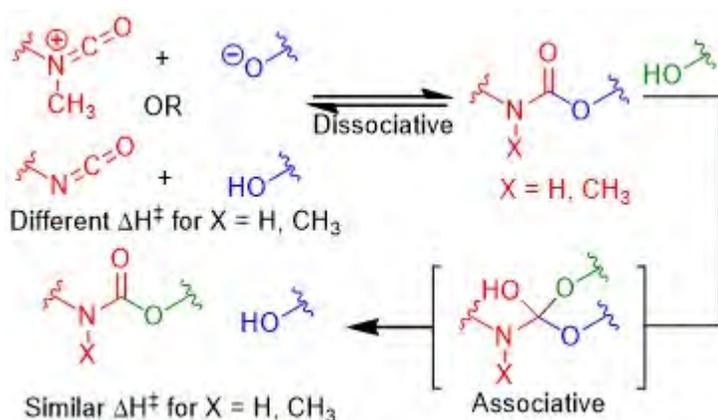
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## POLY 175: Sustainable urethane-based vitrimers

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Cross-linked polymers with controllable healing characteristics have received significant attention over the last decade. However, there is still much to be developed with these materials in the sustainability arena. Herein, we studied the healing capabilities of cross-linked bioderived poly(lactones) through Lewis acid catalyzed exchange reactions. Materials that use isodesmic reactions (e.g., transesterification) for healing are termed vitrimers and have been reported using a diverse range of chemistries. Initial studies focused on the healing properties of amorphous isocyanate cross-linked star-shaped poly( $\pm$ -lactide) utilizing stannous octoate as the exchange catalyst. These materials exhibited remarkably fast stress relaxation rates when compared with previously reported polyester-based vitrimers, exhibiting similar stress relaxation rates at temperatures up to 140 °C lower. Interestingly, the stress relaxation activation energy ( $E_a$ ; ca. 150 kJ/mol) determined was almost double literature values for stannous octoate catalyzed transesterification. Thus, an isocyanate cross-linked polyethylene oxide analogue showed an identical  $E_a$ , revealing urethanes as responsible for stress relaxation. Recently, a collaboration with the Dichtel group was initiated in which cross-linked polyhydroxyurethanes were utilized for a mechanistic study on stress relaxation. An *N*-monosubstituted and an *N,N*-disubstituted urethane network were compared in order to determine whether transcarbamoylation or urethane reversion was the main stress relaxation mechanism. Furthermore, a computational study comparing transcarbamoylation versus urethane reversion was performed to further support the outcome from stress relaxation analysis. These results will be described in this presentation, as well as our ongoing research efforts on utilizing renewable cross-linkers and production of sustainable elastomers.

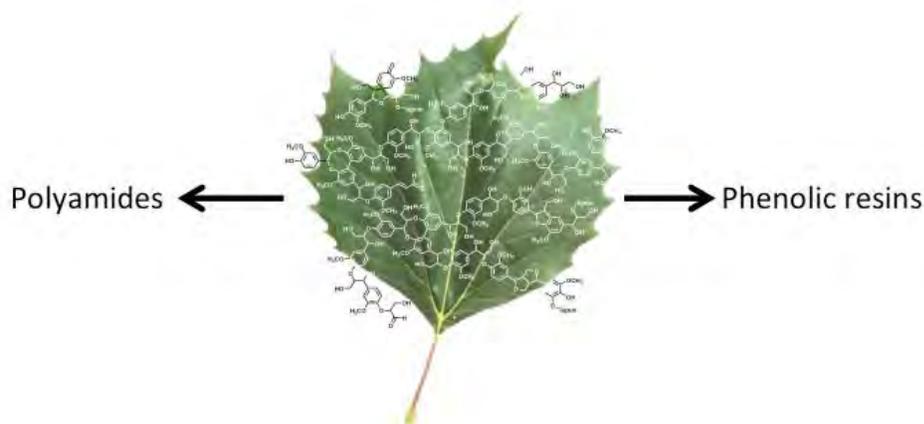


Schematic showing change in  $E_a$  due to *N,N*-disubstitution of the urethane linkages

## POLY 176: Biomass-derived polymers incorporating monolignols

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Commodity polymers and plastics are most commonly derived from petroleum-based chemicals, such as ethylene, styrene and propylene. The global demand for polyethylene, for example, is expected to reach 99.6 million metric tons in 2018 and approximately 26% of that material is likely to be disposed of in a landfill. To reduce dependence on non-renewable resources and impact on the environment, new polymeric materials must be developed. Due to the robust presence of lignin in nature, monolignols (lignin monomers such as coniferyl alcohol and *p*-coumaryl alcohol) provide an ideal framework for the development of novel polymeric and composite materials. A series of bio-based polyamides were synthesized from monolignol dimers and aliphatic or aromatic diamines. The length or the functionality of the diamine was systematically varied to determine effects on the properties of the resulting materials. The functional groups of the monolignol dimer were also varied to study the effects of monolignol substitution. The resulting polymers offered moderate molecular weights as well as moderate thermal stability. In contrast to the monolignol-based polyamides, a series of benzoxazines and polybenzoxazines from monolignols were also synthesized and characterized. These thermosets were shown to have a moderate curing temperature as well as low solubility in common organic solvents making them potentially useful in applications requiring solvent resistance. Polymeric materials from natural sources that mimic the desirable properties of commodity materials are important for both the environment and ability to produce useful materials from renewable sources.

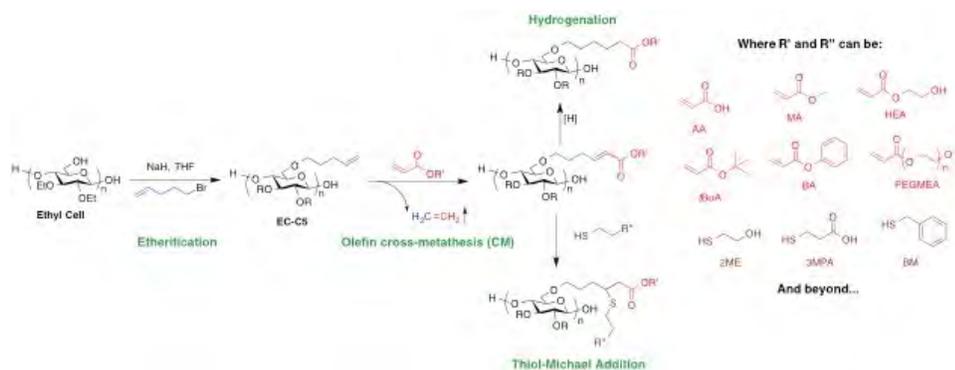


## POLY 177: Multifunctional modification of cellulose ethers via olefin cross-metathesis followed by Thiol-Michael addition

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Olefin cross-metathesis (CM) has been shown to be a valuable and versatile approach for imparting functional variety to cellulose ethers<sup>1</sup> and esters<sup>2-3</sup> providing that an olefin handle for metathesis can be attached. This synthetic pathway gives access to various functional derivatives under very mild conditions and at high efficiency. In general, we are preparing cellulose derivatives (e.g. cellulose ethers<sup>1</sup> and hydroxyalkyl cellulose) with a terminal olefin branch chain as metathesis “handles” via etherification with alkene halide, and we then conduct olefin CM reaction with various partners including acrylic acid (AA), various acrylates (e.g. 2-hydroxyethyl acrylate (HEA), methyl acrylate (MA), *tert*-butyl acrylate (*t*BuA)), and acrylamides.<sup>4</sup> The CM products are then subject to hydrogenation to reduce the conjugated olefin bond and remove the potential issue of radical cross-linking.<sup>2</sup> The products are promising for applications like amorphous solid dispersion to enhance oral drug delivery and waterborne coating. In this project we further investigate the elaboration of these  $\alpha,\beta$ -unsaturated CM products through thiol-Michael addition, not only eliminating the cross-linking instability but also incorporating new functionality. Through the mild and modular three-step procedure, a broad collection of cellulose derivatives with multiple functional groups can be prepared and the structure, property and performance relationship can be further investigated.

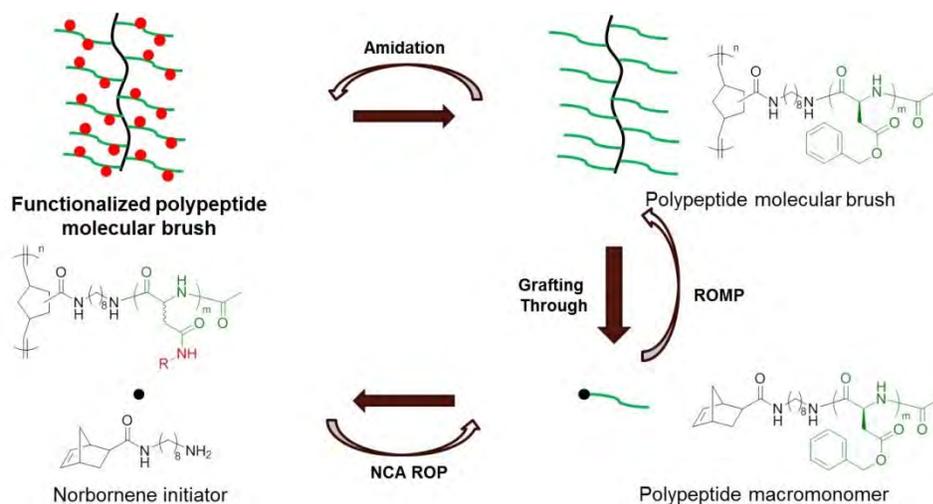
1. Dong, Y.; Edgar, K. J. Imparting functional variety to cellulose ethers via olefin cross-metathesis. *Polym. Chem.* 2015, 6, 3816-3827.
2. Meng, X. T.; Matson, J. B.; Edgar, K. J. Olefin cross-metathesis, a mild, modular approach to functionalized cellulose esters. *Polym. Chem.* 2014, 5, 7021-7033.
3. Meng, X. T.; Matson, J. B.; Edgar, K. J. Olefin cross-metathesis as a source of polysaccharide derivatives: cellulose omega-carboxyalkanoates. *Biomacromolecules* 2014, 15, 177-187.
4. Meng, X.; Edgar, K. J. Synthesis of amide-functionalized cellulose esters by olefin cross-metathesis. *Carbohydr. Polym.* 2015, 565-573.



## POLY 178: Facile syntheses of polypeptide molecular brushes with two-dimensional controlled architectures

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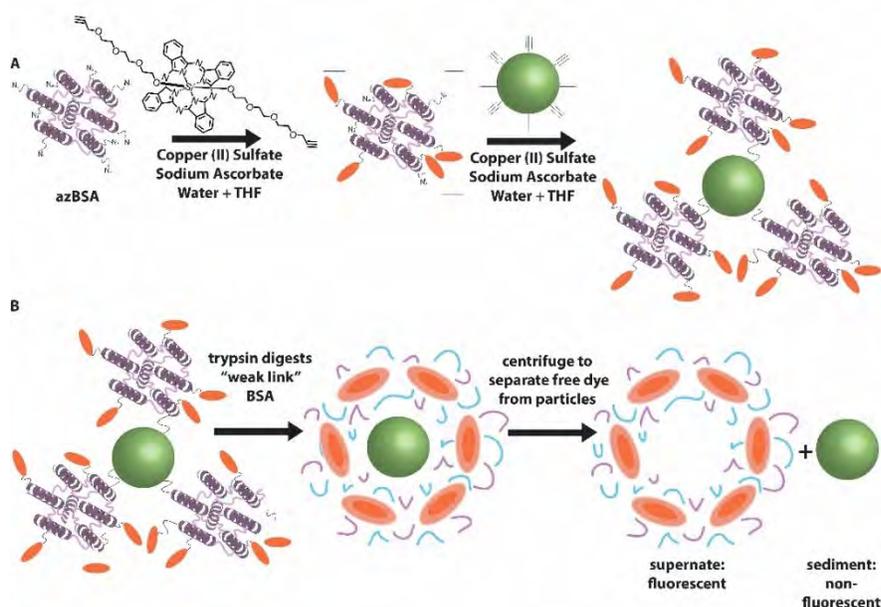
Well-defined brush-like polymers bearing polypeptides as the brush side chains with two-dimensional control over the brush molecular architectures are easily constructed *via* integration of ring-opening polymerizations (ROPs) of amino acid *N*-carboxyanhydrides (NCAs) and ring-opening metathesis polymerizations (ROMPs). This approach is capable of building desirable segment lengths of the polypeptide side chains and brush backbones, independently, in controlled manners. A new type of brush-like polymer, poly(norbornene-*graft*-poly(*b*-benzyl-L-aspartate)) (P(NB-*g*-PBLA)), is synthesized *via* the ROMP of norbornene-terminated polypeptide macromonomers in a mixture of dichloromethane and ionic liquid. The N<sub>2</sub> flow accelerated NCA ROP is utilized to prepare polypeptide macromonomers with different lengths by using norbornene-based primary amine as the initiator. Given the numerous types of NCA monomers and norbornene-terminated macromonomers, this novel synthetic strategy not only allows for exploration of molecular architecture effects on the properties of brush polymers, but also can be expanded to build various hybrid materials with broad applications.



## POLY 179: *in vitro* illustrations: Achieving activated fluorescence in cancer cells

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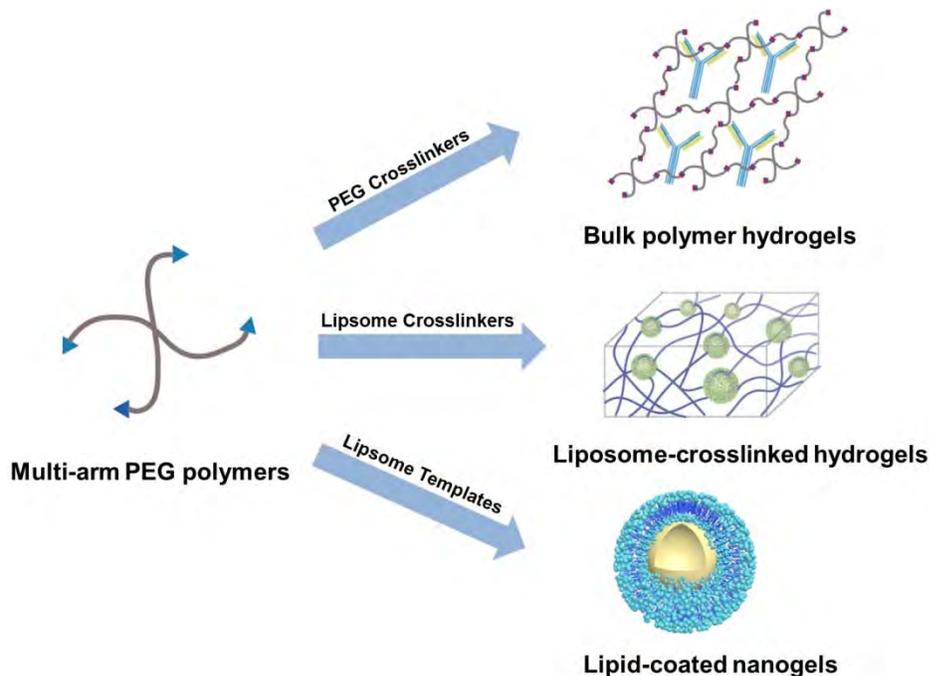
Activated fluorescence was achieved for a poly(propargyl acrylate) (PA) nanoparticle system. In this work, the system consisted of an azide modified bovine serum albumin (azBSA) that had been covalently attached to an alkyne modified silicon phthalocyanine (akSiPc) derivative through a copper catalyzed azide alkyne Huisgen cycloaddition, ("click chemistry"). The azBSA/akSiPc was then covalently attached, via "click chemistry", to the PA particle sized at ca. 67 nm (PA/BSA/akSiPc). The native system had no emission. However, when the system was incubated at 37 °C for 30 min with the digestive enzyme, trypsin, it was seen that the system became fluorescent. This phenomenon is due to the trypsin digesting the "weak link" BSA, which releases free akSiPc, a highly fluorescent dye. The PA/BSA/akSiPc system was confirmed to be biocompatible, and, to investigate activated fluorescence in cancer cells, human non-small cell lung cancer cells (A549 cell line) were used. The PA/BSA/akSiPc system was incubated with the cells at varying time points in a effort to observe a fluorescence increase over time as the cells uptake the system. The particle is taken to the lysosomes and endosomes of the cancer cell. This is where the digestive enzymes are located, and the BSA is digested via endocytosis, resulting in the release of free akSiPc in the cell. It was seen, through live cell scanning confocal microscopy, that the fluorescence was activated in the cell.



## POLY 180: Engineering responsive matrices for controlled drug delivery: From bulk gels to nanogels

**Yingkai Liang**, [yingkai@udel.edu](mailto:yingkai@udel.edu), Kristi L. Kiick. *Materials Science and Engineering, University of Delaware, Newark, Delaware, United States*

Polymeric hydrogels have been extensively explored as drug delivery vehicles due to their high water content, tunable viscoelasticity, and biocompatibility, which allow the release of bioactive molecules from the hydrogel in a controlled manner. Herein, we present the development of various responsive polymeric matrices ranging from bulk to nanoscale for different biomedical applications. First, we describe the engineering of a library of hydrolytically degradable polyethylene glycol (PEG) hydrogels formed by Michael-type addition for the sustained delivery of an anthrax toxin-neutralizing monoclonal antibody. Second, we introduce the design of a glutathione-sensitive, liposome-crosslinked hybrid hydrogel for the controlled and sequential delivery of multiple cargo molecules that are relevant for chemotherapies. Finally, we demonstrate the facile preparation, from liposome templates, of novel, polymeric nanogels that are crosslinked by photo-triggered Michael-type addition. Taken together, these matrix platforms provide a powerful toolbox for the controlled delivery of therapeutic molecules in various biomedical applications.



Polymeric matrices ranging from bulk to nanoscale based on polyethylene glycol polymers.

## POLY 181: Freeform light-responsive spirals

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This lecture will illustrate how shape-persistent, freeform molecular spirals can be created efficiently as single-handed stereoisomers. This synthetic advance has become possible with chirality-assisted synthesis (CAS), a general approach invented by us to control molecular shape (see: Liu, X.; Weinert, Z. J.; Sharafi, M.; Liao, C.; Li, J.; Schneebeli, S. T. *Angew. Chem. Int. Ed.* 2015, Early View, DOI: 10.1002/anie.201506793). While previous freeform structures created with CAS were static, we will now, for the first time, introduce stimuli-responsive, CAS-derived compounds. These polymeric entities (Figure 1) not only adopt well-defined, readily-predictable, chiral shapes in solution, but are also switchable with light to fold and unfold in a selective manner. Drastic changes in the polymers' properties go along with the light-induced changes of nanoscale shape, which can be utilized to investigate the fundamental question of how the shapes of polymers affect their mechanical and electrical properties in general. Furthermore, we envision that our molecular spirals, which contain well-defined, hydrophobic cativites, can encapsulate specific guest molecules (including transition-metal catalysts and drugs). These guests will then, of course, be released as soon as the molecular spirals are unfolded photochemically.

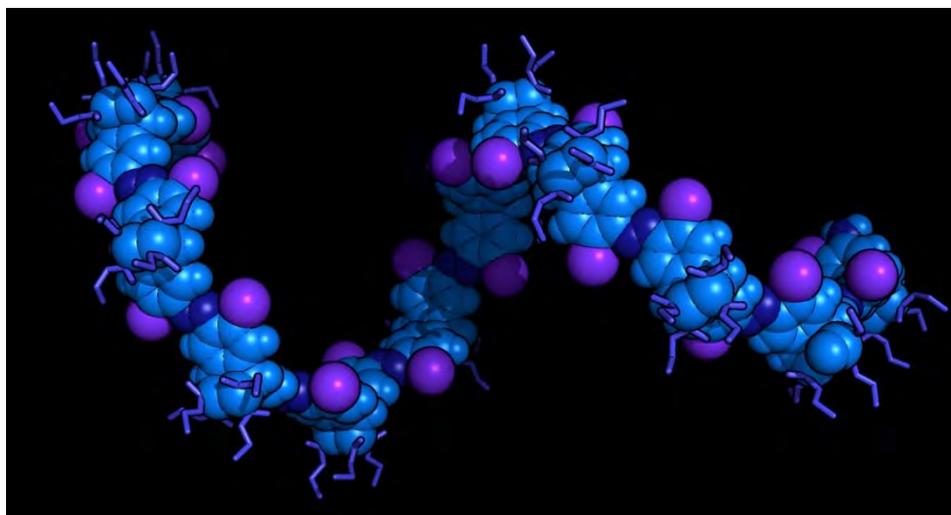
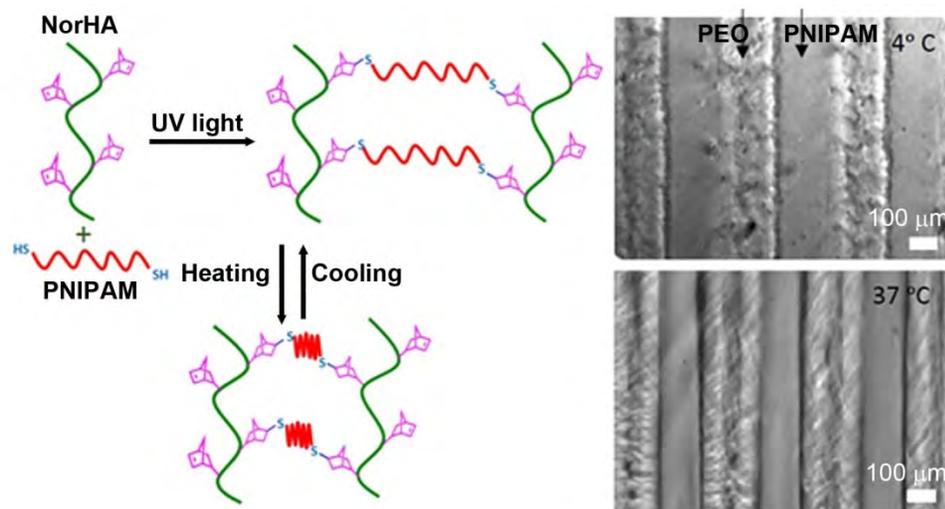


Figure 1. Three-dimensional model of a freeform, light-responsive nanoscale spiral, which can unfold/refold under irradiation with specific wavelengths of light.

## POLY 182: Modular assembly of spatiotemporally patternable, stimuli responsive hydrogels

Nayereh Dadoo, **William Gramlich**, [william.gramlich@umit.maine.edu](mailto:william.gramlich@umit.maine.edu). Department of Chemistry, University of Maine, Orono, Maine, United States

Hydrogels have traditionally been static materials that can provide physical bulk and diffusion controlled drug delivery, heading towards advanced regenerative medicine by mimicking the extracellular matrix (ECM). However, the natural ECM is neither static nor uniform and instead varies spatiotemporally in chemical and physical nature. New materials are needed that can mimic this natural complexity. By utilizing orthogonal, thiol-norbornene click chemistry our group has developed a modular hydrogel system that can be modified spatiotemporally with stimuli responsive crosslinks. To this end, a series of  $\alpha,\omega$ -thiol-terminated poly(*N*-isopropyl acrylamide) (PNIPAM) polymers were synthesized as these thermally responsive crosslinks. The PNIPAM crosslinkers reacted with a norbornene-functionalized hyaluronic acid (NorHA) through a UV-light induced thiol-norbornene reaction to yield stimuli responsive hydrogels. Upon heating above the lower critical solution temperature (LCST), the collapse of the PNIPAM chains into nanoscopic domains yielded macroscopic changes to the hydrogels as measured by the changes in size and mass loss of water. The scale of the thermal response was controlled by the length of crosslinker and the degree of crosslinking, creating hydrogels that could lose up to 40% of their mass upon heating above 37 °C, while containing a majority of hyaluronic acid. The thermal response was reversible, suggesting that these hydrogels could be used as shape memory materials. Moreover, this thermal response could be photopatterned on the micrometer-scale to yield hydrogels with thermal- and non-thermal-responsive regions.

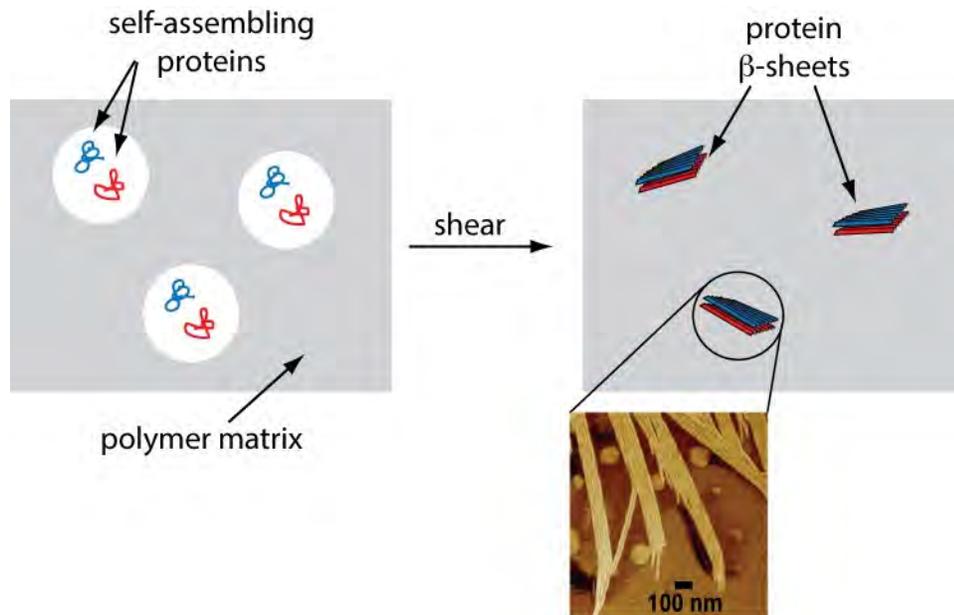


Fabrication and photopatterning of thermally responsive hydrogels.

## POLY 183: *In situ* nanofiller formation in polymer nanocomposites

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Dispersion of nanofillers in polymer nanocomposites is problematic because the nanofillers prefer to agglomerate. Attempts to disperse the nanofiller using extrusion require expensive processing agents and high heat and shear conditions that add significantly to the cost. But, extrusion compounding of nanofillers in polymers is the preferred method to process nanocomposites. Nanofillers can be dispersed in monomers and then the monomers polymerized into the polymer matrix for “*in situ* polymerization” of nanocomposites but this technique is only realistic for a very limited number of polymers. Here, *in situ* nanofiller formation is demonstrated where the nanofiller forms in the polymer matrix. Protein molecules are dispersed in a polymer matrix and the protein molecules self-assemble into a nanostructure called an amyloid that is high in beta sheet content. *In situ* nanofiller formation is demonstrated in nanocomposites formed from solution and melt compounding. The amyloid nanostructure is of high rigidity so the potential to make high performance nanocomposites exists.



*In situ* nanofiller formation in polymers.

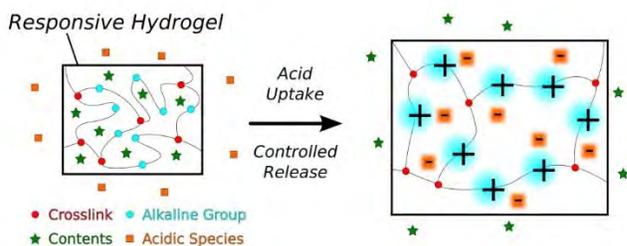
## POLY 184: Quantifying the behavior of a new family of pH-responsive hydrogels

Smruti Patil<sup>2</sup>, Pulkit Chaudhury<sup>3</sup>, Lisa Clarizia<sup>4</sup>, Melisenda J. McDonald<sup>4</sup>, Emmanuelle Reynaud<sup>5</sup>, Peter Gaines<sup>3</sup>, **Daniel F. Schmidt<sup>1</sup>**, Daniel\_Schmidt@uml.edu. (1) Plastics Engineering, University of Massachusetts Lowell, Lowell, Massachusetts, United States (2) Biomedical Engineering & Biotechnology, University of Massachusetts Lowell, Lowell, Massachusetts, United States (3) Biological Sciences, University of Massachusetts Lowell, Lowell, Massachusetts, United States (4) Chemistry, University of Massachusetts Lowell, Lowell, Massachusetts, United States (5) Mechanical Engineering, University of Massachusetts Lowell, Lowell, Massachusetts, United States

Hydrogels represent an important class of responsive materials with significant utility in the biomedical sector in particular. Our own efforts in this area have yielded a large family of (primarily epoxy-based) hydrogel networks – stable, robust, biocompatible materials capable of pH-responsive swelling, absorption and release.

The impetus for the creation of these materials was the hypothesis that it should be possible to create a hydrogel capable of absorbing acidic waste, releasing nutrients and supporting cells in culture. Subsequent studies have borne out this hypothesis, with these materials enabling long-term mammalian cell culture without human intervention. As an example, this is demonstrated in the context of the culture of SA-13 human-human hybridomas. The biocompatibility of these materials is excellent so long as the extractable fraction is kept low, and we have further demonstrated that their presence does not induce differentiation in stem cells. At the same time, these efforts have made clear that different cell lines differ greatly in terms of activity and optimal growth conditions, and that there remains a need not just to create such materials, but to design them to possess very specific properties.

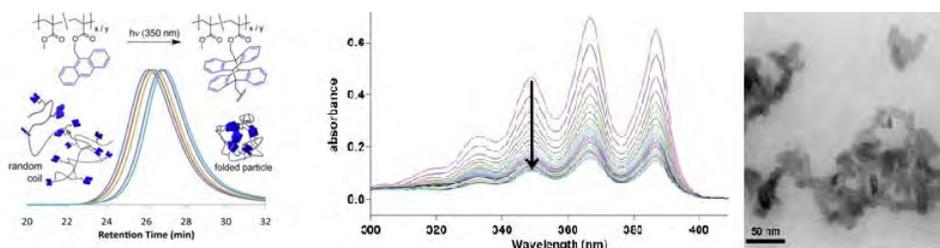
With this in mind, we report on our efforts to quantify and predict the behavior of these hydrogels. Flory-Rehner network theory has been used to predict the maximum extent of swelling, with additional mathematical modeling enabling us to describe swelling kinetics in further detail. Release characteristics are shown to be directly related to the aforementioned swelling metrics, and acid absorption capacity is predicted based on compositional arguments and confirmed to be consistent with observed behavior as well. While there is still work to be done to describe the behavior of pH-responsive hydrogels especially in the partially to fully charged state, these efforts enable us to predict the behavior of any number of new additions to our family of pH-responsive hydrogels in advance of their synthesis. The ability to use simple analytical predictions to guide the design of new and useful responsive materials represents an important step in their continued development.



## POLY 185: Application of Anthracene in the Synthesis and Functionalization of Single-Chain Nanotechnology

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Well defined linear polymers precisely folded into nano-structures, capable of performing complex functions both individually and collaboratively, are abundant in nature. This has inspired numerous researchers around the world with the desire to replicate this synthetically. The effort has been bolstered by recent advances in controlled polymerizations that facilitates a more precise synthesis of polymer chains with varying backbones and placement of functional groups. Based on the discrete folding of these polymer chains, the single-chain nanotechnology is proving itself to be a facile route to functional nano-objects. Anthracene decorated chains offer an advantageous approach via photo-induced folding under mild and ambient conditions, while allowing for further functionalization via Diels Alder chemistry. Additionally, sequential folding can be achieved by incremental exposure to ultraviolet light that allows the precise targeting of nanoparticle size while maintaining uniformity. Herein we report our studies on the photo-folding of anthracene derivatized polymers characterized by multi-detection size exclusion chromatography as well as spectrochemical and microscopic investigations



## **POLY 186: Fabrication and applications of multiresponsive cyclic poly(phthalaldehyde) microcapsules prepared by internal phase separation**

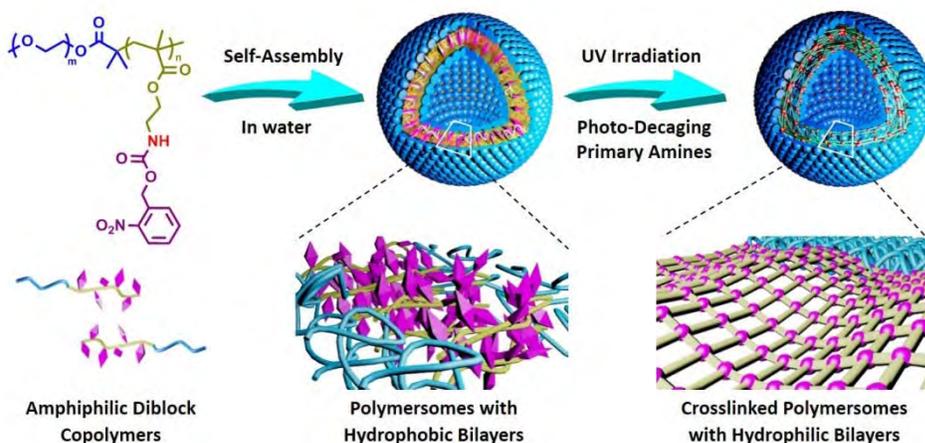
**Shijia Tang**<sup>1,2</sup>, *shijia1224@gmail.com*, Michael Odarczenko<sup>3,2</sup>, Nancy R. Sottos<sup>1,2</sup>, Scott White<sup>3,2</sup>, Jeffrey S. Moore<sup>4,2</sup>. (1) *Materials Science and Engineering, University of Illinois Urbana-Champaign, Urbana, Illinois, United States* (2) *Beckman Institute for Advanced Science and Technology, University of Illinois Urbana-Champaign, Urbana, Illinois, United States* (3) *Aerospace Engineering, University of Illinois Urbana-Champaign, Urbana, Illinois, United States* (4) *Chemistry, University of Illinois Urbana-Champaign, Urbana, Illinois, United States*

Microcapsules based self-healing materials have been applied in restoring mechanical properties, optical properties, conductivity, inhibiting corrosion, etc. In most cases, mechanical activation is required to deliver protective payloads, whereas targeted spatial and temporal delivery of core materials triggered by non-mechanical means remains challenging. Here we show an internal phase separation approach to fabricate multi-responsive core/shell microcapsules using cyclic poly(phthalaldehyde) (cPPA) as shell wall. cPPA is a rising material for stimuli responsive systems with applications in photolithography, controlled release and transient electronics packaging. Degradation of cPPA in organic acid/base is rapid. To expand the triggering conditions, we incorporate acid generators in encapsulation, resulting in acid, UV, and thermal responsive shell walls. Release behavior has been directly visualized using optical microscope and scanning electron microscope. Smooth microcapsule exterior surface erodes after exposing to triggering condition, releasing core materials onto the substrates. Release rate profiles of microcapsules are quantified from UV-vis spectroscopy, <sup>1</sup>H NMR and/or GC-MS using a model core material, hexadecane. Over 90% payload is released within 24h in 1M HCl solution. Ongoing and future work involves optimization in fabricating microcapsules, developing shell wall with different responsiveness and expanding application areas in self-healing coatings, Li battery, electrical devices, etc.

## POLY 187: Traceless crosslinking and bilayer permeability tuning of polymersomes self-assembled from responsive amphiphilic block copolymers

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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 we demonstrate 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  $pK_a$  within hydrophobic milieu. This leads to serendipitous vesicle crosslinking and the process is associated with bilayer hydrophobicity-to-hydrophilicity transition and membrane permeabilization.



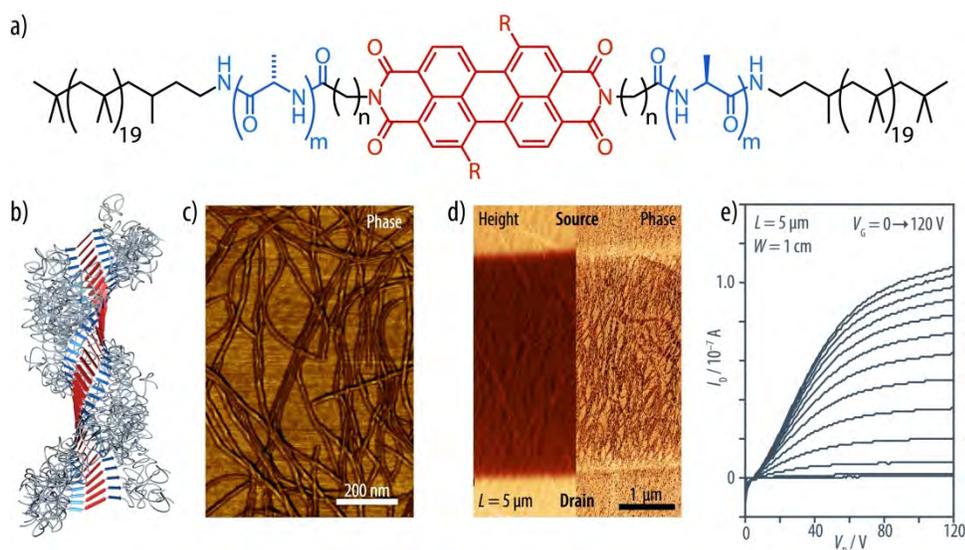
## POLY 188: Unusual photocharge generation in 1D confined organic semiconductor nanostructures

**Holger Frauenrath**, *holger.frauenrath@epfl.ch*, Regina Hafner, Roman Marty. Institute of Materials, EPFL, Lausanne, Switzerland

Organic semiconductors may provide display unusual properties when they become confined to the nanometer length scale in one or two dimensions. We prepared well-defined supramolecular polymers from oligopeptide-substituted chromophore. The supramolecular helicity of these systems resulted in strict confinement to a single, helically twisted stack of the chromophores stacked along the supramolecular polymer.<sup>1</sup> Synergistic hydrogen-bonding of the oligopeptide substituents and  $\pi$ - $\pi$  stacking of the cores resulted in a strong electronic coupling of the chromophores,<sup>2</sup> resulting in an unusual photogeneration of either positive or negative polaron charge carriers in the p-type or n-type nanowires without the addition of any redox-active reagent in either case. The charge carriers were formed reversibly, exhibited life times on the order of many hours, were therefore formed at unprecedented charge densities approaching the insulator-metal boundary, and exhibited unusually low activation energies for charge transport. The supramolecular polymers showed macroscopic hole or electron transport properties, respectively, rendering the n-type systems the first examples of intrinsic electron-conducting organic semiconductor nanostructures. The described systems hence highlight the role of nanoscopic confinement on charge transport phenomena in organic semiconductors, and may be model systems to study spin effects in confined geometries.

(1) Marty, R.; Szilluweit, R.; Sánchez-Ferrer, A.; Bolisetty, S.; Adamcik, J.; Mezzenga, R.; Spitzner, E.-C.; Feifer, M.; Steinmann, S. N.; Corminboeuf, C.; Frauenrath, H. *ACS Nano* 2013, 7, 8498.

(2) Marty, R.; Nigon, R.; Leite, D.; Frauenrath, H. *J. Am. Chem. Soc.* 2014, 136, 3919.



## POLY 189: Self-assembly of pH-regulated supramolecular polymers in water

Hendrik C. Frisch, Patrick Ahlers, **Pol Besenius**, besenius@uni-mainz.de. Institute of Organic Chemistry, University of Mainz, Mainz, Germany

Self-assembly of molecular building blocks into ordered architectures, polymers and materials opens exciting avenues for fundamental developments in nanoscience and applications in biomedical technologies, optoelectronics and catalysis. Our young group designs supramolecular synthons for controlling self-assembly processes in water and on surfaces. I will discuss our latest efforts in controlling supramolecular polymerisations through pH-regulation.

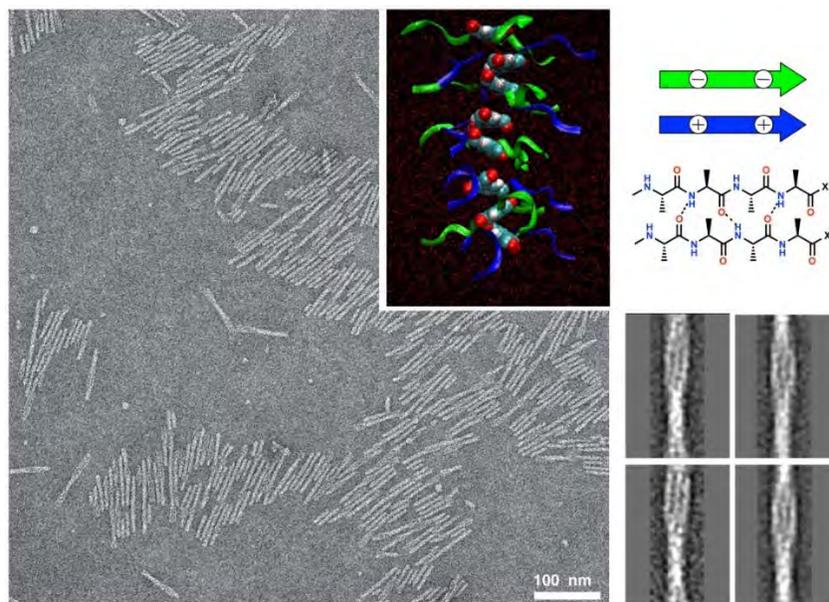
The monomeric building blocks are based on  $\beta$ -sheet encoded anionic and cationic dendritic peptide amphiphiles that form one-dimensional supramolecular alternating copolymers when self-assembled in a 1:1 feed ratio (Fig. 1). These materials have been designed for on-off polymerization in response to pH triggers. The pH at which the transition from polymers to monomers occurs can be tuned by the reactivity of the supramolecular comonomer, behaviour that is in agreement with the self-assembly of protein based morphologies, like virus capsids.

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P. Ahlers, H. Frisch, P. Besenius, *Polym. Chem.* 2015, *in press*. DOI: 10.1039/C5PY01241D.

H. Frisch, Y. Nie, S. Raunser, P. Besenius, *Chem. Eur. J.* 2015, *21*, 3304-3309.

H. Frisch, J.P. Unsleber, D. Lüdeker, M. Peterlechner, G. Bruncklaus, M. Waller, P. Besenius, *Angew. Chem. Int. Ed.* 2013, *52*, 10097-10101.

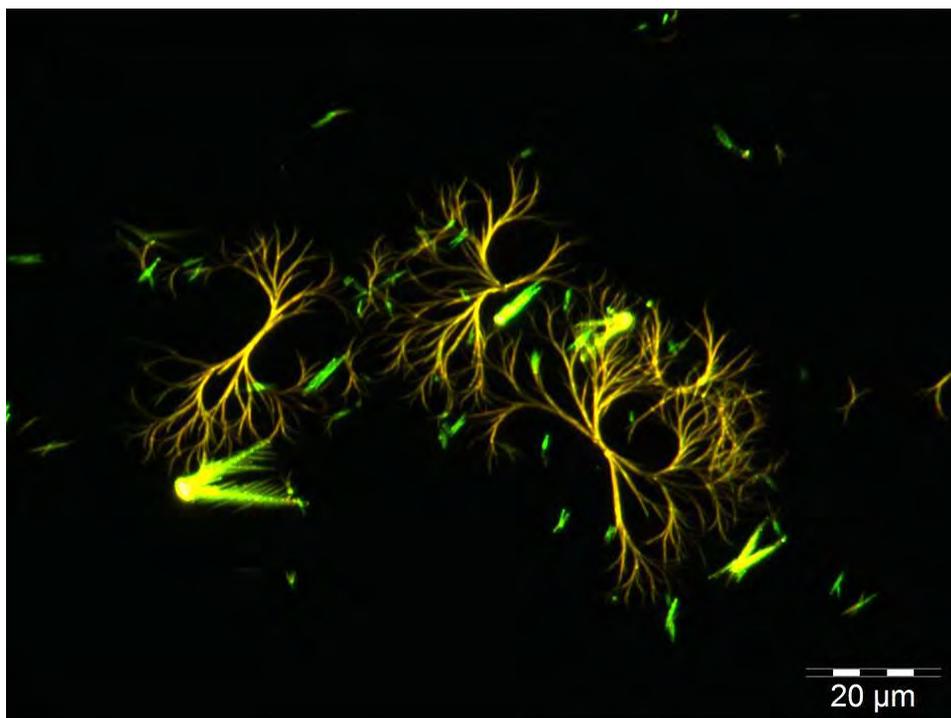


Representation of the pH-switchable supramolecular copolymerization of the anionic/cationic beta-sheet-encoded dendritic peptide amphiphiles and stained TEM micrographs which show supramolecular nanorod morphologies for the copolymers with a number average length distribution of 56 nm.

## POLY 190: Stimuli-responsive supramolecular polymers

**Christoph Weder**, *christoph.weder@unifr.ch*. University of Fribourg, Adolphe Merkle Institut, Fribourg, Switzerland

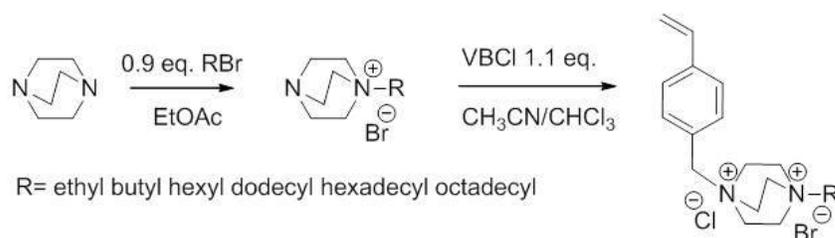
Polymers which change (some of) their physical and/or chemical properties upon exposure to an external stimulus – often referred to as “adaptive”, “smart” or “intelligent” polymers – are of significant academic interest and potentially useful for a plethora of applications that range from debonding on demand to healable coatings to mechanochromic indicators. On account of their dynamic, stimuli-responsive nature, non-covalent interactions represent a useful design element for the creation of stimuli-responsive polymers with unusual functions. Several types of materials that rely on this general design approach and are assembled through hydrogen-bonds,  $\pi$ - $\pi$  stacking, or metal-ligand binding will be discussed in this presentation.



## POLY 191: Doubly Charged Monomers for Enhanced Physical Crosslinking: Are two charges per repeating unit twice as good?

Keren Zhang<sup>2</sup>, Kevin Drummey<sup>2</sup>, Mana Tamami<sup>3</sup>, Shijing Cheng<sup>4</sup>, Sean Hemp<sup>5</sup>, Renlong Gao<sup>6</sup>, Adam E. Smith<sup>1</sup>, **Timothy E. Long<sup>2</sup>**, [telong@vt.edu](mailto:telong@vt.edu). (1) Department of Chemical Engineering, University of Mississippi, University, Mississippi, United States (2) Virginia Tech, Blacksburg, Virginia, United States (3) Lubrizol, Cleveland, Ohio, United States (4) 3M, Woodbury, Minnesota, United States (5) Michelin, Mauldin, South Carolina, United States (6) PPG, Akron, Ohio, United States

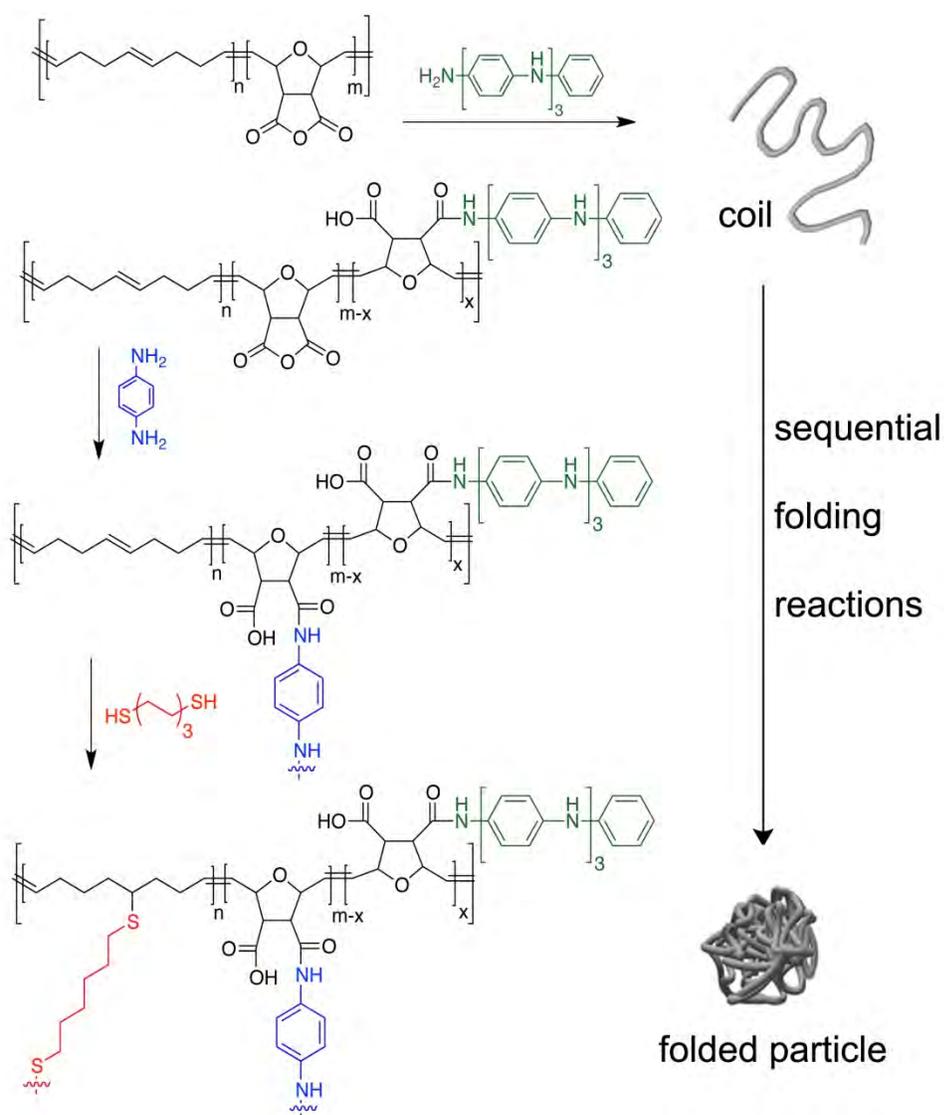
Nature employs a complement of hydrogen bonding and ionic bonding in the design of biomacromolecules used in biological systems. This inspiration demands that scientists envision adhesives and coatings that present novel performance due to this complicated morphological synergy. Moreover, nature employs sequence control in combination with unique molecular architectures. This lecture will focus on the design of block copolymers with a focus on ion-containing acrylics, polyurethanes, and ammonium or phosphonium ionenes for the synthesis of novel materials for coatings. These intermolecular interactions are dynamic and offer impact in the design of novel polymeric materials with self-healing characteristics and stimuli-responsive performance. Particular attention will be devoted to the synthesis of DABCO based doubly charged monomers and the impact of the dications on self-assembly and the formation of physical crosslinks compared to simpler ammonium and imidazolium cations. Physical characterization that the presence of the doubly charged repeating units leads to improved physical crosslinking and enhanced thermomechanical performance for many elastomeric and adhesive applications.



## POLY 192: Application of tetra aniline oligomers in functional single-chain nanoparticles and materials

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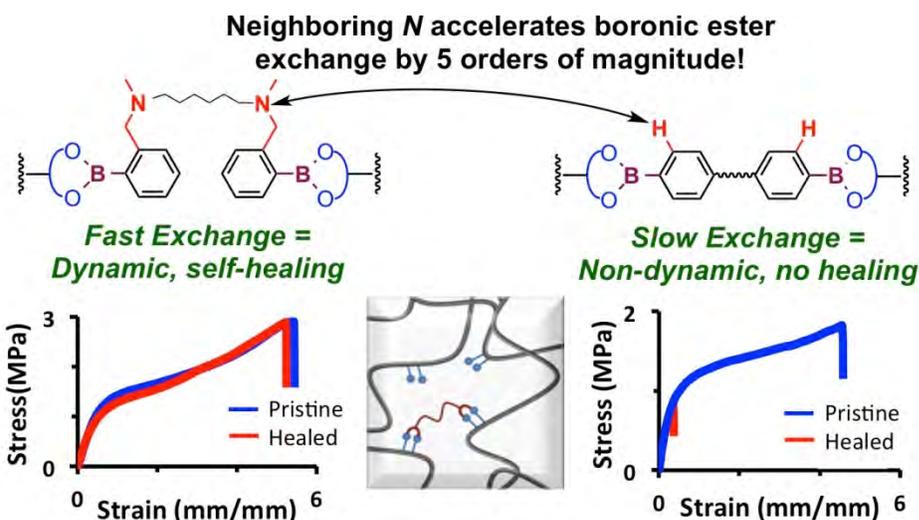
This talk will discuss some of our recent efforts incorporating tetra aniline oligomers into a variety of materials. A bulk of the talk will discuss using these groups to mediate supramolecular folding of linear polymers into a single-chain nanoparticles (figure 1). We will also present work concerning the ability of the aniline tetramer to quench fluorescence of a nearby fluorophore, depending on the oxidation state of the oligomer, as a route to fluorescent sensors for redox active species.



## POLY 193: Dynamic and self-healing polymer design via both supramolecular and dynamic covalent interactions

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The development of polymers that can spontaneously repair themselves after mechanical damage would significantly improve the safety, lifetime, energy efficiency, and environmental impact of manmade materials. Our laboratory has successfully developed several self-healing polymers having strong mechanical properties and autonomous self-healing capability. For noncovalent healing mechanism, we developed multiphase supramolecular thermoplastic elastomers that combine high modulus and toughness with spontaneous healing capability by using hydrogen-bonding (Nature Chemistry 2012, 4, 467) and metal-ligand interactions (J. Am. Chem. Soc. 2014, 136, 16128). For using dynamic covalent interactions, my laboratory has demonstrated both Ru-catalyzed olefin metathesis (J. Am. Chem. Soc. 2012, 134, 14226) and boronic ester exchange (J. Am. Chem. Soc. 2015, 137, 6492) reactions can afford efficient self-healing polymers. In this talk, I will discuss the most recent development from our lab on dynamic and self-healing materials.



Neighboring group accelerates boronic ester exchange for self-healing

## **POLY 194: Tracking the transformation of lead halide complex into organic lead halide perovskite**

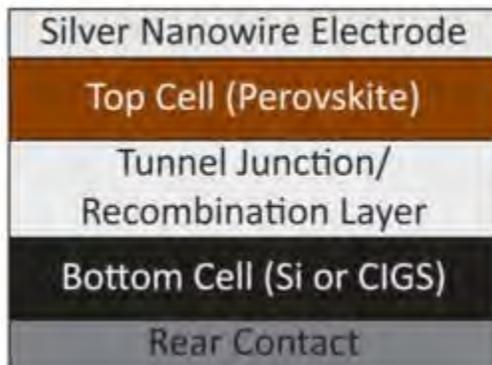
*Prashant V. Kamat, pkamat@nd.edu, Joseph Manser, Seogjoon Yoon. University of Notre Dame, Notre Dame, Indiana, United States*

With the emergence of highly efficient perovskite materials, there is a need to understand the excited state behavior and charge separation events in these new materials. The scientific issue related to the understanding of the excited state behavior of organic metal halide perovskite materials remains a scientific challenge. Photoexcitation of perovskite film leads to efficient charge separation and the fate of charge carriers is determined by the bimolecular recombination rate. Transient absorption spectroscopy measurements reveal the existence of a charge transfer state in addition to the charge separated state. The plumbate complex formed in the precursor solution evolves into a perovskite structure during annealing process. The stronger complexation constant between  $\text{Pb}^{2+}$  and  $\text{Br}^-$  as compared to  $\text{Pb}^{2+}$  and  $\text{Cl}^-$  results in composition dependent excited state behavior. Results that show photoinduced segregation in mixed halide perovskite will be discussed.

## **POLY 195: Towards stable and efficient metal halide perovskite solar cells for hybrid tandems with silicon**

**Tomas Leijtens**, *tomas.leijtens@physics.ox.ac.uk*, **Michael D. McGehee**, **Colin Bailie**, **Kevin Bush**, **Eric Hoke**. *Stanford University, Stanford, California, United States*

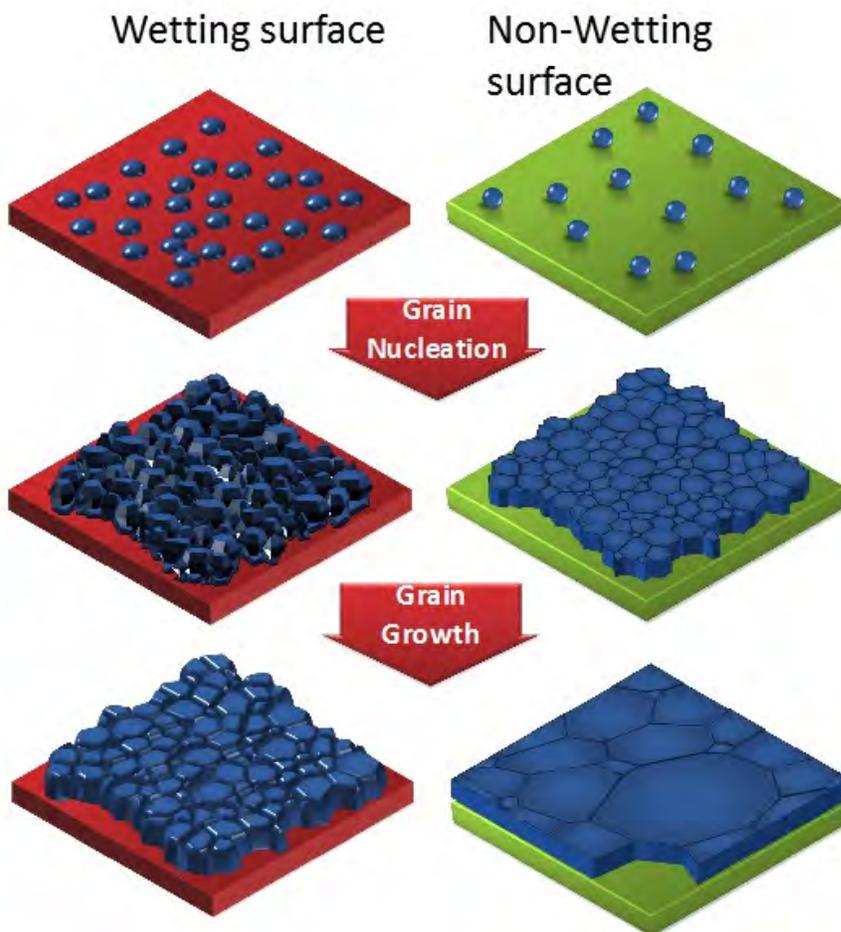
Metal halide perovskite solar cells have rapidly reached performances that make them competitive with traditional inorganic photovoltaic technologies. Still, before this exciting, low cost class of materials can be considered ready for commercialization, it must be proven to be stable to stresses relevant to operating conditions. Here, an overview of the influence of oxygen, water, heat, light, and electrical bias will be presented. Particular attention will be placed on the motion of ions within the crystal structure which can lead to phase segregation in mixed halide systems as well as rapid material decomposition in the presence of moisture and electric fields. Once the material is proven to be stable and ready for real-world application, it becomes important to consider the form which perovskite solar cells will take. Metal halide perovskites, with their tunable bandgaps and low manufacturing costs, are ideal candidates for application in hybrid tandems on top of Silicon solar cells. Initial results on successful two and four terminal perovskite – silicon tandem solar cells will be presented. Strategies for making tandem solar cells using a variety of Silicon solar cells and device architectures will be discussed.



## POLY 196: Influence of surfaces and interfaces on the grain morphology and electronic structures in perovskite solar cells

**Jinsong Huang**, *jhuang2@unl.edu*. Mechanical and Materials Engineering, University of Nebraska Lincoln, Lincoln, Nebraska, United States

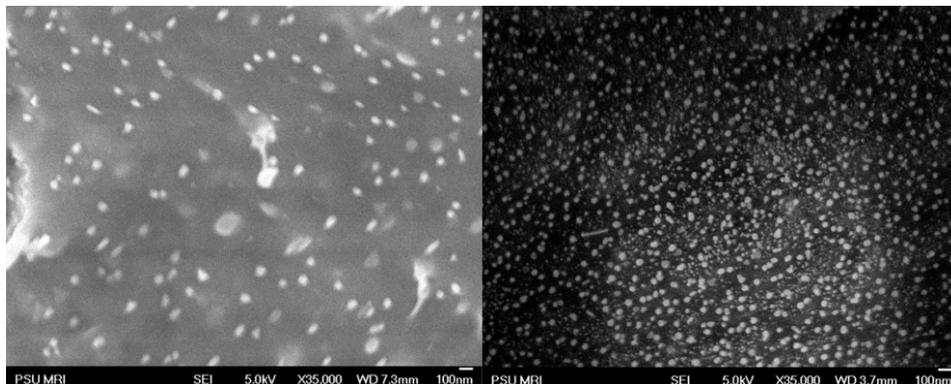
The progress in understanding of perovskite solar cells points to a direction that perovskite solar cells resemble that of traditional thin film solar cells. The low temperature solution process allows the integration of polymer and organic charge transport or buffer layers in perovskite solar cells for optimal energy conversion efficiency, despite that perovskite solar cells can work without these buffer layers at lower performance. It naturally bonds the traditional thin film solar cells and organic solar cells, which adds the versatility of the device designing for reduced cost and new functionalities, in addition to the boosted device efficiency. In this talk, I will present our recent progress in understanding on the important function of the surfaces of the buffer layers on the grain morphology of perovskite films and associated electronic states in perovskite. I will also discuss some of our new strategies to applying unique interfacial layers to understand the origin of several key performance parameters in perovskite solar cells, including charge recombination and open circuit voltage.



## POLY 197: Characterization of PVDF-g-sulfonated polystyrene and PE-g-sulfonated polyarylsulfone proton exchange membranes for direct methanol fuel cells

**Tze-Chiang M. Chung**, chung@ems.psu.edu, Gong Zhang, Changwoo Nam. *Materials Sci.&Eng., Penn State U., State College, Pennsylvania, United States*

In this presentation, we will discuss a new class of polyolefin based proton exchange membranes (PEMs) that show a unique combination of surface and bulk morphology with desirable properties (fuel selectivity, proton conductivity, long term stability, etc.) for direct methanol fuel cell applications. We will focus on synthesis, structure characterization, and evaluation of two graft copolymers, including poly(vinylidene fluoride)-g-sulfonated polystyrene (PVDF-g-SPS) and polyethylene-g-sulfonated polyarylene ether sulfone (PE-g-SPAES) proton exchange membranes. Due to the extreme property difference between a semi-crystalline and hydrophobic PVDF or PE backbone and several amorphous and hydrophilic SPS or SPAES side chains, both PVDF-g-SPS and PE-g-SPAES membrane self-assembles into a unique morphology, with a thin hydrophobic PVDF or PE layer (thickness~1nm) spontaneously formed on the membrane surfaces and many proton conductive SPS or SPAES channels imbedded in the stable and tough PVDF or PE matrix. In the bulk, these membranes show good mechanical properties (tensile strength >30 MPa, Young's modulus >1400 MPa) and low water swelling ( $\lambda < 15$ ) even with high IEC >3 mmol/g in the conducting domains. On the surfaces, the thin hydrophobic and semi-crystalline PVDF and PE layer shows some unusual barrier (protective) properties. In addition to exhibiting higher through-plane conductivity (up to 160 mS/cm) than in-plane conductivity, the PE surface layer minimizes methanol cross-over from anode to cathode with reduced fuel loss, and stop the HO• and HO<sub>2</sub>• radicals, originally formed at anode, entering into PEM matrix. Evidently, the thin PE surface layer provides very desirable protecting layer for PEMs to reduce the fuel loss and to increase chemical stability. Overall, the newly developed PE-g-SPAES membranes offer a desirable set of PEM properties, including conductivity, selectivity, mechanical strength, stability, and cost-effective, for direct methanol fuel cell applications.

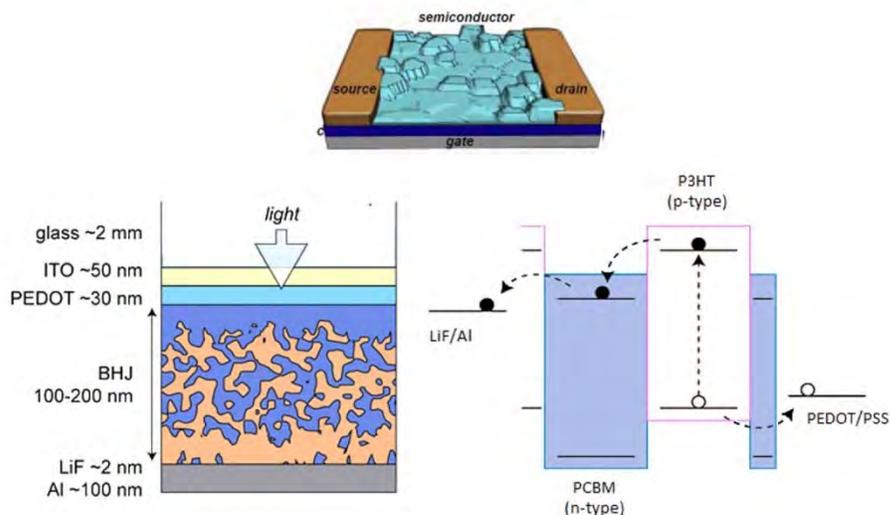


SEM micrograph of surface (left) and bulk (right) of PE-g-SPAES proton exchange membrane

## POLY 198: Morphology studies of contact optimization in organic electronic devices

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Additive manufacturing of active components: emitter, detectors, transistors and devices: sensors, displays, and solar cells by the printing of solution based inks is becoming a reality. Polymers, due to their synthetic and processing diversity play a critical role in ink formulation, as both binders and active material. Charge injection and transport at the interfaces between active layers and either contacts or gates critically determine the performance of thin film devices. In this talk, a series of morphological studies of the interfaces crucial to both transistors and organic photovoltaics will be presented. The role of contact and ink in determining interface composition and active layer structure will be discussed. Additionally, mechanisms for the use of contact modification layers to improve charge injection will be explored.

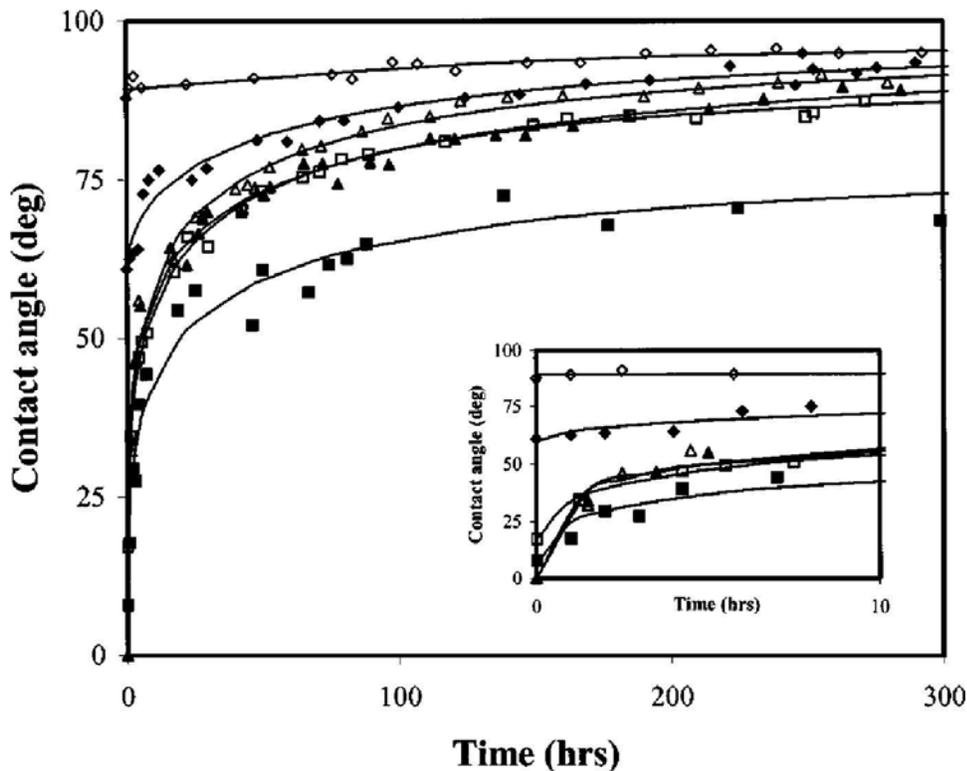


## POLY 199: Silicone high voltage insulation

**Michael J. Owen**, *michaelowen01@chartermi.net*. Michigan Molecular Institute, Midland, Michigan, United States

Most of the surface property related applications of polydimethylsiloxane (PDMS) exploit its familiar low surface energy characteristic. The use of PDMS to produce water-shedding hydrophobic high-voltage insulators is one such application. Severe electrical discharges can cause the surface to lose hydrophobicity, a situation much alleviated by the rapid hydrophobic recovery property of most PDMS materials as shown in the plot from our study [1] of Sylgard® 184 subjected to partial electrical discharge pulses using a needle-to-plane electrode configuration – black symbols are on extracted samples at various discharge levels and exposure times, open symbols are with added low MW PDMS fluid. At low electrical discharge levels the hydrophobic recovery is primarily caused by migration of preexisting fluids from the bulk to the surface. At higher levels the dominant mechanism in the recovery becomes the migration of *in-situ* produced low molecular weight species in the elastomer.

[1] Kim, Chaudhury, Owen, Orbeck (2001), J. Colloid Interface Sci. 244:200



## POLY 200: Nano-membranes for lithium/sulfur batteries

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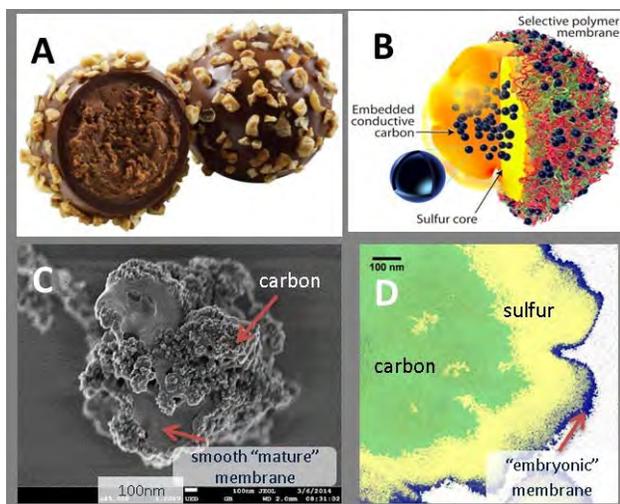
While sulfur has been an attractive cathode for more than 50 years its viability has been hindered by two fundamental challenges which need to be resolved.<sup>1</sup> (1) Enhance the conductivity of elemental sulfur. (Unlike commercial lithium ion cathodes sulfur is a good insulator) (2) Control the diffusion of soluble polysulfide intermediates formed during cycling.

Here we demonstrate a sulfur particle embedded with hollow carbon nanospheres which is encapsulated by conductive nanomembranes built based on the layer-by-layer principle (Fig. 1).<sup>2</sup> Such architecture has multiple advantages: (A) the hollow carbon embedded inside the sulfur core promotes electronic conductivity and sulfur utilization while minimizing the addition of conductive carbon in the electrode. (B) the hollow space inside the carbon structures can accumulate polysulfides and reduce outwards expansion during discharge. (C) the ion-selective nanomembrane limits the escape of polysulfides while permitting the diffusion of lithium ions (D) nanocarbon is also decorating the membrane to promote conductivity and minimize the carbon loading. This truffle inspired nanoarchitecture overcomes the dilemma associated with maximizing the sulfur loading without compromising the electrical conductivity and retention of polysulfides.

Figure 1. Picture of Godiva truffle (A) – our inspiration and a three-dimensional schematic of our concept (B); (C) depicts the typical outer surface of a truffle containing the selective polymer membrane and carbon decoration. A TEM/EELS analysis (D) depicting the embedded carbon (green) the sulfur core (yellow) and the initial (“embryonic”) polymer coating of a sulfur particle (blue). The outer selective membrane and carbon decoration were omitted for clarity.

### References

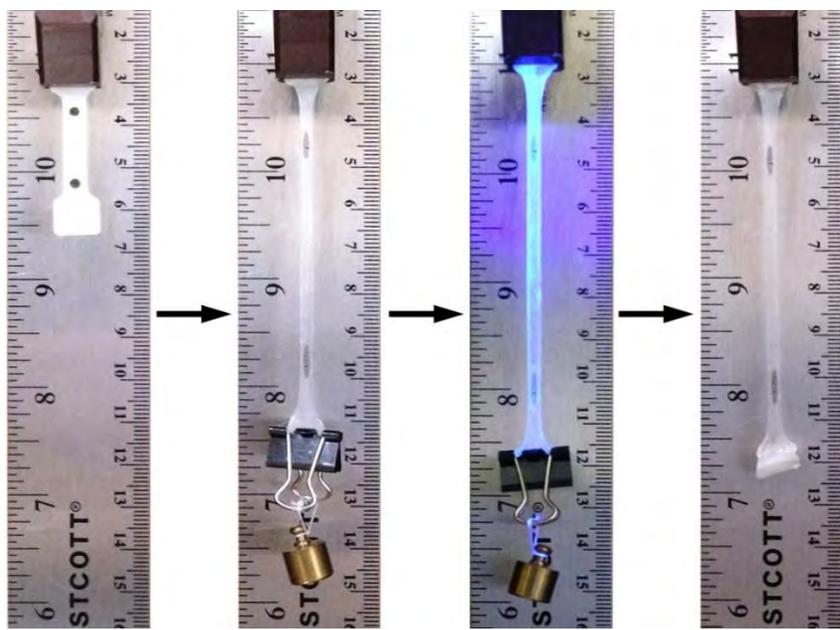
- 1 A. Manthiram, Y. Fu, S.-H. Chung, C. Zu and Y.-S. Su, *Chem. Rev.*, 2014, 114, 11751–11787.
- 2 C. B. Bucur, J. Muldoon, A. Lita, J. B. Schlenoff, R. A. Ghostine, S. Dietz and G. Allred, *Energy Environ. Sci.*, 2013, 6, 3286–3290.



## POLY 201: Main-chain liquid-crystalline elastomers using a two-stage thiol-acrylate reaction for shape-switching biomedical applications

*Christopher M. Yakacki<sup>1</sup>, chris.yakacki@ucdenver.edu, Ross Volpe<sup>1</sup>, Mohand Saed<sup>1</sup>, Amir Torbati<sup>1</sup>, Daniel Merkel<sup>2</sup>, Carl Frick<sup>2</sup>. (1) Mechanical Engineering, University of Colorado Denver, Denver, Colorado, United States (2) Mechanical Engineering, University of Wyoming, Laramie, Wyoming, United States*

Liquid-crystalline elastomers (LCEs) are a class of stimuli-sensitive materials that can display reversible thermo-mechanical actuation, soft-elasticity behavior, and changes in optical properties. Recently, a two-stage thiol-acrylate Michael-addition/photo-polymerization reaction has been introduced to synthesize main-chain LCEs. This presentation will discuss how this two-stage reaction can be used as a platform to create a wide range of shape-changing and biomedical applications. A nematic diacrylate mesogen, RM257, is mixed in a non-stoichiometric ratio with a di-thiol spacer and multi-functional thiol crosslinker. Utilizing an excess of acrylate functional groups, the Michael-addition reaction is a click reaction that is self-limited by the number of thiol groups. This first reaction can be used to create polydomain LCE samples. The second stage photo-polymerization reaction is then used to react the excess acrylate groups in a homopolymerization reaction. The second stage reaction will be shown to program a permanently oriented liquid-crystal monodomain capable of reversible thermal actuation. The magnitude of thermal actuation is shown to increase proportionally with the amount of strain applied during photo-crosslinking. Furthermore, the spatio-temporal control of the UV light can be used to tailor both mechanical and optical properties of the LCE samples. Next, the two-stage reaction process will be combined with electrospun polyvinylalcohol (PVA) fibers to create LCE-PVA mesh composites. By utilizing a water-soluble fiber, such as PVA, the fibers of the composite can be used as a sacrificial template to create an LCE-based filtration device capable of reversible actuation.



## POLY 202: Liquid crystal elastomer composites with aligned, anisotropic fillers as multifunctional actuators

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Bioengineering, The University of Texas at Dallas, Richardson, Texas, United States

Many biological materials derive function from spatial and hierarchical control of structure and composition. This structure is particularly critical at the interfaces between rigid and compliant tissues, such as tendon and bone. Programmable control of shape, modulus and other properties is needed to better interface relatively simple synthetic materials with complex natural tissues. Liquid crystal elastomers are well known to exhibit anisotropic mechanical properties and have been widely studied for the coupling of the nematic director to mechanics. This coupling results in unique behaviors such as soft elasticity and actuation. However until recently, nearly all of these materials have been aligned uniaxially. By directing the self-assembly of liquid crystal elastomers, the highly anisotropic mechanical properties, including thermally induced shape change and elastic modulus, exhibited by these materials can be designed in 2D (**Figure**). These materials can be designed to reversibly change shape with over 50% strain in response heat or solvent. In this work, we leverage recent results in surface-aligned liquid crystal elastomers to demonstrate that mixtures of liquid crystal monomers can be used to spatially align anisotropic microparticles, yielding multifunctional composites. The effect of aligned fillers, such as silicon carbide whiskers, on shape change and modulus is explored. Furthermore strategies to enable liquid crystalline hydrogels that change shape in response to changes in physiological conditions will be described. These liquid crystal elastomer composites provide a strategy towards mimicking the multifunctionality of highly complex biological materials. It is expected that these active, designed monoliths may be leveraged in applications such as coatings for implantable devices.

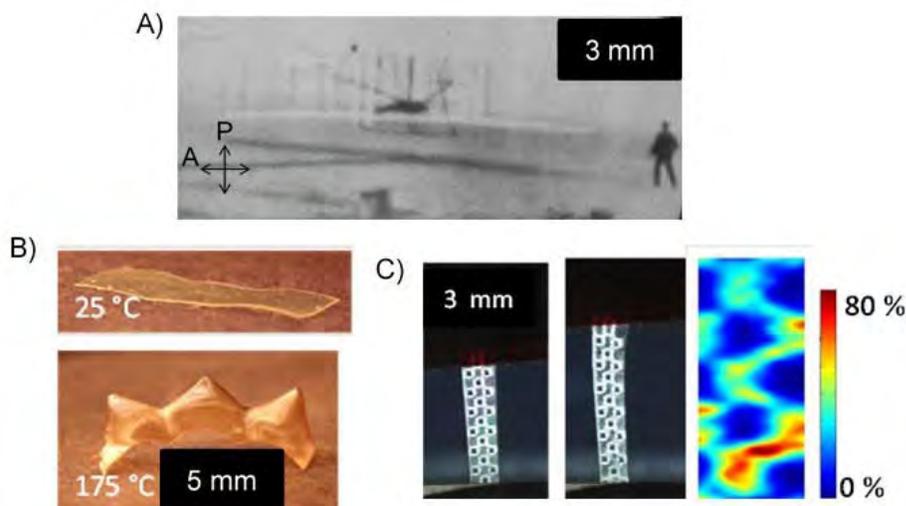


Figure: The director in liquid crystal elastomers can be spatially patterned (a). The resulting monolith can be designed to exhibit complex actuation (b) or to locally control modulus (c). In this work we will use this control to design the microstructure in liquid crystal elastomer composites.

## **POLY 203: Responsive surfaces prepared by programming liquid crystalline elastomers**

**Timothy J. White**<sup>1</sup>, *timothy.white.24@us.af.mil*, Taylor Ware<sup>1,2</sup>, Benjamin Kowalski<sup>1</sup>. (1) *Materials and Manufacturing Directorate, Air Force Research Laboratory, Centerville, Ohio, United States* (2) *University of Texas at Dallas, Dallas, Texas, United States*

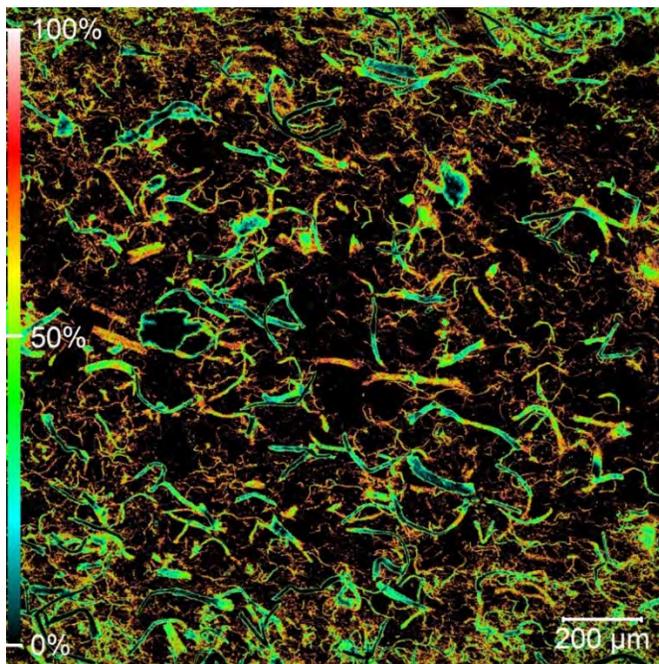
Shape can be a functional property of devices. Shape is derived topology and is designed evident in the planar fold lines of a cardboard box or the mechanical anisotropy of certain natural structures. Building upon recently developed chemistries conducive to photoalignment we report on the demonstration of adaptive shape and surface control within topologically blueprinted liquid crystal elastomers. The display Figure illustrates the dramatic change in shape upon heating a liquid crystal elastomer film in which nine +1 topological defects are subsumed in a 3 x 3 array.



## POLY 204: Study of dynamics at a composite interphase as a result of applied stress using fluorescence imaging

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Composites have percolated into a wide range of material applications, ranging from vehicle light weighting to construction materials. With an increase in demand comes the need for more sustainable sources of components for composites. Understanding the components' interactions at the interphase in composites will help target possible sources for both the reinforcing and matrix portion when designing a composite. Förster Resonance Energy Transfer (FRET) imaging of a composite interphase was pioneered at the National Institute of Standards and Technology previously, through the dispersion of donor dye in a polymer matrix and covalent attachment of the acceptor dye to nanofibrillated cellulose (NFC). Here we probe the interface of epoxy composites with both negative and positive fluorescent response mechanisms. The first being FRET imaging at the interface of two components with covalently locked donor and acceptor, while the second is the mechanical activation of a fluorescent probe bound at the interface of an epoxy fiber composite. Given that FRET is a distance dependent phenomenon that disappears with separation of donor acceptor pairs, the response to interfacial debonding is a loss signal. The mechanically responsive probe is dark prior to activation, and becomes fluorescent in response to stress resulting in a signal increase. We found that the interface can be imaged and monitored for damage through fluorescence imaging using these two activation/deactivation mechanisms.



FRET efficiency image of nanofibrillated cellulose in PE

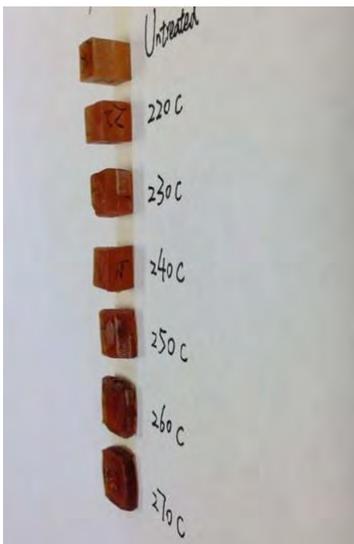
## POLY 205: Enhancing the sustainability of glass-fiber reinforced epoxies

Chris Kuncho<sup>2</sup>, Wenhao Liu<sup>2</sup>, Johannes Moeller<sup>2</sup>, Emmanuelle Reynaud<sup>1</sup>, **Daniel F. Schmidt<sup>2</sup>**, Daniel\_Schmidt@uml.edu. (1) Mechanical Engineering, University of Massachusetts Lowell, Lowell, Massachusetts, United States (2) Plastics Engineering, University of Massachusetts Lowell, Lowell, Massachusetts, United States

Glass fiber reinforced epoxies represent materials of critical importance in a range of industries, offering high specific stiffness and strength and excellent corrosion resistance. Unlike traditional structural materials such as metals, however, they are nearly impossible to recycle. Likewise, in spite of significant efforts to develop more sustainable bio-derived polymeric materials, composite resins remain almost entirely petroleum-based. Here, review our progress in the preparation of high performance, reworkable, bio-derived polymer networks and their glass fiber reinforced composites.

With respect to sustainable, bio-based resins, we show that epoxidized linseed oil represents an excellent basis for the formation of high-performance structural thermosets. We review the various curatives studied and present the results of our most current efforts focused on resin rheology and the properties of networks cured with anhydride blends and reinforced with synthetic clay nanoparticles. These materials display attractive combinations of modulus and heat distortion temperature. In tandem, rheological studies confirm equivalent or better performance vs. conventional materials as far as resin infusion is concerned.

In tandem, we demonstrate that high performance anhydride cured epoxy thermosets may be successfully cured in the presence of various transesterification catalysts to render them thermally reworkable. Complementing an initial screening effort involving simple constant-load creep experiments, we demonstrate the utility of stress-relaxation measurements in generating useful information concerning the time-scales over which reworkability may take place. In addition to enabling for recycling and reuse, the possibility to take advantage of reworkability as a means of manufacturing is also shown.



Reworkable epoxy specimens following compression set experiment

## POLY 206: Refining the design of sustainable polymers with octanol-water partition coefficients

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The pursuit of sustainable polymers faces several interesting dilemmas. These include questions about how to polymerize renewable molecules, what type of physical properties will result, and will these properties meet or exceed current petroleum-based polymers. To enable a better prediction of polymer properties, octanol-water partition coefficients (LogP) offer insight into the hydrophobicity of monomers and polymers. In combination with the 12 Principles of Green Chemistry, LogP values enable the design of sustainable polymers and may improve the ability to target particular physical properties.



Octanol-water partition coefficients (LogP) enable a prediction of polymer properties.

## **POLY 207: Single-step and simultaneous plasticization and compatibilization process for compounding starch and polyolefins**

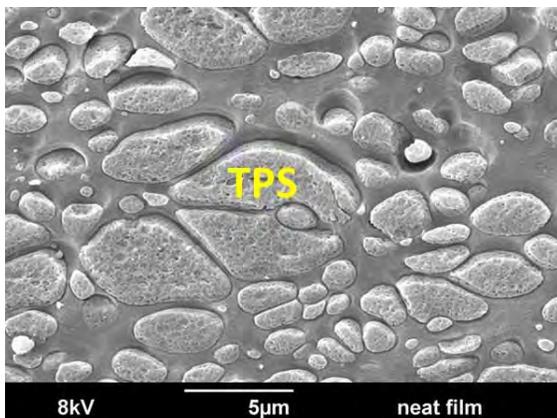
**Amy Chen**<sup>1</sup>, amy.f.chen@kcc.com, James H. Wang<sup>2</sup>, Greg Wideman<sup>1</sup>. (1) Kimberly-Clark, Neenah, Wisconsin, United States (2) SINOPEC, Appleton, Wisconsin, United States

Blending starch into polymer has been studied intensively in the recent decades and starch has been considered as a bio-based and biodegradable component in the composite. Typically, starch has to be converted into thermoplastic starch (TPS) before blending with other polymers, due to the fact that native starch has narrow processing window and poor mechanical properties. The additional plasticizing and converting process creates extra cost during production, which hindered the commercialization of the polymer/starch composite films. To create economic value, there is a need to develop a one-step compounding process of binary polyethylene (PE)/TPS blend films in industry.

In this study, glycerol, as an in-situ plasticizer during compounding process, was injected into the twin-screw extruder to soften the TPS phase and facilitate the processing. Water, as a secondary plasticizer to assist glycerol, was also added into TPS component for a comparison study. The benefit of using water as plasticizer is that it will evaporate during the compounding process; higher mechanical properties will be expected due to the lack of residue plasticizer in the TPS phase. This study also discussed the influence of 1). TPS loading level on the phase structure and mechanical properties of PE/TPS blend films; and 2). the composition, processing temperature, and screw speed on the mechanical properties of Bio-PE/TPS blend films.

In general, the cost of both PE/TPS and Green PE/TPS blend films will be reduced by increasing the loading level of in situ formed TPS, and the renewability of PE/TPS blends will be increased by increasing TPS content. The comparison study of compatibilizers showed that maleic anhydride grafted polyolefin (Fusabond<sup>®</sup>) is a preferred compatibilizer.

This simultaneous plasticization and compatibilization method enabled a single-compounding process to make low-cost, high performance PE/TPS films.



## **POLY 208: Step-growth polymerization of highly efficacious antimicrobial polymers for consumer care products**

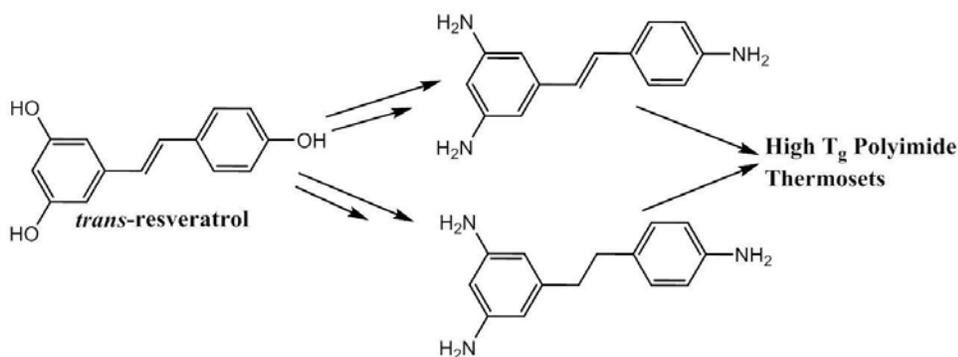
**Musan Zhang**<sup>1</sup>, zhangmn86@gmail.com, Robert Ono<sup>1</sup>, Amanda Engler<sup>4</sup>, Yi-Yan Yang<sup>3</sup>, J L. Hedrick<sup>2</sup>. (1) IBM, San Jose, California, United States (2) IBM Research, San Jose, California, United States (3) Inst Bioengr Nanotech, Singapore, Singapore (4) 3M, Minneapolis, Minnesota, United States

Small molecule antimicrobial agents are pervasive in everyday consumer care products; however, many of these active agents are under scrutiny as potential carcinogens that may lead to antibiotic resistant bacteria. Cationic polymers are a desirable alternative to small molecules due to their membrane description mode of action which eliminates the potential for resistance. Many reports in the literature describe using living polymerization techniques to control molecular weight and polydispersity and synthesis of novel active monomers. However, this approach may not be ideal for cost and industrial scale-up. Therefore, we describe an alternative approach using bulk polycondensation polymerization due to its simplicity, ease of polymer scale-up, and cost-effectiveness. To further improve the scale-up process, commercially available monomers were selected to generate different classes of step-growth polymers including polyamides, polyesters, polyureas, polyguanidiniums, and polyionenes. By carefully selecting monomers with tertiary nitrogen groups, these resulting polymers contained tertiary nitrogens on the polymer backbone which were further quaternized with a variety of alkylating agents. The advantages of this approach addresses not only the polymerization scale-up but also the synthetic versatility necessary to explore a variety of chemical functional groups and tune the polymer amphiphilicity for targeted antimicrobial performance, and haemolysis, and cytotoxicity.

## POLY 209: High temperature thermosetting polyimides derived from sustainable, non-toxic polyanilines

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Methylene dianiline (MDA) is a commodity chemical and an important component of both epoxy resins and thermosetting polyimides. Unfortunately, MDA is also mutagenic and a known carcinogen that poses an unacceptably high health risk to workers in the aerospace industry as well as the general public. The conversion of bio-derived substrates to polyanilines is a promising approach to the development of non-toxic, sustainable alternatives to MDA. In addition to the potential to reduce toxicity, the use of bio-based aromatic compounds allows for the exploration of a variety of novel structural motifs that are not commonly found in petroleum based resins. The structural diversity of renewable materials can also positively impact key polymer properties including glass transition temperature, water uptake, thermo-oxidative stability, and char yield. Further, the use of renewable aromatic compounds can result in more efficient synthetic strategies, improving atom economy and reducing costs. This presentation will discuss the synthesis of novel polyanilines from renewable feedstocks including pine resin, resveratrol, and other bio-based phenols. The cure chemistry and characterization of derivative thermosetting polyimides will then be discussed.

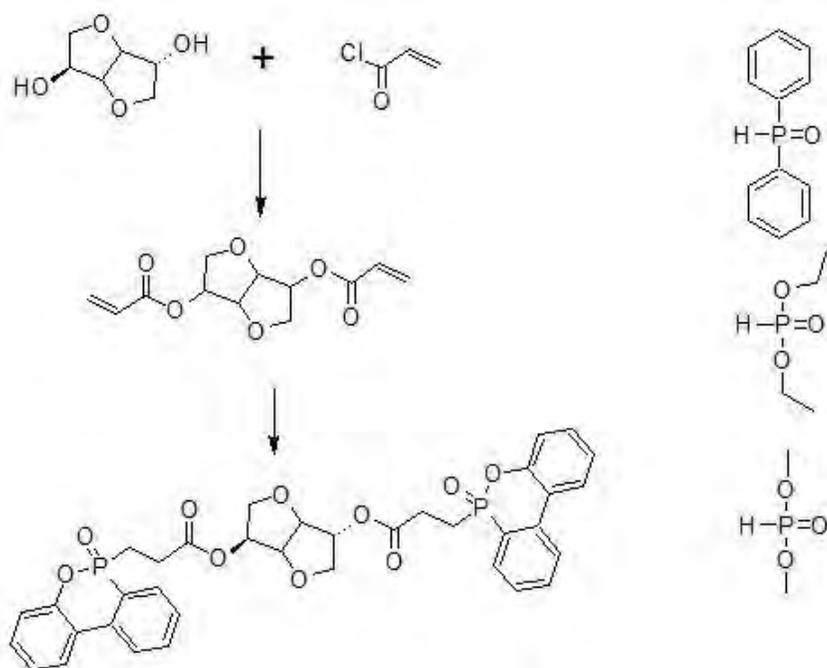


Synthesis of trisanilines and thermosetting polyimides from *trans*-resveratrol

## POLY 210: Phosphorus flame retardants for polymeric materials from isosorbide bis-acrylate

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Polymeric materials are pervasive in modern society. In fact, the high standard of living enjoyed by people of the developed world would not be possible were it not for the availability of these materials. For most applications these materials must be flame retarded. Traditionally, organohalogen compounds, particularly brominated aromatics, have been widely used as effective, low cost flame retardants. However, these compounds are stable in the environment, tend to bioaccumulate and may pose a risk to human health. Consequently, they are coming under increasing regulatory pressure worldwide. As alternatives, phosphorus compounds derived from renewable biosources are particularly attractive. Isosorbide is a dihydroxy ether readily available from starch which is annually abundant from a variety of seed crops. It may be converted to the bis-acrylate ester. This compound undergoes Michael addition of phosphites to generate a number of phosphorus compounds which display good flame retardancy in polymeric materials.



## **POLY 211: Dual functional flame retardants from a non-edible seed oil**

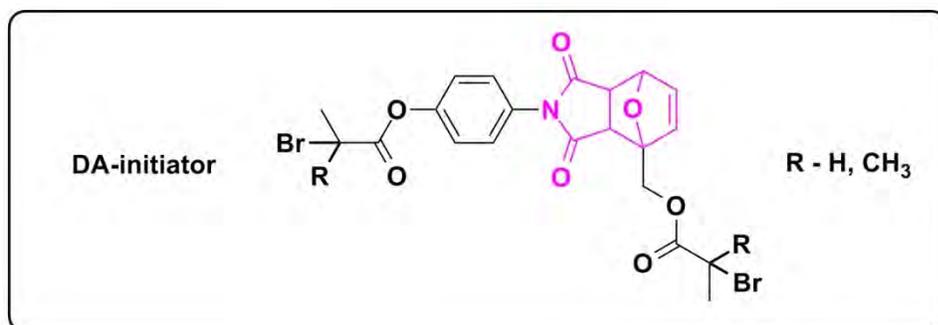
**Eric A. Ostrander**<sup>2</sup>, [Ostra2ea@cmich.edu](mailto:Ostra2ea@cmich.edu), **Bob A. Howell**<sup>1</sup>. (1) Central Michigan Univ, Mount Pleasant, Michigan, United States (2) Central Michigan University, Oscoda, Michigan, United States

As the concern about the potential negative health impacts of the organobromine compounds continues to grow, the need for the development of new, nontoxic flame retardants becomes ever more pressing. Such materials may be based on renewable biomaterials. Castor oil is abundantly available from the seed (bean) of the castor plant widely cultivated in the Far East. This oil contains functionality (hydroxyl group and unsaturation) which may be utilized for the generation of a variety of phosphorus compounds with flame-retarding properties.

## POLY 212: Use of Diels-Alder chemistry to prepare molecular weight changing material

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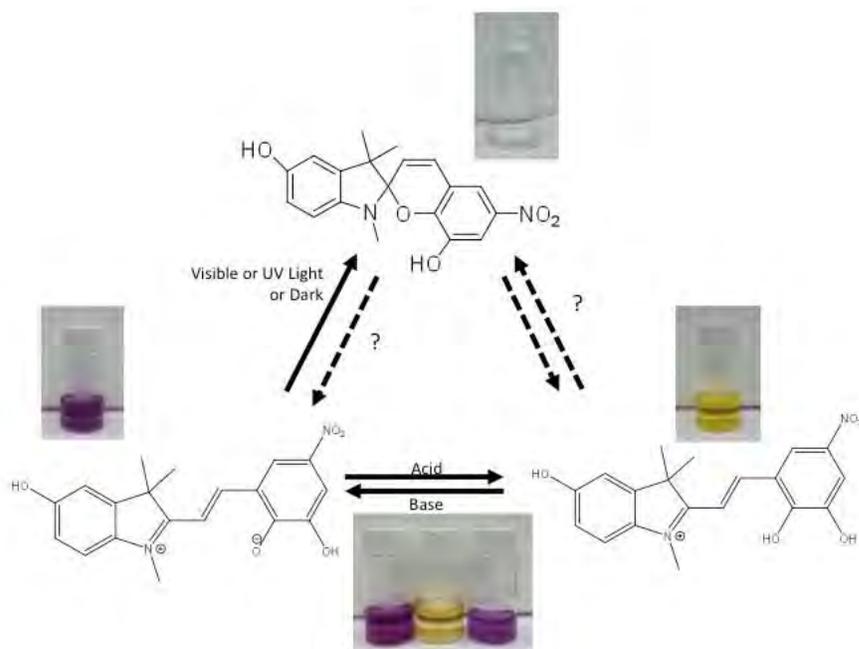
Thermally-responsive materials have been prepared in a multitude of ways for a wide variety of applications. One aspect not previously exploited is the ability to change the molecular weight for dynamic processing. Diels-Alder (DA) chemistry was incorporated within the main chain of the polymer backbone by using a DA-initiator and atom transfer radical polymerization. Next, polymer were utilized as macromonomers and coupled into high molecular species via atom transfer radical coupling. Upon the application of a thermal stimulus, the retro-DA was induced and molecular weight of the polymer was altered. [figure1]



## POLY 213: Synthesis and characterization of activatable dyes for Integration into polymer systems

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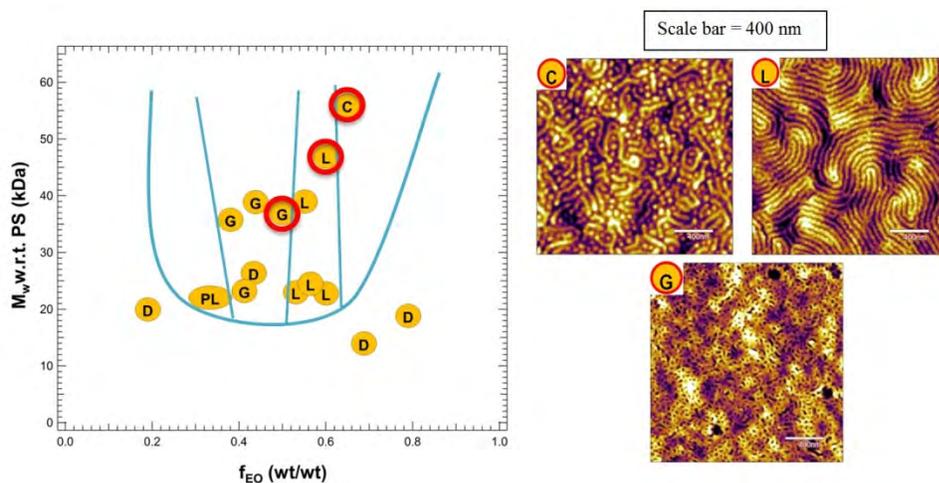
Activatable dyes are an important class of molecules due to their ability to indicate changes in environment by their change in fluorescence and absorbance. Activation can occur through several methods, including acid, base, ultraviolet light and visible light. Mechanophores are a subclass of activatable dyes that become fluorescent with mechanical activation or force. In one type of mechanophore, application of force breaks a chemical bond within the molecule, shifting the equilibrium from a non-fluorescent to a fluorescent isomer. The ability to detect the deformation within a polymer is important to prevent its failure. Integration of these molecules into polymers would allow for the important identification and localization of mechanical stress and damage in a polymer via the visible fluorescence of the stressed dye molecule. The goal of this project is to synthesize and characterize several mechanophore dyes and incorporate them into polymers. The dyes being focused on are synthesized derivatives of spiropyran and rhodamine. Characterization of these dyes is done through absorbance, fluorescence and calculation of a relative quantum yield value. In addition other forms of activation, such as ultraviolet light, acid, base and visible light, for these dyes was studied. These dyes are then integrated into a polymer which can be tension tested, during which the dye should become visibly fluorescent in the polymer.



## POLY 214: Investigation of microphase separation by atomic force microscopy in oligo(ethylene oxide) grafted oxanorbornyl diblock copolymers for use as lithium ion battery electrolyte supports

**Thomas J. Kolibaba**, [tjkolibaba@gmail.com](mailto:tjkolibaba@gmail.com), Dean A. Waldow. Department of Chemistry, Pacific Lutheran University, Tacoma, Washington, United States

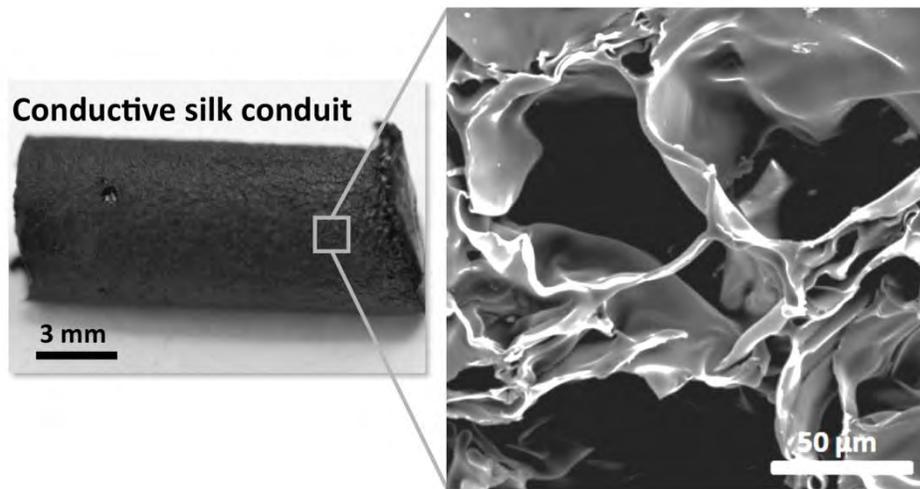
Lithium-ion batteries could potentially be made to be safer by eliminating the use of flammable electrolyte solvents, which could be achieved by the development of solid polymer electrolytes. A series of novel oligo(ethylene oxide) grafted dicarboximide functionalized oxanorbornyl diblock copolymer electrolyte supports were synthesized via ring opening metathesis polymerization. Products obtained were monodisperse, with a variety of ethylene oxide sidechain lengths ( $n=2, 3, 8$ ) and compositions. The nanomorphologies of solvent vapor annealed samples were investigated through the use of atomic force microscopy to determine the phase diagram of the diblock system for each sidechain length and to determine the impact of oligo(ethylene oxide) sidechain length on the phase behavior. It was found that the phase diagrams of the  $n=2$  diblock system appears to deviate from a standard diblock theoretical phase diagram in that it seems to have a much larger gyroidal region and it is shifted toward the ethylene oxide containing block. Future scattering experiments are planned to confirm phase assignments.



## POLY 215: Electrically conductive silk fibroin scaffolds for use as nerve conduits

**Emily Sanders**, sandere3@students.wvu.edu, Sean Severt, Amanda Murphy. Chem Dept, MS9150, Western Washington Univ, Bellingham, Washington, United States

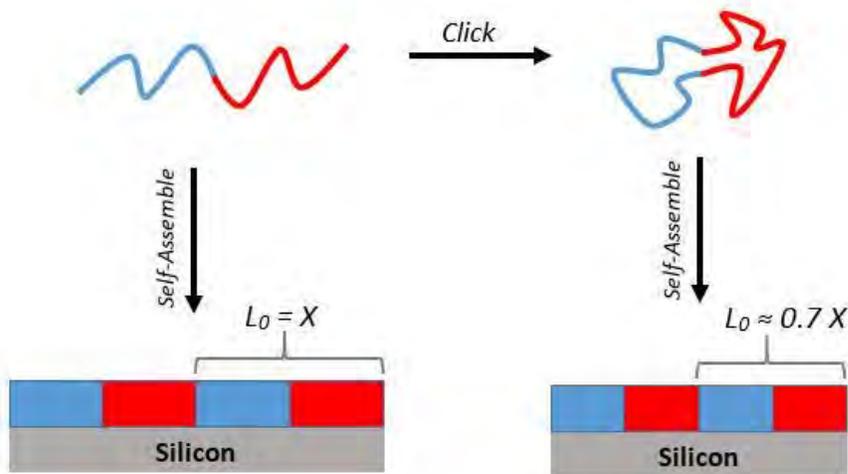
Regaining function of peripheral or central nerves damaged by trauma or disease is a problem that researchers in the field of biomaterials are actively trying to resolve. To bridge nerve gaps and encourage directional axonal growth, conduits made from biocompatible, robust, flexible, degradable, multi-channeled and electrically conductive materials are sought. The silk fibroin protein found in the cocoon of the *Bombyx mori* silkworm is a biopolymer that meets most of these requirements when processed into a 3D form. Previous work in our group has demonstrated that when modified using a diazonium coupling reaction, the fibrous protein gains anionic character and can form a conductive scaffolds containing an interpenetrating network of cationic conducting polymers. Here we describe the optimization of the reaction conditions, morphology, and conducting polymer choice to give materials with chemical and physical properties appropriate for use as nerve conduits.



## POLY 216: Strategic geometries for pitch reduction in self-assembled block copolymer

**Jeffrey L. Self**<sup>3</sup>, [jeff.self@utexas.edu](mailto:jeff.self@utexas.edu), Michael Maher<sup>4</sup>, Christopher J. Ellison<sup>1</sup>, Carlton G. Willson<sup>2</sup>. (1) Chemical Eng, U of Texas At Austin, Austin, Texas, United States (2) Univ of Texas Dept Chem Engr, Austin, Texas, United States (3) Department of Chemistry, University of Texas, Seabrook, Texas, United States (4) Chemistry, University of Texas at Austin, Austin, Texas, United States

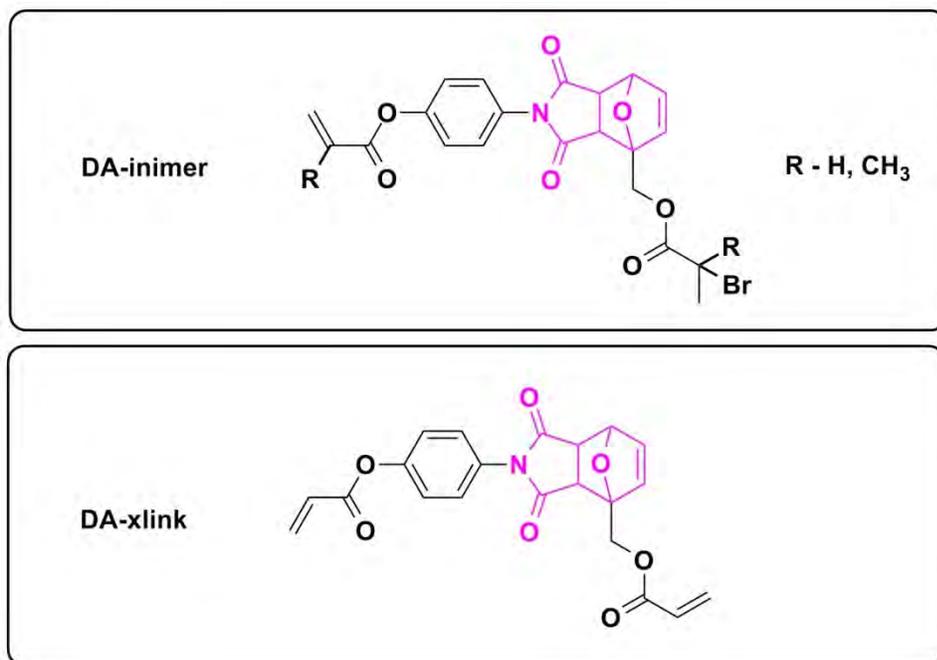
Block copolymers (BCP) offer an alternative to traditional patterning techniques, but have yet to reach the necessary domain spacing to be truly viable. Domain spacing is known to be directly correlated to radius of gyration, which is synthetically controlled by the molecular weights of the individual blocks for linear BCP. Recent studies using ARGET ATRP and click chemistries have shown that the effective radius of gyration can be greatly reduced for cyclic BCP relative to their linear analogs. This suggests that further constraining the radius of gyration via strategic manipulation of the geometry of BCPs would yield greater reductions in domain spacing. A comparative study on linear and cyclic BCPs' behavior in bulk and in thin film would provide the data necessary to elucidate this trend, and further our understanding of BCP self-assembly.



## POLY 217: Thermally responsive materials with dynamic topology based upon Diels-Alder chemistry

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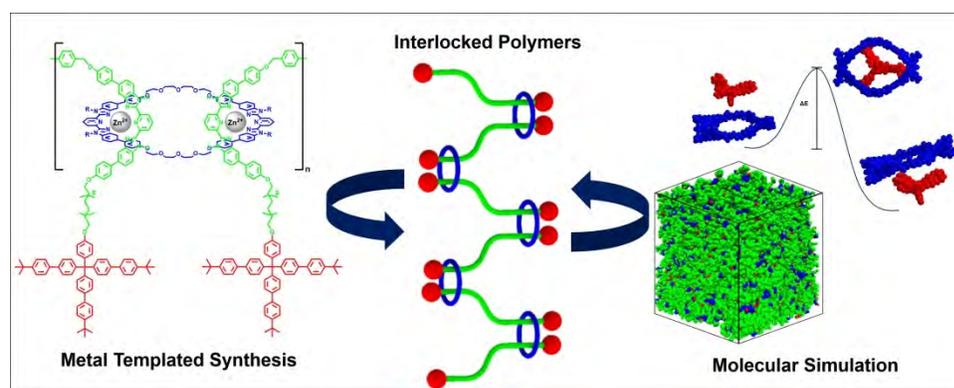
Thermally-responsive materials have been prepared in a multitude of ways for a wide variety of applications. One aspect not previously exploited is the ability to induce changes in polymer architecture. Diels-Alder (DA) chemistry was employed to prepare various topologies with DA linkages at branching points within a non-linear 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]



## POLY 218: Integrated synthetic and computational techniques for the design of poly[3]rotaxanes

*Eric P. Bruckner, epb18@case.edu, Michael J. Hore, Stuart J. Rowan. Case Western Reserve University, Cleveland, Ohio, United States*

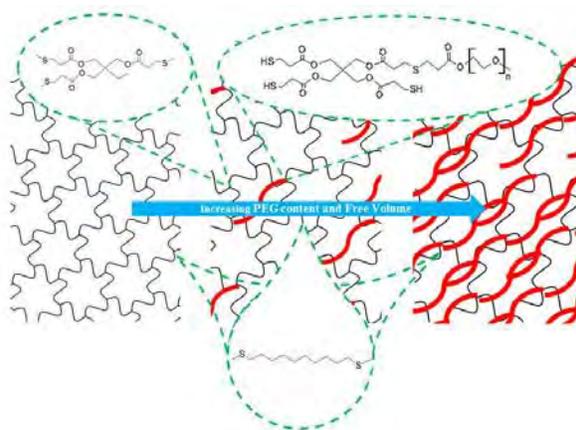
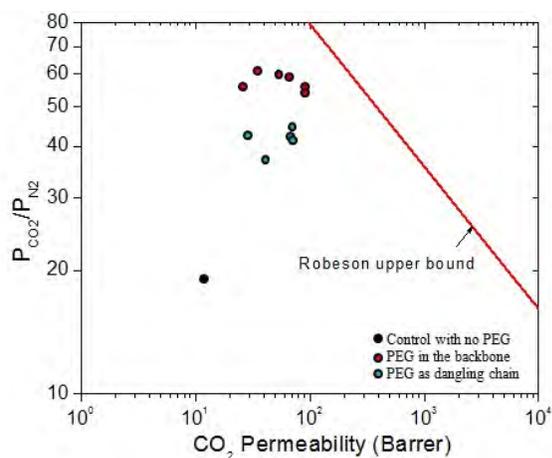
Rotaxanes are a type of mechanically interlocked molecule, consisting of a molecular “dumbbell” threaded through a macrocycle, which can be used as a repeat unit to form larger interlocked polymers (i.e. polyrotaxanes). Since interlocked polymers are primarily composed of mechanical bonds, instead of covalent bonds, the material properties are dominated by component geometry as opposed to chemical structure. Due to the complexity of mechanically interlocked molecules, it is difficult to optimize component geometry by purely synthetic techniques, thereby necessitating the use of an integrated experimental and computational approach. Herein we report the synthesis of a novel double-threaded poly[3]rotaxane by a metal-templating process with the 2,6-bis(N-alkyl-benzimidazolyl)pyridine ligand. Design of the poly[3]rotaxane was supplemented by atomistic simulations used to determine the optimum component geometry to prevent disassembly of the interlocked structure. Further coarse-grained dissipative particle dynamics (DPD) simulations were used to calculate rheological properties of the bulk material in order to understand the relationship between component geometry and material properties. By understanding the structure-property relationships of mechanically interlocked polymers, future materials can be designed more efficiently and with a greater degree of structural control.



## POLY 219: PEG containing thiol-ene network membranes for CO<sub>2</sub> separation: PEG units as dangling chains versus peg units in the backbone

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A family of dangling poly(ethylene glycol) (PEG) containing thiol-ene network membranes were synthesized by photo-polymerizing 1,9-decadiene (DDE) with a trithiol crosslinker (3T). PEG comprising modified trifunctional thiol (4T-PEG) was synthesized by thio-Michael reaction of tetrafunctional thiol pentaerythritol tetrakis(3-mercaptopropionate) (4T) and PEG methyl ether acrylate (PEG-Ac) taken in a 1:1 ratio. The trithiol crosslinker (3T) was gradually replaced with (4T-PEG) to vary the PEG content of the networks. The effect of increasing the amount of bulky PEG chains on glass transition temperature was studied. Changes in free volume as a function of temperature and PEG content were measured using Pressure Volume Temperature (PVT) dilatometry and Positron Annihilation Lifetime Spectroscopy (PALS). Permeability, diffusivity, and solubility of different light gases through the networks were studied at varying PEG content. CO<sub>2</sub>/N<sub>2</sub> permeability-selectivity performance of the membranes were compared to a similar family of membranes with PEG contained in the backbone.



## POLY 220: Chain transfer polymerization of carbon dioxide, cyclohexene oxide and poly(dimethyl)siloxanes utilizing zinc based catalysts

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Aliphatic polycarbonates, derived from carbon dioxide and epoxides, have drawn much attention in the last decades, due to their material properties such as durability, high transparency, heat resistance and gas permeability.<sup>[1]</sup> However, particularly poly(cyclohexene carbonate) (PCHC) suffers from brittleness and a high glass transition temperature ( $T_g$ ).<sup>[2]</sup> In order to modify the material properties, terpolymerization of different epoxides and carbon dioxide<sup>[3]</sup>, as well as chain transfer polymerization were studied.<sup>[4]</sup> In a key work, Lee *et al.* showed that *in situ* formation of ABA or AB block copolymers out of propylene oxide, CO<sub>2</sub> and chain transfer agents such as adipic acid, poly(ethylene glycol), poly(propylene glycol) or polycaprolactone, catalyzed by an ionic cobalt salen complex, is possible.<sup>[4]</sup>

As the main disadvantage of PCHC is brittleness, the idea was to incorporate poly(dimethylsiloxanes) (PDMS) into the PCHC backbone. PDMS have a very low glass transition temperature of commonly -120 °C, are stable in a broad temperature range, are non toxic and hydrophobic. The formation of PCHC out of CO<sub>2</sub> and cyclohexene oxide is effectively catalyzed by various  $\beta$ -diiminato (BDI) zinc catalysts.<sup>[5]</sup> Among these a dinuclear complex, developed in our group, shows the highest reported activity (155000 h<sup>-1</sup>, 350 kg/mol) so far.<sup>[6]</sup> Herein, we present the novel approach of performing chain transfer polymerizations of CO<sub>2</sub>, cyclohexene oxide and polysiloxanes. Our investigations imply a detailed performance analysis of different mononuclear and dinuclear BDI zinc catalysts, as well as a full characterization of the resulting polycarbonate polyols.

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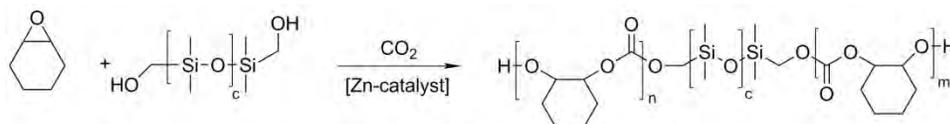
[2] C. Koning, J. Wildeson, R. Parton, B. Plum, P. Steeman, D. J. Darensbourg, *Polymer* 2001, 42, 3995-4004.

[3] J. G. Kim, C. D. Cowman, A. M. LaPointe, U. Wiesner, G. W. Coates, *Macromolecules* 2011, 44, 1110-1113.

[4] A. Cyriac, S. H. Lee, J. K. Varghese, E. S. Park, J. H. Park, B. Y. Lee, *Macromolecules* 2010, 43, 7398-7401.

[5] D. R. Moore, M. Cheng, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* 2003, 125, 11911-11924.

[6] S. Kissling, M. W. Lehenmeier, P. T. Altenbuchner, A. Kronast, M. Reiter, P. Deglmann, U. B. Seemann, B. Rieger, *Chem. Commun.* 2015, 51, 4579-4582.

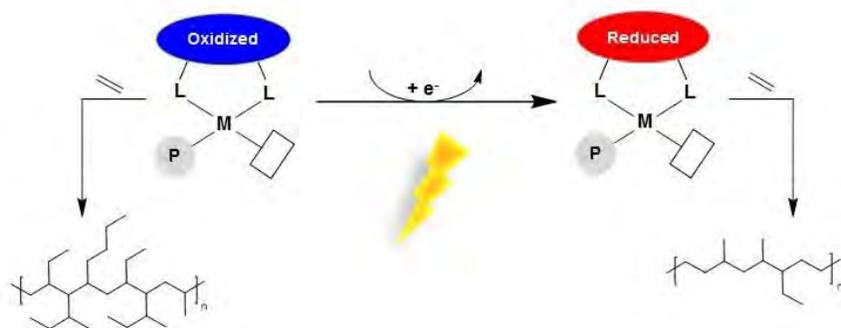


**PCHC-PDMS-PCHC Block Copolymer**

## POLY 221: Introduction of redox-active catalysis to the polymerization of olefins

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Polyolefins represent a class of macromolecules that have made a profound impact on everyday life and are produced on the multibillion lb/yr scale. Many of those commonly produced polyolefins are made via the copolymerization of inexpensive ethylene gas and larger olefinic comonomers providing opportunities for tailored mechanical and thermal properties; however, this method dramatically increases the cost of polymer production. To address this issue, we have used late transition metal olefin polymerization catalysts that may modulate polymer topology based on their redox state, thereby allowing for specially tailored polyolefins without the use of expensive comonomers.



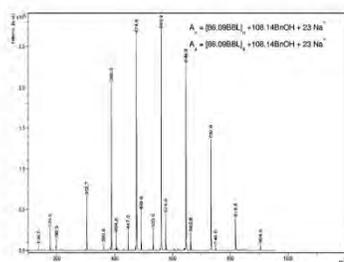
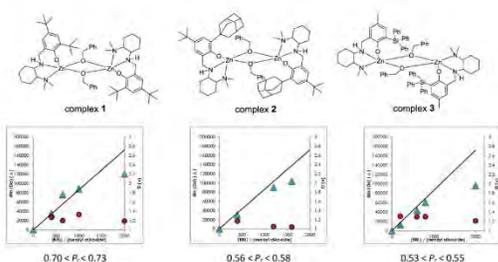
## POLY 222: Highly active and syndioselective zinc complexes for the immortal ring-opening polymerization of $\beta$ -butyrolactone

**Tannaz Ebrahimi**<sup>1,2</sup>, [tannaz@chbe.ubc.ca](mailto:tannaz@chbe.ubc.ca), **savvas hatzikiriakos**<sup>1</sup>, **Parisa Mehrkhodavandi**<sup>2</sup>. (1) Department of Chemical and Biological Engineering, University of British Columbia, Vancouver, British Columbia, Canada (2) Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada

Poly(hydroxybutyrate), as a biodegradable and biocompatible polymer, has received an increasing amount of attention over the last decades due to its significance in a wide variety of applications, ranging from packaging industries to biomedical and drug delivery applications. To tailor the final physical properties of these polymers through controlling the backbone microstructure, several chemical synthetic routes such as ring opening polymerization (ROP) of strained cyclic ester,  $\beta$ -butyrolactone (BBL), based on metallic catalysts have been reported. We have recently shown that chiral alkyl zinc complex (NNiOtBu)Zn(CH<sub>2</sub>CH<sub>3</sub>) forms moderately syndiotactic PHBs (Macromolecules 2015 48 (18), 6672-6681). In this work, syndiotactically enriched PHB ( $P_r$  up to 0.71) is synthesized from ring opening polymerization of rac-BBL using series of chiral alkoxy zinc complexes.

During polymerization, all the complexes are very reactive and have very good control over the molecular weight and form monodispersed syndio-enriched PHBs. This is also the case in the presence of high loadings of alcohols.

Detailed investigations have been also carried out to address the polymerization mechanism. Mechanical and thermorheological properties of these polymers are also studied through investigation of the effect of backbone microstructure and molecular weight on the tensile and melt viscoelastic properties of syndiotactically enriched PHBs.

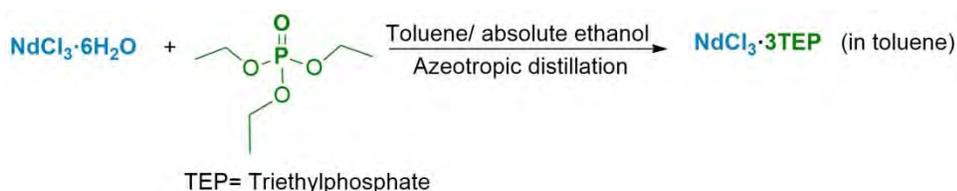


MALDI-ToF spectrum of syndio-PHB oligomers using immortal polymerization of BBL/iBnOH/[Zn] = 20 000/ 5000/ 1

## POLY 223: Highly active neodymium catalyst for polymerization of dienes, vinyl monomers and ring opening polymerization of lactones

**Ruvanthi Kularatne**<sup>1</sup>, *rnk130030@utdallas.edu*, Davy Krang<sup>1</sup>, Annie Yang<sup>1</sup>, Michael C. Biewer<sup>2</sup>, Mihaela C. Stefan<sup>3</sup>. (1) Chemistry and Biochemistry, University of Texas at Dallas, Richardson, Texas, United States (2) Dept of Chemistry, University of Texas at Dallas, Richardson, Texas, United States (3) Dept Chem UT Dallas, Richardson, Texas, United States

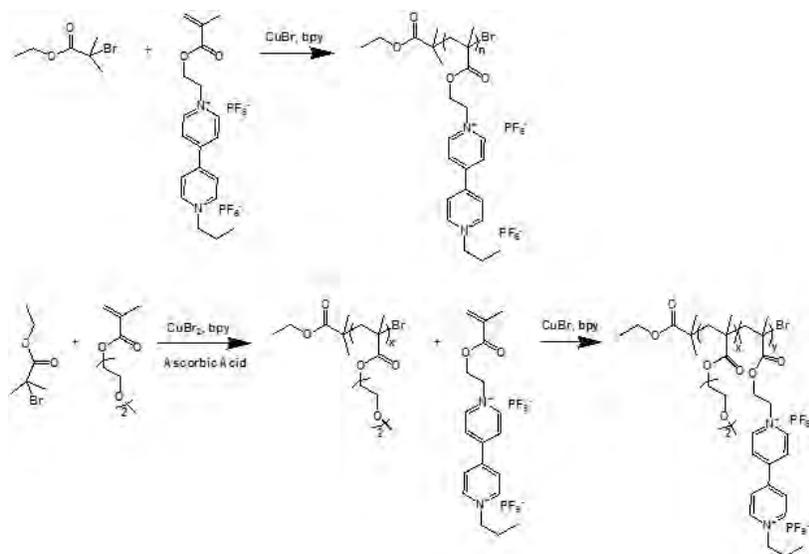
The synthesis and the application of a neodymium based binary catalytic system for the polymerization of dienes, vinyl monomers, and lactones is reported. The proposed catalyst is composed of neodymium trichloride ( $\text{NdCl}_3$ ) and triethylphosphate (TEP) as the ligand.  $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$  and TEP (molar ratio 1:3) were dissolved in toluene-ethanol mixture followed by an azeotropic distillation, which removes the crystallization water of  $\text{NdCl}_3$  and allows the self-complexation of the Nd with the phosphate ligands. The as synthesized catalyst ( $\text{NdCl}_3 \cdot 3\text{TEP}$ ) together with the co-catalyst triisobutylaluminum (TIBA) were used in appropriate ratios with varying temperatures for the polymerization of dienes and vinyl monomers. Homopolymerization of myrcene, isoprene, vinyl acetate, methyl acrylate, methyl methacrylate, and styrene was carried out. The catalytic system was also proven to be active for the ring opening polymerization of  $\epsilon$ -caprolactone. Copolymerization between dienes and diene- vinyl monomers was performed. The *living* nature of the catalyst for the homopolymerization of dienes was demonstrated. The characterization of the catalyst was performed by FT-IR,  $^1\text{H}$  and  $^{31}\text{P}$  NMR analysis. Quantification of the number of ligands was done by  $^{31}\text{P}$  NMR. Characterization of the polymers were carried out by  $^1\text{H}$  NMR and the molecular weights were obtained by size exclusion chromatography (SEC).



## POLY 224: Synthesis of redox-active, fluorescent, and/or thermo-responsive viologen-containing polymers by atom transfer radical polymerization

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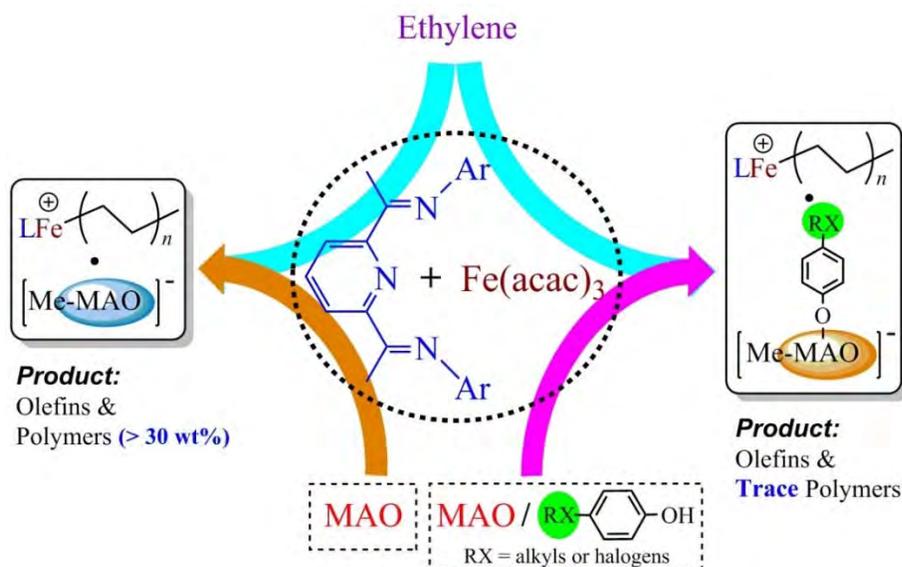
An asymmetric viologen-containing methacrylate monomer (2-methacryloyloxyethyl propyl 4,4'-bipyridinium hexafluorophosphate) was synthesized and polymerized under atom transfer radical polymerization (ATRP) conditions to afford well-defined linear polymers with multiple redox-active and electrochromic viologen pendant groups. The hexafluorophosphate salts of the polymers were hydrophobic, while the chloride salts were hydrophilic and water-soluble. The redox catalytic activity of the prepared materials was studied by UV-vis spectroscopy in aqueous solutions, using hydrazine as the reducing reagent and oxygen from air as the oxidant. Upon reduction, the pendant viologen units were converted to intensely colored radical cations, which had a significantly higher propensity to dimerize by radical coupling compared to low-molecular weight viologens with similar structures. In addition, unlike most low-molecular weight viologens, the polymers with multiple pendant viologen groups were highly fluorescent in aqueous solutions. The intensity of the fluorescence was very sensitive to the salt concentration in aqueous solutions; for instance, the addition of NaCl quenched the viologen fluorescence. To prepare thermally responsive viologen-containing materials, block copolymers were synthesized by ATRP by chain extension of poly(diethylene glycol methyl ether methacrylate)-based macroinitiators with the viologen-based monomer. The macroinitiators were synthesized by low-catalyst concentration (ARGET) ATRP using ascorbic acid as the reducing reagent. The lower critical solution temperatures in aqueous solutions of the block copolymers, in their higher oxidation state and in their reduced form, were determined.



## POLY 225: Phenol-modified methylaluminoxanes for the activation of a bis(imino)pyridine iron catalyst in ethylene oligomerization

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A limitation of bis(imino)pyridine (BIP) iron-catalyzed ethylene oligomerization is the simultaneous production of insoluble polymers. In this presentation, we would introduce the strategy of tuning the product distribution by modification of the methylaluminoxane (MAO) co-catalyst with a series of phenolic compounds. It was found that the polymer share in the total products would be largely reduced with the increasing dosage of the phenols and the enlargement of *para*-substituent size from methyl to *tert*-butyl. Further <sup>1</sup>H NMR studies showed that the phenols could provide MAO profound structural modifications, giving rise to larger MAO aggregates and decoration of phenoxy groups on its surface. This would thus facilitate the active ion pair separation, leading the phenols to be effective polymer-retarding modifiers. Starting from the reaction between 4-*tert*-butylphenol, AlMe<sub>3</sub> and water, a novel phenoxy-aluminoxane could be prepared. Its combination with AlMe<sub>3</sub> enabled the catalyst activation, and gave us a further verification about the important role of phenoxy groups on the MAO surface. Furthermore, introduction of electron-withdrawing groups would improve the reactivity of the -OH group, promoting the interaction between the phenols and MAO. A series of *para*-halogen substituted phenols were thus developed. With the relatively large size of bromo group and the highest reactivity of -OH group, 4-bromophenol was proved to be the most efficient polymer-retarding modifier among the studied phenols in this work. An almost polymer-free ethylene oligomerization could be achieved by this strategy without altering the mono *ortho*-methyl substituted BIP ligand.

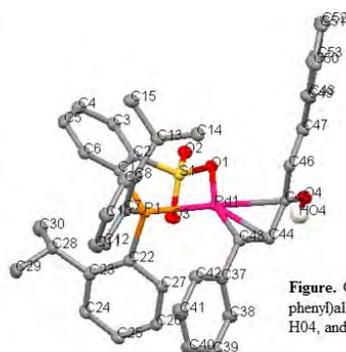
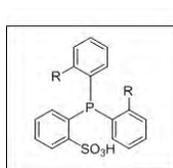


Polymer formation could be efficiently retarded with the activation of phenol-modified MAOs in the iron-catalyzed oligomerization of ethylene

## POLY 226: Structure-activity relationship on palladium phosphine-sulfonates for olefin-polar monomer copolymerization

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Palladium phosphine-sulfonates have been reported as effective catalysts for olefin-polar monomer copolymerization. In this study, a systematic study revealed that substituents at the ortho position of arylphosphines play a critical role on their catalytic property. Introduction of sec-alkyl group enhanced the activity and molecular weight of the produced copolymer, as compared to the n-alkyl analogue. The crystal structure of the isopropyl-introduced complex showed the effective covering with the isopropyl group over the apical position of the center metal. Introduction of oxygen-containing group led to the considerable increase of catalytic activity, which indicates the importance of interaction of the  $d_{z^2}$  Pd orbital with oxygen lone pairs.



**Figure.** ORTEP drawing of (L4){ $\eta^3$ -(1-hydroxy-1'-phenyl-3-phenyl)allyl}Palladium complex. Hydrogen atoms except H04, and two hexyl groups have been omitted for clarify.

**Table 1.** Copolymerization of Ethylene with Methyl Acrylate initiated by Phosphinesulfonate Complex.<sup>a</sup>

Run	R	Activity (g/mol/h)	$M_w$	$M_w/M_n$	$T_m$ (°C) <sup>b</sup>	Incorp. (mol%) <sup>c</sup>
1	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	256,700	44,000	2.0	118.2	1.3
2	-CH(CH <sub>3</sub> ) <sub>2</sub>	577,000	153,000	2.4	118.9	1.3
3	-cyclo-CH(CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub>	1,795,200	168,000	2.1	120.4	0.6
4	-CH <sub>2</sub> OCH <sub>3</sub>	1,794,545	19,000	1.9	121.0	1.2
5	-CH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	2,460,000	40,000	2.0	121.6	1.1
6	-OCH <sub>3</sub>	422,000	14,000	2.0	104.2	3.6

<sup>a</sup> The Polymerization Conditions: (*o*-R-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>P(*o*-SO<sub>3</sub>H-C<sub>6</sub>H<sub>4</sub>)/Pd(dba)<sub>2</sub> = 1, Ethylene 3.0 MPa, [MA]<sup>b</sup> = 1.0 M, Toluene, 80°C.

<sup>b</sup> Measured by DSC. <sup>c</sup> MA incorporation estimated by IR.

## POLY 227: Breaking symmetry-rules for stereoselective polymerization catalysis

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Homogeneous catalysts for propylene polymerization are now available for production of isotactic polypropylene (PP) with stereoselectivities approaching that of heterogeneous Ziegler-Natta (ZN) catalysts.

Ewen<sup>1</sup> and Kaminsky<sup>2</sup> demonstrated that the microstructure of PP was predictable when produced with catalysts operating by site control mechanisms and established the relationships, known as “Ewen’s symmetry rules”, which correlate the chirality and symmetry of the catalyst to the microstructures of PP.

In this communication we report a theoretical analysis by DFT calculations on the propene polymerization promoted by systems formed by N-heteroaryl-pyridylamido tridentate ligands and the corresponding (N,N,N)M<sup>IV</sup>(Me<sub>2</sub>)<sub>2</sub> pentacoordinate complexes (M=Zr, Hf) (systems 1 and 2 in Chart 1).<sup>3</sup>

Our results suggest that for these systems: a) the mechanisms of stereoselectivity contradict the “Ewen’s symmetry rules”; b) the tacticity control is much more subtle and difficult to predict than the one performed by tetrahedral *ansa*-metallocene<sup>4</sup> as well as post-metallocene systems.<sup>5</sup>

Nevertheless, breaking the generally accepted symmetry-rules open new perspectives to achieve stereoselective catalysis.

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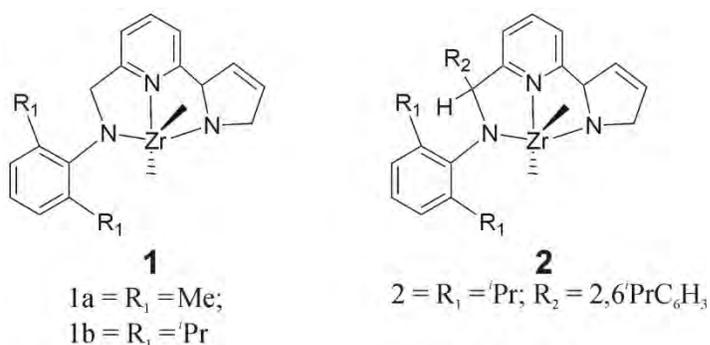
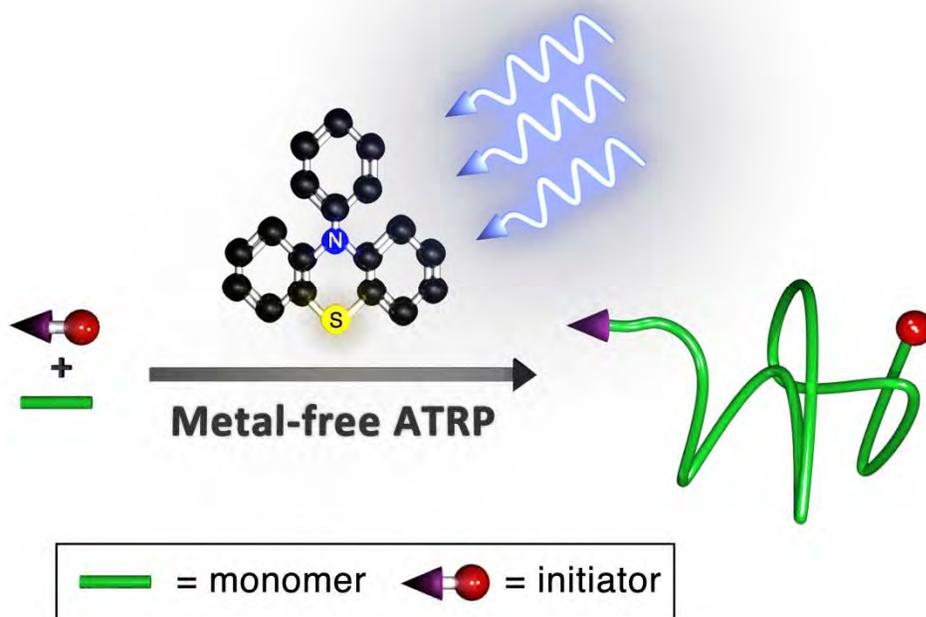


Chart 1. Systems analyzed in this study

## POLY 228: Metal-free atom transfer radical polymerization

**Nicolas J. Treat**<sup>1</sup>, [nicolas.treat@gmail.com](mailto:nicolas.treat@gmail.com), Javier Read De Alaniz<sup>1</sup>, Brett P. Fors<sup>3</sup>, Craig J. Hawker<sup>2</sup>. (1) Materials, UNIVERSITY OF CALIFORNIA, SANTA BARBARA, Santa Barbara, California, United States (2) Univ of California, Santa Barbara, California, United States (3) Cornell, Ithaca, New York, United States

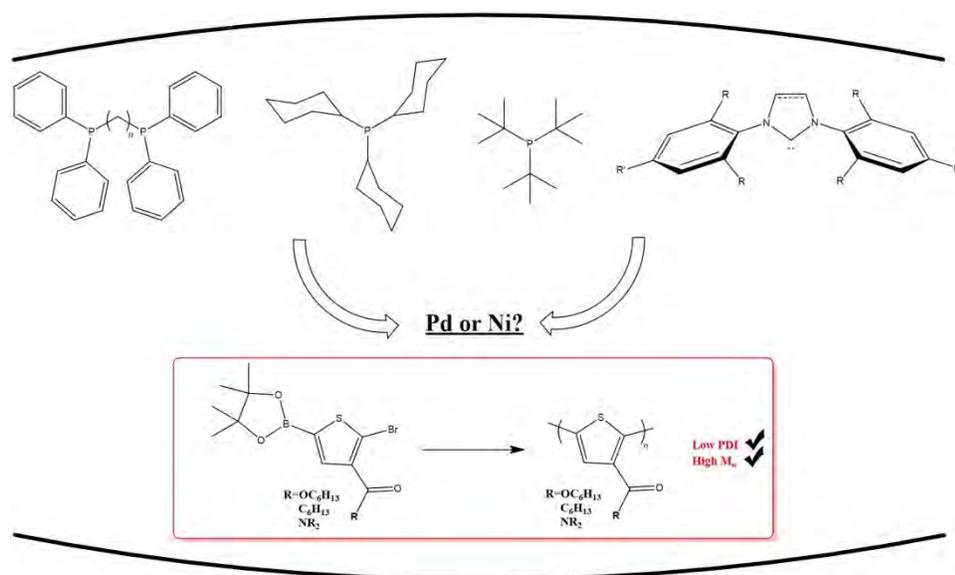
Overcoming the challenge of metal contamination in traditional ATRP systems, a metal-free ATRP process, mediated by light and catalyzed by an organic-based photoredox catalyst, is reported. Polymerization of vinyl monomers are efficiently activated and deactivated with light leading to excellent control over the molecular weight, polydispersity, and chain ends of the resulting polymers. Significantly, block copolymer formation was facile and could be combined with other controlled radical processes leading to structural and synthetic versatility. We believe that these new organic-based photoredox catalysts will enable new applications for controlled radical polymerizations and also be of further value in both small molecule and polymer chemistry.



## POLY 229: Robust catalysts for catalyst-transfer polycondensation of monomers containing electron withdrawing groups

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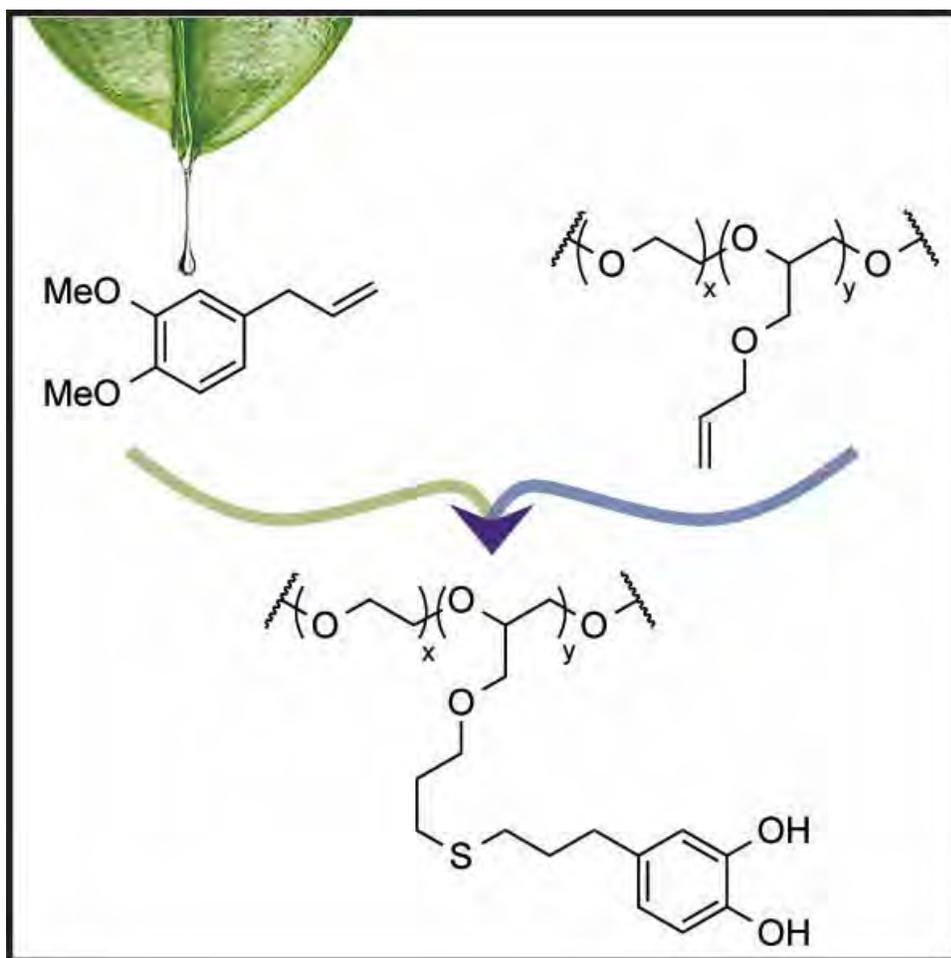
Since the controlled synthesis of poly(3-hexylthiophene) via catalyst-transfer polycondensation (CTP), various catalysts and monomers have been examined. However, the most successful cases have primarily been limited to 1) electron-rich monomers with inert functional groups and 2) catalysts featuring bidentate phosphine ligands or monodentate electron-rich phosphines such as tri-*tert*-butylphosphine. In this presentation I will discuss our advancement of general CTP protocols for monomers displaying relatively sensitive electron withdrawing moieties. The focus will be on exploration of catalysts suitable for cross-coupling methodologies that are recognized for functional group tolerance e.g. the Suzuki–Miyaura reaction.



## POLY 230: Synthesis of catechol-functionalized poly(ethylene oxide) block and random copolymers

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University of California, Santa Barbara, California, United States

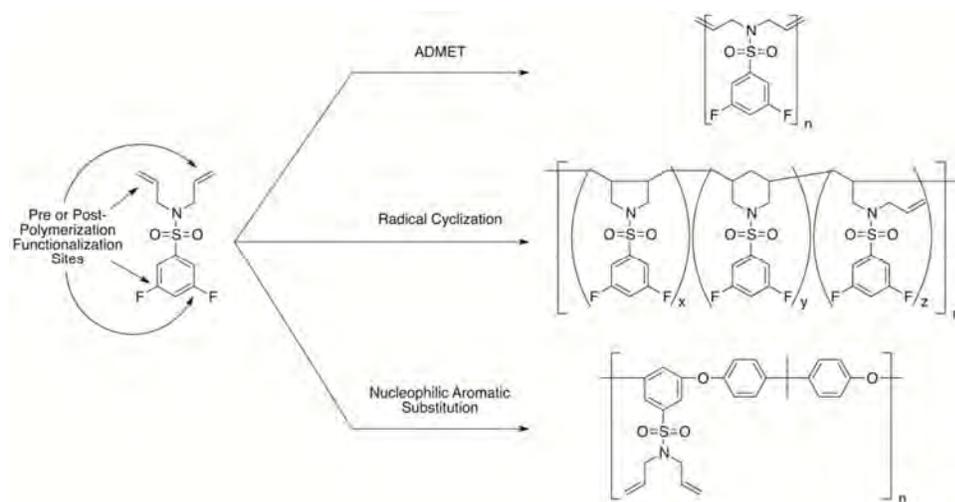
A modular strategy for the functionalization of well-defined polyether copolymers with control over the number and location of catechol groups will be presented. This simple, high-yielding synthesis represents the first time catechols have been controllably dispersed throughout polyethylene oxide (PEO)-based polymer backbones. The precise tunability afforded by this system could allow the effects of polymer architecture, molecular weight, and catechol incorporation on the adhesive properties of surface-anchored PEO to be studied.



## POLY 231: Synthesis, polymerization, and characterization of sulfonamide based bifunctional monomers

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Bifunctional monomers, monomers containing two distinct polymerizable moieties, aid in pre- or post polymerization functionalization. This project seeks to develop bifunctional monomers in which one of the polymerizable moieties can undergo nucleophilic aromatic substitution (NAS) reactions. The overall project has two goals: 1) to synthesize bifunctional monomers, such as *N,N*-diallyl-3,5-difluorobenzenesulfonamide, and 2) to form polymers using acyclic diene metathesis (ADMET), radical cyclopolymerization, and NAS, followed by the appropriate functionalization chemistry. The monomers were prepared via the reaction of diallyl amine with the appropriately substituted benzenesulfonyl chloride. The ADMET and radical cyclopolymerizations were monitored by <sup>1</sup>H NMR spectroscopy, observing the disappearance of signals for the allyl groups and the appearance of broad aliphatic signals. The polymers formed via NAS reactions were followed by DEPT 90 <sup>13</sup>C NMR spectroscopy. Additionally, GPC, DSC, and TGA were used to characterize the polymers, which indicated successful ADMET, cyclopolymerization, and NAS reactions.

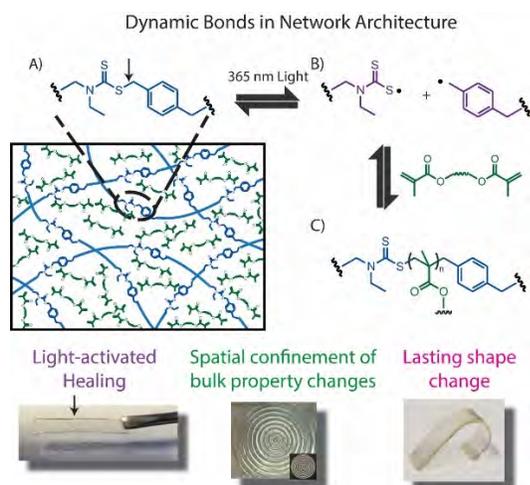


## POLY 232: Dynamic bonds in covalently crosslinked polymer networks for photo-activated strengthening and healing

**Melissa B. Gordon**<sup>1</sup>, [gordonm@udel.edu](mailto:gordonm@udel.edu), **Jonathan M. French**<sup>2</sup>, **Norman J. Wagner**<sup>1</sup>, **Christopher J. Kloxin**<sup>2,1</sup>. (1) Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware, United States (2) Department of Material Science and Engineering, University of Delaware, Newark, Delaware, United States

A new class of photoresponsive materials is described in which a dynamic bond is built into the crosslinks of a polymer network to enable a light-triggered, secondary polymerization which simultaneously strengthens and heals the material under light<sup>1</sup>. Unlike other two-tiered polymerization systems that utilize a leachable photoinitiator to impart dynamic nature to the network, the responsive nature of this material is inherent to the network itself via the light-triggered dissociation of its own crosslinks. Specifically, a crosslinker containing a labile carbon-dithiocarbamate bond (or iniferter) is incorporated into a polyurethane network and initiates a light-triggered, free-radical polymerization. Upon irradiation, the modulus of the network exhibits a two order of magnitude increase. The final modulus is tuned *a priori* by adjusting the concentration of the polymerizable group initially present in the formulation. We show the versatility of this new approach with three demonstrations: 1) photo-induced healing, reforming, and strengthening of a specimen after it has been severed, 2) photopatterning to spatiotemporally control property changes post-cure, and 3) cold-working the polymer film into a 3D configuration and then using light to "lock-in" the film's shape. The simplicity and versatility of this iniferter-based, two-tiered polymerization is readily translatable to other applications, such as functionalizing surfaces, wrinkling and beyond.

1. M. B. Gordon, J. M. French, N. J. Wagner, C. J. Kloxin, *Adv Mater* 2015, Accepted.

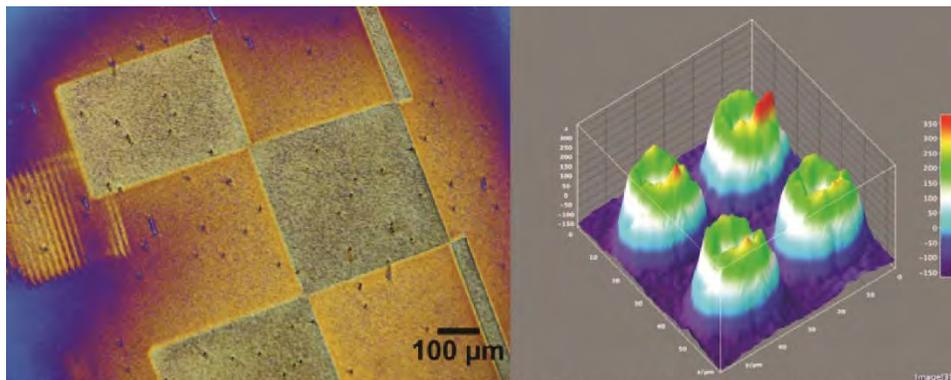


Dynamic bonds are built into the network architecture to enable a light-triggered, secondary polymerization. Three attributes of this material are shown, including: (1) simultaneous photo-induced strengthening and healing, (2) spatial confinement of bulk property changes via photopatterning, and (3) lasting shape change post-cure.

## POLY 233: Postpolymerization modification of liquid crystal alignment in covalent adaptable networks

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Disruption in liquid crystalline polymer networks enables diverse applications ranging from reversible shape memory, photo-induced bending, and adaptable surfaces. Light has been used extensively to change the order of liquid crystalline networks because of the spatial and temporal control of photo-activated processes. In this work, we demonstrate photo-controllable liquid crystal alignment by incorporating allyl sulfides within the crosslinker. When activated, the allyl sulfides begin rearranging and increase the mobility of the liquid crystalline units. Accompanied with heating; the birefringence can be decreased controllably, and with sufficient heating a permanent nematic to isotropic phase transition is observed which only occurs if light is turned on. We further demonstrate the generation of surface features by irradiating surface coatings through a photo-mask and photo-induced bending of thin films without the traditionally used azobenzene avoiding the coloration related to that.

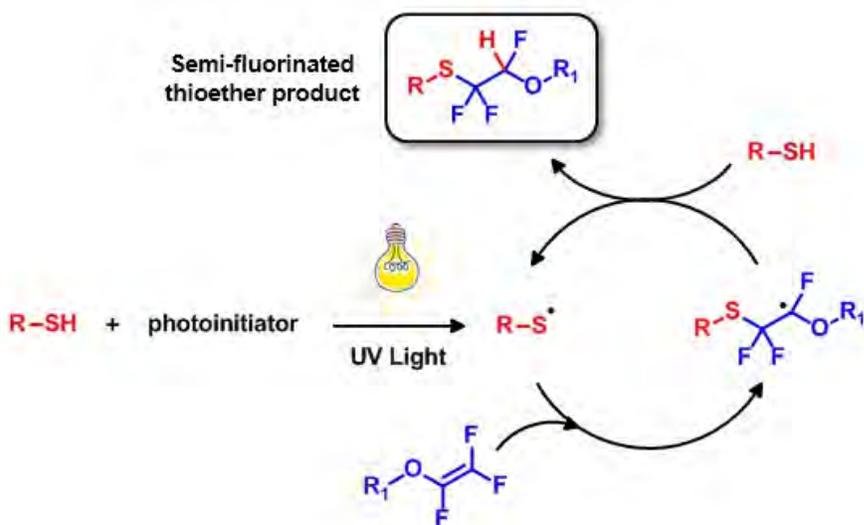


Left: Spatially controlled disruption of the liquid crystals as seen through a polarized optical microscopy. Right: Surface features generated from irradiating LC network through a photo-mask.

## POLY 234: Thiol-trifluorovinyl ether (Thiol-TFVE) photochemistry: A new route to semifluorinated materials

**Brian R. Donovan**<sup>1</sup>, [brian.donovan@eagles.usm.edu](mailto:brian.donovan@eagles.usm.edu), Jason Ballenas<sup>1</sup>, Derek L. Patton<sup>2</sup>. (1) The University of Southern Mississippi, Hattiesburg, Mississippi, United States (2) Campus Box #10076, University of Southern Mississippi, Hattiesburg, Mississippi, United States

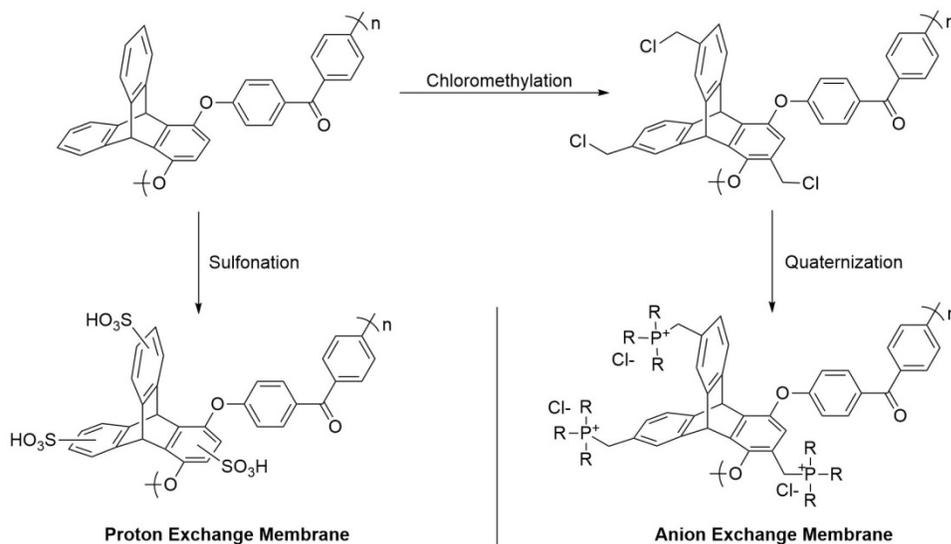
Fluorinated polymers have found prolific use in many high performance applications due to their mechanical strength, high thermal stability, and chemical stability. While desirable, fully fluorinated polymers tend to be highly crystalline, resulting in difficult processing conditions. Semi-fluorinated polymers, however, show improved processing conditions by remaining amorphous, yet demonstrate analogous properties to their fully fluorinated counterparts. Herein, we propose the use of thiol-ene chemistry as a viable route to synthesize semi-fluorinated materials. Specifically, we demonstrate the addition of a thiyl radical to the CF<sub>2</sub> end of a trifluorovinyl ether (TFVE) group in accordance with the thiol-ene radical mechanism, and the ability to form semi-fluorinated networks rapidly and in controlled geometries. The mechanism of addition is confirmed by <sup>1</sup>H and <sup>19</sup>F NMR by careful consideration of the spectrum splitting patterns, and real-time FTIR and thermomechanical analysis reveal kinetic and thermomechanical properties similar to that of a traditional thiol-ene reaction.



## POLY 235: Functionalized triptycene based poly (ether ether ketone) for ion exchange membranes

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Proton and anion exchange membranes are critical dielectric materials used in electrochemical energy storage devices. In this work, triptycene based poly (ether ether ketone) (trp-PEEK) was synthesized and functionalized for use as proton or anion exchange membranes. The triptycene moiety in this poly (ether ether ketone) is designed to increase the free volume in the membrane and provide extra reaction sites for higher degree of functionalization and crosslinking. The resulting membranes thermally stable in air and nitrogen to 300 °C. For proton exchange membranes, trp-PEEK was sulfonated and compared to sulfonated poly (ether ether ketone) to understand the effect of free volume on proton conductivity in these membranes. The resulting membranes showed a range of proton conductivity of 0.1 – 0.15 S/cm in water at 20 °C. For anion exchange membranes, trp-PEEK was first chloromethylated and then quaternized with various ammonium and phosphonium groups. The membranes were then studied for anion conductivity and stability in basic solutions.



## POLY 236: Development of polyimine-based dynamic covalent network: From malleable polymers to high-performance composites

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Recently, dynamic covalent chemistry has been employed to form malleable thermosets, a new class of network polymers which can be reprocessed, and recycled like thermoplastics. The focus of our work is the development of robust, catalyst-free malleable thermosets using exchangeable imine (a.k.a. Schiff-base) chemical links, and exploration of their great potential in fabricating high-performance functional composite materials.

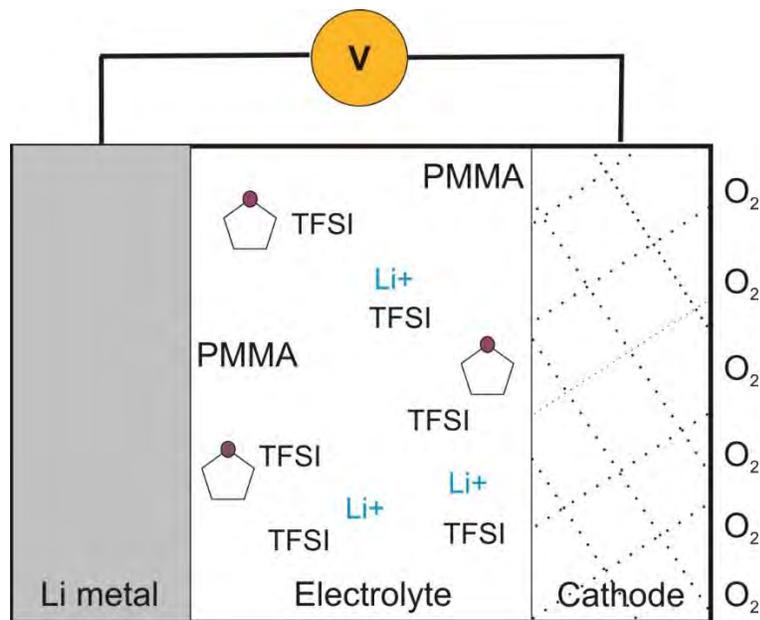


## POLY 237: One-electron process in a gel polymer Li-O<sub>2</sub> battery

**Chibueze V. Amanchukwu**<sup>2</sup>, [chibueze@mit.edu](mailto:chibueze@mit.edu), Hao Hsun Chang<sup>4</sup>, Yang Shao-Horn<sup>1</sup>, Paula T. Hammond<sup>3</sup>. (1) Dept Mech Eng Rm 3-334, MIT, Cambridge, Massachusetts, United States (2) Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Texas, United States (3) Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (4) Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

The development of better energy storage media has generated great interest as a means to support further use of renewable energy technologies, and to electrify transport. Of the battery chemistries of interest, lithium-air batteries have an order-of-magnitude greater gravimetric energy density than commercial lithium-ion batteries. Conventional lithium-air batteries contain non-aqueous electrolytes, and its chemistry is dominated by a two-electron oxygen reduction process to form peroxide species. This two-electron process is unlike other alkali-air battery systems that show a one-electron process, and has been speculated as one reason for observed slower kinetics and low-current rates in Li-air batteries.

In this work, we show that when a gel-polymer electrolyte is incorporated in a Li-air cell, the oxygen reduction chemistry changes to a one-electron process. Flexible free-standing gel polymer electrolytes were developed, and the effect of lithium-ion availability was studied. The change in discharge mechanism that occurs in a gel electrolyte as compared to a non-aqueous cell is discussed. This work shows a method to tune the desired Li-air chemistry, and should bring the field closer to developing Li-air batteries with long cycle life.



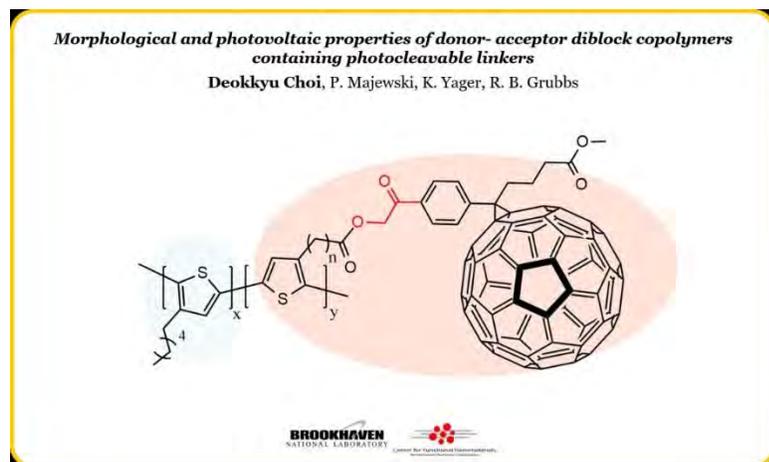
Schematic of a Li-air cell utilizing a gel polymer electrolyte

## POLY 238: Morphological and photovoltaic properties of donor- acceptor diblock copolymers containing photocleavable linkers

**Deokkyu Choi**<sup>1,2</sup>, [deokkyu.choi@stonybrook.edu](mailto:deokkyu.choi@stonybrook.edu), Pawel W. Majewski<sup>2</sup>, Kevin G. Yager<sup>2</sup>, Robert B. Grubbs<sup>1,2</sup>. (1) Chemistry, Stony Brook University, Stony Brook, New York, United States (2) Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, United States

Device performance is intrinsically tied to the morphology of organic photovoltaic (OPV) materials, making the development of new means of controlling nanoscale order extremely important. The introduction of photocleavable linkers between ester-functionalized side chains of donor copolymers and acceptor units provides a potential method for control morphology in bulk heterojunction OPV devices. In this study, we designed, synthesized, and characterized a donor-acceptor conjugated block copolymer (BCP) containing a photolabile phenacyl ester linker.

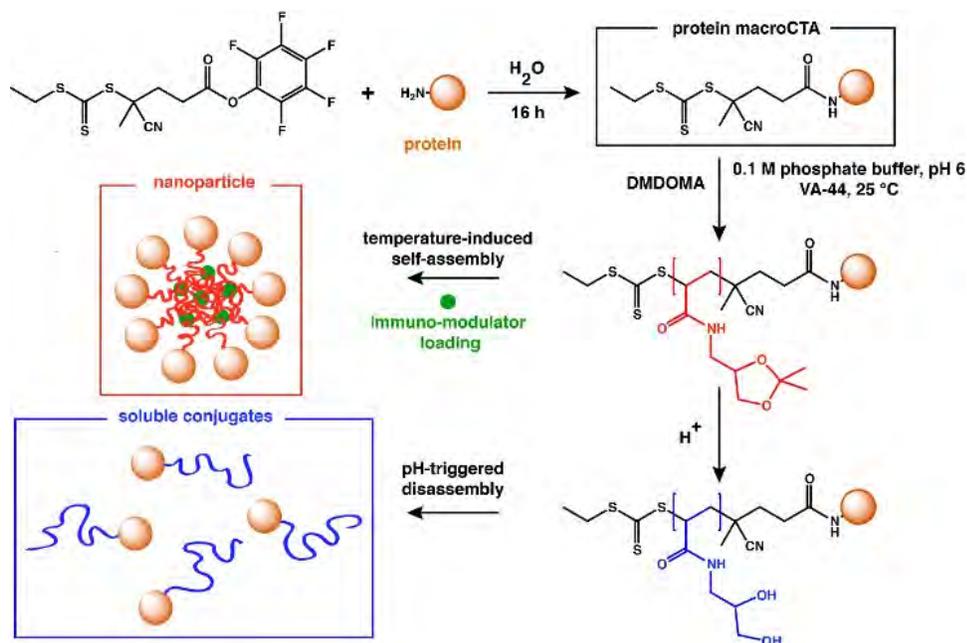
These BCPs are designed to be capable of self-assembly as well as controlled disassembly, where appropriate irradiation and photocleavage can in principle be used to tune the OPV morphology. The BCP consists of a poly(3-hexylthiophene) backbone as the electron donor block with photocleavable PC<sub>61</sub>BM units in the acceptor block. The BCPs were prepared by the Rieke method. The second block consists of PCBM pendent units connected to a polythiophene backbone through a photolabile phenacyl ester linker, and was synthesized by Suzuki coupling between 4-(hydroxyl-1-phenylethan-1-one)phenyl-C<sub>61</sub>-butyric acid methyl ester starting from C<sub>60</sub>, and the carboxylic acid group of poly(thiophene-3-hexanoic acid). The monomer and the polymer structures were confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR and elemental analysis. Photolysis studies on the photocleavable linker in the monomers and in the BCPs were performed by irradiating UV to quantify the changes in morphology. Different molecular weights, ratio and the acceptor contents of the blocks in the BCP were prepared to compare the properties with the photocleavable BCPs. The solar cell devices with the BCPs were fabricated and their photovoltaic properties were measured under optimized processing conditions.



## POLY 239: Transiently responsive protein-polymer conjugates via a grafting-from RAFT approach: For intracellular co-delivery of proteins and immune-modulators

**Nane Vanparijs**, *nane.vanparijs@ugent.be*, Bruno De Geest. Ghent University, Gent, Belgium

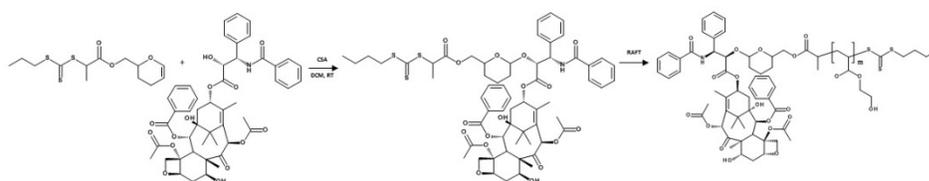
Efficient polymer-protein conjugation is a crucial step in the design of many therapeutic protein formulations including vaccine nano-formulations. Covalent modification with temperature-responsive polymers is particularly of interest to allow the proteins to self-assemble into nanoparticles above the cloud point temperature. Formulating protein antigens as nanoparticles has proven to be a promising strategy to modulate and increase the adaptive antigen-specific CD8<sup>+</sup> T-cell response through the cross-presentation pathway and can further be improved by co-encapsulation of immune-modulators. We report on transiently responsive protein-polymer conjugates that temporarily change protein conformation between soluble and particle-like. 'Grafting-from' RAFT polymerization of a dioxolane-containing acrylamide with a protein macroCTA is used to design polymer-protein conjugates that self-assemble into nanoparticles at physiological temperature and pH. These self-assembled nanoparticles can be used for intracellular co-delivery of proteins and hydrophobic molecules. The latter was demonstrated by delivering an immune-modulating compound that holds potential for vaccine delivery. Acidic triggered hydrolysis of the dioxolane units into diol moieties rendered the conjugates fully water soluble irrespective of temperature.



## POLY 240: Acid-cleavable acetal-linked paclitaxel-polymer conjugates via a drug-functionalized RAFT CTA approach

**Benoit Louage**<sup>2</sup>, [benoit.louage@ugent.be](mailto:benoit.louage@ugent.be), Bruno De Geest<sup>1</sup>. (1) Ghent University, Ghent, Belgium (2) Pharmaceutical Sciences, University Gent, Ghent, Belgium

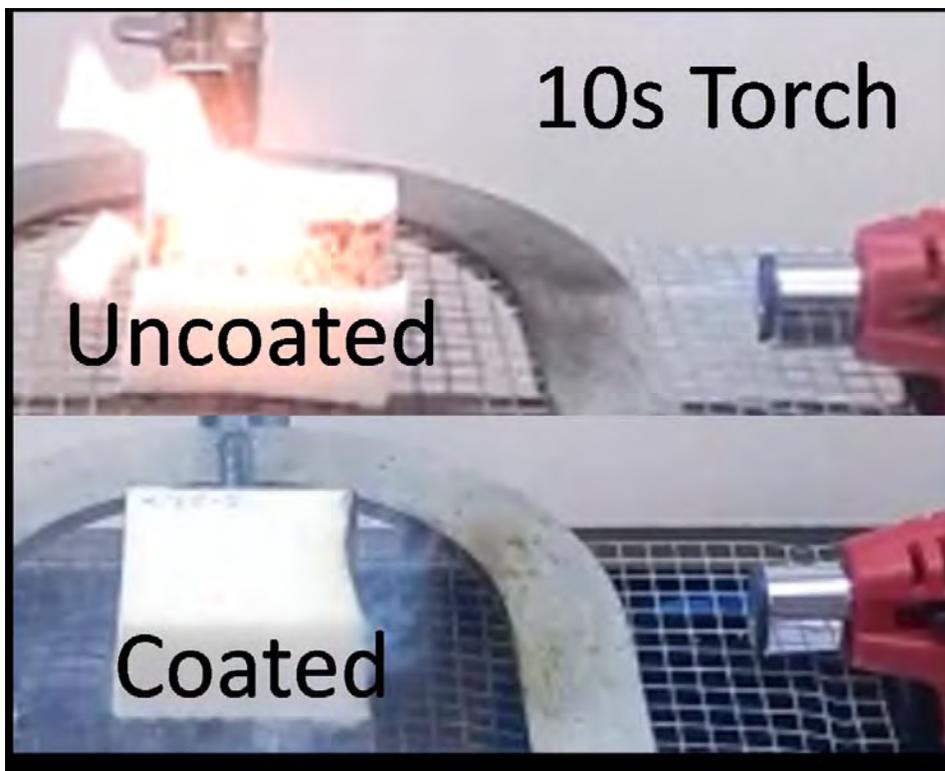
The major hurdle in successful anti-cancer drug delivery remains the inability of potent cytotoxic drugs to be efficiently delivered to tumor tissue while causing minimal side effects to healthy cells and tissues. Here we report on paclitaxel-functionalized RAFT (Reversible Addition-Fragmentation chain Transfer) chain transfer agent (CTA) via an acid-cleavable acetal linkage. Paclitaxel, a widely-used hydrophobic anti-cancer drug and conjugation to a RAFT-CTA comprises a novel strategy for designing responsive polymer-drug conjugates. This paclitaxel-CTA allows excellent control over polymerization of hydrophilic acrylates and acrylamides. Even at low degrees of polymerization the formation of stable soluble or micellar conjugates is obtained. In response to an acidic pH, the acetal bond between the drug and the polymer chain is cleaved, leading to liberation of the original unmodified paclitaxel. We show detailed physico-chemical characterization of the polymer-drug conjugates and assessed the in vitro performance of the system on human ovarian cancer cell lines. In contrast to paclitaxel that is formulated via mere hydrophobic entrapment into amphiphilic such as lipids and block copolymers, our approach could avoid immediate drug release upon administration. Thereby peak drug levels in the bloodstream are avoided and systemic side effects reduced. Furthermore, our approach allows introduction of additional functionality such as tracer molecules (e.g. fluorophores) or targeting ligands, either by co-polymerization or by post-polymerization transformation of the thiocarbonate end-group of the RAFT CTA.



## **POLY 241: Stacking clay-based and intumescent multilayer thin films to completely stop fire on highly flammable polyurethane foam**

**Kevin Holder**<sup>1</sup>, [kevin.m.holder@gmail.com](mailto:kevin.m.holder@gmail.com), Molly Huff<sup>2</sup>, Mario Cosio<sup>2</sup>, Jaime C. Grunlan<sup>3</sup>. (1) Materials Science and Engineering, Texas A&M University, College Station, Texas, United States (2) Chemistry, Texas A&M University, College Station, Texas, United States (3) Texas A&M University, College Station, Texas, United States

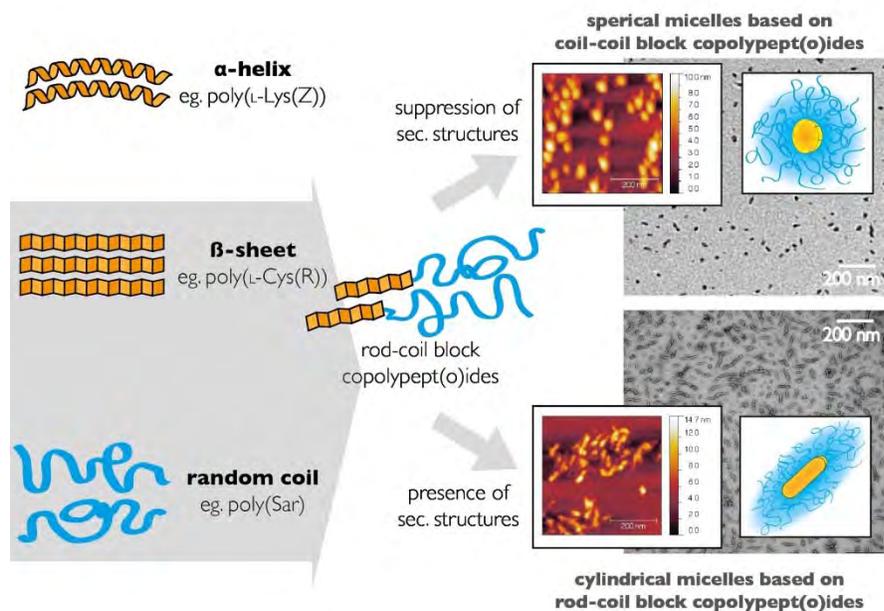
Current polyurethane (PU) foam flame retardant (FR) treatments involving halogenated molecules are facing scrutiny due to their potentially negative environmental impact. Layer-by-layer (LbL) assembly offers a path to uniformly coat every surface of open-celled PU foam using a water-based coating and benign ingredients. This study combines two different coating systems that synergistically create a powerful, environmentally-benign flame retardant. A bilayer system of chitosan (CH) and vermiculite (VMT) clay provides a nanobrick wall exoskeleton that protects the polyurethane long enough for a carbonaceous char forming system of CH and ammonium polyphosphate (APP) to activate and form a thicker intumescent char layer. Stacking these two recipes allows the foam to self-extinguish when exposed to a butane torch without any flame spread or shrinkage of the foam, two things commonly observed with either coating alone. This nanocoating acts as an environmentally-benign template for protecting complex substrates, especially those found in household furnishings.



## POLY 242: Shape-control in self-assembly of bioreducible polypept(o)ides

**Olga Schaefer**, [olga.schaefer@uni-mainz.de](mailto:olga.schaefer@uni-mainz.de), David Huesmann, Kristina Klinker, Matthias Barz. Institute of Organic Chemistry, Johannes Gutenberg-University Mainz, Mainz, Germany

We report on polypept(o)ides based on hydrophilic poly(sarcosine) and hydrophobic poly(*S*-thiosulfonyl-L-cysteine), their secondary structure controlled self-assembly into nanoparticles and core cross-linking by disulfide bond formation. The formed disulfide bonds respond to intracellular reduction potentials and hence provide stability in extracellular medium while degrade inside the cell.

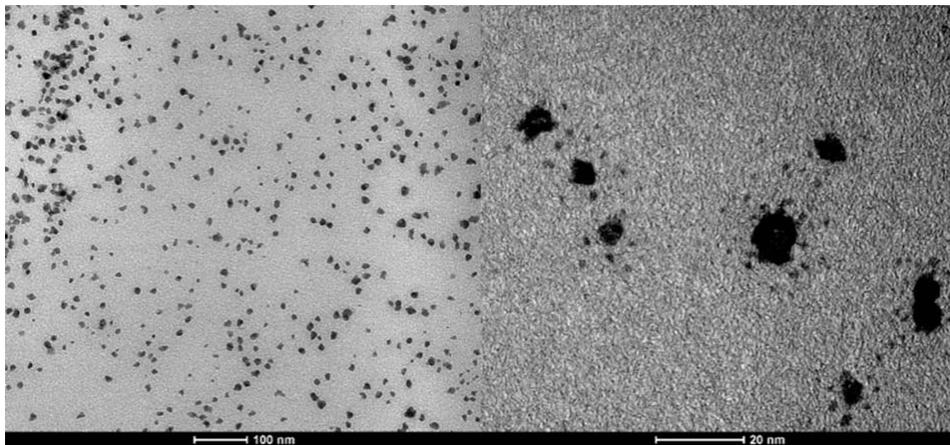


Morphology of self-assembled rod-coil polypept(o)ides based on the occurrence or suppression of secondary structures inside the core as confirmed by AMF and TEM imaging.

## **POLY 243: *In Situ* formation of nanoparticles in polymer matrices using thermal and photothermal processing**

**Fan Zeng**, *fanwzeng@jhu.edu*, James Spicer. *Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland, United States*

A scalable, synthesis process has been used to create nanostructures in polymer matrices to form polymer matrix nanocomposites (PMNCs) with specific photochemical functionalities. Various metal and metal oxide nanoparticles exhibiting catalytic, photocatalytic and photochromic behaviors have been produced directly in polymers using a modified vapor deposition method. Under different processing conditions, the resulting composites display various optical absorption characteristics. We investigate the effects of different thermal processing parameters, such as processing temperatures and dwell times (for vaporization and decomposition of precursors), on nanoparticle size and distribution. We also incorporate laser irradiation as localized heating sources for the polymer matrix in the synthesis process to actively control the precursor diffusional pathways. Spatially adjusting the precursor concentrations in the matrix allows for control of nanoparticle formation and results in a patterned nanocomposite. These results demonstrate the possibility of synthesizing nanocomposites with specific nanoparticle location, size, and distribution in a polymer matrix and outline processes that can be used to pattern materials with tailored photochemical properties.

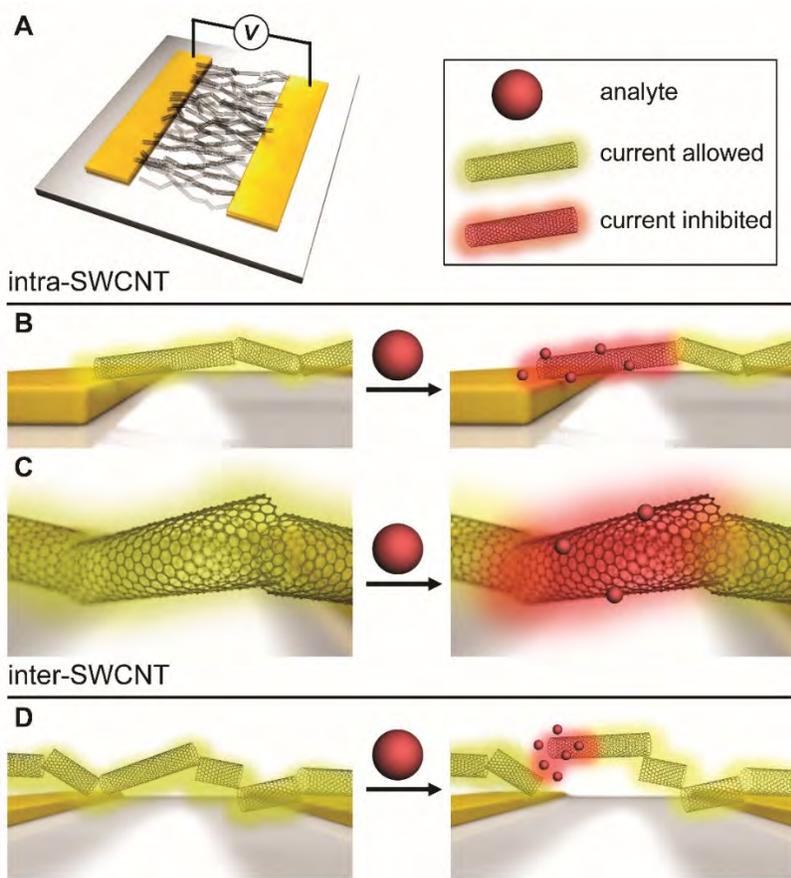


TEM Micrographs of PMNC with  $\text{WO}_3$  Nanoparticles (2 processing cycles)

## POLY 244: Carbon nanotube-polymer composites for chemical warfare agent sensing

**John F. Fennell<sup>2</sup>**, *jfennell@mit.edu*, **Hitoshi Hamaguchi<sup>3</sup>**, **Timothy M. Swager<sup>1</sup>**. (1) MIT, Cambridge, Massachusetts, United States (2) Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (3) Japanese Synthetic Rubber Company, Tokyo, Japan

Chemical warfare agents (CWA) continue to present a threat to U.S. military personnel in operational areas all over the world. Reliable measurements of CWAs are critical to contamination detection, avoidance and remediation. The current deployed systems are accurate but are also large and expensive. Chemiresistors may indeed provide a solution to this operational requirement. Specifically, chemiresistive sensors using single-walled carbon nanotubes (SWCNT) coupled with polythiophene polymer derivatives have been shown to have high sensitivity, endurance and have a simple fabrication process. To improve sensitivity and stability, we have endeavored to develop a SWCNT / poly (3,4-ethylenedioxythiophene (PEDOT) derivative sensor system. Additionally, we have shown that the inclusion of a hexafluoroisopropanol (HFIP) group as a receptor enhances sensitivity to a nerve agent mimic (dimethylmethylphosphonate, DMMP).



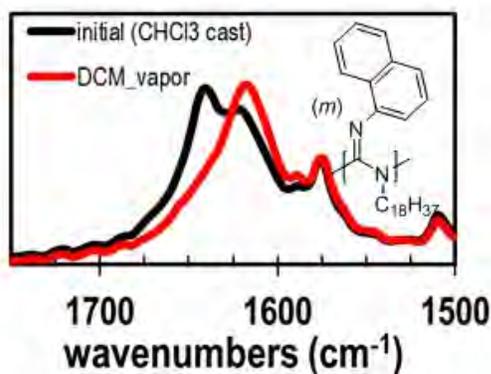
Possible SWCNT-Analyte Conduction Mechanisms

## POLY 245: Serendipitous discovery of an unlikely polycarbodiimide switch and recent application to VOC sensing

**Raymond Campos**<sup>5,1</sup>, [raymond.campos.32@gmail.com](mailto:raymond.campos.32@gmail.com), James F. Reuther<sup>3,1</sup>, Dennis Kovalev<sup>2</sup>, Nimmy R. Mammootil<sup>1</sup>, Christian Merten<sup>4</sup>, Bruce M. Novak<sup>2</sup>. (1) Chemistry, The University Of Texas At Dallas, Dallas, Texas, United States (2) School of Natural Sciences Mathematics, University of Texas at Dallas, Richardson, Texas, United States (3) Chemistry, The University of Texas at Austin, Austin, Texas, United States (4) a Fakultat fur Chemie und Biochemie, Ruhr-Universitat Bochum, Bochum, Germany (5) Aerospace Systems Directorate, ERC, Inc., Air Force Research Laboratory, Edwards, California, United States

The increasing precision of the primary (e.g. microstructure sequence, molecular weight dispersity, etc.) and secondary structure (helical sense, persistence length, thermal stability, etc.) of polycarbodiimides has resulted in chiroptical switching without the use of chiral monomers, solvents, or additives, and without any obvious sensing functional groups on alternating pendant groups. The initial design and chiroptical properties of poly(*N*-(*n*-octadecyl)-*N'*-(1-naphthyl)carbodiimide), or polyNOC, will be described along with previous studies elucidating the presence of an equilibrium of expanded (state A) and contracted (state B) conformations.

Recent characterization of polyNOC surfaces and bulk phases will be presented that suggests the state A/B population is concentration independent and can be kinetically trapped in the solid-state. Once trapped in the solid state the state A/B population can be reversibly modulated with solvent exposure. VOC sensing using the state A/B population of polyNOC films will be introduced for the first time, using ATR-FTIR spectroscopy for transduction. An example of biasing the population of polyNOC in the solid state is shown in figure 1 using chloroform and dichloromethane vapor. Additional examples will be presented including non-polar hydrocarbons and common laboratory solvents. Complimentary differential scanning calorimetry and grazing incidence, X-ray diffraction studies will also be presented that further elucidate the conformation switching mechanism.

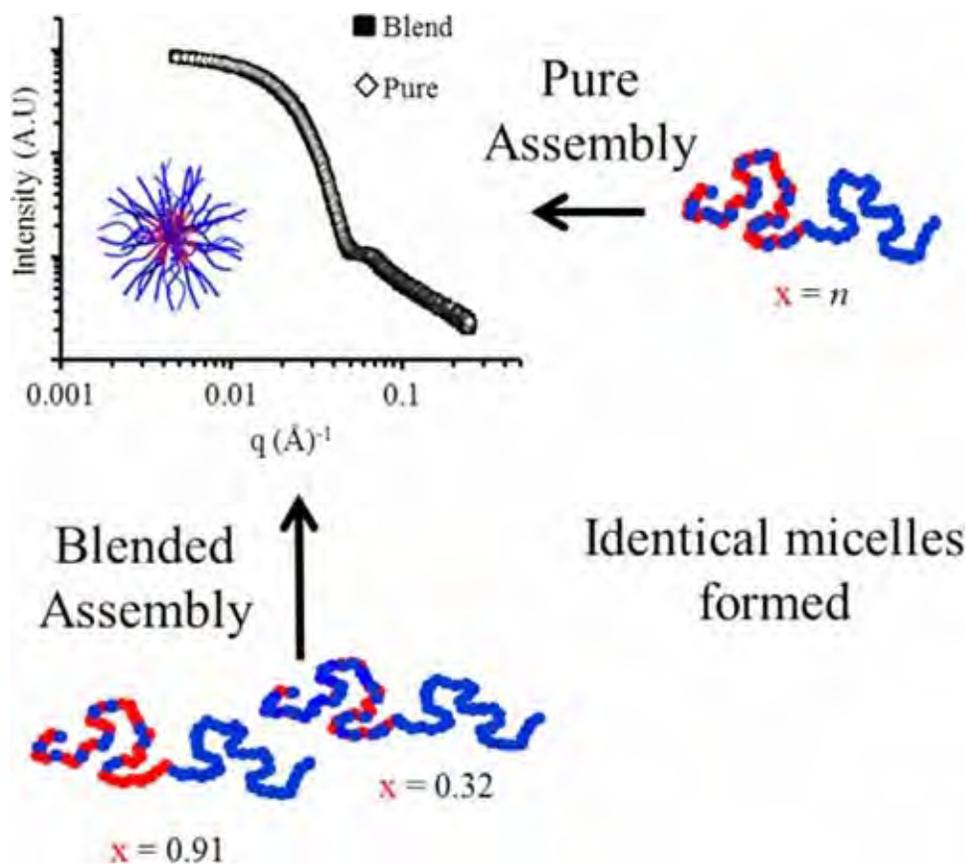


Infrared spectrum of the imine stretching region of (M)-polyNOC (inset structure) cast from chloroform (black trace) and after exposure to dichloromethane vapor (red trace).

## POLY 246: Blending approach for the assembly of micellar nanoparticles

**Daniel Wright**<sup>3</sup>, *d.b.wright@warwick.ac.uk*, **Joseph P. Patterson**<sup>3</sup>, **Nathan C. Gianneschi**<sup>3</sup>, *christophe.chassenieux*<sup>2</sup>, *Olivier Colomban*<sup>2</sup>, *Rachel K. O'Reilly*<sup>1</sup>. (1) Dept of Chemistry, University of Warwick, Coventry, United Kingdom (2) PCI, Université du Maine, Le Mans, France (3) Chemistry and Biochemistry, University of California, San Diego, San Diego, California, United States

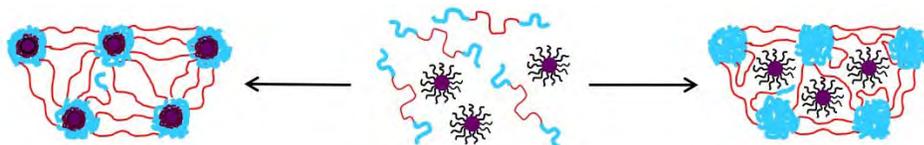
Polymer solution self-assembly is a simple strategy for the preparation of smart yet complex nanomaterials. To access specific assemblies extensive synthesis of the polymers is habitually required. Nevertheless, we show by controlling the synthesis of diblock copolymers a range of nanostructures under thermodynamic control can be produced. In addition we show that blending two diblock copolymers that form thermodynamically controlled structures can be used as a method to access a range of assemblies, with intermediate characteristics between the parent polymers. These blend nanostructures were shown to be identical to those formed with the directly synthesized copolymer, of the same composition, by an array of analytical techniques. This new assembly approach presents researchers a simple and accessible route to access precision self-assembled structures under thermodynamic control. The utility of this method is then highlighted with a catalytically active demonstrator system.



## POLY 247: Hybrid hydrogels of thermosensitive block copolymers and hairy nanoparticle

**Bin Hu**, *bhu6@vols.utk.edu*, Roger A. Wright, Daniel M. Henn, Sisi Jiang, Bin Zhao.  
Department of Chemistry, University of Tennessee, Knoxville, Tennessee, United States

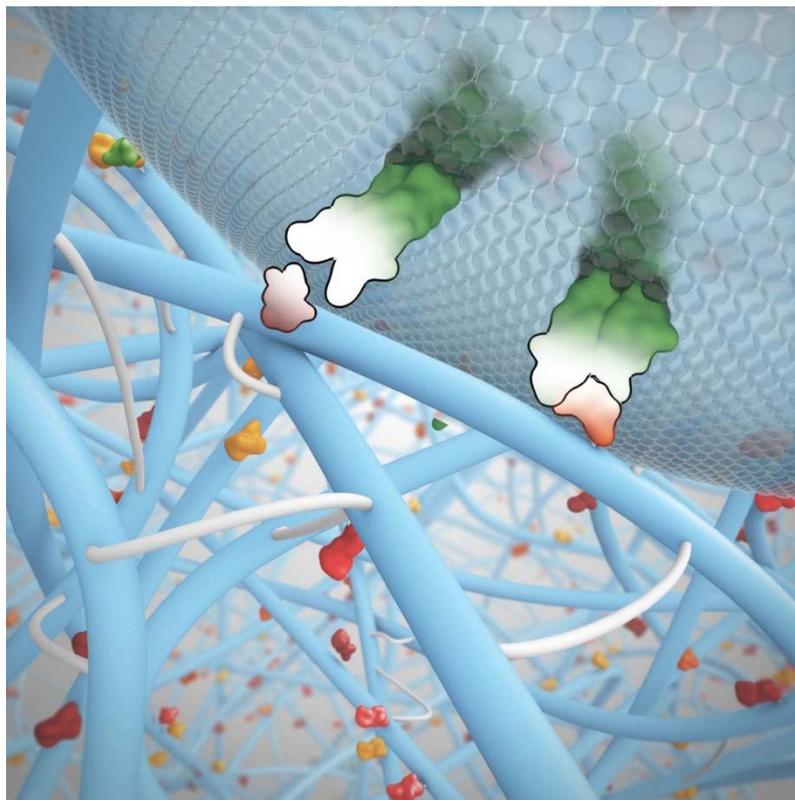
Thermosensitive block copolymer hydrogels have great potential in a wide variety of applications. Rationally incorporating nanoparticles (NPs), which often exhibit intriguing properties that are not associated with polymers, into hydrogels can produce composite hydrogels with synergistic effects. We have developed a method to control the spatial location of NPs in hybrid hydrogels of thermosensitive ABA triblock copolymers and polymer brush-grafted NPs (hairy NPs) via the tuning of the lower critical solution temperature of hairy NPs ( $LCST_{NP}$ ) relative to that of the thermosensitive block copolymers ( $LCST_{ABA}$ ). When the  $LCST_{NP}$  is similar to the  $LCST_{ABA}$ , the NPs reside in the core of micelles upon heating. When the  $LCST_{NP}$  is significantly higher, the NPs are located outside the core of micelles as confirmed by FRET. The effects of different NP locations and  $LCST_{NP}$  of hairy NPs on gel properties are studied by rheometry. The sol-gel transition temperature ( $T_{sol-gel}$ ) and dynamic storage modulus  $G'$  of the gels with NPs inside the core of micelles do not change much with increasing NP-to-polymer mass ratio. In contrast, for the hydrogels containing NPs with significantly higher  $LCST$ s, the  $G'$  decreases appreciably with increasing NP-to-polymer ratio. A sharp increase of  $G'$  is observed around the  $LCST_{NP}$  for all hybrid gels with NPs initially located in the interstitial space. This is believed to be caused by the collapsed brushes on NPs adsorbing dangling or loop polymer chains, increasing the density of bridging chains in the gel network.



## POLY 248: Bioinspired supramolecular polymers

**Matthew B. Baker**<sup>2,1</sup>, [dnbgy4@gmail.com](mailto:dnbgy4@gmail.com), **Lorenzo Albertazzi**<sup>3,1</sup>, **Christianus Leenders**<sup>1</sup>, **Anja Palmans**<sup>1</sup>, **Egbert W. Meijer**<sup>1</sup>. (1) Institute for Complex Molecular Systems, Eindhoven University of Technology, Eindhoven, Netherlands (2) MERLN, Maastricht University, Maastricht, Netherlands (3) IBEC, Barcelona, Spain

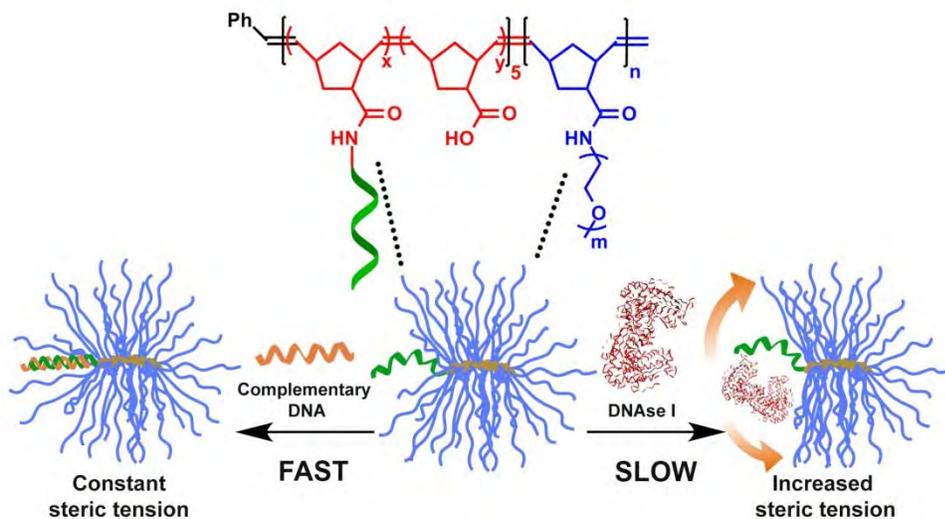
Supramolecular polymers hold great promise to form the foundation of our next generation of smart materials. Held together by weak, dynamic, and responsive non-covalent interactions, the fundamental forces that enable supramolecular polymers are also heavily utilized in biological systems. Due to this “dynamic reciprocity,” it is hypothesized that bioinspired supramolecular materials can have a distinct advantage with interfacing dynamic and complex biological systems. Utilizing the popular 1,3,5-benzenetricarboxamide (BTA) supramolecular motif, I will discuss a series of water soluble supramolecular fibers that have been designed and explored towards use as a next generation biomaterial. In addition to several novel methods of characterization (STORM and FRET), these BTA based supramolecular polymers have provided key insight into the behavior and design of supramolecular systems. Furthermore, knowledge gained has been used to create extracellular matrix mimics for intestinal organoid culture and growth. Insight from these studies as to the limiting factors in the design and use of supramolecular biomaterials will also be discussed.



## POLY 249: Utilizing the steric congestion of brush polymers: From nucleic acid delivery to self-assembly

**Ke Zhang**, *k.zhang@neu.edu*, Xueguang Lu, Xuyu Tan, Fei Jia. *Chemistry and Chemical Biology, Northeastern University, Boston, Massachusetts, United States*

Brush polymers have a dense arrangement of side chains, which induce steric congestion. We have developed a brush polymer-oligonucleotide conjugate system, which relies upon the steric congestion to achieve interesting properties that are absent for free or polyplexed oligonucleotides. These properties include selectivity towards complementary strands vs. proteins, and directionality in binding with other particles. We have applied these properties to the design of new structures for DNA delivery and for programmable materials self-assembly.

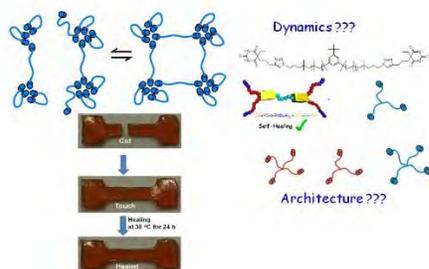


## POLY 250: Responsive polymers by supramolecular design : Self-healing materials and pressure sensitive chemistry

Senbin Chen, Philipp Michael, Diana Döhler, **Wolfgang H. Binder**,  
wolfgang.binder@chemie.uni-halle.de. Faculty of Natural Sciences II, Martin-Luther  
University Halle-Wittenberg, Halle, Germany

Self-healing materials have created a new vision in material science, together with the exploitation which basic chemical and physical principles<sup>1-3</sup> display upon healing systems. In particular, the introduction of supramolecular bonds (such as hydrogen-bonds)<sup>4</sup> into linear, branched and crosslinked polymers enables multiple SH principles taking into account the relevant timescales of self-healing<sup>5</sup>. The current presentation addresses principles of self-healing polymers active via supramolecular healing concepts, combining healing principles to obtain multiple healing-cycles together with a the achievement of mechanically stronger material<sup>6</sup>. Issues of linear-, star- and partially crosslinked supramolecular systems<sup>6-8</sup> are addressed, studying the influence of the supramolecular polymers' architecture onto the self-healing properties of the resulting material. Finally, pressure sensitive supramolecular polymers are presented and discussed, where pressure is inducing rupture of supramolecular bonds and in turn generates catalytic activity<sup>9</sup> able to provide a method to detect stress-detection within solid materials.

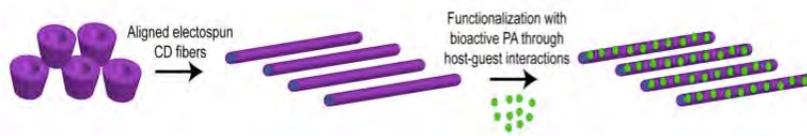
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## POLY 251: Functionalization of electrospun polycyclodextrin fibers with bioactive peptide molecules and their biological applications

**Seren Hamsici**, *seren.hamsici@bilkent.edu.tr*. Bilkent University, ANKARA, Turkey

Electron-spinning technique enable to obtain cyclodextrin (CD) fibers with high surface area and porosity. These fibers can be functionalized through host-guest chemistry via interactions of hydrophobic CD cavity with bioactive peptide molecules. In this study, aligned and non-aligned electrospun CD fibers were functionalized with laminin mimetic peptide molecules as being complex bioactive scaffolds for neural tissue engineering. The physical and chemical characterizations of the bioactive peptide functionalized fibrous CD scaffold are completed using different techniques such as FT-IR, ITC binding experiment, XPS and elemental analysis etc. In addition, we aim to understand the effects of both alignment and bioactivity of the designed fibrous structures on cellular behaviors including viability, adhesion and neural differentiation.



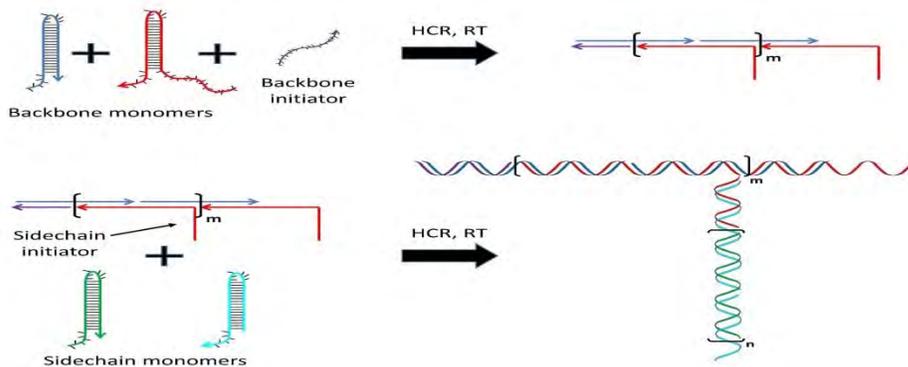
Schematic representation of host-guest interactions with electrospun and aligned CD fibers with bioactive peptide epitope

## POLY 252: Design and characterization of supramolecular DNA bottlebrushes

**Laura Lanier**<sup>2</sup>, [llanier@mail.pse.umass.edu](mailto:llanier@mail.pse.umass.edu), **Harry Bermudez**<sup>1</sup>. (1) University of Massachusetts, Amherst, Massachusetts, United States (2) Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, Massachusetts, United States

Through the use of a self-assembly technique called hybridization chain reaction (HCR), we have created noncovalent supramolecular bottlebrushes of DNA. In an HCR scheme two single-stranded DNA (ssDNA) monomers isothermally react in the presence of an initiator ssDNA to form a nicked supramolecular polymer of DNA. Analogous to chain polymerization, an initiator reacts with a monomer, thereby activating the monomer to react with the other monomer. This chain reaction continues until monomer supply is exhausted. The ratio of monomer to initiator concentration is inversely proportional to molecular weight, allowing for control over size.

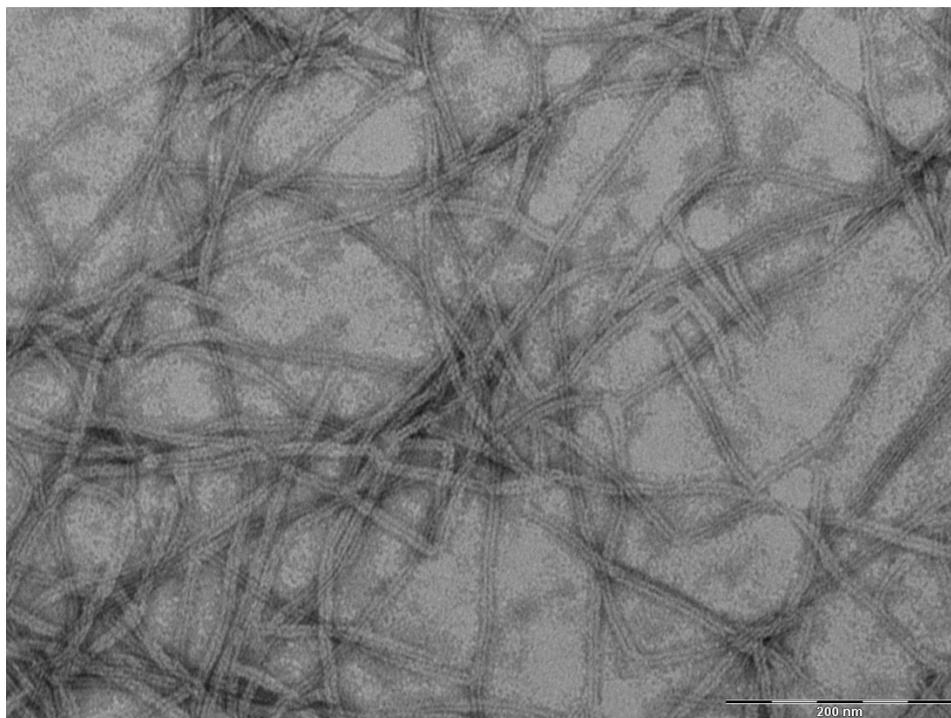
We have created a supramolecular bottlebrush of DNA held together by noncovalent interactions by rational design of ssDNA monomers. To create supramolecular bottlebrushes, sequences for the backbone monomers were adapted from literature to add a sidechain initiating sequence. The sidechain monomer sequences were designed using NUPACK. Assembly of the backbone into a supramolecular polymer by HCR was confirmed by polyacrylamide gel electrophoresis (PAGE). PAGE was also used to confirm the independent assembly of the sidechain supramolecular polymer. Addition of sidechain monomers to pre-assembled supramolecular backbone polymers demonstrates a product with lower mobility in PAGE, suggestive of a larger structure and consistent with the formation of a bottlebrush. This bottlebrush structure was confirmed by PAGE to be distinct from the mixture of backbone and sidechain supramolecular polymers, ruling out nonspecific association. Because these bottlebrushes are made by HCR, both length and radius of the brushes are tuned by changing the stoichiometry of the monomers. Thus these noncovalent supramolecular polymers allow for variation of characteristic dimensions. Dynamic light scattering is being used to study the size distribution of the bottlebrushes. The bottlebrushes will also be imaged by transmission electron microscopy and/or atomic force microscopy to directly visualize the distribution of radii and lengths.



## **POLY 253: Disassembly and immolation pathways of drug-based supramolecular polymers**

*Pengcheng Zhang<sup>2</sup>, **Honggang Cui**<sup>1</sup>, cuihonggang@gmail.com, Ran Lin<sup>3</sup>. (1) 221 Maryland Hall, JHU Chemical and Biomolecular Engineering, Baltimore, Maryland, United States (2) SIMM, Shanghai, China (3) Johns Hopkins University, Baltimore, Maryland, United States*

The ability of supramolecular nanostructures to break down in response to physiological stimuli is a prerequisite for their use as drug or imaging agent carriers. The pathways and kinetics of disassembly would have an important impact on cargo release rates and their ability to fulfill their biological roles. In this presentation, I will report our recent progress in understanding of the disassembly and immolation pathways of drug-based supramolecular polymers. Our results revealed that the reducing agent glutathione could directly attack supramolecular assemblies at defects of packing, which leads to a cascade of nanostructures breakdown and reassembly.



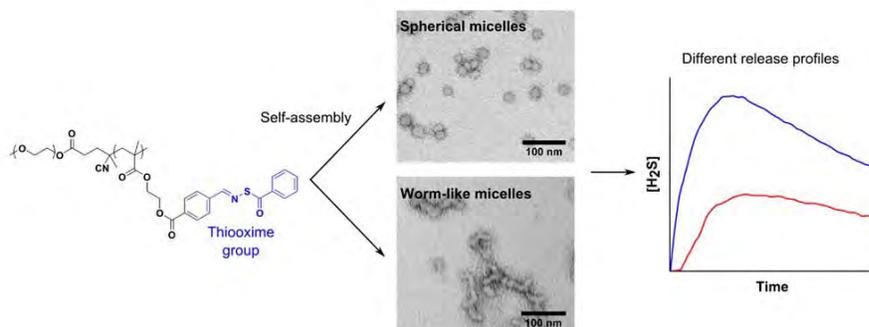
## POLY 254: Morphological control of the release profile of H<sub>2</sub>S-releasing micelles

Jeffrey Foster<sup>1</sup>, jefff23@vt.edu, John B. Matson<sup>2</sup>. (1) Virginia Tech, Blacksburg, Virginia, United States (2) Chemistry, Virginia Tech, Blacksburg, Virginia, United States

Gasotransmitters such as hydrogen sulfide (H<sub>2</sub>S) are biologically produced signaling gases with physiologically relevant activities. For example, H<sub>2</sub>S suppresses oxidative stress, modulates inflammation, and protects endothelial tissue via vasodilation.<sup>1</sup> In addition to these potential therapeutic targets, the short *in vivo* half-life of H<sub>2</sub>S coupled with its capability to permeate cell membranes makes H<sub>2</sub>S an attractive alternative to traditional small molecule therapeutics. To achieve a desired therapeutic outcome *in vivo*, H<sub>2</sub>S must be delivered locally and at the correct concentration. Therefore, the vehicle of delivery must be rationally designed to release H<sub>2</sub>S at the desired rate. A number of H<sub>2</sub>S-releasing compounds have been reported including S-arylothiooximes, which release H<sub>2</sub>S controllably (sensitive to thiooxime structure) in response to thiol functionality.<sup>2</sup> Thiooximes have been successfully conjugated to methacrylate polymers with pendant aldehyde functionality in a post-polymerization modification approach.<sup>3</sup> We discuss here thiooxime-functionalized block copolymers that self-assemble in aqueous solution to form stable colloidal dispersions. The kinetics of H<sub>2</sub>S-release can be tuned by manipulating either the thermal properties of the parent polymer (i.e., glass transition temperature) or the solution morphology of the assembly (i.e., spheres, worms, or vesicles). In the latter case, multiple release profiles can be achieved using a single polymer simply by changing the type of supramolecular assembly. In general, the release reactions occur on the timescale of days, in contrast to most H<sub>2</sub>S-releasing small molecule compounds that exhibit full release in a few hours.

### References

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**POLY 255: Microvascular materials for carbon capture and self-improvement:  
How do we make materials that make themselves better?**

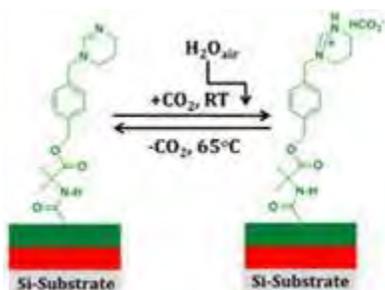
**Aaron P. Esser-Kahn**<sup>1</sup>, *apekay@gmail.com*, **Maya Kleiman**<sup>3</sup>, **Kyle Brubaker**<sup>2</sup>, **Du T. Nguyen**<sup>4</sup>. (1) *Test, Irvine, California, United States* (2) *UCI, Irvine, California, United States* (3) *Natural Sciences II, Univ California Irvine, Irvine, California, United States* (4) *Physics, University of California, Irvine, Irvine, California, United States*

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. We are focused on mass transfer applications for the capture of CO<sub>2</sub>. 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. We will also focus on the development of a novel process for shaping microstructures which can be used to improve the mass transfer capabilities of the exchangers using reaction and diffusion programmed inside of materials.

## POLY 256: Reversible CO<sub>2</sub> capture from an amidine functionalized polymer thin film

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The ability of block copolymers (BCPs) to spontaneously organize into microphase segregated structures in solution and thin films are the origin of many useful and potential applications. Dually-reactive BCPs comprised of poly(glycidyl methacrylate) (PGMA) and deuterated poly(vinyl dimethyl azlactone) (PVDMA<sub>d6</sub>), denoted PGMA-*b*-PVDMA<sub>d6</sub>, were utilized to generate surface scaffolds in which film thickness, surface grafting density, and functionality can be tailored. The reactive pendant group of PVDMA<sub>d6</sub> was functionalized with a benzyl alcohol derivative bearing a cyclic amidine group “4-(N-methyltetrahydropyrimidine) benzyl alcohol” (MTHBPA). Amidines are highly basic functional moieties which have been shown to be able reversibly capture CO<sub>2</sub> at room temperature. The ability of the functionalized polymer film to reversibly capture and release CO<sub>2</sub> was investigated by attenuated total reflectance infrared spectroscopy (ATR-FTIR), quartz crystal microbalance (QCM), and neutron reflectometry. ATR-FTIR was utilized to monitor the peak at 1650 cm<sup>-1</sup> which is attributed to the formation of a resonance stabilized amidinium structure [-N-CH=N<sup>+</sup>- ↔ -N<sup>+</sup>=CH-N-] upon CO<sub>2</sub> binding. Changes in film mass as a function CO<sub>2</sub> binding was measured by QCM. In addition, preliminary neutron reflectometry data indicate changes to the overall film structure upon CO<sub>2</sub> binding and release.



Reversible CO<sub>2</sub> capture with PGMA-*b*-dPVDMA-MTHBPA thin film.

## POLY 257: Improved carbon dioxide separation performance in amidoximated polydimethylsiloxane-norbornene membranes

**Tao Hong**<sup>3</sup>, [thong1@vols.utk.edu](mailto:thong1@vols.utk.edu), Sabornie Chatterjee<sup>3</sup>, Shannon M. Mahurin<sup>1</sup>, De-en Jiang<sup>2</sup>, Brian K. Long<sup>3</sup>, Jimmy W. Mays<sup>3,1</sup>, Alexei P. Sokolov<sup>3,1</sup>, Tomonori Saito<sup>1</sup>. (1) Chemical Sciences Division, Oak Ridge National Laboratory, Knoxville, Tennessee, United States (2) Department of Chemistry, University of California, Riverside, Riverside, California, United States (3) Department of Chemistry, University of Tennessee, Knoxville, Tennessee, United States

A climate change caused by a greenhouse effect is one of the most challenging problems we face today, and the development of high performance materials for CO<sub>2</sub> separation and capture will significantly contribute to a solution of the problem. Passive membranes present one of the promising and energy efficient solutions. However, materials with high CO<sub>2</sub> permeability and good CO<sub>2</sub>/N<sub>2</sub> selectivity are needed for the use in these membranes, and only a few materials have been developed to meet the requirement. Based on our previous study on cross-linked (Bicycloheptenyl) ethyl terminated polydimethylsiloxane (PDMSPNB) membranes[1], we herein report the work on the incorporation of the CO<sub>2</sub>-philic amidoxime group into the PDMSPNB matrix. The membranes were synthesized by using *in-situ* ring-opening metathesis polymerization followed by post modification. The degree of amidoximation was controlled by varying the functionalization time and significantly affected both CO<sub>2</sub> permeability and CO<sub>2</sub>/N<sub>2</sub> selectivity. Our best performing amidoximated PDMSPNB membranes showed excellent CO<sub>2</sub> permeability and achieved the performance above the Robeson upper bound line (CO<sub>2</sub> permeability ~8,000 Barrer and CO<sub>2</sub>/N<sub>2</sub> ~18). The elemental analysis, gas solubility and differential scanning calorimetry measurements are carried out to further elucidate the key parameters leading to this excellent performance. The study contributes to foster the fundamental understanding of gas transport through polymer membranes for CO<sub>2</sub> separation as well as many other applications.

[1] Hong et al. DOI:10.1002/cssc.201500903

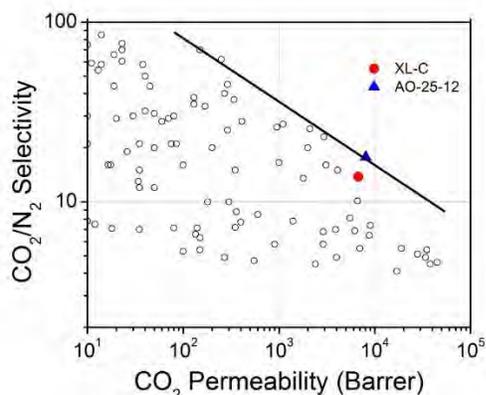
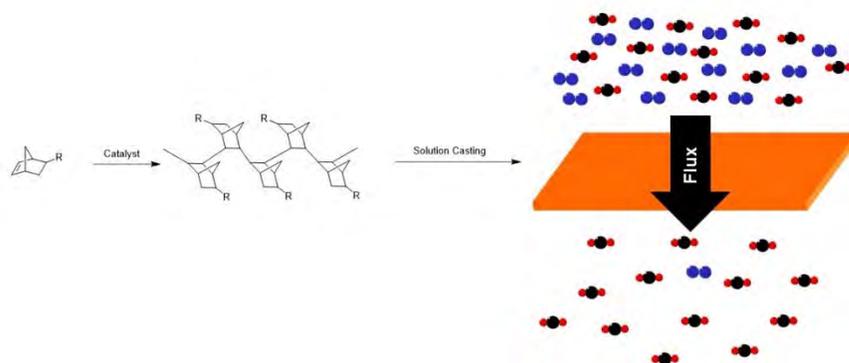


Figure 1. Representative data of cross-linked PDMSPNB (XL-C) [1], and PDMSPNB amidoxime membranes (AO-25-12) in the Robeson plot.

## POLY 258: Development and characterization of advanced gas separation membranes using vinyl-added polynorbornenes bearing CO<sub>2</sub>-philic functionalities

**Kevin R. Gmernick<sup>2</sup>**, *krger6910@gmail.com*, **Eunice Hong<sup>2</sup>**, **Tao Hong<sup>2</sup>**, **Tomonori Saito<sup>1</sup>**, **Brian K. Long<sup>2</sup>**. (1) *Chemical Sciences Division, Oak Ridge National Laboratory, Knoxville, Tennessee, United States* (2) *Dept of Chemistry, University of Tennessee, Knoxville, Tennessee, United States*

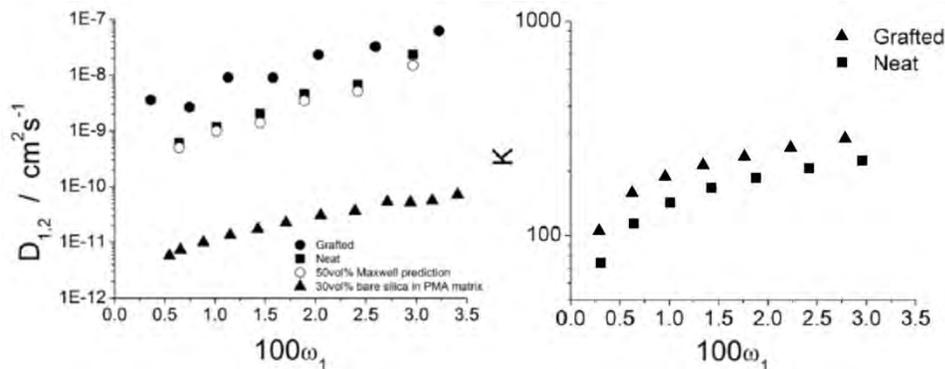
With federal incentives calling for widespread reductions in greenhouse gas emissions over the next few decades, the power sector is in dire need of cost effective solutions to minimize carbon dioxide emissions without hindering their efficiency. Amongst the various methods used for the separation of carbon dioxide from gas mixtures, polymer membranes operate by a passive diffusion mechanism that will significantly reduce operating costs when compared to other methods such as physical adsorption or cryogenic distillation. However, separating carbon dioxide from gas mixtures that are roughly 75 percent nitrogen using polymer membranes remains a grand challenge due to their similar molecular size, kinetic diameters of 3.30 Å and 3.64 Å respectively. We present polymer membranes fabricated from high molecular weight, addition-type polynorbornenes that were functionalized with CO<sub>2</sub>-philic pendant groups to enhance the diffusion of CO<sub>2</sub> gas molecules while hindering the diffusion of nitrogen. These polymer membranes exhibit excellent CO<sub>2</sub>/N<sub>2</sub> selectivity, can be recycled due to their excellent solubility in common organic solvents, and are integral in the design of more complex membrane materials



## POLY 259: Polymer nanocomposite membrane for gas separation

**Yucheng Huang**<sup>1</sup>, butan15@gmail.com, Eileen Buenning<sup>2</sup>, Connor Bilchak<sup>2</sup>, Lei Wang<sup>1</sup>, Sanat Kumar<sup>2</sup>, Brian C. Benicewicz<sup>1</sup>. (1) Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina, United States (2) Chemical Engineering, Columbia University, New York, New York, United States

Polymer membranes are commercially utilized for gas separations, e.g., removal of CO<sub>2</sub> from natural gas, H<sub>2</sub>/CO<sub>2</sub> separation in hydrocarbon fuel processing, etc. The membrane should have both good permeability and selectivity. However, these polymer membranes are limited, as defined by Robeson's upper bound correlation. Furthermore, the current polymer membranes exhibit an aging phenomenon, which can decrease their efficiency. Mixing the polymer matrix with inert fillers can affect the diffusivity and solubility of the polymer membrane. It was reported that the diffusivity of n-alkyl acetate decreased in poly(methyl acrylate) (PMA) filled with silica nanoparticles (NPs), which was consistent with conventional composite theory. Motivated by recent work in filled polymer systems, we are investigating the use of membranes formed by polymer grafted nanoparticles for gas separation. In this work, we synthesized polymer membranes using PMA-grafted silica nanoparticles, prepared by RAFT polymerization. The results showed increases of both diffusivity and solubility of ethyl acetate in these films.



Diffusivity and solubility of ethyl acetate in membrane

## **POLY 260: Ionically-crosslinked polymer and nanoplatelet multilayer films for gas separation**

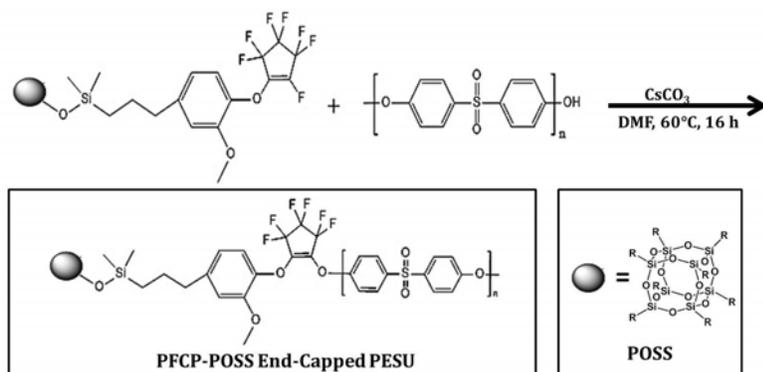
**Jaime C. Grunlan**<sup>1</sup>, [jgrunlan@tamu.edu](mailto:jgrunlan@tamu.edu), Benjamin A. Wilhite<sup>2</sup>. (1) Texas A M Univ, College Station, Texas, United States (2) Texas AM University, College Station, Texas, United States

The production of inexpensive, high purity hydrogen remains a critical challenge to improving the sustainability of fossil fuels and for realizing renewable and clean energy sources capable of displacing fossil fuels. Polymeric gas separation membranes combining low production costs with robust mechanical properties have found broad industrial application for O<sub>2</sub> and N<sub>2</sub> enrichment of air, upgrading of natural gas and hydrogen recovery from ammonia. In the absence of structure (i.e. in amorphous glassy or rubbery films), increasing the free volume of size-selective polymer membranes improves the permeability at the cost of reducing the permselectivity. This translates to an upper bound in separation performance achievable by dense, homogeneous and amorphous polymeric films. We recently demonstrated that layer-by-layer (LbL) deposition provides a robust, low-cost means to introduce size-selective functionality via manipulation of polymer processing conditions. Extension of the LbL assembly technique to gas purification membranes promises the ability to tune overall gas permeability and permselectivity through manipulation of film nanostructure by varying deposition conditions. The alternate deposition of branched polyethylenimine (PEI) and poly (acrylic acid) (PAA) produces a “scrambled salt” structure, resulting in a highly interpenetrating network of high density which exhibits size selective gas separation in excess of Robeson’s ‘upper boundary,’ which we attribute to the structure imparted by a high degree of ‘ionic-crosslinking.’ Specifically, this ionically crosslinked assembly exhibits H<sub>2</sub>/N<sub>2</sub> and H<sub>2</sub>/CO<sub>2</sub> selectivities in excess of 1000:1 and 100:1, respectively, which are superior to the properties of any organic, inorganic or mixed-matrix membrane outside of dense metallic (e.g. Pd) or electroceramic (e.g., BaYxCe<sub>1-x</sub>O<sub>3</sub>) films reported in the open literature. This unique thin film overcomes the drawbacks of common polymeric membranes (i.e., low selectivity and poor mechanical properties), making it a significant advance in polymeric membranes for gas separation.

## POLY 261: Functionalization and surface characterization of sulfone polymers with partially fluorinated POSS chain-ends

**Sarah E. Morgan**<sup>4</sup>, *sarah.morgan@usm.edu*, **Katrina M. Knauer**<sup>1</sup>, **Abby R. Jennings**<sup>2</sup>, **Scott T. Iacono**<sup>3</sup>. (1) School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, Mississippi, 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 (4) School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, Mississippi, United States

Polyethersulfone (PESU) and Polysulfone (PSU) are aromatic thermoplastics that demonstrate excellent mechanical properties and hydrolytic stability leading to applications in filtration membranes, biomedical devices, and high performing coatings. However, such applications require precise control of surface composition, structure, and properties. Thus, post processing surface modifications are often necessary in order to meet the performance requirements. We have previously reported the preferential surface segregation of polyhedral oligomeric silsequioxane (POSS) additives in POSS/polyphenylsulfone nanocomposites prepared by melt blending. While POSS segregation can have a dramatic effect of the surface properties of polymer systems, the aggregation size and crystallinity can be difficult to control in a melt blended composite. However, modifying polymer chain ends (CEs) with POSS analogues results in a covalent attachment to the polymer chain and allowing for more uniform POSS surface coverage. Additionally, the preferential segregation of POSS CEs near the air-interface is an alternative route to exploit the desirable POSS properties at the surface of the polymer while maintaining the bulk polymer properties (i.e. low concentration of CE's in the bulk). Herein we report the synthesis and characterization of perfluorocyclopentenyl (PFCP)-POSS end-capped sulfone polymers. PFCP-POSS structure and grafting efficiency of the POSS molecules to the polymer chain was verified via fluorine (<sup>19</sup>F) NMR. Surface composition and depth profiles were measured using X-ray photoelectron spectroscopy (XPS) and neutron reflectivity (NR) techniques. Crystallinity of the POSS modified systems was investigated via X-ray diffraction (XRD). Finally, the surface properties of solution cast films were characterized with quantitative nano-mechanical mapping-atomic force microscopy (QNM-AFM) and contact angle goniometry.

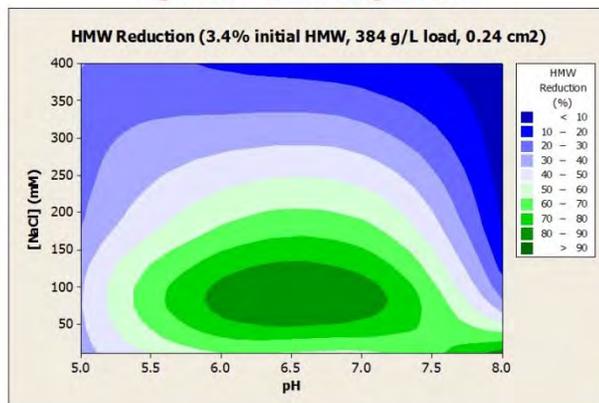


## POLY 262: Novel ligand functionalized membranes for monoclonal antibody purification

**Semra Colak Atan**, [semracolak@gmail.com](mailto:semracolak@gmail.com), Andrew Vail, Jerald K. Rasmussen, Cathy Bothof, George Griesbraber, Federica Sgolastra. 3M Center, 3M, Saint Paul, Minnesota, United States

One of the most challenging areas of biopharmaceutical drug production is the filtration/purification process of therapeutic monoclonal antibodies. Removal of contaminants such as aggregates, host cell proteins, nucleic acids, and viruses is an essential part of this process. To be able to overcome this filtration problem; fine tuning of the ligand chemistry on the filtration media is essential. Currently there are no commercial products on the market that specifically target monoclonal antibody aggregate removal. The main objective of this work is to develop a platform of novel mixed-mode functional monomers and investigate their applicability as ligands for functionalized membranes for biopharmaceutical purification. This presentation will summarize our efforts in synthesis of novel multifunctional monomers as ligands, grafting these ligands to various substrates to generate filtration media, and testing their effectiveness in monoclonal antibody purification.

### High molecular weight impurity removal performance of a multi-modal ligand in flow-through mode:

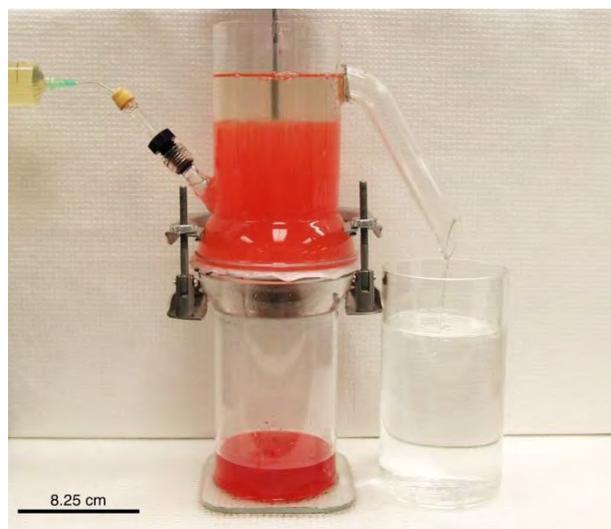


## POLY 263: Hygro-responsive membranes for high efficiency separation of miscible liquids

**Ethan R. Post**<sup>2</sup>, [erpost@umich.edu](mailto:erpost@umich.edu), **Gibum Kwon**<sup>4</sup>, **Arun K. Kota**<sup>4</sup>, **Chao Li**<sup>4</sup>, **Josiah T. Reams**<sup>1</sup>, **Joseph M. Mabry**<sup>1</sup>, **Anish Tuteja**<sup>3</sup>. (1) AFRL/RZSM, Air Force Research Laboratory, Edwards AFB, California, United States (2) Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States (3) Mat Sci Eng HH Dow Bldg, University of Michigan, Ann Arbor, Michigan, United States (4) Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States

Separation of miscible liquid mixtures is critical for a wide variety of industries, including the oil refining and energy industries. For example, crude oil must be fractionated into useable cuts, biofuels extracted from fermentation broth, and impurities removed from final products. Distillation is typically employed for these separations. High-energy costs associated with boiling the entire liquid mixture, similar component boiling points, and azeotropes are some of the challenges currently associated with the distillation process. Liquid-liquid extraction, another technique used for the separation of miscible liquids, solves some of these challenges by adding a second, immiscible extractant to the original mixture and preferentially extracting a component.

In our work, we have developed a novel, energy-efficient, separation methodology that combines liquid-liquid extraction, using surfactant-stabilized emulsions, and solely gravity-driven separation of these emulsions into a single unit operation, using hygro-responsive membranes. The hygro-responsive surface allows polar compounds to pass through, while repelling emulsified non-polar ones. Several systems were investigated to show the process' utility in removing dye, sulfurous compounds, and biofuel impurities. The results from using the surfactant-stabilized emulsions showed significant enhancement in extraction efficiency, and increased partition coefficients, leading to significantly lower separation costs when compared with distillation.



## **POLY 264: Superoleophobic-superhydrophilic surfaces via thiol-ene photopolymerization for efficient oil-water separations**

*Li Xiong, Wei Guo, **Derek L. Patton**, derek.patton@usm.edu. School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, Mississippi, United States*

This presentation will focus on recent efforts in the Patton Research Group to use thiol-ene photopolymerizations to fabricate thin, crosslinked polymer networks with surface properties aimed at high efficiency oil-water separations. Balancing the composition of hydrophilic nanoparticles in a perfluorinated thiol-ene resin provides surfaces in the superoleophobic-superhydrophilic wetting regime. The spray-deposition process provides a scalable route to functional textiles and membranes for highly efficient oil-water separations – even in the presence of common surfactants.

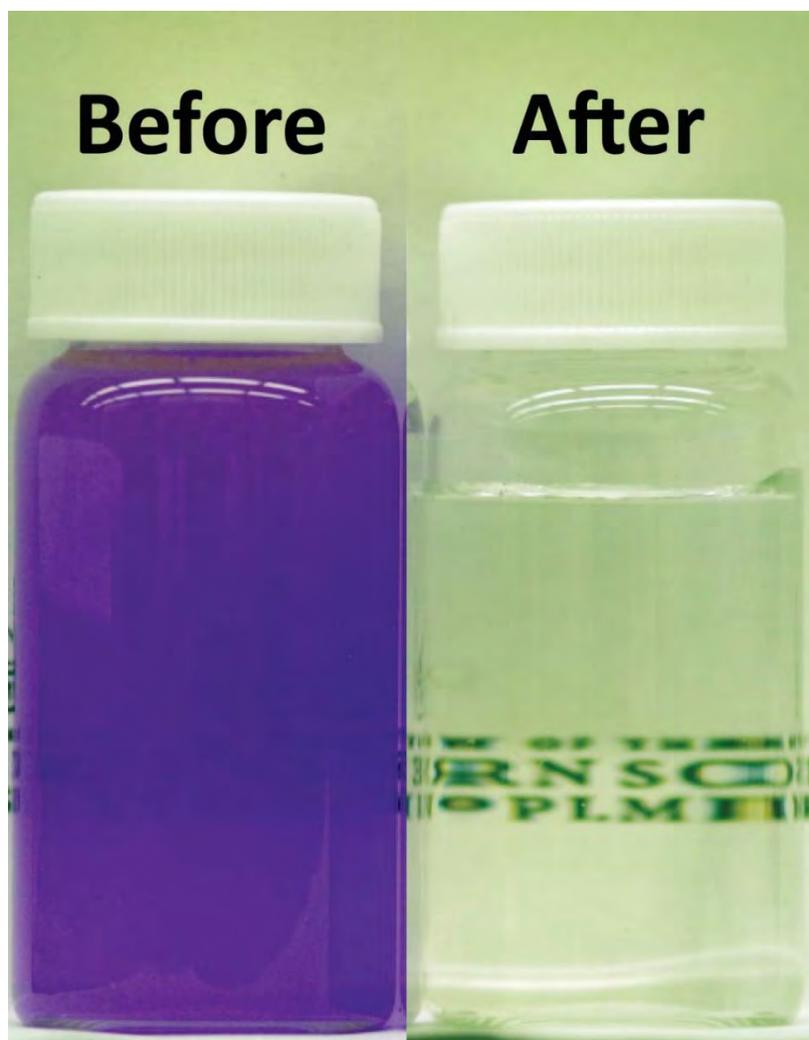


Figure 1. Separation of hexadecane and Nile red-in-water emulsion using a superoleophobic-superhydrophilic membrane fabricated by thiol-ene photopolymerization.

## **POLY 265: Materials design for novel nanotherapeutics based on control of gaseous molecules in vivo\**

**Yukio Nagasaki**<sup>2,1</sup>, [nagasaki@nagalabo.jp](mailto:nagasaki@nagalabo.jp). (1) WPI-MANA, NIMS, Tsukuba, Ibaraki, Japan (2) Department of Materials Science and Medical Sciences, University of Tsukuba, Tsukuba, Ibaraki, Japan

Recently, gaseous molecules such as oxygen, nitric oxide, carbon monoxide and hydrogen sulfide have been reported to play important roles in numerous biological events. New strategies utilizing these gaseous molecules have been proposed. For example, selective elimination of excessively generated reactive oxygen species (ROS) such as superoxide and hydroxyl radical improves versatile serious diseases. Control of nitric oxide generation induces angiogenesis and apoptosis depend on its concentration. This paper deals with our materials design for novel nanotherapeutics based on control in ROS and NO by newly developed nanoparticles.

## POLY 266: Acid-triggered oxidative stress amplifying polymeric micelles: Applications in anticancer and antibacterial therapy

**Dongwon Lee**<sup>1</sup>, *dlee@chonbuk.ac.kr*, **Hoyeon Park**<sup>1</sup>, **Eunbyeong Jung**<sup>1</sup>, **Donghyuck Yoo**<sup>2</sup>. (1) Polymer Nano Science and Technology, Chonbuk National University, Jeonju, Korea (the Republic of) (2) BIN Convergence Technology, Chonbuk National University, Jeonju, Korea (the Republic of)

Reactive oxygen species (ROS) are a collective term of highly reactive chemical species and radicals, including hydrogen peroxide, superoxide anion and hydroxyl radical. Compared to normal cells, cancer cells are under oxidative stress associated with the elevated level of ROS and are more vulnerable to oxidative stress induced by ROS generating agents. In addition, ROS produced by host phagocytes exert antibacterial action against a variety of pathogens and ROS-induced oxidative stress is the governing mechanism for the antibacterial activity of major bactericidal antibiotics. Thus, manipulation of the ROS level provides a logical approach to kill cancer cells and bacteria specifically, without toxicity to normal cells. Cinnamaldehyde, a major active compound of cinnamon, exerts antibacterial and anticancer activity by generating ROS. However, its clinical uses are limited by poor bioavailability and low therapeutic efficacy. In order to overcome these limitations, we developed dual acid-responsive polymeric micelle-forming cinnamaldehyde prodrugs, poly[(3-phenylprop-2-ene-1,1-diyl)bis(oxy)bis(ethane-2,1-diyl)diacrylate]-co-4,4'-(trimethylene dipiperidine)-co-poly(ethylene glycol), termed PCAE. PCAE is designed to incorporate cinnamaldehyde *via* acid-cleavable acetal linkages in its pH-sensitive backbone and self-assemble to form stable micelles which can encapsulate common therapeutic agents. PCAE self-assembles to form micelles which release drug payloads and cinnamaldehyde in pH-dependent manners. PCAE micelles induce apoptotic cell death through ROS generation and exert synergistic therapeutic effects with a payload in a mouse model of tumor xenografts. Moreover, PCAE micelles encapsulating ferrocene could perform Fenton reaction to generate hydroxyl radicals which kill bacteria in a mouse model of bacterial infection. We anticipate that ROS-generating PCAE has great potential for anticancer and antibacterial therapy.

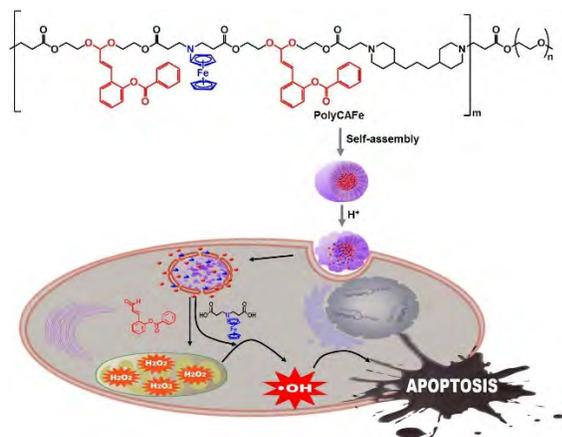


Figure. Acid-sensitive oxidative stress amplifying polymeric micelles

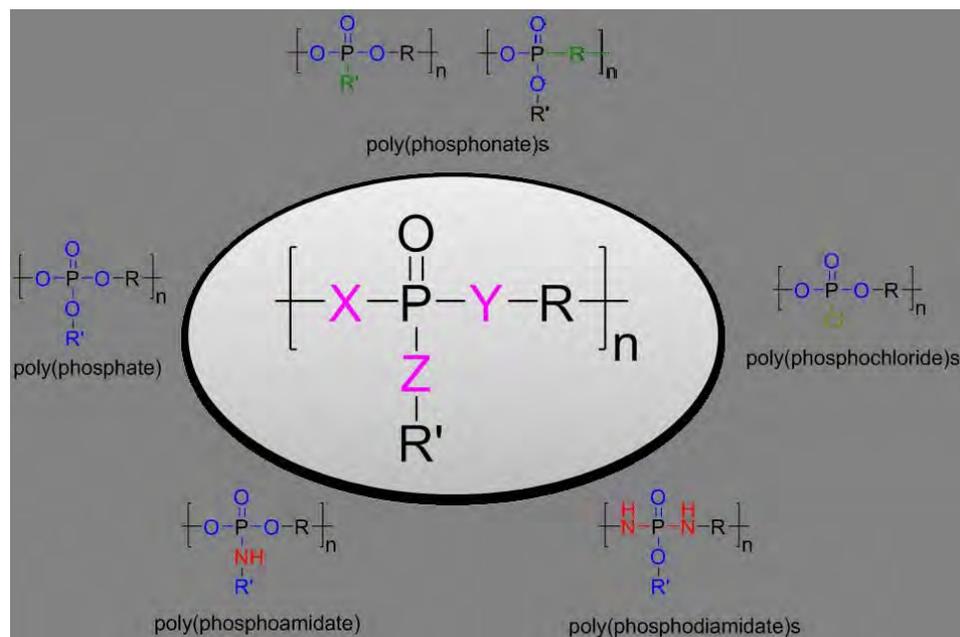
## POLY 267: Poly(phosphoester)s: From adhesives to stealth polymers

**Frederik Wurm**, [wurm@mpip-mainz.mpg.de](mailto:wurm@mpip-mainz.mpg.de), Thomas Wolf, Greta Becker, Mark Steinmann, Hisaschi Tee, Alper Cankaya. Max Planck Institut für Polymerforschung, Mainz, Germany

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. The incorporation of uncharged phosphates or phosphonates into polymers allows us 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.

The materials range from very hydrophobic to highly water soluble PPEs. With the natural phosphate building block a reliable access to biodegradable, biomimetic PPEs is possible. We have developed a robust protocol based on olefin metathesis for the synthesis of PPEs with tunable hydrophilicity and degradation rate, high reactivity or adhesion properties. Further, we develop the anionic ring-opening polymerization of five-membered cyclic phosphoesters to novel water-soluble polymers with stealth properties similar to polyethylene glycol, however having the great benefit of being biodegradable.

The combination of the pentavalence of phosphorus with modern polymer chemistry allows the synthesis of a platform for a broad variety of applications, ranging from adhesives or optical applications to tissue engineering scaffolds or polymer therapeutics.



## POLY 268: Highly porous polymers and hydrophobic-hydrophilic bicontinuous polymers for bio-related applications through emulsion templating

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

PolyHIPEs are highly porous polymers synthesized within high internal phase emulsions (HIPEs) [1,2]. Biodegradable crosslinked poly(urethane urea) (PUU) polyHIPEs for tissue engineering applications were synthesized using the step-growth polymerization of oligomeric polycaprolactone (PCL) polyols and renewable resource polymers (castor oil, polysaccharides) [3]. Cell growth studies demonstrated the potential of these polyHIPEs for tissue engineering applications. Bicontinuous, hydrogel-filled hydrophobic polymers for controlled release applications and for water-sensitive shape-memory applications were synthesized using simultaneous polymerizations in the HIPE's organic external phase and aqueous internal phase [4-6]. The release behavior reflected the highly tortuous bicontinuous morphology. The "dual lock" shape-memory behavior reflected contributions from both the crystalline hydrophobic polymer and the hydrogel.

[1] Silverstein MS. *Prog Polym Sci* 2014;39:199-234.

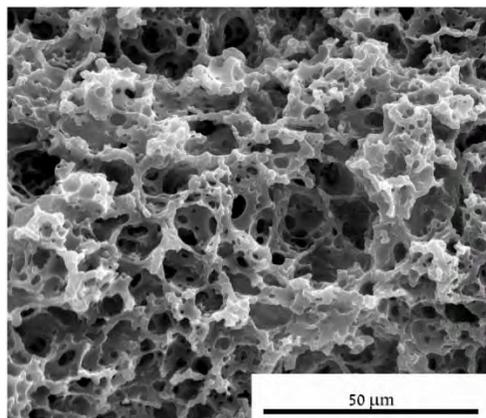
[2] Silverstein MS. *Polymer* 2014;55:304-320.

[3] David D, Silverstein MS. *J Polym Sci A, Polym Chem* 2009;47:5806-5814.

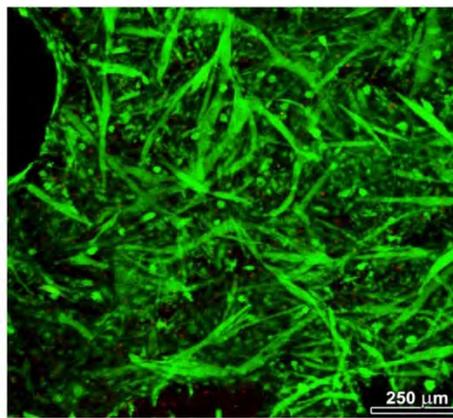
[4] Gitli T, Silverstein MS. *Soft Matter* 2008;4:2475-2485.

[5] Gitli T, Silverstein MS. *Polymer* 2011;52:107-115.

[6] Gurevitch I, Silverstein MS. *Soft Matter* 2012;8:10378-10387.



PUU PolyHIPE: Highly interconnected porous structure

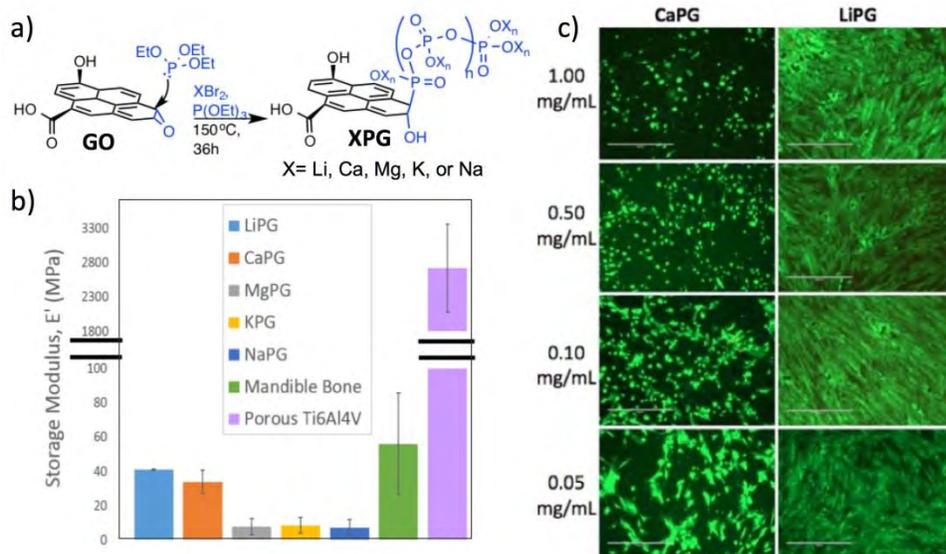


PUU PolyHIPE: Cell growth

## POLY 269: Osteomimetic graphene composite scaffolds for bone regeneration

**Stefanie A. Sydlik**, [ssydlik@mit.edu](mailto:ssydlik@mit.edu), Anne Arnold, Brian Hold, Zoe Wright. Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States

Graphene oxide (GO) is thought to have great potential as a component of biomedical devices. Although this nanomaterial has been demonstrated to be cytocompatible in vitro, its compatibility in vivo in tissue sites relevant for biomedical device application is yet to be fully understood. Here, we evaluate the compatibility of GO with two different oxidation levels following implantation in subcutaneous and intraperitoneal tissue sites, which are of broad relevance for application to medical devices. We demonstrate GO to be moderately compatible in vivo in both tissue sites, with the inflammatory reaction in response to implantation consistent with a typical foreign body reaction. Leveraging this information, the Sydlik group has further modified GO using an Arbuzov reaction to install hydroxyapatite-like polyphosphates onto GO (Figure 1a). With this sophisticated control of the surface chemistry, we are able to incorporate specific biomimetic moieties that simultaneously control the physical properties of the material, including stiffness (Figure 1b) and degradation rate, as well as the biological response (Figure 1c) through the incorporation of signaling molecules. To further enhance the compatibility and integration, we have are developing a modified methyl methacrylate bone cement that encourages cell recruitment and osteogenesis at the critical tissue-scaffold interface. This material offers unprecedented control of the mechanical and biological properties of a scaffold material and here we present our efforts towards developing it as a scaffold for bone regeneration.

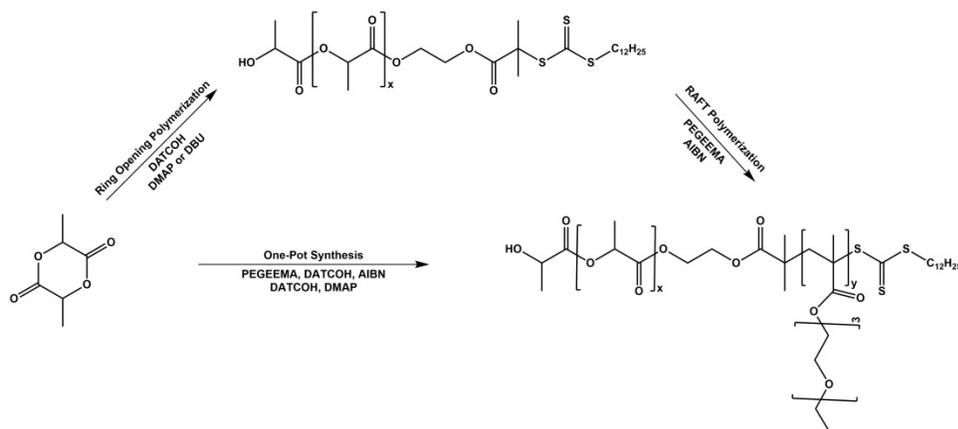


## POLY 270: One-pot synthesis of poly(lactide)-based block copolymers for bone tissue engineering applications

**Patrizia P. Smith**<sup>1</sup>, *pasmith@mines.edu*, **Amanda L. Rightler**<sup>2</sup>, **Daniel Price**<sup>3</sup>, **Stephen G. Boyes**<sup>1</sup>. (1) *Chemistry and Geochemistry, Colorado School of Mines, Northglenn, Colorado, United States* (2) *Chemistry and Biochemistry, University of Tulsa, Wildwood, Missouri, United States* (3) *Columbine High School, Littleton, Colorado, United States*

Biodegradable aliphatic polyesters such as poly(lactide) (PLA) have been extensively used as scaffold materials for tissue engineering applications. However, the inherent hydrophobicity associated with PLA homopolymers can adversely affect cell adhesion, proliferation, differentiation and ultimately new tissue formation. In order to improve the overall hydrophilicity and biocompatibility, amphiphilic block copolymers based on PLA and hydrophilic poly(meth)acrylates can be prepared. Typically, this requires the sequential combination of two mechanistically different polymerization types, namely ring opening polymerization (ROP) and reversible addition-fragmentation chain transfer (RAFT) polymerization or atom transfer radical polymerization. In order to simplify this process, a one-pot approach allowing for the simultaneous synthesis of the PLA block as well as the bio block could be beneficial, thus providing a means for a facile route to synthesize well-controlled amphiphilic block copolymers without an intermediate purification process.

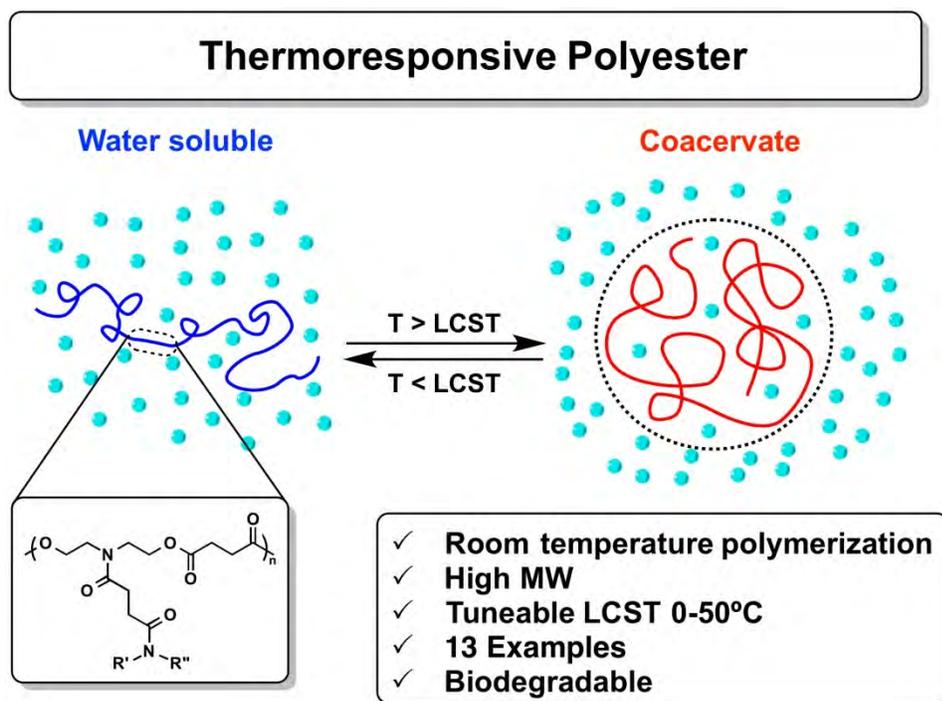
This research seeks to investigate the kinetics of the RAFT polymerization of poly(ethylene glycol) ethyl ether methacrylate (PEGEEMA) and the ROP of lactide in order to gain a better understanding of the feasibility of the synthesis of amphiphilic block copolymers such as PLA-b-PPEGEEMA via a one-pot approach. A unique bifunctional agent, bearing a hydroxyl group as well as a trithiocarbonate moiety, serves as the initiator for the ROP of lactide as well as the chain transfer agent for the RAFT polymerization of PEGEEMA. Previous research in our group has shown that PLA-b-PPEGEEMA block copolymers exhibit improved hydrophilicity and *in vitro* cell attachment. By investigating both the sequential as well as simultaneous synthesis of PLA-b-PPEGEEMA block copolymers, this research aims to further and improve the preparation of well-controlled and well-defined block copolymers used for tissue engineering applications.



## POLY 271: Highly tunable library of thermoresponsive, biodegradable polyesters based on N-substituted diols

**John P. Swanson**<sup>2</sup>, johnpswan@gmail.com, Michael R. Martinez<sup>1</sup>, Leanna R. Monteleone<sup>1</sup>, Fadi Haso<sup>2</sup>, Philip J. Costanzo<sup>1</sup>, Tianbo Liu<sup>2</sup>, Abraham Joy<sup>2</sup>. (1) Chemistry, California Polytechnic State U, San Luis Obispo, California, United States (2) Polymer Science, The University of Akron, Akron, Ohio, United States

Temperature responsive smart materials, such as poly(acrylamides) (PAs), undergo a reversible hydrophilicity change at a lower critical solution temperature (LCST) which makes them particularly attractive for biomedical applications such as targeted drug delivery. However, the nondegradable backbone of PAs and many other thermoresponsive polymers ultimately limit their use for a number of applications. To date, few examples of thermoresponsive, biodegradable polymers exist. Recently, our lab has developed a library of thermoresponsive polyesters (TR-PEs) based on PAs and thermoresponsive elastin-like peptides (ELPs). A modular synthetic design allows for polyesterification of a variety of N-substituted amide-diol monomers, yielding a library of TR-PEs. The LCST range can be tuned between 0-50°C, dependent on polymer structure and cosolutes, as evidenced by UV-Vis, <sup>1</sup>H NMR, and DLS. Additionally, the hydrophilic nature of TR-PEs prevents full dehydration above the LCST, resulting in the formation of polymer-rich coacervates. The degradable polyester backbone enables hydrolytic degradation over time. These features make TR-PEs attractive candidates for applications such as controlled drug release and degradable scaffolds.



## POLY 272: Synthesis and characterization of NIPAM and acrylic acid-based polymer-lysozyme conjugates

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Enzymes are the foundation of any biological system, especially the human body. Their stability, great affinity and selectivity, catalytic efficiency, and reusability are just a few factors that distinguish enzymes from small molecules and make them ideal for pharmaceutical uses. While there has been much progress since the first use of enzymes as a treatment in the 1920's, there are still many challenges that hinder the expansion in usage of this potent form of drugs. Our work stems from these challenges, such as instability at room temperature and degradation by the body's proteolytic mechanisms, and seeks to use polymer conjugation to optimize enzyme properties for pharmaceutical uses. Polymers are ideal because they have specific controllable characteristics such as molecular weight, mechanical strength, and biocompatibility. *N*-Isopropylacrylamide (NIPAM) has thermoresponsive properties and has been shown to help increase stability of enzymes via conjugation. Furthermore, acrylic acid has pH-responsive properties and can increase the enzyme's catalytic efficiency. NIPAM and acrylic acid-based homopolymers and copolymers have been synthesized using radical polymerization techniques. The enzyme we have chosen is lysozyme, which is easy to acquire, well characterized, and currently being developed as an antibiotic. It is functionalized with polymers through lysine residues using carbodiimide-mediated coupling. Polymers were coupled either through their end groups or pendant carboxylic acids within the main chain (Figure 1). The success of the conjugation was confirmed by gel electrophoresis and the thermal and kinetic properties of the bioconjugates were evaluated.

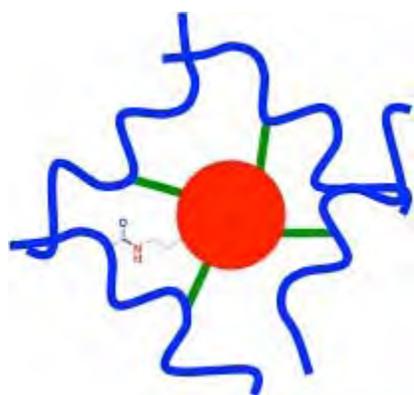
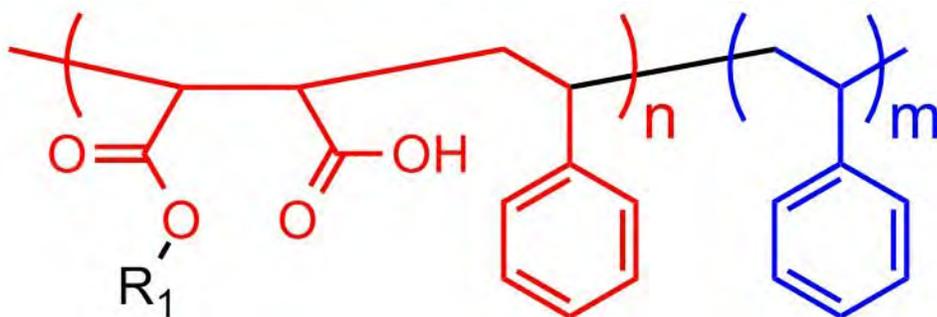


Figure 1: Enzyme (red)-polymer (blue) conjugate showing coupling via amide bond (green).

## POLY 273: Synthetic design of block copolymer amphiphiles for nanomaterial dispersion

**Benjamin Alameda**, *balameda@calpoly.edu*, **Simone Feist**, **Hannah Heintzmann**,  
**Philip J. Costanzo**, *phil.costanzo@gmail.com*. Chemistry, California Polytechnic State  
U, San Luis Obispo, California, United States

Amphiphilic block copolymers were prepared with a variety of controlled radical polymerization techniques, including RAFT and ATRP. Length of the hydrophobic and hydrophilic block were adjusted to determine optimum dispersion of various hydrophobic nanomaterials. The prepared water-borne dispersions were subsequently utilized for a wide variety of applications. [figure1]



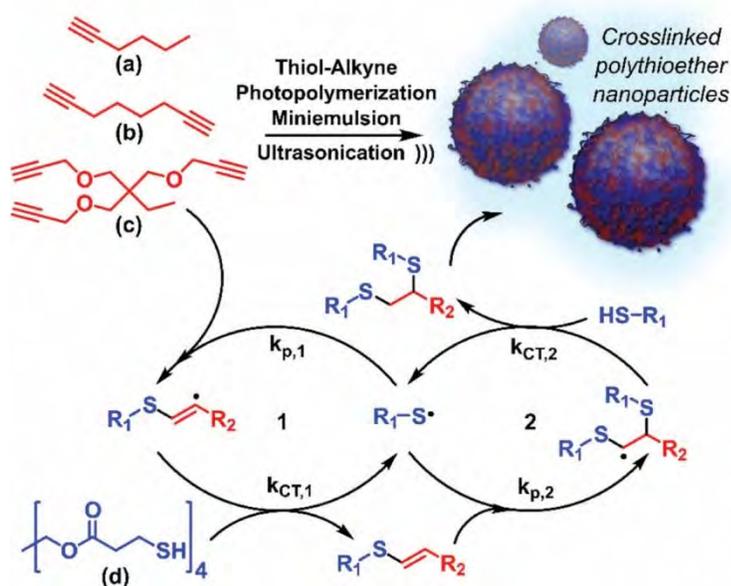
## POLY 274: Functional, composite polythioether nanoparticles via thiol-alkyne photopolymerization in miniemulsion

**Susan E. Walley**<sup>1</sup>, *susan.walley@eagles.usm.edu*, **Dahlia N. Amato**<sup>1</sup>, **Douglas V. Amato**<sup>1</sup>, **Jananee Narayanan**<sup>1</sup>, **Brian R. Donovan**<sup>1</sup>, **Jessica R. Douglas**<sup>1</sup>, **Alex S. Flynn**<sup>2</sup>, **Derek L. Patton**<sup>1</sup>. (1) School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, Mississippi, United States (2) Department of Biology, University of Southern Mississippi, Hattiesburg, Mississippi, United States

Emulsion-based processes – such as miniemulsion polymerizations – provide well-studied synthetic routes to polymer nanomaterials. Miniemulsion polymerizations are characterized as aqueous dispersions of small, narrowly distributed monomer droplets created through high shear and stabilized against Ostwald ripening/collisional degradation by addition of an appropriate surfactant and costabilizer. In this work, thiol-alkyne photopolymerization in miniemulsion is demonstrated as a simple, rapid, and one-pot synthetic approach to polythioether nanoparticles with tuneable particle size and clickable functionality.

Nanoparticles with mean particle diameters ranging from 45 nm to 200 nm were synthesized through simple modifications to the miniemulsion formulation and processing parameters.

Facile access to thiol or alkyne functional nanoparticles, and subsequent postpolymerization modifications of these functional moieties using thiol-Michael, thiol-ene, and CuAAC click reactions are explored. The strategy is also useful in the synthesis of composite polymer-inorganic nanoparticles such as silver.



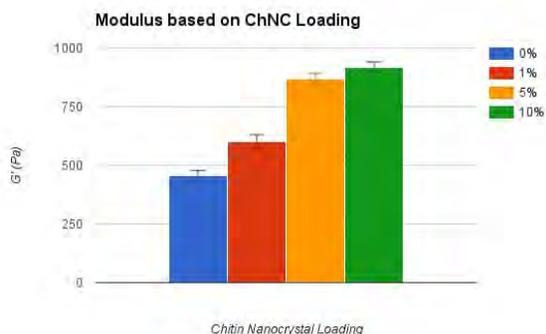
Scheme 1. Various multifunctional alkynes (a-c) and tetrafunctional thiol (d) used to generate polythioether nanoparticles *via* thiol-alkyne photopolymerization in miniemulsion. Thiol-alkyne involves sequential addition and hydrogen abstraction steps of primary alkynes (1) and subsequent vinyl sulfides (2) to generate crosslinked nanoparticles.

## POLY 275: Mechanically tunable pullulan-chitin nanocrystal scaffold for biological application

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As disease modeling, tissue engineering and lab on a chip systems advance, it is imperative that the new scaffolding systems are developed to establish long-term models. These scaffolds must be biocompatible, have limited and controlled degradation profiles, and should mimic the mechanical properties of the native tissue. As scaffolds are often combined with extracellular matrix proteins these systems must limit the contraction of ECM gels when cells are present and should be robust to allow researchers to manipulate the samples as needed.

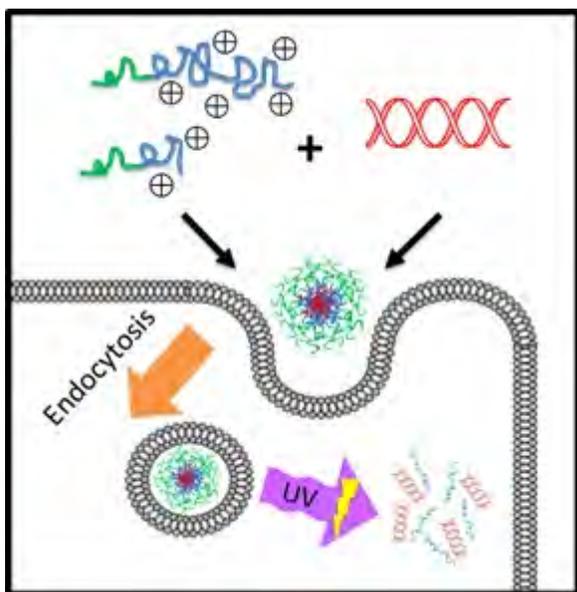
We report a mechanically tunable chitin nanocrystal-enriched hydrogel made from pullulan covalently cross-linked by sodium trimetaphosphate (STMP). Chitin nanocrystals, products of the acid hydrolysis of chitin, were added to the hydrogel in various loading percentages. The viscoelastic properties of the crosslinked hydrogel nanocomposites were determined by linear rheology through frequency sweeps. The surface and internal morphology of the freeze-dried nanocomposite scaffolds were characterized by scanning electron microscopy. The total amount of water that the hydrogels could hold and their ability to retain water was also characterized and found to be comparable to that of current crosslinked hydrogel systems. The neutral scaffolds also do not inhibit mammalian cell growth with routes for improving cell adhesion being explored. Pullulan is an extracellular polysaccharide, excreted by *Aureobasidium* and has been explored for stem cell encapsulation, and enhancing survival in high oxidative stress environments. Both pullulan and sodium trimetaphosphate are classified as Generally Recognized as Safe (GRAS) by the Food and Drug Administration. Chitin also has the potential to be bioresorbed into the body through enzymatic degradation pathways and requires further study to determine its viability in tissue engineering applications. The prepared hydrogel nanocomposites scaffolds offer a unique pathway towards controlling scaffold mechanical properties, internal morphology, and water retention while being non-toxic to human cells.



## POLY 276: Optimizing gene silencing in light-responsive siRNA polyplexes by varying polymer block lengths

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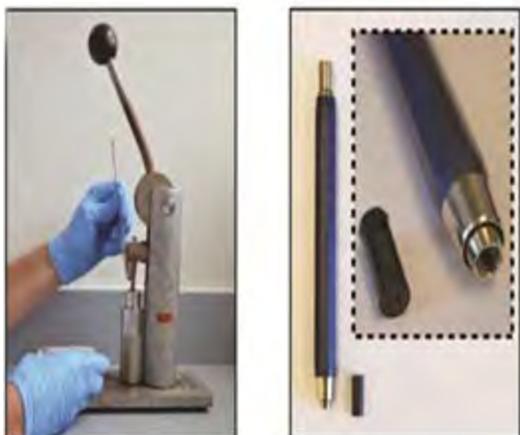
Small interfering RNA (siRNA) therapeutics have emerged as a means to post-transcriptionally silence gene expression and treat a wide range of genetic diseases; however, the therapeutic delivery of siRNA to cells is limited by enzymatic degradation, rapid clearance from circulation, and limited cellular uptake. To improve delivery, siRNA can be packaged into polyplexes. These polyplexes must be stable enough to deliver siRNA into targeted cells while simultaneously promoting siRNA release within these cells. To meet these contradictory demands, this effort uses photo-responsive *m*PEG-*b*-poly(5-(3-(amino)propoxy)-2-nitrobenzyl methacrylate) (*m*PEG-*b*-P(APNBMA)) diblock copolymers to create polyplexes that efficiently encapsulate siRNA, while also providing a method for modulating siRNA release *via* light-mediated charge reversal of the cationic polymer block. In this work, we studied two polymers consisting of identical PEG blocks but different lengths of the cationic block. The shorter polymer was shown to release siRNA more efficiently in response to the photo-stimulus; however, the longer polymer exhibited better siRNA encapsulation and stability. By formulating mixtures of the two polymers, we were able to optimize both cellular uptake and targeted gene silencing upon transfection of the polyplexes into NIH-3T3 cells. Additionally, the improved gene silencing designs coupled with mass action kinetic modeling approaches provided opportunities to predict siRNA, mRNA, and protein concentrations during the gene silencing process and thereby adjust polyplex dosing protocols to further enhance siRNA efficacy. These results demonstrate the ability to effectively tune gene silencing through small changes in polymer composition.



## **POLY 277: Characterization of reagent pencils for solvent-free deposition of reagents onto paper-based diagnostic device**

**Cheyenne H. Liu**<sup>1</sup>, *clui16@calpoly.edu*, **Hayden T. Mitchell**<sup>1</sup>, **Isabelle C. Noxon**<sup>1</sup>, **Chad E. Immoos**<sup>2</sup>, **Nathaniel Martinez**<sup>3</sup>, **Andres W. Martinez**<sup>4</sup>, **Philip J. Costanzo**<sup>1</sup>, *phil.costanzo@gmail.com*. (1) Chemistry, California Polytechnic State U, San Luis Obispo, California, United States (2) California Polytechnic State U, San Luis Obispo, California, United States (3) California Polytechnic State Univ, San Luis Obispo, California, United States

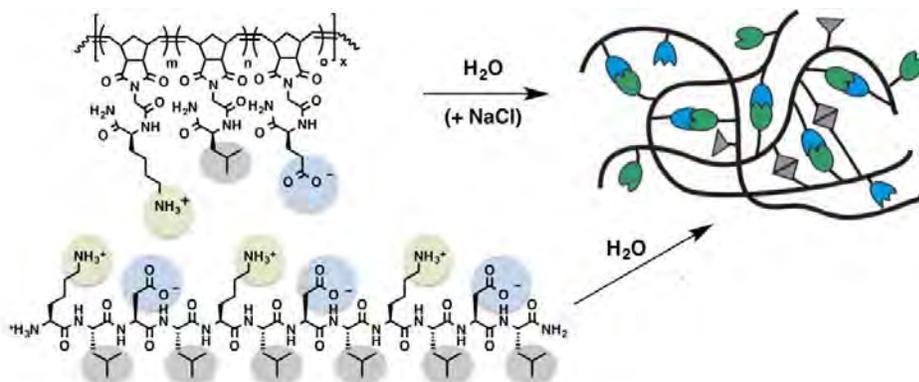
In an effort to improve the utility and effectiveness of microfluidic paper-based analytic devices (microPADs), reagent pencils were developed. The straightforward methodology of reagent pencils is advantageous in its allowance for rapid solvent-free deposition of reagents, longer reagent shelf life stored in a solid matrix, and lack of specialized equipment. Poly(ethylene glycol) was found as the most reliable and versatile polymer to incorporate into reagent pencils. PEG/graphite systems were tested for its wear resistance and colorimetric signal strength at different molecular weights. In general, the hardness of PEG/graphite systems used for reagent pencils can be customized by varying the diameter of the pencil core or changing the molecular weight of PEG itself. A new parameter was devised correlating wear to reagent deposition. It was determined that lower molecular weight PEG deposited more reagent onto microPADs than systems that incorporated higher molecular weight PEG. In the future, this parameter may be used as a comparison tool between different, more sensitive reagents. Reagent pencils provide a more facile method of preparing low-cost diagnostic assays that can be delivered to a point of care out in the field.



## POLY 278: Amino acid-modified norbornyl polymers as analogues to hydrogel-forming peptides

Dustin Crystal<sup>1</sup>, Angela P. Blum<sup>5</sup>, Andrea S. Carlin<sup>2</sup>, Swagat Sahu<sup>3</sup>, **Francisco J. Hidalgo**<sup>1</sup>, fhidalgoruiz@ucsd.edu, Nathan C. Gianneschi<sup>4</sup>. (1) UCSD, San Diego, California, United States (2) Chemistry and Biochemistry, University of California - San Diego, La Jolla, California, United States (3) University of California San Diego, La Jolla, California, United States (4) Chem M/C 0343, University of California, San Diego, La Jolla, California, United States (5) Chemistry and Biochemistry, University of California, San Diego, San Diego, California, United States

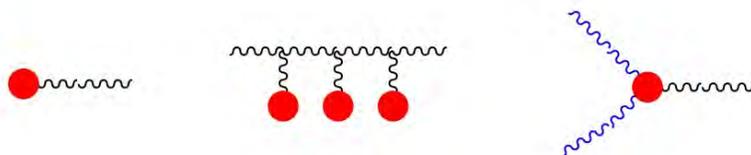
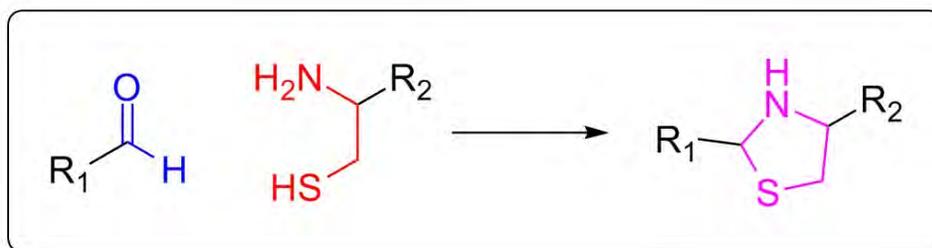
Hydrogels have been widely explored for use as materials in assorted biomedical applications, including as tissue engineering scaffolds, antifouling surfaces, and drug delivery vehicles. A number of peptides have been reported to self-assemble into robust hydrogels via inter-strand crosslinking. However, peptide-based materials pose practical and clinical challenges as a result of their susceptibility to proteolytic degradation and the relative difficulty associated with chemical functionalization of their side chains. Here, we present a series of polymer mimics of one particular peptide that forms hydrogels by a combination of electrostatic and hydrophobic interactions as a result of the repeating Lys-Leu-Asp-Leu units that comprise its sequence. In our design, analogues of these amino acids are prepared as modified norbornene monomers and polymerized by ring opening metathesis polymerization (ROMP). With this strategy, the peptide backbone is replaced with a norbornene backbone that is resistant to proteolytic degradation and can be easily modified to include a wide range of chemical functionality. In this work, we present a comparison between the physical properties of our polymer mimics to those of the parent peptide and describe intriguing variations whose gelation can be controlled by changes in solution salt concentration.



## POLY 279: Employment of cysteine and thiazolidine chemistry for novel polymer coupling and architectures

**Karoline E. Eckhart**, [keckhart@calpoly.edu](mailto:keckhart@calpoly.edu), Austin M. Ventura, Anthony J. Varni, Clement DeHoe, **Philip J. Costanzo**, [phil.costanzo@gmail.com](mailto:phil.costanzo@gmail.com). Chemistry, California Polytechnic State U, San Luis Obispo, California, United States

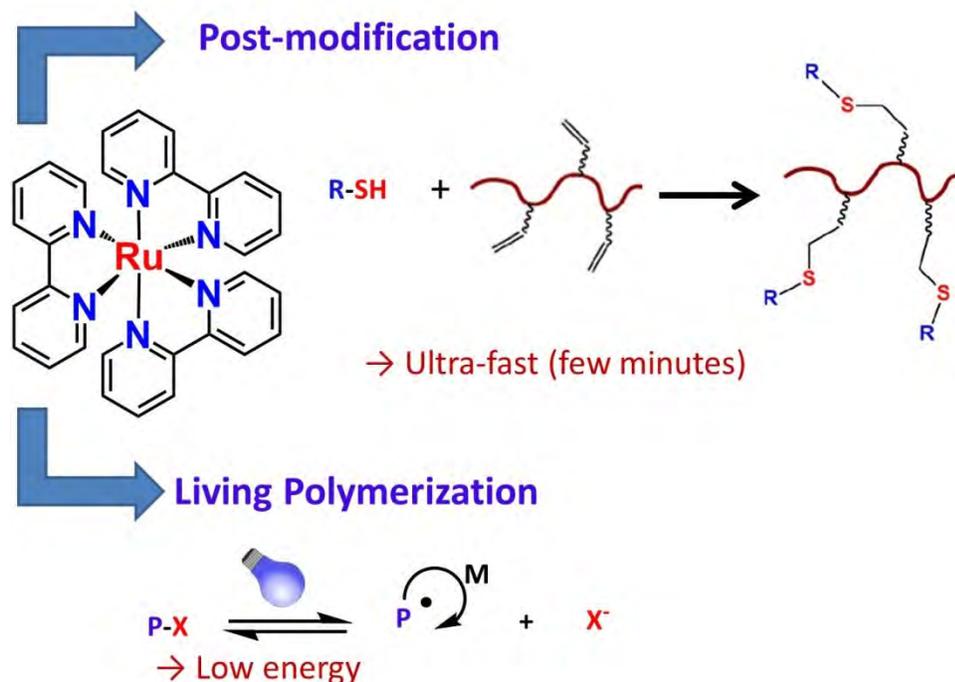
The development of simple and efficient crosslinking techniques is sought after for a variety of applications including bioconjugation, material synthesis and design, and surface functionalization. This work focuses upon the decoration of latent cysteine functional groups at the terminus and along the backbone that undergo thiazolidine coupling upon the introduction of aldehyde. A protected cysteine residue was prepared and utilized and incorporated via chain end modification and as an initiating site for atom transfer radical polymerization (ATRP) and reversible addition fragmentation transfer (RAFT) polymerization techniques.[figure1]



## POLY 280: Photoredox catalysts: An efficient tool for click chemistry and polymer post-modification

**Cyrille Boyer**, [cboyer@unsw.edu.au](mailto:cboyer@unsw.edu.au). Chemical Engineering, UNSW Australia, Sydney, New South Wales, Australia

Photoredox catalysts have emerged as an efficient tool to perform complex organic transformation under visible light to yield complex organic compounds in high yield and purity. In this communication, we would like to introduce this concept for polymer post-modification. In this talk, several examples of post-modification reactions will be discussed. For instance, an elegant approach for fast polymer post-functionalization and step-growth polymerization (via addition reaction) under aerobic condition was developed from visible light photocatalytic thiol-ene “click” reaction, employing  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  as photoredox catalyst and *p*-toluidine as redox mediator. The nature of the photoredox catalyst, thiol substrates and solvents were extensively investigated for this reaction with two types of alkene polymers, polybutadiene and poly(allyl methacrylate)s. The use of *N*-methyl-2-pyrrolidone as the solvent and *p*-toluidine as redox mediator remarkably improved the reaction rates and limited the formation of side products. This highly efficient thiol-ene reaction was employed for the synthesis of polymers by step-growth addition polymerization. In another example, the addition of halide compounds will be presented to yield functional polymers or to functionalize surface. Finally, this talk will give an example of application of photoredox catalysts for living polymerization.



Example of application of photoredox catalysts for polymer synthesis

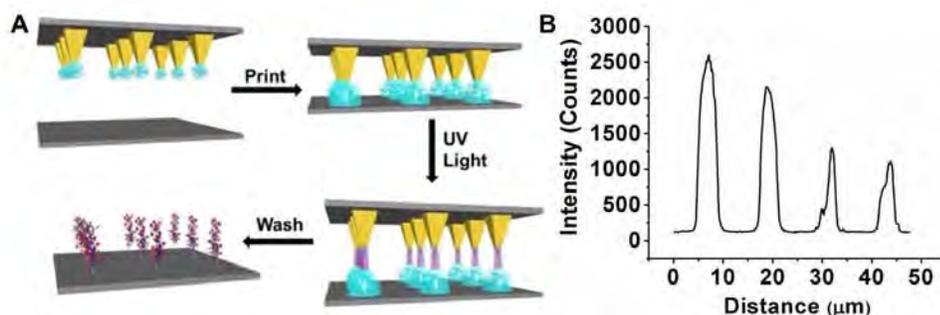
## POLY 281: Multiplexed nanoarrays via 4D surface photochemistry

**xiaoming liu**<sup>2</sup>, [lx39@miami.edu](mailto:lx39@miami.edu), Yeting Zheng<sup>1</sup>, Adam Braunschweig<sup>1</sup>, yiwen ji<sup>1</sup>. (1) Chemistry, University of Miami, Miami, Florida, United States (2) chemistry, university of miami, Miami, Florida, United States

Massively parallel tip based lithographies have garnered widespread attention because of (1) their compatibility with soft organic- and biologically-active materials, (2) their low-cost, and (3) their ability to produce arbitrary patterns with sub-micrometer feature dimensions.<sup>[1]</sup> We have recently demonstrated (Figure) that these patterning techniques are an excellent method for performing localized photochemical polymerizations, and we have used these to grow fluorescent and glycan labelled brush polymers with nanoscale control over feature position and height (3D nanolithography)<sup>[2]</sup> Incorporating microfluidics into our printing platform allows for the additional control over chemical composition at each point, thereby resulting in a 4D printing device. This new nanolithography strategy will enable breakthrough advances in biotechnology, materials science, and organic chemistry.

[1] Braunschweig, A. B. et al. "Molecular Printing" *Nat. Chem.*, 2009, 1, 353–358.

[2] Bian, S. et al. "Beam Pen Lithography as a New Tool for Spatially Controlled Photochemistry, and its Utilization in the Synthesis of Multivalent Glycan Arrays" *Chem. Sci.*, 2014, 5, 2023 – 2030.



## **POLY 282: Click chemistry dye conjugate dendrimers containing controlled ratios of dye per particle: Synthesis, characterization, and biological evaluation**

**Mark M. Banaszak Holl**<sup>1</sup>, [mbanasza@umich.edu](mailto:mbanasza@umich.edu), Casey A. Dougherty<sup>3</sup>, Sriram Vaidyanathan<sup>4</sup>, Stassi C. Dimaggio<sup>2</sup>, Janet M. Manono<sup>5</sup>. (1) Univ of Michigan, Ann Arbor, Michigan, United States (2) Xavier University of Louisiana, Metairie, Louisiana, United States (3) Chemistry, University of Michigan, Ann Arbor, Michigan, United States (4) Biomedical Engineering, University of Michigan, Ann Arbor, Michigan, United States (5) Chemistry, Xavier University of New Orleans, New Orleans, Louisiana, United States

Fluorescent dyes are commonly attached to polymers and nanoparticles in order to image the location of the particle in a cell or track a process over a period of time. Although substantial effort has been made to control the number of fluorophores on a polymer, the synthesis of controlled ratios of fluorescent dyes per polymer particle has been a major challenge in synthetic materials chemistry. Typically, these materials are synthesized with an average number of dyes and contain a distribution of dye/particle ratios. We have employed click chemistry to synthesize Generation 5 PAMAM dendrimers with a controlled number of fluorescent dyes per particle by using a method we developed with reverse phase high performance liquid chromatography (rp-HPLC). The resulting materials can be separated into controlled dye/particle ratio fractions based on the hydrophobicity of the click ligand, either azide or alkyne, or based on the hydrophobicity of the clicked dye conjugate.

We then tested if variation in the number of dyes per particle affected uptake into HEK293A cells. We found that using uncorrected mean fluorescence measurements for such materials is problematic because the extent of dye-dye quenching, and thus fluorescence intensity, varies with dye/particle ratio. Dye/particle ratio was found to impact cellular uptake rates. In addition, the dye particle ratio was found to have a substantial impact on intracellular fluorescence lifetime.



## **POLY 283: Thiol-Yne photo-click chemistry: Towards biocompatible and tough photopolymers for 3D printing**

**Thomas Griesser**, *thomas.griesser@unileoben.ac.at*. Chair for Chemistry of Polymeric Materials & Christian Doppler Laboratory for Functional and Polymer Based Ink-Jet Inks, University of Leoben, Leoben, Austria

Recent years have seen an increasing interest in the development of photo-polymerizable monomers providing low cytotoxicity and high impact resistance in their cured state. This fact can mainly be explained by the rapid progress in UV based additive manufacturing technologies such as stereolithography, digital light processing or 3D ink-jet printing which enables the fast, accurate and individual fabrication of biocompatible structures for hard tissue engineering. In this contribution, the versatility of the thiol-yne photo-click reaction for the fabrication of biocompatible photopolymers is shown at the example of tailor-made bi- and multifunctional alkyne and thiol monomers. This reaction leads to highly uniform polymeric networks exhibiting a sharp and defined thermal glass transition together with outstanding impact resistance [1] making these polymers interesting for challenging applications such as medical implants. A particular focus was set on the development of low odour thiols as promising alternatives to commercially available mercapto propionic acid derivatives. Thiol-yne resins based on these monomers provide both, high reactivities comparable to those of acrylates and mechanical properties appropriate for the fabrication of medical devices in their cured state. Not only non-degradable, but also degradable monomers were designed, enabling the selective adjustment of the resorption behaviour of the resulting polymers. The herein described monomers pave the way towards the fabrication of tailor-made photopolymers suitable for hard tissue engineering.

[1] Thiol-X Chemistries in Polymer and Materials Science Andrew B. Lowe and Christopher N. Bowman Editors, Royal Society of Chemistry, Cambridge 2013.

## POLY 284: Retro-Staudinger cycloaddition enabled by polymer mechanochemistry

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Polymer mechanochemistry enables a variety of remarkable chemical transformations including the ring-opening of spiropyran, activation of latent catalysts, and even formally forbidden reactions like the disrotatory electrocyclic ring-opening of benzocyclobutene. Increasing the repertoire of mechanochemical transformations remains a critical goal in this emerging field, particularly for applications such as self-healing materials where the production of functional groups with exquisite reactivity is necessary. Here, we present the discovery of a mechanically facilitated formal [2+2] cycloelimination reaction of a  $\beta$ -lactam mechanophore to generate ketene and imine functional groups, i.e., a mechanochemical retro-Staudinger cycloaddition. The mechanochemical reactivity of the  $\beta$ -lactam motif was predicted by DFT calculations and confirmed experimentally through a combination of kinetic analyses, UV-vis absorption measurements, and polymer end-group analysis using <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The  $\beta$ -lactam group is the newest addition to the mechanophore family and the mechanical generation of highly reactive ketene groups provides a promising platform for the realization of materials with dynamic functionality including self-healing properties.

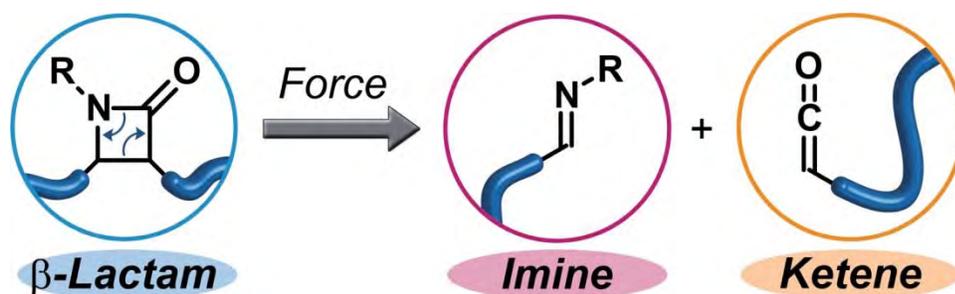
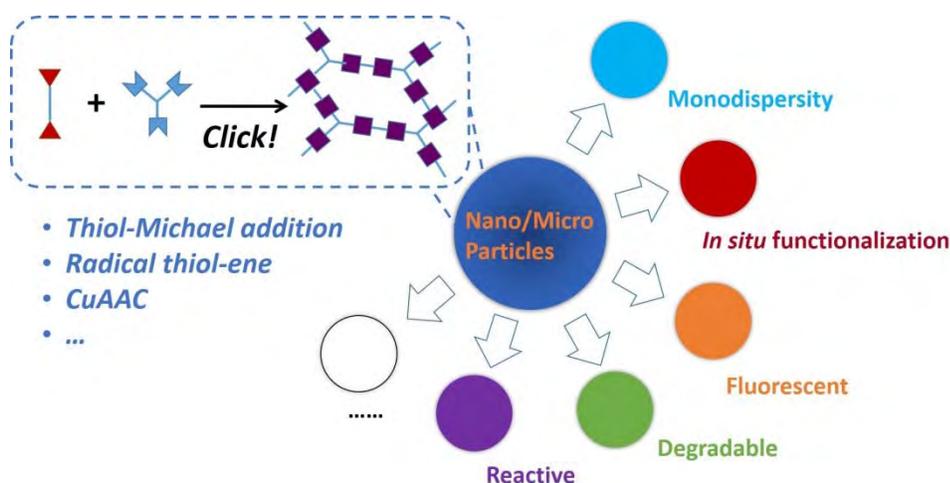


Figure 1. The  $\beta$ -lactam mechanophore undergoes a formal [2+2] cycloelimination reaction under mechanical force to generate imine and ketene functional groups. Due to the versatile reactivity of the ketene group, this retro-Staudinger cycloaddition represents a promising new platform for producing advanced, functional materials.

## POLY 285: Step-growth clickable nano/micro-particles

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Herein we demonstrate the implementation of “Click” chemistries in heterogeneous polymerizations, for the realization of colloidal polymers from step-growth polymerizations. Step-growth polymers have been rarely used in the preparation of polymeric particles, mainly due to the low efficiency and the intolerance to aqueous/alcohol media of conventional condensation/addition reactions. We find that many “Click” reactions, including copper catalyzed azide-alkyne cycloaddition, thiol-Michael addition and radical mediated thiol-ene reaction, are ideal candidates for conducting heterogeneous step-growth polymerizations. We have systematically investigated thiol-Michael addition and radical thiol-ene reactions in dispersion polymerization systems, generating monodisperse crosslinking microparticles with quantitative yields. Step-growth mechanism enables off-stoichiometric reactions while maintains crosslinking. Off-stoichiometric polymerizations offer microparticles with well-defined physiochemical properties, and more importantly they are *in situ* functionalized with “clickable” reactive moieties that are ready for further modifications. Also, step-growth mechanism allows the manipulation of polymer backbones simply by altering the monomer structure between “clickable” groups. We have been able to incorporate particular functional groups that realize particles with degradability, photo-responsiveness, etc. In miniemulsion polymerization systems, nano-particles are achieved with the abovementioned properties integrated. These “clickable” step-growth nano/micro particles provide a novel family of colloidal polymers. We expect they will find use in many applications such as composite material, bio-imaging and drug delivery systems.

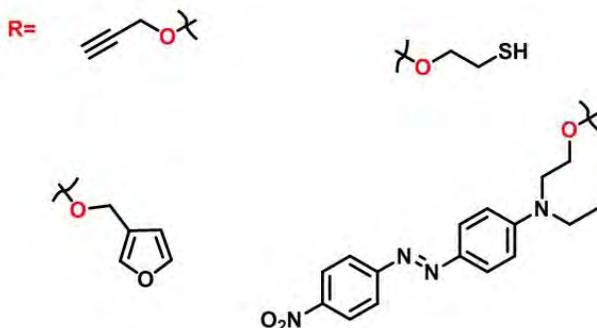
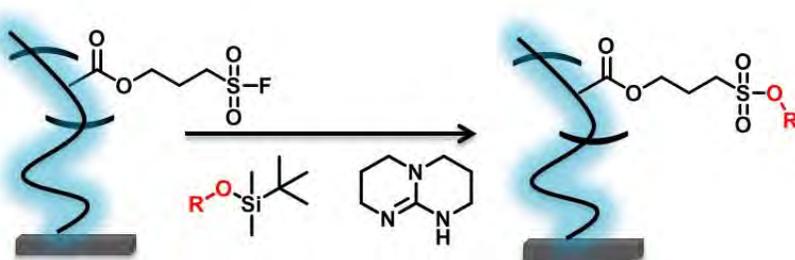


Scheme for the preparation and application of nano/micro-particles from step-growth "click" polymerizations.

## POLY 286: Sufex on the surface: A flexible platform for postpolymerization modification of polymer brushes

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Polymer brushes present a unique architecture for tailoring surface functionalities due to their distinctive physicochemical properties. However, the polymerization chemistries used to grow brushes place limitations on the monomers that can be grown directly from the surface. Several forms of click chemistry have previously been used to modify polymer brushes by postpolymerization modification with high efficiency, however, it is usually difficult to include the unprotected moieties in the original monomer. We present the use of a new form of click chemistry known as SuFEx (sulfur(VI) fluoride exchange) on the surface, which allows a silyl ether to be rapidly and quantitatively clicked to a polymer brush grown by free radical polymerization containing native -SO<sub>2</sub>F groups with rapid pseudo-first-order reaction rates as high as 0.04 s<sup>-1</sup>. Furthermore, we demonstrate the use of SuFEx to facilely add a variety of other chemical functional groups to brush substrates that have highly useful and orthogonal reactivity, including alkynes, thiols, and dienes.



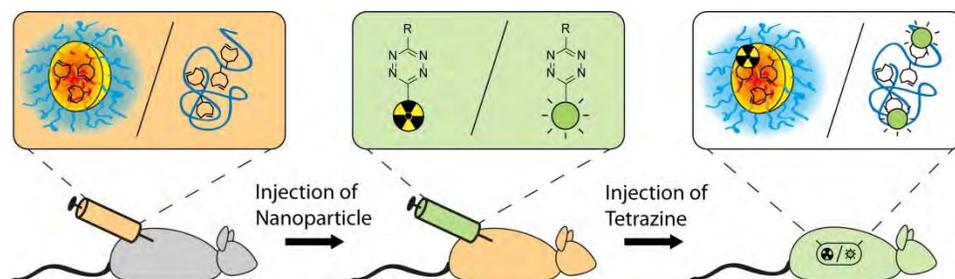
Post-polymerization SuFEx modification of free-radically grown polymer brushes with moieties which are suitable for other click reactions. Useful functional groups such as thiols, alkynes, and dienes can be facilely added to the backbone under ambient conditions to provide access to highly reactive functionalities which are poorly compatible with typical free-radical polymerization.

## POLY 287: From imaging to therapy: Polymeric nanoparticles for in vivo click chemistry

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In vivo click chemistry utilizes the site selectivity of strain promoted inverse electron demand Diels-Alder reaction to link chemical entities to each other in the complex environment of living organisms.

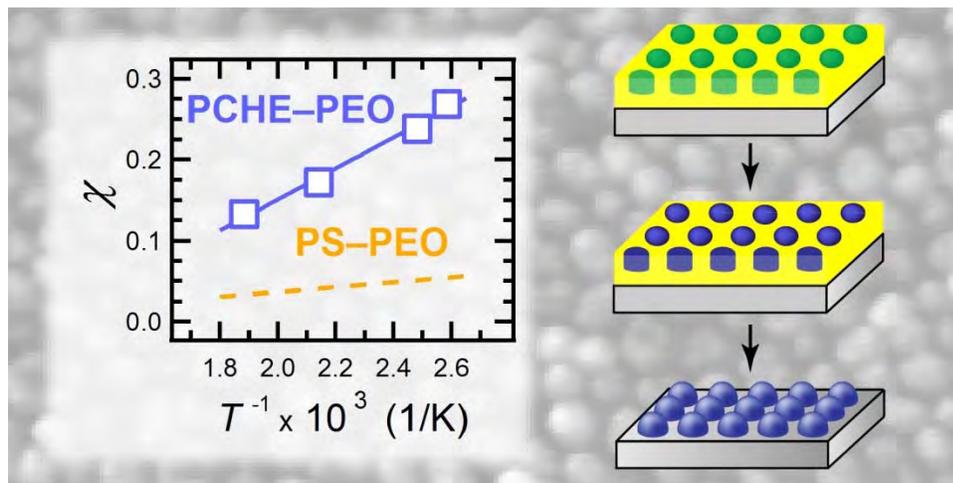
We report the synthesis, characterization and in vivo evaluation of polypept(o)idic nanoparticles with trans-cyclooctenes and functional tetrazines. The accumulation of polypept(o)idic nanoparticles is visualized in animal models utilizing a functional tetrazine (fluorescently and radiolabeled). We demonstrate the feasibility of the in vivo click chemistry for different polypept(o)idic nanoparticles in complex biological settings and report first applications in diagnostics.



## POLY 288: Poly(cyclohexylethylene)-*block*-poly(ethylene oxide) block polymers for metal oxide templating

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Dense arrays of nanostructured metal oxides offer diverse functionality for a broad range of technologies, including optoelectronics, magnetic storage, and photocatalysis. Block polymer lithography has emerged as a powerful bottom-up technique to spatially template high density arrays. In this work, we synthesized a series of poly(cyclohexylethylene)-*block*-poly(ethylene oxide) (CEO) block polymers through tandem anionic polymerizations and heterogeneous catalytic hydrogenation. The substantial chemical dissimilarity of the two blocks enables (i) the formation of exceptionally small feature sizes due to a relatively large interaction parameter and (ii) selective inclusion of an inorganic precursor within the PEO domain following the simple spin-coating of a precursor solution atop the solvent-annealed CEO film. UV/ozone treatment following incorporation produces an ordered arrangement of oxide nanodots and simultaneously removes the block polymer template. Herein, we report the smallest particles ( $6 \pm 1$  nm) templated from a selective precursor insertion method to date and an approximate 5-fold increase of the interaction parameter over the unreduced poly(styrene)-*block*-poly(ethylene oxide) analogue.



## POLY 289: Design and synthesis of nitrogen-doped hierarchical carbon for selective carbon capture and electrocatalysis

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Porous carbon is an interesting class of materials with desirable properties, including high surface area, tunability over pore geometries, and flexibility of heteroatom doping. An ideal sorbent should possess a hierarchical structure, in which ultramicropores provide high selectivity and capacity while mesopores allow fast gas diffusion. However, such hierarchical structures remain challenging to rationally design and synthesize in carbon materials.

We reported a “designer carbon” with controlled synthesis of a N-doped hierarchical carbon that exhibits outstanding performances in both CO<sub>2</sub> capture and electrochemical catalysis. Our porous carbon was prepared using low temperature process ( $\leq 500$  °C) of a rigid conjugated polymer framework synthesized through co-assembly and polymerization of a molecular designed pyrrole monomer and a soft-template. These processes allow controllability over the ultramicropore volume and nitrogen functional groups, which are essential for CO<sub>2</sub> adsorption under post-combustion conditions. This lead to a record-high Henry’s law CO<sub>2</sub>/N<sub>2</sub> selectivity ( $\sim 200:1$  at 323 K) among physisorptive carbons while possessing high adsorption capacity.

Excellent performance for both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) was also exhibited by this hierarchical carbon, as demonstrated by means of fundamental electrochemical studies as well as integration into oxygen electrode of a regenerative fuel cell. The activities observed for both the ORR and the OER are comparable to that achieved by state-of-the-art Pt and Ir in an alkaline environment, but at much lower costs. These results are paramount for the deployment of energy storage systems that utilize O<sub>2</sub>-H<sub>2</sub>O chemistries such as regenerative fuel cells and metal-air batteries.

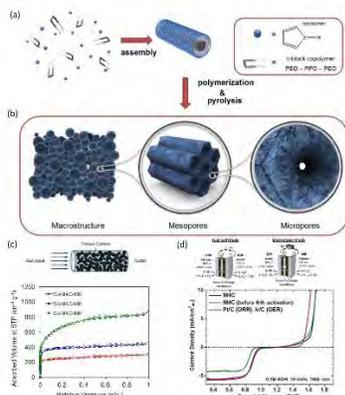


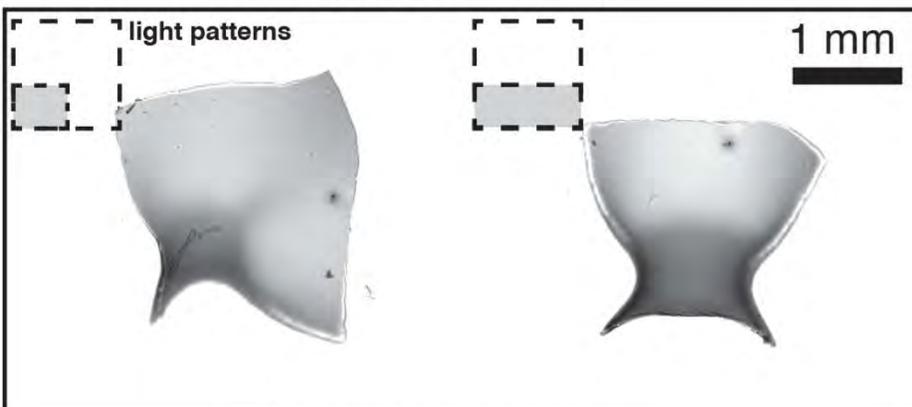
Figure 1 shows the co-assembly process of the molecular engineered monomer; b shows the hierarchical nature of the porous carbon; c shows the gas adsorption behavior of the porous carbon with high adsorption capacity of CO<sub>2</sub>; d shows the fabrication of the regenerative fuel cell device with high performance as a bifunctional catalyst for ORR and OER reactions.

## POLY 290: Optically reprogrammable buckling of nanocomposite polymer films

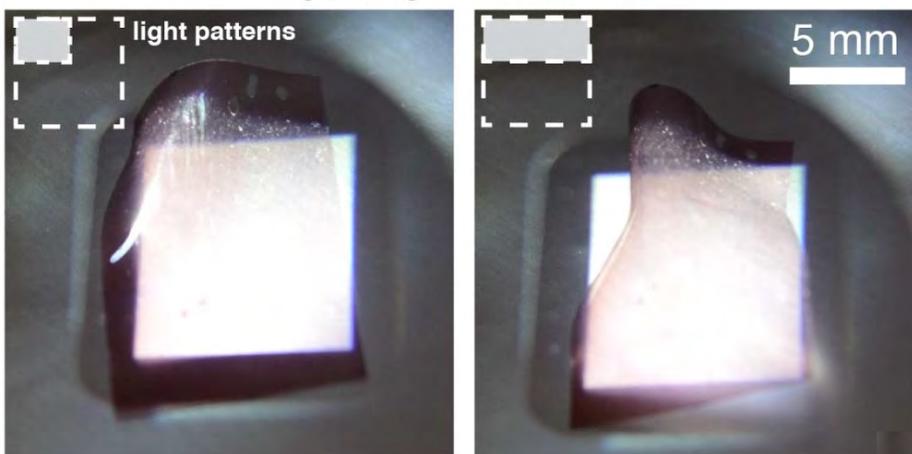
**Adam W. Hauser**<sup>1</sup>, [awhauser@mail.pse.umass.edu](mailto:awhauser@mail.pse.umass.edu), Arthur A. Evans<sup>3</sup>, Danqing Liu<sup>2</sup>, Kyle C. Bryson<sup>1</sup>, Jun-Hee Na<sup>1</sup>, Dirk Broer<sup>2</sup>, Ryan C. Hayward<sup>1</sup>. (1) Polymer Science & Engineering, University of Massachusetts, Amherst, Massachusetts, United States (2) Chemical Engineering & Chemistry, Eindhoven Technical University, Eindhoven, Netherlands (3) Mathematics, University of Wisconsin-Madison, Madison, Wisconsin, United States

Patterned in-plane deformation of thin sheets has attracted great attention as a means to create complex 2D to 3D shape transformations. Several interesting methods to pre-program such strains have been shown, but generally allow only a single type of transition from flat to a particular buckled state, or in rare cases, switching between a few pre-programmed shapes. Here, we show that photothermally responsive isotropic nanocomposite gels and anisotropic monodomain liquid crystal networks can be reversibly reconfigured into several buckled forms through projected patterns of white light. Predictable and easily controllable steady-state shape control is demonstrated, which may find uses in soft robotics, microfluidics, or any application that requires externally actuated complex deformation.

### *hydrogel networks*



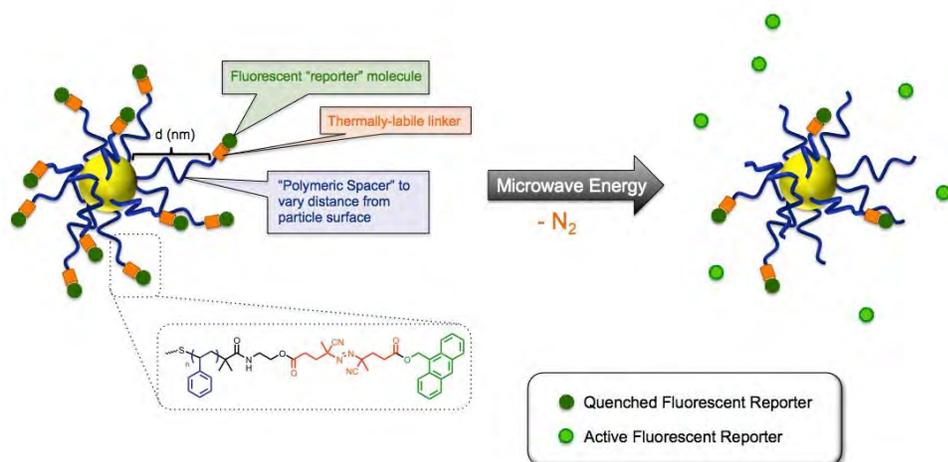
### *liquid crystal networks*



## POLY 291: Probing the surface-localized hyperthermia of gold nanoparticles in a microwave field using polymeric thermometers

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The surface-localized hyperthermia of gold nanoparticles under microwave irradiation was examined. Gold nanoparticles with a hydrodynamic diameter of ~6 nm stabilized by polymeric “thermometers” were used to gather information on the extent of heating as well as its spatial confinements. Reversible addition–fragmentation chain transfer polymerization was employed to synthesize well-defined, functional polymers of predetermined molecular weights, allowing for estimation of the distance between the nanoparticle surface and the polymer chain end. The polymers were conjugated with a fluorescent dye separated by a thermally-labile azo linkage, and these polymeric ligands were bound to gold nanoparticles via gold–thiolate bonds. Conventional heating experiments elucidated the relationship between temperature and the extent of dye release from the gold nanoparticle using fluorescence spectroscopy. The local temperature increase experienced under microwave irradiation was calculated using the same methodology. This approach indicated the temperature near the surface of the nanoparticle was nearly 70 °C higher than the bulk solution temperature, but decreased rapidly with distance.



## **POLY 292: Polyhomologation: Another version of monomer activated anionic polymerization**

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Access to well-defined (high degree of structural, molecular weight and compositional homogeneity) polyethylenes (PEs) and PE-based copolymers is necessary in order to elucidate the structure-properties relationships and evaluate potential applications. Recently, Shea developed a novel polymerization methodology leading to perfectly linear PEs. The general reaction scheme involves the formation of an organoboron zwitterionic complex between a methylide (monomer, anion) and a trialkylborane Lewis acid (activator/initiator) which breaks down by the intramolecular 1,2-migration. As a consequence, the activated methylene group of methylide is randomly inserted one by one into the three branches of the trialkylborane leading to a 3-arm PE star. The resulting star is subsequently oxidized/hydrolysed to give perfectly OH-end-capped linear PEs.

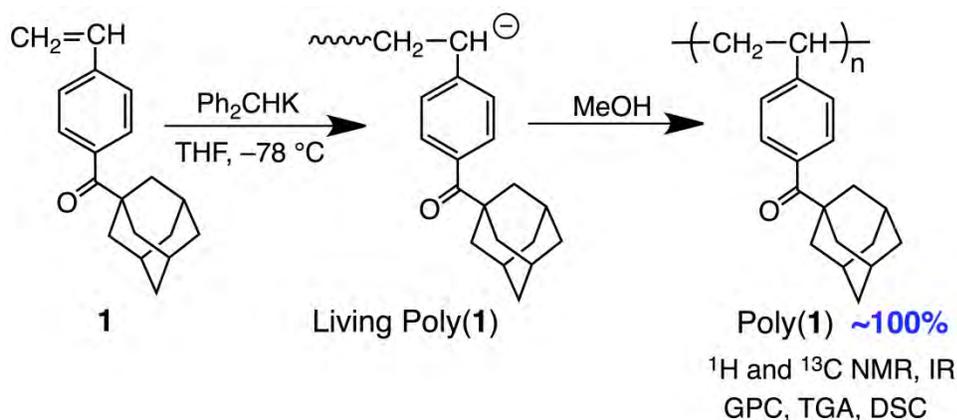
Our group is developing both novel borane initiators and ylides monomers and combines polyhomologation with other living polymerizations to synthesize model polymethylene (or PE)-based polymeric materials.

## POLY 293: Living anionic polymerization of 1-adamantyl 4-vinylphenyl ketone

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It has been believed that the anionic polymerization of styrene derivatives carrying ketone moieties is very difficult, since electrophilic carbonyl moieties readily react with the nucleophilic anionic initiators and the propagating carbanions. Furthermore, acidic alpha-hydrogens in the ketone moieties also prohibit the anionic polymerization via the proton abstraction. Therefore, a well-defined poly(4-acetylstyrene) has been obtained by the anionic polymerization of *tert*-butyldimethylsilyl enol ether of 4-acetylstyrene and the following deprotection. In this case, the electrophilic acetyl group was converted to the electron-rich silyl enol ether of monomer, and the acidic alpha-hydrogen of CH<sub>3</sub>CO group was eliminated to prevent the side reaction with the basic anionic species. In this study, we focus on the anionic polymerization behavior of a novel styrene derivative, 1-adamantyl 4-vinylphenyl ketone (1), which has a bulky adamantyl substituent without acidic alpha-hydrogen.

No polymerization of 1 occurred with *sec*-BuLi in THF at -78 °C for 48 h, and 1 was quantitatively recovered from the polymerization system. On the other hand, the mixture of 1 and diphenylmethylpotassium (Ph<sub>2</sub>CHK) showed a characteristic dark red color in THF at -78 °C, and the polymerization of 1 quantitatively proceeded within 24 h to form the polymers with predicted molecular weights and narrow molecular weight distributions ( $M_w/M_n = 1.1$ ). These results indicate that bulky *p*-conjugated initiators and larger counter cation of initiators are preferable for the successful polymerization of styrene derivative carrying ketone functionality to prevent side reactions as well as the bulky adamantyl group. In addition, the propagating carbanion of poly(1) was effectively stabilized by the electron-withdrawing carbonyl group. The resulting poly(1) had a high glass transition temperature at 193 °C, indicating the effect of introduced bulky adamantyl group.



## POLY 294: Synthesis of randomly branched polymers by anionic chain-transfer polymerisation

**Lian R. Hutchings**, *l.r.hutchings@durham.ac.uk*. University of Durham, Durham, United Kingdom

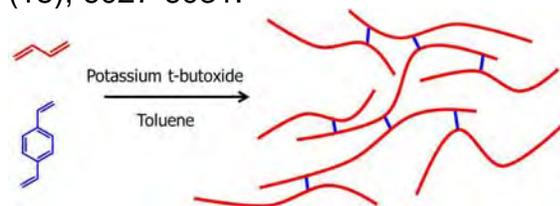
The synthesis of long-chain branched polymers has long been of interest to both academic and industry. In the past decade we have reported the synthesis of well-defined, nearly monodisperse DendriMacs<sup>1,2</sup> which were designed and synthesised for structure-property correlation studies. The synthesis of DendriMacs is extremely tedious and exploits time-consuming methodologies based on the coupling of AB<sub>2</sub> macromonomers. We have also reported the synthesis of HyperMacs<sup>3</sup> and HyperBlocks<sup>4</sup> by a more facile and scalable one-pot coupling reaction of AB<sub>2</sub> macromonomers, which results in rather polydisperse branched polymers with defined linear segments between branch points.

However, we report here today a new synthetic strategy for the production of randomly-branched, long-chain polymers prepared by anionic chain-transfer polymerisation. The described methodology is an adaption of the previously reported “Strathclyde route” developed by Sherrington *et al* in which highly branched polymers were prepared by free radical polymerisation using a divinyl comonomer in presence of a chain transfer agent to prevent gelation<sup>5</sup>.

We will describe how living anionic polymerisation may be adapted to allow the copolymerisation of simple commercial monomers with readily available difunctional comonomers to produce branched, soluble polymers by a commercially scalable approach. This new approach has been shown to be viable for the synthesis of branched polymers from dienes, methylmethacrylate and for the production of branched copolymers from styrene/diene.

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5. N. O'Brien, A. McKee, D. C. Sherrington, A. T. Slark, A. Titterton. *Polymer* 2000, 41 (15), 6027-6031.



Schematic of randomly branched polymer synthesized by anionic chain transfer polymerization

## POLY 295: Synthesis and application benefits of 1,3-butadiene and divinylbenzene copolymers

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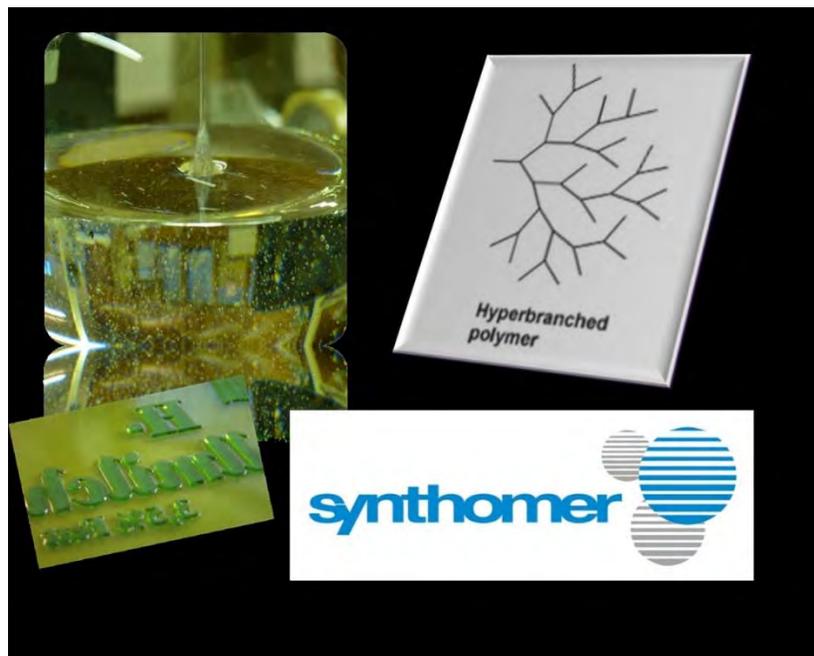
Synthesis and Application Benefits of 1,3-Butadiene and Divinylbenzene Copolymers  
*Malcolm McInnes, Carl A. Roeschlaub, Peter L. Shaw, Solomon Kimani and Paul Ross-Gardner, Synthomer UK Ltd, Harlow, UK*

Ionic polymerisation of 1,3 butadiene in the presence of controlled amounts of divinyl benzene and a Schlosser base generates a bimodal distribution of products containing both linear and cross-linked moieties. The result is a material that delivers the benefits a higher molecular weight material without increasing viscosity that may lead to processing complications.

Development products with target molecular weights ( $M_{\text{target}}$ ) from 10 000 up to 250 000g mol<sup>-1</sup> were synthesised and our study shows that the molecular weight and polymer architecture can be controlled by careful management of reagent addition.

The microstructure of the resulting polymers was calculated by <sup>1</sup>H-NMR and FTIR and polydispersity data and branching analysis was obtained by Size Exclusion Chromatography, equipped with refractive index, viscosity index and light scattering detectors.

The ability to “tune” the structure and properties should allow the development of product to serve a range of applications.

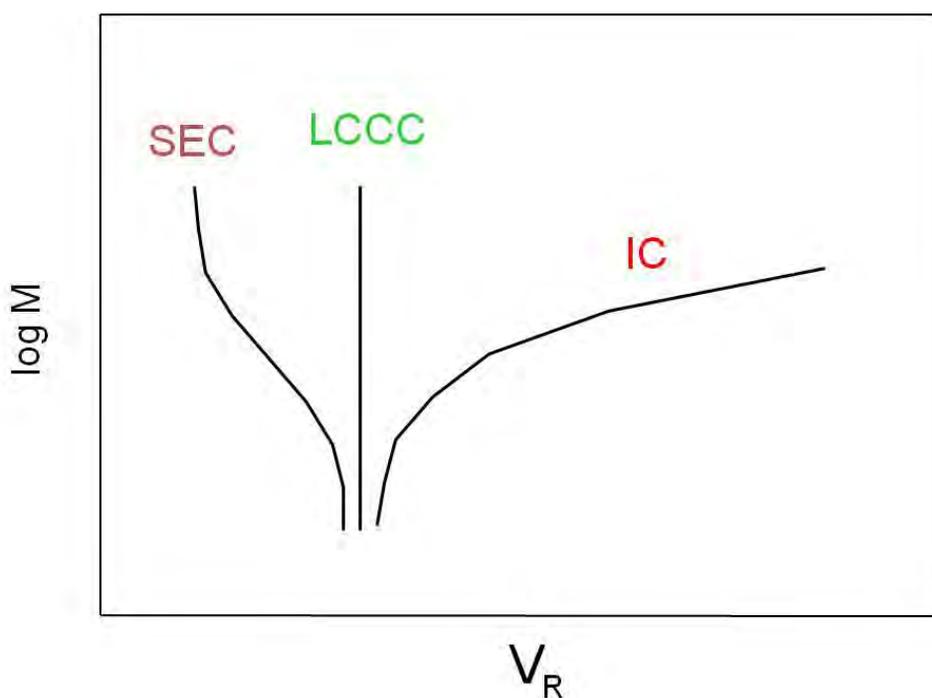


## POLY 296: Precise characterization of polymers prepared by anionic polymerization

**Taihyun Chang**, 30019351@acs.org. Pohang Univ Chemistry Dept, Pohang, Korea (the Republic of)

Synthetic polymers are not homogeneous molecules but have distributions in many molecular characteristics such as molecular weight (MW), chemical composition, chain architecture, and so on. Among the various separation methods of polymers, size exclusion chromatography (SEC) has been used. However, SEC separates macromolecules in terms of molecular size not MW, thus SEC has its limitation in resolving branched polymers or copolymers according to MW.

Interaction chromatography (IC) mainly utilizes the enthalpic interaction of polymeric solutes with the stationary phase. The enthalpic interaction depends on chemical composition as well as MW while less sensitive to chain architecture. Therefore, IC can complement the weakness of SEC effectively. In addition, band broadening is much lower in IC than SEC, thus IC exhibits a far better resolution than SEC. In Temperature gradient interaction chromatography (TGIC), the column temperature is controlled in a programmed manner during the elution to control the interaction strength of polymeric solutes with the stationary phase. TGIC exhibits much higher resolution than SEC in the separation according to MW and it allows many useful detectors for polymer characterization to be utilized, which is impossible in the solvent gradient elution. TGIC has been applied to resolve a number of long-standing problems in polymer characterization, particularly for the polymers prepared by anionic polymerization. In this presentation, the principle and representative applications of TGIC will be presented.



3 different modes in HPLC separation of polymers

## POLY 297: New synthetic strategy for the synthesis of amphiphilic PDMS-PEO block copolymer and characterization of heterobifunctional PEO using normal phase-interaction chromatography

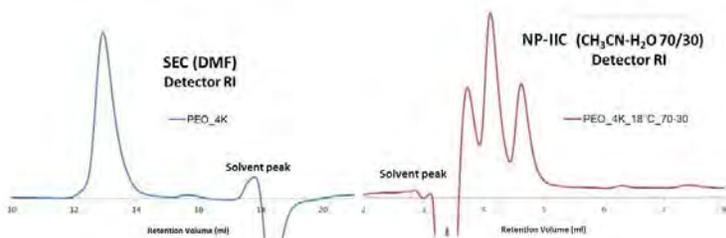
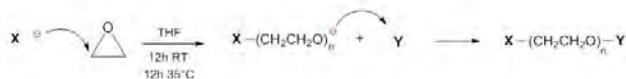
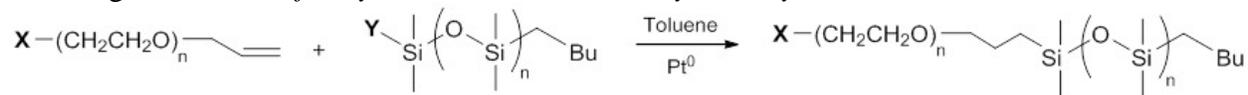
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Silicones or polysiloxanes are widely produced by anionic ring-opening polymerization (ROP) of cyclic trimers such as hexamethylcyclotrisiloxane (D<sub>3</sub>) to obtain poly(dimethylsiloxane) (PDMS). In order to widely exploit the unique properties of polysiloxanes, PDMS is often incorporated into block copolymer structures with a variety of different comonomers especially with hydrophilic poly(ether)s, like poly(ethylene oxide) (PEO) attached to the PDMS as linear copolymers or grafted onto the PDMS backbone. Given the promising role of silicone-based amphiphilic block copolymers in a whole set of applications, we present here a novel approach consisting of few synthetic steps for the preparation of end-functionalised amphiphilic PDMS-PEO block copolymers (scheme 1).

In addition to, we report on the synthesis of heterobifunctional PEO polymers of structure X-PEO-Y and particularly on the analysis of the polymers using Interaction Chromatography (IC) and Size Exclusion Chromatography (SEC) techniques<sup>1</sup>. The most direct method to obtain heterobifunctional PEO is the AROP of EO from a functional anionic initiator (X), followed by termination with a different functional group (Y) (scheme 2). The characterization of PEO and derivatives using HPLC techniques, including normal-phase (NP) and reversed-phase (RP) liquid chromatography have been generally used to separate the oligomers basing on the molecular weights<sup>2</sup>. Our main goal is to develop conditions for the Normal Phase Isothermal Interaction Chromatography (NP-IIC) analysis of end-functionalised PEO and to establish whether IC can provide additional information to SEC analysis about the molecular structure of PEO. It is known that NP-IC can be very useful for its ability to separate polymers in terms of functional groups, but we believe this is the first work showing how to discriminate PEO polymers based on their chain-end functionalities by using NP-IIC as evidenced in figure 2.

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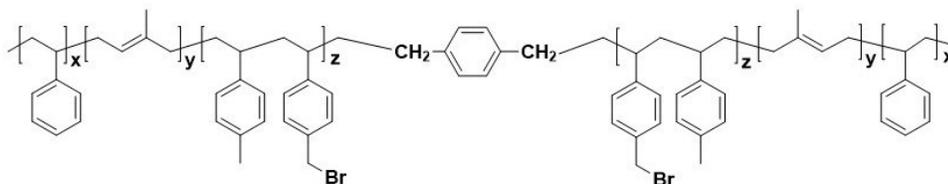
2. Chang T., *Journal of Polymer Science Part B-Polymer Physics*, 2005, 43, 1591-1607



## POLY 298: High conductivity durable anion conducting membranes

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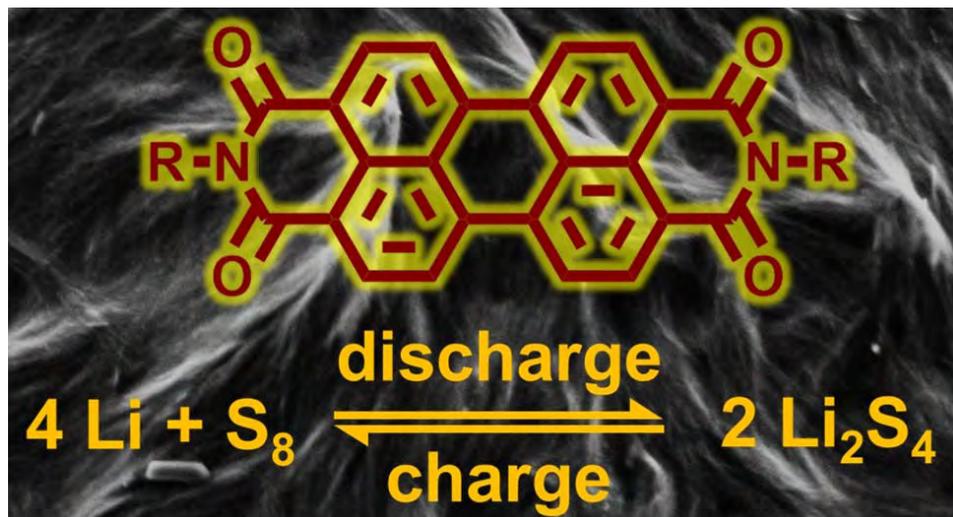
The goal of this technology is to develop highly conducting durable anion exchange membranes (AEMs) and demonstrate them as alkaline fuel cells (AFCs). A new type of a polystyrene copolymer with Br-methyl ring substituents was synthesized with well-defined polydispersity and degree of functionalization. Imidazole cross-linkers were used to simultaneously introduce cationic sites in order to improve the mechanical properties and to manipulate the chemical properties of the polymer. More specifically, anionic polymerization and high vacuum techniques, combined with click-chemistry, were employed in order to synthesize a pentablock copolymer consisting of two polystyrene outer blocks, two hydrogenated intermediate poly(isoprene) blocks and a partially brominated poly(4-methylstyrene) middle block. Molecular characterization was performed by using size exclusion chromatography (SEC), equipped with two angle laser light scattering (TALLS), and proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectroscopy. Conductivity measurements of the crosslinked pentablock with dicationic bis-imidazole groups in DI H<sub>2</sub>O showed promising results (74 mS/cm) at 25<sup>o</sup>C.



## POLY 299: Supramolecular redox mediators for lithium-sulfur batteries

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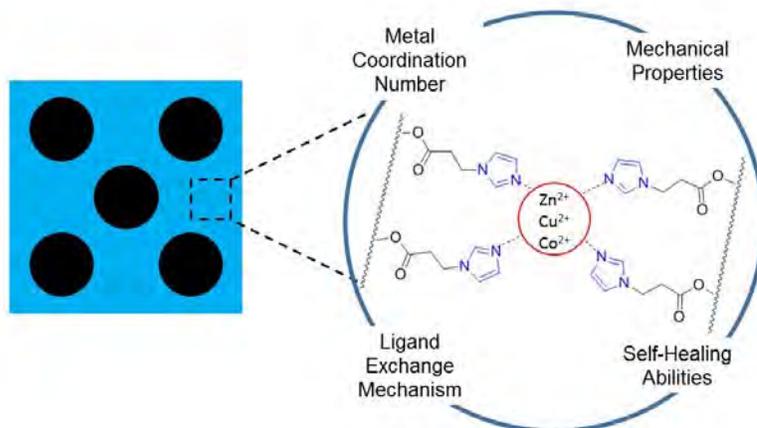
Redox-active molecular networks assembled from polycyclic aromatic hydrocarbons are well-positioned to be integrated in electrochemical devices where charge-transport bottlenecks limit device performance. This includes their application as nanostructured redox mediators, given the exceptionally low reorganization energy required for charge transfer to (or from) them across electrolyte-current collector interfaces. I will discuss in depth how to design and apply supramolecular design principles to such nanostructured redox mediators in the context of lithium-sulfur batteries.



## POLY 300: Role of metal-ligand bond strength and exchange dynamics on the mechanical properties of self-healing metallopolymers

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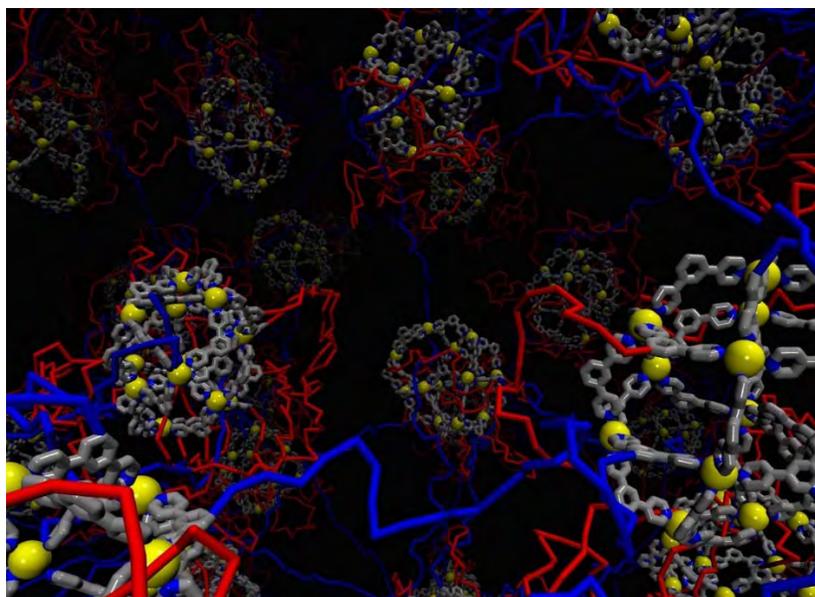
Understanding the chemical origin of bulk mechanical properties is a promising route toward design and synthesis of advanced materials. Traditionally, the mechanical performance of polymeric materials is controlled by chain packing, molecular weight, or crosslink density. Here, we use transient metal – ligand crosslinks to study the effects of metal coordination number and ligand exchange mechanisms on bulk mechanical properties and self-healing abilities. Specifically, an imidazole-containing brush copolymer system is crosslinked with zinc(II), copper(II), or cobalt(II) metal ions. This polymer design enables exquisite control over the imidazole to metal ratio, which provides tunability over stiffness and extensibility, as well as insight into metal – imidazole complexes in the system. We are able to observe a clear relationship between the established characteristics of metals and their rheological and uniaxial tensile data. We anticipate this study will further efforts towards understanding the chemical origin of mechanical properties in advanced and biological materials.



## POLY 301: Highly branched and loop-rich polymer metal-organic-cage gels

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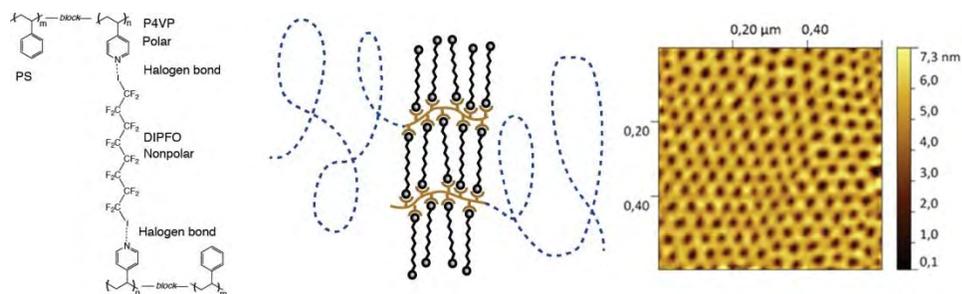
Gels formed via metal-ligand coordination typically have very low branch functionality,  $f$ , as they consist of ~2-3 polymer chains linked to single metal ions that serve as junctions. Thus, these materials are very soft and unable to withstand network defects such as dangling ends and loops. This talk will describe a new class of gels assembled from polymeric ligands and metal-organic-cages (MOCs) as junctions. Two examples of such "polyMOCs" – a low- $f$  gel based on a  $M_2L_4$  paddlewheel cluster junction and a higher- $f$  one based on a  $M_{12}L_{24}$  cage – will be described. These compositionally isomeric materials have completely different properties that arise from their self-assembled junction structures. The cage-based polyMOC with  $M_{12}L_{24}$  junctions features large shear moduli, but also a very large number of elastically inactive loop defects that can be subsequently exchanged for functional ligands with no impact on the gel's mechanical properties. Such a ligand substitution is not possible in low- $f$  gels, including the  $M_2L_4$ -based polyMOC.



## POLY 302: Halogen bond directed self-assembly of block copolymer complexes

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Supramolecular complexation of low molecular weight compounds to block copolymers allows hierarchical self-assemblies and routes for functional materials (O. Ikkala, G. ten Brinke, *Science*, 295, 2407, 2002). Therein hydrogen bonds, coordination, and ionic interactions have been feasible. On the other hand, halogen bonds are directional physical bonds that have become attractive in supramolecular chemistry of crystal engineering and liquid crystallinity (G. Cavallo, P. Metrangolo, T. Pilati, G. Resnati, M. Sansotera, G. Terraneo, *Chem. Soc. Rev.*, 39, 3772, 2010) They have recently also been used to control polymeric self-assemblies (N. Houbenov, R. Milani, M. Poutanen, J. Haataja, V. Dichiarante, J. Sainio, J. Ruokolainen, G. Resnati, P. Metrangolo, O. Ikkala, *Nature Comms*, 5, 4043, 2014). Here we show that perfluorinated low molecular weight compounds can be halogen bonded selectively to one block of a diblock copolymer to control the self-assemblies. In particular, we use polystyrene-block-poly(4-vinylpyridine), PS-*b*-P4VP, where ditopic rod-like 1,8-diiodoperfluorooctane molecules bond nominally at their both ends to the pyridines of P4VP. Due to the rod-like halogen bonded low-energy perfluorinated complexes, we foresee new options for block copolymer-based hierarchical self-assemblies and functionalizations.

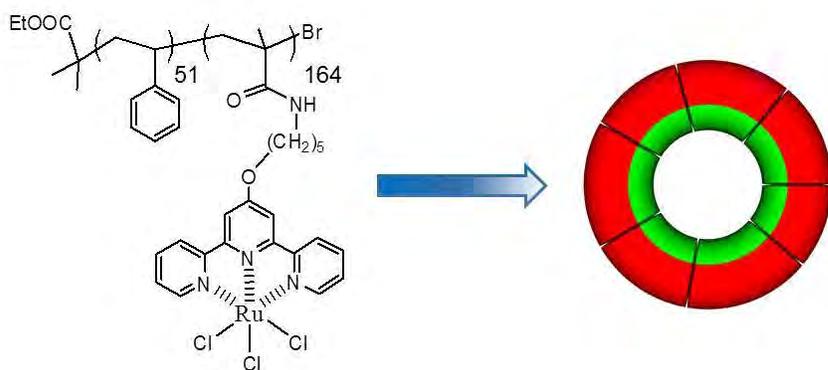


Halogen bonded supramolecular complex of polystyrene-block-poly(4-vinyl pyridine) and 1,8-diiodoperfluorooctane and AFM image of the resulting block copolymer length scale cylindrical self-assembly.

## POLY 303: Novel metal ligand containing block copolymers and their assembly

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Supramolecular chemistry has evolved into a powerful strategy for the creation of new materials. Metal-ligand bonds exhibit both strong and directional interactions in which the selection of metal ion and ligand can guide the strength of the association. To this end, we have established a program to incorporate metal binding ligands into polymers and copolymers to create new materials with tunable properties. A focus on blocky architectures and networks will be discussed.



## **POLY 304: Living crystallization-driven self-assembly: A versatile, seeded growth approach to functional supramolecular materials**

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Although chemical synthesis has evolved to a relatively advanced state, the ability to prepare well-defined materials of controlled shape, size, and structural hierarchy on a length scale from 10 nm – 100 microns is still in its relative infancy and currently remains the virtually exclusive domain of biology. In this talk recent advances concerning a promising new route to well-defined 1D and 2D materials within this size regime, termed “living 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 (PFS) metalloblocks. Living CDSA offers a versatile new route to monodisperse cylindrical micelles and 2D platelets, block comicelles with segmented non-equilibrium structures, and complex, hierarchical materials with controlled dimensions and a variety of potential applications. The seeded growth approach characteristic of living CDSA can be regarded as a type of “living supramolecular polymerization” that is analogous to living covalent (e.g. anionic) polymerizations of molecular monomers [1]. The process is performed under conditions that yield kinetically-trapped non-covalent assemblies in which potential dynamic behavior is switched off. Seeded growth approaches characteristic of living CDSA appear to be applicable to a wide range of other block copolymers with crystallizable blocks, including biodegradable and  $\pi$ -conjugated materials, and also to molecular amphiphiles that form  $\pi$ -stacked supramolecular polymeric assemblies [2].

### References

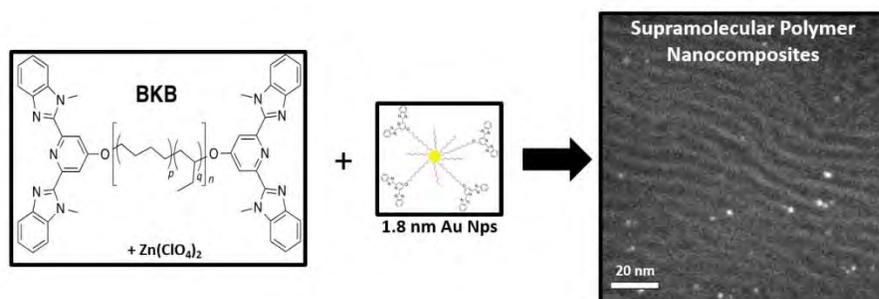
[1] J.B. Gilroy et al *Nature Chem.* 2010, 2, 566.

[2] Recent work from our group: M. Robinson et al *Chem. Comm.* 2015 DOI: 10.1039/C5CC06606A

## POLY 305: Synthesis and characterization of metallo-supramolecular nanocomposites

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A series of optically healable metallo-supramolecular nanocomposites was synthesized using the supramolecular assembly of poly(ethylene-co-butylene) telechelic oligomers and functionalized gold nanoparticles. After synthetic optimization of the functionalized gold nanoparticles using a direct synthesis approach, the nanoparticles were dispersed in chloroform and the assembly solution. Utilizing the metal-coordination bonds of 2,6-bis(1'-methylbenzimidazolyl)pyridine (MeBIP) ligands with a zinc metal ion, these supramolecular assemblies were formed with 0.1 wt% to 10 wt% octanethiol-functionalized gold nanoparticles or MeBIP-functionalized gold nanoparticles. The order of addition of gold nanoparticles, zinc salt, and telechelic oligomer in the assembly process proved essential to reduce nanoparticle aggregation and improve oligomer-nanoparticle interactions. The resulting morphologies of the solution-cast films were characterized with small angle X-ray scattering and transmission electron microscopy. The morphological effects of incorporating functionalized nanoparticles directly into the supramolecular polymer backbone will be discussed.

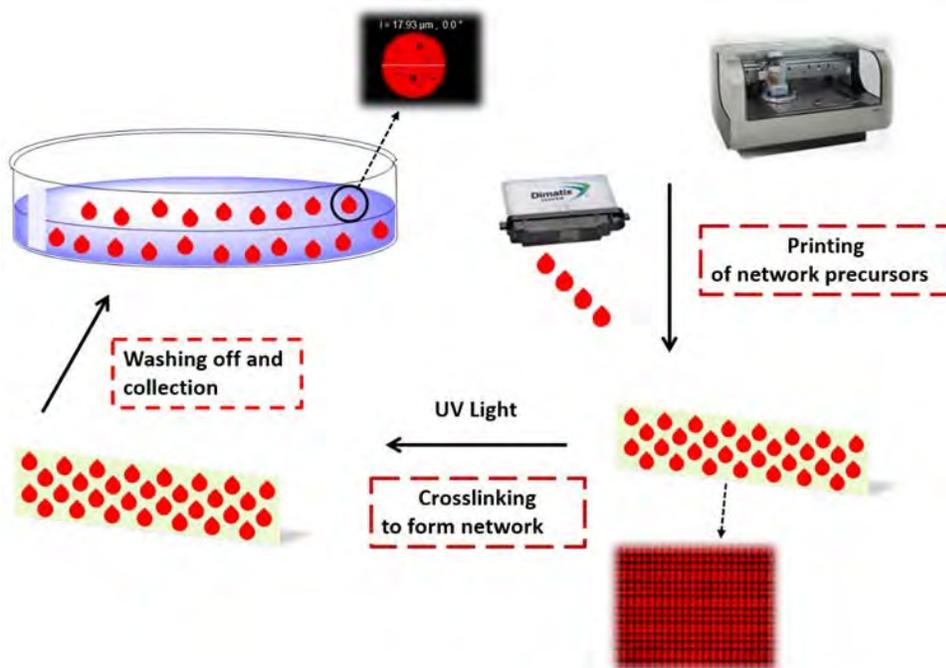


Components of the supramolecular polymer nanocomposite assemblies and a resulting HAADF STEM micrograph of a solution cast film.

## POLY 306: Printing of polymer hydrogel microparticles as drug delivery vehicles

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A method for the fabrication of monodisperse hydrogel microparticles via inkjet printing has been developed. This technique allows for the synthesis 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 in the presence of the desired cargo with a dithiol species via thiol-ene click to form the hydrogel microparticles in the range of 10-30  $\mu\text{m}$ . This process has been implemented to create hydrophobic, hydrophilic, and amphiphilic structures which can be loaded with a range of 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). Particles formed from crosslinked poly(glycidol)s have shown intriguing physical characteristics and will be investigated for their application in inhalants and vaccines.

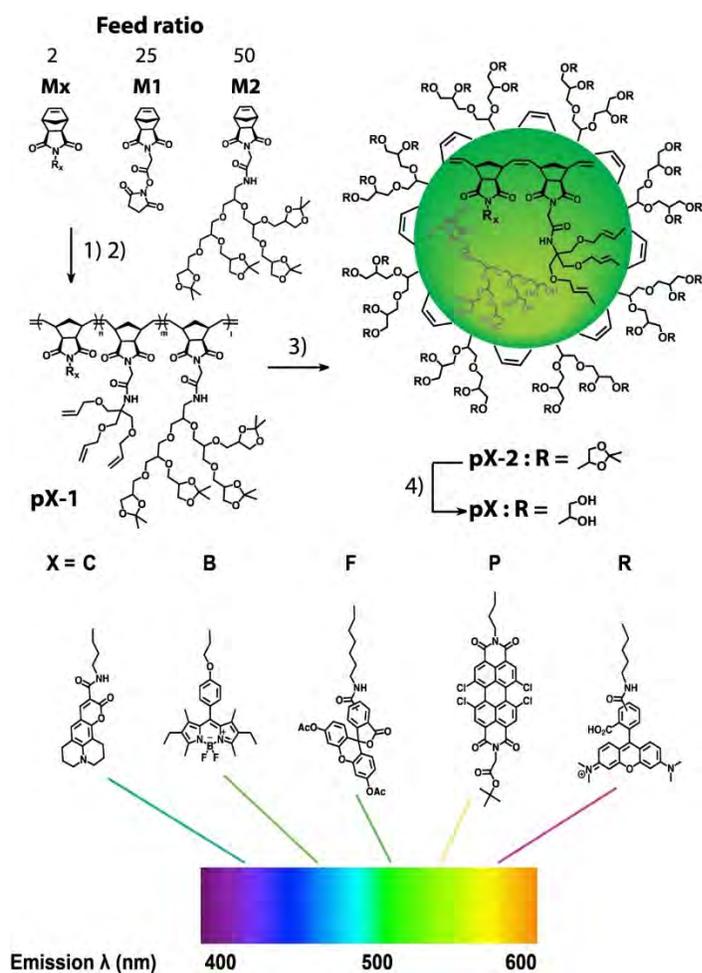


Hydrogel particle printing process.

## POLY 307: Crosslinked dendronized polyols as a general approach to brighter and more stable fluorophores

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Crosslinked dendronized polyols (CDPs) that are fluorescent and aqueous soluble are obtained through a sequential ring-opening metathesis polymerization (ROMP), intra-chain ring-closing metathesis (RCM) and hydrolysis process. This strategy renders this process a general approach to improve the quantum yields (QYs), brightness and photostability of fluorophores of different families. In addition, the polymers' ability to escape endosome after cellular uptake open the doors to more applications in bioimaging and intracellular delivery.

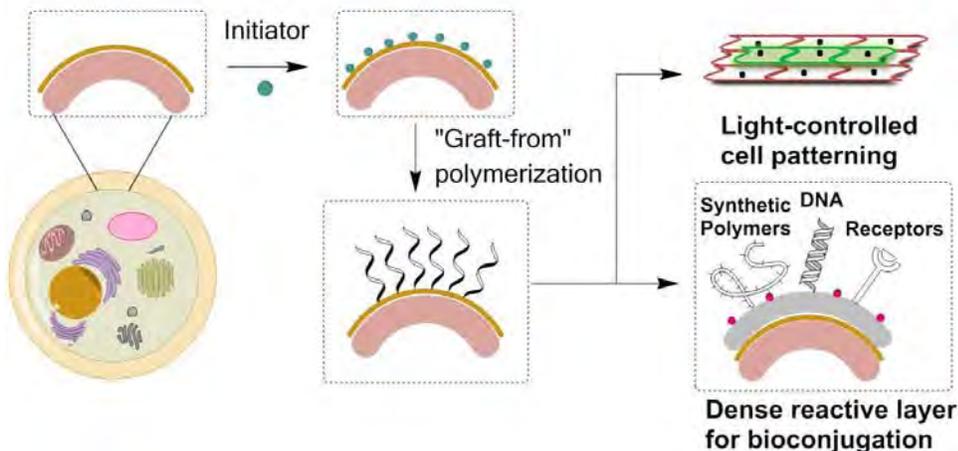


The synthetic scheme of the crosslinked dendronized polymer pX. 1) 3<sup>rd</sup> Grubbs catalyst, DCM; 2) tri-*O*-allyl tris, nitrobenzene, DCM, 40 °C; 3) 1st Generation Grubbs catalyst, DCM, high dilution condition; 4) TFA, DCM, Acetone, H<sub>2</sub>O, 40 °C. X represents the specific dye incorporated. The corresponding emission wavelengths of different dyes are displayed on the visible spectrum.

## POLY 308: Development of a light-mediated, cytocompatible controlled radical polymerization technique for cell surface engineering applications

**Jia Niu**<sup>2,3</sup>, [jniu@mrl.ucsb.edu](mailto:jniu@mrl.ucsb.edu), Lior Dassau<sup>3</sup>, Craig J. Hawker<sup>1</sup>. (1) Univ of California, Santa Barbara, California, United States (2) Materials Research Laboratory, University of California, Santa Barbara, Santa Barbara, California, United States (3) California NanoSystems Institute, University of California, Santa Barbara, Santa Barbara, California, United States

Synthetic polymers as cell surface modification materials have attracted significant research and development efforts due to their macromolecular nature that enables improved mechanical property, higher density and diversity of functional groups, and structures more closely resembling the natural protein receptors. However, the majority of the existing synthetic polymer cell surface engineering approaches have been based on the conjugation of pre-made synthetic polymers to the cell surface (the “graft-to” strategy). While the graft-to approaches are relatively straightforward to execute, the lacks of efficiency in polymer conjugation to the cell surface and the ability to spatially and temporally control the reaction limit the density and functionality of the graft-to polymers on cell surface. Herein, we report a light-mediated controlled radical polymerization approach that directly initiate polymer growth on the cell surface. Such a “graft-from” approach still maintains high cell viability while generating a dense polymer coating with various functional side chains on the cell surface. Regulated by light, the polymer growth is spatially and temporally controlled, resulting in a patterned cell surface with the light-directed distribution of the grafted functional synthetic polymers. This technique can provide a powerful tool for potential applications such as programmable cell-cell interaction and bottom-up three-dimensional tissue construction.



## POLY 309: Biodegradable polyesters from renewable resources

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Using materials from renewable resources such as glycerol and sugar alcohols (sorbitol, erythritol and xylitol), biocompatible and biodegradable polyesters were enzymatically synthesized using *Candida Antarctica* type B (CAL-B) lipase. Due to regioselectivity of the lipase enzyme, these multiple hydroxyl containing structures along with divinyladipate, produce linear polyesters possessing unreacted hydroxyl groups on their backbone.

In another attempt cross-linkable, biodegradable polyesters based on fumaric acid were synthesized. Yet in another approach water soluble functional polyesters based on tartaric acid and a series of ethylene glycols have also been synthesized. Initial results have shown that these polymers along with boronic acid form biodegradable hydrogels. Figure 1 shows the chemical structure of poly(sorbitol adipate) which is truly water soluble.

Poly(glycerol adipate), poly(xylitol adipate) and poly(sorbitol adipate) were grafted with different amounts of saturated and unsaturated fatty acids. Structure analysis of these grafted chains was done using XRD. Liquid crystalline nanoparticles of these grafted polyesters were prepared using the interfacial deposition method and dynamic light scattering measurements were carried out to find their particle size [1]. Further analysis of these particles was done using negative staining TEM and cryo-Tem. All the synthesized products were characterized by NMR- and IR-spectroscopy and their thermal behavior was analyzed by DSC.

### References

[1] Weiss, V. M.; Naolou, T.; Hause, G.; Kuntsche, J.; Kressler, J.; Mäder, K. *J. Control. Release* 2012, 158, 156–164.

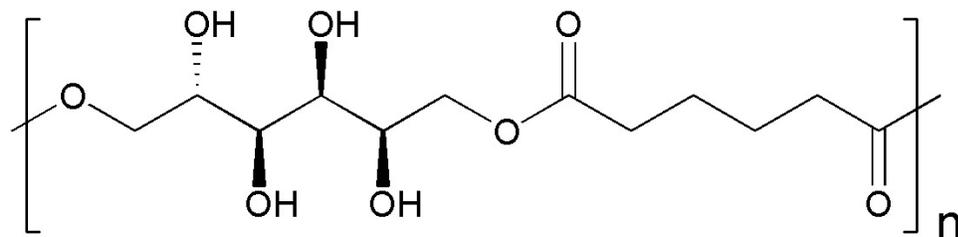


Figure 1: Chemical structure of poly(sorbitol adipate).

## POLY 310: New amphiphilic polymers for peptide complexation

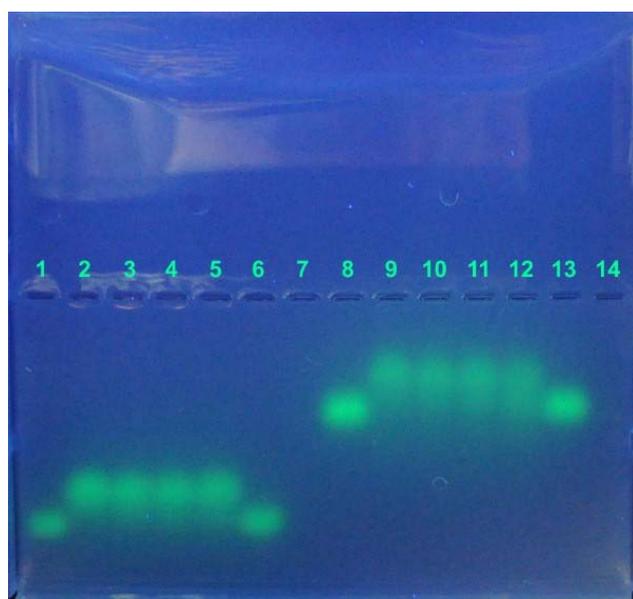
**Oksana Zholobko**<sup>1</sup>, oksana.zholobko@ndsu.edu, Ananiy Kohut<sup>2</sup>, Shane Stafslie<sup>1</sup>, Lyndsi VanderWal<sup>1</sup>, Ihor Tarnavchyk<sup>1</sup>, Andriy S. Voronov<sup>1</sup>. (1) Coatings and Polymeric Materials, North Dakota State University, Fargo, North Dakota, United States (2) Organic Chemistry, Lviv Polytechnic National University, Lviv, Ukraine

Swine influenza virus [SIV] is the second most economically significant pathogen of swine. Despite decades of research, developing vaccines that can produce robust and broad protection against the many strains of influenza viruses is a challenge. Polymer-conjugated proteins and peptides as vaccines are a rapidly expanding area of research, due to the discovery of new proteins/peptides and a better understanding of the mechanism(s) of their actions *in vivo*.

Synthesized in our group two polymer types, pseudo poly(amino acids) (PSAA) and amphiphilic invertible polymers (AIPs) are employed for complexation with peptides. PSAA are polymers with the confirmed ability to entrap a variety of potential antigens. Selected PSAA was synthesized from poly(ethylene glycol) (PEG, 300 g/mol), N-lauroyl-glutamic acid and glutamic acid to yield PEG:Glu(Boc):Glu(Lauryl) – 1.14 : 0.77 : 0.23 composition.

It was expected that by self-assembling of AIPs, the micellar invertible assemblies become capable of peptide complexation. Selected AIP D10 was synthesized from poly(ethylene glycol) (PEG, molecular weight 1000) and dodecanedioic acid. Both synthesized polymers were characterized using <sup>1</sup>H NMR spectroscopy, FTIR spectroscopy, GPC, acid-base titration methods, zeta-potential and cytotoxicity measurements.

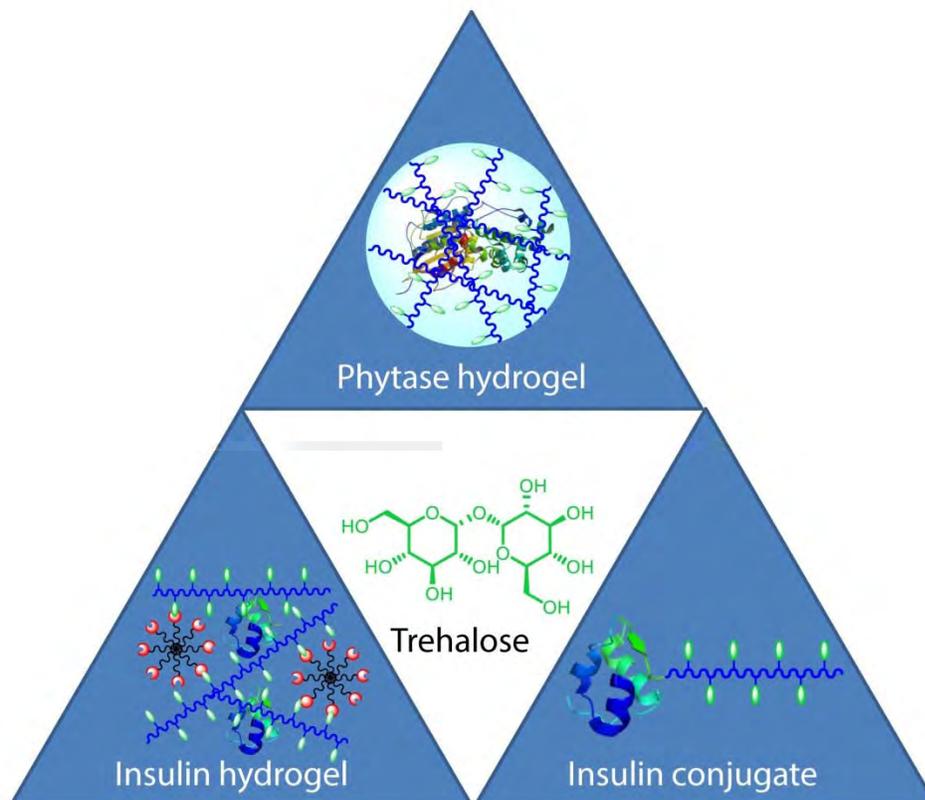
The polymer ability to form complexes with peptides was tested using HA and V5 peptides. Using gel electrophoresis it was demonstrated that the formation of complexes is determined by polymer-peptide ratio and the stability of polymer-peptide complexes varies depending on the pH value and polymer concentration.



## POLY 311: Trehalose polymers for stabilization of industrially important proteins

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Proteins are important as therapeutic drugs and enzymes for industrial processing, sensing applications, and laboratory reagents. However, they are unstable to heat and other environmental stressors and are thus limited in their applications. We have previously synthesized glycopolymers based on trehalose, a natural protein-stabilizing disaccharide, and have stabilized various proteins to stressors such as heat, lyophilization, and even electron beam irradiation. We have extended this platform to synthesize trehalose-based materials to stabilize industrially important proteins. First, industrially scalable hydrogel synthesis was used to generate trehalose hydrogel that stabilized phytase, an important enzyme in the animal feed industry. We have also used trehalose-boronic acid hydrogel that can release insulin upon addition of glucose, which is relevant for diabetes treatment. Moreover, the hydrogel stabilized insulin to heating. Finally, trehalose polymer was conjugated to insulin as a model protein drug to improve its pharmacokinetics and stability. We expect that these strategies will be applicable to stabilization of a wide range of proteins.



Stabilizing industrially important proteins

## POLY 312: Molecular design for dual modulation effect of amyloid protein aggregation

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Modulation of protein self-assembly has been a powerful strategy for controlling and understanding amyloid protein aggregation. Most modulators of amyloid aggregation only involve simple inhibition or acceleration. We recently developed a new multivalent molecular motif, the polyethyleneimine–perphenazine (PEI-P) conjugate which has a dual “acceleration–inhibition” modulation effect on amyloid  $\beta$  ( $A\beta$ ) aggregation. Dose dependent results from Thioflavin T fluorescence assays, circular dichroism, and atomic force microscopy show that PEI-P conjugates accelerate formation of  $A\beta$  prefibrillar intermediates and then inhibit  $A\beta$  fibrillation. Furthermore, compared to perphenazine alone, PEI-P conjugates exhibit an enhanced inhibitory effect due to multivalency. Cell viability assays indicate that the PEI-P conjugates reduce the cytotoxicity of  $A\beta$  aggregates in a dose-dependent manner. This new modulation strategy may shed light on controlling amyloid aggregation, which offers a general concept for designing new modulators.

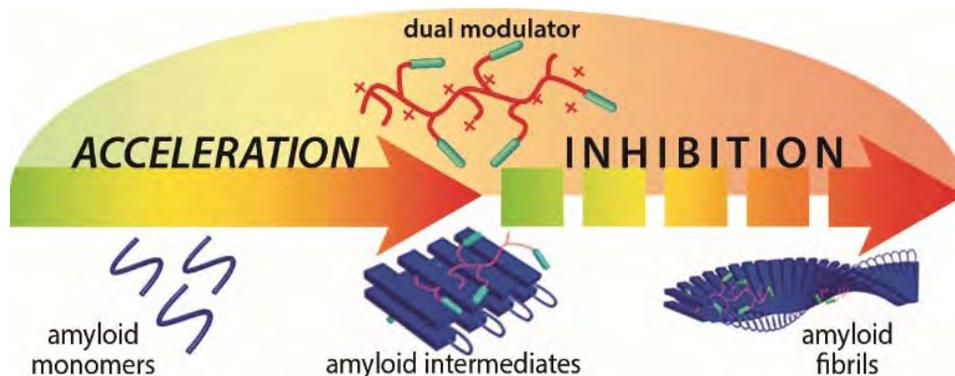
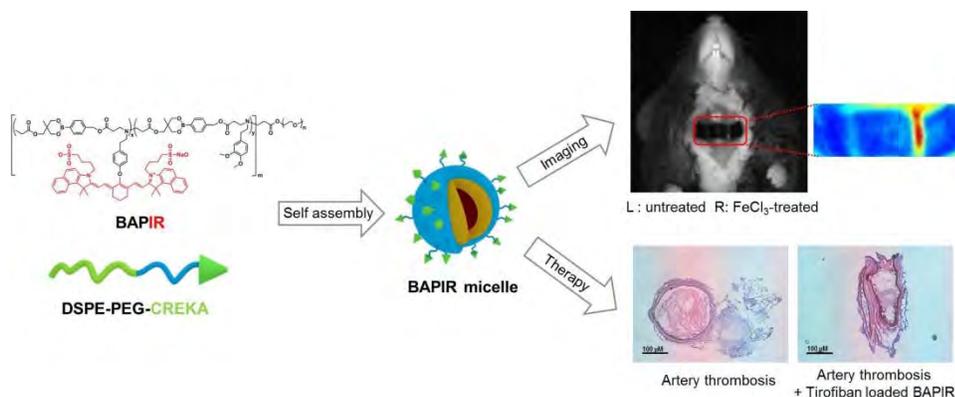


Figure. Dual modulation effect of amyloid protein aggregation by polyethyleneimine-perphenazine conjugates

## POLY 313: H<sub>2</sub>O<sub>2</sub>-activatable and clot-targeting antithrombotic polymeric nanoparticles

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Thrombosis (blood clot) is characterized by the recruitment and aggregation of platelets and fibrin deposition. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is a key mediator of platelet activation and aggregation and H<sub>2</sub>O<sub>2</sub>-mediated platelet activation is one of mechanisms leading to prothrombotic phenotypes. H<sub>2</sub>O<sub>2</sub> activates platelet-endothelium interactions, facilitating inflammation and development of atherosclerotic vascular diseases. As a clotted plasma protein, Fibrin exists in the form of cross-linked mesh deposited both inside and on the surface of atherosclerotic plaques and plays an important role in the stabilization of thrombus. By taking advantages of elevated level of H<sub>2</sub>O<sub>2</sub> and abundance of fibrin during thrombus formation, we developed a novel thrombus-targeted imaging and antithrombotic nanopatform, which is able to specifically target thrombus, scavenge H<sub>2</sub>O<sub>2</sub> and inhibit thrombus formation in injured vasculature. The nanopatform was formulated with antioxidant and anti-inflammatory boronate polymer (BAP-IR) and fibrin targeted lipopeptides (DSPE-CREKA). BAP-IR was designed to covalently incorporate H<sub>2</sub>O<sub>2</sub>-scavenging boronate and near infrared fluorescent IR-820 and release bioactive hydroxybenzyl alcohol (HBA) after H<sub>2</sub>O<sub>2</sub>-mediated boronate oxidation. BAP-IR rapidly scavenged H<sub>2</sub>O<sub>2</sub> and underwent H<sub>2</sub>O<sub>2</sub>-triggered hydrolysis to release HBA. BAP-IR and lipopeptides were self-assembled to form thermodynamically stable micelles with a mean diameter of ~120 nm. The micelles could target blot clots and reduce the generation of H<sub>2</sub>O<sub>2</sub> in platelets activated by calcium chloride and thrombin *in vitro*. In the study of a mouse model of ferric chloride-induced carotid artery thrombosis, the micelles could image ferric chloride-induced thrombus, reduce inflammatory responses and significantly inhibited blot clotting. When anti-thrombotic drug, tirofiban was loaded in the micelles, they exerted remarkable anti-thrombotic effects. Given their excellent biocompatibility, antioxidant and anti-inflammatory activity, BAP-IR has great potential as an imaging and therapeutic agent for obstructive thrombosis.



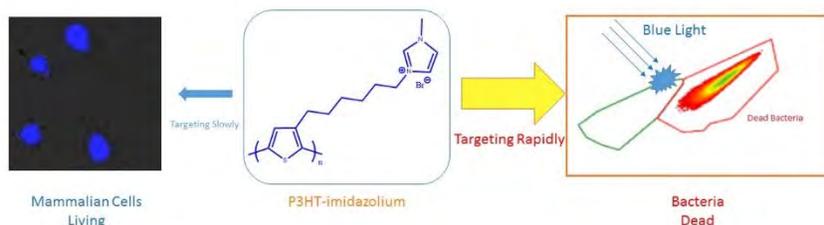
A schematic diagram of H<sub>2</sub>O<sub>2</sub>-activatable and clot-targeting antithrombotic nanoagents

## POLY 314: Targeting rate dependent selective imaging and inactivation of bacteria over mammalian cells by regioregular polythiophene with imidazolium solubilizing groups

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The increase of antibiotic-resistant bacteria has become a serious public health concern, and it is essential to develop an alternative strategy to pathogenic bacteria without harming human cells. In effort to address these concerns, we synthesized a regioregular head-to-tail poly {3-[6-(1-methylimidazolium-3-yl)hexyl]thiophene-2,5-diyl bromide} (P3HT-imidazolium,  $M_n = 12,000$ ) by Grignard metathesis controlled polymerization. In water, P3HT-imidazolium exhibits a broad absorption band in the visible region from 390-550 nm. Additionally, fluorescence quenching studies performed in methanol or water revealed that P3HT-imidazolium undergoes amplified quenching when using anionic electron acceptor sodium anthraquinone-2,6-disulfonate. A triplet-triplet transient absorption with a lifetime of 1.51  $\mu\text{s}$  was observed, confirming the existence of a triplet excited state. Sensitization of singlet oxygen by the polyelectrolyte was measured according to singlet oxygen phosphorescence at 1270 nm in deuterated methanol.

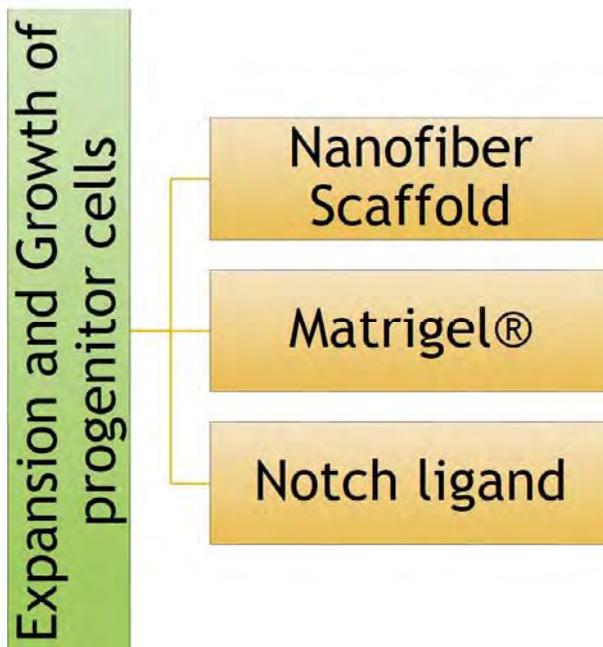
The biocidal activity of 10  $\mu\text{g/mL}$  P3HT-imidazolium has been demonstrated with Gram-positive *Staphylococcus aureus* and Gram-negative *Escherichia coli*; in the presence of near-visible light (420 nm), 2 log (99%) kill is achieved after one hour. Moreover, preliminary results suggested that P3HT-imidazolium is nontoxic to mammalian cells at concentrations  $\leq 20 \mu\text{g/mL}$  over a short time scale ( $\leq 1$  hour) in the dark or when irradiated with blue light, due to relatively slow targeting rates. To the best of our knowledge, this is the first study to demonstrate the capability of a simple cationic polymer to achieve selective imaging and inactivation of bacteria over mammalian cells by utilizing different targeting rates, indicating that P3HT-imidazolium is particularly well-suited for addressing antibiotic-resistant bacteria in the clinical setting.



## POLY 315: Nanofiber scaffolds as an ex-vivo method for stem cell growth

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Current treatment of Sickle Cell Disease (SCD) involves either a bone marrow or a stem cell transplant. The issues involved with bone marrow transplants, such as graft failure or difficulty in donor matching, suggest that stem cell transplants may be a more effective treatment approach. This work presents an ex-vivo approach for expansion of progenitor cells in the treatment of SCD. Nanofiber scaffolds consisting of Matrigel® and Notch Ligand have been developed to support CD34+ hematopoietic stem cell (HPC) growth and expansion. These nanofiber scaffolds were constructed using a 15% polycaprolactone (PCL)-8% chitosan (CS) blend. The surface morphology of the scaffolds were studied using SEM and TEM. It was observed that the fibers are aligned, uniform, and measure around 400 nm in diameter. Preliminary findings show that the developed PCL/CS scaffolds show promise as successful substrates for enrichment and expansion of CD34+ hematopoietic stem cells.



## POLY 316: PHEMA hydrogels filled with nanogels of polyhexylacrylate (HA) core and polyethylene glycol (PEG) Shell: Preparation and Properties

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Hydrogels are crosslinked polymeric materials with swelling capacity in water. They can be prepared in sizes ranging from nanometers (nanogels) to centimeters (macrogels). Hydrogels are widely investigated due to its countless biological applications. Poly (2-hydroxyethyl methacrylate) (PHEMA) hydrogels, are widely used in the biomedical field due to their easy polymerization, oxygen permeability, and high biocompatibility. PHEMA hydrogels are glassy materials in the dry state at room temperature, however, this behavior can be modified to be soft at room temperature and resistant at physiological conditions. The present work was undertaken to prepare improved PHEMA macrogels by introduction of nanogels with core-shell structure; having a flexible core of poly(n-hexyl acrylate) (PHA), and a biocompatible shell of polyethylene glycol methacrylate (PEGMA), which allows for a good interface between the macrogel and nanogel. The nanogels were prepared by surfactant-free emulsion polymerization (SFEP) method and PHEMA macrogels, filled and unfilled, were prepared by photocrosslinking polymerization. The results of swelling, compression and thermal analysis show that the incorporation of the PHA/PEGMA nanogels increased the compressive modulus in the swollen state, the thermal stability in the dry state and the overall flexibility of the macrogels. This behavior depends on the concentration and the diameter of the nanogels incorporated into the macrogel.



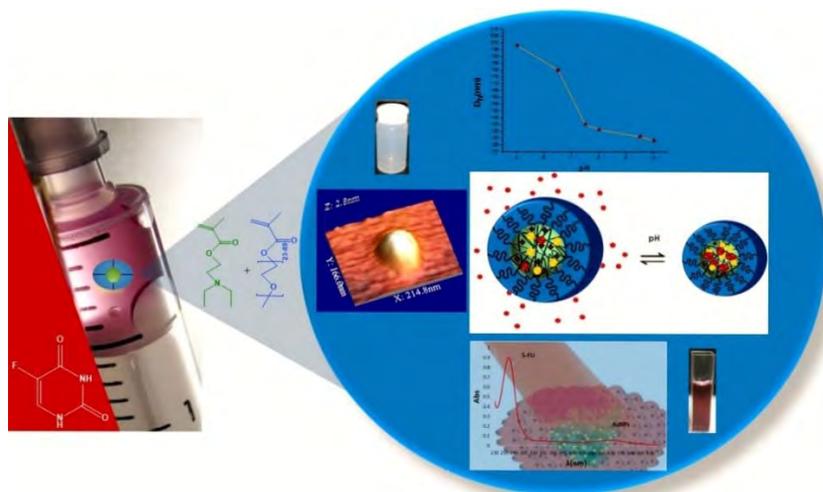
## POLY 317: Pegylated cationic nanogels based on PDEAEM for drug delivery

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Nanogels are nanosized polymer networks swollen in a liquid, i.e. water. Nanogels that respond to certain pH changes by changing its volume have gain great importance due to the fact that tumor tissues are known to show slightly acidic pH compared to healthy tissues. Therefore pH sensitive nanogels are good candidates for biomedical applications, for example, for pH triggered drug delivery.

In this contribution a synthetic approach has been established for the preparation of nanogels formed by a pH responsive core of poly(*N,N*-diethylaminoethyl methacrylate) (PDEAEM) and a shell of the biocompatible polymer polyethylene glycol (PEG). The methodology used for the synthesis was the “soap-less” emulsion polymerization, i.e. an emulsion polymerization reaction without surfactant, where a methacrylate functionalized PEG (PEGMA) acts as stabilizer for the monomer droplets while it was incorporated by free radical reaction as shell over the crosslinked PDEAEM nanoparticle. For stabilizing the polymeric nanoparticles and providing them with a network structure, three different crosslinkers were tested: ethylene glycol dimethacrylate (EGDMA), *N,N*-bis(acryloyl)cystamine (BAC), and a divinylacetal compound (DVA), furthermore the effect of the type of water soluble initiator, an azo compound (AIBA) and two persulphate initiators (APS and KPS) has been studied.

Dynamic light scattering results show that the average diameter of the nanogels decreased from 274 nm down to 73 nm with increasing PEGMA content in the recipe, while maintaining a narrow size distribution. It has been observed under similar synthetic conditions that the crosslinker type and initiator affects the average diameter and the size distribution. Furthermore, with the aim to develop dual therapy nanogels, gold nanoparticles were prepared *in situ* and also *ex-situ* and incorporated in addition to 5-Fluorouracil, into selected nanogels and tested in drug delivery experiments.



Scheme of PEGylated poly(*N,N*-diethylaminoethyl methacrylate) pH responsive nanogels acting for 5-FU delivery vehicle in cancer treatment.

## POLY 318: Investigating the unique structure and physical properties of spider prey wrap silk with electron microscopy and solid-state NMR

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Spiders use aciniform silk to wrap and immobilize their prey and also in the construction of egg cases. It is the finest of the spider silks having a fiber diameter approximately an order of magnitude smaller compared to spider dragline silk. For the spider species *Argiope aurantia*, we find aciniform silk fiber diameters are  $500 \pm 100$  nm compared to  $3.5 \pm 0.5$   $\mu\text{m}$  for dragline spider silk (see Figure 1). Aciniform spider silk has been scarcely studied compared to other spider and silkworm silks. Yet, it has been shown that the mechanical properties are superior compared to the highly touted dragline silk with regards to toughness because of a unique combination of high modulus and extensibility.<sup>1,2</sup> There is some primary amino acid sequence information available on the protein that comprises aciniform spider silk, aciniform spidroin 1 (AcSp1), that illustrates it is a highly repetitive protein similar to other spider silk proteins, but lacks the common repeat units found in other spider silks. For example, the poly(Ala) and Gly-Ala couplets that form the nanocrystalline  $\beta$ -sheet structures that impart dragline spider silk its high modulus are poorly represented in the primary amino acid sequence of AcSp1.<sup>1</sup> By feeding the spiders <sup>13</sup>C/<sup>15</sup>N-labeled amino acids we can label the prey wrap silk enabling advanced multidimensional magic angle spinning (MAS) solid-state NMR techniques to characterize the silk protein structure. We find that this silk, unlike other spider and silkworm silks, has a predominant  $\alpha$ -helical structure compared to the  $\beta$ -sheet hallmark structure of other spider and silkworm silks. This structural information helps to explain the greater extensibility and toughness observed for prey wrap spider silk compared to the dragline silk.

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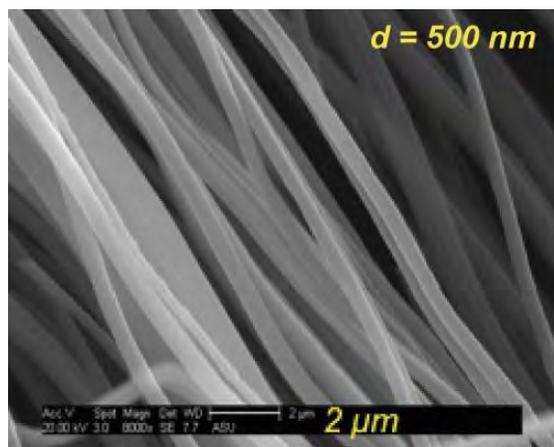
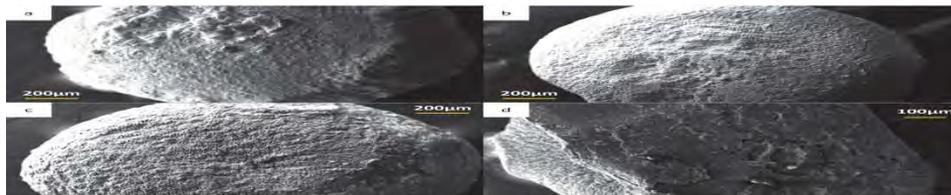


Figure 1. Scanning Electron Microscope (SEM) image of spider prey wrap silk.

## POLY 319: Controlled release of plant hormones for agricultural purposes

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Massive amounts of agriculture run-off water carrying a variety of contaminants are discharged by agricultural operations. Without proper disposal this situation can lead to alarming levels of water pollution. One possible approach to solve this problem is to discharge agricultural chemicals via controlled release formulations. This work explores the properties and performance characteristics of polysaccharide beads as reservoirs/carriers for controlled release of plant hormones. The beads were formulated with different types of low cost natural polysaccharides, including alginate, starch, cellulose powder, xylan, and nanocrystalline cellulose (NC). To improve their mechanical properties as well their plant hormones controlled release characteristics, kaolin and a positively charged polyelectrolyte, polyethylenimine (PEI) were incorporated into the beads. The sizes, swelling ratios, surface morphologies and mechanical strength of the beads were evaluated and the cumulative release of a model plant hormone, phenylacetic acid, was measured and related to the composition of the beads.

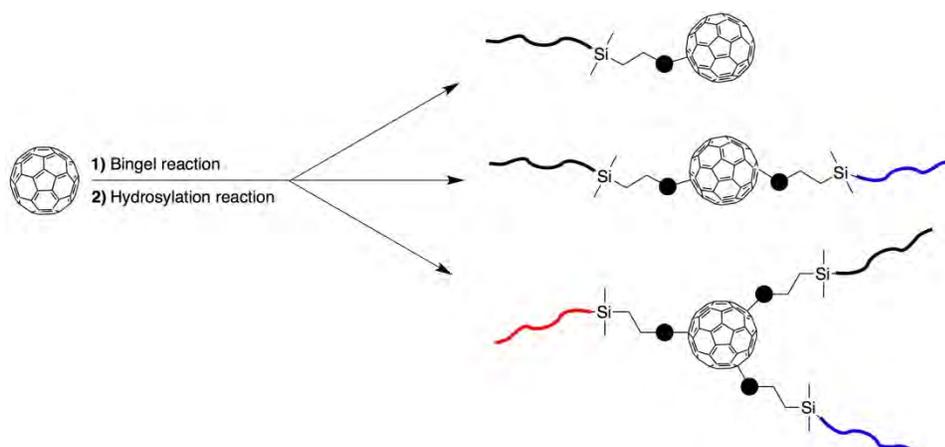


Surface morphologies of crosslinked beads (2% w/v alginate, 2% kaolin, 1% xylan) (a) without coating, (b) 2% PEI coating, (c) 4% PEI coating, (d) cross section of (b)

## POLY 320: Well-defined synthesis of miktoarm star polymers with a fullerene core

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$C_{60}$  is a fascinating allotrope of carbon that possesses perfect structural symmetry and exceptional electronic properties. The preparation of new fullerene derivatives has been extensively studied in the past two decades, with particular attention to the combination of  $C_{60}$  with versatile polymer chemistry. Numerous  $C_{60}$  containing polymers have been successfully synthesized, including  $C_{60}$ -endcapped polymers,  $C_{60}$  dendrimers, star-shaped polymers bearing  $C_{60}$  core, etc. So far, star architectures containing a  $C_{60}$  core are mainly synthesized by attachment of polymer chain-end living anions or living radicals, however these reactions produce a highly complicated mixture of mono-, bis- and multiple adducts in the product. In this work, we present an indirect grafting-to method to introduce functionalized polymers onto the  $C_{60}$  core in sequence. This synthetic approach enables various star polymers bearing a  $C_{60}$  core to be obtained by first producing mono functionalized  $C_{60}$  derivative with a vinyl linker through a Bingel reaction. The well-defined polymer arms are synthesized, and subsequently end-capped with chlorodimethyl silane, by anionic polymerization using high vacuum and glass-blowing technique. The final step of the synthesis employs the hydrosylation reaction between the functionalized  $C_{60}$  core and silyl end-capped polymer to produce the desired  $C_{60}$ -containing star polymer. Since the efficiency of hydrosylation reaction is relatively high in nature, this process can be reiterated multiple times to yield miktoarm star polymers. The resulting polymers are characterized by  $^1H$  NMR,  $^{13}C$  NMR, and mass spectrometry. In addition, the molecular weight and polydispersity of the star polymers were obtained by gel-permeation chromatography. This successful methodology will give rise to a new realm of research in a variety of applications including organic electronics, nanoscience and nanotechnology using their self-assembly, thermoplastic elastomers, with the possibility of additional tailoring to creating more interesting composites.



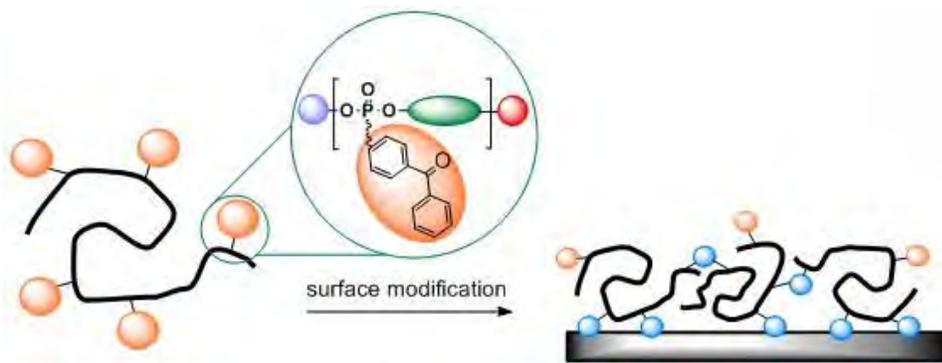
Scheme of  $C_{60}$  star polymer synthesis

## POLY 321: Sticky poly(phosphoester)s: UV triggered surface modification

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Poly(phosphoester)s (PPEs) are a very interesting, yet rather neglected class of polymers. The chemical structure of PPEs is highly modular, they are degradable and their degradation time can be adjusted by precise chemistry. Poly(ethyl ethylene phosphate) (PEEP) is a water-soluble polymer. In biomedical applications it can be a potential biodegradable alternative to today's gold standard: poly(ethylene glycol).

Herein, we present PPE-coated surfaces. For this purpose, a new photoreactive phosphate monomer was synthesized. It can be copolymerized with ethyl ethylene phosphate (EEP) by controlled anionic ring-opening polymerization to obtain "linear functionalized PEEP". The polymer then can be attached to a surface via C,H insertion reaction when exposed to UV-light. In this way, PPEylated surfaces can be generated which may find useful application in biomedical applications, e.g. implants tissue engineering. The surfaces were characterized in detail.

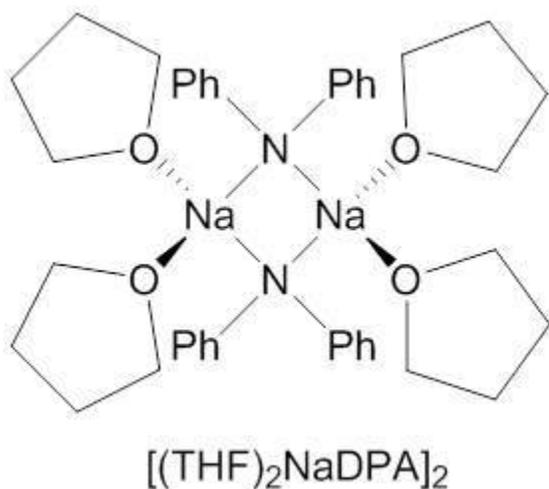


Schematic view of modification of surfaces with PPEs

## POLY 322: Revealing the initiation mechanism of aggregated sodium diphenylamide in anionic polymerization of isocyanates

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Since polyisocyanates as a class of dynamic helical polymers were discovered in 1959, their distinct conformational and morphological features have become exclusively studied subjects for attractive research fields such as chiroptical switches, macromolecular vehicles, liquid crystals, and photonic crystals. The primary work to take advantage of desired properties of polyisocyanates is to achieve the controlled molecular weight (MW) and narrow polydispersity. We have found anionic polymerization using sodium diphenylamide (NaDPA) initiator fulfills this prerequisite. NaDPA typically associates into a tetrasolvated dimer in THF. The polymerization behaviors were strongly affected by several types of additives. The initiation efficiency of NaDPA in the presence of several base ligands including THF was shown to be 40~50%. Surprisingly, the addition of sodium tetraphenylborate a common ion salt raised the initiation efficiency of NaDPA quantitatively, as well as the kinetic of propagation indicated the living nature. The aggregation structures of NaDPA are expected to strongly affect the initiation mechanism.



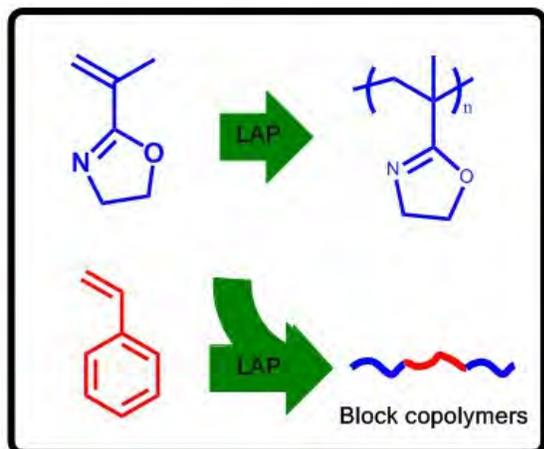
Tetrasolvated dimer structure of NaDPA initiator in THF.

## POLY 323: Synthesis of well-defined poly(2-isopropenyl-2-oxazoline) via living anionic polymerization

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2-isopropenyl-2-oxazoline (IPOx) is a water-soluble monomer and IPOx-containing polymers are used widely for many applications of bio-medical, polymer therapeutics, nano science, etc. IPOx has isopropenyl moiety, which can undergo free radical, reversible-addition-fragmentation chain transfer (RAFT) polymerization. It also contains oxazoline moiety which is capable of polymerization under acid catalysis via ring-opening polymerization. On the other hand, the successful synthesis of well-defined poly (2-isopropenyl-2-oxazoline) (PIPOx) via anionic polymerization has not been reported yet. Therefore, it is still a big challenge of establishing controllable polymerization anionically. This poses the question: can living anionic polymerization of IPOx be truly possible?

In this study, the synthesis of well-defined water-soluble PIPOx via living anionic polymerization using two initiation systems of i) potassium naphthalenide and ii) diphenylmethyl potassium/diethyl zinc through high-vacuum and glass-blowing techniques was investigated. The resulting PIPOx with controlled molecular weight from 6,000g/mol to 720,000g/mol and narrow molecular weight distribution, 1.04~1.15 was successfully synthesized for the first time and characterized by <sup>1</sup>H, <sup>13</sup>C-nuclear magnetic resonance spectroscopy (NMR), size exclusion chromatography (SEC), matrix assisted laser desorption ionization (MALDI-TOF) mass spectrometry, viscometry and neutron scattering. Moreover, the reactivity of living PIPOx was investigated by cross-over polymerization with styrene (st), 2-vinyl pyridine (2VP), methyl methacrylate (MMA) and ethylene oxide (EO). We found living PIPOx can be initiated by living P2VP and living PMMA. Furthermore, PIPOx-b-PS-b-PIPOx tri-block copolymers with different block ratios were carried out and the morphology and solution self-assembly behavior were studied by transmission electron microscopy (TEM).



## POLY 324: Synthesis and TGIC characterisation of H-shaped polymers: The macromonomer approach

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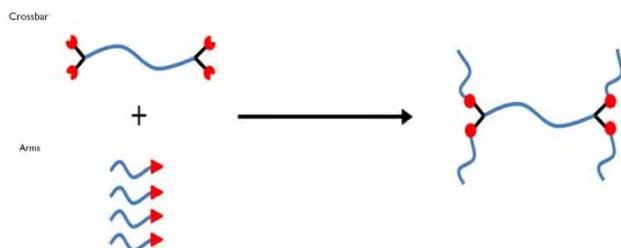
We present the synthesis and characterisation of H-shaped polybutadienes via the “macromonomer” approach. This approach has previously been exploited for the synthesis of star branched polymers<sup>1</sup>, dendritically branched polymers, DendriMacs<sup>2</sup> and HyperMacs<sup>3,4</sup>, involves the use of polymers with reactive chain-end functionalities introduced via a functionalised protected initiator or a functionalised protected end capping agent. The functional macromonomers can then be coupled together in a post-polymerisation reaction (Fig. 1). The traditional method of H-shaped polymer synthesis involves the use of chlorosilane coupling reactions, which can produce multiple side products. The macromonomer approach allows for the construction of branched polymers in much simpler terms with greater control over properties such as molecular weight and molecular weight distribution over each chain in the polymer and we describe here the synthesis of a series of homologous H-shaped polymers in which the MW of the crossbar can be absolutely identical in each case whilst the arm molecular can be systematically varied or vice versa.

All macromonomers were prepared using living anionic polymerisation resulting in well-defined polymers with narrow molecular weight distributions. The telechelic “crossbar” polymer was prepared in a one-pot, one shot copolymerisation exploiting monomer reactivity ratios to control monomer sequence distribution as previously described<sup>5</sup>.

The crossbar, arms and final H-shaped polymers were characterised using size exclusion chromatography as well as normal-phase temperature gradient interaction chromatography to establish the extent of chain-end functionalisation and reverse-phase temperature gradient interaction chromatography to analyse the structural homogeneity of the final product.

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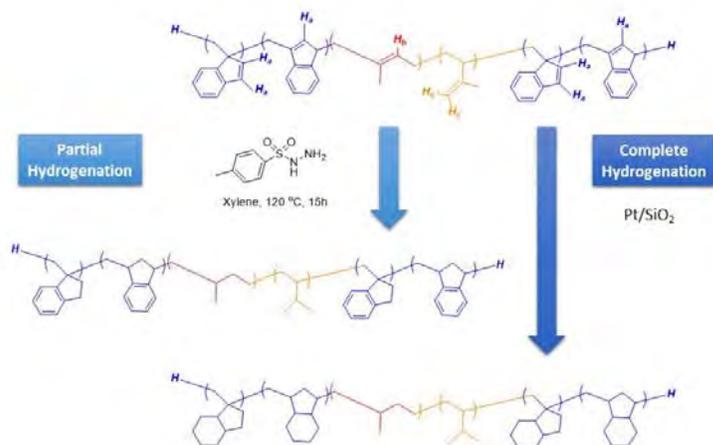
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## POLY 325: Developing high temperature thermoplastic elastomers based on benzofulvene by living anionic polymerization in hydrocarbon solvent at room temperature

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Thermoplastic elastomers (TPEs) are of great importance both academically and technologically. Currently TPEs are predominating styrenic-diene copolymers. However, these styrenic TPEs have serious limitations in applications, especially at higher temperature, because of their low upper service temperature (UST). Here we present a new class of TPEs with higher UST based on benzofulvene, an anionically polymerizable monomer in hydrocarbon solvent at room temperature. Polybenzofulvene-*b*-polyisoprene-*b*-polybenzofulvene (FIF) triblock copolymers of four different compositions were synthesized through a difunctional lithium-based initiator (DLI) in benzene. These synthesized triblock copolymers retained their storage modulus up to 150°C before dropping off proved by dynamic mechanical analysis (DMA). Tensile test revealed FIF with 14 vol% of polybenzofulvene has maximum 1400% strain with a tensile strength of 17 MPa. Small angle X-ray scattering showed microphase separation between polybenzofulvene and polyisoprene but without long range order. Partial and complete hydrogenation of FIF triblock were performed and resulting polymers showed different mechanical properties but improved thermal stability. Study of 1,2- and 1,4- microstructure of polybenzofulvene homopolymers was carried out in benzene with different polar additives such as *sec*-Butoxide (*sec*-BuOLi), 1,2-dipiperidinoethane (DiPIP), 1,2-dimethoxyethane (DME). The glass transition temperature analyzed from differential scanning calorimetry (DSC), respectively, were 153°C, 161°C and 191°C at molecular weight of 20kg/mol. Thus, synthesizing high temperature thermoplastic elastomers with potential of tunable service temperature by incorporating polybenzofulvene as a new building blocks is possible.



## POLY 326: Synthesis and characterisation of poly(dimethylbutadiene) copolymers

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2,3-dimethyl-1,3-butadiene (DMB), typically referred to as dimethylbutadiene is a colourless liquid monomer that was used in the production of synthetic poly(dimethylbutadiene) (PDMB) commonly called methyl rubber. This polymer, first synthesized by Kondakov<sup>1</sup> in 1900, is considered the first commercial synthetic rubber. PDMB was developed in Germany as a replacement for natural rubber however there is very little published data on this monomer and its polymers. Any academic interest seems to have largely died after the conclusion of WWI. Natural rubber is always considered a material with excellent mechanical properties. These features are usually attributed to its ability to stress-crystallise<sup>2</sup>. This property is highly dependant upon the microstructure of the polymer backbone. According to Henderson<sup>3</sup>, in the case of PDMB this property is influenced mainly by the content in 1,2 and *trans*-1,4 microstructures in the polymer backbone (Fig. 1).

We describe herein the synthesis of homopolymers and copolymers of DMB in different polarity solvents. DMB was copolymerised with styrene and butadiene to obtain statistical copolymers and with divinylbenzene (DVB) in order to explore the synthesis of randomly branched copolymers. The target molecular weights ( $M_{\text{target}}$ ) of the obtained materials ranged from 10000 up to 100000 g mol<sup>-1</sup>.

The microstructure of the resulting polymers was calculated by <sup>1</sup>H-NMR. Molecular weight and polydispersity data was obtained by Size Exclusion Chromatography using both a triple detector (with refractive index, viscosity and light scattering detectors).

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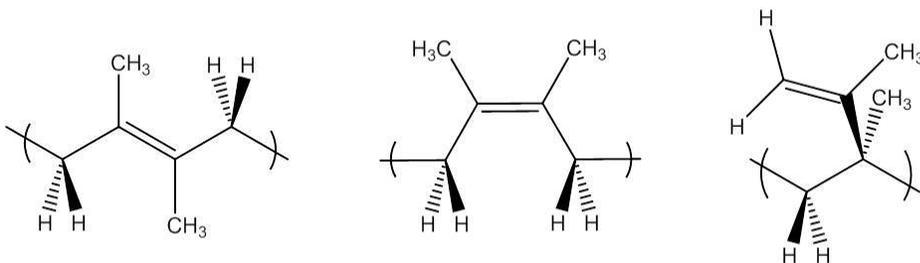


Figure 1. PDMB possible microstructures. From left to right: *trans*-1,4, *cis*-1,4 and 1,2.

## **POLY 327: Efficacy of phytochemical-based antimicrobial coatings**

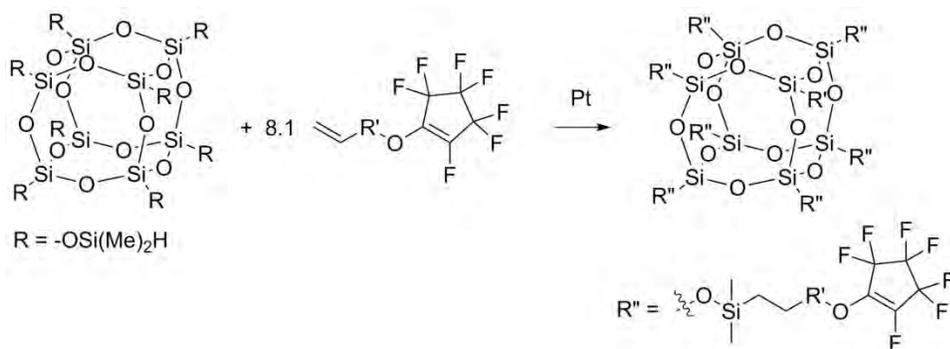
*Wai Yi HUI, wyhuiaa@connect.ust.hk, Ying Li, Jong Hong LEE, King Lun Yeung. The Hong Kong University of Science and Technology, Hong Kong, Hong Kong*

Essential oils are containing phytochemical components derived from plants. Their antimicrobial properties enable to disinfect or inhibit the growth of microorganisms, which may be harmful to plants or humans. The aim of our research is to develop a formula using antimicrobial capsules and essential oils. The research is to examine phytochemical-based antimicrobial formulation into coating materials for sustained surface disinfection, controlled-release and anti-adhesion properties. An understanding of the inhibition and inactivation mechanisms of these phytochemicals is essential for their optimal formulation. Target microorganisms will include Gram+ and Gram- bacteria, and fungal spores and tests will be carried out under conditions that simulate practical use. Finally, the coating will be reformulated to optimize bactericidal efficiency and durability by examining the impact factor of chemicals used. Several experiments were launched to optimize the formula, for example, the amount of each component used was reduced to minimize the usage and maximize bactericidal efficacy. Release rate test and long term bactericidal test were launched on glass medium. It shows that the coating can remain over 90% bactericidal performance in a month.

## POLY 328: Synthesis and applications of partially fluorinated organically modified silicas

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Fluorinated organically modified silicas (F-ORMOSILs) are unique organic-inorganic hybrid materials which have been extensively used for non-wetting surfaces and coatings. Our current research endeavors focus on developing new fluorinated monomers utilizing perfluorocyclopentene. The monomers were designed such that they contain terminal reactive groups, allowing them to easily be incorporated into organically modified silicas through the implementation of solution-gelation and hydrosilylation chemistries. The monomer synthesis and their use in the preparation of F-ORMOSILs; including silsesquioxanes, nano-metered sized silica particles, aerogels, and surfaces will be discussed in detail. Furthermore, the ability to synthetically post-modify the F-ORMOSILs and utilize them for hydrophobic coatings will be investigated.



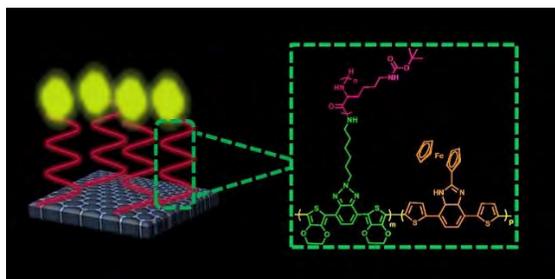
## POLY 329: Synthesis and characterization of conducting polymers containing polypeptide and ferrocene side chains as ethanol biosensors

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Conducting polymers are used as excellent immobilization platform for biomolecules led to the development of efficient biosensors, taking the advantages of ease of processability, ability of conduct the electricity and low cost<sup>1</sup>. Combining synthetic polymers with polypeptide segments becomes a promising approach in the field of enzyme immobilization since polypeptides segments possess remarkable biocompatibility and exhibit a 3D conformation under certain conditions<sup>2</sup>. Also, development of ferrocene polymer modified electrodes provides superior characteristics such as relatively low molecular mass, reversibility and generation of stable redox forms due to their nature of excellent electron transfer mediator<sup>3</sup>. Herein, we report electrochemically simple synthetic approach, capable of yielding random conducting copolymer possessing both polypeptide side chains and ferrocene units. While polypeptide segments created a fascinating biocompatible environment for enzyme immobilization as well as enabling covalent attachment of the enzyme, the ferrocene units improve biosensor performance without any leaching. Alcohol oxidase was used as a model enzyme was immobilized onto the proposed matrix covalently in the presence of glutaraldehyde as the crosslinking agent. The intermediates and final conducting copolymer before and after enzyme deposition were fully characterized. The designed biosensor combining the advantages of each component was tested as the ethanol sensing system and the biosensor design becomes a promising complementary method for ethanol analysis in alcoholic beverages. The fabricated sensor offers fast response time (9 s), wide linear range (0.17 mM and 4.25 mM) and low detection limit (0.28 mM) with high sensitivity (12.52  $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$ ). Kinetic parameters  $K_M^{app}$  and  $I_{max}$  were determined as 2.67 mM and 2.98  $\mu\text{A}$ , respectively. The applicability of the biosensor in analyzing ethanol content in real alcoholic samples was also tested and the results approves reliability and accuracy of the biosensor.

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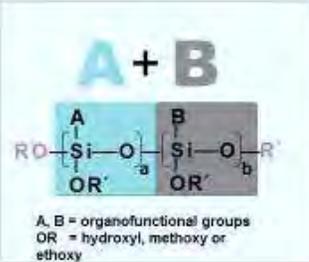
## POLY 330: Neat and aqueous novel functional siloxane oligomers for adhesive and coating applications

*Tim N. Biggs, tim.biggs@evonik.com. Evonik, Piscataway, New Jersey, United States*

Evonik's Silane R&D group has developed neat and aqueous novel siloxane oligomers for adhesive and coating applications. Previously, silane monomers provided good performance in these applications; however, as demand for improved performance (e.g. adhesion) and lower environmental impact increased, unique silane oligomers were generated that provided better adhesion, better mechanical properties, easier processing and much lower environmental impact. Both neat and aqueous oligomers and co-oligomers were designed for flexibility in the end-user application whether 100% solids or water based. Additionally, a variety of functional groups are available in these materials to give the user wide latitude with a variety of adhesive/coating resins and reagents as well as substrates.

### Evonik Silane Oligomer Multifunctional System™





A, B = organofunctional groups  
OR' = hydroxyl, methoxy or ethoxy

- **Chemical multifunctionality within one product**
- **Storage stable, low viscous liquid, easy dosing**
- **Reduced VOC**
- **High flash point, no evaporation (enhanced product processability and safety)**
- **Better compatibility to polymers/resins**
- **One diffusion rate and one reactivity**
- **Improved film forming properties on fillers**
- **Excellent reactivity and surface modification**
- **Polymer by OECD definition**

### Key Benefits



1. **Better performance & low VOC content**
2. **Multifunctionality**
3. **Safer handling & less environmental impact**
4. **Low water uptake during storage**

Dynasylan®

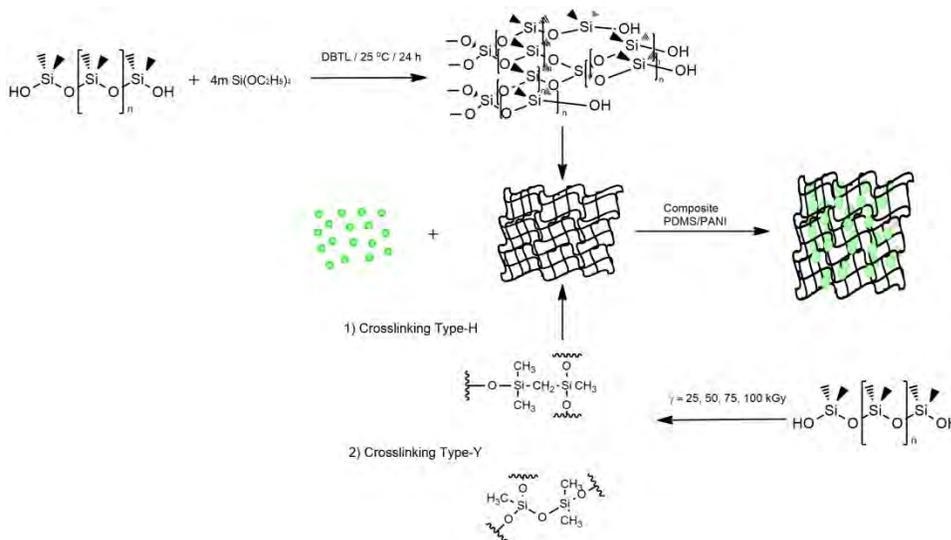
Page 1

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## POLY 331: Polydimethylsiloxane/Polyaniline composite: Study and structural characterization of the elastomeric matrix obtained by gamma radiolysis and polycondensation route

**Miguel Angel Melendez Zamudio**<sup>1</sup>, *ma.melendezzamudio@ugto.mx*, Antonio Villegas<sup>1</sup>, Melendrez Rodrigo<sup>2</sup>, Jorge A. Cervantes<sup>1</sup>. (1) Universidad de Guanajuato, Guanajuato, Mexico (2) Universidad de Sonora, Sonora, Mexico

Polysiloxanes are the most used and studied inorganic polymer. One of the fields of applications is the synthesis of composites with remarkable properties. The aim of this project is the preparation of a composite integrated by an elastomeric matrix of poly(dimethylsiloxane) (PDMS) and a conductive polymer such as polyaniline (PANI) as a filler, with potential application as biosensor. The elastomeric matrix was obtained by the polycondensation reaction between PDMS-OH and TEOS catalyzed by di-n-butyrtin dilaurate (DBTL). Then, the cross-linked of the polymer was performed using gamma radiation with different doses (25, 50, 75 and 100 kGy). The degree of crosslinking is critical because it would play a fundamental role in the mechanical properties of the composite. The study of the PDMS networks obtained by the chemical route includes solubility tests in toluene to obtain the yield of crosslinking ( $X_v$ ) and characterization by solid state NMR of  $^{29}\text{Si}$  at different gelation times. To obtain the quantum yield of crosslinking ( $\phi(x)$ ) and the chemical bonding yield (G-values) of the samples irradiated with gamma radiation, it was performed the analysis on the molecular weight modification of the samples using a coupled system of GPC/LS. In addition, NMR, FTIR and Raman spectroscopies were done to study the modification of structure in the samples irradiated with gamma radiation. The samples exhibited an increase in the molecular weight with the increase of the radiation dose. The results suggest that this methodology would let to adjust the degree of crosslinking required in the polymer matrix in accord to the potential use of the composite as a biosensor. The authors want to thank CONACYT-México and the University of Guanajuato.



## POLY 332: Using highly branched silicone oils to tailor the properties of gels

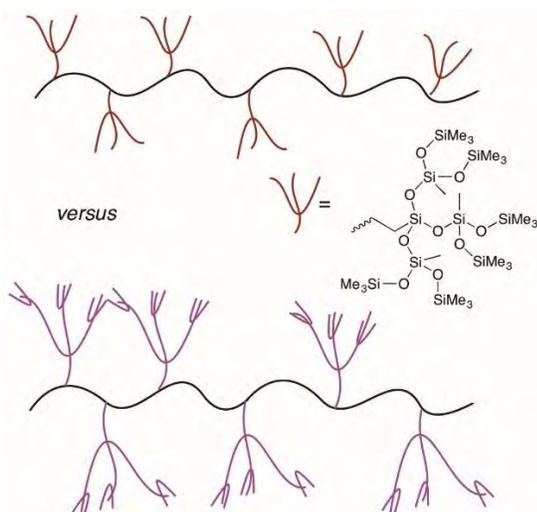
**Jennifer Morgan**, *jmorgan@mcmaster.ca*, Tong Chen, Michael A. Brook. *Chemistry and Chemical Biology, McMaster University, Hamilton, Ontario, Canada*

Silicone gels are prepared by curing elastomers in the presence of silicone oils and then used in a variety of applications, ranging from implantable devices to sealants for HEPA filters. Traditionally, linear silicone oils are used to prepare the gel but, over time, the oils are known to bleed from the gel into the surrounding environment. This can pose several problems including loss of viscoelasticity for sealants and potential implications for bleed from a biomedical device in vivo. Since the viscosity of linear polymers has been shown to increase by adding linear branches to the backbone,<sup>1</sup> we are exploring the possibility that more elaborate branches of different architectures can be used to further increase the viscosity and in turn, cause the oil to be better retained within a gel.

Linear silicone polymers bearing SiH functional sites of uniform molecular weight were prepared by equilibration with acid. A hydrosilylation reaction was used to functionalize the polymers with three different silicone side chains. The control sidechain, a linear polymer, was prepared using ring-opening polymerization. Two highly branched silicones were prepared using the Piers-Rubinsztajn (PR) reaction and a second generation, dendrimer-like side chain was prepared by alternating PR and hydrosilylation reactions (Scheme).<sup>2</sup> The degree of branching with these distinct branched groups along the polymer backbone was varied. Residual SiH groups were capped with vinylpentamethylidisiloxane to prevent undesirable crosslinking into the network and the viscosities of the uncapped and capped materials were compared. Gels were synthesized with the capped oils. We will report on the viscosity properties and trends of the silicone oils as a function of frequency and size of branching, as well as our preliminary studies of their behaviour in gels.

1Charlesby. *Polym. Sci.* 1955, 17, 379-390.

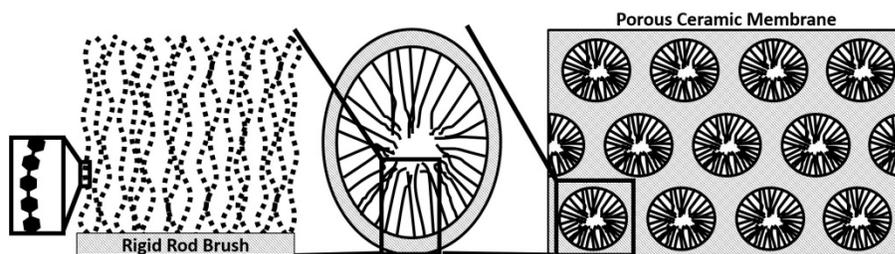
2Grande et al. *Polym. Chem.* 2014, 5, 6728-6739.



## POLY 333: Rigid rod chain-growth polyaramid brushes: Improved synthesis, solubility, and potential applications

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Conventional polymer brushes consist of surface-grafted random coil polymers, typically synthesized using a combination of the grafting from method and a living radical polymerization technique. This technique limits the particular studies to a very narrow field with limited functionalities. The advent of polymer brushes with more rigid-rod character, however was assisted by the discovery of the chain growth condensation polymerization technique. This new class of polymer brush will allow for research into brush architectures never before realized. Our research is an extension and improvement upon our published work on chain-growth condensation polyaramid brushes. We have been examining how to extend the brushes to thicker regimes, by increasing the molecular weight by improving the solubility of the polymer and the liberated alkoxide salts. We also are investigating potential application of these systems in various areas, including hybrid ceramic-polyaramid reverse osmosis and nanofiltration membranes for water desalination.

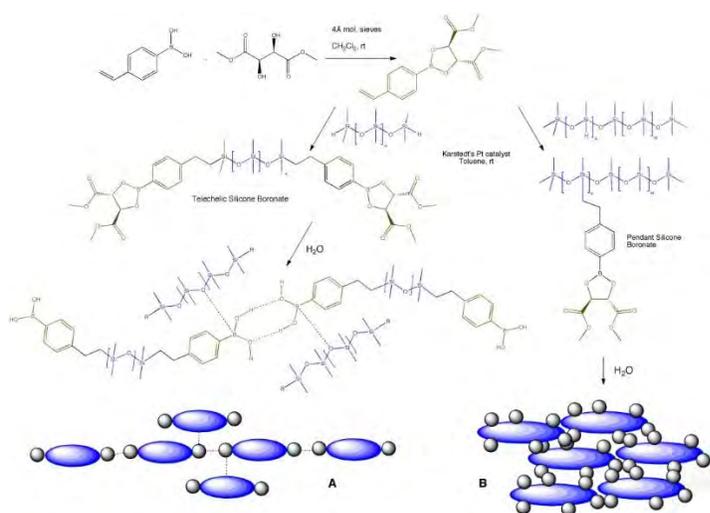


## POLY 334: Synthesis of spread and set silicone boronic acid elastomers activated by contact with aqueous surfaces

**Benjamin J. Macphail**, [macphaib@mcmaster.ca](mailto:macphaib@mcmaster.ca), Laura Dodge, Michael A. Brook.  
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Highly labile boronic esters hydrolyse on contact with aqueous interfaces producing the corresponding boronic acids.<sup>1</sup> Boronic acids form complexes with a variety of ligands including other boronic acids.<sup>2</sup> Silicone elastomers are normally crosslinked through covalent linkages. We were interested in examining the use of this boronic acid complexation, initiated by contact with water, as a new way to make silicone elastomers. Both pendant and telechelic tartrate ester-protected silicone-boronic acid polymers with different molecular weights and boronic acid densities were synthesized via hydrosilylation.<sup>3</sup> These polymers were exposed to moisture, which led to hydrolysis of tartrate protecting groups and an immediate and dramatic change in physical properties (Scheme 1). Low viscosity oils were transformed into viscoelastic films even in the absence of coordinating Lewis bases. Although the protected oil spreads readily, upon water exposure very rapid boronic ester hydrolysis occurs at a water-silicone interface and the free boronic acids adhere both to water and other boronic acids: 1:1 complexes form, which facilitates crosslinking. Additional crosslinking arises from O-B dative bonds forming between chains. The stability of these films was tested to better understand the impact of molecular weight and density of boronic acid appendages on mechanical properties. We will discuss the surprisingly high level of control over mechanical properties that is possible simply by changing these two parameters.

1. Achilli, C.; Ciana, A.; Fagnoni, M.; Balduini, C.; Minetti, G., *Cent. Eur. J. Chem.* 2013, 11, 137-139.
2. Mansuri, E.; Zepeda-Velazquez, L.; Schmidt, R.; Brook, M. A.; DeWolf, C. E., *Langmuir* 2015, 31, 9331-9339.
3. Dodge, L.; Chen, Y.; Brook, M. A., *Chem. Eur. J.* 2014, 20, 9349-9356.



Scheme 1. Telechelic (A) and pendant (B) silicone boronic ester synthesis and polymerization by boronic acid complexation via hydrolysis.

## POLY 335: Amphiphilic polymer-mediated surface modification and colloidal dispersion of nanoparticles

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We consider colloidal dispersions of silica nanoparticles in aqueous media containing amphiphilic polymers of the poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) type (Pluronics), with a specific interest on how solution conditions such as pH and temperature [1], and the presence of electrolytes [2], polar organic solvents [3], or PEO homopolymers [4] affect the (i) organization of the amphiphilic polymers on the nanoparticle surface and in the bulk solution, (ii) ensuing colloidal interactions between nanoparticles, and (iii) macroscopic properties of the dispersions. The fundamental knowledge thus gained for these systems informs the design of oil-in-water dispersants incorporating nanoparticles and the clean-up of mineral surfaces contaminated with petroleum. Particle-polymer-solvent interactions are also important to nanocomposites processing [5] and nanomaterials synthesis [6].

[1] Sarkar, B.; Venugopal, V.; Tsianou, M.; Alexandridis, P. "Adsorption of Pluronic Block Copolymers on Silica Nanoparticles" *Colloids Surfaces A: Physicochem. Eng. Aspects* 2013, 422, 155-164.

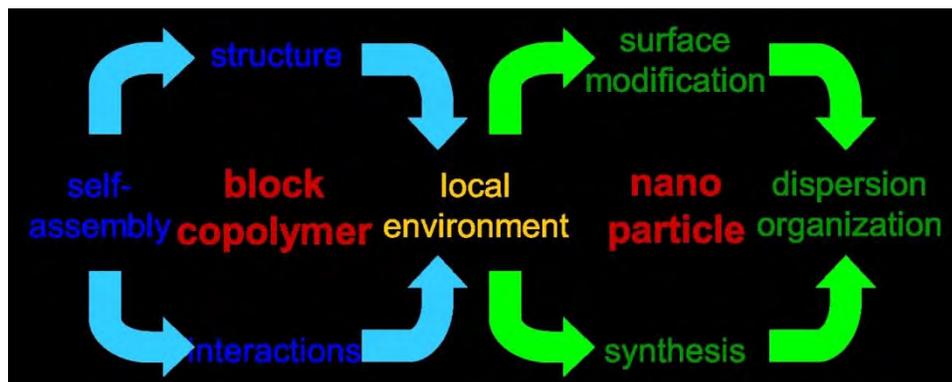
[2] Bodratti, A. M.; Wu, J.; Jahan, R.; Sarkar, B.; Tsianou, M.; Alexandridis, P. "Mono- and Divalent Salts as Modifiers of PEO-PPO-PEO Block Copolymer Interactions with Silica Nanoparticles in Aqueous Dispersions" *J. Dispersion Sci. Tech.* 2015, 36 (12), 1806-1815.

[3] Sarkar, B.; Venugopal, V.; Bodratti, A. M.; Tsianou, M.; Alexandridis, P. "Nanoparticle Surface Modification by Amphiphilic Polymers in Aqueous Media: Role of Polar Organic Solvents" *J. Colloid Interface Sci.* 2013, 397, 1-8.

[4] Bodratti, A. M.; Sarkar, B.; Song, D.; Tsianou, M.; Alexandridis, P. "Competitive Adsorption between PEO-Containing Block Copolymers and PEO Homopolymers at Silica" *J. Dispersion Sci. Tech.* 2015, 36 (1), 1-9.

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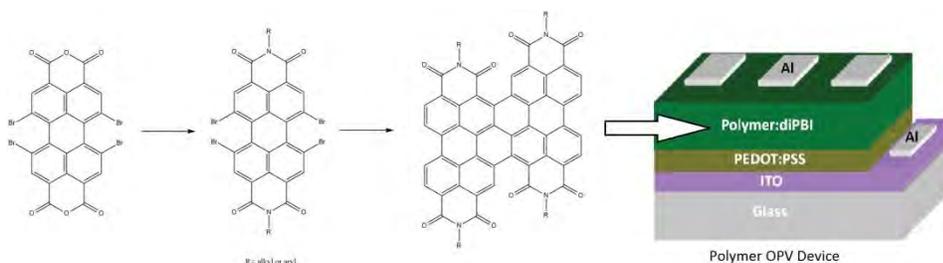
[6] Alexandridis, P.; Tsianou, M. "Block Copolymer-Directed Metal Nanoparticle Morphogenesis and Organization" *Eur. Polym. J.* 2011, 47 (4), 569-583.



## POLY 336: Di-perylene bisimides as alternative acceptor molecules for polymer photovoltaics

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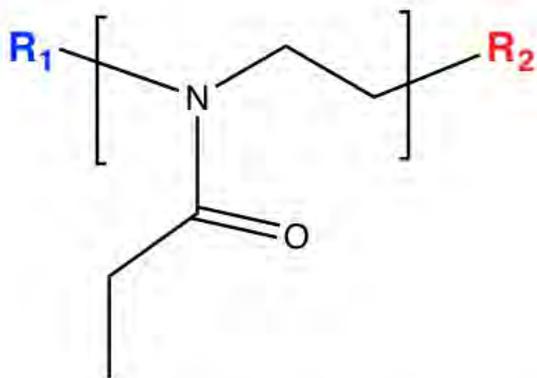
Organic photovoltaics (OPVs), in contrast to conventional silicon-based solar cells, have the potential to be produced at much lower costs due to the manufacturing methods involved, like spin coating and inkjet printing onto flexible substrates. Present high-performance polymer OPV technologies utilize fullerene derivatives as the electron accepting and transport material, however there is a shift away from fullerenes toward alternative acceptors due to their limitations, like their narrow light absorptivity, environmental instability, and poor processability. A new acceptor series with the potential to address these concerns based on dimers of perylene bisimides (di-PBIs), was synthesized via an Ullmann-style coupling reaction, and characterized via NMR and MALDI-TOF. Optical and electronic properties were determined with UV-Vis spectroscopy and cyclic voltammetry. The di-PBIs were blended with donor polymers, spin cast into thin films, and incorporated into OPV devices. These devices were processed in air on ITO-patterned glass as the anode, PEDOT:PSS as the hole transporting layer, the active layer at a 1:1 weight ratio of donor to acceptor, and thermally evaporated aluminum as the cathode layer. Morphologies of the active layer blends were characterized via atomic force microscopy.



## POLY 337: Functionalized poly(2-ethyl-2-oxazoline), a “click-like” polymer ready to simplify syntheses

**Kevin M. Kayne**<sup>1</sup>, [kmkayne@polychemistry.com](mailto:kmkayne@polychemistry.com), **Laura Stratton**<sup>2</sup>, **Bernard Gordon III**<sup>1</sup>.  
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Poly(2-ethyl-2-oxazoline), Aquazol, is a versatile non toxic polymer that is soluble in water and many organic solvents. Aquazol also has a low  $T_g$  for ease of thermal processing. Research has shown how effective specific end group functionalization can be towards simplifying syntheses. Functional groups currently being studied include and forms of the following; diol, amine, methacrylate, alcohol, and dodecane terminated. These end groups compliment further syntheses such as click-like applications due to their benign, and neat reaction synthesis and readily available termination with an appropriate nucleophile. Functionalized Aquazol has been seen in multi-block copolymers, amino acid building blocks, macro-monomers, macro-initiators and more. For example, “clicking” two poly lactic acid blocks to a central Aquazol backbone to change the biodegradability rate, is now an easier process than preparing a block copolymer in a one-pot method. Functionalized Aquazol has  $\geq 95\%$  functionality, as determined by NMR, mass spectroscopy, and GPC. The current experimental molecular weight ranges are 1,000 MW - 25,000 MW, with higher molecular weights still in development. Functionalized Aquazol has a poly dispersity index (PDI) of less than 1.5, allowing for researching specific molecular weights in targeted applications.

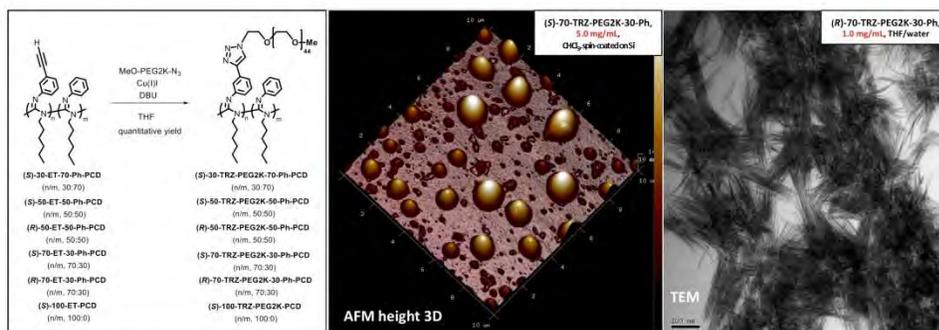


$R_1 / R_2 = \text{OH, NH}_2, \text{Phenyl, Methacrylate, Diol, and more}$

## POLY 338: Self-assembly of the PEGylated rod-coil block copolymers derived from helical (*R*)- and (*S*)-triazolepolycarbodiimides inspected by TMAFM and TEM

**Oleg V. Kulikov**<sup>1</sup>, [oleg.kulikov.chem@gmail.com](mailto:oleg.kulikov.chem@gmail.com), Dumindika Siriwardane<sup>1</sup>, Gregory McCandless<sup>1</sup>, Bruce M. Novak<sup>2</sup>. (1) Chemistry, University Of Texas at Dallas, Richardson, Texas, United States (2) School of Natural Sciences Mathematics, University of Texas at Dallas, Richardson, Texas, United States

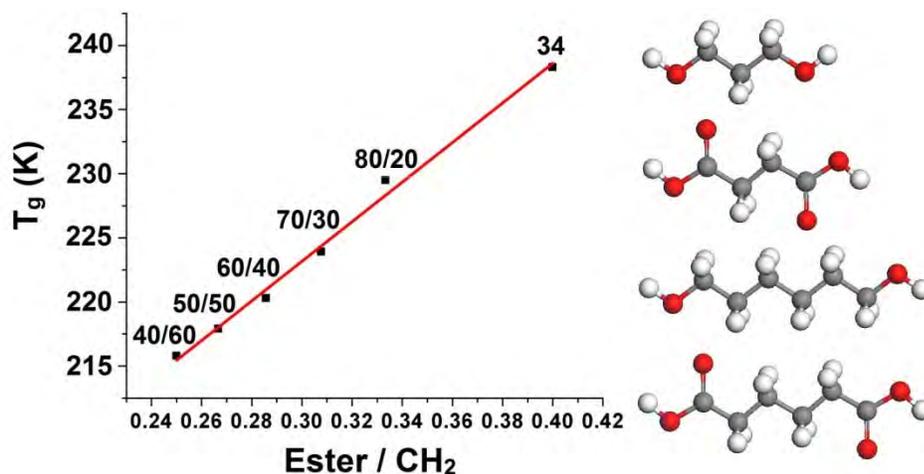
Family of helical rigid-rod (*R*)- and (*S*)-polycarbodiimides bearing PEG2K pendants on their periphery have been successfully obtained from the corresponding ethynyl precursors *via* click reaction. TMAFM dilution series showed them to aggregate into spherical assemblies of a size varying from several microns to ~ 200 nm depending on concentration. Supposedly, dewetting phenomenon has dramatic effect on a process leading to the formation of spheroids observed. Investigation of PEGylated polycarbodiimides by TEM technique clearly exhibited bundled nanorods that may be resulted from association of the long (~ 44 ethylene oxide units) hydrophilic PEG-chains belonging to the adjacent polycarbodiimide macromolecules. Overall, self-assembly of these species is mostly driven by a massive PEG-corona rather than by rigid polyguanidine helical scaffold.



## POLY 339: Glass transition temperatures of amorphous linear aliphatic polyesters

**Jialong Shen**, [jjalongshen@gmail.com](mailto:jjalongshen@gmail.com), Yavuz Caydamli, Alper Gurarlan, Alan E. Tonelli. North Carolina State University, Raleigh, North Carolina, United States

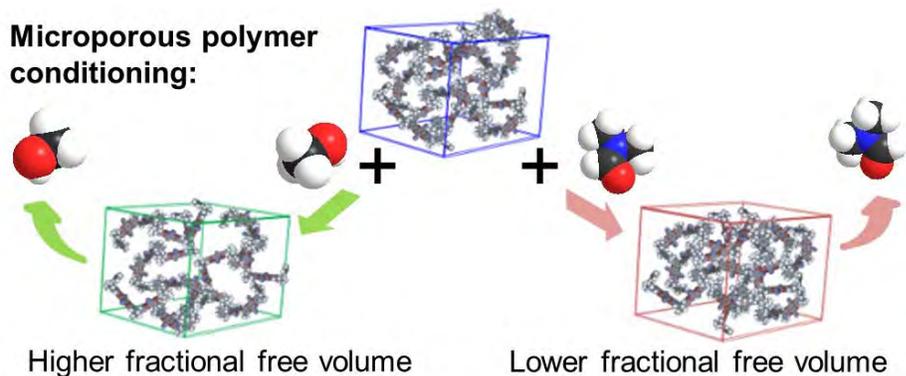
The profound effect of crystallinity on polymer glass transition temperatures ( $T_g$ s) necessitates obtaining wholly amorphous samples for the purpose of studying their  $T_g$ s. Such samples are usually prepared through a melt-quenching process which could possibly introduce large cooling rate effects on their  $T_g$ s and is not feasible for all polymers. In this study, a series of wholly amorphous linear aliphatic co- and tetra-polyesters were synthesized *via* bulk melt step-growth polymerization, and their glass transition temperatures were determined using Differential Scanning Calorimetry (DSC). With the irregularity introduced by the inherent expected randomness from step-growth copolymerization, the crystallinities of copolymers were significantly reduced to near or wholly amorphous states, leaving the  $T_g$ s of the polymer samples essentially unaffected by crystallinity. The glass transition temperatures of the polyesters increase linearly with the ratio of ester groups per methylene group. Extrapolation of the ratio to zero ester group content gives a  $T_g$  of 177K for amorphous polyethylene (PE). The calculated  $T_g$ s of this polyester series using Van Krevelen's group contribution method manifest similar linearity with the ester group content and are 3 to 17 K higher than the measured  $T_g$ s. The intramolecular equilibrium flexibilities were evaluated through the calculation of conformational entropies of individual polymer chains approximated by considering solely the short range interactions between neighboring groups, as embodied in their RIS conformational models. Their calculated conformational entropies decrease linearly with increasing ester group content. This suggests the dominant effect of intramolecular interactions on the  $T_g$ s of linear aliphatic polyesters over the entire range of ester group content explored experimentally in this study.



## POLY 340: Sorption and diffusion of organic vapors into PIM-1 and the effects of methanol conditioning

**Melinda Jue**, [mjue8@mail.gatech.edu](mailto:mjue8@mail.gatech.edu), **Ryan P. Lively**. *Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States*

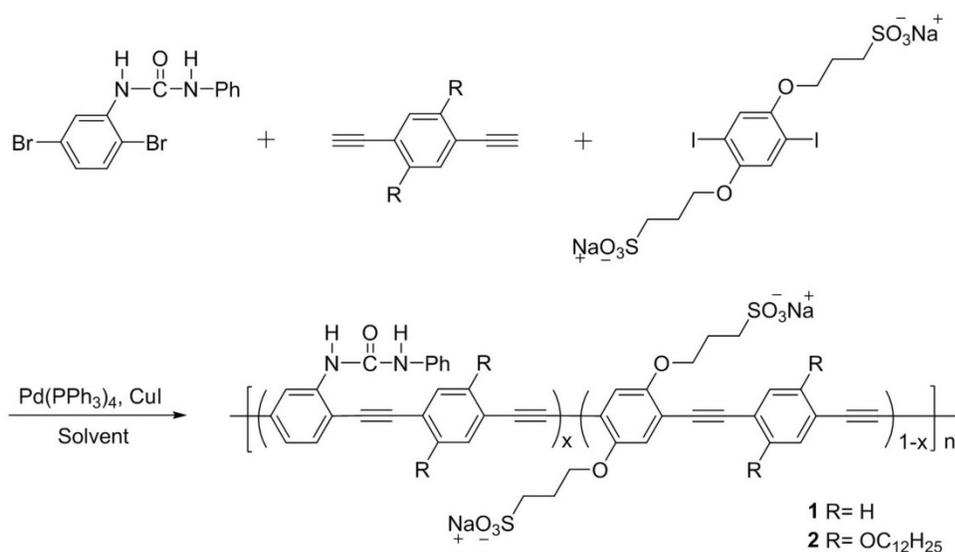
Polymers of intrinsic microporosity (PIMs) are an emerging class of polymers that have been of significant interest for a variety of separations due to their favorable permeability and selectivity. High free volume polymers like PIMs are typically soaked in methanol and dried before permeation and sorption analysis to remove any processing history effects and to improve experimental reproducibility. This methanol preconditioning step is thought to remove residual trapped solvent in the micropores as well as erase the past thermal processing history. While few studies have investigated this process in great detail, this work examines methanol treatments as a means to reverse the effects of organic solvent exposure on PIM-1. Gravimetric vapor sorption analysis is used to determine the diffusion coefficients of organics in neat PIM-1. Thermogravimetric analysis, surface area, and pore volume analysis are used to determine the efficacy of methanol treatments at removing residual solvent from the polymer.



## POLY 341: Design and synthesis of fluorescent conjugated polyelectrolytes for sensing fluoride ions

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Department of Chemistry, State University of New York at Binghamton, Binghamton,  
New York, United States

Fluorescent conjugated polymers (FCPs) have received intense research interest for fabricating chemosensors to screen various metal cations, and more recently to differentiate anions. Fluorescent conjugated polyelectrolytes (FCPEs) are a new approach to build highly emissive, water-soluble sensory materials. Facile structural adjustment of the receptors attached to the conjugated backbones can be made for specific sensing requirements. This research outlines the design and synthesis of novel FCPEs to detect fluoride anion. To achieve this aim, urea groups that are capable of sensing fluoride have been incorporated as the receptors into the polyelectrolyte systems via Sonogashira coupling reaction (Scheme 1). Two polyelectrolytes with different alkyl pendent chains were obtained with more than 60% yield, and their structures were confirmed by Nuclear Magnetic Resonance (NMR) and Fourier Transform Infrared Spectroscopy (FTIR). Molecular weight and distribution were determined through Gel Permeation Chromatography (GPC). Photophysical characterization including UV-vis absorption, time resolved fluorescence emission, quantum yield determination, and Stern-Volmer analysis have been investigated to evaluate the newly constructed chemosensory molecules.

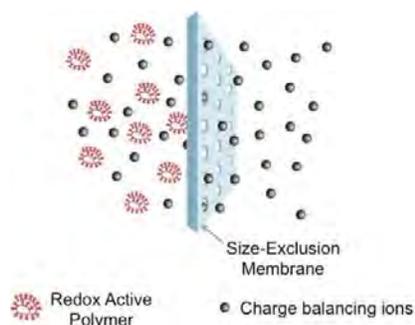


Synthesis of new fluorescent conjugated polyelectrolytes for sensing fluoride anion.

## POLY 342: Investigation of nitrobenzene-based redox-active polymers for non-aqueous redox flow batteries

**Kevin J. Cheng**<sup>2</sup>, [kvn.j.cheng@gmail.com](mailto:kvn.j.cheng@gmail.com), Etienne Chenard<sup>4</sup>, Elena B. Montoto<sup>2</sup>, Nagarjuna Gavvalapalli<sup>1</sup>, Rylan D. Dmello<sup>5</sup>, Jingshu Hui<sup>6</sup>, Kyle C. Smith<sup>5</sup>, Joaquin Rodriguez Lopez<sup>3</sup>, Jeffrey S. Moore<sup>2</sup>. (1) Chemistry, University of Illinois, Urbana, Illinois, United States (2) Chemistry, University of Illinois at Urbana-Champaign, Champaign, Illinois, United States (3) School of Chemical Sciences, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States (4) universit  de montr al, Montreal, Quebec, Canada (5) Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Ur, Illinois, United States (6) Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States

Non-aqueous redox flow batteries (NRFBs) are a possible energy storage solution for intermittent renewables (solar, wind). Their long cycle lifetimes and capability to store large quantities of energy make NRFBs attractive for grid level storage, to capture energy during periods of low energy consumption. However, the low energy density and tendency of NRFBs to lose capacity over time result in a high energy cost (approximately \$500 per kWh) that hinder them from wider incorporation in grid systems. The problems arise from use of small metal ions as electrolytes in conjunction with expensive ion-exchange membranes (IEMs) that inadequately prevent the crossover of charge-carrying species between compartments. We utilized relatively inexpensive, commercial off-the-shelf (COTS) porous separators in place of IEMs and redox-active polymers (RAPs) in place of metal ions in non-aqueous solvents. In our initial studies, we examined the diffusion rates of varying viologen polymer chain lengths through COTS separators and observed a reduction in polymer crossover with increasing chain lengths (up to 85%), showing size-enhanced rejection of electroactive species. The results demonstrate the feasibility of polymers as charge storage materials but further improvements are required to make NRFBs viable for grid incorporation. Incorporation of organic moieties such as nitrobenzene in RAPs displayed superior electrochemical performance (1.6 V) and solubility (6.0 M) compared to viologen polymers (0.8 V and 2.8 M). Further synthetic modifications on nitrobenzene-based polymers exhibited enhanced electrochemical performance capable of achieving energy cost targets (\$180 per kWh), demonstrating the potential of NRFBs to meet grid level storage.

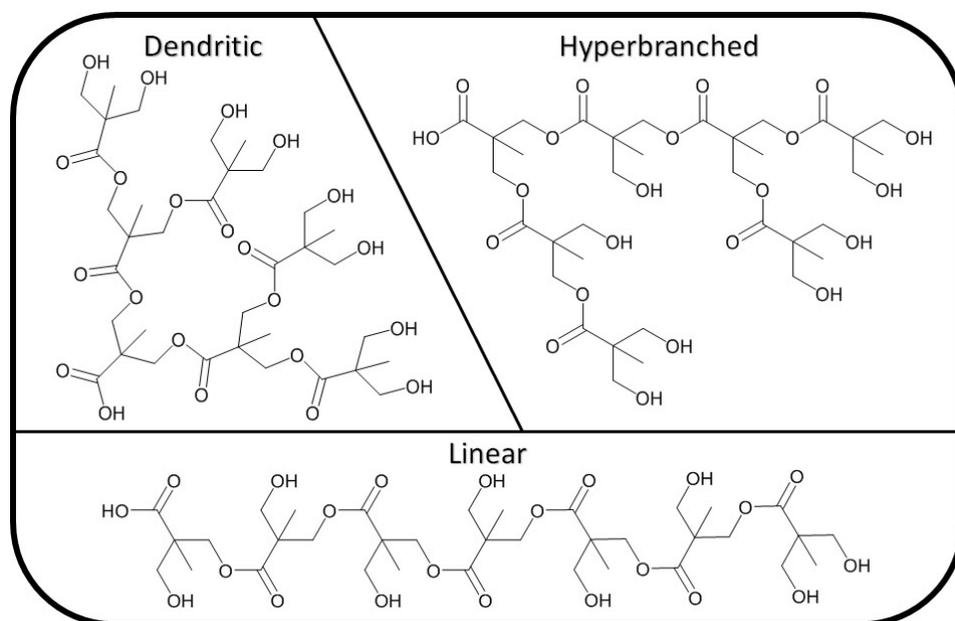


RAPs are prohibited from diffusion through the membrane by their large size but small charge balancing ions freely diffuse to allow battery operation.

## POLY 343: Effect of branching on bis-MPA polymers: A comparative study of polymer architecture

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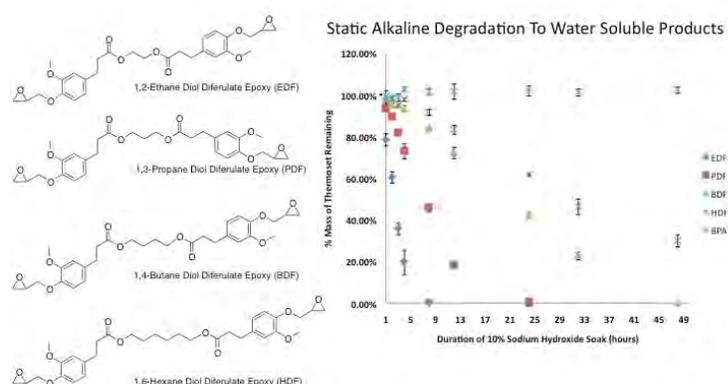
Polymer architecture (i.e. linear, dendritic, hyperbranched, star, cyclic, etc.) plays a critical role in the chemical and physical properties of these types of polymers. Recently, there has been much synthetic and analytic work done to elucidate the behavioral differences between cyclic polymers and their linear precursors. It has long been known how to synthesize dendritic and hyperbranched 2,2-bis(hydroxymethyl) propionic acid (bis-MPA) polymers. Bis-MPA is a biologically relevant monomer for dendritic and hyperbranched materials due to high biocompatibility, biodegradability, and low toxicity, which has made it of particular importance as of late. Hyperbranched materials of this monomer are desirable because of their ease of synthesis and inexpensive starting materials and are already commercially available as Boltorn™. However, the random branching inherent with this type of one-pot synthesis yields hyperbranched materials possess large, wide and relatively uncontrolled polydispersities and stringent requirements by the FDA on drugs and drug delivery agents, limits may exist to their biological scope. In order to more accurately understand how and to what degree this imperfect branching affects the hyperbranched material's chemical properties and physical characteristics, it is critical to compare these randomly branched materials with both the perfectly branched, monodisperse dendritic materials and the completely unbranched linear polymers. Therefore, linear, dendritic and hyperbranched bis-MPA polymers were synthesized and a comparative study of these three architectures was undertaken.



## POLY 344: Degradable ferulic acid based epoxy thermosets

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Epoxy thermosets are typically employed for their excellent modulus, high glass transition temperature, low viscosity, wettability, and no condensation products during cure. Epoxy thermosets are becoming more prevalent in different applications from structural adhesives to wind turbine blade construction and they are almost impossible to degrade and ultimately are not sustainable. Herein we prepared liquid epoxy resins from dihydroferulate esters derived from ferulic acid and a series of aliphatic alkyl diols including ethylene glycol, 1,3-propane diol, 1,4-butane diol, and 1,6-hexane diol. Ferulic acid is a biobased platform chemical that can be derived from sugar beet roots, rice and wheat bran and bagasse, and aliphatic alkyl diols are becoming available from biomass at pilot plant level scale. Our goal was to explore the effect of diol length on epoxy resin performance with a cycloaliphatic diamine crosslinker. Decreasing the length of the diol linker increased both the glass transition temperature and the glassy modulus that eventually surpass stiffness of resins derived from bisphenol A. Additionally, the internal aliphatic ester can be used to selectively degrade the thermoset under static mild alkaline conditions with tunable degradation times ranging from under 5 hours to days. This family of biobased epoxy resins represents a new class of degradable epoxy resins that has the potential to reduce costs for continuous fiber reinforced composites by enabling recycling of fillers.

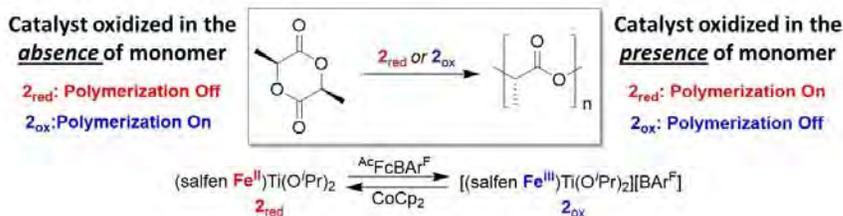


Epoxy resin structure allows for fine tuning of chemical degradation to completely water soluble products by length of diol linker increasing time required for chemical recycling.

## POLY 345: Enhancing lactide polymerization control through the use of redox-active catalysts

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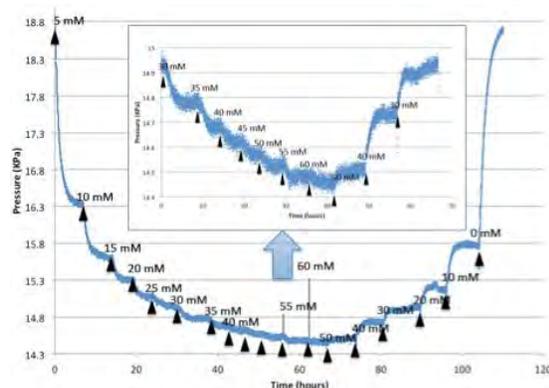
Poly lactides have proven to be relevant in biomedical applications as well as packaging materials because the monomer can be obtained from a renewable agricultural source and the polymer is biocompatible/biodegradable. Previous studies have shown that single-site redox-switchable catalysts can modulate lactide polymerization behavior. However, the titanium catalyst first used in this capacity was comprised of a salen ligand bearing two redox-active ferrocenyl moieties distal to the active metal center. In this study, we synthesized a single-site titanium catalyst bearing a ferrocenyl moiety in much closer proximity to the active metal site. We will show that not only is the redox-active moiety location important to polymerization behavior, but that the inclusion of monomer during oxidation can also greatly affect the performance of this group IV catalyst.



## POLY 346: Effect of electrostatic interactions on the response of zwitterionic glucose sensitive hydrogels designed for bioprocess sensing

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A glucose sensitive hydrogel (GSH) containing both anionic phenylboronic acid (PBA) groups and cationic tertiary or quaternary amines reversibly shrinks in response to increases in the environmental glucose concentration. Such stimuli-responsive behavior makes these hydrogels promising candidates for use in glucose sensors needed for various applications in medicine and bioprocess control. In bioreactors, for example, the glucose concentration is an important parameter to control because it crucially affects bioreactor productivity and pharmaceutical product quality. For this application, a GSH needs to be able to respond to changes in glucose at high concentration values, function over a relatively wide pH range, and in the presence of a variety of cell-metabolites. We demonstrate a new approach in the design of GSHs obtained by manipulating the electrostatic interactions of these polyelectrolyte hydrogels. The method entails changing hydrogel composition in order to shift the isoelectric point (IEP) of the GSH to a value that is higher than that of the intended medium of use. The IEP is defined as the pH value at which there are an equal number of fixed positive and negative charges along the polymer backbone. Hence shifting the IEP to a higher value makes the GSH more positively charged during normal usage. This is found to strongly increase the glucose response magnitude of the hydrogel, thereby enhancing its potential utility in glucose sensing. We postulate that this enhancement arises from an increase in electrostatic attraction between the negatively-charged PBA moieties bound to glucose, and the positively-charged tertiary or quaternary amines. This demonstrates that electrostatic forces play a significant role in hydrogel response with respect to glucose. It also helps explain why PBA-containing hydrogels without cationic amines swell, rather than shrink, in response to increases in environmental glucose concentration.



Reversible response of glucose sensitive hydrogel with glucose concentration from 0-60 mM tested by a pressure sensor.

## POLY 347: Anti-cancer activity of H<sub>2</sub>S-releasing micelles

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Gasotransmitters such as hydrogen sulfide (H<sub>2</sub>S) are biologically produced signaling gases with physiologically relevant activities. For example, H<sub>2</sub>S suppresses oxidative stress, modulates inflammation, and protects endothelial tissue via vasodilation.<sup>1</sup> Of particular interest is the mounting evidence that H<sub>2</sub>S can exert both pro- and anti-apoptotic activity on cultured cells. For example, Lee et. al. reported a time- and concentration-dependent activity of H<sub>2</sub>S on human cancer cells, with low concentrations of H<sub>2</sub>S applied over a period of days resulting in inhibited cancer cell proliferation as well as apoptosis.<sup>2</sup> To achieve a desired outcome *in vivo*, H<sub>2</sub>S must be delivered locally and at the correct concentration. Therefore, the vehicle of delivery must be rationally designed to release H<sub>2</sub>S at the desired rate. A number of H<sub>2</sub>S-releasing compounds have been reported including S-arylthiooximes, which release H<sub>2</sub>S controllably (sensitive to thiooxime structure) in response to thiol functionality.<sup>3</sup> Thiooximes have been successfully conjugated to methacrylate polymers with pendant aldehyde functionality in a post-polymerization modification approach.<sup>4</sup> This philosophy was extended to the preparation of H<sub>2</sub>S-releasing nanoparticles by preparing thiooxime-functionalized block copolymers that self-assemble in aqueous solution to form spherical micelles. In this case, the kinetics of H<sub>2</sub>S-release can be tuned by manipulating various parameters of the polymer aggregates (i.e., polymer thermal properties, particle size, aggregate morphology, etc.). This release reaction occurs on the timescale of days, in contrast to most H<sub>2</sub>S-releasing small molecule compounds that exhibit full release in a few hours. These H<sub>2</sub>S releasing micelles exhibit anti-cancer activity on human colon cancer cells *in vitro* but are well-tolerated by healthy cells.

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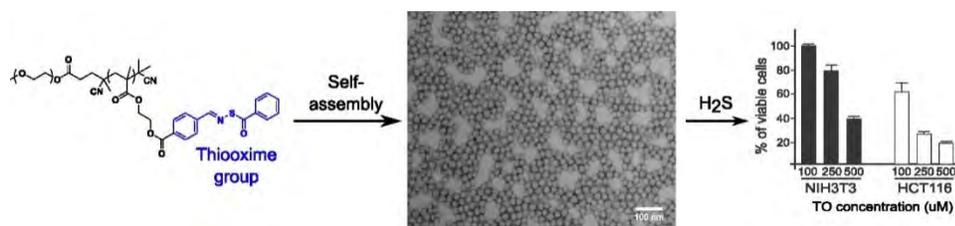
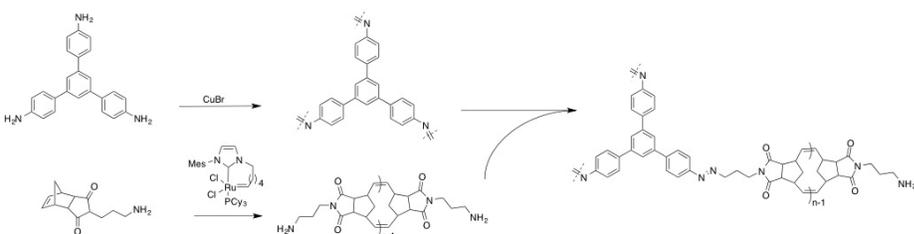


Figure 1. H<sub>2</sub>S release from thiooxime micelles exhibits anti-cancer activity on human cancer cells (HCT116) but is well-tolerated by healthy cells (NIH3T3).

## POLY 348: Nanoporous cyclic brush polymers for selective carbon dioxide capture

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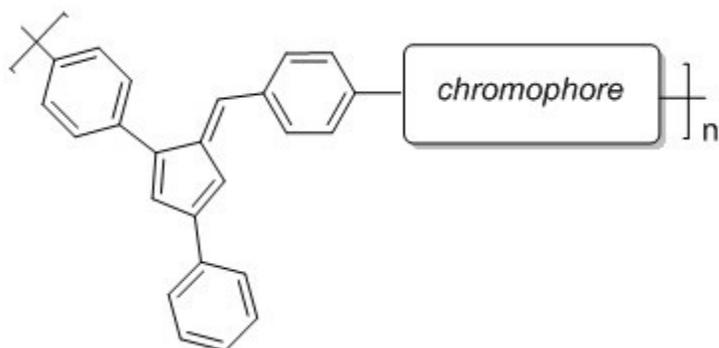
This work describes advanced synthetic methodologies to afford nanoporous materials with selective uptake affinity towards carbon dioxide and large gas storage capacities. An increase in porosity and uptake capacity in azo-linked porous organic polymers (ALP) for carbon dioxide capture as well as increased thermal stability of these materials by the incorporation of a cyclic backbone will be discussed. Cyclic polymers show remarkably different behaviors than their linear counterparts, and are expected to provide a highly tunable system for removing impurities such as carbon dioxide from breathing air aboard space vessels. The tunability will be further enhanced by the construction of ALP-based molecular brush polymers, which behave significantly differently from linear polymer analogs, and allow for pre-established molecular design parameterization facilitated by the covalent connectivity combined with solution- and solid-state assembly processes. Cyclic brush polymers, achieved by ring-expansion metathesis polymerization (REMP), combined with highly dense networks of azo-linkages, recently shown to be efficacious for selective carbon dioxide uptake, are achieved by “grafting to” strategies. A simple, scalable synthesis of a cyclic brush polymer system with highly tunable porosity and surface morphology that can be utilized for selective capture of carbon dioxide will be outlined, as well as a better fundamental understanding of the physicochemical behaviors and functionalization potential of these systems with regard to their applications in space technology as lightweight, nanoporous materials.



## POLY 349: Synthesis of fulvene containing polymers for use in light-harvesting material

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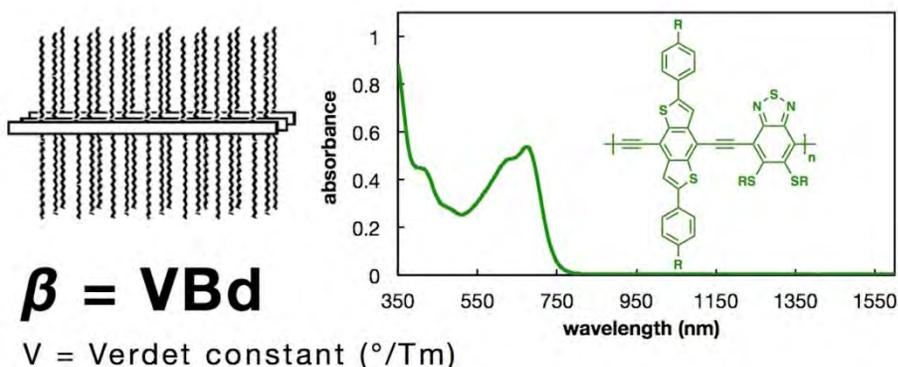
Conjugated polymers containing donor and acceptor groups have received considerable attention as possible light-harvesting materials. One area of research that remains largely unexplored is the incorporation of fulvene-based donor/acceptor moieties within the polymer backbone. The unique structure-property relationships associated with fulvenes are promising in the field of organic electronics. In this work, dibromo-substituted 1,3,6-triphenylfulvenes were copolymerized via palladium-catalyzed cross-coupling and 1,3-diphenyl-6-norbornenylfulvenes were polymerized via ROMP to form the first reported examples of fulvene-containing polymers that keep the fulvene core intact. The synthesized polymers were characterized by NMR, ATR-FTIR, GPC, TGA, DSC, UV-Vis, and fluorescence measurements. Model reactions and DFT calculations were also performed on small molecule fulvene chromophores prior to polymerization reactions to support experimental observations of the chain-extended systems. Possible applications of these cross-conjugated polyfulvene in relation to the field of organic electronic materials will also be addressed.



## POLY 350: Highly ordered polymers for magneto-optical applications

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Regioregular polythiophenes and other highly ordered conjugated polymers have recently been found to display large Faraday rotations, though the mechanism leading to this phenomenon is the subject of ongoing research. In this work, we sought to explore the structure-property relationships in conjugated polymers that could lead to the observation of large Faraday rotations, with particular emphasis on the investigation of materials with high degrees of solid-state order. We synthesized a series of poly(arylene ethynylene)s (PAEs) with highly biaxial structures containing “rigid-rod” type backbones and long alkyl side chains. In addition, by incorporating strong donor–acceptor character into the polymer backbones, we sought to promote interchain  $\pi$ -stacking and further enhance solid-state organization and electronic delocalization. The solid-state order of the polymers will be characterized via XRD, and Faraday rotations will be measured. We envision that these types of materials could find application in the development of magnetic field sensors with high sensitivities.



## POLY 351: Incorporation of different conjugated linkers into low band gap polymers based on 5,6-bis(octyloxy)-2,1,3 benzooxadiazole for tuning efficiency of organic photovoltaics

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Research on organic photovoltaics has gained immense interest in recent years due to the increasing demand for sustainable clean energy. Bulk-heterojunction (BHJ) solar cells based on interpenetrating networks of electron-donating  $\pi$ -conjugated polymers and electron-accepting fullerene derivatives promise several advantages such as low cost, large-area manufacturing compatibility and the ease of material processing.<sup>1</sup> Molecular design and device optimization played a significant role for a rapid development in the field of PSCs over the past decade. One of the most efficient strategies to achieve superior photovoltaic properties is the donor-acceptor approach, combination of electron-rich donor and electron deficient acceptor moieties in the polymer backbone. 2,1,3-benzooxadiazole (BO) is one of the strong electron withdrawing moieties widely used in PSCs due to its planar, rigid geometry, excellent stability and optoelectronic characteristics.<sup>2</sup> Due to its capability to adopt the quinoid structure in the polymer, benzooxadiazole based polymers have a low-band gap and coplanar structures. Conjugated linkers remarkably affect the interaction between donor and acceptor units and thus the optical, electrochemical, charge transport and photovoltaic properties of the resulting D- $\pi$ -A conjugated copolymers. In this study, carbazole and fluorene units were used as the donor and 2,1,3-benzooxadiazole was used as acceptor building blocks in the polymer chain bridged by different heteroaromatic rings as shown in Figure 1. Selenophene and furan units were selected as conjugated linkers. The effect of different conjugated linkers and donor moieties on electrochemical and photovoltaic properties were investigated.

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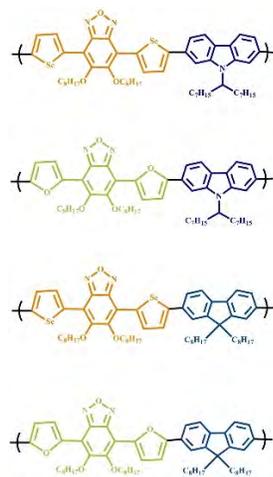


Figure 1

## POLY 352: Coumarin-based fluorescent tag for art conservation epoxy visualization

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Epoxies are commonly used in art conservation as adhesives for artifact reconstruction and repair. However, with the development of colorless epoxies, it has become more difficult to detect repair work. Fluorescent epoxies would allow for easy detection of the epoxy joints by simple visual inspection under UV light while remaining unnoticeable under normal display lighting. We have developed a coumarin modified epoxy monomer that makes the resulting adhesive fluoresce blue under shortwave UV. The monomer was synthesized by glycidylation of 7-hydroxycoumarin. It was soluble in commercial epoxies and was strongly fluorescent at 0.01 M in the epoxy formulation. Lap shear adhesive testing showed that addition of the coumarin to specialty conservation epoxy Epo-Tec 301 did not weaken the adhesive, but actually slightly strengthened it. Concentrations higher than 0.01 M gave stronger fluorescence, but resulted in weaker bonds. Control experiments with non-covalently bound coumarin dye at the same concentration weakened the adhesive bonds, demonstrating the value of covalent attachment.



## POLY 353: Comparison of the $\pi$ -electron delocalization in 2-oxazolines and esters

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In the field of medical and medicinal application, the regioselectivity during the initiation of the cationic ring-opening polymerization CROP of 2-oxazoline monomers [1] is a prerequisite for the synthesis of materials with well-defined structures. The microwave-assisted polymerization of 2-oxazolines enhances the polymerization times by factors of up to 400 and, hence, it is necessary to investigate whether the initiations occur regioselectively at the nitrogen atom or not.

The single crystal X-ray analysis of an ester-functionalized 2-oxazoline monomer (Figure 1) reveals  $p$ -electron delocalization along the N-C-O segment in 2-oxazolines: While the observed C=N bond length in 2-oxazolines and the measured C=O bond length in the ester group are in good alignment with the literature values for the corresponding double bonds, the observed C-O “single” bonds in 2-oxazolines and esters exhibit a value intermediate between a single and double C-O bond.

This delocalization renders a partial negative charge to the nitrogen atom and a partial positive charge to the oxygen atom [2;3]: The delocalization of  $p$ -electrons occurs at a similar degree comparable to that in esters along the O-C-O segment. This data is supported by quantum chemical calculations performed for the ester-functionalized monomer using the MRCC program [4].

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**Figure 1:** Left and Right: Schematic representation of delocalization in 2-oxazolines and esters. Middle: X-ray crystal structure analysis of EstOx.

## POLY 354: Synthesis of PDPP2F-2E-T (polydifurodiketopyrrolopyrrole-diethynyl-hexylthiophenes) as low band gap polymers

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This research examines the effects of alkyl substituents on the solubility in organic solvents of proposed low band gap polymers, polydifurodiketopyrrolopyrrole-diethynyl-hexylthiophene (PDPP2F-2E-T), which will be incorporated into hybrid solar cells. DPP polymers synthesized from 2-ethylhexyl, tetradecyl, and 2-octyldecyl substituents includes acetylene spacers between the aromatic and thiophene monomers to lessen steric interactions. The DPP monomers are derived from  $S_N2$  reactions of the sodium salt with long chain alkyl halides. Many of these alkyl halides are not commonly available thus XtalFluor-E was employed to provide such from the corresponding primary alcohols. The synthetic scheme which utilizes Sonogashira coupling of the DPP monomers with hexyl dibromothiophene is outlined in Figure 1. Solid-state ultraviolet-visible spectroscopy was used to monitor the optical band gaps which were intended to be about 1.4 eV.

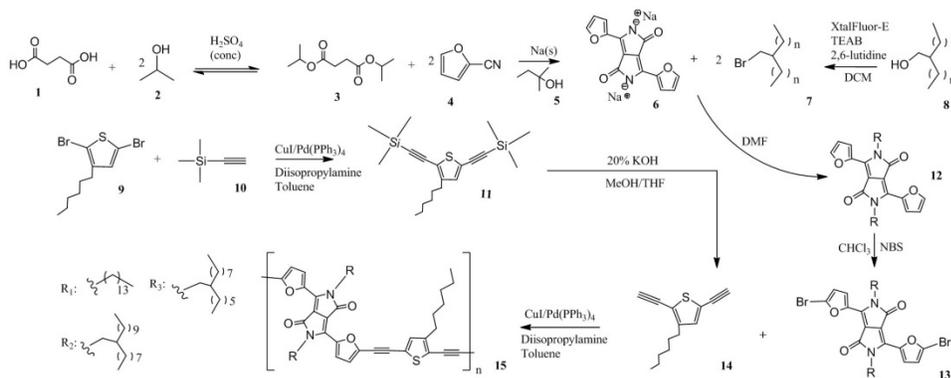


Figure 1: Synthetic scheme for the synthesis of PDPP2F-2E-T polymers

## POLY 355: CO<sub>2</sub> capture by sulfur-bridged nanoporous covalent organic polymers

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It is well known that CO<sub>2</sub> is the most important component of greenhouse gases resulting in global warming. During the past few years, the increase in burning fossil fuels and petroleum products has led to the higher concentrations of CO<sub>2</sub> in the atmosphere. Moreover, the adjustment of global atmospheric circulation and the extension of climate zones to polar regions has caused climate anomalies and natural disasters[1]. To begin such an endeavour, capturing of CO<sub>2</sub> generated by large point sources, such as fossil-fuel-fired power gasification plants, is essential. Conventionally, the most widely adopted approach to absorb CO<sub>2</sub> uses aqueous organic amine solutions as chemical sorbents at fossil fuel-burning power plants, but severe economic burden and corrosion to the production plant are very cumbersome[2]. Developing porous materials which stores and releases CO<sub>2</sub> with fast kinetics and high reversibility over multiple cycles is of widely discussed strategy for a viable adsorption process in CO<sub>2</sub> separations[3]. Several porous materials such as mesoporous silica, activated carbon, metal-organic frameworks (MOFs), covalent-organic frameworks (COFs), and porous covalent-organic polymers with excellent CO<sub>2</sub> adsorption capacities have been reported[4].

The present work focus on the capturing CO<sub>2</sub> by adsorption process utilizing the sulfur-bridged triazine-based porous covalent organic polymers (PCOPs). This new PCOP networks were fully characterized. The BET surface area of PCOP network was found to be 50.3092 m<sup>2</sup>/g as shown in Table 1. The research results displayed that this PCOPs adsorbant has a good adsorption capacity of 5.1282 cm<sup>3</sup>/g for CO<sub>2</sub>.

### Acknowledgements

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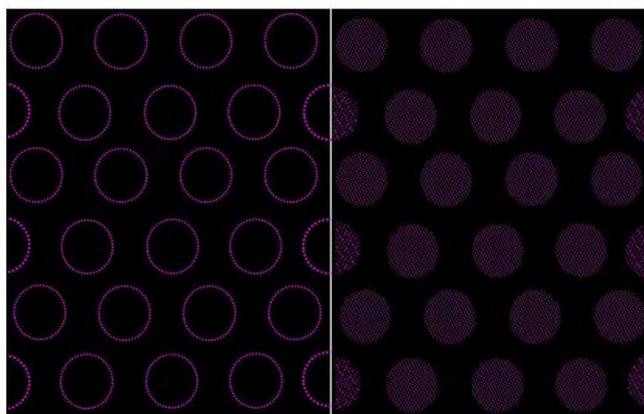
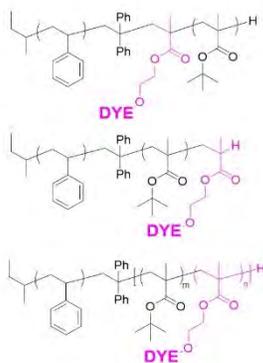
**Table 1** Textural parameters calculated from N<sub>2</sub> adsorption isotherms at 77 K

Parameters	PCOP
BET surface area (m <sup>2</sup> /g)	50.3092
Langmuir surface area (m <sup>2</sup> /g)	70.5250
Average pore size (nm)	23.730
Pore volume(cm <sup>3</sup> /g)	0.259100

## POLY 356: STORM Imaging of phase morphology of PS-*b*-PtBMA copolymer bio-interfacial thin films

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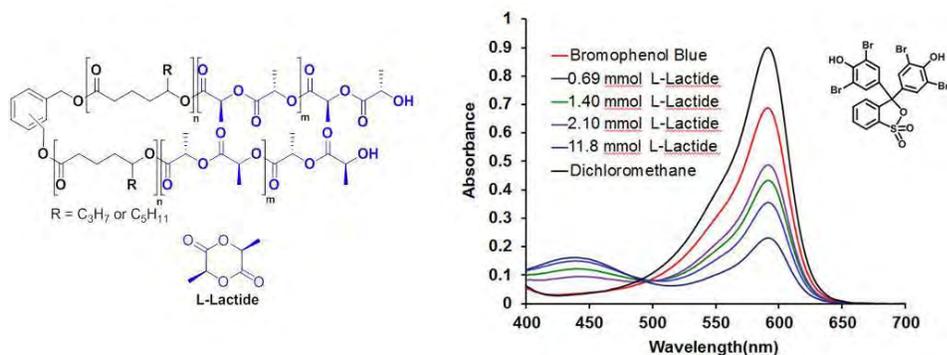
Super-resolution microscopy has revolutionized the field of non-destructive imaging in biology over the past 20 years. Through its use of blinking fluorescent dyes it has overcome the diffraction limited imaging barrier, and now provides an avenue to achieve sub-20 nm resolution with optical microscopy techniques. Although it has found widespread use in biological applications, owing largely to its non-destructive and flexible nature, it is just beginning to be seen as a useful tool in materials applications, such as in the imaging of block copolymer phase morphology. In this study, several Polystyrene-*block*-Poly(*tert*-butyl methacrylate) (PS-*b*-PtBMA) copolymers, with small amounts of Poly(hydroxyethyl methacrylate) (PHEMA) incorporated at several different locations along the polymer chain, were synthesized by anionic polymerization for imaging by stochastic optical reconstructive microscopy (STORM). PHEMA was used to add a hydroxyl group as an attachment point for labeling with fluorescent dyes. Labelling was done at different points along the copolymer chain: in between blocks, at the end of the PtBMA block, and randomly incorporated throughout the PtBMA block. These labelling geometries allow us to probe architecturally regiospecific effects of the incorporation of the dye at the phase boundary or dispersed throughout one block. This understanding will open up the ability to apply STORM imaging to block copolymer morphological studies, particularly in bio-related applications where non-destructive *in situ* imaging is required.



## POLY 357: Modification of macromolecular scaffolds for water purification using ring opening polymerization of biorenewable monomers

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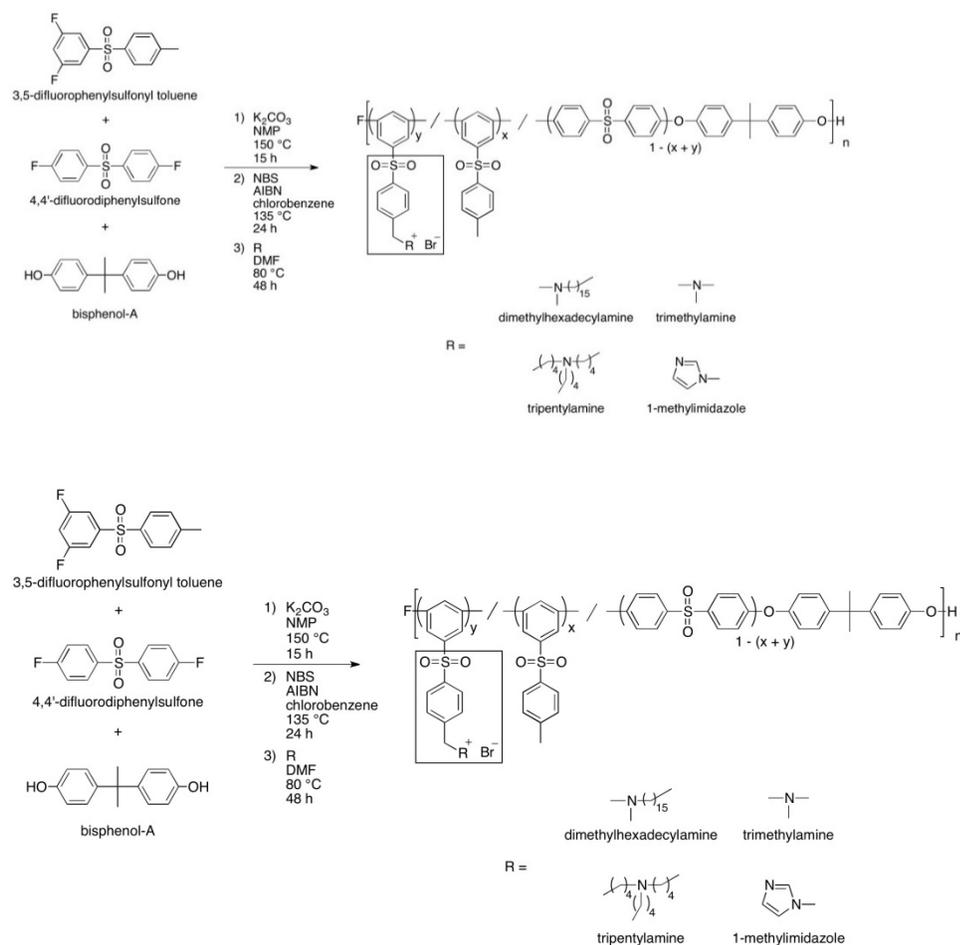
Polymer-based materials for water purification typically utilize a “patching” approach in which the periphery of a known architecture is modified with specific functionalities and are not optimized to encapsulate small molecules. Thus, studies are needed to develop structure-activity relationships which provide insight into what functional groups in these systems are required to remove organic pollutants from water. Several closely related triblock copolymer systems prepared from hydrophobic and hydrophilic biorenewable monomers have been synthesized and evaluated as scaffolds for the removal of photochromic dyes from water. The synthesis of these polymers was accomplished using ring opening polymerization conditions with minimal purification. Monomer composition and molar ratio of the different block sections impact the effectiveness in removing the dye pollutant from water. A discussion of these results will be presented.



## POLY 358: Poly(arylene ether)s with ammonium groups located on pendent phenyl sulfonyl moieties for use as anionic exchange membranes

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A series of poly(aryl ether)s with varying percentages of ammonium groups, located on truly pendent positions, was prepared and characterized. The initial polymers were prepared by nucleophilic aromatic substitution (NAS) polycondensation reactions of varying ratios of 3,5-difluorophenylsulfonyl toluene and 4,4'-difluorodiphenylsulfone, with bisphenol-A as the nucleophilic reaction partner. The tolyl groups in the resulting polymers were subjected to radical bromination with *N*-bromosuccinimide, followed by amination with four different amines: trimethylamine, triethylamine, dimethylhexadecylamine, and *N*-methylimidazole. The polymers were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, thermogravimetric analysis, and differential scanning calorimetry. With the exception of the 100% functionalized polymers, tough films were observed after casting from solutions in dimethylformamide. The films were evaluated for potential use as alkaline exchange membranes (AEM) by determining their water uptake and ion exchange capacity values.



## POLY 359: Synthesis and characterization of novel cardo-containing copolyimide membranes for gas separation

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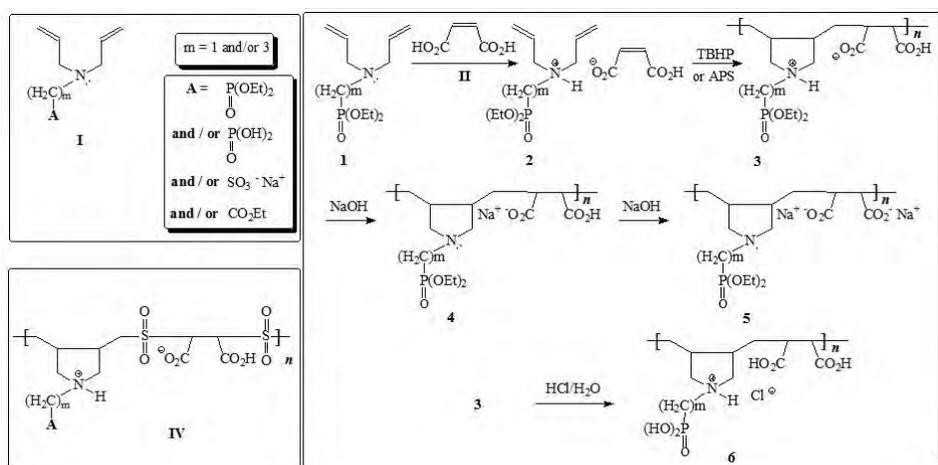
A series of copolyimides were successfully synthesized via a polycondensation reaction of a dianhydride and two cardo-types of diamines. The molar composition of the copolyimide was controlled to investigate the effect of hydroxyl group on gas permeation properties. The synthesized cardo copolyimides were soluble in common organic solvents and had excellent thermal stabilities. CO<sub>2</sub> permselectivity of the copolyimide membrane containing hydroxyl group was higher than that of polyimide without hydroxyl group. CO<sub>2</sub> permeability of the polyimide membrane was improved by the incorporation of hydroxyl group, which increased the solubility of carbon dioxide. The copolyimides containing the hydroxyl group were thermally converted to poly(benzoxazole-imide) at 425 °C for improvements in the gas permeability. The hydroxyl group in the polymer membrane led to the internal free volumes within the polybenzoxazole polymer matrix, which resulted in the increase of gas permeation properties.



## POLY 360: Synthesis of a new class of alternate ionic cyclocopolymers and their potential use as antiscalants

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An array of diallylamine salt monomers I containing methyl- and propyl-phosphonate, methylcarboxylate, and propylsulfonate pendants have been synthesized and subjected to copolymerization with maleic acid II using Butler's cyclopolymerization protocol to obtain a variety of pH-responsive alternate copolymers III, which were then subjected to pH-controlled conversion into cationic, zwitterionic and zwitterionic/anionic polymers. The copolymerization of the monomer containing phosphonate motifs with maleic acid along with the interconversions to different ionic polymers is illustrated in Scheme 1. Also, monomers I and II have been terpolymerized with sulfur dioxide leading to a novel class of pH-responsive polymers IV with interesting solution properties. The efficacy of these polymers as antiscalants are being evaluated to inhibit  $\text{CaSO}_4$  and/or  $\text{CaCO}_3$  scale formation which hinders smooth operation of desalination plants.

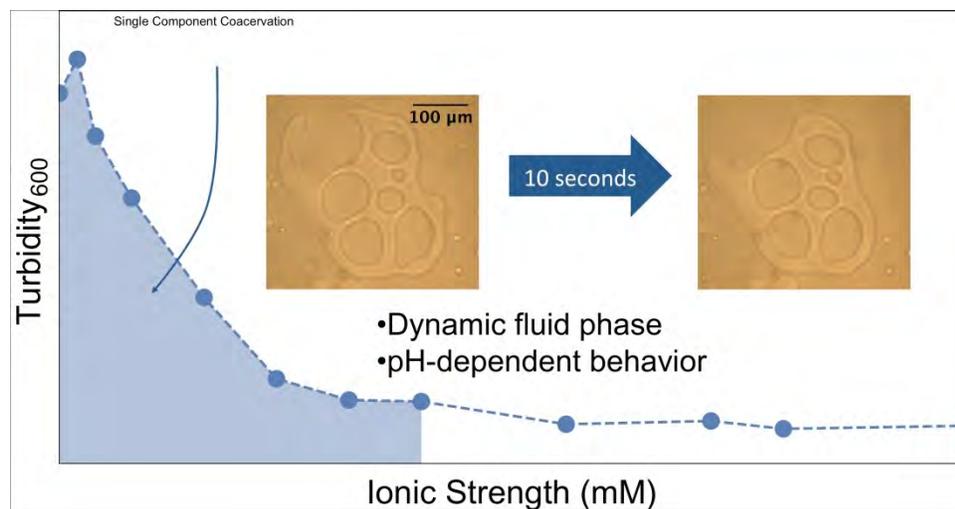


Scheme 1: Cyclopolymerization of diallylamine salt monomers containing various motifs

## POLY 361: Phase behavior of single component coacervates composed of random copolymers

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Coacervates are fluid-fluid phase separations of hydrated polyelectrolytes that have been implicated in the creation of mechanically robust materials by several marine organisms. While currently not well understood, coacervates have been shown to exhibit novel mechanical properties including low surface energy, shear thinning behavior, low surface friction, as well as high degrees of wear protection, making them ideal candidates for durable coatings. In recent years, there has been a considerable effort to understand the “complex coacervation” of polycation and polyanion mixtures, but little is known about the single component coacervation of mixed-charge species. In the presented work, we show that the post-functionalization of sodium polyacrylate with histamine affords random copolymers that undergo coacervation in response to ionic strength as well as pseudo charge cancellation determined by the solution pH. These copolymers represent a fundamentally new class of coacervate-forming polyelectrolytes than previously reported in the literature. Here we present the phase behavior of these copolymers using turbidity measurements and optical microscopy.



## POLY 362: Multifunctional cancer-targeting strategy for encapsulating doxorubicin by folate-conjugated and quercetin-anchored pluronic mixed micelle systems

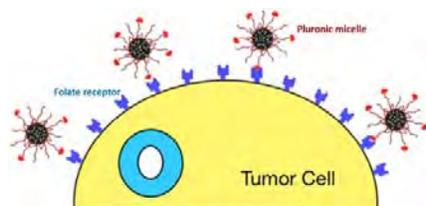
**Zhaoxuan Feng**<sup>2</sup>, [zhaoxuan@kth.se](mailto:zhaoxuan@kth.se), **Salman Hassanzadeh**<sup>2</sup>, **Torbjorn Pettersson**<sup>1</sup>, **Minna Hakkarainen**<sup>2</sup>. (1) KTH Royal Institute of Technology, Stockholm, Sweden (2) Chemical science and engineering, KTH Royal Institute of Technology, Stockholm, Sweden

Amphiphilic pluronic copolymers consisting of hydrophilic poly (ethylene oxide) (PEO) and hydrophobic poly (propylene oxide) (PPO) blocks are popular drug delivery systems known to form micelles by self-assembly. Specific advantages of pluronic-based micelles as drug carriers lie in 1) biocompatibility and nontoxicity, 2) feasibility of structural and functional modification and 3) ability to encapsulate water-insoluble bioactive drugs. However, pluronic micelles suffer from several weak points which have impeded further applications. Pluronics normally have relatively high CMCs due to the weak hydrophobic driving force of PPO which consequently decrease the micelle stability in human body, leading to micelle disintegration and sudden burst of drug. Additionally pluronic systems have relatively low hydrophobic drug loading capacity.

Here, a new strategy to design a multifunctional mixed pluronic micelle system aiming to overcome the above inherent weaknesses was reported through molecularly modification of Pluronic, F127 (PEO-PPO-PEO, Mn=12,500 g/mol) and reversed pluronic, 10R5 (PPO-PEO-PPO, Mn=2000 g/mol).<sup>1</sup> Folic acid was covalently conjugated to the chain ends of F127 to introduce a cancer cell-targeting functionality, while hydrophobic quercetin was selected as a chemical anchor for the PPO chain ends of 10R5 to reduce the CMC, increase the encapsulation capacity as well as control release rate of the hydrophobic anti-cancer drug DOX. The modified polymers were successfully identified by <sup>1</sup>H NMR, FTIR, DSC and UV-Vis. Reduced CMC and promoted DOX encapsulation efficiency (from 19% to 43%) was also proved. Colloidal probe AFM further indicated that adhesion force between DOX coated probe and quercetin anchored pluronic was approximately doubled compared to the adhesion between DOX and unmodified pluronic.

### References:

1. Hassanzadeh, S., et al., *A proof-of-concept for folate-conjugated and quercetin-anchored pluronic mixed micelles as molecularly modulated polymeric carriers for doxorubicin*. *Polymer*, 2015. 74: p. 193-204.



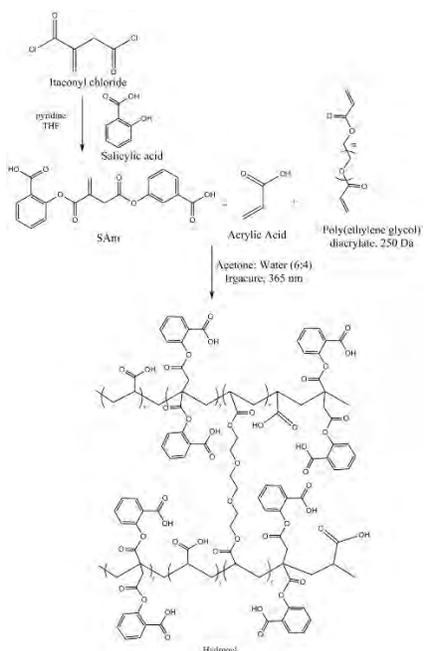
Multifunctional pluronic micelle conjugated with folic acid ligand targeting at the overexpressed folic acid receptor on the tumor cells

## POLY 363: Novel salicylic acid-based chemically cross-linked pH sensitive hydrogels for biomedical applications

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Salicylic acid (SA), an anti-inflammatory drug, has shown potential to prevent many diseases including diabetes and cancer. In this research, SA chemically incorporated into hydrogel systems. Hydrogels have been received attention in many biomedical applications including, protein delivery and wound dressing owing to their ability to tune easily and similarity to natural living tissue. In this research, SA was chemically incorporated into hydrogel systems via attachment of SA to an itaconate moiety followed by crosslinking using acrylic acid and poly(ethylene glycol) diacrylate via UV initiation.

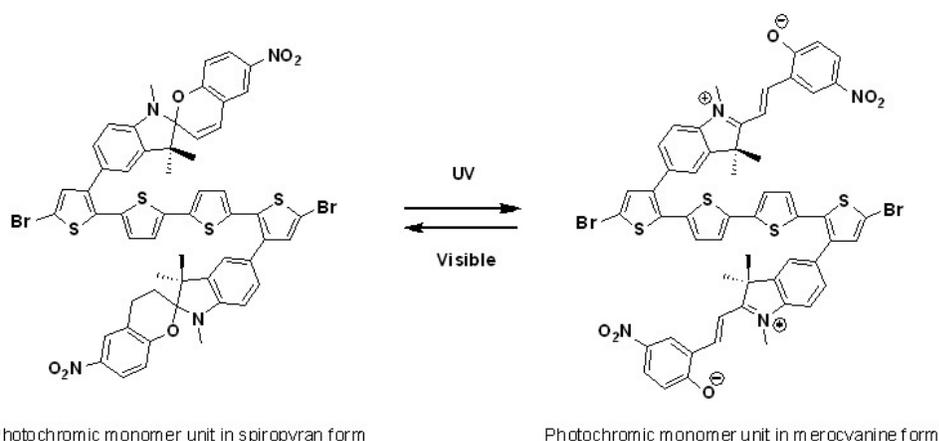
SA-based hydrogels showed pH-responsive behavior, collapsing at acidic pH (pH 1.2) and swelling at higher pH (pH 7.4). The structure, swelling behavior, pore structure, SA release, rheological, and mucoadhesion behavior of these hydrogels were studied. These networks exhibit promising pore size for physically encapsulating of drugs and proteins. Furthermore, SA release behavior of these hydrogels was evaluated. The hydrogel systems exhibit a pH-dependent SA release profile. In pH 1.2, SA release was much slower compared to pH 7.4. Under acidic pH, 30% SA was released after 24 h, and 100% SA was released in a sustained manner within 24 h in pH 7.4 buffer. In addition, rheological studies of the hydrogels proved that these systems are mechanically strong and robust. Moreover, these hydrogel systems also showed mucoadhesive behaviors, which is important for drug delivery applications. These results suggest that SA-based hydrogels can be potentially used for oral delivery of proteins and small molecules in combination with SA to treat cancer and diabetes.



## POLY 364: Novel synthetic route towards incorporating photochromic spiropyrans into thiophene based semiconducting polymers

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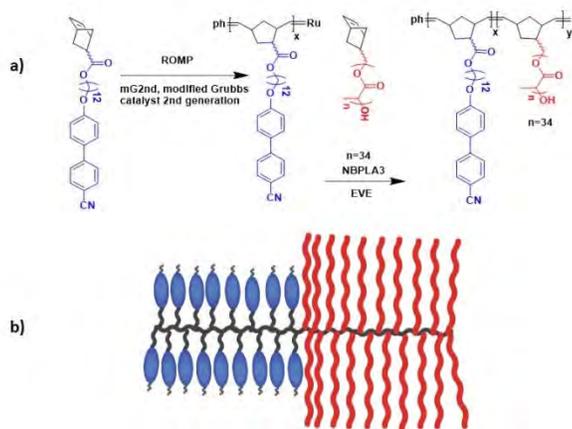
The use of thiophene based conducting polymers in organic field effect transistors (OFETs) have been extensively studied over the past several years. Photochromism is the ability of a molecule to undergo reversible structural changes upon absorption of a photon. It is possible to observe interesting properties when the photochromic effect is coupled to a conducting polymer as light is an ideal, harmless, selective external trigger signal. Among different classes of photochromic materials indoline spiropyrans are notable for their high sensitivity and resolving power, exhibiting photochromic properties in solution, in polymeric matrices and even in solid state, which is very convenient for their practical applications. Even though the chemical doping of spiropyran with thiophene based conducting polymers is reported, their application is limited due to the use of low amounts to suppress phase separation. Here we report a novel synthetic route to incorporate photochromic spiropyran as a pendant group to polythiophene.



## POLY 365: Molecular weight dependence of domain spacing in novel liquid crystalline brush-like block copolymers

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We introduce a novel Liquid Crystalline Brush-like Block Copolymer (LCBBC) architecture in order to study the effect of molecular weight on microdomain spacing for a series of symmetric composition samples,  $\Phi_{LC} = 0.5$ . Sequential Ring-Opening Metathesis Polymerization of n-alkyloxy cyanobiphenyl and poly(D,L-lactide) (PLA) functionalized norbornene monomers yields low polydispersity block copolymers with its novel architecture. Samples with molecular weights of 25, 50, 100, 200 and 400 Kg/mol having symmetric compositions are prepared for this study. The microdomain spacing displays power law scaling with molecular weight with an exponent of 0.6,  $L_0 \sim MW^{0.6}$ , which represents strong departure from the behaviour of bottlebrush block copolymers where  $L_0 \sim MW^1$ . While we study the dependence of molecular weight on microdomain spacing, we have also studied the phase behavior of these LCBBCs with a constant overall molecular weight and asymmetric compositions. We observe a display of conventional linear block copolymer (LBC)-like morphologies of both PLA and liquid crystalline blocks. Presence of sub-linear scaling of microdomain spacing with molecular weight and morphological variety like LBCs set this system clearly apart from bottlebrush block copolymers, perhaps retaining some of the beneficial characters of bottlebrush block copolymers, including higher chain mobility and larger domain spacings relative to linear diblocks.

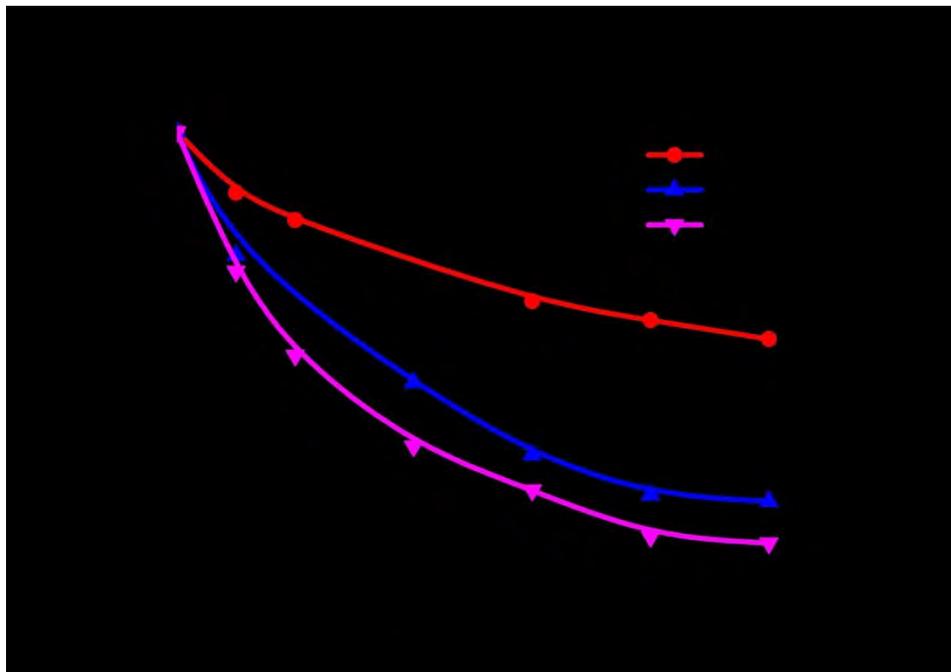


Synthetic scheme for ring opening metathesis polymerization for the poly(D,L-lactide) (PLA) based liquid crystalline brush-like block copolymers (LCBBC) (b) Schematic illustration of molecular architecture of LCBBCs with symmetric composition.

## POLY 366: Enhancement of magnetic field on the ultrasonic degradation of polymer chains of spherical polyelectrolyte brushes

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The magnetic field was found to be able to promote the ultrasonic degradation of polyelectrolytes. With the existence of magnetic field, the thickness of spherical poly(2-aminoethyl methacrylate hydrochloride) brushes decreased significantly after ultrasonic irradiation. The scission of poly(2-aminoethyl methacrylate hydrochloride) chains enhanced upon increasing the magnetic field intensity and ultrasonic frequency while decreasing the temperature.



Thickness change of PS-PAEMH chains under different magnetic field intensities.  $T = 303 \text{ K}$ ,  $f = 35 \text{ kHz}$ ,  $P = 0.086 \text{ W}$ .

## POLY 367: Six-arm star-shaped poly( $\epsilon$ -caprolactone)-b-poly(*n*-vinylcaprolactam) micelles as nanocarriers of 5-fluorouracil

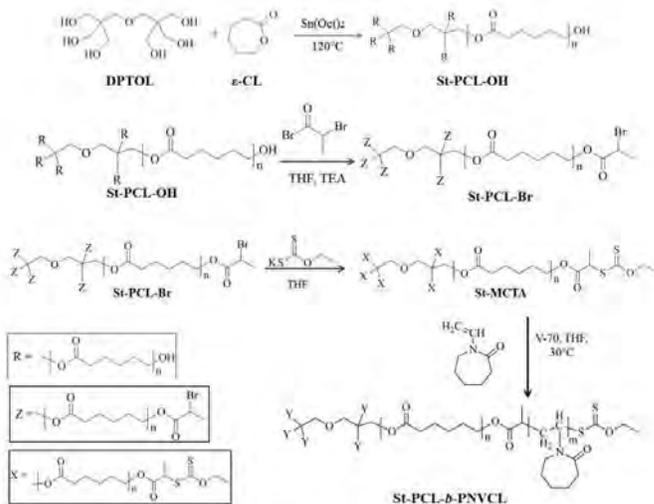
**gema danira d. garcia olaiz**, *gg.gemmagarcia@gmail.com*, norma aide cortez lemus.  
Instituto tecnologico de tijuana, Tijuana, Baja California, Mexico

Currently releasing systems more selective and effective cancer drugs are sought. In recent decades have been studied polymeric micelles formed by stars as they can have a higher efficacy as drug delivery system because of its greater storage area and compactness, this can be modulated by varying the synthesis conditions.

In this project, the synthesis of six arms star-shaped Poly( $\epsilon$ -caprolactone)-b-poly(*N*-vinylcaprolactam) block copolymers were synthesized by first time, by combining ring opening polymerization (ROP) of  $\epsilon$ -caprolactone (CL) and reversible addition-fragmentation chain transfer (RAFT) polymerization of *N*-vinylcaprolactam (NVCL). SPCL-OH six arm star polymers with different PCL chain lengths were successfully synthesized. The molecular weights from GPC were 3035 g mol<sup>-1</sup> to 14,820 g mol<sup>-1</sup> with PDI less than 1.23. After functionalization with xanthates, controlled copolymerization of NVCL moiety to PCL-macroRAFT was carried out. Global blocks with molecular weights were obtained from 12,440 g mol<sup>-1</sup> to 73,000 g mol<sup>-1</sup>. The resulting star copolymers were characterized using <sup>1</sup>H NMR, GPC and UV-vis. We also demonstrated that the reactive xanthate groups were still retained in polymer chain ends using UV-vis.

The star-shaped block copolymers self-assembled in solution into micelles with sizes varying from 25 to 250 nm. The effect of length of hydrophobic and hydrophilic segments on drug loading, micelle size and drug release was investigated. Micelles were characterized by atomic force microscopy (AFM), dynamic light scattering (DLS) and scanning electron microscopy (SEM).

Furthermore, 5-fluorouracil was used as the model drugs to evaluate the potential of micelles prepared from star-shaped copolymers based on poly( $\epsilon$ -caprolactone)-block-poly(*N*-vinylcaprolactam) for drug loading.

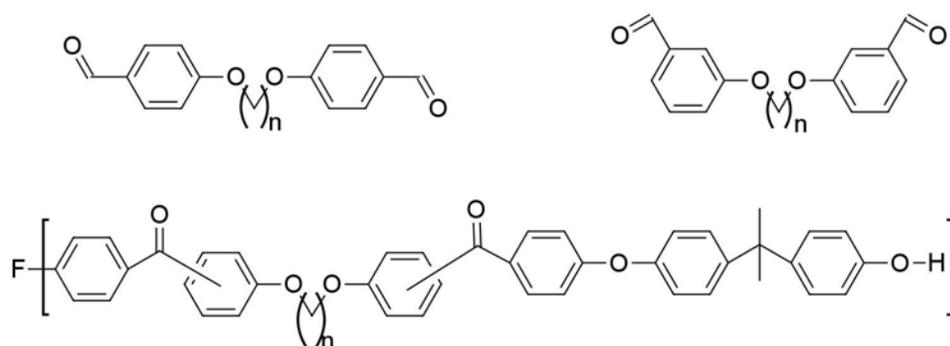


Synthetic route.

## POLY 368: Alkylenedioxy containing PEEK polymers containing meta linkages

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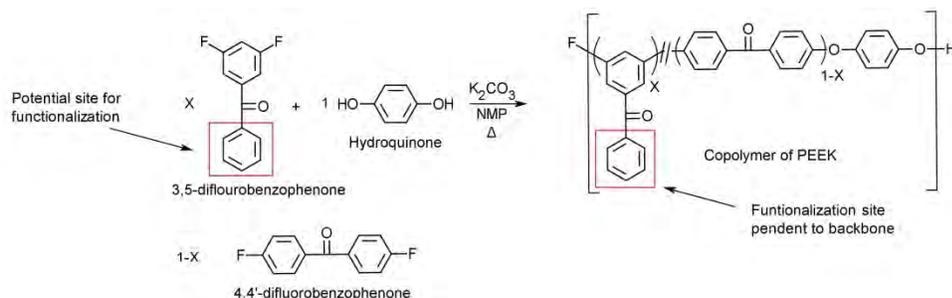
Poly(ether ether ketone)s (PEEK) polymers are known for their unique properties including excellent thermal stability, solvent resistance and mechanical properties. Since their discovery, various alterations have been done to enhance their properties one of which has been the inclusion of alkylenedioxy linkages with all para linkages. A series of meta substituted PEEK monomers have been synthesized via a three-step process involving alkylenedioxy dibenzaldehyde synthesis, Grignard reaction to add the addition of fluorophenyl groups and subsequent oxidation to form a fluorophenyl ketone. Polymerization occurred in an A2+B2 fashion with bisphenol-A under NAS conditions (NMP, toluene, potassium carbonate). Characterization of the meta substituted polymers will be presented in comparison to the previously reported para systems.



## POLY 369: Synthesis of functionalized PEEK analogues via "one-pot" reaction

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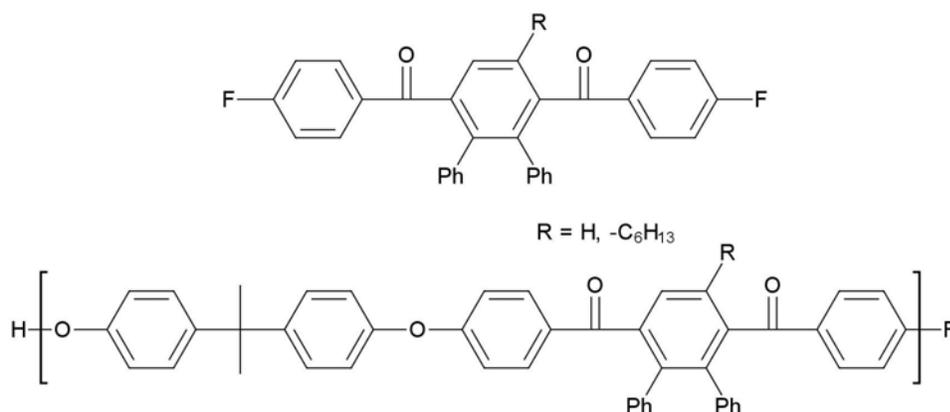
Poly(ether ether ketone), PEEK, is known for its high thermal stability, chemical and corrosion resistance, and versatility. When functional groups are introduced to PEEK, crystallinity is often disrupted causing some of the desirable properties to diminish. Synthetic routes that allow functionalization, but permit the crystallinity to be maintained are highly desirable. This presentation will focus on our attempts to prepare functional, semi-crystalline PEEK analogues. The overall project has two goals: 1) to demonstrate semi-crystalline properties in copolymers of PEEK with pendent functionalization sites, and 2) to synthesize copolymers of PEEK with pendent functional groups. The optimum percentage of traditional PEEK in the copolymers was investigated, as was the importance of the monomer addition order. The level of crystallinity was determined via DSC and X-ray diffraction analyses. Copolymers of PEEK containing up to 25 % of repeat units derived from 3,5-difluorobenzophenone remain semi-crystalline, but with better solubility than PEEK.



## POLY 370: Phenylated PEEK containing pendant alkyl substituents

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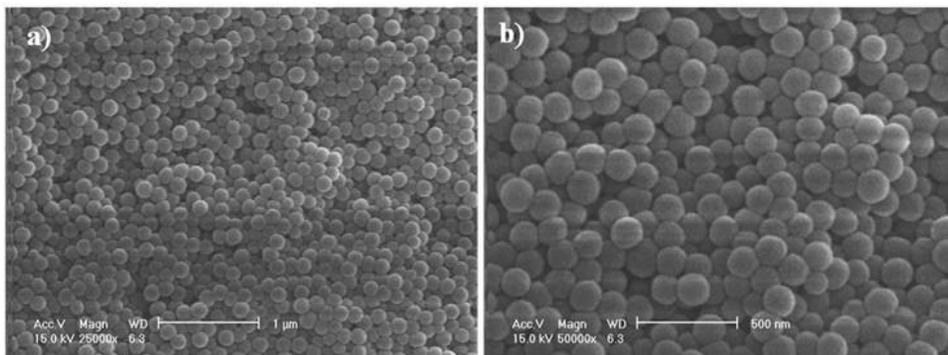
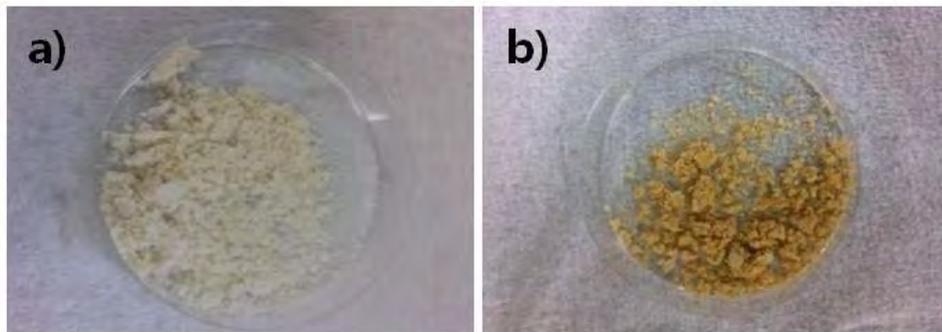
Poly(ether ether ketone)s (PEEK) are extensively used in industries where a robust, nonreactive material is desired. They retain their mechanical strength and chemical resistance even at high temperatures. These properties come from a rigid structure and the low reactivity of its functional groups. However, this leads to higher working temperatures and more difficult processing conditions. Previously reported phenylated PEEK polymers showed higher solubility, lower glass transition temperatures and equivalent thermal stability compared to nonphenylated analogs. The addition of an alkyl chain on the phenylated bis(fluorobenzoyl) monomer provides additional control of the glass transition temperature to improve processability and solubility. The bis(fluorobenzoyl) monomer, prepared by a three-step procedure, was polymerized with a series of bisphenols.



## **POLY 371: Synthesis and characterization of sulfonated PEEK/polymeric nanoparticles composite membrane for fuel cell application**

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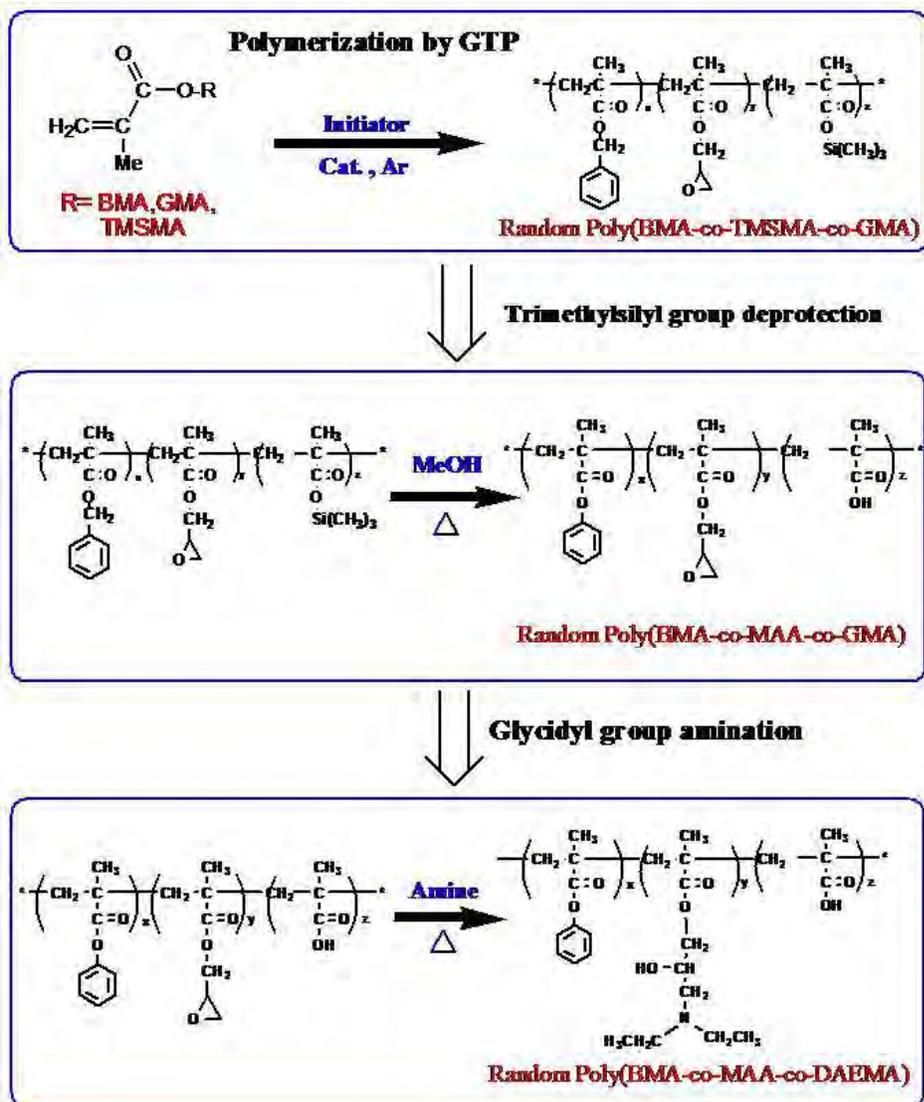
Emulsion polymerization and post sulfonation methods are used to prepare polystyrene nanoparticles with a uniform size and particle size distribution, and sulfonated poly(etheretherketone) (sPEEK) for the fabrication of composite membranes. The polystyrene particles are functionalized with sulfonation reagents in order to enhance the proton conductivity. This study compares the performance of polymer electrolyte membrane fuel cells with different amounts of sulfonated nanoparticles and sulfonation reaction time of the PEEK polymer. The optimum composition of PS-SO<sub>3</sub>H particles is determined based on the mechanical properties, the behavior of water in the membrane, and the level of proton conductivity. The composite membrane has higher levels of proton conductivity than the pure sPEEK membrane. An increase in the content of PS particles increases the proton conductivity due to the incorporation of hydrophilic nanoparticles. These properties enable the composite membranes to become candidates for proton exchange membrane fuel cell applications



## POLY 372: GTP synthesis of the multifunctional polyacrylate and their analysis of functional group

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Multifunctional polyacrylate copolymers consisting of benzyl methacrylate, trimethylsilyl methacrylate, and (dimethylamino)-ethyl methacrylate as monomers were synthesized by group transfer polymerization. The molecular weights and molecular weight distributions of the copolymers were determined by gel permeation chromatography in THF, and their number-average degrees of polymerization and copolymer compositions were calculated by <sup>1</sup>H-NMR. These molecular weights and degrees of polymerization corresponded closely to the values expected from the monomer/initiator ratios. The polydispersities were low as expected for GTP, and ranged from 1.6 to 1.85

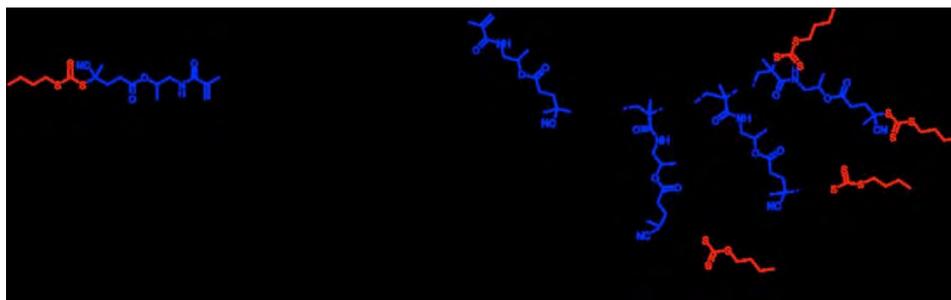


Overall scheme of GTP for multifunctional polyacrylate

## POLY 373: Hyperbranched poly[(*n*-2-hydroxypropyl) methacrylamide] via RAFT self-condensing vinyl polymerization

**Jawaher A. Alfurhood**<sup>2</sup>, jawaher1@ufl.edu, Hao Sun<sup>1</sup>, Patricia Bachler<sup>1</sup>, Brent S. Sumerlin<sup>1</sup>. (1) Department of Chemistry, University of Florida, Gainesville, Florida, United States (2) chemistry, university of florida, Gainesville, Florida, United States

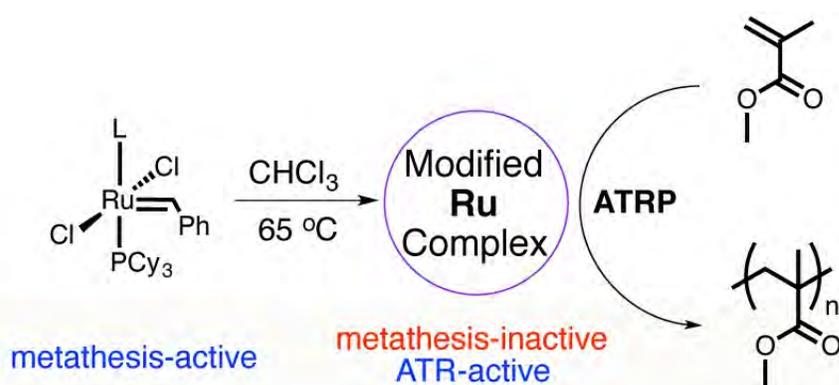
We report the first synthesis of hyperbranched poly[(*N*-2-hydroxypropyl) methacrylamide] (HB-PHPMA) using reversible addition-fragmentation chain transfer (RAFT) self-condensing vinyl polymerization (SCVP). The synthesis of these sophisticated, well-defined architectures involved the copolymerization of HPMA with a chain transfer monomer (CTM). The polymerization kinetics, as well as the effects of initiator and monomer concentration, were studied. The resulting polymers show high molecular weights and controlled branching frequencies in close alignment with the theoretical values. Due to their inherent amphiphilic nature, these hyperbranched structures self-assemble into aggregates in water. Additionally, we determined the cloud point of the HB-PHPMA to be in the range of 29-40 °C. These interesting results provide access to a new class of thermoresponsive PHPMA polymers with potential to be used in drug delivery and other biological applications.



## POLY 374: Evidence for in situ catalyst modification in atom transfer radical reactions with ruthenium benzylidene complexes

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Since the first report of ruthenium-based catalysts in atom transfer radical addition (ATRA, also called Kharasch addition) and atom transfer radical polymerization (ATRP), this area of research has attracted widespread interest. Well-defined ruthenium benzylidene complexes, commonly used as olefin metathesis catalysts, have also been reported to catalyze ATRA and ATRP. The ability of ruthenium benzylidene complexes to promote two reactions with such markedly different mechanisms has been utilized in various tandem reactions in which olefin metathesis and atom transfer radical (ATR) reactions take place in one pot. While the mechanism by which ruthenium benzylidenes initiate and catalyze olefin metathesis has been studied in great detail, little is known regarding the mechanism of ATR reactions promoted by these complexes. In the present study, <sup>1</sup>H NMR kinetics revealed that ruthenium benzylidene complexes are rapidly converted into new metathesis inactive species under typical ATRA conditions. When ruthenium benzylidene complexes were pre-incubated prior to substrate addition, the resulting activated species exhibited enhanced kinetic reactivity in ATRA with no significant difference in overall product yield compared to the original complexes. Kinetic measurements along with additional mechanistic and computational investigations show that metathesis-inactive ruthenium species, generated in situ from ruthenium benzylidene complexes are active catalysts in ATR reactions including ATRA and ATRP.



## POLY 375: Sterically-driven selectivity in ADMET polymerization of asymmetric $\alpha,\omega$ -dienes for sequence-controlled polyolefins

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Monomer sequence control plays a vital role in biology and is a prerequisite for crucial features of life, such as molecular recognition and data storage. Bridging the gap between synthetic polymers and biopolymers has been a grand challenge for polymer chemists during the last few decades. Inspired by nature's way of sequence-controlled materials, strategies to control the primary structure of synthetic macromolecules to develop new highly-organized materials have become an active area of research. Although progress has been made in manipulation of polymer architecture, the complexity of biomacromolecules cannot be fully reproduced because the methods available to tailor polymer microstructures are still rudimentary. In this work, we investigate sterically-driven metathesis selectivity as an innovative approach towards sequence-controlled polyolefins via acyclic diene metathesis polymerization (ADMET) of asymmetric  $\alpha,\omega$ -dienes. The asymmetric monomers contain an unhindered Type I alkene as the  $\alpha$ -terminus and a hindered Type II/III protected tertiary allylic alcohol as the  $\omega$ -terminus. By increasing the steric bulk of the tertiary allylic alcohol, the  $\omega$ -terminus is expected to transform from Type II to Type III, leading to selective head-to-tail additions. Successful demonstration of sequence-controlled polyolefins via ADMET will lead to a vast array of new monomer design for sequence-controlled polymers and their utilization in improved technologies.

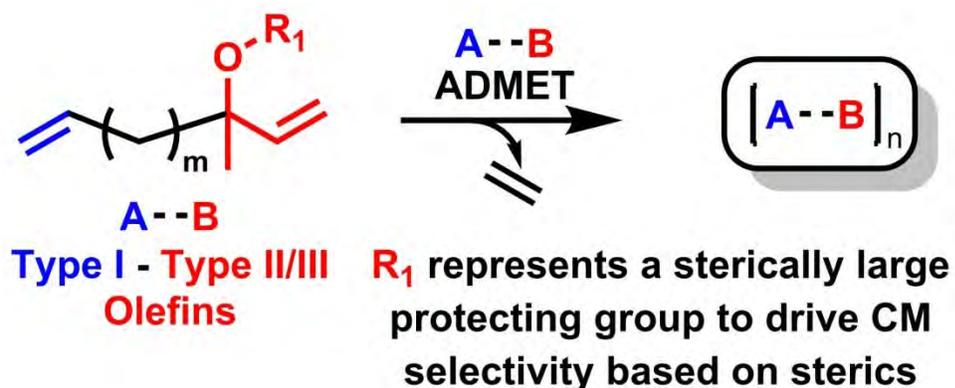
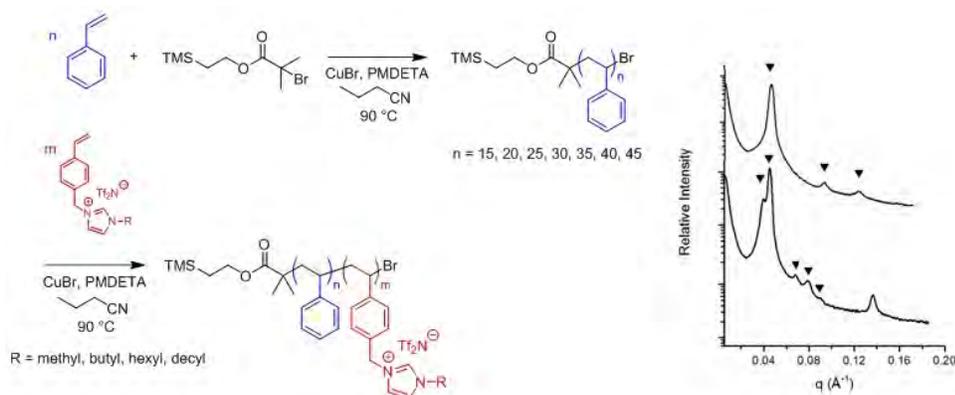


Figure 1. Sterically-driven selectivity in ADMET polymerizations using asymmetric  $\alpha,\omega$ -dienes based on terminal alkenes and protected tertiary allylic alcohols.

## POLY 376: Synthesis and morphological phase behavior of ordered, microphase-separated, imidazolium-containing diblock copolymers made by ATRP

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Polymerized ionic liquids (poly(IL)s) are macromolecules with charged repeat units that are prepared from or structurally related to ionic liquids (ILs). The development of ordered, microphase-separated polymeric systems containing poly(IL) segments has considerable implications toward a range of transport-dependent, energy-based technology applications. A series of imidazolium-based noncharged-charged diblock copolymers with total of 50 repeat unit and repeat unit ratios range of 15:25 to 45:5 were synthesized by the direct, sequential atom-transfer radical polymerization of styrene and styrenic imidazolium bis(trifluoromethyl)sulfonamide (Tf<sub>2</sub>N<sup>-</sup>) monomers. Size-exclusion chromatography and <sup>1</sup>H NMR endgroup analysis confirmed low MW distributions and the expected block ratios. Small-angle X-ray scattering studies on the thermally annealed block copolymers showed that they can form different ordered nanostructures (i.e., sphere, hexagonal, and possibly gyroid phases) in their neat states via varying both the block ratio and the length of the alkyl side-chain (methyl, *n*-butyl, *n*-hexyl, and *n*-decyl) on the imidazolium monomer.

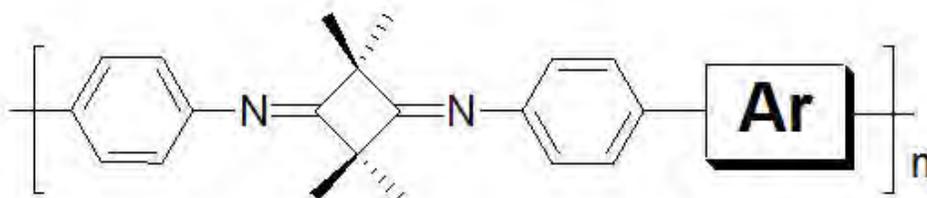


Synthesis and SAXS profile of imidazolium-containing diblock copolymers

## POLY 377: Synthesis and properties of polyimines containing 2,2,4,4-tetramethyl-1,3-cyclobutadiimine moiety

Yeong-Beom Lee<sup>3</sup>, **Woohyung Lee**<sup>1</sup>, woohyung2@gmail.com, Annick Anctif<sup>2</sup>, James J. Worman<sup>3</sup>, Brian J. Land<sup>2</sup>, Chulsung Bae<sup>1,3</sup>. (1) Dept. of Chemistry Chemical Biology, Rensselaer Polytechnic Institute, Troy, New York, United States (2) Chemical Engineering, Rochester Institute of Technology, Rochester, New York, United States (3) Department of Chemistry, University of Nevada Las Vegas, Las Vegas, Nevada, United States

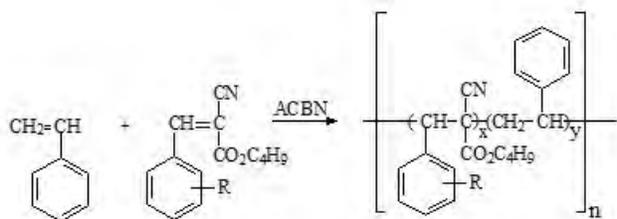
Although 2,2,4,4-tetramethyl-1,3-cyclobutadiimine (TMCBDI) has been known for more than 50 years, it has never been used for formation of polymers primarily due to inefficiency of direct polycondensation reaction. A series of new TMCBDI-based polymers were synthesized using Pd-catalyzed Suzuki coupling polymerization; the TMCBDI monomer was polymerized with aromatic diboron components including fluorene, benzene and thiophene. The polyimines from fluorine and benzene have good solubility in common organic solvents, while the polymer from thiophene which lacks a soluble alkyl group was insoluble. All polymers showed good thermal stability over 340 °C and high glass transition temperature over 220 °C in thermal analysis. The effects of different aromatic units on the TMCBDI-based polyimine backbones, solubility, thermal properties, UV absorption spectra, and energy levels properties of the resulting copolymers were investigated.



## POLY 378: Novel copolymers of styrene with oxy ring-disubstituted butyl 2-cyano-3-phenyl-2-propenoates

**Sara M. Rocus**, sroculus3@gmail.com, Gregory B. Kharas, Varun Elangovan, Anna Kovaleva, Sarah Malik, Ogechi Nwosu, Amanda Piche, Lopa A. Patel, Scott J. Rosengarden. Chemistry, DePaul University, Chicago, Illinois, United States

Novel trisubstituted ethylenes, oxy ring-disubstituted butyl 2-cyano-3-phenyl-2-propenoates,  $RPhCH=C(CN)CO_2C_4H_9$  (where R is 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 4-ethoxy-3-methoxy, 3,4-dibenzyloxy, 2-benzyloxy-3-methoxy, and 3-benzyloxy-4-methoxy) 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,  $^1H$  and  $^{13}C$ -NMR. All the ethylenes were copolymerized with styrene in solution with radical initiation (ACBN) at  $70^\circ C$ . The compositions of the copolymers were calculated from nitrogen analysis and the structures were analyzed by IR,  $^1H$  and  $^{13}C$ -NMR. Decomposition of the copolymers in nitrogen occurred in two steps, first in the  $200-500^\circ C$  range with residue (2-17 % wt.), which then decomposed in the  $500-800^\circ C$  range.

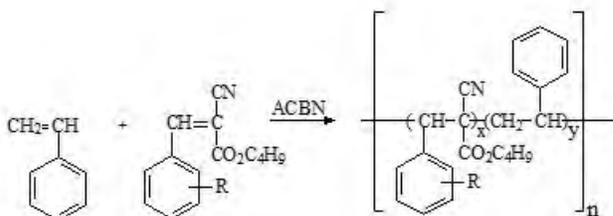


Copolymerization of Styrene with Oxy Ring-disubstituted Butyl 2-cyano-3-phenyl-2-propenoates

## POLY 379: Novel copolymers of styrene and fluoro ring-disubstituted butyl 2-cyano-3-phenyl-2-propenoates

**WILLIAM S. SCHJERVEN**, WSCHJERVEN@GMAIL.COM, Gregory B. Kharas, URIEL A. BARAY, SAMANTHA CHAN, MICHAEL T. COLE, ALEXANDER F. HADDAD, JOSEPH A. LUCENTE, KAYNE J. PATTERSON, Arthur Ralko, KATIE N. REGET, CATHERINE A. SHAMBLIN, EMILY M. WHITMORE. Chemistry, DePaul University, Chicago, Illinois, United States

Electrophilic trisubstituted ethylenes, ring-disubstituted butyl 2-cyano-3-phenyl-2-propenoates,  $RPhCH=C(CN)CO_2C_4H_9$  (where R is 2-fluoro-4-methoxy, 2-fluoro-5-methoxy, 2-fluoro-6-methoxy, 3-fluoro-4-methoxy, 4-fluoro-3-methoxy, 5-fluoro-2-methoxy, 3-fluoro-2-methyl, 3-fluoro-4-methyl, 4-fluoro-2-methyl, 4-fluoro-3-methyl, 5-fluoro-2-methyl) were prepared and copolymerized with styrene. The monomers were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-disubstituted benzaldehydes and butyl cyanoacetate, and characterized by CHN analysis, IR,  $^1H$  and  $^{13}C$ -NMR. All the ethylenes were copolymerized with styrene in solution with radical initiation (ACBN) at  $70^\circ C$ . The compositions of the copolymers were calculated from nitrogen analysis and the structures were analyzed by IR,  $^1H$  and  $^{13}C$ -NMR. Decomposition of the copolymers in nitrogen occurred in two steps, first in the  $200$ - $500^\circ C$  range with residue (3.1-6.5 % wt.), which then decomposed in the  $500$ - $800^\circ C$  range.

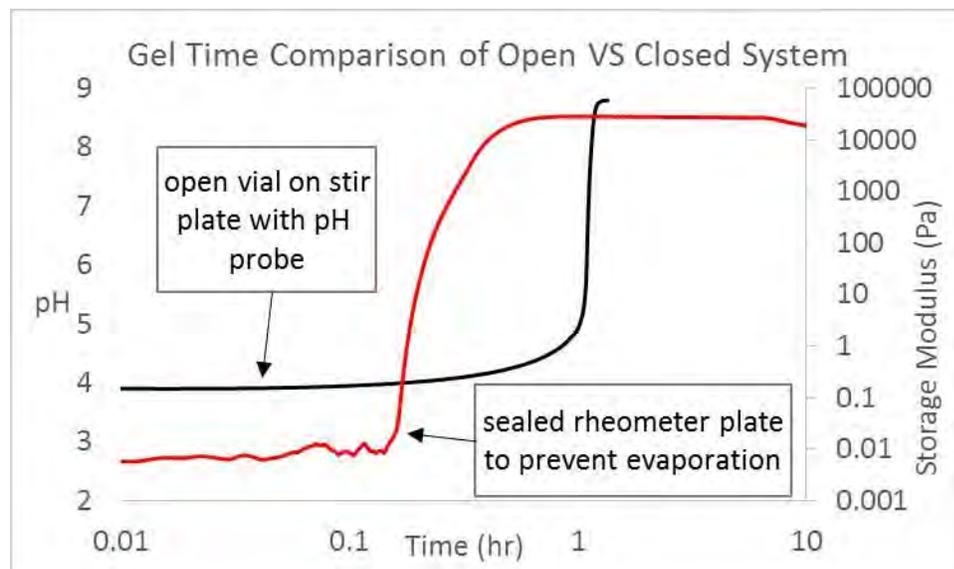


Copolymerization of Styrene with Fluoro Ring-disubstituted Butyl 2-cyano-3-phenyl-2-propenoates

## POLY 380: Thiol-acrylate hydrogels prepared via a new time-lapse polymerization method

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A new time-lapse polymerization system has been developed which employs a benign clock reaction to trigger the base-catalyzed Michael addition of a water-soluble trithiol to a water-soluble diacrylate. The clock reaction is the urea-urease clock, and the monomers are Thiocure® ETTMP 1300 and PEGDA 700. The concentration dependent clock and gel times have been studied. The hydrogel polymer formed has been characterized by rheometry, DMA compression, DMA tensile, DSC, and TGA. Swelling studies have also been performed to determine the equilibrium swelling ratio. The degradation time of the crosslinked ester hydrogel varies with changing reagent concentrations and has been studied. Increased urea and urease concentrations led to increased clock and gel times, but decreased degradation times and conversion of the hydrogel. The opposite is true for increased monomer concentrations.



Ammonia evaporation can lead to delayed clock and gel times. However, the same trends with changing concentrations are observed with both. In these graphs, the concentrations of reagents are 0.01 M urea, 0.5 mg/mL urease, 0.10 M thiol, and 0.15 M acrylate.

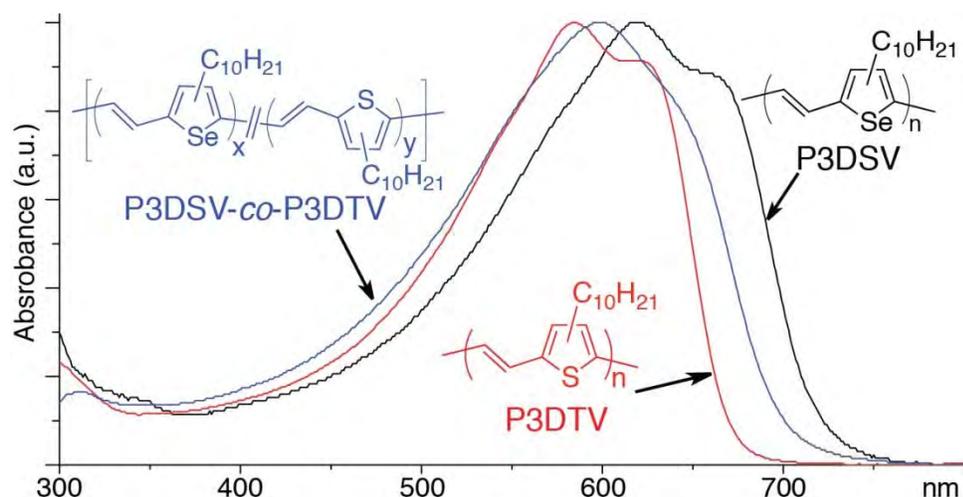
## POLY 381: Novel poly(chalcogenylene vinylene)s with systematically tunable physical and electronic properties through acyclic diene metathesis (ADMET)

**Zhen Zhang**, zhangzh2013@unm.edu, Yang Qin. University of New Mexico, Albuquerque, New Mexico, United States

Conjugated polymers have found widespread applications in thin film electronic devices. Among a plethora of examples, low bandgap poly(thienylene vinylene) (PTV) derivatives have attracted increasing attention due to high charge mobilities, environmental and thermal stability, and recently discovered singlet fission processes. However, these PTVs possess extremely short exciton lifetimes that significantly limit their applications in organic optoelectronic devices. Thus, structural modifications and a better understanding on structure-property relationships are necessary, which has been explored to a very limited extent mainly due to the limitations in conventional synthetic methodologies.

Here, we report two distinctive methods for modifying PTV structures and properties. First, we synthesized poly(3-decylselenylene vinylene) (P3DSV) homopolymers and poly(3-decylselenylene vinylene)-co-poly(3-decylthienylene vinylene) (P3DSV-co-P3DTV) copolymers through acyclic diene metathesis (ADMET) polymerization techniques.<sup>1</sup> By replacing sulfur atoms with selenium, P3DSV was found to possess reduced crystallinity and a smaller bandgap of ca. 1.6 eV, and P3DSV-co-P3DTV shows physical/electronic properties between those of the corresponding homopolymers. Secondly, we successfully prepared a series of novel PTV derivatives functionalized with F, Cl, Br and I atoms at the 4-positions of thiophene rings through ADMET. Such halogenation not only displays capabilities of fine-tuning polymer properties but also provides opportunities for further functionalization through cross-coupling reactions. Our methodologies provide new ways to systematically study the structure-property relationships of low bandgap poly(chalcogenylene vinylene)s, which has been rarely explored previously.

<sup>1</sup> Zhang, Z. and Qin, Y. *ACS Macro Lett.* 2015, 4, 679.



## POLY 382: Ruthenium catalyzed ring-opening metathesis polymerization of cyclic olefins

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Olefin metathesis is a powerful and versatile method in synthetic organic and polymer chemistry. In particular ring-opening metathesis polymerization (ROMP) has become an extremely valuable tool for the preparation of functionalized homopolymers.

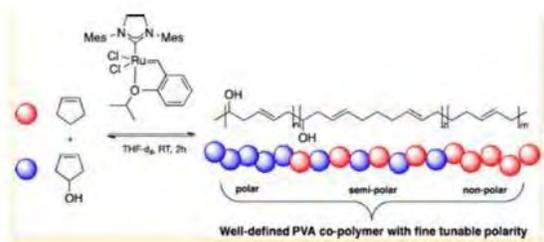
The ROMP of strained cyclic olefins to linear polymers provides an interesting class of stereoregular polymers. Of particular interest is *trans*-poly(pentenamer) which has unique relevance among the synthetic rubbers since it has similar physical properties to natural rubber.<sup>1</sup> Furthermore, *trans*-poly(pentenamer) can be easily synthesized by utilizing dicyclopentene or cyclopentadiene that are produced as waste products by the petrochemical industries, to reduce environmental pollution.

In the past several living ROMP of cyclic olefins have been reported based on a range of metals, including titanium, tantalum, tungsten and molybdenum metathesis catalytic systems.<sup>2,3</sup> However, despite the high catalytic activity of these early transition-metal catalyst, their relatively limited functional group tolerance, high sensitivity towards moisture and atmospheric oxygen often render them difficult to use. Over the last decade several ruthenium based catalysts have attracted considerable attention because of their remarkable efficiency, stability and excellent tolerance towards a variety of functional groups. Nevertheless, ruthenium catalyzed ROMP studies of cyclopentene and its functionalized derivatives are rare.

Herein we will focus on the use of non-supported and soluble polymer supported N-heterocyclic carbene (NHC) Ru metathesis catalysts for the equilibrium ROMP of cyclic olefins. Moreover, well defined poly(Vinyl Alcohol) (PVA) copolymers.

(a) K. Sanui, W. J. MacKnight and R. W. Lenz, *Macromolecules*, **1974**, 7, 101. (b) J. K. Gillham and J. A. Benci, *J. Appl. Polym. Sci.*, **1974**, 18, 3775.

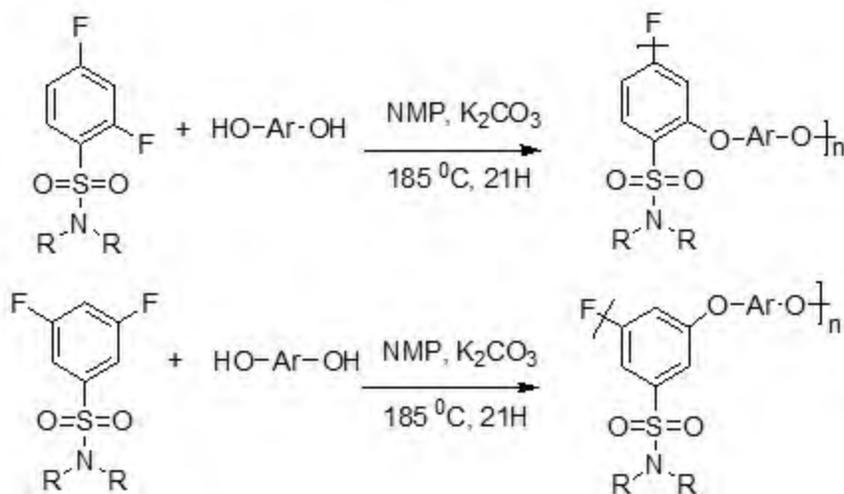
(a) Natta, G.; Dallasta, G.; Mazzanti, G.; Pasquon, I.; Valvassori, A.; Zambelli, A., *Makromolekulare Chemie* 1962, 56, 224-227. Schrock, R. R., 1990, 23 (5), 158-165.



## POLY 383: Comparison of the thermal properties of poly(arylene ether)s prepared from of *N,N*-dialkyl-2,4-difluorobenzenesulfonamide and *N,N*-dialkyl-3,5-difluorobenzenesulfonamide

*James waweru*<sup>2</sup>, *kanyosh06@yahoo.com*, *Eric Fossum*<sup>1</sup>, *Steven Ujvary*<sup>2</sup>, *Jasper van den Hoek*<sup>2</sup>. (1) Department of Chemistry, Wright State University, Dayton, Ohio, United States (2) chemistry, wright state university, Dayton, Ohio, United States

A series of poly(arylene ether)s was synthesized by the nucleophilic aromatic substitution (NAS) polycondensation reactions of *N,N*-dialkyl-2,4-difluorobenzenesulfonamide and *N,N*-dialkyl-3,5-difluorobenzenesulfonamide. The sulfonamide-activated monomers were synthesized by reacting 2,4- and 3,5-difluorobenzenesulfonyl chloride with a series of dialkyl amines, ranging from *n*-propyl to *n*-octyl. The poly(arylene ether)s, prepared with bisphenol-A as the nucleophilic reaction partner, were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, TGA, DSC and SEC. The thermal properties of the *N,N*-dialkyl-2,4-difluorobenzenesulfonamide polymers were compared to those of the *N,N*-dialkyl-3,5-difluorobenzenesulfonamide system. Poly(arylene ether)s prepared from the 2,4-monomers possessed consistently higher glass transition temperatures than those from the 3,5-monomers. While the 5% weight loss temperatures were similar for both systems, there were observable differences in the TGA traces, indicating that the decomposition pathways may not be the same



R = propyl, iso-propyl, butyl, hexyl, cyclohexyl, octyl, and iso-octyl.

## POLY 384: Aliphatic polycarbonates based on carbon dioxide, furfuryl glycidyl ether, and glycidyl methyl ether: Reversible functionalization and crosslinking

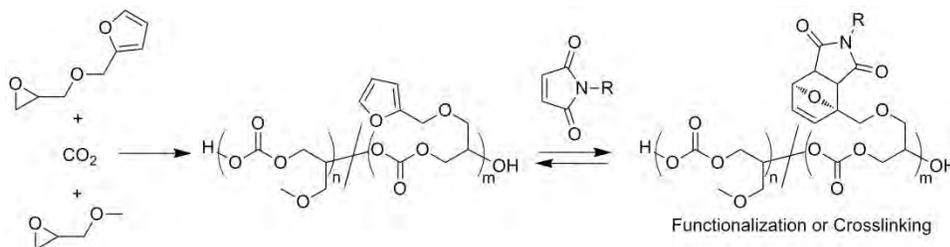
**Markus Scharfenberg**, *scharfen@students.uni-mainz.de*, Holger Frey, Johannes Gutenberg University, Mainz, Germany

Carbon dioxide (CO<sub>2</sub>) is an attractive carbon source for materials synthesis with respect to resource utilization, as it is nontoxic, renewable, and readily available in large quantities and high purity. In combination with tailored epoxides, multifunctional polymers can be synthesized. Usually, propylene oxide or cyclohexene oxide have been used for the synthesis of novel aliphatic polycarbonates (APCs). The resulting materials are promising for a variety of applications, such as ceramic binders, adhesives, coatings, and packaging materials as well as for biomedical functions, since they are biodegradable into nontoxic compounds.<sup>[1]</sup> Increasing demand for more versatile biomaterials has also revived the interest in APCs for biomedical purposes, for which their degradability, low glass transition temperature, and elasticity of APCs, previously perceived as their major drawbacks, may turn into advantages.

We have synthesized novel aliphatic multifunctional polycarbonates, as random copolymer, via terpolymerization of furfuryl glycidyl ether (FGE), glycidyl methyl ether (GME) and carbon dioxide in a facile one-step, solvent-free synthesis. Polymers with 26%–100% FGE content and molecular weights between 2300 and 4100 g mol<sup>-1</sup> were obtained under mild reaction conditions. They were characterized by FT-IR, NMR, SEC and DSC. The polycarbonate copolymers were functionalized and crosslinked reversibly with a variety of different tailored maleimide derivatives using a convenient [4+2] cycloaddition transformation. DSC measurements revealed the thermal properties of the crosslinked systems and required the temperature for de-crosslinking via retro-Diels-Alder reaction.<sup>[2]</sup>

[1] Zhu, K. J.; Hendren, R. W.; Jensen, K.; Pitt, C. G., *Macromolecules*, 1991, 24, 1736.

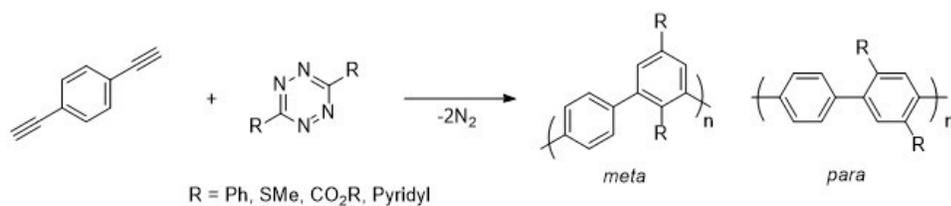
[2] Hilf, J; Scharfenberg, M.; Poon, J.; Moers, C.; Frey, H., *Macromol Rapid Comm*, 2015, 36, (2), 174.



## POLY 385: Polybiphenylenes by cycloaddition co-polymerization of 1,2,4,5-tetrazines with 1,4-diethynylbenzene

**Robb E. Bagge**<sup>3</sup>, [rbagge@email.arizona.edu](mailto:rbagge@email.arizona.edu), Dylan Boday<sup>1</sup>, Douglas A. Loy<sup>2</sup>. (1) IBM, Tucson, Arizona, United States (2) Materials Science and Engineering, The University of Arizona, Tucson, Arizona, United States (3) Chemistry, University of Arizona, Tucson, Arizona, United States

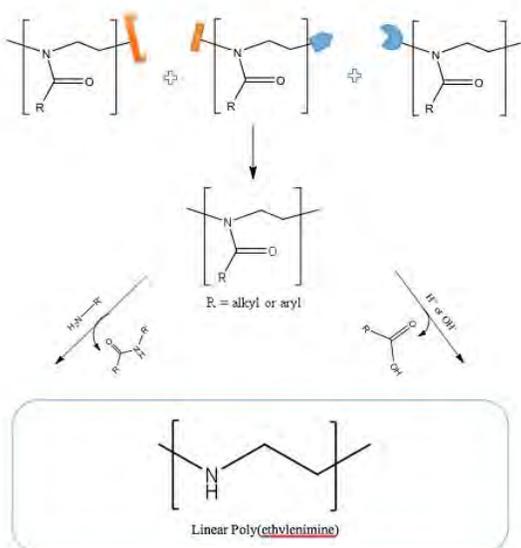
One widely used method for preparing high substituted polyphenylenes is through cycloaddition copolymerizations of 1,4-diethynylbenzene with highly phenylated bis-cyclopentadienones. Due to the reactivity of the cyclopentadienone, only highly phenylated polyphenylenes can be prepared by this approach. Here we would like to report a new cycloaddition copolymerization based on 3,6-disubstituted-1,2,4,5-tetrazines with diethynylbenzene that permits polybiphenylenes with only two substituents per repeat unit to be prepared. These reactions are performed at 140 °C in dimethylacetamide under argon in 24 hours. The tetrazine reacts with the first ethyne in a [4+2] cycloaddition reaction, followed by cheletropic elimination of nitrogen to afford an ethynylphenyl substituted pyridazine. The pyridazine group then reacts with a second ethynyl group by a [4+2] cycloaddition followed by cheletropic elimination of a second equivalent of nitrogen. Monomers with pyridyl, and chloro substituents have been successfully polymerized. Details of the polymers preparation and characterization will be presented.



## POLY 386: Linear poly(ethylenimine) synthesis: Traditional and innovative approaches

**Benjamin Zarin**<sup>1</sup>, [ben@polychemistry.com](mailto:ben@polychemistry.com), **Bernard Gordon III**<sup>2</sup>, **Laura Stratton**<sup>3</sup>. (1) *Polymer Chemistry Innovations Inc., Tucson, Arizona, United States* (3) *Poly Chemistry, Tucson, Arizona, United States*

One of the most typical routes for obtaining poly(ethyleneimine) involves the ring opening polymerization of aziridine, however, the resulting polymer is highly branched with the presence of primary, secondary, and tertiary amino groups. In contrast, linear poly(ethyleneimine), LPEI, can be conveniently obtained by the hydrolysis of poly(2-alkyl-2-oxazoline) precursors. The poly(2-alkyl-2-oxazolines) are attractive starting materials due to their thermal stability, overall linear structure, low poly dispersity, and the ability to synthesize these over a wide range of molecular weights. LPEI synthesis is investigated from several routes including evaluating traditional methods used, and via non-traditional routes such as click-like reactions or transamidation of varying precursors. The most commonly used precursor from this class of polymers is poly(2-ethyl-2-oxazoline), Aquazol<sup>®</sup>, due to its commercial availability and high water solubility. The kinetics of this process are well-defined such that the degree of hydrolysis can be tailored for specific applications. The fully hydrolyzed product is crystalline and water-insoluble, whereas the partially hydrolyzed product is readily soluble in methanol. An example where partial hydrolysis is desired would be when LPEI is used for transfection into mammalian cells, where it is preferred that the polymer be left with 10-12% of the poly(2-ethyl-2-oxazoline) precursor. Despite the convenience of using commercial precursors, limitations exist in terms of the maximum molecular weights obtained after hydrolysis, due to known long-chain branching of Aquazol<sup>®</sup> at high M/I ratios. To combat this undesirable branching, poly(2-phenyl-2-oxazoline) can be used as an alternative precursor where long-chain branching is not apparent presumably due to the bulk and electron donating ability of the phenyl moiety, minimizing side reactions that promote branching.



## **POLY 387: Photochemical stability of Various RAFT agents and their uses in the polymerization of *N*-vinylpyrrolidone**

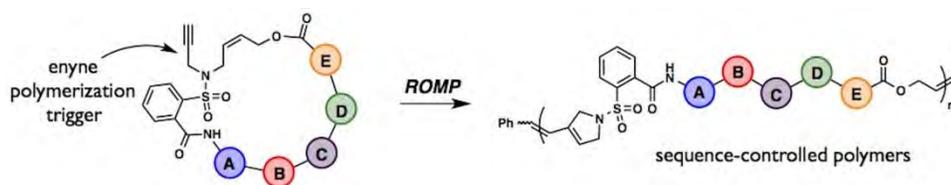
**Joon Hee Cho**, *harrycho90@gmail.com*, *Young-Je Kwark*. Dept Organic Materials and Fiber Engineering, Soongsil University, Seoul, Korea (the Republic of)

Poly(*N*-vinylpyrrolidone) (PVP) is widely used in pharmaceutical, medical, and cosmetic applications due to its solubility in water, good biocompatibility, and low toxicity. PVP can be generally obtained by free radical polymerization (FRP) of *N*-vinylpyrrolidone (VP). Even though, there are several controlled FRP, such as atom transfer radical polymerization (ATRP), nitroxide-mediated polymerization (NMP), and reversible addition-fragmentation chain transfer process (RAFT), controlling molecular weight (MW) and its distribution (MWD) of non-conjugated monomer, such as VP, are relatively difficult. In this work, we used photo-initiated RAFT process to synthesis PVP with controlled MW and MWD. To achieve successful photo-initiated RAFT process, it is required to use photo-chemically stable chain transfer agent (CTA), along with additional photoinitiator, BAPO. On testing various xanthate CTA for thermal RAFT of VP, methyl (ethoxycarbonothioyl)sulfanyl propionate (MESP) was identified as an effective RAFT agent for the polymerization of VP. However, when photo-initiation process was applied, the polymerization system loses its control to give high polydispersity index. The reason of the poor control was turned out to be the decomposition of MESP under the conditions of UV irradiation. A set-up of varying UV energy was developed by using LEDs with different wavelength to prevent the decomposition of MESP. Detailed results about the photo-chemical stability of various CTA under different UV wavelength and photo-initiated RAFT process of VP under the conditions will be discussed.

## POLY 388: General strategy for sequence-controlled polymerization using macrocyclic ROMP

**Will Gutekunst**, *willgute@ucsb.edu*, **Craig J. Hawker**, *University of California Santa Barbara, Santa Barbara, California, United States*

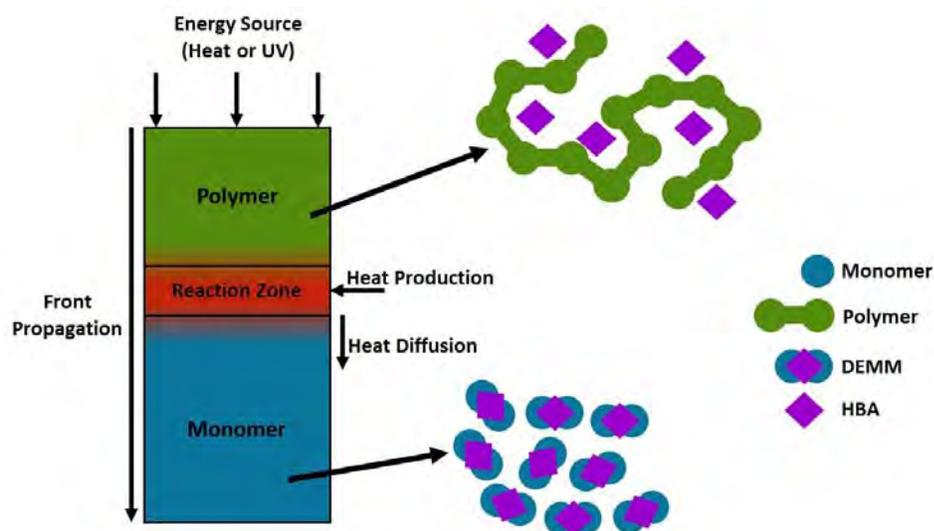
Biopolymers, such as proteins and DNA, demonstrate how a defined polymer sequence can lead to exquisite functions such as catalysis, molecular recognition, and data storage. Likewise, control of primary structure has far reaching possibilities for the future of synthetic polymers, but methodologies for their preparation remain limited. In this poster, a general strategy for the synthesis of sequence-defined polymers is detailed that uses relay metathesis to promote the ring-opening polymerization of unstrained macrocycles. The short, scalable and practical synthesis of a small molecule polymerization trigger allows for facile sequence incorporation and enables the controlled, unidirectional polymerization of the macrocyclic monomers. Using this system, a diverse range of functionality can be incorporated into the polymer backbone with high levels of control over molecular weight and molecular weight distribution.



## POLY 389: Free-radical frontal polymerization properties of vinylic monomers in deep eutectic monomer mixtures

**Kylee F. Fazende**, *kfazenz2@lsu.edu*, John A. Pojman. *Chemistry, Louisiana State University, Baton Rouge, Louisiana, United States*

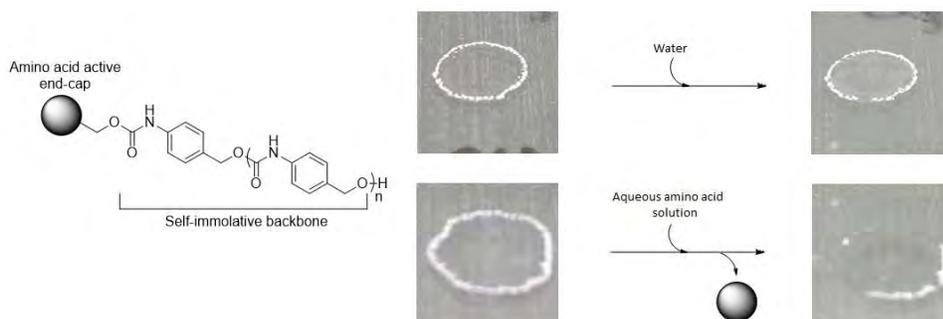
The free-radical frontal polymerization properties of vinylic acids were examined when the acids were used as the hydrogen bond donor (HBD) for a deep eutectic monomer mixture (DEMM). The presence of the hydrogen bond acceptor (HBA) for the DEMM seemed to change the frontal polymerization properties of the monomer and was therefore replaced with a variety of inert materials to determine if this was the case. Decreased front temperature and increased front velocity were seen with the DEMM systems but not with any inert materials. Acrylamide-acid comonomer DEMMs were also prepared to examine the ability of copolymers to form during frontal polymerization of DEMMs as well as the ability to decrease initiator concentration without a loss in front velocity.



## POLY 390: Synthesis of self-immolative coatings responsive to an aqueous amino acid solution

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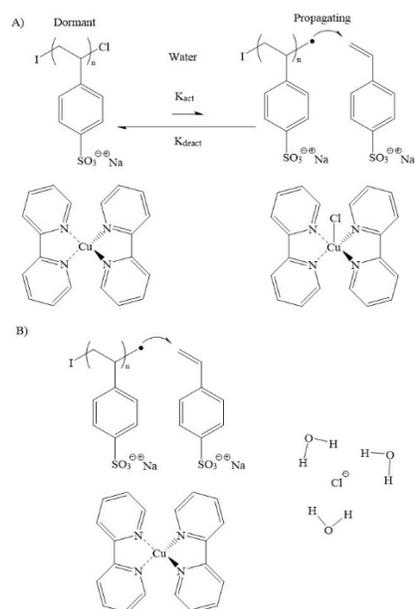
There are many applications that require the use of temporary coatings that can be safely and easily removed. Unfortunately, coatings and polishes are generally created to be permanent, meaning their removal often requires the use of harsh chemicals or solvents. An ideal coating would need to retain these long-lasting properties, while being easy and safe to remove. I propose creating easily removable polishes and coatings using self-immolative (SI) polyurethane materials with a novel amino acid activated trigger. SI polymers are kinetically stable materials that degrade into individual monomer components upon the activation and release of a trigger molecule. Their unique ability to amplify a signal by releasing multiple reporters per activation event has stimulated interest in their use. Since SI polymers only require a catalytic amount of stimulus to initiate degradation, their use would require significantly shorter exposure times for removal. Using an aqueous amino acid solution to remove coatings may provide a less harmful alternative to the organic solvents currently used.



## POLY 391: Sprinkle of salt to aid the synthesis of sodium polystyrene sulfonate via atom transfer radical polymerization

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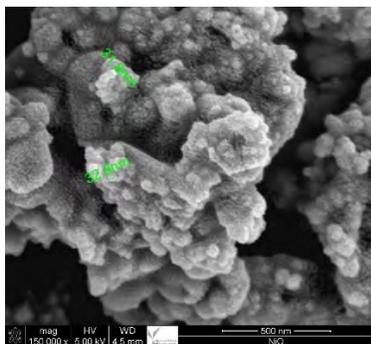
The role of salt in the synthesis of sodium polystyrene sulfonate (NaPSS) via atom transfer radical polymerization (ATRP) was investigated through gel permeation chromatography coupled with multiple-angle light scattering (GPC/MALS), differential refractometry and NMR. It is proposed that the CuCl complex becomes hydrolyzed in an aqueous reaction which renders the activation/deactivation mechanism central to ATRP ineffective. This could be due to inability of Cl<sup>-</sup> to reversibly bind with the Cu complex as the Cl<sup>-</sup> are dissociated in solution. NaCl provides Cl<sup>-</sup> ions for the reaction and furthermore the ratio of NaCl added to CuCl was found to effect molecular weight, PDI and reaction kinetics. Less added salt and therefore a lower [NaCl]/[CuCl] value resulted in a broader molecular weight distribution range. Increasing the [NaCl]/[CuCl] composition narrowed the molecular weight range but also reduced the molecular weight of the final NaPSS polymer for reactions conducted on the same time scales. This finding suggests that increasing the [NaCl]/[CuCl] ratio slows reaction kinetics, quite possibly due to the polymerization favouring the radical deactivated step as excess Cl<sup>-</sup> ions are available to cap the propagating chain. The realization of high molecular weight, up to 900 000 g/mol, and a polydispersity index (PDI) as low as 1.02 indicate the efficacy of adding salt to this synthetic approach of NaPSS. dn/dc values of NaPSS at 488 nm were found to decrease from 0.197 mL/g with no added NaCl to 0.171 mL/g at a [NaCl]/[CuCl] ratio of 100. Values of dn/dc at 488 nm at a fixed [NaCl]/[CuCl] value of 10 increased from 0.185 mL/g to 0.198 mL/g as the reaction time was extended from 0.5 to 96 hrs respectively. Three broad peaks at chemical shifts of approximately 7.5, 6.5 and 1.3 ppm were determined by H NMR and are consistent with the proton environment of NaPSS.



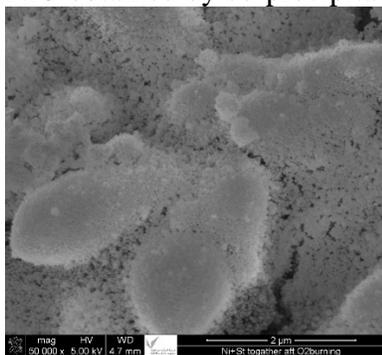
## POLY 392: Synthesis, characterization, and use of mesoporous polymer as hard template for the fabrication of spherical nickel oxide nanoparticles

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Mesoporous polymers are useful materials for the synthesis of hierarchically porous, shape-controlled metal oxide nanoparticles, which have numerous applications in catalysis, optoelectronics, magnetism, and many others. In this context, we have utilized emulsion technique using cetyltrimethylammonium bromide (CTAB) as a surfactant for synthesizing polystyrene nanospheres (PSNS, 46-75 nm), which found to have a specific surface area of 93.14 m<sup>2</sup>/g and average pore size of 129.34 Å. The fabricated PSNS was then used as a hard template for the co-precipitation of nickel hydroxide with PSNS. Another alternative route is to incorporate nickel(II) ions within PS beads by the addition of nickel nitrate in the emulsion medium. Nickel oxide was obtained by calcination of the nickel/polymer containing materials under air at 500°C for three hours. Both methods resulted in mesoporous, size-controlled nickel oxide nanospheres. Nickel oxide, obtained by inclusion of nickel during polymerization, had a specific surface area as ~1.5 as that of the nickel oxide, obtained by co-precipitation method.



NiO obtained by co-precipitation of nickel hydroxide with polystyrene nanospheres



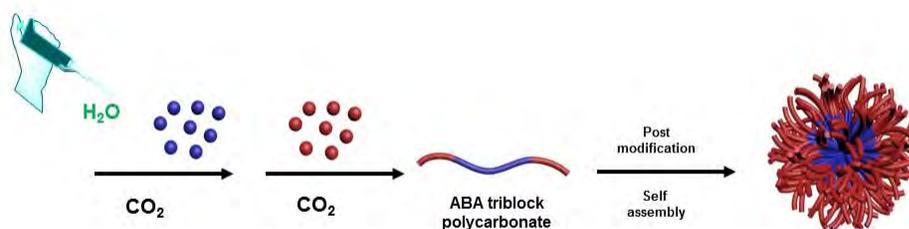
NiO obtained by inclusion of nickel in the emulsion medium during polymerization of styrene monomer

## POLY 393: Construction of Versatile and Functional Nanostructures Derived from CO<sub>2</sub>-based Polycarbonates

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Using the abundant, nontoxic and inexpensive CO<sub>2</sub> as a renewable C1 feedstock, the coupling of CO<sub>2</sub> and epoxides provides an attractive way for preparing polycarbonates and has been commercialized in recent years. The hydrophobic nature and lack of functionalities of the commonly studied CO<sub>2</sub>-based polycarbonates however, have prevented their use in functional materials, especially for biomedical applications. In order to expand the use of CO<sub>2</sub>-based polycarbonates towards improved material performances, it is necessary to synthesize more diverse CO<sub>2</sub>-based polymers with functionalities.

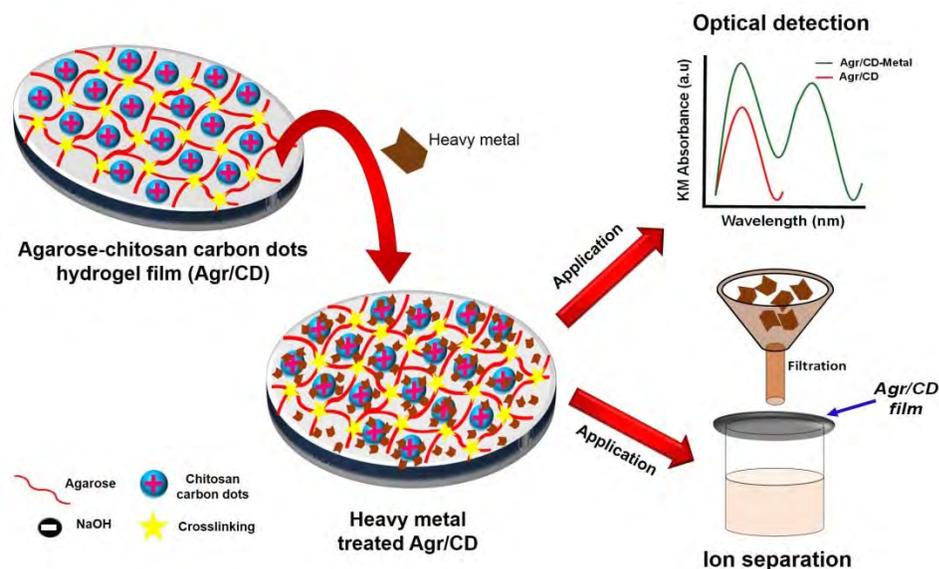
In this work, we demonstrate the facile preparation of diverse and functional nanoparticles derived from CO<sub>2</sub>-based triblock polycarbonates system. By judicious use of water as chain-transfer reagent in the propylene oxide/CO<sub>2</sub> polymerization, PPC diols are successfully produced and serve as a macroinitiator in the subsequent allyl glycidyl ether/CO<sub>2</sub> coupling reaction. The resulting ABA triblock polycarbonate can be further functionalized with various thiols by radical mediated thiol-ene click chemistry. The functionalized triblock polycarbonates readily form spherical nanoparticles with different charges upon suspension in DI water. This class of amphiphilic polycarbonates could provide a powerful platform for biomedical applications.



## POLY 394: Carbon dots rooted agarose hydrogel hybrid platform for optical detection and separation of heavy metal ions

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A robust solid sensing platform for an on-site operational and accurate detection of heavy metal is still a challenge. We introduce chitosan based carbon dots rooted agarose hydrogel film as a hybrid solid sensing platform for detection of heavy metal ions. The fabrication of the solid sensing platform is centred on simple electrostatic interaction between  $\text{NH}_3^+$  group present in carbon dots and  $\text{OH}^-$  groups present in agarose. Simply on dipping the hydrogel film strip into heavy metal ion solution, in particular  $\text{Cr}^{6+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$  the strip displays color change, viz.,  $\text{Cr}^{6+}$ →yellow,  $\text{Cu}^{2+}$ →blue,  $\text{Fe}^{3+}$ →brown,  $\text{Pb}^{2+}$ →white,  $\text{Mn}^{2+}$ →tan brown. The optical detection limit of the respective metal ion is found to be 1 pM for  $\text{Cr}^{6+}$ , 0.5  $\mu\text{M}$  for  $\text{Cu}^{2+}$  and 0.5 nM for  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$  by studying the changes in UV-visible reflectance spectrum of the hydrogel film. Moreover, the hydrogel film finds applicability as an efficient filtration membrane for separation of these quintet heavy metal ions. The strategic fundamental feature of this sensing platform is the successful capability of chitosan to form colored chelates with transition metals. This proficient hybrid hydrogel solid sensing platform is thus the most suitable to employ as an on-site operational, portable, cheap colorimetric-optical detector of heavy metal ion with potential skill in their separation. Detailing of the possible mechanistic insight into the colorimetric detection and ion separation is also discussed.



The pictorial representation of agarose/CD (Agr/CD) hydrogel film and its applicability as optical sensor and filtration membrane for separation of quintet heavy metal ions  $\text{Cr}^{6+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$ .

## POLY 395: Synthesis and characterization of hard and soft nanocomposites derived from $\beta$ -cyclodextrin ( $\beta$ -CD) and hyperbranched polyglycerol (HPG) templates

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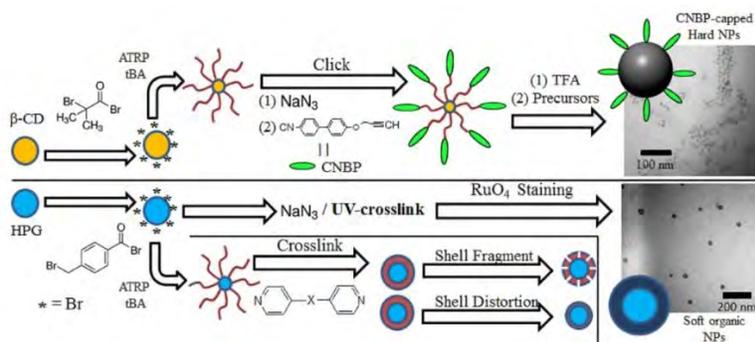
Beta cyclodextrin ( $\beta$ -CD) and Hyperbranched polyglycerols (HPG) possess several abilities which motivate their use in functional hard and soft polymeric nanocomposite fabrication in an analogous fashion to the tedious synthesis of dendrimers. Both  $\beta$ -CD and HPG contain surface hydroxyl groups which can be functionalized to serve as sites for crosslinking, atom transfer radical polymerization (ATRP) initiation and click-reactions.

The goal of this work is to use both starting materials to produce novel and functional hard and soft nanomaterials. In the first project, a pro-mesogenic (liquid crystal-like) molecule is attached to a  $\beta$ -CD block copolymer via click chemistry to produce a 21-arm star-like poly(acrylic acid)-4-isocyano-4'-(prop-2-yn-1-yloxy)biphenyl polymer (21- $\beta$ -CD-CNBP). This material can be used as an additive in LC mixtures and act as a nanoreactor for making pro-mesogen-capped nanoparticles. These particles have the potential for improved solubility in liquid crystals and offer a novel route to multi-responsive liquid crystal materials [1].

In the second project, monodisperse ( $PDI < 1.4$ ) samples of HPG are synthesized by ring-opening multi-branching polymerization (ROMBP) yielding samples with 83, 126 and 170 reactive  $-OH$  sites per molecule. In the first study, HPG is crosslinked with passive and active materials (disulfide and azo groups) to produce soft, biocompatible, nanoparticles with diameters ranging from 50 to 150 nanometers. The first iteration is a novel photo-crosslinked organic nanoparticle based on HPG-4-bromomethyl benzoyl bromide using UV-induced crosslinking.

In the second study, HPG is converted into an ATRP macroinitiator and used to produce diblock and triblock star-like copolymers (HPG-b-PAA-b-PS-Br and HPG-b-PS-b-PAA-b-PS-Br) that will serve as templates for the nucleation of inorganic nanoparticles. Both projects offer routes to producing hard and soft nanocomposites that possess a high degree and variety of surface functionality. With applications from medicine to energy, star-like nanocomposites offer a starting point for many end-uses on an industrial scale and at low costs.

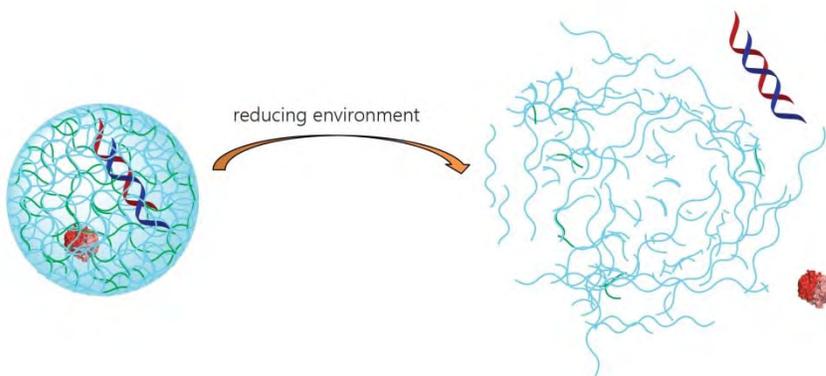
1. Icozzia, J., et al. *RSC Advances*, 2014, 4, 50212-50219.



## POLY 396: Redox responsive nanogels for hydrophilics delivery

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We propose a redox responsive polymeric nanoparticle platform for biologics delivery. These stimuli responsive nanoparticles were synthesized using inverse emulsion methodology using a redox responsive polymeric crosslinker. Polymeric nanogels were synthesized In situ while sequestering biologic cargo such as plasmid DNA, siRNA, m RNA and proteins with high efficiency. The size of these nanoparticles are in the range of 100-200 nm and are non-toxic to the mammalian cell lines. Upon application of stimuli, the size of these particles decrease drastically as tested from dynamic light scattering experiments and also release the entrapped biologics confirmed through gel electrophoresis experiments. These evidences show complete disassembly of the nano aggregates upon application of redox trigger. These particles also possess surface functionalization feature which will be helpful in conjugation of ligands specific for cell surface receptors of interest. The cell uptake study of these nanoparticles was tested using confocal microscopy and the cells show good uptake of these nanoparticles into the cytosol.

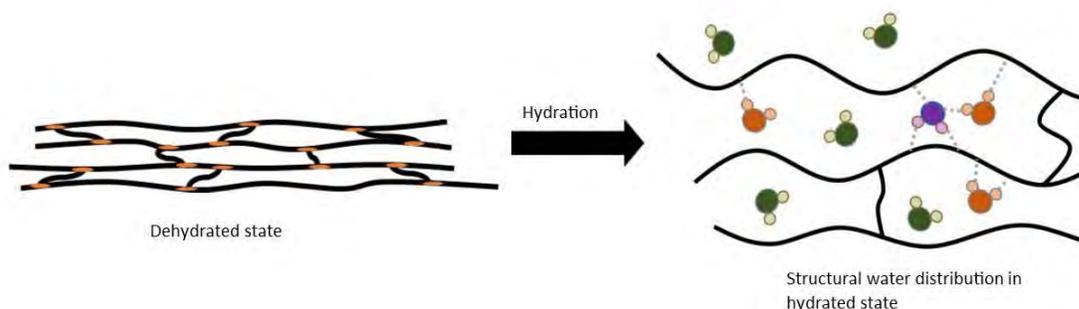


Pictorial representation of redox responsive nanogels for encapsulation and stimuli responsive release of biologics

## POLY 397: Synthesis of stereospecific glycopolymer hydrogel networks for the determination of the effects of network architecture on water content and structure

**April Fogel**, *april.fogel@eagles.usm.edu*, Sarah E. Morgan. School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, Mississippi, United States

Hydrogels are capable of absorbing many times their weight in water but are insoluble in water due to the crosslinked nature, making them ideal materials for use in biomedical applications such as drug delivery systems. Water within hydrogel networks play a pivotal role in dictating network properties such as mechanical stability, permeability, and network architecture. Three discrete states of water (bound, restricted, and free) exist within hydrogel networks, which are described by the degree of hydrogen bonding that occurs between molecular water and the network. As shown in the schematic, bound water is tightly held to the network often undergoing 3 to 4 modes of hydrogen bonding, restricted water is loosely held undergoing 1 to 2 modes of hydrogen bonding and free water is unassociated with the network. The purpose of this study is to gain a fundamental understanding of the influence of structural parameters on water uptake and morphology for acrylamide based glycopolymer hydrogels containing stereospecific glucose and galactose pendant moieties, synthesized via UV initiated free radical polymerization. A fractional factorial experimental design was utilized to systematically elucidate the influence of monomer concentration, crosslinker to monomer ratio, UV exposure time, and solvent system on water uptake and structure characterized via thermogravimetric analysis, TGA, and DSC.



## POLY 398: Mesoporous polymers by selective swelling of block copolymers with different alcohols

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Swelling of block copolymers by selective solvents has emerged as a simple and efficient process to produce nanoporous materials with well-controlled porosities. It has been demonstrated that a number of parameters including the compositions of the copolymers, the swelling temperatures and durations strongly influence the swelling behaviors and consequently the porous morphologies of the copolymers. However, it remains unclear on the role of the swelling agents in this selective swelling-induced pore generation. Here we investigate the evolution of morphology, thickness, and surface chemistry of thin films of polystyrene-block-poly (2-vinyl pyridine) (PS-*b*-P2VP) soaked in a series of alcohols with changing carbon atoms and hydroxyl groups in their molecules. It is found that, in addition to a strong affinity to the dispersed P2VP microdomains, the swelling agents should also have a moderate swelling effect to PS to allow an appropriate plastic deformation of the PS matrix. Scanning electron microscopy demonstrates that monohydric alcohols with longer aliphatic chains exhibit larger ability to induce the pore formation, and ellipsometry reveals that a remarkable increase in film thickness is associated with the pore formation. High-carbon alcohols including *n*-propanol, *n*-butanol, and *n*-hexanol provide strong ability to induce the pore formation and produce cylindrical micelles upon prolonged exposure for their strong affinity toward the PS matrix. In contrast, methanol and polyhydric alcohols including glycol and glycerol show very limited effect to swell the copolymer films as their affinity to the PS matrix is low; however, characterizations by water contact angles and x-ray photoelectron spectroscopy reveal that they evidently induce the surface segregation of P2VP blocks for the rich presence of hydroxyl groups in their molecules and consequently highest possibility to form hydrogen bonds with P2VP blocks.

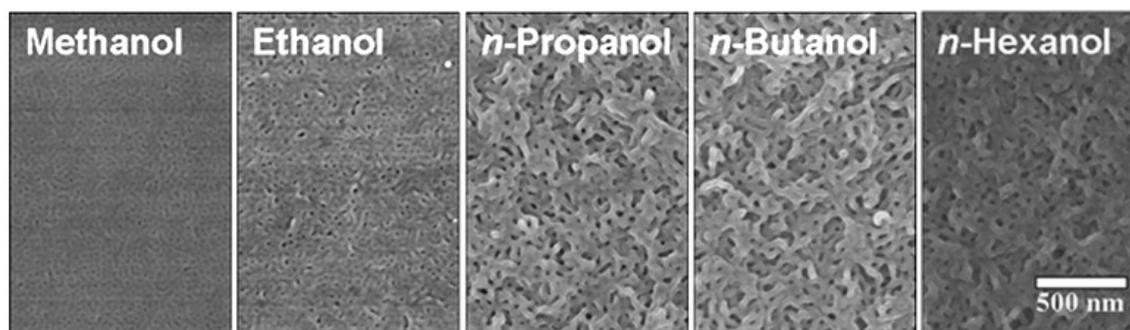
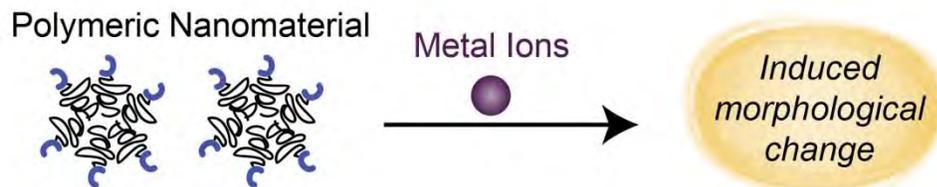


Figure 1. The surface morphologies of S2VP films after swelling treatment in various alcohols.

## POLY 399: Bioinspired control of polymer self-assembly via ligand-metal ion interactions

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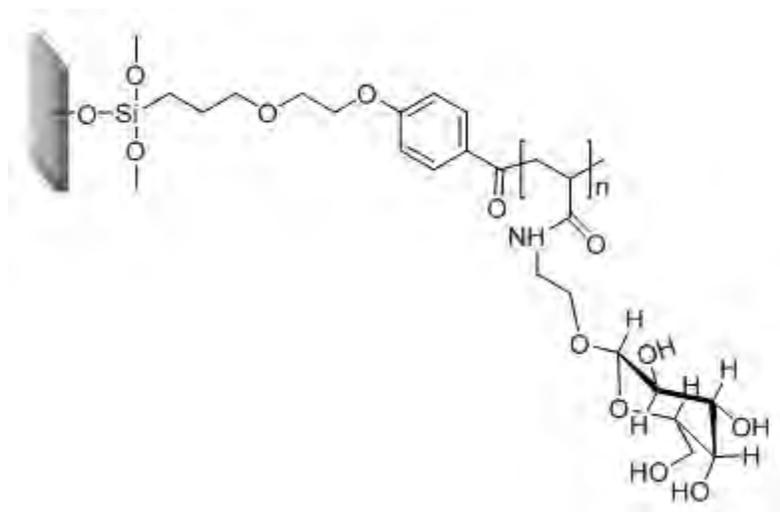
Nature has created a vast array of responsive polymeric architectures for structural (i.e. collagen and microtubules) and functional applications (i.e. enzymes and DNA). Researchers, however, have just begun to develop responsive synthetic systems with similar capabilities. In order to create more of these systems, techniques are required to create responses to a wide range of chemical and physical stimuli. We are working towards developing a new technique to achieve morphological control of synthetic systems, specifically using specific ligand-metal ion interactions to modulate the assembly of novel nanomaterials with biological applications.



## POLY 400: Synthesis of stereospecific glycopolymers as models to mimic amyloid- $\beta$ peptide/saccharide interactions

**Pradipta K. Das**<sup>1</sup>, Pradipta.Das@eagles.usm.edu, Wei Guo<sup>2</sup>, Vijay Rangachari<sup>4</sup>, Derek L. Patton<sup>3</sup>, Sarah E. Morgan<sup>5</sup>. (1) Polymer Science, The University of Southern Mississippi, Hattiesburg, Mississippi, United States (2) School of Polymers and High Performance Mater, The University of Southern Mississippi, Hattiesburg, Mississippi, United States (3) Campus Box #10076, University of Southern Mississippi, Hattiesburg, Mississippi, United States (4) Dept of Chemistry Biochemistry, University of Southern Mississippi, Hattiesburg, Mississippi, United States (5) School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, Mississippi, United States

The process of aggregation and subsequent deposition of the peptide amyloid- $\beta$  (A $\beta$ ) on neuronal membranes, which causes disruption of the normal neuronal functions, is generally accepted to be one of the fundamental causes of Alzheimer's disease (AD). The factors responsible for A $\beta$  aggregation and the mechanism of aggregation are not yet fully understood. Among other factors, ganglioside GM1 is believed to act as a modulator which promotes the aggregation of A $\beta$ . However, the role of the individual saccharides of GM1 ganglioside in A $\beta$  aggregation is not known. In the current research, acrylamide based glycomonomers with either glucose or galactose pendant groups were synthesized, maintaining the stereochemistry of the saccharides in GM1. The monomers were characterized via <sup>1</sup>H-NMR and ESI. Stereospecific glycopolymers were synthesized in solution via aqueous reversible addition-fragmentation chain transfer polymerization (RAFT) and glycopolymer brushes were synthesized on the surfaces of silicon wafers via UV-initiated free radical polymerization. Glycopolymers synthesized in solution and on surfaces will be utilized as models to mimic A $\beta$ /GM1 saccharide interactions in the neuronal membranes.



**POLY 401: Synthesis and characterization of nanohydrogels prepared by gamma irradiation of thermosensitive micelles of poly(*N*-vinyl caprolactam)-*b*-poly(hexyl acrylate)**

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Micelles with anfifilic characteristics have been widely research over the past few years due to their possible applications as drug carriers. *N*-Vinylcaprolactam has been long study because its biocompatible material approve by the FDA, making it ideal for applications as biomaterials. In this work we have synthesized micelles with anfifilic characteristics of block copolymers of poly (*N*-Vynilcaprolactam-*b*-hexile acrylate) in water dispersion, block copolymers were polymerize by RAFT polymerization, getting controlled molecular weight and polydispersity, polymers were characterized by dynamic light scattering. Micelles were formed by dispersion in water; right conditions of micellization were obtained. The results obtained demonstrated that anfifilic micelles of block copolymers poly (*N*-Vynilcaprolactam-*b*-hexile acrylate) can be prepared via RAFT polymerization obtaining good molecular weight control while having low polydispersity, these micelles prove to be pH and temperature responsive. These results suggest that these micelles can have a potential use as drug carriers.

## POLY 402: Accelerated degradation of hydrogen peroxide sensitive polymeric nanoparticles by releasing of acid and reducing their local pH

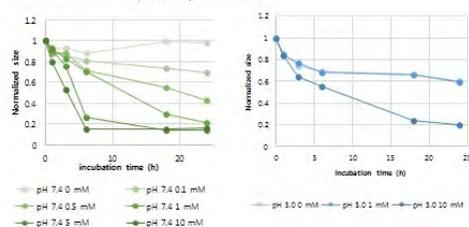
**Sangeun Lee**<sup>1</sup>, *mirukoo86@gmail.com*, **Alexandra Stubelius**<sup>4</sup>, **Jason Olejniczak**<sup>2</sup>, **Adah Almutairi**<sup>3</sup>. (1) University California, San Diego, San Diego, California, United States (2) University of California San Diego, San Diego, California, United States (3) Pharmaceutical Sciences MC 0600, University of California San Diego, La Jolla, California, United States (4) Skaggs School of Pharmacy and Pharmaceutical Sciences, University of California, San Diego, San Diego, California, United States

Previously, we reported a polymer which is degrading by UV light. The mechanism behind the polymer is that the ortho-nitrobenzyl group in the polymer is removed by UV irradiation, and then releasing acid. This released acid is supposed to attack the acid sensitively cleavable group in the polymer backbone. This sophisticatedly designed polymer, however, has a limitation for biomedical application because of the trigger source, UV. In here, we report another polymer which has same degradation strategy but which utilize hydrogen peroxide ( $H_2O_2$ ) as a trigger.

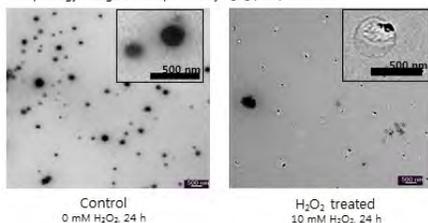
Hydrogen peroxide is one of the reactive oxygen species (ROS) which is over expressed in neurodegenerative disease, chronic obstructive pulmonary disease (COPD), arthritis, cancer, and inflammation. Thus, it is one of the widely used source as an internal stimuli for stimuli responsive biomaterials. Therefore, pinacol boronic ester group, sensitively and quantitatively reactive group with  $H_2O_2$ , was introduced into the polymer in this study.

Designed polymer was successfully synthesized and degradation of the polymer by  $H_2O_2$  was examined using size exclusion chromatography (SEC). The prepared polymer was degraded by  $H_2O_2$  as expected and formulated into nanoparticle through nanoprecipitation method. Size of the formulated nanoparticle was ~200 nm, and it was observed by DLS and TEM that the size of nanoparticle was decreased by  $H_2O_2$  treatment (figure). To evaluate the nanoparticle for drug delivery application, dye (IR 780) was encapsulated and release of it was estimated. As a result, the dye loaded nanoparticle was releasing their encapsulates by stimulus and its degradation. The particle was more evaluated for biological application.

### • Size decrease of nanoparticle by stimulus (DLS)



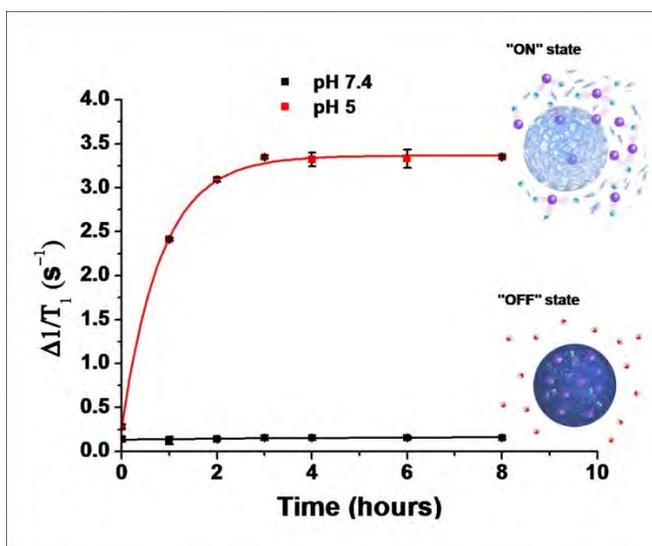
### • Morphology change of nanoparticle by $H_2O_2$ (TEM)



## POLY 403: Highly sensitive activatable polymeric nanoparticles for magnetic resonance imaging diagnostic

**Alexandra Foucault-Collet**<sup>3</sup>, acollet@ucsd.edu, Mathieu Viger<sup>4</sup>, Noah J. Johnson<sup>3</sup>, Sha HE<sup>5</sup>, Guillaume Collet<sup>2</sup>, Adah Almutairi<sup>1</sup>. (1) Pharmaceutical Sciences MC 0600, University of California San Diego, La Jolla, California, United States (2) Skaggs School of Pharmacy and Pharmaceutical Sciences, University of California San Diego, La Jolla, California, United States (3) a. Skaggs School of Pharmacy and Pharmaceutical Sciences, University of California San Diego, La Jolla, California, United States (4) a. Skaggs School of Pharmacy and Pharmaceutical Sciences, University of California San Diego, San Diego, California, United States (5) Nanoengineering Department, UC San Diego, San Diego, California, United States

Most clinically used magnetic resonance imaging (MRI) contrast agents have been developed and used to enhance the signal from water protons in close proximity. However, these contrast agents (e.g. gadolinium (Gd) chelates) being active all the time (always "ON") can only distinguish pathological from healthy tissue by degree of accumulation, which limits sensitivity for diagnostic. In order to maximize signal to noise ratio, we designed highly sensitive activatable MRI probes that will activate only in pathological microenvironment (e.g., acidic pH). Our strategy involves suppressing the MRI signal of Gd-based contrast agents by encapsulating them in bioresponsive and hydrophobic polymeric nanoparticles (NPs). Encapsulation limits water availability and hence their relaxation enhancement capabilities. Polymer degradation, in response to biochemical cues of disease, activates the silenced MRI probes by releasing them from the particle, allowing greater interaction with water protons and faster relaxation. This concept was successfully applied to NaGdF<sub>4</sub> nanocrystals (4 nm diameter) containing a very high fraction of superficial Gd atoms, which strongly influences the longitudinal relaxation of neighboring water protons. Upon acid-triggered release of the quenched NaGdF<sub>4</sub>, T<sub>1</sub> relaxation rate increased as much as 200 times. If designed for tumor recognition, this strategy could be beneficial in cancer or cardiovascular diseases diagnostic and could significantly increase the sensitivity and specificity of detection.



## POLY 404: Detecting inflammation *in vivo* using NIR activatable fluorescence imaging

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Conventional fluorescence imaging strategies rely on imaging agents that are “always on”, emitting constant signal regardless of their proximity or interaction with target tissues, cells, or markers of disease. As a result, the large volume of nonspecific signal makes the tissue or anatomical feature of interest more difficult to distinguish. Optical contrast agents whose fluorescence properties may be switched from OFF to ON in response to specific biological stimuli could minimize background signal and thus improve sensitivity and specificity.

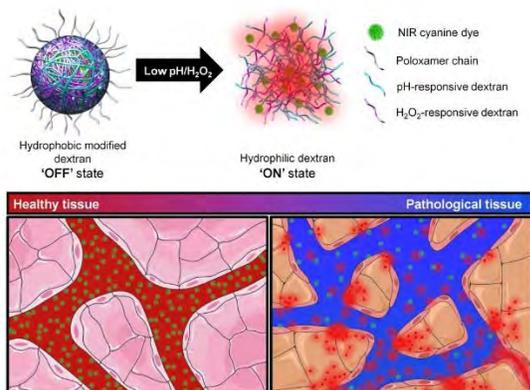
Herein, we report the development of an activatable fluorescence imaging agent capable of detecting hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and acidic microenvironments, two important biomarkers shared by numerous diseases and inflammatory conditions (e.g. tumors, rheumatoid arthritis, atherosclerosis).

This imaging agent consists of H<sub>2</sub>O<sub>2</sub>- and acid-responsive polymeric particles packed with a high concentration of near infrared (NIR) dyes. The close proximity of the dye molecules quenches their fluorescence, thus creating an “off-state”

The signal of this agent is “turned on” through the cleavage of protecting moieties on the polymer backbones upon exposure to either H<sub>2</sub>O<sub>2</sub> or acidic pH, which reveals hydroxyl groups and thus increases the material’s hydrophilicity. Upon this solubility switch, dye molecules diffuse out of the polymer matrix, relieving the particle from intense fluorescence quenching (“on-state”).

We have demonstrated the activation of our agent in three *in vivo* models: serum transfer-induced arthritis, carrageenan-induced paw inflammation, and breast tumor. In all three mouse models, regions of inflammation exhibit a unique fluorescence signal amplification mechanism, which enable detection of inflamed areas with target-to-background ratios reaching as high as 22, only 3 h post-injection.

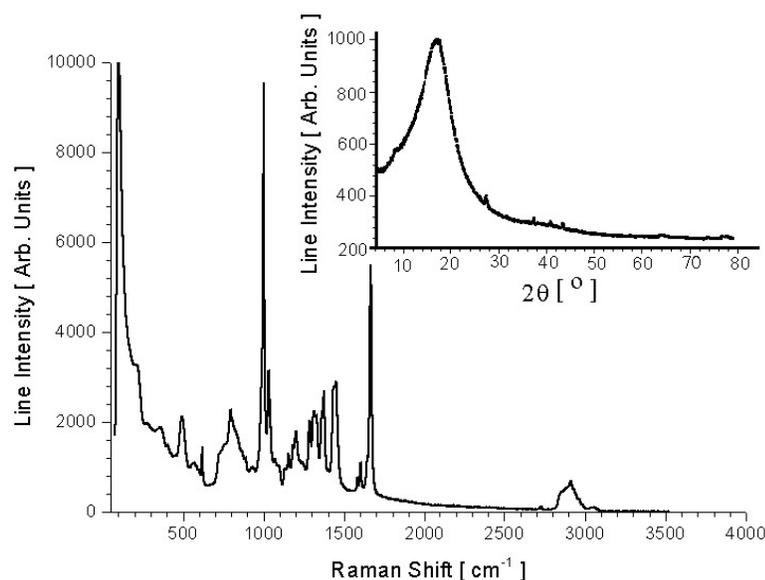
These results suggest that our novel activatable bioimaging agent could be applied to detect inflammation *in vivo* for clinical diagnosis of inflammatory conditions or to assess inflammation in various animal models.



## POLY 405: Raman investigations on nanocomposites of colloidal silver in block copolymers

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Polymer based nanocomposites were obtained by dispersing colloidal silver within a three block copolymer (polystyrene - block polyisoprene - block polystyrene) purchased from Sigma Aldrich. The silver colloids were synthesized from AgNO<sub>3</sub> water solution. The polymer-based nanocomposite was obtained by dissolving the polymer in chloroform, adding the homogenized colloidal silver water solution to the polymer solution, followed by sonication of the fluid mixture at 800 W using a high power sonicator. The mixture was sonicated for one hour without cooling. The as obtained homogenized solution was poured on a glass slide and the solvent was removed by heating in an oven at 90 °C for about 10 hours. Half of the as obtained nanocomposite was labeled as generation 1 sample and kept for spectroscopic investigations. The other half of the nanocomposite was again dissolved in chloroform. The as obtained solution was stirred for 2 hours, sonicated for 1 hour without cooling and finally poured on a glass slide and placed into a oven heated at 90 °C for about 10 hours. This series was labelled as generation 2. The generation 2 nanocomposites contained almost no water traces. Nanocomposites of generation 1 and 2 containing various amounts of silver have been prepared. The as obtained films have been investigated by Raman spectroscopy using a Renshaw InVia spectrometer, operating at 785 and 532 nm, by FTIR using a Bruker spectrometer, and by Wide Angle X-Ray Spectroscopy using a Bruker Discover 8 spectrometer. The research focuses on the potential use of nanocomposites for surface enhanced Raman, where the potential landscape generated by the self-assembly of the block copolymer may provide the required roughness for an efficient enhancement of the Raman effect.



## POLY 406: Periodical mesoporous polymers from H-bonding-modulated block copolymer supramolecules

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Pore geometry and size uniformity dictate the performances and durability of porous materials in diverse applications. There is a constant demand for methodologies to design and realize tailor-made pores with sizes down to sub-100 nm with affordable expense. Block copolymers (BCPs) which undergo microphase separation allow the accessibility of a library of well-defined, periodical mesoscale structures. Controlled conversion of these structures which are the dispersed phases embedded in the matrix would yield porosity with the geometries coining the parent structures.

In this work, we fabricate ordered porous materials with different pore geometry by incorporating 3-n-pentadecylphenol (PDP) onto the P4VP moieties of cylinder-forming polystyrene-*b*-poly (4-vinylpyridine) (PS-*b*-P4VP) through hydrogen bonding, followed by ethanol treatment. Well-defined, periodical porous structures with the pore geometry of cylinders, lamellae, and gyroid are achieved by tuning the ratio of PDP and P4VP as well as the evaporation rate of the solvent in which the BCP and PDP are dissolved. Particularly, we obtain membranes with perpendicular through pores with length up to 65 microns, and prove their pore size can be adjusted in a larger scale by ethanol treatment at elevated temperatures. Ethanol treatment washes out the H-bonded PDP on one hand and swells the P4VP domains. Such membranes with adjustable thickness are obtained by controlling the evaporation of solvent, and the surface morphology transformations are investigated in this evaporation process for the first time.

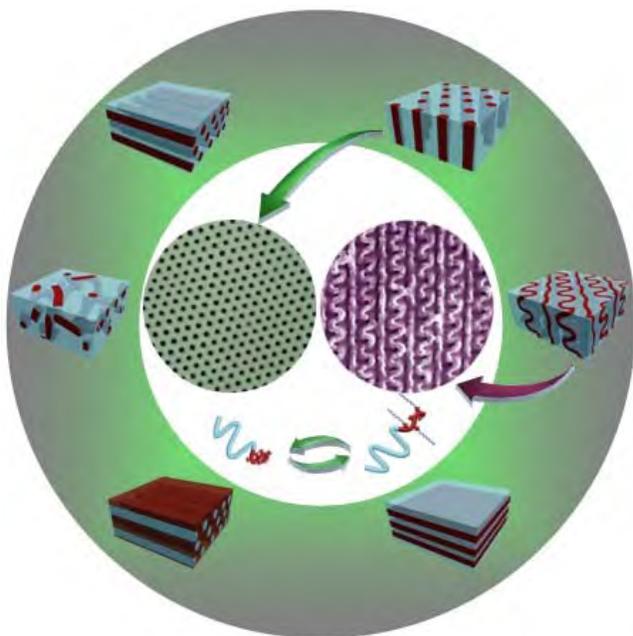
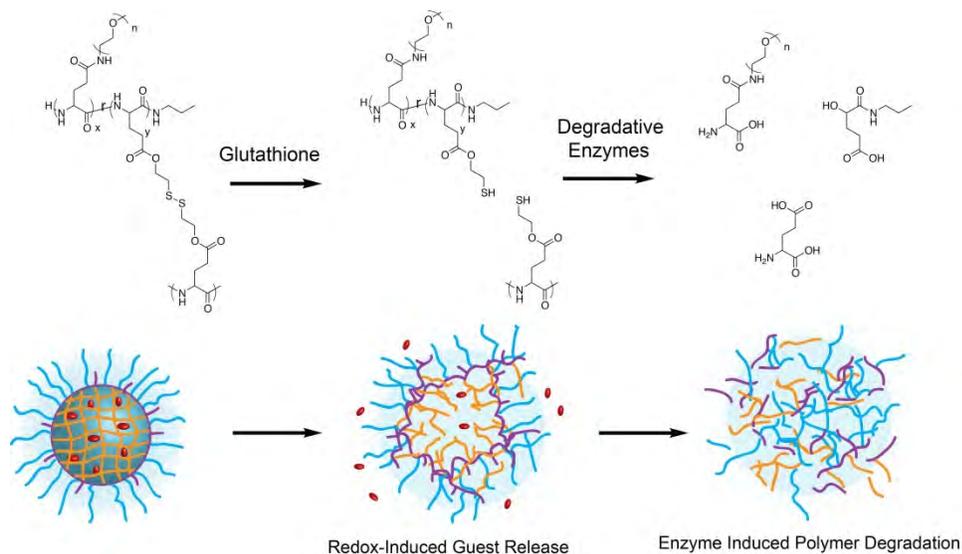


Figure 1. Periodical Mesoporous Polymers from H-Bonding-Modulated Block Copolymer Supramolecules

## POLY 407: Poly(glutamic acid)-based nanogels for drug delivery applications

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Biodegradable nanocarriers that have specific stimuli-induced drug release and subsequent degradation would be ideal for a variety of drug delivery applications. The objective of this work is to develop a polymeric nanogel comprised of a biodegradable and non-toxic poly(glutamic acid) backbone, hydrophilic PEG surface and hydrophobic and a glutathione-responsive disulfide cross-linked core. With the appropriate hydrophilic/lipophilic balance, these polymers self-assemble into micellar aggregates in aqueous conditions and are capable of sequestering lipophilic guests. Following addition of a deficient amount of reducing agent DTT, the crosslinked aggregates have enhanced encapsulation stability and stimuli-induced guest release at a cytosol-relevant GSH concentration. Further, poly(glutamic acid) is susceptible to enzyme proteolysis, but with a surface PEG component that reduces non-specific interactions with biological milieu, we expect that in a stable nanogel assembly the degradation would largely occur due to proteolysis in the lysosome following cell-internalization and guest release.

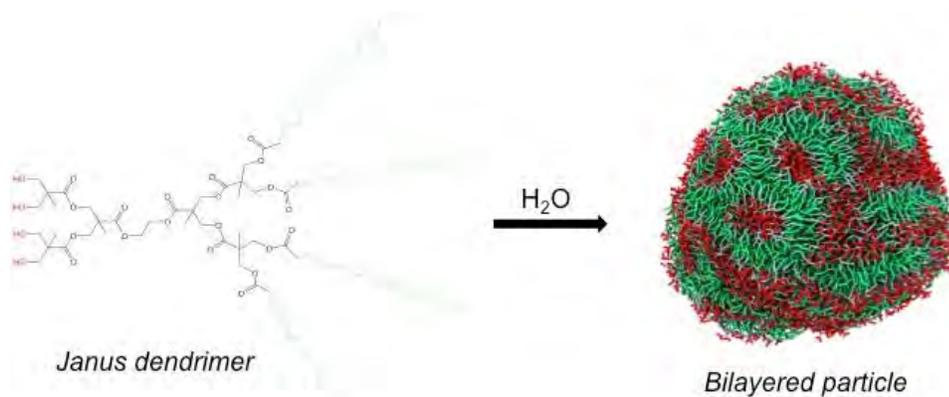


Self-assembled and crosslinked polymeric nanogels release encapsulated guest in response to a cytosol-relevant concentration of glutathione, and the polymers degrade in response to proteolytic enzymes.

## POLY 408: Synthesis of an amphiphilic Janus dendrimer and evaluation of its self-assembly process in water

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(1) Universidad Andrés Bello, Santiago, Chile (4) Instituto Tecnológico y de Estudios Superiores de Monterrey, Monterrey, Mexico (5) Fundación Fraunhofer Chile Research, Santiago, Chile

Dendrimers are monodisperse, highly branched macromolecules with well-defined three-dimensional structures and a large number of terminal groups, these physical characteristics make them ideal candidates for evaluation as drug delivery vehicles. Amphiphilic Janus dendrimers are a kind of dendrimers composed of highly polar and highly nonpolar regions distributed onto its surface that self-assemble in water to form vesicles similar to liposomes. The aim of this work was to synthesize a second generation amphiphilic Janus dendrimer and evaluate its aggregation behaviour in water. The dendrimer was obtained by mixed divergent and convergent synthesis pathways using 2,2-bis(hydroxymethyl)propionic acid as repeating unit, myristic acid bounded to the peripheral groups as nonpolar region and ethylene glycol as nucleous; and was characterized by <sup>1</sup>H NMR and FTIR. For the evaluation of dendrimer aggregation behaviour in water, we made dispersion in this media, using liposome preparation protocols (film hydration and ethanol injection) and we also encapsulated hydrophobic and hydrophilic dyes to identify domains with different polarity in the aggregates. Resulting particles were characterized by light and transmission electron microscopy. Experimental data was compared with coarse grained molecular dynamics simulation. The obtained <sup>1</sup>H NMR and FTIR results confirmed the amphiphilic Janus dendrimer synthesis. Preliminary experimental and theoretical data obtained show that the dendrimer aggregates into bilayered particles in water. The presence of hydrophobic and hydrophilic domains inside the particles makes them potential candidates for the encapsulation of therapeutic molecules.



Particle formed by self-assembly of the Janus dendrimer in water, obtained after 13  $\mu$ s of coarse grained molecular dynamics simulation.

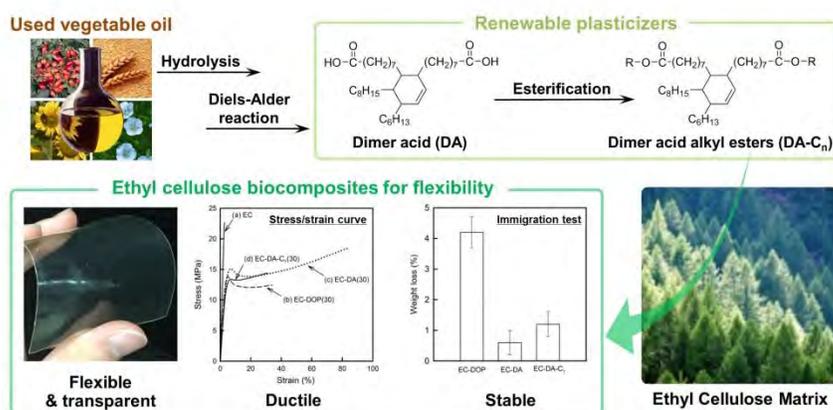
## POLY 409: Ethyl cellulose composite with dimer acid alkyl ester plasticizer derived from used vegetable oil

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Flexible composites were prepared with ethyl cellulose (EC) as a base polymer and dimer acid (DA) derivatives as a plasticizer. Dimer acid and dimer acid esters (DA-C<sub>n</sub>), having short to long alkyl chains were synthesized through the Diels–Alder reaction of fatty acids prepared by hydrolysis of used vegetable oil and the subsequent esterification. <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, Fourier transform infrared (FT-IR), and chemical titration resulting total acid number (TAN) were performed to characterize the renewable plasticizers. The thermal stability was studied with thermal gravimetric analysis (TGA), showing higher thermal degradation temperatures of DA and DA-C<sub>n</sub> than dioctyl phthalate (DOP) which is one of popular petroleum-based plasticizer. To evaluate compatibility between EC and the plasticizers, FT-IR, UV-vis transmittance, and scanning electron microscopy (SEM) analysis were carried out, proving good dispersion of plasticizers in EC matrix and enhanced optical clarity in a micro-scale of EC composites using DA and DA-C<sub>1</sub>. In particular, dynamic mechanical analysis (DMA) and tensile test showed viscoelastic properties and ductile behaviors having enhanced elongation and toughness on the addition of DA in the EC composites. Immigration test of the EC composites revealed that DA was released more slowly than DOP from the EC matrix. In conclusion, DA and DA-C<sub>1</sub> ester could act as effective eco-friendly and renewable plasticizers for EC.

### References

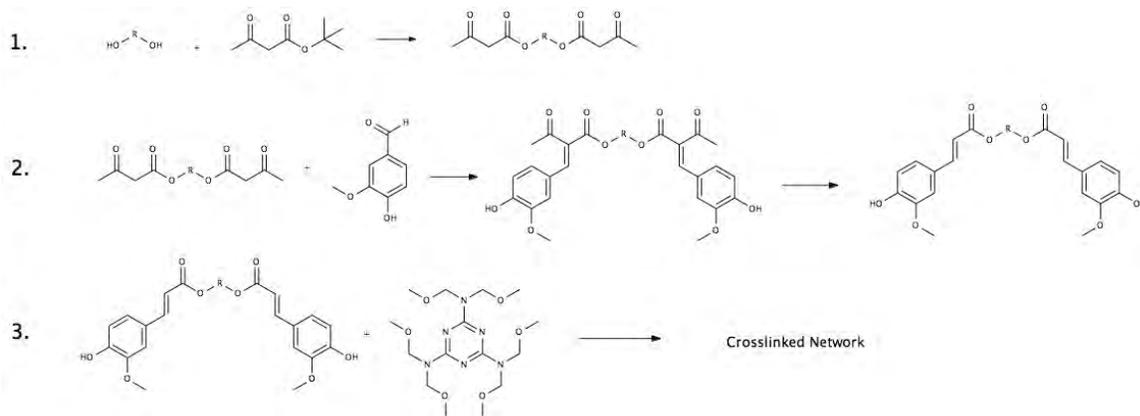
1. Lee, S.; Shin, J.; Kim, Y.-W. et al. *Carbohydrate Polymers* 2015, 121, 284–294.



## POLY 410: Vanillin: A biobased crosslinker for melamine-formaldehyde coatings

**Alison Rohly**<sup>1</sup>, *alison.rohly@ndsu.edu*, **Dean C. Webster**<sup>2</sup>. (1) *Coatings and Polymeric Materials, North Dakota State University, Fargo, North Dakota, United States* (2) *Dept 2760, North Dakota State University, Fargo, North Dakota, United States*

In recent efforts to reduce dependency on petrochemical-based materials, many biobased alternatives are currently under investigation. One material of interest, lignin, may be depolymerized to form low molecular weight compounds, the most abundant being vanillin. Although little research has been done, vanillin offers great potential as a biobased crosslinker in thermoset coatings systems due to its unique functionality. The current research is therefore focused at incorporating lignin-derived vanillin into melamine-formaldehyde thermoset coatings. To begin, several polyols were acetoacetylated using tert-butylacetoacetate (TBAA). The addition of vanillin resulted in a Knoevenagel Condensation between the aldehyde on vanillin and the activated methylene hydrogens on the acetoacetate. Then, the free phenolic groups on vanillin were further crosslinked with a melamine-formaldehyde resin, forming durable coatings with excellent solvent resistance, hardness and toughness.



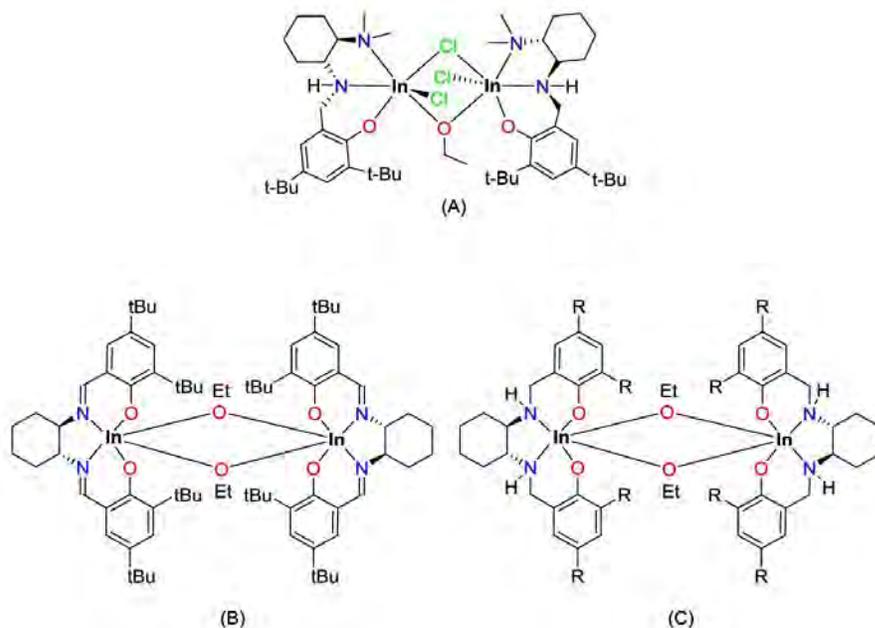
## POLY 411: Moisture resistant indium complexes for ring opening polymerization of lactide

**Tannaz Ebrahimi**<sup>2,1</sup>, [tannaz@chbe.ubc.ca](mailto:tannaz@chbe.ubc.ca), **Dinesh Aluthge**<sup>2</sup>, **savvas hatzikiriakos**<sup>1</sup>, **Parisa Mehrkhodavand**<sup>2</sup>. (1) Chemical and Biological Engineering, University of British Columbia, Vancouver, British Columbia, Canada (2) Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada

Poly(lactic acid) (PLA) is a biodegradable and biocompatible polyester that has received a great deal of interest as an alternative to biostable petroleum based thermoplastics. To improve macro and microstructural properties of PLA, several metal based catalysts have been reported as initiators for ring opening polymerization of lactide to form PLAs of different microstructures.

We have previously introduced dinuclear indium alkoxide complexes bearing chiral tridentate NNO (A) and salen ligands (B) as stereoselective complexes capable of producing isotactically enriched and stereoblock PLAs in a controlled fashion. In this work, indium salen complexes (C) are introduced as highly active and heteroselective complexes for the ring opening polymerization of lactide.

Followed by this, moisture resistance of the aforementioned indium complexes are investigated. The hydroxylated species appear to be highly stable under ambient atmospheric conditions with no degradation observed after long time exposure to the moist air. Excellent molecular weight control and narrow dispersities of the produced PLAs revealed *in-situ* regeneration of the active complexes from the hydroxylated ones in the presence of added alcohols.



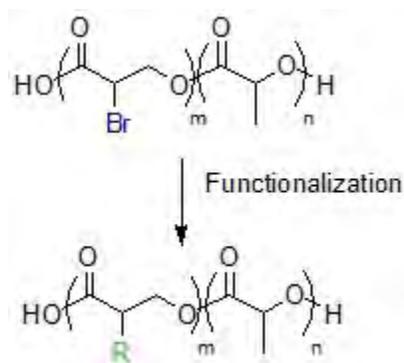
## POLY 412: Synthesis and functionalization of PLA-based systems

**Carolyn Scherger**<sup>2</sup>, [cm94@zips.uakron.edu](mailto:cm94@zips.uakron.edu), **Colin Wright**<sup>3</sup>, **Coleen R. Pugh**<sup>1</sup>. (1) Department of Polymer Science, The University of Akron, Akron, Ohio, United States (2) Polymer Science, The University of Akron, Akron, Ohio, United States (3) University of Akron, Akron, Ohio, United States

Poly(lactic acid) (PLA) is currently an attractive material as a promising alternative to commodity petroleum-based plastics. It is biodegradable and derived from renewable resources. However, PLA has some synthetic limitations: the only two convenient locations for functionalization are the end groups. To overcome this problem, we currently copolymerize lactic acid with 2-bromo-3-hydroxypropionic acid by a step-growth mechanism using *p*-toluene sulfonic acid as a catalyst.<sup>1-3</sup> This 2-bromo-3-hydroxypropionic acid comonomer provides a unique site for functionalization along the polymer backbone: the halogen alpha to the carbonyl is activated to a variety of chemistries. Another approach to synthesize higher  $M_n$  and lower polydisperse PLA is through the ring-opening polymerization (ROP) of lactide. We are looking at ROP as an approach to produce this functional PLA by using this 2-bromo-3-hydroxypropionic acid as a starting material to synthesize both polyester macrocycles and a 6-membered carboxyanhydride ring. Polymerization routes of these molecules are currently being established.

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2. Pugh, C.; Singh, A.; Samuel, R.; Bernal Ramos, K.M. *Macromolecules* 2010, *43*, 5222-5232.
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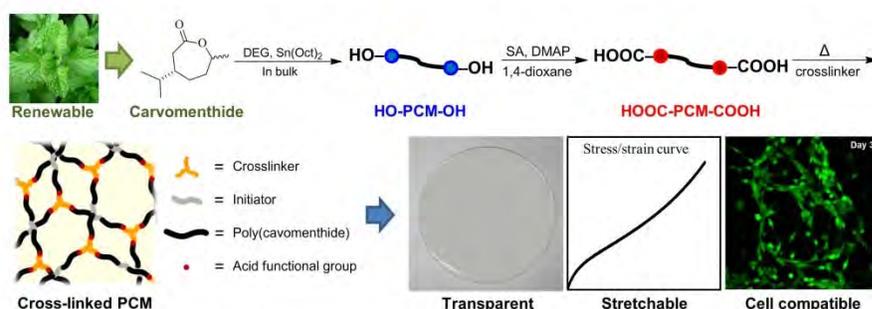
## POLY 413: Renewable crosslinked elastomer derived from carvomenthide

**Sangjun Lee**<sup>1,2</sup>, [sangjunlee@ust.ac.kr](mailto:sangjunlee@ust.ac.kr), Young-Wun Kim<sup>2,1</sup>, Jihoon Shin<sup>2</sup>. (1) Department of Green Chemistry and Environmental Biotechnology, Korea University of Science & Technology (UST), Daejeon, Korea (the Republic of) (2) Center for Biobased Chemistry, Korea Research Institute of Chemical Technology (KRICT), Daejeon, Korea (the Republic of)

Three dimensional cross-linked polymers were synthesized using plant-based monomer carvomenthide prepared via alternative green procedure. Ring-opening transesterification polymerization of carvomenthide using diethylene glycol as an initiator gave telechelic hydroxyl poly(carvomenthide) (HO-PCM-OH). Adjusting monomer to initiator ratio, target molar masses of 3, 6, and 12 kg mol<sup>-1</sup> were precisely controlled with narrow dispersity. Subsequently, hydroxyl functional groups were converted to carboxyl acid resulting acid-terminated poly(carvomenthide) (HOOC-PCM-COOH) by esterification with excess succinic anhydride. Transesterification or polymer chain scission was minimized during esterification, showing unimodal trace and low dispersity in size-exclusion chromatography (SEC). Thermal curing process of the resulting prepolymers was carried out at 180 °C with trifunctional aziridine to give cross-linked elastomers (XL-PCM). All polymers including HO-PCM-OH, HOOC-PCM-COOH, and thermoset elastomers exhibited high thermal resistance. The mechanical behavior of the thermoset elastomers were evaluated using dynamic mechanical analysis and tensile tests under static and cyclic loads, proving viscoelastic properties and rubbery behaviors with exceptional elongation at break, tensile strength, and elastomeric recovery properties. Cell adherence and proliferation on the elastomer surface were investigated for *in vitro* cytocompatibility. Therefore, this thermoset elastomer system derived from renewable materials offer useful approaches for the tissue engineering scaffold applications.

### References

1. Lee, S.; Kim, Y.-W.; Shin, J. et al. *Biomacromolecules* 2015, 16, 246–256.
2. Martinez, H.; Hillmyer, M. A. *Macromolecules* 2014, 47, 479–485.



## **POLY 414: Development and evaluation of a physical-mechanical board based recycled polyethylene acacia wood farnesiana**

**Mario Solís**, *msolis@ubiobio.cl. de Quimica, Universidad del BioBio, Concepción, Concepción, Chile*

This research is focused on the development and characterization of prototype-based panels of recycled high-density polyethylene and acacia wood, using the gypsum binder. Because nowadays synthetic adhesives dominate reconstituted wood industry, it is important to reduce such toxicity problems.

This descriptive study with quantitative approach, describes the process of making a board based on wood fiber aramo solid waste, in order to obtain a competitive construction element that complies with current regulations.

Regarding the experimental development, it can be concluded:

It is possible to manufacture a board type construction element to be used as lining, nonstructural using a mixed feedstock based on recycled high density polyethylene and acacia wood composite.

Cold water resistance, impact resistance and flexural strength were also compared to the technical requirements of drywall plasterboard was determined experimentally.

Finally, it notes that sustainable development in construction is a strategy of development of the industry, which is here to stay, and studies like these help our country does not fall behind in innovation, incorporating these materials in processes production.

The authors acknowledge the technical and financial support of the Department of Chemistry, Faculty of Science, University of Bio Bio, Concepción, Chile. It also corresponds to thank the Center for Advanced Polymer Research at the University of Bio Bio.



## **POLY 415: Optimization via microwave synthesis of non-halogenated phosphorus flame retardants**

**Robbie K. Mahaffey**, *rkm3i@mtmail.mtsu.edu. Chemistry, Middle Tennessee State University, Murfreesboro, Tennessee, United States*

Due to combustible household items, such as computers, chargers, televisions, and other appliances, civilization has come to require a strong need for the prevention of fire. Two major issues that arise, in order to solve this matter, is the ability for materials to resist flames and interrupt the combustion cycle of the flame. Due to environmental concerns, a non-halogenated and phosphorus based compound is a solution that is already in use. In order to synthesize a more thermally stable fire retardant, the phosphorus based compounds are going to be synthesized into solids as it is hypothesized that they are best in their solid phase, which allows for higher molecular weight. Optimization of the synthesis process for 1,3,5-tris(diphenoxyphosphoryl)benzoate, 1,3,5-tris(phenoxyphosphoryl) dibenzoate, and 1,3,5-tris(phenoxyphosphoryl) tribenzylidicarboxylic acid will be done via a microwave synthesis in bulk. Finally, characterization of the finished products will be done using Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR), and thermogravimetric analysis (TGA), in order to determine each compounds capability as a high quality flame retardant polymer.

## **POLY 416: Effects of exohelical functionalization on structure of water-soluble meta-poly(phenylene ethynylene) foldamers**

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The biomimetic oligomer meta-poly(phenylene ethynylene) (mPPE) is modeled to gain an understanding of the functionality of many transmembrane proteins, which are similar in structure, but often too large and computationally expensive to model. Most of the prior studies feature mPPEs that are known experimentally to be water-insoluble, which places limitations on the applicability of these studies' findings to biologically relevant problems. The objective of this study was to parameterize models for experimentally-known mPPE foldamers, propose and test a collection of metrics for water-solubility of mPPE foldamers, and to study diffusion of solvent and ions through the cavity of mPPE helices. Models of the mPPE were constructed based on the intramolecular parameters in the CHARMM General Force Field (CGenFF) and CHARMM35 force field. Appropriate partial charges for the monomers were computed using the MP2/6-31G(d) level of theory and the Merz-Kollman scheme. Production runs of simulations were run in the dynamics package NAMD2. Using the computational models developed, metrics of solubility were elucidated from simulations of foldamers known to be experimentally water-soluble (hexaethylene glycol and ethylammonium side chains) and water-insoluble (triethylene glycol, methyl ester, and ethylamine side chains). The metrics developed include number of monomers per turn of helix, numbers of solvent molecules within helix, and solvent accessible surface area. The kinetics of the diffusion of ions through the center of the helix were also examined. The solvophobic interactions involved in the diffusion process were studied, as well as the effects of helix length and adding an endohelical side chain. Endohelical functional groups were found to have a significant impact on the diffusion rates through the helix. The use of polar or charged endohelical functional groups could functionalize the foldamers as chemoselective molecular sieves. Furthermore, synthetic proteins could possibly forge a future approach towards facilitated transport through membrane barriers.

## POLY 417: Online resources for the polymer education community

Katherine Aubrecht<sup>3</sup>, Erik B. Berda<sup>6</sup>, Kevin A. Cavicchi<sup>5</sup>, Philip J. Costanzo<sup>1</sup>, Gregory J. Gabriel<sup>2</sup>, Christopher Goh<sup>10</sup>, **Sarah L. Goh**<sup>9</sup>, [sgoh@williams.edu](mailto:sgoh@williams.edu), Scott T. Iacono<sup>4</sup>, Sarah E. Morgan<sup>7</sup>, Daniel A. Savin<sup>8</sup>. (1) Chemistry, California Polytechnic State U, San Luis Obispo, California, United States (2) Chemistry and Biochemistry / MD #1203, Kennesaw State University, Kennesaw, Georgia, United States (3) SUNY Stony Brook, Stony Brook, New York, United States (4) Department of Chemistry, United States Air Force Academy, Colorado Springs, Colorado, United States (5) University of Akron, Akron, Ohio, United States (6) Department of Chemistry, University of New Hampshire, Durham, New Hampshire, United States (7) School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, Mississippi, United States (8) Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, Mississippi, United States (9) Williams College, Williamstown, Massachusetts, United States (10) Dept of Chemistry, Williams College, Williamstown, Massachusetts, United States

The 2015 ACS Guidelines for Bachelor's Degree Programs now require that some course time be devoted to the introduction of polymers (synthetic and/or biological) and the discussion of meso- and nanoscale materials. Polymer Undergraduate Network of Knowledge, PUNKpolymer.org, is designed to be an online resource for the polymer community. Providing course content from lecture slides and laboratory experiments to textbook reviews and sample writing assignments, PUNKpolymer.org will serve to fill the knowledge gaps in polymer science by providing content that will be accessible for both introductory and upper level courses. This poster will introduce the website and its contents.

**PUNK: Polymer Undergraduate Network of Knowledge**

- Home
- Lecture Slides**
  - Polymer Synthesis 1
  - Polymer Synthesis 2
  - Polymer Synthesis 3
  - Classification: Biological or Synthetic?
  - Environmental Issues and Polymers**
- Demonstrations
- Lab Experiments
- Problem Sets
- Surveys
- Forum
- Writing Resources
- Outside Links

News Highlights

Abstracts Now Open for San Diego!

POLY/PMSE abstracts due Oct 12, 2015

CHED abstracts due Oct 26, 2015

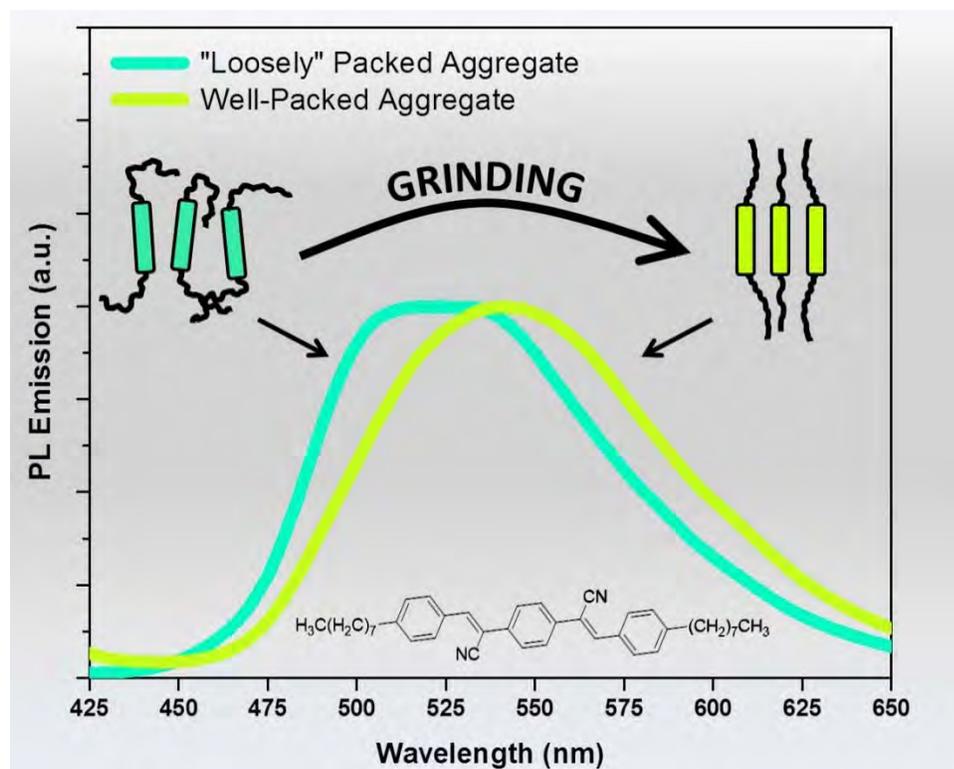
PUNKpolymer.org

Figure 1. Sample page of the PUNKpolymer.org website.

## POLY 418: Stimuli responsive cyano-oligo(phenylene vinylenes)

**Jasmine Davila**<sup>1</sup>, [jdavila@monmouthcollege.edu](mailto:jdavila@monmouthcollege.edu), **Mitchell Woellner**<sup>2</sup>, **Joseph Lott**<sup>3</sup>. (1) Chemistry, Monmouth College, Moline, Illinois, United States (2) School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, Mississippi, United States (3) University of Southern Mississippi, Hopkins, Minnesota, United States

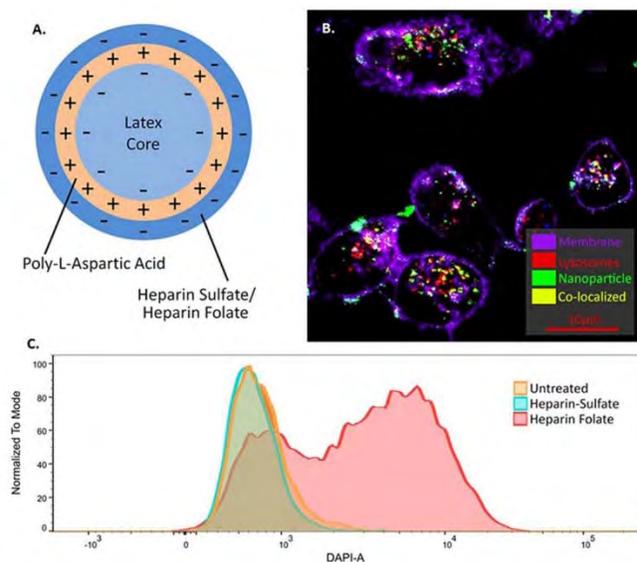
A series of four cyano-containing oligo(phenylene vinylene) (cyano-OPV) chromophores was synthesized via Knoevenagel condensation. Functional groups with varying electron donating strength were incorporated to explore their effect on the “push-pull” conjugated system. The optical properties of the chromophores were analyzed via UV-VIS and fluorescence spectroscopy. As the donating groups changed from hydrogen to alkyl to methoxy, both the absorbance and emission maxima were increasingly red-shifted. Binary, on-off fluorescent emission was observed and was related to the rigidity of the chemical environment. Liquid solutions of all chromophores displayed no fluorescence, while frozen samples were highly emissive. Piezochromic stimuli response of a novel chromophore was discovered. Using mechanical grinding, a color change easily discernable to the eye, corresponding to a shift in maximum emission wavelength from 523 to 540 nm was observed. This piezochromic behavior could be controlled at the molecular level via the length of aliphatic tails on the terminal ends of the cyano-OPVs.



## POLY 419: Generation of layer-by-layer nanoparticle library to selectively target ovarian cancer

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Layer-by-layer (LbL) assembly allows researchers to make hierarchical, multifunctional materials in a highly controlled manner. LbL works by the sequential absorption of oppositely charged materials, creating layers held together by electrostatic attraction. Modification of nanoscale drug-carriers allows incorporation of novel therapeutics, tuning of drug release and active targeting. Surface chemistry plays a major role in cancer-cell targeting and cellular uptake, and is easily modulated on LbL particles by choosing a particular terminal layer. In this work we focus on targeting ovarian cancer, which has seen little improvement in survival rates in the past thirty years. We aim to improve the delivery of therapeutic payloads by terminating LbL drug-carriers with novel layers composed of biocompatible polymers conjugated to active targeting moieties. Here we show preliminary data that demonstrates the benefits of modifying heparin sulfate by conjugating it to folate (heparin-folate). Heparin sulfate is strongly charged and native to the human body; using NHS addition chemistry, we modified it with folate, a B-vitamin whose receptors are over expressed in ovarian cancer. Flow cytometry determined nanoparticle association levels to treated cells and indicated that the heparin-folate outperformed unmodified heparin nanoparticles. Confocal microscopy showed that cancer cells were endocytosing heparin-folate nanoparticles, as indicated by co-localization with lysosomes. This promising data indicates potential for modulating nanoparticle-cell interactions by careful selection of the terminal layer on LbL nanoparticles. Continued exploration of modified native polymers can combine characteristic advantages of different biomolecules. In particular, future work will focus on the modification of linear polypeptides and polysaccharides with novel targeting moieties. LbL nanoparticle systems with synthetic terminal layers possess great potential in targeted drug delivery.



## POLY 420: UV-Initiated free-radical polymerization of acrylamide based glucose and galactose glycomonomers

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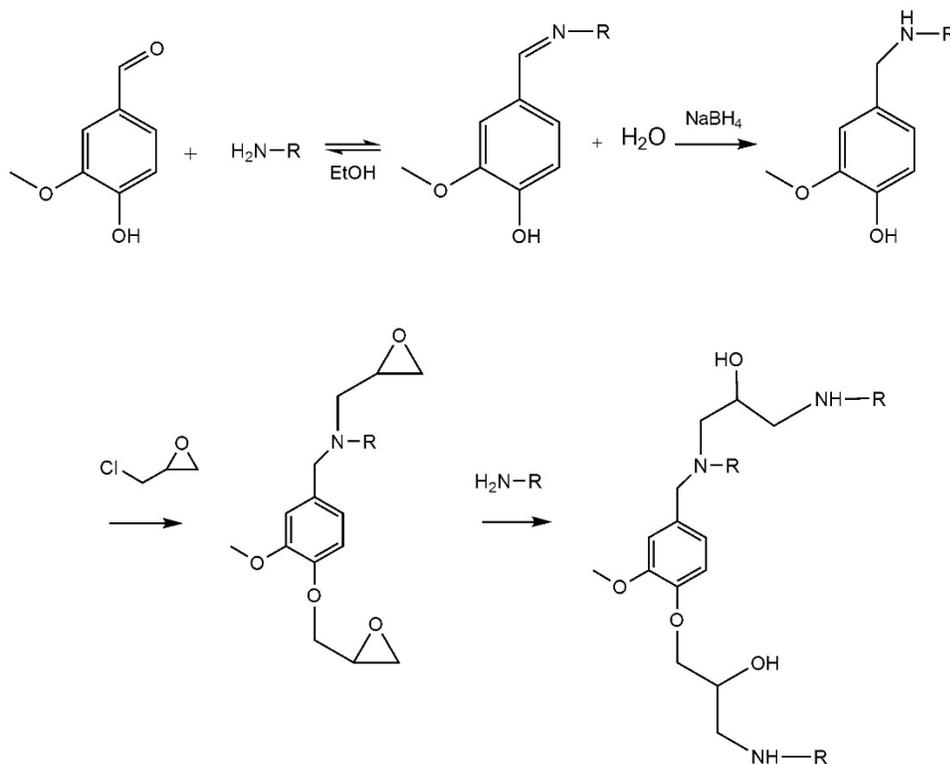
Glycopolymers are synthetic analogues of naturally occurring polysaccharides that contain a carbon-carbon backbone with hydrophilic saccharide pendant moieties. Due to their inherent biocompatibility and extreme hydrophilicity, glycomonomers have been utilized in the design and fabrication of hydrogel networks that can be applied in biomedical applications such as drug delivery systems and biodegradable scaffolds. Hydrogel network structure and properties are influenced by bulk water absorbency, as well as the structure or type of water within the network. Water molecules within hydrogel networks are defined as free, restricted and bound, which vary in relation to the degree of hydrogen bonding within the polymeric network. This research focuses on the homopolymerization of two acrylamide based glycomonomers with pendant glucose (GlcEAm) and galactose (GalEAm) moieties, shown in Figure 1, using UV-initiated free radical polymerization in water. Through this study, the extent of conversion and the corresponding molecular weight of linear homopolymers comprised of GlcEAm and GalEAm is evaluated via <sup>1</sup>H-NMR and dynamic light scattering, respectively. The information pertaining to the polymerization parameters elucidated through this study will be used in the design and fabrication of crosslinked glycopolymer networks.



## POLY 421: Study of vanillin-amine systems for potential uses in coatings

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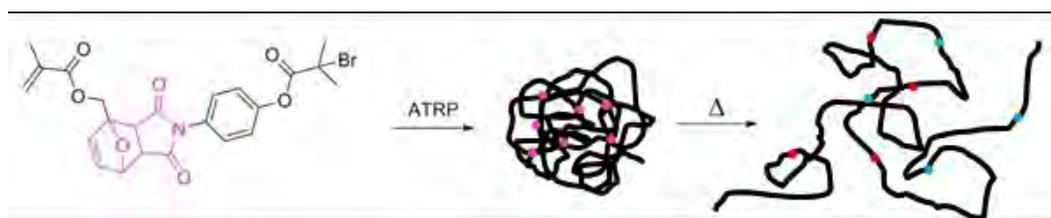
Recent efforts to replace petrochemical materials with biobased alternatives remains a high priority to reduce dependency on oil. Vanillin is a compound of interest due to its biobased origin and functionality. Vanillin is readily obtained through the depolymerization of lignin, a naturally occurring biopolymer that is considered a waste product of the Kraft Pulp process. Vanillin has many applications in the food and drug industries, however there is sparse research on utilizing this compound for coating systems. This study focuses on the synthesis of Schiff-Base compounds via the reaction of vanillin with various amines. The Schiff-Base compounds produced vibrant colors, which is believed to be a result of the conjugation between the imine and aromatic functionality. Reduction of the imines using sodium borohydride was hypothesized to result in loss of color. After reduction, these compounds were reacted with epichlorohydrin to form epoxidized vanillin-amine compounds, which were then crosslinked with amines to form cured thermosets.



## POLY 422: Incorporation of Diels-Alder chemistry into polymer matrices via an inimer approach

**Kyle S. Barcus**, *kbarcus@calpoly.edu*, **Erik D. Crenshaw**, **Philip J. Costanzo**, *phil.costanzo@gmail.com*. *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]



## **POLY 423: Synthesis and characterization of novel polyester polyols derived from bio-based succinic acid and various diols**

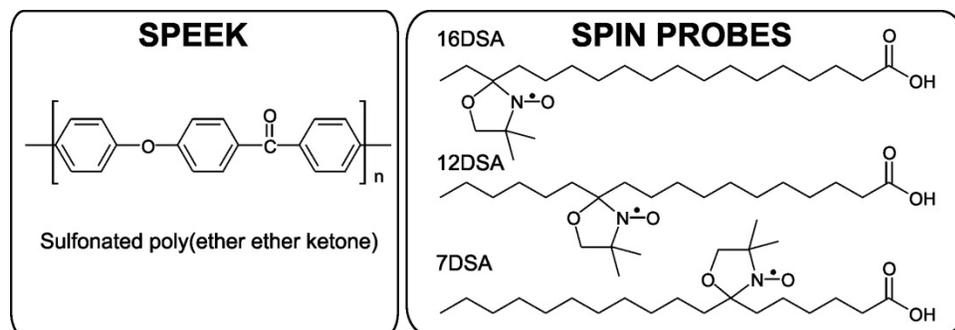
**Cathlene Del Rosario**<sup>1</sup>, *cndelrosario@yahoo.com*, **Kenneth D. Ulrich**<sup>1</sup>, **Baylen Thompson**<sup>1</sup>, **William D. Coggio**<sup>2</sup>, **Alan Schrock**<sup>1</sup>. (1) *Chemistry, University of West Florida, Pensacola, Florida, United States* (2) *BioAmber Inc., Plymouth, Minnesota, United States*

Bio-based polyester polyols were synthesized from the reaction between bio-based succinic acid (SA) and various diols. The bio-based succinic acid was produced by BioAmber via a fermentation biotechnology process to yield this renewable organic diacid building block. The acid is converted to hydroxy-terminated polyesters polyols by condensation polymerization with a variety of diols such 1,3-propanediol, 1,4-butanediol, 3-methyl-1,5-pentanediol, 2,2-dimethyl-1,3-propanediol, and diethylene glycol. The molecular weight of the final polyols was controlled to approximately 1,000 g/mol as determined by NMR end group analyses. The structure-property relationships of the polyols, as influenced by the glycols, were determined for both succinate polyester polyols and adipate polyester polyols. As anticipated, the diol structure and the ratio of the diols influenced the key physical properties such as viscosity, glass temperature and melting point. Succinate polyols tended to have higher glass temperatures and viscosity compared to adipates, but at temperatures > 50° C, the succinates and adipates were found to possess comparable viscosities. This poster will discuss these findings and how such materials are being designed to perform in key applications such as coatings, adhesives, and elastomers.

## POLY 424: Dynamics and location of doxyl-stearic acid spin probes in sulfonated poly(ether ether ketone) ionomer deduced from electron spin resonance studies

**Brooke Hosea**<sup>3</sup>, hoseabe@udmercy.edu, Marek Danilczuk<sup>2</sup>, Shulamith Schlick<sup>1</sup>. (1) Univ Detroit Mercy, Detroit, Michigan, United States (2) University of Detroit Mercy, Detroit, Michigan, United States (3) Chemistry and Biochemistry, University of Detroit Mercy, Detroit, Michigan, United States

The phase separation in sulfonated poly(ether ether ketone) (SPEEK) was previously studied by our group as a function of the degree of sulfonation (DS) and the water content, using the nitroxide radical 4-oxo-TEMPO (Tempone) as a spin probe. We present more detailed information on specific regions of the microphase-separated SPEEK with DS of 68 %, based on a series of doxyl-stearic acid (DSA) spin probes with different polarities, using the electron spin resonance (ESR) method. The chosen DSA spin probes were 7DSA, 12DSA and 16DSA. The ESR spectra of the spin probes were measured as a function of temperature in the range of 110-350 K in order to obtain information on the dynamical properties and distribution of the spin probes in the various regions of the SPEEK ionomer. Two components, fast and slow, were detected in the ESR spectra of the three spin probes. At 350 K, all spectra had dominant slow components, but as the distance between the nitroxide group and the acid group of the probe increased, the intensity of the fast component peaks also increased. The mobility of the spin probes depends on their polarity and reflects on their location in the ionomer.

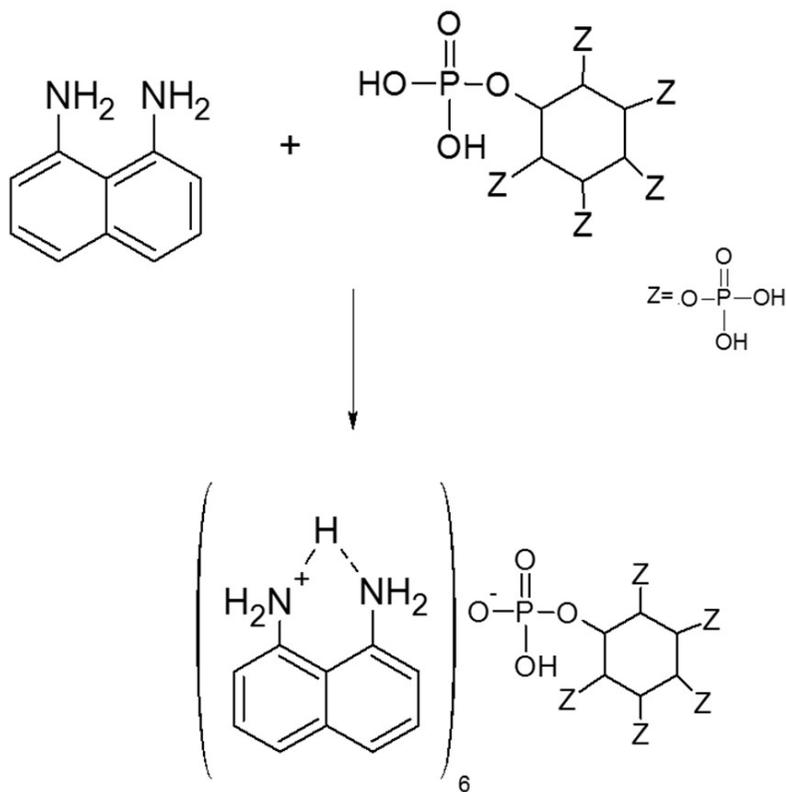


## POLY 425: Salts of natural plant acid as nontoxic flame retardants for polymeric materials

**Amanda Dembski<sup>2</sup>**, dembs1ak@cmich.edu, Bob A. Howell<sup>1</sup>. (1) Central Michigan Univ, Mount Pleasant, Michigan, United States (2) Chemistry and Biochemistry, Central Michigan University, Mt. Pleasant, Michigan, United States

As the potential risk to human health posed by organohalogen flame retardants, particularly brominated aromatics, become of increasing concern, the greater is the need for the nontoxic, nonhalogen alternatives. Alternatives based on renewable biosources are most attractive. Not only do they remove a dependence on petroleum but, since they are based on compounds normally present in the environment, they are unlikely to display major toxicity.

Phytic Acid is a bioacid generated by plants as a nutrient storage compound that is present in various crop seeds to provide a nutrient source to allow new plants to develop to the point of root growth for extraction of nutrients from the soil. This acid is a cyclohexane derivative containing six phosphoric acid groups. These acid groups are capable of protonating sufficiently basic amines or phosphines to form stable salts. These salts contain a high level of phosphorous and should function as high-temperature flame retardants.

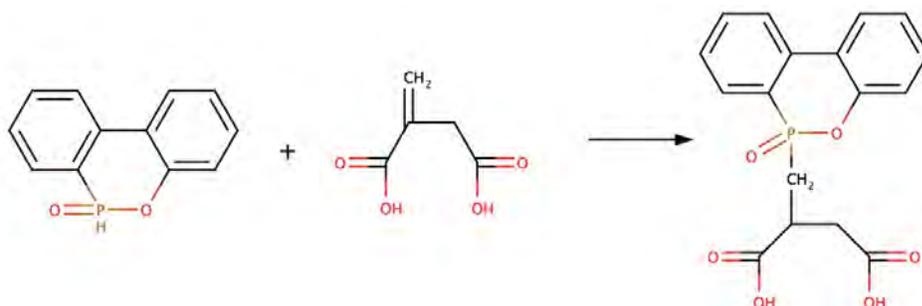


Salt formation between Phytic Acid and 1,8 Diaminonaphthalene

## POLY 426: Phosphorylated itaconic acid monomer for the preparation of nonmigrating flame retardants

**Victoria R. Hill<sup>2</sup>**, hill2vr@cmich.edu, **Bob A. Howell<sup>1</sup>**. (1) Central Michigan Univ, Mount Pleasant, Michigan, United States (2) Chemistry and Biochemistry, Central Michigan University, Mount Pleasant, Michigan, United States

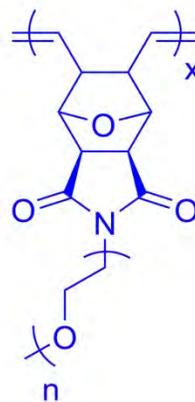
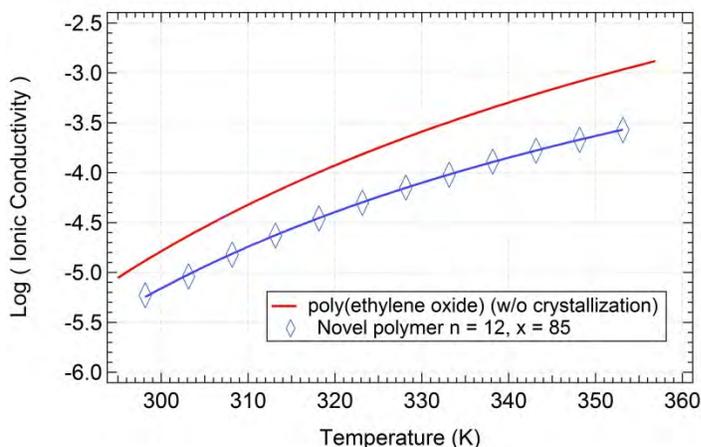
The need to supplant organohalogen flame retardants, which tend to bio accumulate and may pose a risk to human health has generated great interest in the development of nontoxic, nonmigrating and biodegradable replacements. Itaconic acid is a four-carbon diacid containing a methylene group at the 2-position. The double bond is in conjugation with the carbonyl group making it susceptible to Michael addition by a number of phosphorus derivatives. The resulting phosphorus derivatives are difunctional carboxylic acids. These acids may be polymerized with bio-based diols [isosorbide, 2-5-bis (hydroxymethyl) furan, for example] to generate oligomers containing a phosphorus moiety in each repeat unit. These oligomers should function as non-migrating, effective flame retardants for polymeric materials.



## POLY 427: Applications of impedance spectroscopy: Exploring the temperature dependence of ionic conductivity in novel oligo(ethylene oxide) brush homopolymers as solid electrolyte supports

**Colin Peterson**, *petersch@plu.edu*, Dean A. Waldow. Department of Chemistry, Pacific Lutheran University, Tacoma, Washington, United States

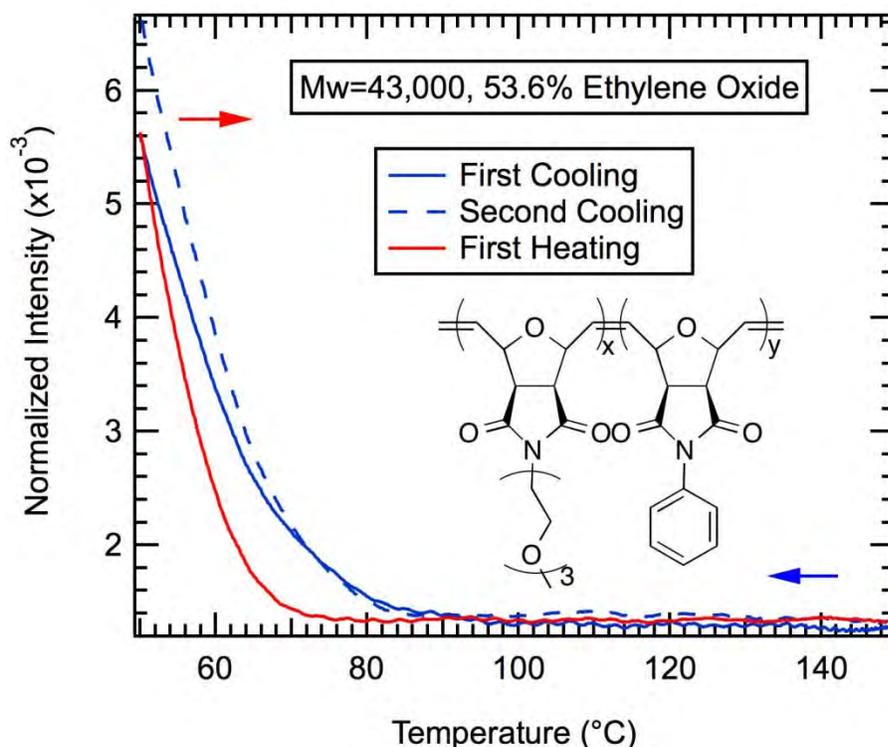
Novel polymers with a rigid oxanorbornyl backbone and oligo(ethylene oxide) 'brush' have been synthesized as an alternative solid polymer electrolyte support for lithium ion batteries. The ionic conductivity of lithium bis(trifluoromethane)sulfonimide through the polymer was measured by impedance spectroscopy. The effect of different sample preparation techniques on the conductivity due to variable ambient water content was also explored. The temperature dependence of the conductivity was also investigated and fit to the Vogel-Fulcher-Tammann equation, examining trends in temperature dependence between samples with different oligo(ethylene oxide) lengths, as well as different degrees of polymerization. For example, samples with the highest molecular weight in the  $n=12$  group were found to have an ionic conductivity at 298 K of  $5.9 \times 10^{-6}$  S/cm, while poly(ethylene oxide) would be approximately  $1.6 \times 10^{-5}$  S/cm if crystallization could be inhibited. These polymers are approaching competitive conductivities with poly(ethylene oxide) without the issues of crystallization.



## POLY 428: Investigation of phase transition temperatures of oligo(ethylene oxide) grafted oxanorbornyl diblock copolymers for solid polymer electrolytes supports

Dean A. Waldow, **Sevryn P. Modahl**, modahlsp@plu.edu. Department of Chemistry, Pacific Lutheran University, Tacoma, Washington, United States

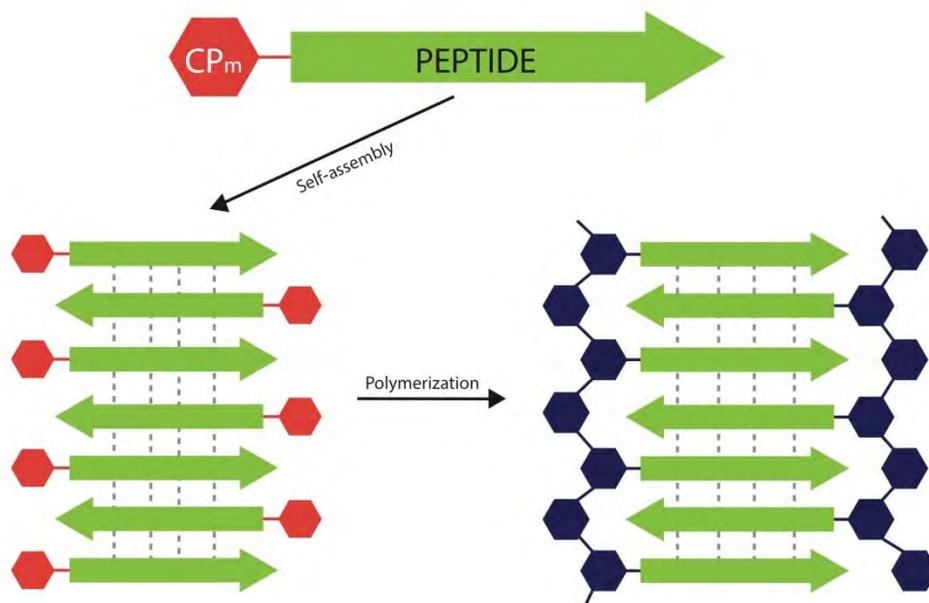
Solid polymer electrolytes (SPEs) offer a potentially safer alternative to current electrolytes used in lithium-ion batteries by removing the use of flammable solvents. The ionic conductivity of SPEs are tied to the segmental motion of the polymer backbone. Most common SPEs are poly(ethylene oxide), which can crystallize at room temperature and offers no resistance to dendrite growth. Polymers with a bulky backbone and a conductive tail may decouple the ionic conductivity from the segmental motion. The addition of a high modulus block to the polymer can cause the formations of nanomorphologies that may lead to ionic pathways as well as a structural region that can prevent dendritic growth. Nine oligo(ethylene oxide, N=3) grafted oxanorbornyl diblock copolymers with narrow polydispersities were synthesized using ring opening metathesis polymerization with varying compositions and molecular weights. The order-disorder transition temperature ( $T_{ODT}$ ) and order-order transition temperature ( $T_{OOT}$ ) of the nanomorphologies and the Flory-Huggins interaction parameter of these diblock copolymers were investigated through the use of optical birefringence and small angle x-ray scattering.



## POLY 429: Controlling nanoscale organization of thiophene-based conducting polymers with self-assembling peptides

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Chem Dept, MS9150, Western Washington Univ, Bellingham, Washington, United States

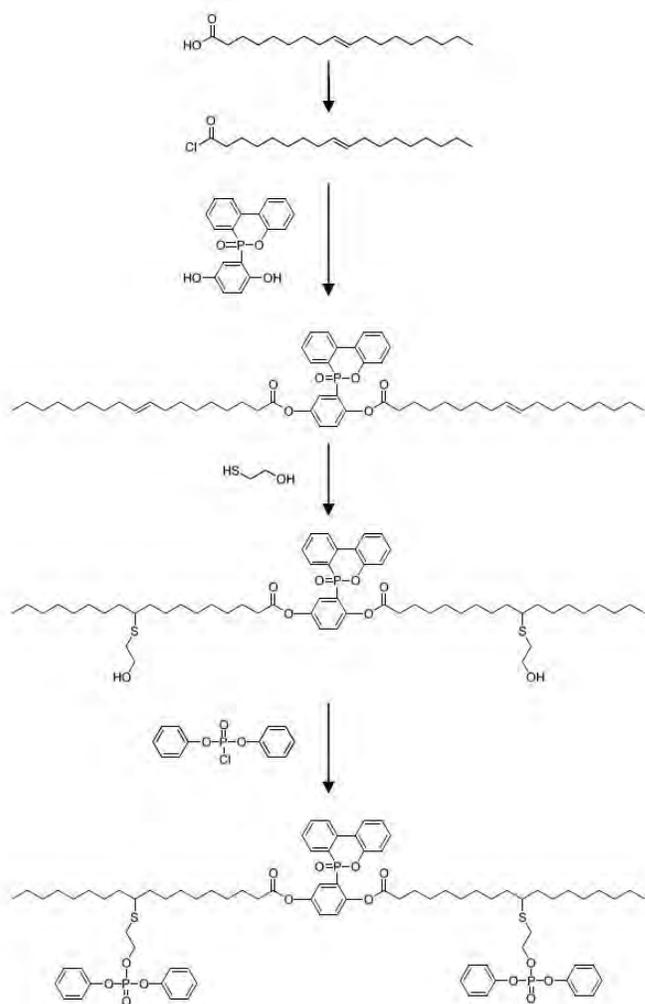
To control the morphology and improve the mechanical properties of conducting polymers, a short silk-inspired peptide capable of self-assembly was installed directly onto a thiophene-based monomer. Self-assembly of the peptide was found to drive 2D organization of the covalently linked monomer, and at high concentrations produced a 3D gel with a fibrous, porous structure. Subsequent polymerization of the thiophene monomer following self-assembly resulted in the formation of electrically conductive gels that retain the fibrous structures. Changes in concentration, temperature, solvent, pH, and amino acid sequence of the peptide was found to influence the 2D and higher-order 3D structures, producing materials with unique morphologies. This simple yet powerful method can be further exploited to produce conducting polymers with controlled nanoscale organization for use in a variety of biomedical applications.



## POLY 430: Phosphorus flame retardants for polymeric materials from a renewable plant oil

**Gavan W. Lienhart<sup>2</sup>**, [gavanlienhart@gmail.com](mailto:gavanlienhart@gmail.com), **Bob A. Howell<sup>1</sup>**. (1) Central Michigan Univ, Mount Pleasant, Michigan, United States (2) Chemistry and Biochemistry, Central Michigan University, Haslett, Michigan, United States

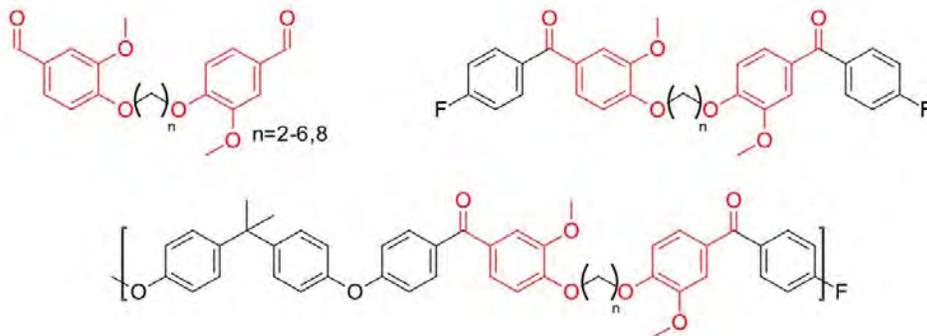
As the potential health risks associated with the use of organohalogen flame retardants becomes more apparent, the need to develop new effective and nontoxic alternatives becomes increasingly urgent. Such materials may be generated from renewable plant oils. Oleic Acid is readily available from saponification of triglycerides from a variety of crop seeds, most notably soybeans. Esterification of this acid with 2-dopyl-1,4-benzenediol generates a diester containing unsaturation which can be subjected to thiol-ene reaction using 2-hydroxyethanethiol to afford a diol from which a variety of phosphorus esters may be generated. These compounds have the potential to function as nontoxic flame retardants for polymeric materials.



## POLY 431: Dioxyalkylene PEEK polymers containing vanillin subunits

**James Herbort**, *James.Herbort@hotmail.com*, **Nicholas Yahna**, *Yahna.5@wright.edu*,  
*William A. Feld*. *Wright State Univ, Dayton, Ohio, United States*

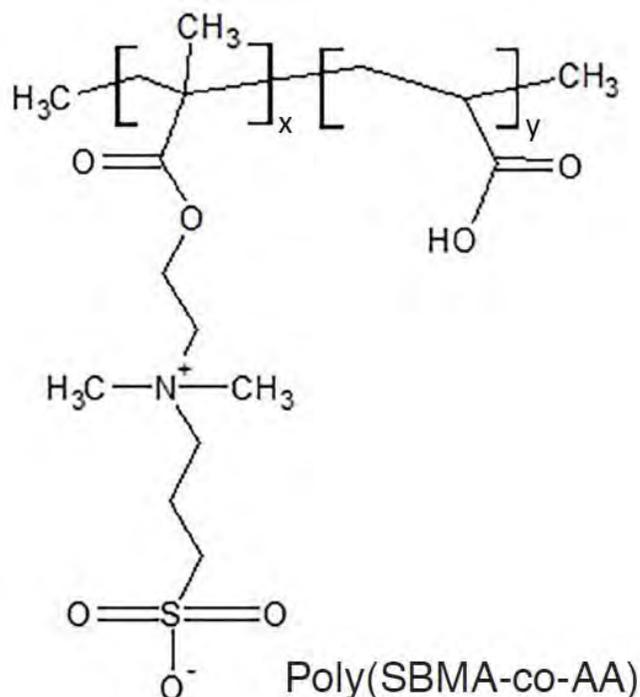
Vanillin has many interesting properties and is frequently used as a building block in organic synthesis. Poly (ether ether ketone)s (PEEK) have been known to exhibit thermal stability, solvent resistance, and mechanical properties. A series of dioxyalkylene peek based monomers containing vanillin subunits were generated via a three-step process, 1) Williamson ether synthesis, 2) Grignard reaction with p-bromofluorobenzene, and 3) Jones oxidation. The monomer was then polymerized in an A<sub>2</sub>B<sub>2</sub> NAS polymerization with Bisphenol A. The oxidation procedure can be modified by using Green methods such as TEMPO/sodium hypochlorite oxidation in an effort to become more environmentally friendly.



## POLY 432: Synthesis and characterization of sulfobetaine containing copolymers

**Katherine Mullen**, *kdm14209@huskies.bloomu.edu*, Mark A. Tapsak. Department of Chemistry and Biochemistry, Bloomsburg University, Bloomsburg, Pennsylvania, United States

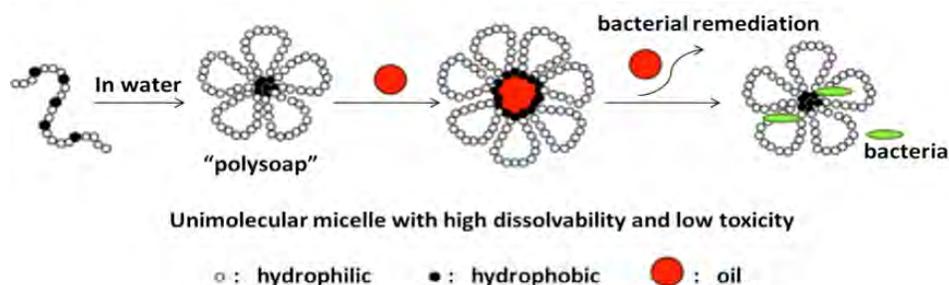
Sulfobetaine based zwitterionic polymers are a relatively new set of biocompatible polymers that exhibit nonspecific protein adsorption and antifouling properties. Their importance as biocompatible synthetic materials has been recognized by many researchers. Biocompatibility is generally defined by the absence of a foreign body response when a biomaterial is implanted into the body. The foreign body response is a series of cellular processes that occurs, for example, when a tissue is injured because of the implantation of a medical device. Improved biocompatibility limits adverse effects for implanted sensors and drug delivery devices. In this study, copolymers of acrylic acid (AA) and sulfobetaine methacrylate (SBMA) were synthesized with varying feed ratios from 50:50, 75:25 and 100:0 of SBMA:AA respectively. The copolymers were then purified using a novel mixed solvent precipitation method. Dried polymers were characterized by NMR and FTIR spectroscopy. Proton NMR spectroscopy was used to determine that the ratio between SBMA and AA in the final products is significantly different from the initial feed ratios, and this data are compared to other polymer preparation schemes that have been previously reported in the literature. Our analysis shows that these copolymers incorporate more SBMA than AA as compared to their given feed ratios. Future work for these materials will include the crosslinking of these water soluble copolymers into films so that their specific protein absorption may be studied *in vitro*.



## POLY 433: Structurally controlled anionic polysoaps to serve as dispersants for hydrocarbon uptake in aqueous media: Investigating the structural contributions of hydrophobic content, and molecular weight

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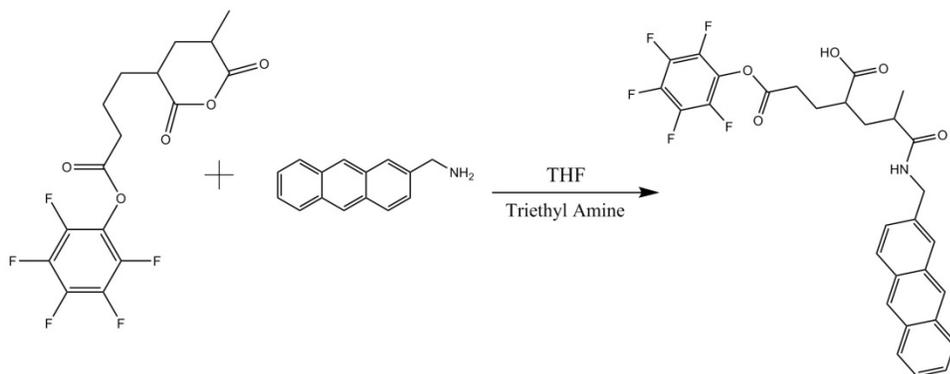
Conventional surfactants used for oil spill remediation are ineffective due to enormous dilution effects when applied in open sea waters. Developing a concentration-independent surfactant with lower toxicity is the main goal of this work. Anionic amphiphilic polymeric surfactants (“polysoaps”) have been prepared via RAFT polymerization resulting in controlled molecular weights and narrow molecular weight distributions. Initial studies have shown that polysoaps prepared by statistical copolymerization of the hydrophobic dodecyl acrylamide monomer and the hydrophilic AMPS monomer form micelles in water that can sequester pollutants. Several of the anionic polysoaps exhibit uni-molecular micelle behavior with increased capabilities to sequester hydrocarbon and up to 60x less cytotoxicity when compared to the small molecule surfactant analog, SDS. It is evident in these studies that hydrophobic content has an effect on polysoap properties. However, what remains to be studied is the molecular weight contribution on hydrocarbon uptake and micelle formation. This work investigates the hydrophobic content and molecular weight contribution to polysoap performance. By varying the composition and molecular weight of the polysoaps, the behavioral properties and concentration dependence of the micelle formation can be studied. The conceptual aspect of this approach, as well as the synthesis, characterization and behavioral properties of the uni- vs. multi-molecular micelles will be discussed.



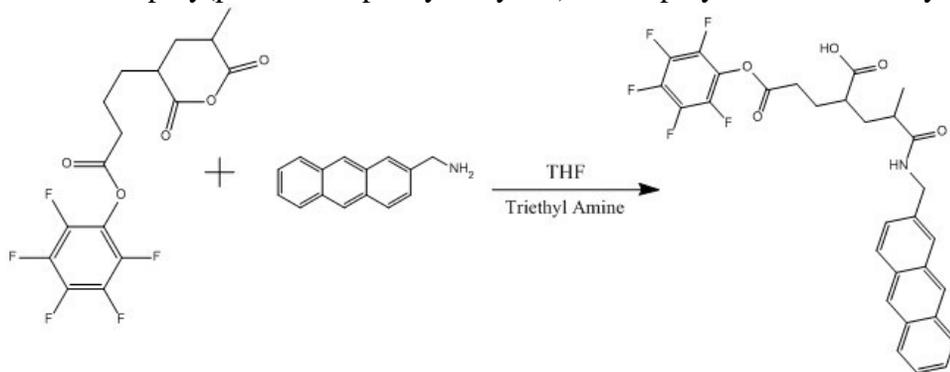
## POLY 434: Solid-state upconversion with CdSe nanocrystals and anthracene

**Gabriela Tablas**<sup>2</sup>, [gtabl001@ucr.edu](mailto:gtabl001@ucr.edu), Duane Simpson<sup>3</sup>, Xin Li<sup>3</sup>, Zhiyuan Huang<sup>1</sup>, Jesse Tamayo<sup>3</sup>, Ming Lee Tang<sup>1</sup>. (1) Department of Chemistry, UC Riverside, Riverside, California, United States (2) University of California Riverside, Riverside, California, United States (3) Chemical Sciences, University of California, Riverside, Moreno Valley, California, United States

Upconversion is the process of converting lower-energy photons to higher energy photons. Here, we study the upconversion of incoherent light using semiconductor nanoparticles to absorb the low energy photons, and molecular annihilators to emit the high energy photons. Two triplet excited states ‘annihilate’ each other to give one molecule in the ground state, and the other in its first excited singlet state, thus upconverting light. This platform can be used to inexpensively enhance the efficiency of solar cells. In this work, we use a poly(pentafluorophenyl acrylate) PFPA polymer to covalently bind anthracene. This creates a solution-processible thin film that allows controllable loading of anthracene and CdSe nanocrystals, while preventing spontaneous crystallization. This precludes undesirable phase separation that results in physical isolation of the nanocrystal light absorber from the anthracene annihilator. The design, synthesis and characterization of this thin film is vital to harnessing this hybrid upconversion platform in third-generation photovoltaic cells.



Scheme of poly(pentafluorophenyl acrylate) PFPA polymer to covalently bind anthracene.

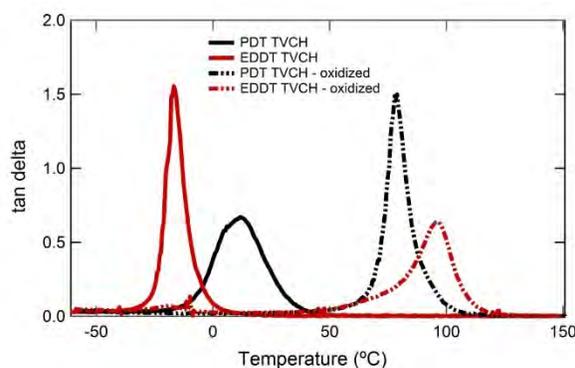
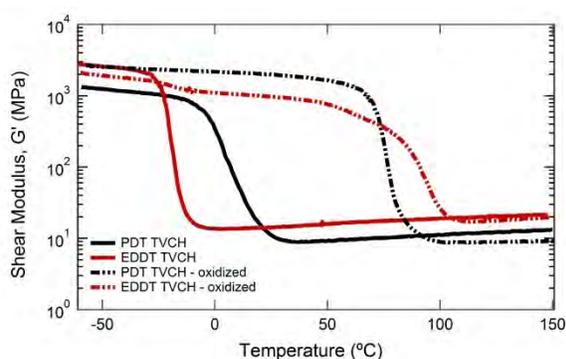


Scheme of poly(pentafluorophenyl acrylate) PFPA polymer to covalently bind anthracene.

## POLY 435: Influence of dithiol length on the thermomechanical properties of oxidized thiol-ene polymers

**Allie Dyson**<sup>3</sup>, [dyson.allie@gmail.com](mailto:dyson.allie@gmail.com), Benjamin Gardner<sup>5</sup>, Alex Spiride<sup>6</sup>, Radu Reit<sup>1</sup>, Benjamin R. Lund<sup>4</sup>, Walter Voit<sup>2</sup>. (1) Bioengineering, The University of Texas at Dallas, Garland, Texas, United States (2) UT Dallas, Richardson, Texas, United States (3) University of Texas at Dallas, Dallas, Texas, United States (4) Dept of Chemistry MS RL 10, University of Texas at Dallas, Richardson, Texas, United States

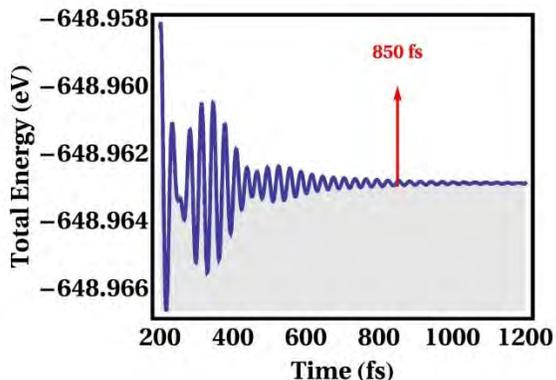
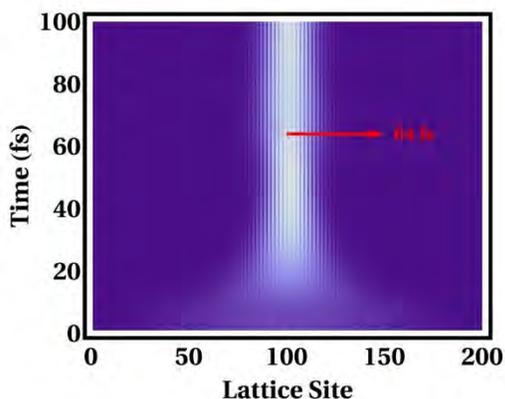
Thiol-ene networks have a broad range of applications, including dendrimer synthesis and biosensing. When exposed to an oxidizing agent, the thioether linkage in these networks becomes oxidized to a sulfoxide or sulfone. The length and structure of the thiol monomer will influence the thermomechanical properties seen in the oxidized thiol-ene polymer in the form of an increased glass transition temperature ( $T_g$ ). Our work explored the thermomechanics of networks using various lengths of dithiol monomers to observe the effect of increasing thioether molarity of the degree of increase in the  $T_g$ . Using the alkene 1,2,4-Trivinylcyclohexane (TVCH) and the thiol monomers 1,3-Propanedithiol (PDT) and 2,2'-(Ethylenedioxy)diethanethiol (EDDT), we created 1mm thick films and sulfonated them using 30% hydrogen peroxide. Upon this oxidization, dynamic mechanical analysis was used to determine thermomechanical differentiation between the networks as shown by the respective peaks in their tangent deltas. Results show that PDT TVCH has a  $T_g$  around 80°C, an increase of 65°C from the initial  $T_g$  of 15°C. Meanwhile, EDDT TVCH has a  $T_g$  around 100°C, an increase of 110°C from the initial  $T_g$  of -10°C. From this data, increased thioether molarity appears to lead to a decreased  $T_g$  due to the oxidation of the sample. Through modifying the thiol monomer used in the polymer, we can modify the thermomechanical properties associated with that polymer. A wide range of thiols can be used in an oxidized thiol-ene polymer to see if its thermomechanical properties are suitable for future usage in biological, chemical, and medical applications.



## POLY 436: Localization and relaxation of singlet exciton formation in conjugated polymers under photoexcitation

**Cong Wang**<sup>2,3</sup>, wangimagine@gmail.com, Li-qing Zhuang<sup>3</sup>, Ren-Ai Chen<sup>4</sup>, Sheng Li<sup>3</sup>, Thomas F. George<sup>1</sup>. (1) Office of the Chancellor, University of Missouri-St. Louis, Saint Louis, Missouri, United States (2) chemistry, university of illinois at chicago, CHICAGO, Illinois, United States (3) Zhejiang Normal University, Jinhua, Zhejiang, China (4) Fudan University, Shanghai, China

This paper employs a molecular dynamics approach to uncover the time profile of exciton formation, which can be divided into two stages: localization of electron-hole pairs and relaxation process (nuclear and electronic). Under photoexcitation, an electron-hole pair is formed by an electronic transition, and the pair in turn becomes localized through the electron-lattice interaction, which triggers the total energy to shift violently and oscillate. The oscillation during the first 40 fs induces the excitation to step into the second stage, i.e., relaxation. After the relaxation process of about 850 fs, the total energy, lattice energy, and electron energy reach certain values whereas the lattice configuration and electron remain localized, indicating the formation of a singlet exciton.



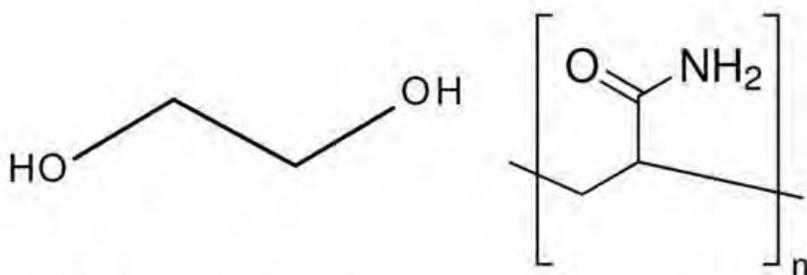
## POLY 437: Ballistic properties of Kevlar-shear thickening fluid in combination with polymeric networks

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This study explores the combination of Kevlar fabric with shear thickening fluids (STF's) maintained in polymeric networks. Previous work with STF's eventually found that the solvent was not required indicating the enhanced protection from that body of work is not due to STF's. The question remains as to whether or not STF's can increase ballistic protection. We are examining STF's in combination with various polymerized acrylamide monomers in several different solvents (ethylene glycol, diethylene glycol, diethylene glycol monoethyl ether and glycerol) to ensure the solvent remains in the treated fabrics. Preliminary results suggest that several of these solvents may prove useful for maintaining solvents in the STF's. Targets are made from 5 in<sup>2</sup> treated layers of Kevlar fabric which are then heat sealed into HDPE bags prior to ballistic testing. This is followed by placing the target on ballistic gel prior to firing. Results of the testing done to date will be presented.

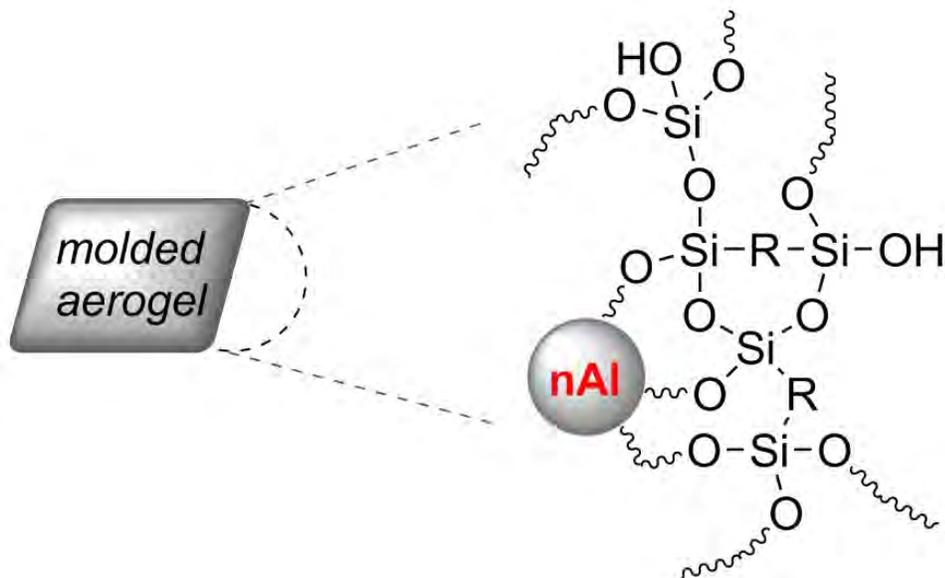


Acrylamide polymerized in ethylene glycol will provide the foundation of the sheer thickening fluids.

## POLY 438: Metalized fluorosilicone aerogel thermites for highly energetic materials

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Previous investigations by our laboratory have focused on utilizing oligomeric perfluoropolyether and nanometer-sized aluminum (nAl) for energetic composites. Being that silicon has a larger enthalpy of formation with fluorine and larger energy density than aluminum, the incorporation of silicon into an energetic composite may serve as a better alternative to current formulations. Furthermore, the use of silicon as a fuel source in highly energetic materials is a largely uninvestigated field. In this work, a fluorinated-silane monomer was prepared and used in the synthesis of fluorinated silicon based aerogels. By incorporating nAl into the framework of the aerogel, the effects on energetic output of the metalized thermite could be studied. The synthesis, characterization, and properties of the metalized fluorosilicone aerogel thermites will be presented.



## POLY 439: Solution processable dioxithiophene polymers as active materials in aqueous and organic supercapacitors

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Supercapacitors are devices to use in situations where high charge/discharge rates and long cycle life are important. In particular, electrochemical supercapacitors (ESC) are devices that bridge the gap between batteries (high energy, low power) and capacitors (high power, low energy).<sup>1</sup> Commercially available ESCs store less charge than batteries as they are limited by storing charge electrostatically at the electrode-electrolyte interface. To increase the charge storage capability while minimizing the amount of active material needed, we focus on using electroactive polymers as active materials in ESCs. They are capable of storing charge both at the electrochemical double layer and in the film itself through faradaic charge transfer (pseudocapacitance). Our current efforts are focused on optimizing soluble co-polymers containing 3,4-propylenedioxythiophene (ProDOT) and 3,4-ethylenedioxythiophene (EDOT) units that can be coated onto an electrode with a variety of roll-to-roll compatible methods. ProDOT:EDOT<sub>2</sub> can be functionalized with different side-chains to tune solubility and electrolyte compatibility. This polymer is synthesized with tetraester side-chains (A in Fig. 1) that make it organic soluble and compatible for devices with propylene carbonate-based (PC) electrolytes. If this polymer is hydrolyzed to a polyelectrolyte form it becomes water-soluble (B in Fig. 1). This is especially attractive for safer processing conditions and reducing environmental impact.<sup>2</sup> Treating the films with an acid renders the films solvent resistant (C in Fig. 1), allowing for devices to be made using both organic and aqueous electrolytes. We show that by optimizing side chain and electrolyte, we can fabricate solution processable ESCs with subsecond discharge rates while maintaining stable capacitance.

1. Österholm, A.M.; Shen, D. E. et al. *ACS Appl. Mater. Interfaces*. 2013, 5, 13432.
2. Ponder, J. F.; Österholm, A.M.; Reynolds, J. R. submitted to *Adv. Mater.* 10/2015

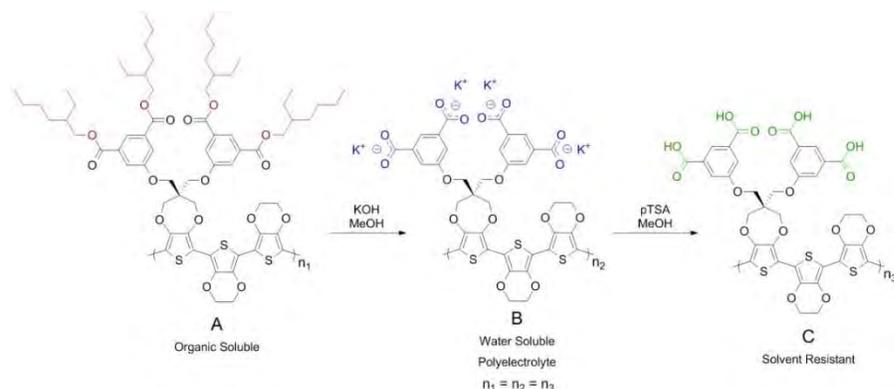
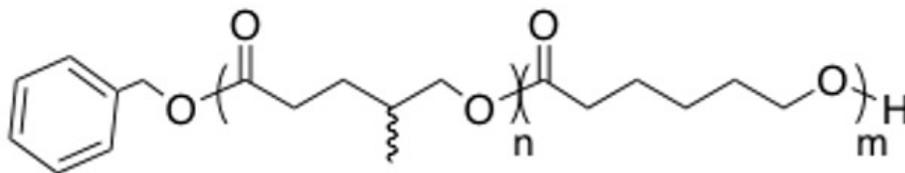


Figure 1 – ProDOT:EDOT<sub>2</sub> Structures

## POLY 440: Sustainable copolymers with tailored thermal properties

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(1) *Chemical and Biomolecular Engineering, Tulane University, Newberg, Oregon, United States* (2) *University of Minnesota, Minneapolis, Minnesota, United States* (3) *Chemistry, University of Minnesota, Magnolia, Minnesota, United States*

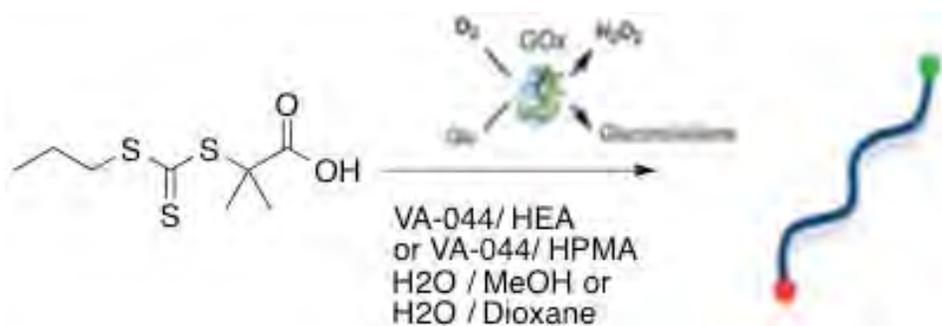
A major challenge facing modern polymer scientists is how to make affordable high-performance polymers that are environmentally benign. Poly(lactide), is both biorenewable and biodegradable, and has achieved great commercial success. However, its thermal and mechanical properties limit its potential uses. Previous work has shown poly( $\epsilon$ -caprolactone-co- $\epsilon$ -decalactone) to have tunable thermal properties, but the high cost of the  $\epsilon$ -decalactone monomer inhibits its commercial viability. My work investigates poly( $\gamma$ -methyl- $\delta$ -valerolactone) homopolymers and poly( $\gamma$ -methyl- $\delta$ -valerolactone-co- $\epsilon$ -caprolactone) (P( $\gamma$ MVL-co-CL)) statistical copolymers as potential new sustainable materials. These polymers can be produced in high yield with no byproducts and minimal waste, using bulk, room temperature polymerizations. Depending upon its composition and the sample preparation, P( $\gamma$ MVL-co-CL) can be either amorphous or semicrystalline with a range of possible melting temperatures. Interestingly, the thermal properties of the P( $\gamma$ MVL) homopolymers depend upon tacticity. Atactic P( $\gamma$ MVL) is amorphous whereas isotactic P( $\gamma$ MVL) is semicrystalline with improved thermal stability relative to caprolactone. The ability to tailor the thermal profiles of these sustainable polymers makes them extremely attractive for a wide variety of potential commercial applications.



## POLY 441: Enz-RAFT polymerization in continuous flow

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Reversible addition fragmentation chain transfer (RAFT) radical polymerization is an effective and reliable way to synthesize polymers of a specific chain length. RAFT can be performed under both batch and flow conditions - however ambient oxygen can interfere with the reaction by scavenging radicals during polymer propagation. Glucose oxidase (GOx) has been used as a degassing agent during RAFT polymerization under batch conditions to remove oxygen ("Enz-RAFT") at low concentrations. Enz-RAFT has now been deployed under continuous flow conditions using hydroxyethyl acrylate and 2-hydroxypropylmethacrylamide in order to increase the efficiency of Enz-RAFT polymerization.



## POLY 442: Neutron reflectivity studies of polymer multilayers prepared by sequential spin coating

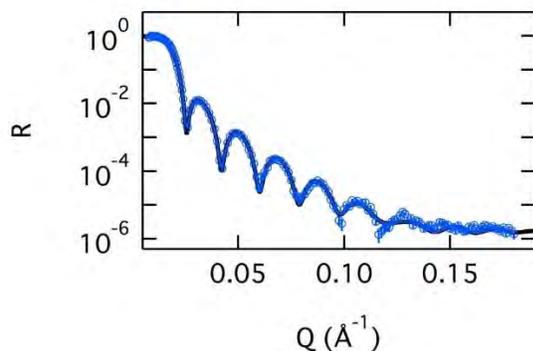
**Thomas A. Seery**<sup>1</sup>, [seery@mail.ims.uconn.edu](mailto:seery@mail.ims.uconn.edu), David Schwärzle<sup>3</sup>, Oswald Prucker<sup>3</sup>, Jürgen Rühle<sup>3</sup>, Mark D. Dadmun<sup>2</sup>. (1) Univ of Connecticut, Storrs Mansfield, Connecticut, United States (2) Univ of Tennessee, Knoxville, Tennessee, United States (3) IMTEK, University of Freiburg, Freiburg, Germany

Schuh<sup>1</sup> and co-workers have recently reported on a general procedure for preparing robust multilayered polymer structures using C-H insertion reactions. Designed polymer multilayers can be prepared from sequential steps of spincoating followed by thermal or photochemical crosslinking steps. This approach is comparable to layer by layer deposition or Langmuir Blodgett methods in that multilayers are formed but should generalize the preparation of such structures to the set of polymers containing C-H bonds. The crosslinking approach has the advantage that chemical bonds are formed across the interfaces leading to superior adhesion between layers.

In the current study we have prepared thin multilayer films containing pendant benzophenone moieties with layers that are alternately hydrophilic or hydrophobic. The benzophenone groups are capable of UV activated crosslinking. Neutron reflectivity was used to study the importance of crosslinking to interlayer mixing. In order to generate contrast between layers, a PMMA copolymer was prepared from deuterated (d8) MMA monomer and 5% comonomer containing the benzophenone photocrosslinker. The hydrophilic polymers were selected from a series of copolymers containing dimethylacrylamide, acrylic acid and the benzophenone crosslinking moiety.

Multilayers were prepared on thick silicon wafers by application of ca. 1 mg ml<sup>-1</sup> solutions of polymer and thicknesses checked by ellipsometry. Film robustness was demonstrated as films could be removed by simply spinning the wafer with solvent prior to UV exposure. After UV exposure, multiple attempts to remove the layers in this manner were unsuccessful. Neutron reflectivity experiments were performed at NIST on the NG7 beamline.

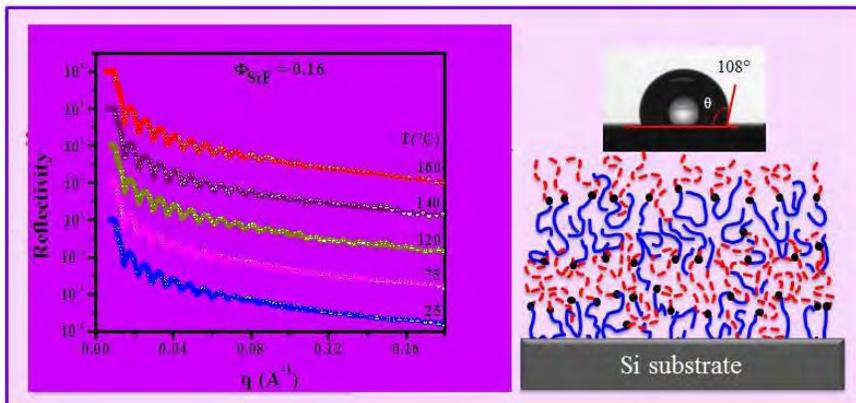
1. Schuh, K., Prucker, O. and Rühle, J. (2013), Tailor-Made Polymer Multilayers. *Adv. Funct. Mater.*, 23: 6019–6023. doi: 10.1002/adfm.201300846



## POLY 443: Semifluorinated diblock copolymer under confinement: A neutron reflectivity study

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Fluorinated segments in copolymer impact their bulk structure and interfacial properties. Here we probe the interfacial response of the thin films of polytrifluoro propyl methyl siloxane-*b*-polystyrene to temperature change using atomic force microscopy, contact angle measurement and neutron reflectometry. Thin films with volume fractions of the fluorinated block ranging from 0.03 to 0.46 were annealed at the temperatures above the glass transition temperature of the diblock. Surface induced layering was observed for all volume fractions of fluorinated block with the air interface rich with the fluorinated segments and the substrate interface was dominated by protonated block. Surprisingly the film did not dewet even at the temperature significantly higher than that of the diblock.



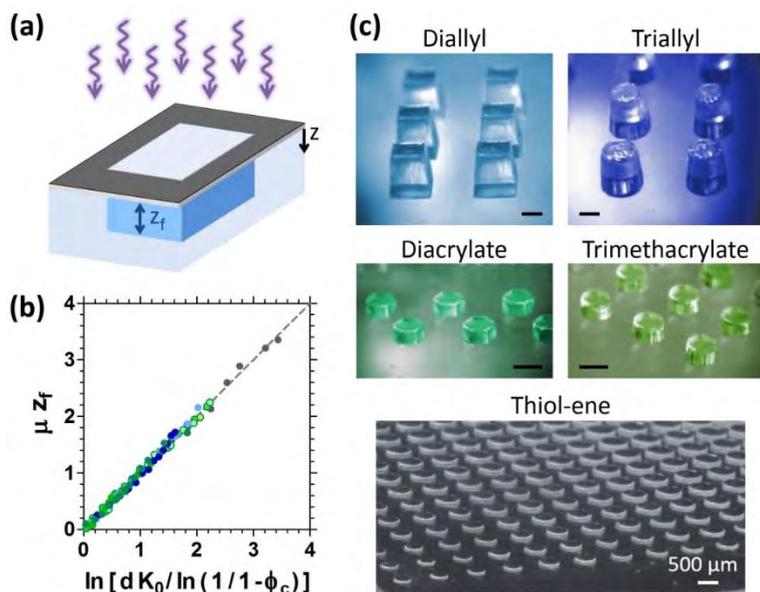
Temperature responsive semifluorinated interfaces as reflected in neutron reflectometry and contact angle measurements.

## POLY 444: Unified approach for polymeric patterning via controlling the propagation of frontal photopolymerization waves

**Alessandra Vitale**, *a.vitale@imperial.ac.uk*, **Matthew G. Hennessy**, **Omar K. Matar**, **Joao T. Cabral**. *Department of Chemical Engineering, Imperial College London, London, United Kingdom*

Patterning of soft matter provides an exceptional route for the generation of micro/nanostructured and functional surfaces. We describe a general, simple and exceptionally well-controlled patterning approach for photocurable monomers based on frontal photopolymerization (FPP). FPP is a significant case of photopolymerization reaction, where illumination results in the development of a solidification front which propagates in the form of a planar wave, invading the monomer bath.

The general patterning strategy for FPP presented in this work is applicable to the fabrication of polymeric structures with prescribed dimensions set by the illumination field. This approach holds for a range of radical photopolymerizing systems, including thiol-ene and acrylic monomers. The factors governing the planar solidification process, including front position, profile shape and thermal effects, are explicitly investigated and quantified. We find the FPP process to be controlled by tuning selected photopolymerization parameters, such as monomer chemistry, optical properties, time and intensity of irradiation, in a remarkably general and simple fashion. A minimal model accurately describes the frontal solidification kinetics and we propose a unified mathematical expression for patterning via FPP. Building on this understanding, we design and fabricate polymeric patterns with well-defined dimensions from representative radical photopolymerizing systems using our predictive FPP approach.

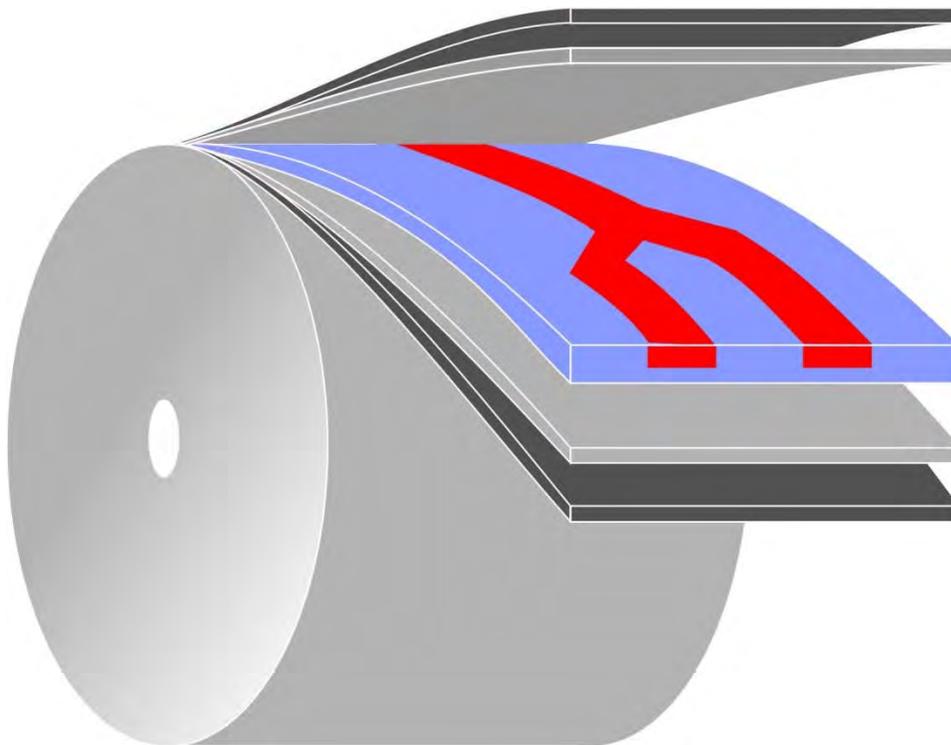


(a) Schematic of the FPP setup showing the photopolymerization front propagation from the UV illuminated surface into the monomer medium, and a photomask defining the lateral pattern shape. (b) Master curve for the prediction of final polymeric pattern thickness. (c) Examples of patterns, obtained using FPP predictive parameters, for different radical polymerizing systems.

## POLY 445: Thin surface-attached polymer networks for planar optronic system

*Martin Körner, Anne-Katrin Schuler, Raimund Rother, Michael Henze, Oswald Prucker, Claas Müller, **Jürgen Rühle**, ruehe@imtek.uni-freiburg.de. Imtek Univ of Freiburg, Freiburg, Germany*

Optronic systems entirely produced from polymers may serve as sensor foils for many applications such as structural monitoring. It is crucial for such applications to control the optical properties of all materials in use but it is of equal importance to master all surfaces and interfaces involved in such systems. These can be numerous: Optical elements like light sources, wave guides or sensors need to be fixed on substrate or carrier foils, claddings need to wrap waveguides, connections join different elements and protective coatings shield all functional units from scratches or finger prints. We have developed chemistries to generate surface-attached polymer networks on other polymers using polymers with thermally or photochemically reactive groups for C,H insertion crosslinking (CHIC) reactions. The presentation will describe how these materials are used to generate waveguides and other optically active units such that optical properties can be varied over a fairly wide range. In addition, we will show that C,H insertion reactions can also proceed across interfaces such that a strong adhesion between the various layers can be assured by basically generating monolithic multilayer assemblies. Aside from these practical implications we will also present theoretical studies that allow us to understand the crosslinking reactions and to predict the performance of such materials in such applications.

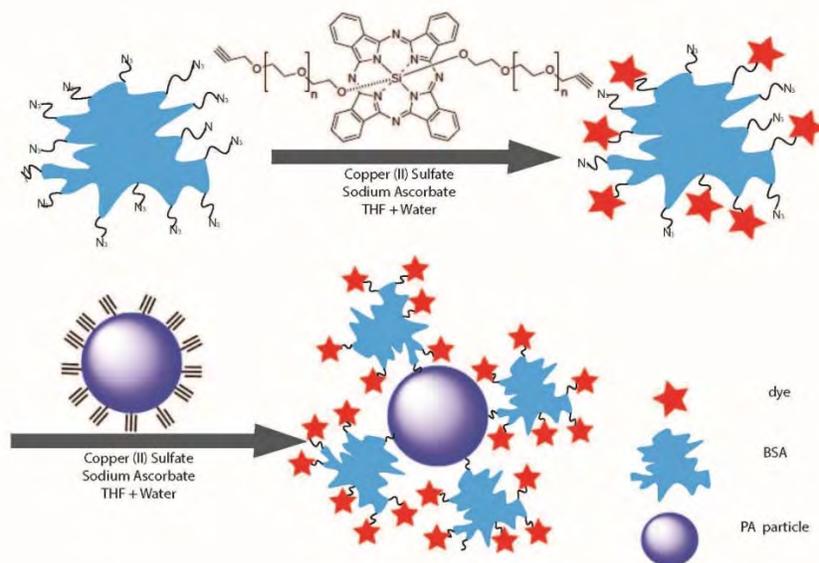


Schematic representation of a multilayer optical foil.

## POLY 446: Reducing background noise in near-infrared medical imaging: Routes to activated fluorescing through surface modification of colloidal particles

Mary Burdette<sup>2</sup>, Iurii Bandera<sup>2</sup>, **Stephen H. Foulger**<sup>1</sup>, [foulger@clemson.edu](mailto:foulger@clemson.edu). (1) Clemson University, Anderson, South Carolina, United States (2) Materials Science, Clemson University, Clemson, South Carolina, United States

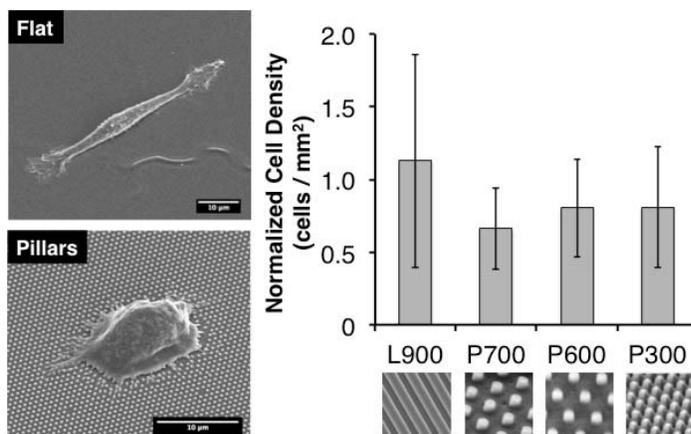
The majority of organic near-infrared emitters utilized in diagnostic and therapeutic imaging exhibit low quantum yields when optically excited. In an effort to reduce the background noise and to localize the emission, it is advantageous to “activate” the emission only in regions of interest. To this end, a colloidal nanoparticle platform was developed that can facilitate the transfer of quenched NIR fluorophores to the interior of cells and only within the cells is the emission permitted. This platform is demonstrated with sub-100 nm poly(propargyl acrylate) (PA) nanoparticles that have been surface modified with an azide modified bovine serum albumin (azBSA). The azBSA was covalently attached to the particles through a copper catalyzed azide alkyne Huisgen cycloaddition (i.e. “click” transformation). To the azBSA, alkyne modified silicon phthalocyanine (akSiPc) fluorophores were attached through a click reaction. As a free molecule in phosphate-buffered saline (PBS), the akSiPc exhibited a 780 nm emission with a 630 nm excitation, though once attached to the PA particles via the azBSA, the emission was quenched. The emission of the akSiPc could be recovered with the incubation of the PA/BSA/akSiPc particles with trypsin, a protease which cleaves peptide chains. The trypsin digested the azBSA and “freed” the quenched akSiPc. The PA/BSA/akSiPc particles were incubated with human non-small cell lung cancer cells (A549) and live cell scanning confocal microscopy at varying time points was employed to study the particles uptake into the cells and subsequent emission activation. It was speculated that particles localized in the lysosomes of the cells where the azBSA was digested, releasing the fluorophores.



## POLY 447: Controlling cell adhesion on device surfaces by nanotopography

**Elena Liang**<sup>1</sup>, [eiliang@uci.edu](mailto:eiliang@uci.edu), Emma Mah<sup>2</sup>, Susan Wu<sup>2</sup>, Mary Nora Dickson<sup>2</sup>, Michelle Digman<sup>3,2</sup>, Albert F. Yee<sup>2,1</sup>. (1) Biomedical Engineering, University of California, Irvine, Irvine, California, United States (2) Chemical Engineering and Materials Science, University of California, Irvine, Irvine, California, United States (3) Biomedical Engineering, University of California, Irvine, Irvine, California, United States

The ability to control cell adhesion on material surfaces is critical for integration of medical implants. Of particular interest to our research is developing an understanding of the role of surface topography in cell adhesion in order to engineer the surfaces of implants without having to chemically modify them. Hu *et al.* showed that nanopillars of varying aspect ratios and surface energies have strong effects on cell morphology, discouraging cell spreading (Hu *et al.* 2010). Kong *et al.* discovered that human embryonic stem cells grown on nanopillar structures have a significantly reduced number of focal adhesions per cell and concordantly exhibit increased cell motility on the nanopillars (Kong *et al.* 2013). Based on these findings, we hypothesize that the pillar nanostructures would prevent cells from adhering. We fabricated a library of nanopillars of different width and spacing on poly(methylmethacrylate) (PMMA) films by nanoimprint lithography using commercially available silicon and nickel molds. Nanopillars were characterized with scanning electron microscopy and atomic force microscopy. To evaluate cell adhesion, we counted the number of fibroblasts adhering to flat PMMA, nanolines and the nanopillars, and examined cell morphology on each pattern. We examined the focal adhesions using fibroblasts transfected with green fluorescent protein (GFP) tagged paxillin, a major protein in the focal adhesion complex. After 24 hours, fewer cells adhered on nanopillars compared to flat PMMA. Cells adopted different morphologies, indicating changes in adhesion dynamics. Fibroblasts show a spread, spindle-shaped morphology on the flat film while the cells on pillars are smaller and equiaxed. In addition, cells on pillars have increased motility compared with cells on flat PMMA and nanolines. Our study shows that nanopatterns in the 100-500 nm range affect adhesion dynamics and can be used to modulate cell adhesion to surfaces of implants.

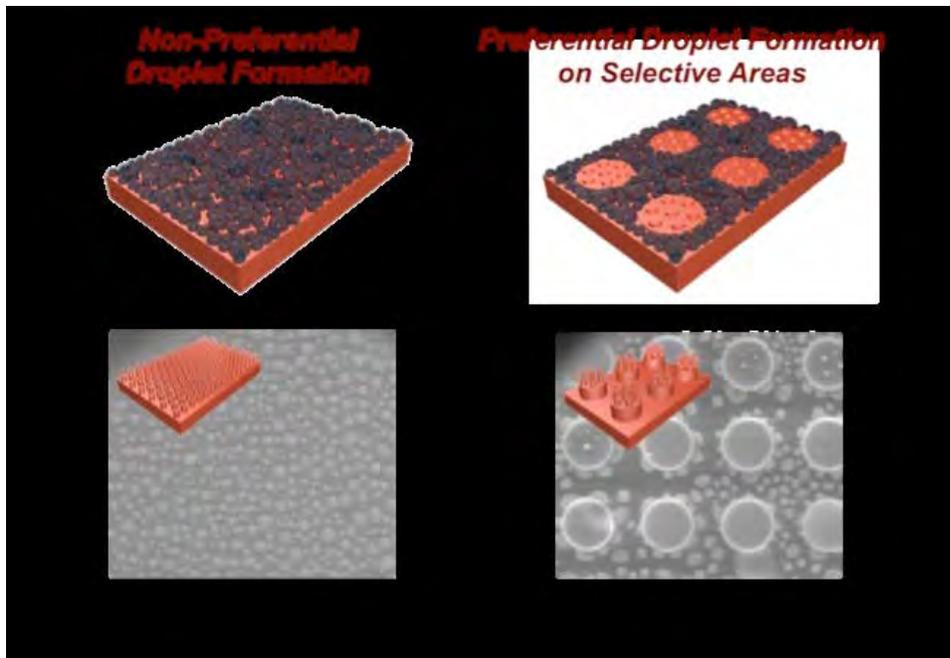


Fewer cells adhered on the nanopillared surfaces compared to flat PMMA. Fibroblasts are spindle-shaped on the flat film while those on pillars are smaller and equiaxed.

## POLY 448: Spatially selective nucleation and growth of water droplets on hierarchically patterned polymer surfaces

Younghyun Cho, Tae Soup Shim, **Shu Yang**, [shuyang@seas.upenn.edu](mailto:shuyang@seas.upenn.edu). University of Pennsylvania, Philadelphia, Pennsylvania, United States

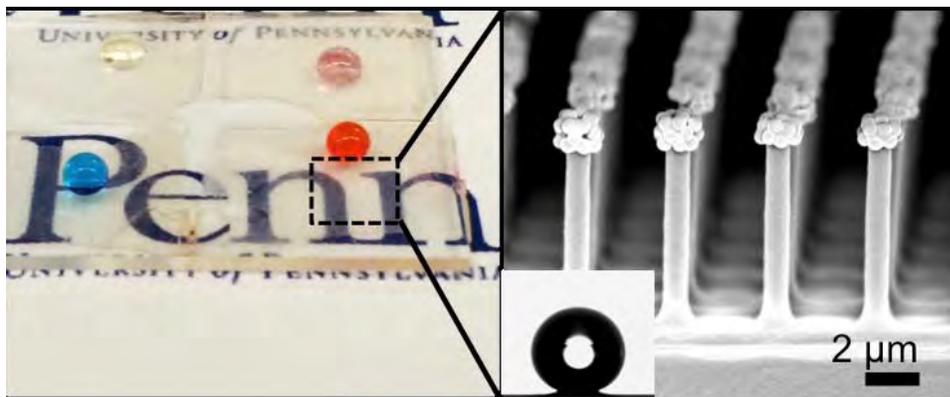
Hierarchical polymer pillar arrays are fabricated using a hierarchically porous anodized aluminum oxide (AAO) membrane as a template. First, a microporous epoxy membrane (pore diameter of 10 - 100  $\mu\text{m}$ ) is placed on an aluminum plate as the anodization mask to direct AAO nanopore (300 nm in diameter) formation within the micropores. The hierarchical AAO template is then replica molded into polyurethane acrylate and epoxy. The combination of micro- and nanostructures dramatically increases the wettability contrast and surface roughness vs. the non-patterned regions. On such surfaces, water droplets are found to nucleate and grow selectively in the grooves between the microposts as the vapor pressure increases. In contrast, surfaces consisting of microposts or nanopillars only do not show such selectivity. Since the roughness of nanopillars is much smaller than the initial water droplet condensed from atmosphere ( $\sim 1 - 40 \mu\text{m}$ ), they can prevent the nucleation of water droplets within or on top of nanopillars. In addition, because the nanopillars sit only on top of the microstructures, thus, they are isolated from each other, which further prevent water nucleation. Importantly, the spatial selectivity of water nucleation and growth demonstrated here is achieved solely by structural hierarchy on a chemically homogeneous surface.



## POLY 449: Transparent and superamphiphobic surfaces from mushroom-like polymer micropillar array

Su Yeon Lee, Yudi Rahmawan, **Shu Yang**, [shuyang@seas.upenn.edu](mailto:shuyang@seas.upenn.edu). University of Pennsylvania, Philadelphia, Pennsylvania, United States

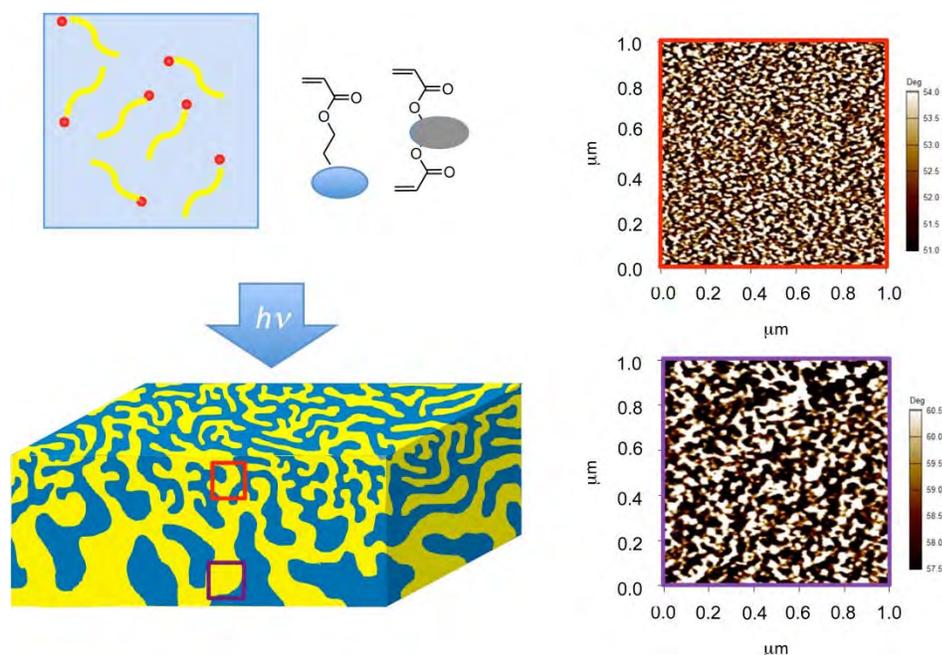
Transparent, superamphiphobic surfaces that repel both water and oils are prepared from mushroom-like micropillar arrays consisting of nanoparticles only at the top of the pillars by controlled compartment filling of silica nanoparticles into the bottom of the pillars by controlled compartment filling of silica nanoparticles into the bottom of the poly(dimethylsiloxane) (PDMS) mold, followed by infiltration of epoxy and UV curing. Since silica nanoparticle decorated pillar heads are more resistant to O<sub>2</sub> plasma than the polymer pillars, we can precisely control the head size of micropillars and nanoroughness on top of the pillar heads by varying the O<sub>2</sub> plasma time. The combination of nanoroughness and mushroom-like micropillars leads to superhydrophobicity and oil repellency to different organic solvents. High transparency is achieved when increasing the spacing ratio of micropillars. Last, we demonstrate anisotropic wetting on the hierarchical surface can be achieved by combining photolithography, replica molding, and self-assembly techniques.



## POLY 450: Unique gradient nanostructure formation in photo-cured coatings via photo-driven controlled radical polymerization

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Photo-induced controlled radical polymerization has attracted recent attention for on-demand on/off control of polymerization. Organo-catalyzed iodine-transfer controlled radical polymerization is a promising approach to obtain colorless polymers with low polydispersity. The polymeric dormant containing stable C-I endgroup was prepared and utilized for chain extension/crosslinking reaction under UV irradiation. Polymerization-induced microphase-separation from miscible mixture of polymeric dormant and mono- and bi-functional acrylate monomers yielded bicontinuous morphology. Unique gradient nanostructure in thickness evolved via controlled photo-curing was investigated by cross-sectional AFM and TEM tomography. Metal (oxide) nanoparticles were selectively integrated into such well-defined nanostructures and their optical- and electronic properties will be discussed.



**Figure.** Bicontinuous and gradient domain formation via controlled photo-curing. Cross-sectional AFM phase images for top and bottom of the coating.

## POLY 451: Characterization of solid-supported ultrathin films and molecular interactions using MP-SPR

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Surface Plasmon Resonance (SPR) has been used already for a few decades for label-free detection and characterization of biochemical kinetics and affinities of many different types of analytes. However, the physical phenomenon is not limited to biochemistry, but is applicable to other nanoscale characterization of thin films [1]. Multi-parametric surface plasmon resonance (MP-SPR) is a new approach to the physical phenomenon, which utilizes full SPR angular spectral measurement and allows also new type of thin film characterization methods to be used.

MP-SPR can be used to characterize ultrathin nanoscale films for both thickness and refractive index with two methods. It is possible to characterize the films either by measuring them in two different media with high  $R_I$  difference, such as air and water [1,2], or by measuring the films with two or more wavelengths of light [2,3]. The method effectiveness has been extensively demonstrated using different ultrathin films systems [2-4].

Stearic acid (SA) LB films showed approximately  $2.5 \pm 0.2$  nm thickness with both 2M and 3W methods, and linear increment with layer number. Similarly the polyelectrolyte multilayer of polystyrenesulfonate and polyallylaminehydrochloride (PSS:PAH) was characterized to grow in 3-3.5 nm steps per layer pair. Lipid bilayers spread from vesicles showed typical thickness of approximately 5 nm. The refractive index of all studied thin films correlated well to earlier literature values. Ex-situ depositions of nanofibrillated cellulose (NFC) by spin coating were characterized by the 2W method to form  $14 \pm 3.4$  nm layers.

Thus the MP-SPR based characterization methods for ultrathin films appear to be effective, especially for applications requiring both measurement of the film properties and interactions of different compounds with the film.

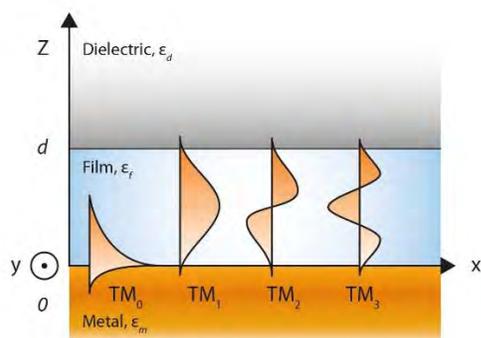
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[4] Kontturi et al., J. Mater. Chem. A, 2013, 1, 13655-13663

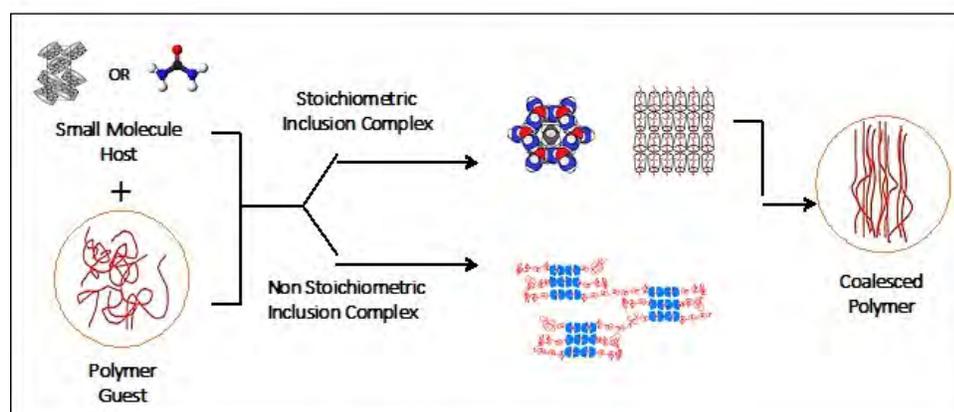


## POLY 452: Restructuring polymers *via* nano-confinement and subsequent release

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### Abstract

During the past several years my students and I have been utilizing small-molecule hosts [cyclodextrins and urea] to nanostructure polymers. This is accomplished by first forming non-covalently bonded inclusion complexes (ICs) between these small-molecule hosts and guest polymers, followed by the careful removal of the host molecule crystalline lattice to obtain a coalesced bulk polymer. We have repeatedly observed such coalesced polymer samples to behave distinctly from those produced from their solutions or melts. Coalesced amorphous homopolymers exhibit higher glass-transition temperatures, while crystallizable coalesced homopolymers evidence higher melting and crystallization temperatures, and sometimes different crystalline polymorphs. When ICs are formed with block copolymers or with two or more different homopolymers the resulting coalesced samples can evidence intimate mixing between the copolymer blocks or between entire homopolymer chains, respectively. All the distinct behaviors observed for polymers coalesced from their ICs is a consequence of the structural organization of polymer-host-ICs. Polymer chains in IC crystals are confined to occupy narrow diameter (~0.5 – 1.0nm) channels formed by the crystallization of the small-molecule hosts around the guest polymers. This results in the high extension and separation of guest polymer chains, which leads to unique behaviors for bulk coalesced polymer. In addition, when excess polymer is used to form ICs with CD hosts, non-stoichiometric [(n-s)] ICs, with partially un-included chains, are formed. We will describe several applications for bioabsorbable-biodegradable polymers coalesced from their ICs and for (n-s)-polymer-CD-ICs.



Formation of and release of guest polymers from CD- and U-ICs

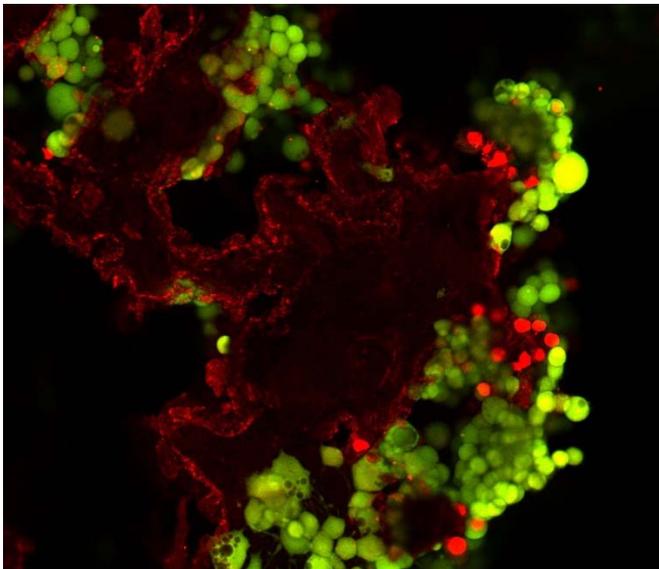
## POLY 453: Scaffolds of chitosan grafted onto poly(3-hydroxybutyrate)

**Roberto Olayo**<sup>1</sup>, *oagr@xanum.uam.mx*, **Maykel Gonzalez-Torres**<sup>2</sup>, **Rogelio Rodríguez-Talavera**<sup>2</sup>, **Rosa M. Toral-Morales**<sup>1</sup>, **Susana Vargas-Muños**<sup>2</sup>, **Juan Morales-Corona**<sup>1</sup>. (1) *Física, Universidad Autónoma Metro, Mexico Df, D.F., Mexico* (2) *Ingeniería Molecular, CFATA,, Universidad Nacional Autónoma de Mexico , Queretaro, Queretaro, Mexico*

Tissue Engineering scaffolds consist of a main support and a good surface interaction with the host mainly through the cell anchor. Polyesters are biodegradable polymers with different biodegradation rate and with good support properties, but not to good cellular interaction. Chitosan is a polymer with good cell interaction because of the primary amines in its main chain but stiff and breakable. In this work chitosan (CS) was grafted into poly(3-hydroxybutyrate) (PHB) to produce a material with good biodegradability and good cell interaction. Scaffolds of this material were made by porogen leixidation and cell cultures were made on the material to test the viability of the cells.

The synthesis of the PHB grafted with CS (PHB-g-CS) was done by irradiating the two polymers at the same radiation level. <sup>60</sup>Co gamma-ray source was used at a dose of about 12 kGy, with 2 kGy/h dose rate measured with a Fricke dosimeter. Scaffold was prepared by the addition and mixing of 0.1 g of PHB-g-CS powder, sodium acid carbonate (NaHCO<sub>3</sub>) and polyurethane (polyester hydroxylated resin/polyisocyanate 1/4 (v/v)). Cell cultures were characterized with optical microscopy and confocal microscopy.

Chitosan was successfully grafted onto poly(3-hydroxybutyrate) by radiation-induced polymerization. FTIR confirm the successful grafting. The freeze-dried broken scaffolds showed that the size of the pores ranges from 100 to 250 μm, with porosity and mean pore size of 80 % and μm respectively. Cell culture of hepatic (HEPG2) and a hybrid of rat neuroblastoma and glioma (NG 108-15). Cells showed good proliferation and viability.

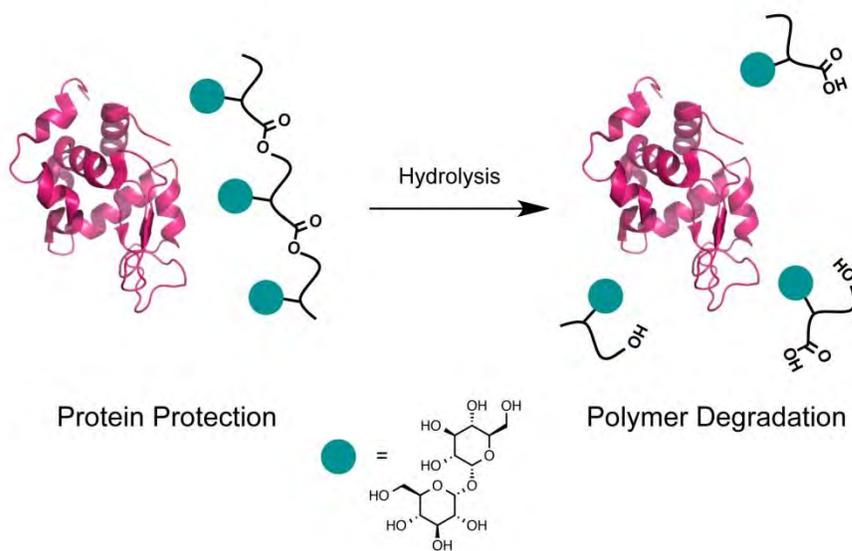


Cell viability by the calcein AM/ethidium homodimer method.

## POLY 454: Biodegradable trehalose glycopolymers for protein stabilization

**Emma Pelegri-O'Day**, [epelegrioday@gmail.com](mailto:epelegrioday@gmail.com), Uland Lau, Heather D. Maynard.  
UCLA, Los Angeles, California, United States

Protein-polymer conjugates combine diverse therapeutic applications with high biological specificity and are widely used in medicine. However, protein instability during transport, storage, and delivery increases costs for both patients and researchers. Additionally, bioaccumulation of synthetic polymers may lead to long-term toxicological effects upon repeated dosage. We have previously synthesized polymers containing trehalose side-chains, which stabilize proteins against environmental stressors. Here, we describe the redevelopment of these bioinspired polymers to contain a hydrolytically degradable ester in the backbone, resulting in biodegradable trehalose glycopolymers. These polyesters can be used as additives or protein-reactive end-groups may be installed for covalent conjugation to relevant proteins. Retention of protein activity was then measured after subjection to environmental stressors. Additionally, cytotoxicity of the polymer and degradation products were measured in cell culture. Synthesis of polymers and conjugates, ability to retain protein activity in the presence of stress, and cytotoxicity, as well as their relevance to next-generation protein-polymer conjugates will be discussed.



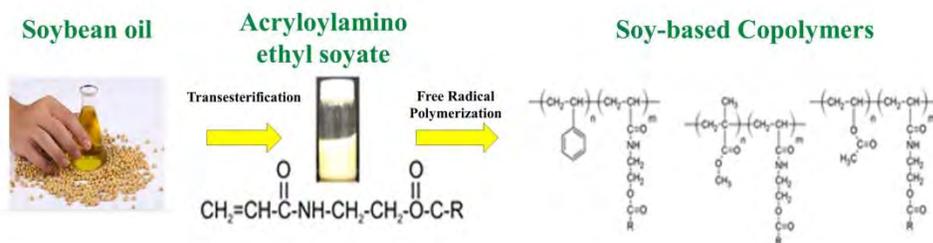
## POLY 455: Synthesis of bio-based copolymers via free radical polymerization of novel vinyl monomer from soybean oil

**Zoriana Demchuk**, [zoriana.demchuk@ndsu.edu](mailto:zoriana.demchuk@ndsu.edu), Ihor Tarnavchyk, Andriy Popadyuk, Andriy Voronov. *Coatings and Polymeric Materials Department, North Dakota State University, Fargo, North Dakota, United States*

A new bio-based acrylic monomer, was developed by one-step method that converts soybean oil into (acryloylamino)ethyl soyate using direct transesterification of crude soybean oil with N-(hydroxyethyl)acrylamide. The synthesized monomer combines vinyl double bond (acryloyl functional group) and isolated double bonds of fatty acids. The vinyl bond is reactive in conventional chain radical polymerization by facilitating macromolecular chain growth. Monomer reactivity ratios ( $r_1$ ,  $r_2$ ) in copolymerization of the new soy-based acrylic monomer (SBA) with styrene, methyl methacrylate, and vinyl acetate, as well as the Q-e parameters of the SBA, were determined. The obtained data indicate that copolymerizations can be described with the classical Mayo–Lewis equation. The SBA can be classified as an acrylic monomer in terms of polymerizability. Glass transition temperature ( $T_g$ ) of the SBA-MMA copolymers decrease considerably with enhances in the fraction of the soybean oil-derived fragments in the synthesized macromolecules. The double bonds of the fatty acid chains are mainly unaffected during the free radical polymerization process that yields linear macromolecules. These unsaturated fatty fragments with double bonds make the resulting macromolecules capable of post-polymerization oxidative reactions to form cross-linked polymer coatings, or of modification of unsaturated fatty acid chains in resulting macromolecules.

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- [2] I. Tarnavchyk, A. Voronov Bio-based Acrylic Monomers and Polymers Thereof U.S. Patent application 044 288, filed August 7,2015.



## POLY 456: Preparation of cubosomes using poly(glycerol adipate) grafted with oleic acid

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Department of Chemistry, Martin-Luther-Universität Halle-Wittenberg, Halle, Germany

Biodegradable functional polyesters from renewable resources like glycerol and various reduced sugars were synthesized. All these compounds contain multiple hydroxyl groups and their enzymatic polymerization with divinyl adipate (DVA), using lipase from *Candida Antarctica* CAL-B, makes it possible to produce linear polyesters with pendant functional OH-groups for further modifications [1].

Linear polyester chains were modified with hydrophobic chains like saturated and unsaturated fatty acids to produce amphiphilic polymers. Poly(glycerol adipate) (PGA) was modified with different amounts of oleoyl chains (see Figure 1) and a nanophase separation of the polymer in bulk was studied using small angle x-ray scattering. Initial results have shown that these amphiphilic polymers can be used to stabilize the cubic crystalline nanoparticles (cubosomes), obtained from monoolein. These cubosomes show a good long-time stability in water.

In another approach PGA was grafted with polycaprolactone bearing alkyne moieties, which after “click” reaction with azide terminated PEO, produce amphiphilic polymers [2]. These graft copolymers are able to form stable worm-like micelles in water.

In addition, aliphatic polyester chains having pendant azide groups were also prepared from 2-azidopropane-1,3-diol and DVA. Water soluble graft copolymers were obtained after doing “click” reaction with mono-alkyne PEO [3].

Polymers were characterized by NMR and IR spectroscopy and the thermal behavior of polymers were analyzed by DSC. The self-assembly behavior was confirmed by dynamic light scattering (DLS), transmission and scanning electron microscope. Potential applications in pharmacy will be discussed. The cubosomes are of special interest as templates for the folding of transmembrane proteins.

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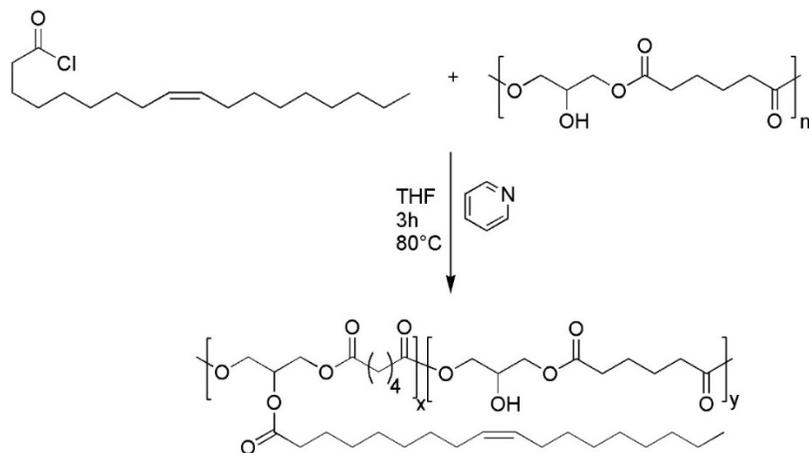


Figure 1: Synthesis of PGA modified with oleoyl chains.



## POLY 458: Designing visible light cured thiol-acrylate hydrogels for studying cell fate processes in 3D

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A visible light initiated thiol-acrylate photopolymerization scheme was used to synthesize dually degradable PEG-peptide hydrogels. We evaluated the effect of immobilized mono-thiol pendent peptide on gel crosslinking and presented methods to tune hydrogel crosslinking, including adjusting co-monomer concentration or using multifunctional peptide crosslinker. Specifically, gel stiffness was reduced when mono-thiol peptides were immobilized in the network (Fig 1A-B). Increasing co-monomer concentration (Fig 1C) or by using multi-thiol peptide linker improved the stiffness of the hydrogels. The thioether ester bonds formed after gel crosslinking render the gels hydrolytically labile (Fig 1D). No significant difference was found between different formulations though the groups with greater total thiol or RGDS concentration degraded slightly faster. If the di-thiol peptide linkers are sensitive to proteases, the thiol-acrylate hydrogels can also undergo partial proteolysis (Fig 1E). The thiol-acrylate PEG-peptide hydrogels have tunable stiffness and integrin ligand presentation, which permits the study of hepatic cancer cell fate *in vitro*. Current work is focused on characterizing the influence of matrix stiffness and integrin signaling on the activation of the HIPPO pathway.

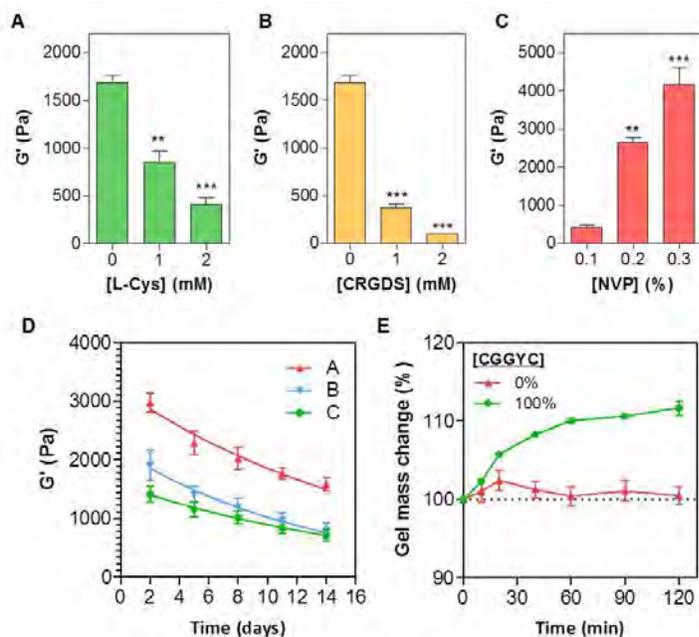
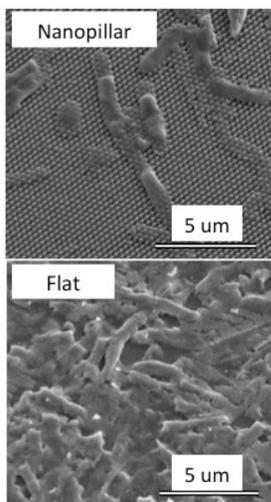


Fig. 1. Effect of (A) [L-Cysteine] and (B) [CRGDS] on shear modulus ( $G'$ ) of hydrogels formed with 0.1 vol% NVP. (C) Effect of [NVP] on  $G'$  of hydrogels formed with 2mM L-Cysteine. Other gel conditions: 10wt% 3.4 kDa PEGDA, 7.5 mM DTT, 0.1 mM eosin-Y, and 5-min visible light exposure. Shear moduli were measured at 2-hr post-gelation (\*\* $p < 0.001$ , \*\*\* $p < 0.0001$ ). (D) Hydrolytic degradation of PEGDA (10 wt%, 3.4 kDa) hydrogels with different crosslinkers: A: 7.5mM DTT; B: 7.5mM DTT and 2 mM CGGYC; C: 5.5mM DTT and 2mM CGGYC. (E) Proteolytic degradation of 10wt% PEGDA thiol-acrylate hydrogels induced by exogenous chymotrypsin (2mg/mL) treatment.

## POLY 459: Towards a scalable, biomimetic antibacterial polymer surface

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Nanopillars on cicada wings are inherently antibacterial, irrespective of surface chemistry. Application of nanopillars to polymer surfaces would result in inherently antibacterial surfaces without use of antibiotic drugs or biocide chemicals. Nano- and microstructured antibacterial surfaces have been previously proposed; none of these approaches can be used on ordinary polymer surfaces or easily scaled up. Thus, we applied industrial polymer nanostructuring techniques to generate biomimetic antibacterial nanostructures at the surfaces of poly(methylmethacrylate) (PMMA), a material commonly used in medical devices. We employed nanoimprint lithography, an industrially viable fabrication process, to produce our nanostructures. We utilized several molds for our process: a nano-holed (negative) mold, a commercially available nickel antireflective nanopillar (positive) mold, and a black silicon nanopillar (positive) mold fabricated with reactive ion etching. We treated these oxide surfaces with a fluorinated silane release coating (perfluorodecyltrichlorosilane) using molecular vapor deposition. These molds were used to fabricate PMMA nanopillar arrays or to generate polydimethylsiloxane nanohole arrays to be used for subsequent PMMA nanopillar molding. The replication processes resulted in large, flat PMMA nanopillar arrays. Compared to flat films, PMMA nanopillar arrays 1) exhibited reduced surface adhesion of live *E. coli* determined by a standard fluorescence based viability assay, and 2) killed these bacteria, as evidenced AFM and SEM showing punctured bacterial cells on nanopillar arrays. Recent efforts have focused on optimizing the bactericidal performance of pillars to assess effectiveness against gram-positive bacteria. Our surfaces could be used for a wide variety of environmental and medical applications.



Above: *E. coli* bacteria on a nanopillared PMMA surface. Below: *E. coli* bacteria on a flat PMMA surface. Bacteria on PMMA seem deflated as they sink into pillars. Bacteria on flat surface are clustering and remain rod shaped.

## POLY 460: Polymer-modulated bacteria behavior: Unifying bacteria aggregation and biofilm formation

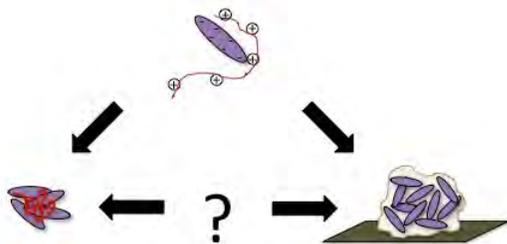
**Leanna Foster**<sup>2</sup>, [lfoster@umich.edu](mailto:lfoster@umich.edu), Haruko Takahashi<sup>2</sup>, Shin I. Yusa<sup>1</sup>, Kenichi Kuroda<sup>2</sup>. (1) University of Hyogo, Himeji, Japan (2) University of Michigan, Ann Arbor, Michigan, United States

Biofilm formation is a significant concern due to their increased resistance to antibiotics, and increased likelihood of surgical site infection when developed on medical implants. However, the factors that influence the formation of biofilms are not well understood. In general, biofilm formation begins by spontaneous attachment of bacteria to material surfaces or interface, and is not governed by bacteria behavior in solution. Details linking physical interactions of planktonic bacteria (such as aggregates) with biofilm formation behavior remain elusive. Based on the traditional view of biofilms as modulated by physical bacteria interactions, bacteria aggregation should modulate biofilm formation, specifically as they could satisfy critical population densities and enhance the kinetics of biofilm formation.

We challenge this traditional view and aim to provide a unifying theory of planktonic bacteria physical interactions as they relate to biofilm behavior. As opposed to providing a catalyst for biofilm formation, polymer induced physical interactions may be capable of sequestering planktonic bacteria as aggregates.

Our approach to address the fundamental knowledge gap between planktonic bacteria physical interactions and biofilm behavior is to utilize cationic polymers as a model material to evaluate the mechanism of biofilm formation, via physical interaction evaluation and biofilm behavior. The objective of this study is to connect the polymer-induced physical aggregation in solution with bacterial responses leading to biofilm formation on surfaces.

The expected outcomes of this research is the quantitative determination of polymer induced physical interactions as they relate to biofilm mass. The determination of critical biological factors will contribute to the understanding of bacteria behavior in solution and how solution behavior dictates biofilm formation. This new information facilitates a new method for governing biofilm growth, toward the development of new materials for targeted drug-delivery, water purification, and biofuels.

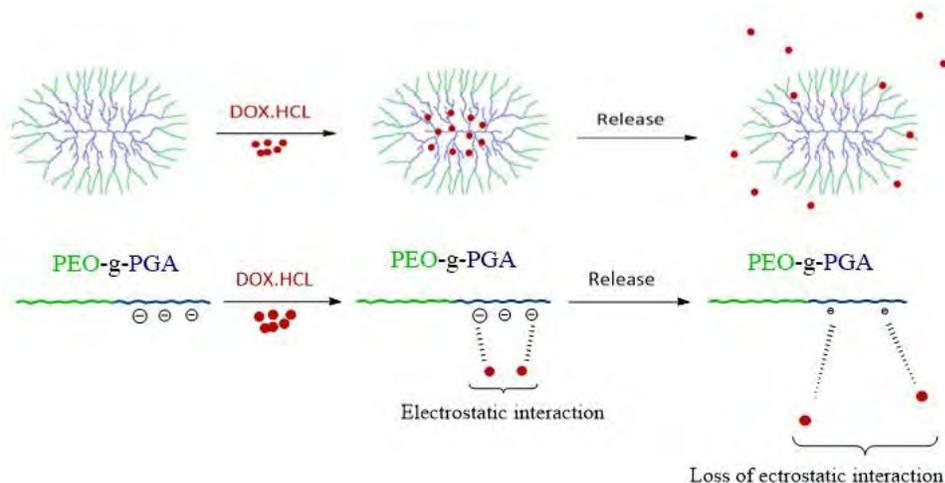


## POLY 461: Unimolecular micelles based on arborescent polypeptides for sustained drug delivery

**Mosa Alsehli**, [malsehli@uwaterloo.ca](mailto:malsehli@uwaterloo.ca), Mario Gauthier. Institute for Polymer Research, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada

Polymeric micelles have attracted much attention in recent years as nanocarriers for sustained drug delivery. While polymer micelles are often obtained by the self-assembly of amphiphilic block copolymers, unimolecular (covalently bonded) micellar structures have significant advantages as delivery vehicles due to their stable structure, insensitive to solvency conditions. The synthesis of biocompatible dendritic unimolecular micelles was accomplished by grafting poly(ethylene oxide) segments onto dendritic graft (arborescent) poly( $\gamma$ -benzyl L-glutamate) (PBG) substrates. The dendritic substrates were synthesized by successive cycles of partial deprotection and grafting reactions of PBG chain segments. The coupling reactions were optimized through systematic variations in the reaction conditions.

The encapsulation and release properties of these unimolecular micelles were investigated using doxorubicin (DOX) as a model hydrophobic anticancer drug, that was efficiently encapsulated via physical entrapment within the core of the arborescent poly( $\gamma$ -benzyl L-glutamate)-*g*-poly(ethylene oxide) (PBG-*g*-PEO) micelles. Doxorubicin hydrochloride (DOX.HCl) was also loaded into hydrophilic arborescent poly(L-glutamic acid)-*g*-poly(ethylene oxide) (PGA-*g*-PEO) copolymers via electrostatic interactions. The drug-loaded unimolecular micelles exhibited pH-responsive drug release behavior, with a slower release rate at physiological pH (7.4) than at pH 5.5.



Schematic illustration of drug loading and drug release in pH-responsive arborescent PGA-*g*-PEO amphiphilic copolymers.

## POLY 462: Endowing nanoparticles with orthogonal functionalities via a core/shell/shell architecture

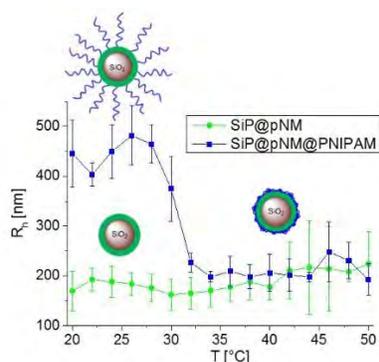
**Annabelle Bertin**<sup>1,2</sup>, [annabelle.bertin@bam.de](mailto:annabelle.bertin@bam.de), Asad Asadujjaman<sup>1</sup>, Knut Rurack<sup>3</sup>. (1) Federal Institute for Materials Research and Testing (BAM), 6.0 Materials Protection and Surface Technologies, Berlin, Germany (2) Free University Berlin, Institute of Chemistry and Biochemistry, Berlin, Germany (3) Federal Institute for Materials Research and Testing (BAM), 1.9 Chemical and Optical Sensing, Berlin, Germany

Dual orthogonal functionality in a single material is highly desirable in many fields such as bio-imaging, sensing, coating or diagnostic and therapy.<sup>[1,2]</sup> However, combining two different functionalities in a precise and controlled way is still a challenging task. Here we present how simply dual functional hybrid nanoparticles consisting of a silica core with a fluorescent and a thermoresponsive polymeric layers can be prepared. As a first step of this work, silica core particles were coated by a fluorescent layer using surface-initiated reversible addition-fragmentation chain transfer polymerization. Afterwards, the fluorescent silica nanoparticles were completely enclosed in a switchable protective coating made of thermoresponsive poly(*N*-isopropylacrylamide). The thermoresponsive poly(*N*-isopropylacrylamide) changes its properties with varying the surroundings temperature and this behavior is reversible and controllable.<sup>[3]</sup> To the best of our knowledge these types of hybrid dual functional core-shell-shell nanoparticles have not yet been prepared, despite the prospect of many potential applications.

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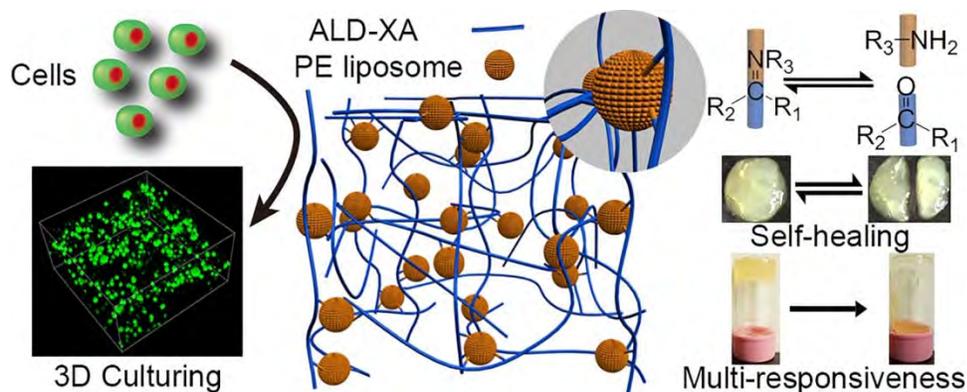


Temperature dependent hydrodynamic radius ( $R_h$ ) of thermoresponsive core/shell/shell particles.

## POLY 463: Biodegradable and injectable polymer-liposome hydrogel: A promising cell carrier

**Yong-Hao Ma<sup>1</sup>**, *mayunghao@gmail.com*, Xiaolin Lu<sup>1</sup>, Zhan Chen<sup>2</sup>. (1) Southeast University, Nanjing, Jiangsu, China (2) Univ of Michigan, Ann Arbor, Michigan, United States

Biodegradable and injectable hydrogels are widely used in many important applications such as cell culturing, tissue engineering, drug delivery, and cell therapy. Here we developed an inexpensive and facile method to prepare a biodegradable and injectable polymer–liposome hydrogel using aldehyde modified xanthan gum (ALD-XA) as the matrix material and phosphatidylethanolamine (PE) liposomes as cross-linkers. To the best of our knowledge, we believe that this is the first time for hydrogels containing crosslinked lipid liposomes to be prepared. The hydrogel was formed through dynamic Schiff base linkages between aldehyde groups of ALD-XA and amino groups of PE liposomes. After mixing ALD-XA and PE liposome solutions, the xanthan gum-based liposome hydrogel could be rapidly prepared within 5 min at room temperature. Owing to the dynamic equilibrium of the Schiff base bonds, the hydrogel responds to various stimuli, including physical stimulus (heat), chemical stimulus (pH variation), and biological stimulus (histidine exposure). Additionally, the hydrogel could easily be biodegraded by papain as a result of the digestion of xanthan gum backbones by enzymes. The hydrogel also exhibits excellent self-healing capability. Cells encapsulated in the prepared hydrogel are viable for a long period of time, indicating that it is an excellent carrier material suitable for three-dimensional (3D) cell culturing. These advantages suggest that the xanthan gum-based liposome hydrogel is a promising candidate for smart cell carrier for cell therapy and excellent cell culturing scaffold for tissue engineering.



## POLY 464: Aggregation-based polymer platforms for ratiometric fluorescence sensing and imaging

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Among ratiometric fluorescent sensors<sup>1</sup>, polymer assemblies can allow for the noninvasive and real-time optical imaging of cellular dynamics and processes, received much attention recently. Herein, we introduced aggregation-induced emission (AIE)<sup>2</sup> and aggregation-induced Förster resonance energy transfer (FRET) into two different polymer systems, respectively, resulted in efficient aggregation-based polymer platforms for ratiometric fluorescence sensing and imaging.

We designed and synthesized an amphiphilic conjugated polymer based on 2,2'-biimidazole and 2,1,3-benzothiadiazole units. In the light of the unique feature of aggregation-dependent FRET, this polymer has been demonstrated to be an excellent multifunctional sensing platform with multicolor fluorescence response for detection of water, Ag<sup>+</sup>, Hg<sup>2+</sup> ions, and cysteine.

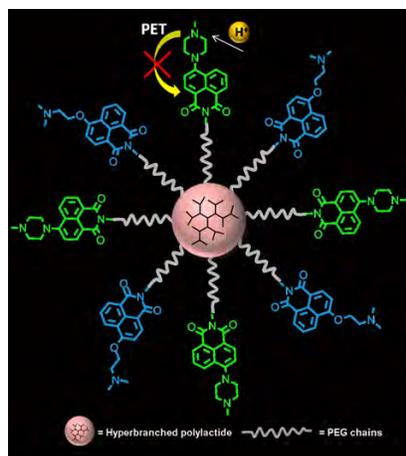
On the other hand, we prepared a tunable ratiometric fluorescent pH nanosensor by incorporating aggregation-induced emission-active fluorophores to hyperbranched poly(lactide) (PLA) nanoparticles (Fig.1), which exhibits excellent sensing properties for intracellular pH. More importantly, quantitative analysis of intracellular pH in HeLa cells has been successfully performed with this ratiometric nanosensor.

In summary, two aggregation-based polymer sensing platforms have been constructed by introducing AIE and aggregation-induced FRET effect, respectively, which provide new choices for future development of ratiometric fluorescent nanosensors, targeting various analytes of biological interest.

Acknowledgements: Ministry of Science and Technology of China (2007CB936401) and Tsinghua-KUL Bilateral Scientific Cooperation (BIL09/08) are acknowledged for financial support.

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**Fig. 1.** Ratiometric pH nanosensors based on hyperbranched PLA nanoparticles

## **POLY 465: Stimulus-responsive nanoparticle for ablating drug-resistant tumors**

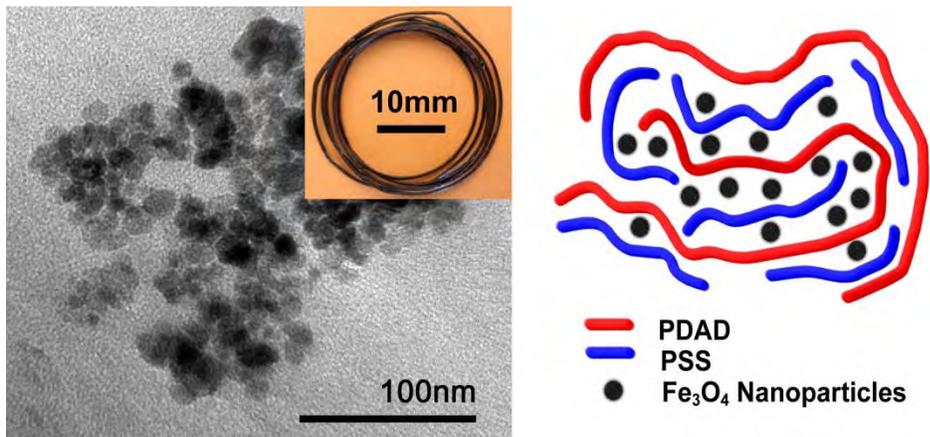
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Cancers cause high mortality rate and pose a major threat to human health. Drug resistance is a major yet frequent cause of failure in cancer chemotherapy. Analysis on the cancer drug resistance mechanisms indicates that agents targeting non-intracellular substances/pathways may be an effective approach for treating drug-resistant cancers. Comparisons on the mechanisms of cancer drug resistance and bacterial antibiotic resistance reveal that lessons learned from the latter may inform the former. Antimicrobial peptides (AMPs) and the synthetic mimics of antimicrobial peptides (SMAMPs) act by disrupting bacterial membrane integrity and are thus widely viewed as a promising source of novel anti-infective agents. Unfortunately, as anticancer agents, AMPs and SMAMPs suffer significantly from their intrinsic lack of selective cytotoxicity to cancerous over normal cells and their intrinsically poor pharmacokinetics. In this work, we show a stimulus-responsive, SMAMP-integrated nanoparticle that enables spatiotemporally controlled treatment with minimal invasiveness and leads to 100% survival for mice bearing drug-resistant tumors.

## POLY 466: Synthesis and characterization of extruded superparamagnetic Fe<sub>3</sub>O<sub>4</sub>-nanoparticle polyelectrolyte composites

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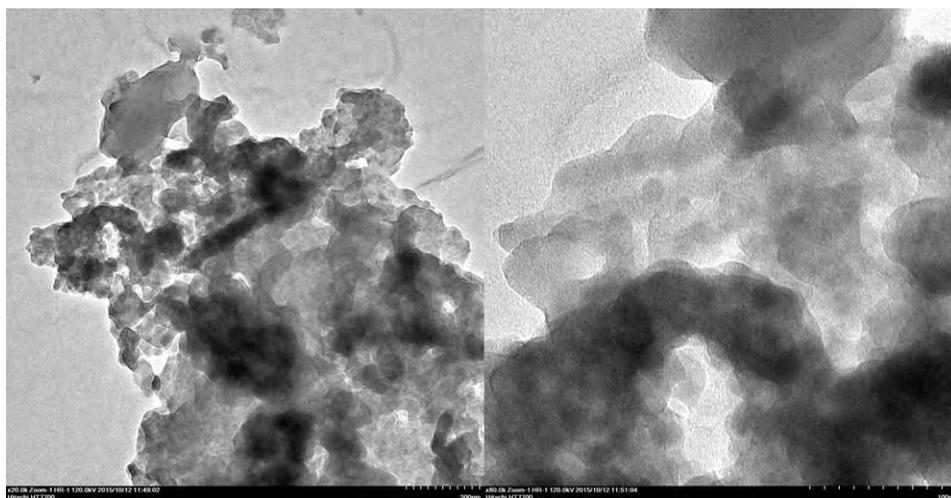
Polyelectrolyte complexes made from poly(styrenesulfonate) and poly(diallyldimethylammonium) were filled with iron oxide nanoparticles of diameter ca. 12 nm. These nanocomposites were extruded into dense, tough fibers after being plasticized with salt water. Superparamagnetic properties and the saturation magnetization of these composites scaled with the content of nanoparticles. These composites were remotely heated by applying a radiofrequency. The tensile strength and toughness of the fiber composites increased with the addition of nanoparticles, while no significant change was observed in the modulus of fibers.



## POLY 467: Diatom drug composite for drug delivery

**Megha Thakkar**, *mt69@njit.edu*, **Aditya Railkar**, **Somenath Mitra**. *Chemistry, New Jersey Institute of Technology, Newark, NJ, United States Minor Outlying Islands*

Diatoms are unicellular, photosynthetic microalgae that are widely distributed in fresh and seawater. Frustules or the rigid amorphous silica cell wall of the diatoms have unique porous architecture. In this paper we present the use of diatom frustule for delivery of Griseofulvin, a poorly water soluble drug. Drug composite developed from diatom silica, celluloses and surfactants show incorporation of the active molecule into the pore structure. Dissolution profiles of the pristine drug, the composite and the drug composite with cellulose and surfactants were studied. The diatom composite resulted in highest drug release of 70% within first 30 mins and 100% in 3 hrs. These results confirm that drug molecules can be loaded on the pores of Diatom silica for effective drug delivery.

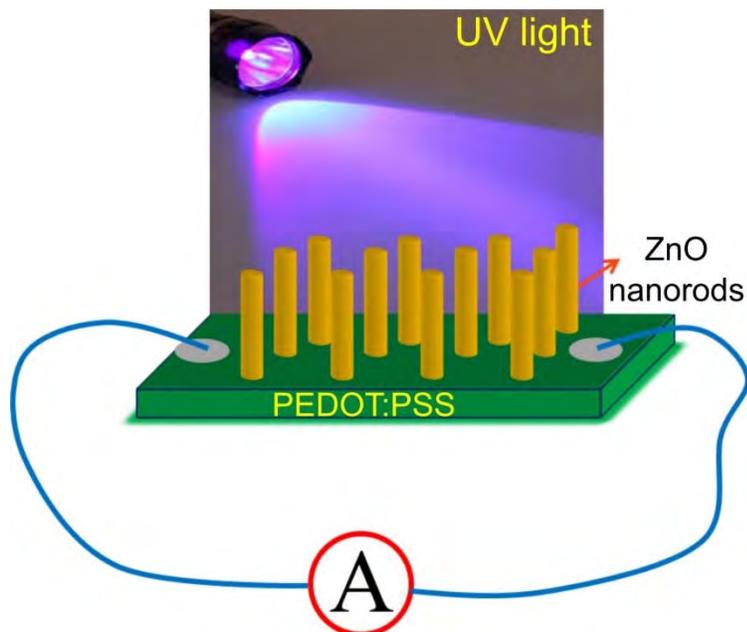


TEM of Diatom-Drug composite

## POLY 468: Synthesis of hierarchical ZnO nanorod/ PEDOT: PSS nanostructures for UV photodetection

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Growth of metal oxide on conducting polymer may lead to unique hierarchical nanostructures and interesting electronic/optical properties for various applications such as flexible/wearable sensors. However, the stringent reaction conditions (e.g. elevated temperature) for synthesis of metal oxide often makes it difficult to prepare such hybrid metal oxide/conducting polymer nanostructures. This work reports a facial approach of low-temperature seeding and hydrothermal growth of ZnO nanorod on conducting polymer, poly(3,4-ethylene dioxythiophene)/ poly(styrene sulfonic acid) (PEDOT:PSS). Seeds of ZnO are deposited on a PEDOT:PSS film by spin-coating of a zinc ammonium complex aqueous solution followed by heat treatment under 100 °C. Subsequently, ZnO nanorods are grown *via* a hydrothermal method in an aqueous solution of zinc nitrate hexahydrate and hexamethylenetetramine. The hydrothermal reaction conditions (including concentration, reaction temperature and time) are optimized to achieve controllable growth of ZnO nanorods. The conductivity of the hierarchical ZnO/PEDOT:PSS nanostructure is measured under UV exposure. The effects of PEDOT:PSS film thickness, the UV light intensity, and the kinetics of UV response are investigated.



Schematic of ZnO nanorods/ PEDOT:PSS device for UV photo-detection

## POLY 469: CuAAc and thio-bromo-click-chemistry as tools to achieve responsivity in polymer science

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Although methods of click-chemistry have reached organic, polymer- and bioorganic chemistry in their molecular dimension, their use as chemical concepts in material-design is surprisingly less developed. We here describe the design of self-healing materials<sup>1</sup>, based on the consequent use of click-chemistry-concepts, their use as crosslinking reactions to induce self-healing capabilities into polymers, based on fast and efficient crosslinking at room temperature or below. Specific catalyst design, in particular the generation of Cu/graphene nanocatalysts<sup>2,3</sup> is required to achieve self-healing nanocomposites. Both, the nature of the catalytically active species, together with an understanding of crosslinking kinetics allows the design of these materials. Subsequently, a concept to achieve pressure-sensitive click-reactions<sup>4</sup> is presented, allowing to site-specifically address curing of the damaged location. A second part shows the use of the thio/bromo-click-reaction<sup>5</sup> as a versatile and Cu-free method to achieve efficient functionalization of polymers, most of all the attachment of functional groups, responsive to stress, in turn enabling self-healing properties to be introduced into the final material<sup>6</sup>.

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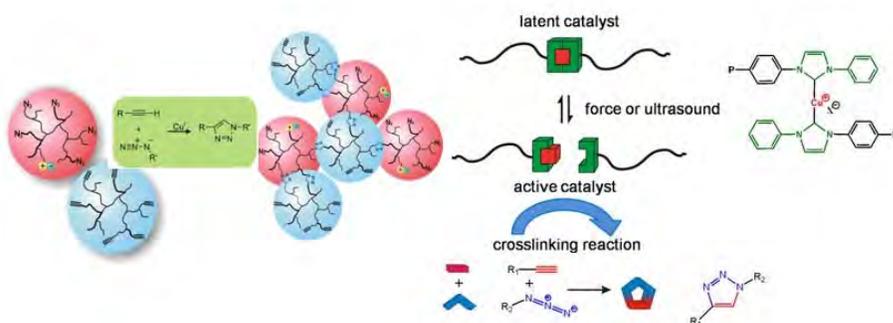
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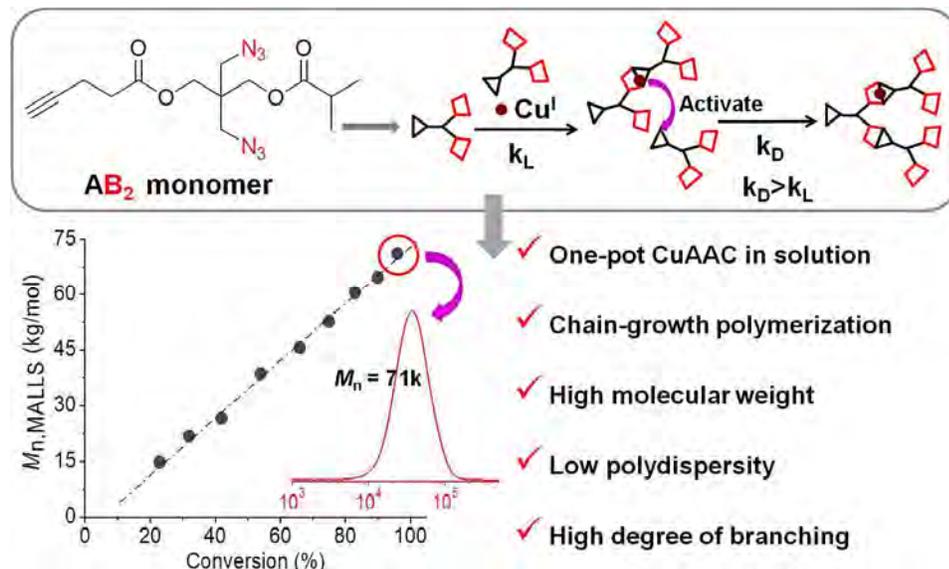
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## POLY 470: Synthesis of hyperbranched polymers following a chain-growth CuAAC click polymerization

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This talk presents our recent development of one-pot chain-growth copper-catalyzed azide-alkyne cycloaddition (CuAAC) polymerization of  $AB_m$  ( $m \geq 2$ ) monomers for synthesis of hyperbranched polymers with controlled molecular weights ( $MW = 20\text{-}1000 \times 10^3$ ), low polydispersity ( $M_w/M_n < 1.1$ ) and high degree of branching ( $DB = 0.9$ ). Complexation of  $Cu^I$  to the in-situ formed triazole groups bound all  $Cu^I$  catalysts in the polytriazole cores at low monomer conversion, and caused subsequent CuAAC reactions only occurring around the polymer proximity between polymers and monomers. The polymerization exhibited linear increase of molecular weight versus conversion and clean chain extension in multiple batches of monomer addition, demonstrating key feature of chain-growth polymerization mechanism. The produced hyperbranched polymers can be easily functionalized with various reactive groups in different layers for potential applications as unimolecular containers.



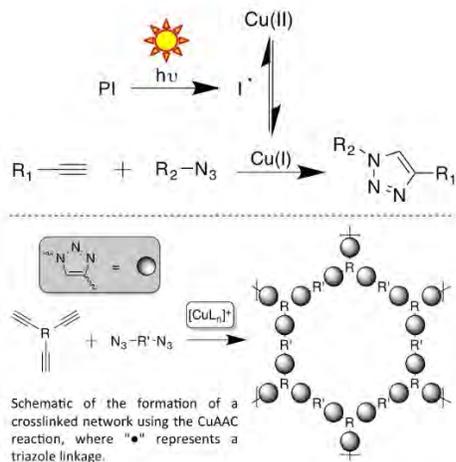
Chain-growth CuAAC polymerization to produce uniform hyperbranched polymers.

## POLY 471: Enhanced material properties from photo-initiated Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) based networks

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“Click” chemistry can be described as efficient reactions that achieve quantitative conversion under mild conditions and because of this it has warranted great interest in the area of polymer chemistry. These reactions allow unprecedented control over materials chemical and physical properties with simple and easily synthesized starting materials. 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 a CuAAC polymerization the triazole adducts formed possess excellent thermal and chemical stability and the rigid-aromatic linkers leads to a higher glass transition temperature ( $T_g$ ) 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 analogues thiol-ene based material. Lastly, the growing list of azide and alkyne monomers capable for use in the photo-initiated CuAAC polymerization renders ideal for broad applications within polymer science.



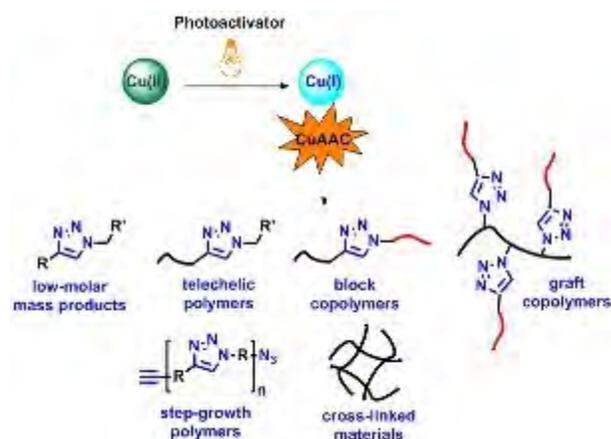
## POLY 472: New approaches for photoinduced CuAAC click reactions

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Click reactions (CuAAC) is a member of coupling processes with unique features such as modularity, versatility, rapidity and efficiency.<sup>1</sup> Due to these intrinsic advantages, CuAAC reactions attract intensive attention from the synthetic polymer community.<sup>2</sup> However, the requirement of low oxidation state copper (Cu(I)) catalysts, forces the process to be conducted in inert atmospheres or under vacuum. In recent studies, Cu(I) salts were simultaneously generated in the reaction media by reducing their Cu(II) associates using photoactivators as reducing agents to overcome such limitations.<sup>3</sup> These photo-induced approaches comprise the utilization of free radical photoinitiators and polyaromatic sensitizers as reducing agents, which enable synthesis of various macromolecular structures.<sup>4</sup> Previous studies in our laboratory demonstrated the possibility of efficiently synthesizing low-molar mass coupling products, telechelic polymers, block and graft copolymers, step-growth polymers and hydrogels and organogels through such redox processes.<sup>5</sup>

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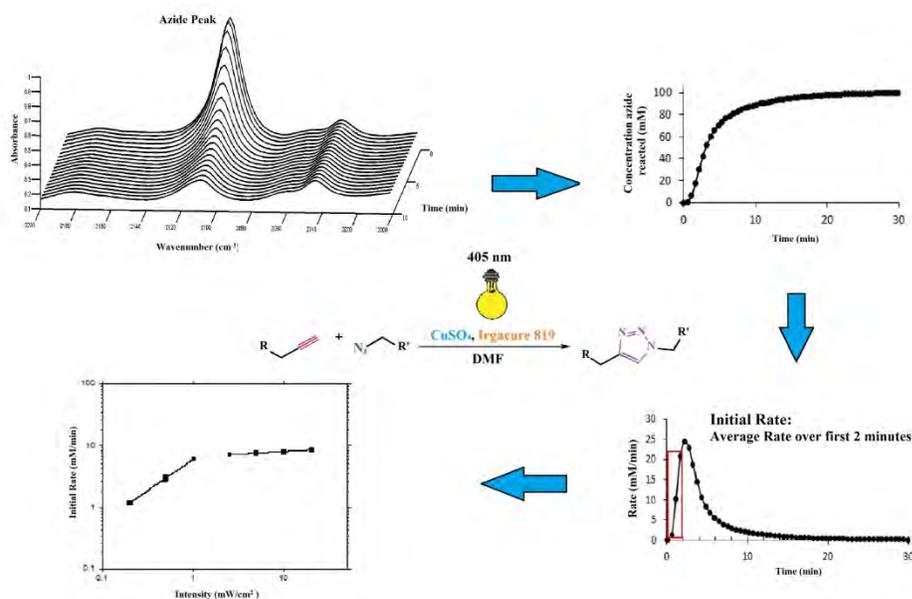
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## POLY 473: Kinetic effects and applications of copper, photoinitiator and intensity on the photo-induced Copper(I) Catalyzed Azide-Alkyne Cycloaddition (CuAAC) reaction

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Click chemistry refers to a collection of high yielding organic chemical reactions with limited or easily removable byproducts which proceed under simple reaction conditions. In addition to the versatility and ease in the implementation of these reactions, a few click reactions are initiated by light, thereby providing spatiotemporal control. One of the most widely used click reactions is the copper(I) catalyzed azide-alkyne cycloaddition (CuAAC) reaction. Despite the potential of the photo-CuAAC reaction in applications such as bioconjugation and materials synthesis, the kinetics and the limitations of this reaction are still relatively unexplored. In the work presented here, we identify the key variables associated with the photo-CuAAC reaction and illustrate how the reaction rate and conversions can be controlled. We demonstrate the sensitivity of a model photo-CuAAC reaction to copper(II) and photoinitiator concentration as well as light intensity, which can limit the maximum achievable reaction rate and extent. These results are translated into a polymer network-forming system to demonstrate the applicability of our model results. Importantly, the reaction kinetics show distinctly different behavior from the traditional, non-photo CuAAC reaction. The quantitative trends presented here will provide fundamental insights into the photo-CuAAC reaction, enabling its implementation over a broad range of applications.



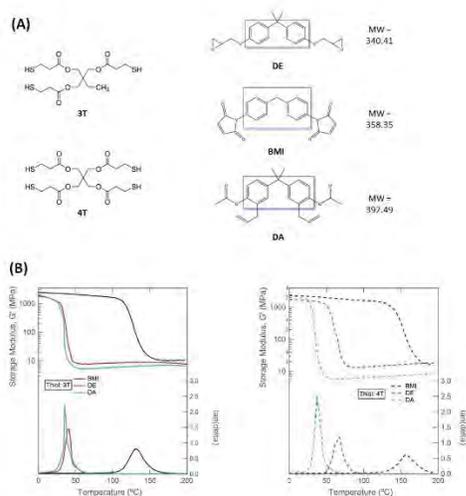
## POLY 474: High glass transition thiol-click networks from maleimides

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High-performance polymer applications such as medical devices, aerospace components and others have led to a demand for polymers with stable and robust properties at elevated temperatures. Traditional polymers used in these environments, such as polyimides, are often synthesized using prepolymers, requiring solvent based depositions and removal of side products. Inclusion of these volatile species presents a challenge for post-processing of bulk samples, where leachable or volatile molecules can exit the final network and react further with outside packaging. Thiol-ene polymers, a potential candidate for these applications, are often polymerized via radical or nucleophilic (Michael addition) means. However, both routes generally require catalytic stimulation to proceed in a timely fashion. Using a copolymer network composed of maleimides and multi-functional thiols, a softening, high glass transition ( $T_g$ ) thiol-click network is described for use as a viable option for applications in high heat environments.

In this study, several comparable networks are formed to investigate the mechanical properties of final polymer networks—such as  $T_g$ , Young's modulus, thermal degradation temperatures, and other characteristics—to isolate the contribution made by the succinimide thioether linkage, specifically for the increased glass transition above  $100^\circ\text{C}$  for an amorphous polymer network. The terminal reactive groups in question (alkenes, epoxies, and maleimides) are copolymerized with multi-functional thiols, and the thermomechanical properties and Fourier Transform Infrared (FTIR) spectrograms are explored.

These polymers show promise as a possible softening thiol-click network for use in high temperature, small molecule sensitive environments such as high vacuum systems and the semiconductor industry.

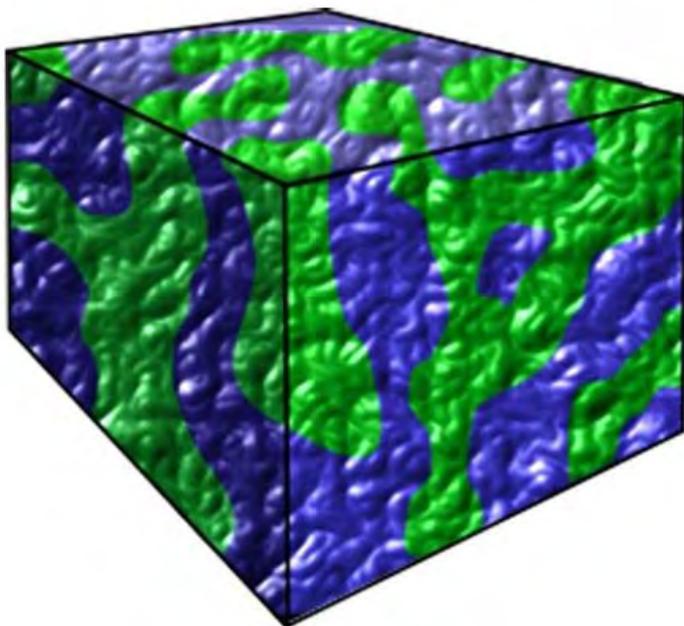


**Figure 1:** Molecular composition and thermomechanical properties of thiol-ene, thiol-epoxy, and thiol-maleimide networks. (A) Monomers used for comparable thiol-click reactions for isolating contributions of the succinimide thioether linkage to  $T_g$  of final networks. (B) DMA comparisons of networks formed with various counter reactive groups to the thiol monomer described in each graph, demonstrating the largely increased  $T_g$  due to the succinimide thioether linkage.

## POLY 475: Thiolene addition across norbornene enables novel co-networks and multi-block copolymers

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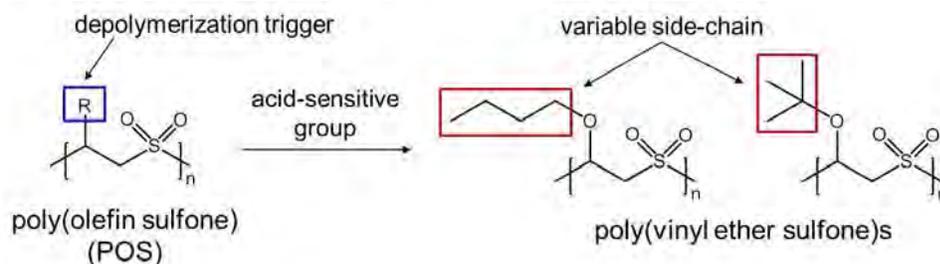
Phase-separated and self-assembled co-network materials offer a simple route to bicontinuous-like morphologies, which are expected to be highly beneficial for applications such as ion, charge, and oxygen transport. Despite these potential advantages, the systematic definition of co-network structures 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  $60 \text{ }^\circ\text{C}$ ), thermal properties (two glass transitions, low PEG crystallinity), and mechanical properties (storage modulus  $\gg 90 \text{ MPa}$  at  $30 \text{ }^\circ\text{C}$ ) remained similar. These findings demonstrate that this approach to thiol-ene co-networks is a versatile platform to create bicontinuous morphologies.



## POLY 476: Poly(vinyl ether sulfone)s as acid-sensitive polymers for transient materials

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Stimuli-responsive materials that undergo depolymerization in response to a specific trigger are of interest as substrates or packaging for transient electronic devices. Poly(olefin sulfone)s (POS)s have been demonstrated to undergo depolymerization in response to heat, base, and ionizing radiation. Our group has recently demonstrated a heat-sensitive POS polymer, namely, poly(vinyl *tert*-butyl carbonate sulfone) that depolymerizes at approximately 85 °C to yield volatile monomers, however the low onset of degradation makes the polymer relatively unstable under ambient conditions. Here, we modify the depolymerization trigger of the POS by incorporating an ether functional group, which is known to undergo hydrolysis in the presence of strong, nucleophilic acids. The poly(vinyl ether sulfone)s exhibit high thermal stability. We vary the degree of substitution of the triggerable group and examine the effect on the thermal stability and sensitivity to acid-triggered depolymerization.

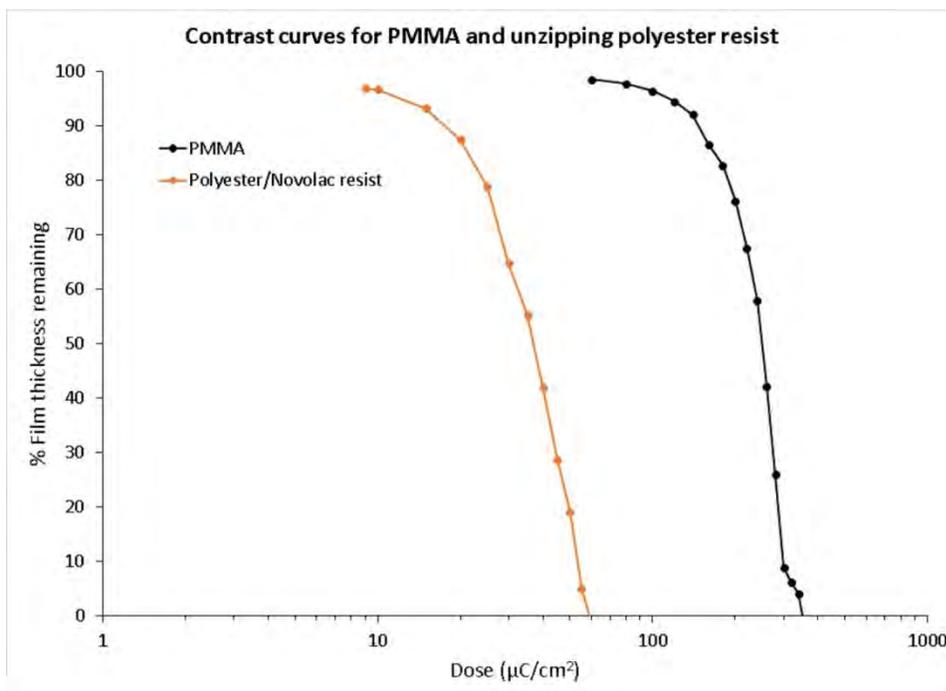


**Figure 1.** Incorporation of an acid-sensitive functional group into a POS polymer and variable degree of chain substitution.

## POLY 477: Self-immolative aromatizing polyester for next-generation lithography

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We have auditioned a new self-immolating polyester as a highly sensitive resist system for next-generation lithography. Upon exposure to either UV or electron beam radiation, the polymer irreversibly depolymerizes to generate toluene and carbon dioxide. When blended with Novolac, the polyester functions as a dissolution inhibitor and displays both high contrast and sensitivity when compared to a positive-tone, high resolution resist such as PMMA. Our research for this material is motivated by new advances in next-generation patterning techniques, such as extreme ultraviolet (EUV) lithography. An ideal EUV resist system must have both high sensitivity and low LER to compensate for the weak intensity of the light source. Unfortunately, traditional chemically amplified resist (CAR) systems suffer from blur caused by acid diffusion which results in poor image quality. To achieve sensitivity without the blur caused by catalyst diffusion, our resist system leverages the amplification power of a self-immolating polymer, which can fully depolymerize in response to a single photochemical event. Combined with the high etch selectivity of a phenolic resin such as Novolac, we can achieve high contrast and sensitivity in a non-CAR system that is compatible with current photolithographic processes. We have optimized our polyester resist system using electron beam lithography (EBL) as a substitute for EUV and compared its lithographic performance to high resolution EBL resists such as PMMA and ZEP as well as a commercial chemically amplified resist for 193 nm lithography.



## POLY 478: ROS responsive Se/Te-containing polymers

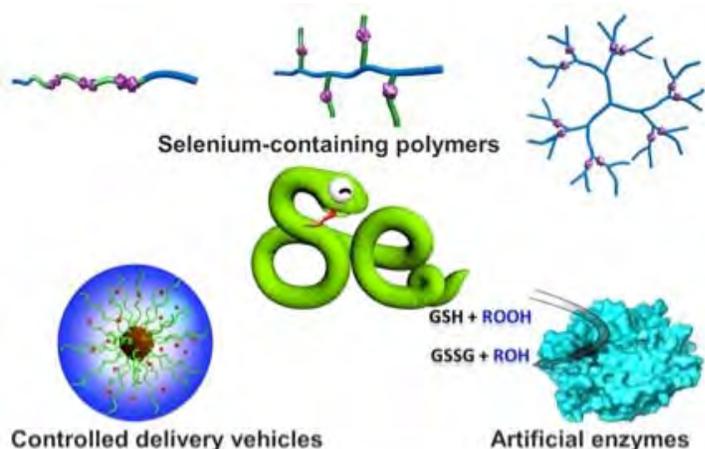
**Huaping Xu**, *xuhuaping@mail.tsinghua.edu.cn*. Tsinghua University, Beijing, China

As reactive oxygen species (ROS) are natural by-products of oxygen metabolism that may cause chronic diseases such as cancer and heart disease, great effort has been put to synthesize numerous antioxidant compounds based on selenium-containing small molecules. However, literatures on selenium-containing polymers are rather scarce. Here we are going to highlight the most recent advances on selenium-containing polymers and their potential bio-applications as ROS-responsive drug delivery vehicles. Take the linear polymer for example, diselenide-containing amphiphilic block copolymer micelles exhibited unique dual redox triggered disassembly behavior in response to a very dilute concentration of ROS ( $\text{H}_2\text{O}_2$ , 0.01%, v/v) or reductant (glutathione, 0.01 mg/mL).<sup>1,2</sup> The diselenide bonds could also be cleaved by ROS generated by photosensitizer under light radiation.<sup>3</sup> As gamma rays is one of the most widely used radiation in clinical application and that gamma radiation on water could also produce ROS, selenium-containing polymers were also used for the combination of chemotherapy and radiotherapy.<sup>4,5</sup>

Our work also suggested that the telluride molecules tend to be oxidized to higher valence much more easily than the selenide and sulfide compounds, which means that tellurium-containing compounds are highly sensitive to ROS. The ultra-sensitive and programmable nature of tellurium can be further employed to construct smart materials for future applications in biomedical engineering etc.

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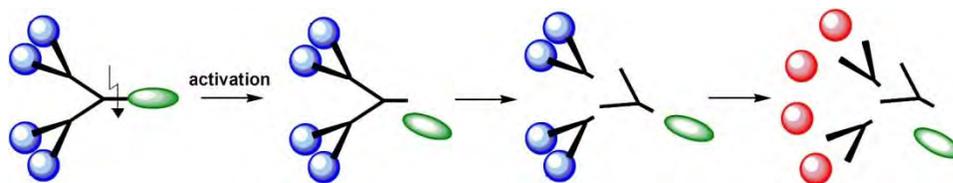
Selenium-containing polymers: promising biomaterials for controlled release

## POLY 479: Self-immolative molecular systems

**Doron Shabat**, *chdoron@post.tau.ac.il*. Department of Chemistry, Tel-Aviv University, Tel Aviv, Israel

Molecular amplification is a helpful and useful approach for various applications in science. Over the last years, we developed a novel class of dendritic and polymeric molecules with programmed disassembly pathway. These molecules were equipped with a head trigger; reaction at the trigger with a specific analyte initiated the fragmentation of a dendritic/polymeric molecule to its building blocks in a domino-like manner with consequent release of drug/reporter-units. We demonstrated the distinctive ability of these systems to achieve molecular amplification of the initial triggering signal. The unique amplification effect obtained by self-immolative dendrimers and polymers is useful in the fields of drug delivery and diagnostic applications. This presentation summarizes the design, function, and applications of our self-immolative molecular systems.

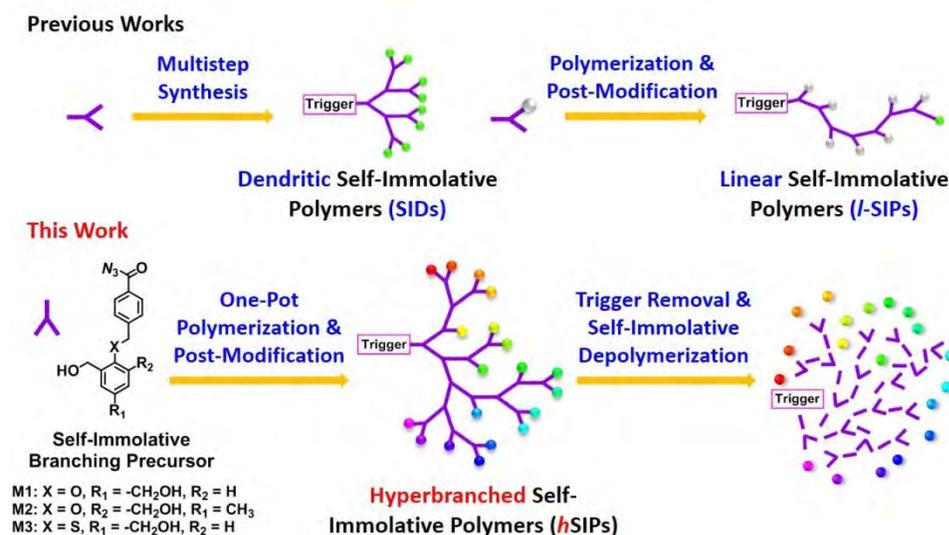
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## POLY 480: Hyperbranched self-immolative polymers (*hSIPs*) for programmed payload delivery and ultrasensitive detection

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Upon stimuli-triggered single cleavage of capping moieties at the focal point and chain terminal, self-immolative dendrimers (SIDs) and linear self-immolative polymers (*l*-SIPs) undergo spontaneous domino-like radial fragmentation and cascade head-to-tail depolymerization, respectively. The nature of response selectivity and signal amplification has rendered them an unique type of stimuli-responsive materials. Moreover, novel design principles are required for further advancement in the field of self-immolative polymers (SIPs). Herein, we report the facile fabrication of water-dispersible SIPs with a new chain topology, hyperbranched self-immolative polymers (*hSIPs*), by utilizing one-pot AB<sub>2</sub> polycondensation methodology and sequential post-functionalization. The modular engineering of three categories of branching scaffolds, three types of stimuli-cleavable capping moieties at the focal point, and seven different types of peripheral functional groups and polymeric building blocks affords both structurally and functionally diverse *hSIPs* with chemically tunable amplified-release features. Based on the *hSIP* platform, we explored myriad functions including visible light-triggered intracellular release of peripheral conjugated drugs in a targeted and spatiotemporally controlled fashion, intracellular delivery and cytoplasmic reductive milieu-triggered plasmid DNA release via on/off multivalency switching, mitochondria-targeted fluorescent sensing of H<sub>2</sub>O<sub>2</sub> with a detection limit down to ~20 nM, and colorimetric H<sub>2</sub>O<sub>2</sub> assay via triggered dispersion of gold nanoparticle aggregates. To further demonstrate the potency and generality of *hSIP* platform, we further configure it into biosensor design for the ultrasensitive detection of pathologically relevant antigens (e.g. human carcinoembryonic antigen) by integrating with enzyme-mediated cycle amplification with positive feedback and enzyme-linked immunosorbent assay (ELISA).



## POLY 481: Cutting to the chase: Azo-containing polymeric materials

**Yoan C. Simon**, [yoan.simon@unifr.ch](mailto:yoan.simon@unifr.ch). Adolphe Merkle Institute, University of Fribourg, Marly, Switzerland

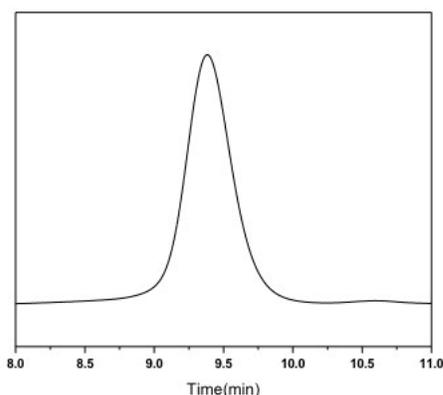
Azo motifs have been extensively used as initiators for radical polymerization but interestingly only a few studies have demonstrated their usefulness as stimuli-responsive motifs embedded covalently into polymeric materials. Such systems are particularly interesting since azo moieties can be activated by temperature or light. This activation results in the cleavage of the C-N bonds leading to the evolution of N<sub>2</sub> and the formation of C-centered tertiary radicals that can further react. More importantly, these materials when multiple reactive groups are incorporated either into linear or network systems, these materials can be depolymerized and mechano-morphing materials can be obtained. Here several examples of azo-containing materials (solution, bulk, gels) will be presented and their chain scission under various stimuli (light, ultrasound and heat) studied. The utilization of such systems in the context of stimuli-responsiveness will also be broached.



## POLY 482: Well-defined block copolymers containing high dielectric constant blocks: Synthesis and application

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**Abstract:** Polar organic polymers have become an appealing and promising new class of materials with a large variety of applications such as piezoelectrics, ferroelectrics.<sup>1-2</sup> Sulfone groups are of particular interest, as they possess an unusually high dipole moment (4.48 Debye), which much exceeds most other functional groups.<sup>3</sup> Vinyl sulfones, however, are in general difficult monomers for any type of polymerization. In this contribution, we describe anionic polymerizations of vinyl methyl sulfone (VMS) under different conditions (initiators, additives, temperatures). Typical side reactions can be suppressed with certain additives. Under certain condition, relatively well-defined poly(vinyl methyl sulfone) (PVMS) were obtained. The synthesis of block copolymers with other monomers (including acrylates, styrene) and the application of these polymers in energy storage is also described.

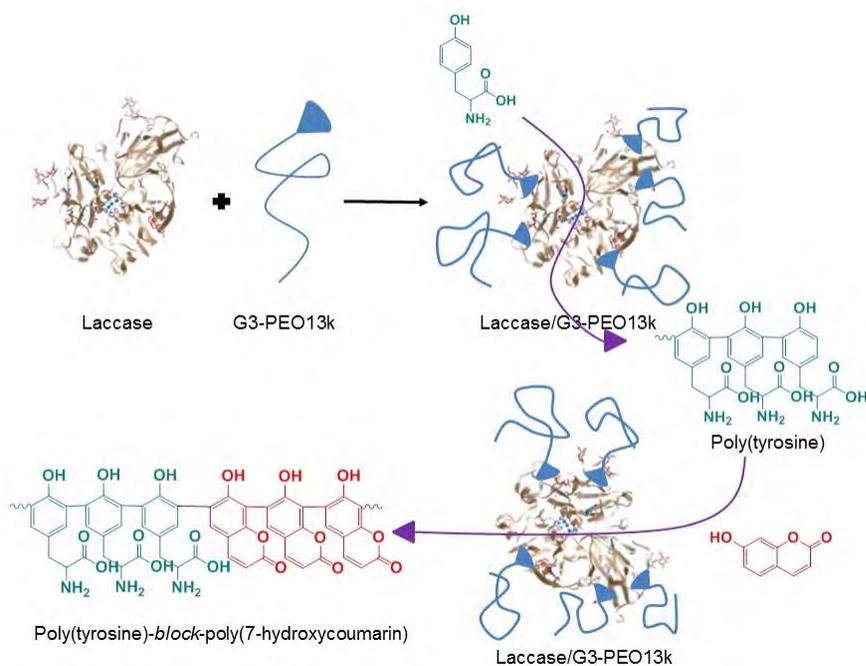


GPC trace of a PVMS in DMF

## POLY 483: Enzyme-mediated quasi-living polymerization: New “green” route to block copolymers

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Living polymerizations are of continual interest to the scientific community for the precision control in molecular mass and end-group functionality they afford. One of the attractive advantages of these reactions is the possibility to form block copolymers with composition and structure tailored to specific applications. Enzymes have also attracted significant attention as polymerization catalysts because of their ability to mediate reactions with high stereo- and regio-specificity under “green” reaction conditions. While they were sporadically used in the synthesis of random copolymers no block copolymerization attempts have been successfully accomplished so far. Here we report a new method for the construction of block copolymers based on a “pseudo-living” environmentally friendly polymerization catalyzed by laccase. Block copolymers of tyrosine and 7-hydroxycoumarin, *N,N*-bis-(*m*-hydroxyphenyl)-3,4,9,10-perylenetetracarboxylic-3,4,9,10-diimide, or 4-(pyren-1-yl-methoxy)-phenol were synthesized in aqueous medium yielding fluorescent water soluble polymers. All of them show interesting composition-dependent solution behavior. The development of this novel method of block copolymerization will open avenues to interesting materials for multidisciplinary use.



Synthesis of block copolymer mediated by linear-dendritic enzyme complex

## POLY 484: Living anionic polymerization of activated aziridines

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The ugly brothers of epoxides: aziridines are typically polymerized by uncontrolled cationic polymerization. Only scarcely anionic ring-opening polymerization (ROP) has been described. The presentation will introduce a whole new monomer class of sulfonamide-activated aziridines that can undergo anionic ROP. In most cases the polymerization mechanism follows a living mechanism and can be combined with other anionic polymerization setups easily. We believe that the anionic ROP of aziridines will provide straightforward access to novel polyamides and –amines with interesting properties for many applications. The presentation will show the progress in the control on sequencing, monomer design, and combination to oxyanionic polymerization.

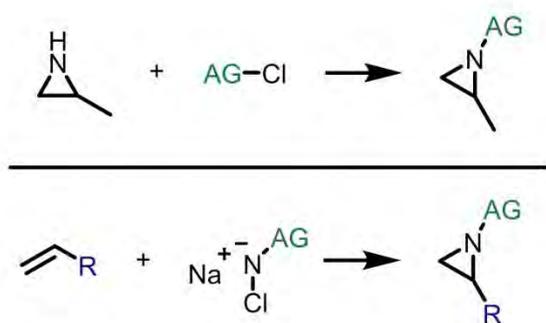


Figure 1: Monomer Synthesis.

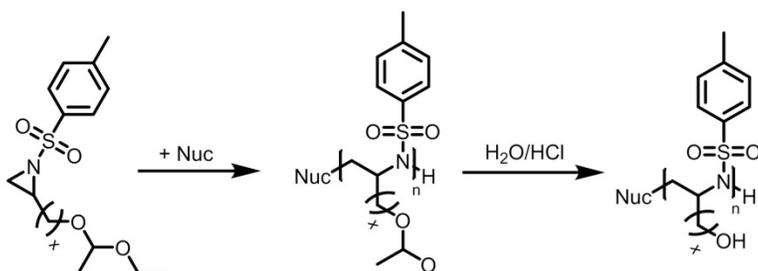
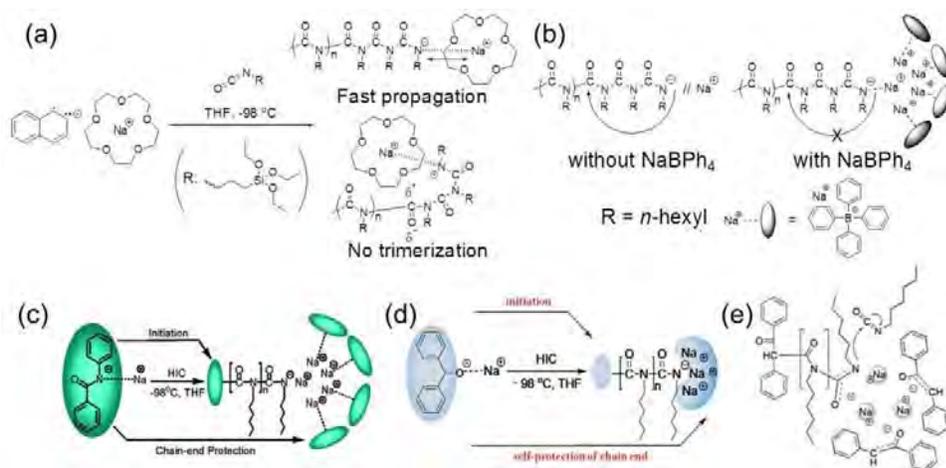


Figure 2. Living anionic polymerization of an acetal-protected aziridine.

## POLY 485: Living anionic polymerization of isocyanates

Chang-Geun Chae, Ho-Bin Seo, In-Gyu Bak, **Jae-Suk Lee**, [jslee@gist.ac.kr](mailto:jslee@gist.ac.kr). School of Materials Science and Engineering, Gwangju Institute of Science and Technology, Gwangju, Korea (the Republic of)

Since polyisocyanates as a class of dynamic helical polymers were discovered in 1959, their distinct conformational and morphological features have become exclusively studied subjects for attractive research fields such as chiroptical switches, macromolecular vehicles, liquid crystals, and photonic crystals. Their macroscopic helical conformation is also similar to structural features of biological macromolecules such as DNA, RNA and proteins. Although many scientists have tried to obtain polyisocyanates with a controlled molecular weight and a narrow weight distribution, the trimerization precluded controlled polyisocyanate formation. To overcome the lack of a living nature, special anionic polymerizations were invented. The use of effective additives and dual functional initiators stabilized the living chain end to prevent the trimerization. These polymerizations eventually achieved the living nature indicating quantitative yield, predictable molecular weight, and a narrow molecular weight distribution. The state of art of anionic polymerization of isocyanates and the effective functionalization techniques led to synthesis of well-defined linear-, telechelic-, chiral-, star-, rod-coil block- and graft polymers. From the controlled molecular architectures, a comprehensive understanding on helical properties and morphologies for polyisocyanates and their block copolymers has been accomplished.

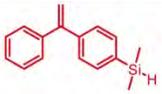
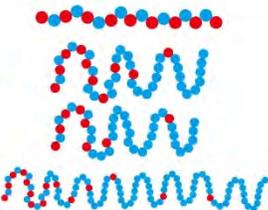
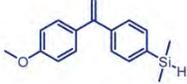
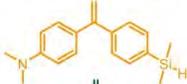
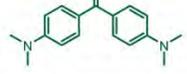


Advances in anionic polymerization of isocyanates: (a) 1<sup>st</sup> generation, (b) 2<sup>nd</sup> generation, and (c-e) 3<sup>rd</sup> generation.

## POLY 486: Sequence-determination and sequence-control in living anionic copolymerization of styrene and 1,1-diphenylethylene derivatives

**Hongwei Ma**, mahw@dlut.edu.cn. Polymer Science and Engineering, Dalian University of Technology, Dalian, China

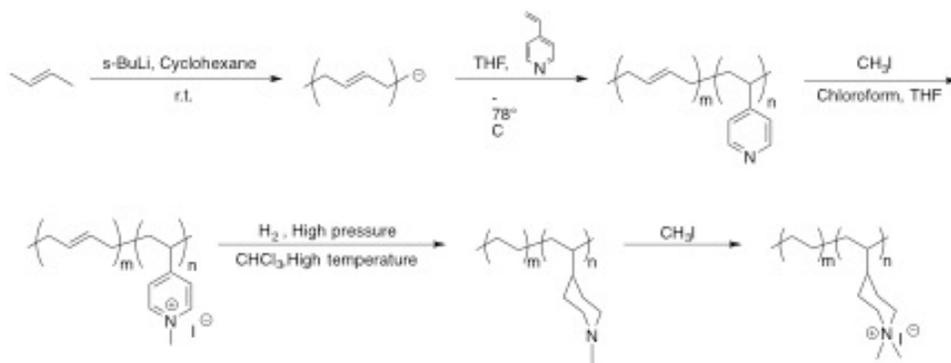
To synthesize the “sequence-controlled” polymers has become a novel area for polymer chemistry. Taking into consideration the special co-polymerization characteristic of 1,1-Diphenylethylene derivatives (DPE-Rs, which cannot be homopolymerized), well-defined control of monomer sequence with DPE derivatives as monomers has been carried out utilizing living anionic polymerization. The approximately alternating in-chain functionalized polymers with DPE functional derivatives as monomer have been synthesized successfully. Meanwhile, sequence determination has been carried out in the anionic copolymerization of styrene and DPE-SiH, DPE-OMe/SiH, DPE-NMe<sub>2</sub>/SiH and DPE-(NMe<sub>2</sub>)<sub>2</sub> via timing-sampling method under high vacuum condition. With varying of the feed ratios of St/DPEs and DPE structures, the sequential arrangements of functional DPE units in copolymer chains were regulated effectively. The sequence of copolymer chains was characterized and given by MALDI-TOF-MS and <sup>1</sup>H NMR.

DPE Structure	r <sub>St</sub>	S/D	Statistical sequence structure	Chain structure
	<b>DPE-SiH</b> 0.38 (r <sub>th</sub> )	0.5	<b>Alternating</b> 3 DS <sub>1</sub> DS <sub>2</sub> DS <sub>3</sub> DS <sub>4</sub> DS <sub>5</sub> DS <sub>6</sub> DS <sub>7</sub> DS <sub>8</sub> DS <sub>9</sub> DS <sub>10</sub> 4 DS <sub>1</sub> DS <sub>2</sub> DS <sub>3</sub> DS <sub>4</sub> DS <sub>5</sub> DS <sub>6</sub> DS <sub>7</sub> DS <sub>8</sub> 6 DS <sub>1</sub> DS <sub>2</sub> DS <sub>3</sub> DS <sub>4</sub> DS <sub>5</sub> DS <sub>6</sub> DS <sub>7</sub> DS <sub>8</sub> DS <sub>9</sub> DS <sub>10</sub> DS <sub>11</sub> DS <sub>12</sub> DS <sub>13</sub> DS <sub>14</sub> DS <sub>15</sub> DS <sub>16</sub> DS <sub>17</sub> DS <sub>18</sub> DS <sub>19</sub> DS <sub>20</sub>	
	<b>DPE-SiH/OMe</b>	1.17	4 DS <sub>1</sub> DS <sub>2</sub> DS <sub>3</sub> DS <sub>4</sub> DS <sub>5</sub> DS <sub>6</sub> DS <sub>7</sub> DS <sub>8</sub> DS <sub>9</sub> DS <sub>10</sub>	
	<b>DPE-SiH/NMe<sub>2</sub></b>	1.29	4 DS <sub>1</sub> DS <sub>2</sub> DS <sub>3</sub> DS <sub>4</sub> DS <sub>5</sub> DS <sub>6</sub> DS <sub>7</sub> DS <sub>8</sub> DS <sub>9</sub> DS <sub>10</sub>	
	<b>DPE-(NMe<sub>2</sub>)<sub>2</sub></b>	54	DS <sub>106</sub> DS <sub>30</sub> DS <sub>24</sub> DS <sub>18</sub> DS <sub>6</sub> DS <sub>3</sub> DS <sub>1</sub> D	

## POLY 487: Polybutadiene-block-poly(4-vinylpyridine) by living anionic polymerization as precursors to polyethylene-block-poly(4-vinyldimethylpiperidinium)

*Feilong Liu*<sup>2</sup>, *fliu@mymail.mines.edu*, *Daniel M. Knauss*<sup>1</sup>. (1) *Colorado School of Mines, Golden, Colorado, United States* (2) *chemistry, Colorado school of mines, Golden, Colorado, United States*

Living anionic polymerization can be used to prepare high 1,4-content polybutadiene. Hydrogenation of the high 1,4-polybutadiene leads to polyethylene. Living anionic polymerization can also be used to prepare poly(4-vinylpyridine) and its hydrogenation leads to poly(4-vinylpiperidine). In this work, block copolymers of high 1,4-polybutadiene and poly(4-vinylpyridine) are prepared as precursors to polyethylene-b-poly(4-vinylmethylpiperidine) and polyethylene-b-poly(4-vinyldimethylpiperidinium). The latter is designed for use in anion exchange membrane applications. The synthetic procedure to obtain the target polymer is depicted in Scheme 1. In the penultimate step, the polymer can be processed into films and then reacted with methyl iodide to produce the polyelectrolyte block copolymer. The block copolymer membranes were characterized to determine water uptake and ion exchange capacity and were examined by electrochemical impedance spectroscopy, thermal gravimetric analysis, differential scanning calorimetry, dynamic vapor sorption analysis, and small angle X-ray scattering.



Scheme 1. Synthesis of polyethylene-block-poly(4-vinyldimethylpiperidinium)

## **POLY 488: Flexible tubing development with K-Resin® SBC resins**

*Jin-Ping J. Zhou, jinpings65@yahoo.com. 95G, BRTC, K Resin Technology, Chevron Phillips Chemical Co, Bartlesville, Oklahoma, United States*

K-Resin® SBC resin, a styrene-butadiene copolymers (SBC) containing high styrene content (>50% by wt), is produced by anionic solution polymerization technique. In contrast to low styrene content (<50% by wt) styrene-butadiene block copolymers used as thermoplastic elastomers (S-TPE), K-Resin® SBC resin grades are transparent thermoplastic with high impact strength in general and various rigidity, which are determined by morphologies beside styrene contents.

The quest to develop flexible medical tubing using styrenic block copolymers can be trace back to 1970s. The major challenge is to balance the properties of kink resistance and flexibility and stickiness. With expanded understanding in styrenic polymer morphology and their structure-property relationship, a new K-Resin® SBC grade has been developed recently. This new resin grade can be extruded into flexible medical tubing and is suitable for other applications. The flexible tubing possesses good kink resistance, comparable to traditional plasticized PVC tubing, but contains no plasticizer. In addition, the tubing made with K-Resin® SBC resins has good solvent bondability and is suitable for ethylene oxide, E-beam and gamma sterilization.

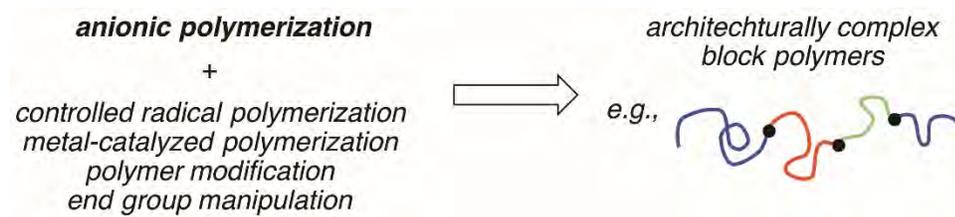


Kink Resistance Measurement

## **POLY 489: Marrying anionic polymerization with other controlled polymerizations for architecturally complex block polymers**

**Marc A. Hillmyer**, [hillmyer@umn.edu](mailto:hillmyer@umn.edu). University of Minnesota, Minneapolis, Minnesota, United States

It is well established that anionic polymerization is a powerful tool for the preparation of architecturally complex macromolecules. We have utilized anionic polymerization in combination with other controlled polymerizations and polymer modification techniques to prepare multiblock polymers with arbitrary block connectivity and symmetry to explore the phase behavior and applications of these interesting self-assembling materials. In this talk I will focus on precision synthetic techniques we have employed to prepare "mechanistically-incompatible" block polymers that can self-assemble to give advanced materials useful in technologies ranging from membrane separations to nanopatterning.



## **POLY 490: Supramolecular chemistry in skin-inspired electronic materials**

**Zhenan Bao**, [zbao@stanford.edu](mailto:zbao@stanford.edu). *Chemical Engr Dept MC 4125, Stanford University, Stanford, California, United States*

In this talk, I will discuss two examples of the applications of supramolecular chemistry for electronic materials. In one example, we used supramolecular polymers for the sorting of semiconducting carbon nanotubes. In another example, I will describe the development of self-healing electronic materials based on polymer networks formed through supramolecular chemistry.

## **POLY 491: Dynamic biomolecular supramolecular polymers**

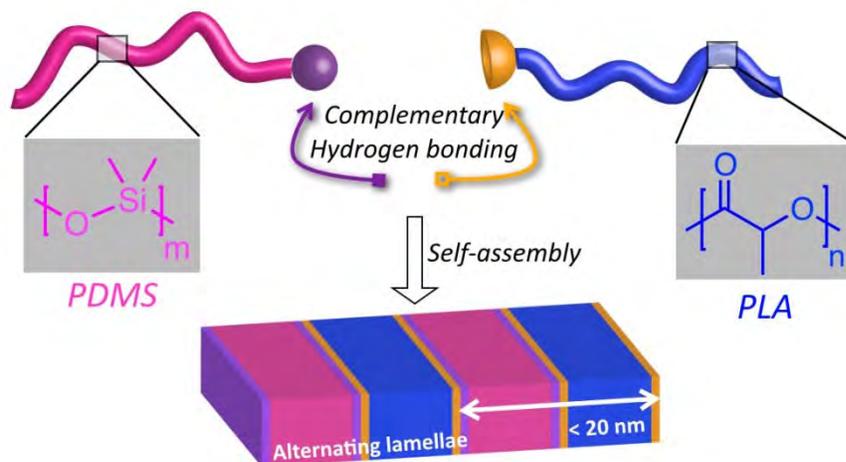
**Samuel I. Stupp**, *s-stupp@northwestern.edu*. Northwestern University, Evanston, Illinois, United States

Supramolecular soft matter has the potential to mimic the structures and dynamics of biological systems, and it is therefore a rich platform for the development of bio-inspired materials. Supramolecular polymers represent a very promising class of this genre of soft matter and one of their unique features is the potential for highly dynamic behavior. This can lead to materials that are highly responsive to external stimuli, with capacity to self-heal defects, or adapt to an environment through structural rearrangements, among many other possibilities. This lecture will describe supramolecular polymers built from monomers containing biomolecular structural units that include peptides, nucleic acids, and glycans. Systems will be described that adapt structurally to bind proteins, others which utilize Watson-Crick pairing to generate hierarchical structures, and also peptide based systems that can catalyze covalent polymerizations.

## POLY 492: Supramolecular block copolymers from hydrogen bonding between highly immiscible segments

**Louis Pitet**<sup>1</sup>, [louis.pitet@dsm.com](mailto:louis.pitet@dsm.com), **Edward J. Kramer**<sup>3</sup>, **Craig J. Hawker**<sup>4</sup>, **Egbert W. Meijer**<sup>2</sup>. (1) DSM, Maastricht, Netherlands (2) Institute for Complex Molecular Systems, Eindhoven University of Technology, Eindhoven, Netherlands (3) Univ of Cali at Santa Barbara, Santa Barbara, California, United States (4) Univ of California, Santa Barbara, California, United States

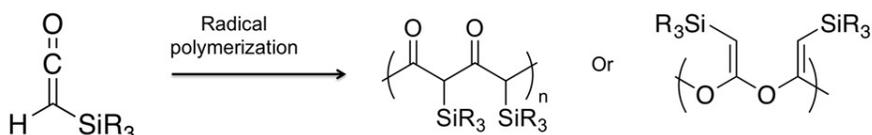
Block copolymers with highly immiscible segments are proving to be promising candidates for preparing nanoscale patterns with exceptionally small features (< 10 nm). A remarkably rich variety of distinct functionalities have been incorporated into block copolymers to realize sophisticated patterns and responsiveness to various chemical stimuli. In an effort to further enhance the potential versatility of this class of materials, the conventional covalent linkage connecting different blocks were replaced with reversible, non-covalent hydrogen bonding units. This work discloses the synthesis of homopolymer segments carrying functional motifs that are capable of directional, four-fold hydrogen bonding with a complementary partner. The synthetic procedure was demonstrated with poly(lactide) and poly(dimethylsiloxane). Mixtures of these homopolymer segments in various proportions led to a hierarchical self-assembly process; initially, four-fold hydrogen bonding occurs, effectively linking the two incompatible homopolymers in suitable solvents. Upon removal of solvent, this is followed by the adoption of nanostructures according to the well-known phenomena exhibited in conventional diblock copolymers. The adoption of organized nanostructures is acutely sensitive to the mixing conditions, providing a handle for manipulating the self-assembly behavior. These materials are promising for various nanotechnologies, where selective removal of blocks in a template can be expedited with supramolecular block copolymers, and thus used to produce masks for nano lithography for example.



## POLY 493: Designing new monomers for radical polymerization

**Emily Pentzer**, *ebp24@case.edu*. Chemistry, Case Western Reserve University, Cleveland, Ohio, United States

Radical polymerization has been performed on the industrial scale for decades, and researchers across academia have focused on controlling radical polymerization to dictate polymer molecular weight and dispersity, end group functionality, and architecture. However, one area that has been relatively little underexplored is the development of new monomers for radical polymerization to give novel backbone chemistries and alter inter and intrachain interactions. This work will address the development of silyl ketenes as monomers for radical polymerization and highlight the difference in the polymerization of these structures compared to traditional olefin-based monomers such as styrene.

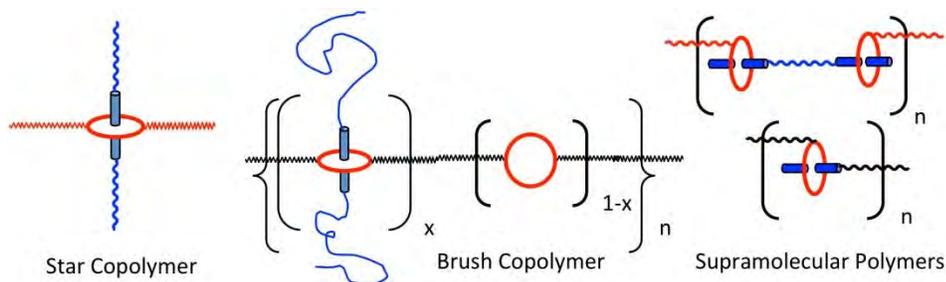


## POLY 494: Supramolecular polymer chemistry: Entanglements by design

**Harry W. Gibson**<sup>1</sup>, [hwgibson@vt.edu](mailto:hwgibson@vt.edu), Terry Price<sup>2</sup>, Daniel Schoonover<sup>3</sup>, Arunachalam Murugan<sup>1,4</sup>, Hanlie R. Wessels<sup>1</sup>, Fiorella Mazzini<sup>1</sup>. (1) Chemistry, Virginia Tech, Blacksburg, Virginia, United States (4) Chemistry, Gandhigram Rural Institute, Dindigul, India

Following extensive studies, we have developed pyridino cryptands that afford association constants in the range of  $10^4$  to  $10^6$  M<sup>-1</sup> with paraquats.[1] Moreover, we have developed template-based methods for formation of the precursor crown ethers and the cryptands in high yields. Functionalized versions of these powerful hosts now enable new avenues to create supramolecular polymeric structures beginning with both functionalized polymers as well as monomeric species. Combined with modern polymerization methodologies these systems enable efficient formation of star, block, graft and brush copolymers. They also provide routes to high molecular weight supramolecular polymers. These procedures will be discussed along with characterization of the resultant novel materials.

1. a) Zhang, M.; Zhu, K.; Huang, F. *Chem. Comm.* 2010, 46, 8131-8141; b) Deska, M.; Kozłowska, J.; Sliwa, W. *ARKIVOC* 2013, 66-100; c) Zhang, M.; Yan, X.; Huang, F.; Niu, Z.; Gibson, H. W. *Acc. Chem. Res.* 2014, 47, 1995-2005; d) Arunachalam, M.; Gibson, H. W. *Progr. Polym. Sci.* 2014, 39, 1043-1073.

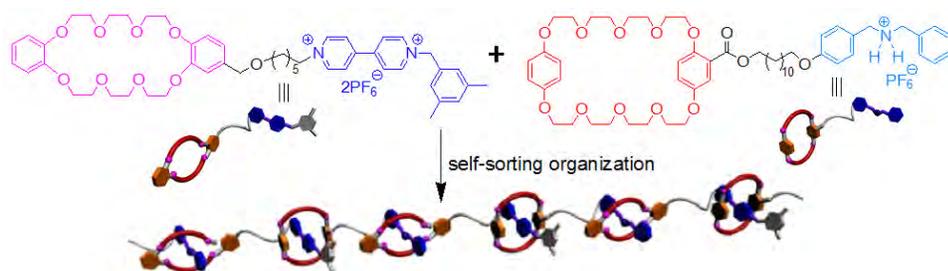


Mechanically Linked Polymeric Architectures via Host-Guest Chemistry

## POLY 495: Supramolecular polymers based on host-guest molecular recognition motifs

**Feihe Huang**, [fhuang@zju.edu.cn](mailto:fhuang@zju.edu.cn), Feng Wang, Xuzhou Yan, Shengyi Dong, Mingming Zhang, Zibin Zhang, Jianzhuang Chen. Department of Chemistry, Zhejiang University, Hangzhou, Zhejiang, China

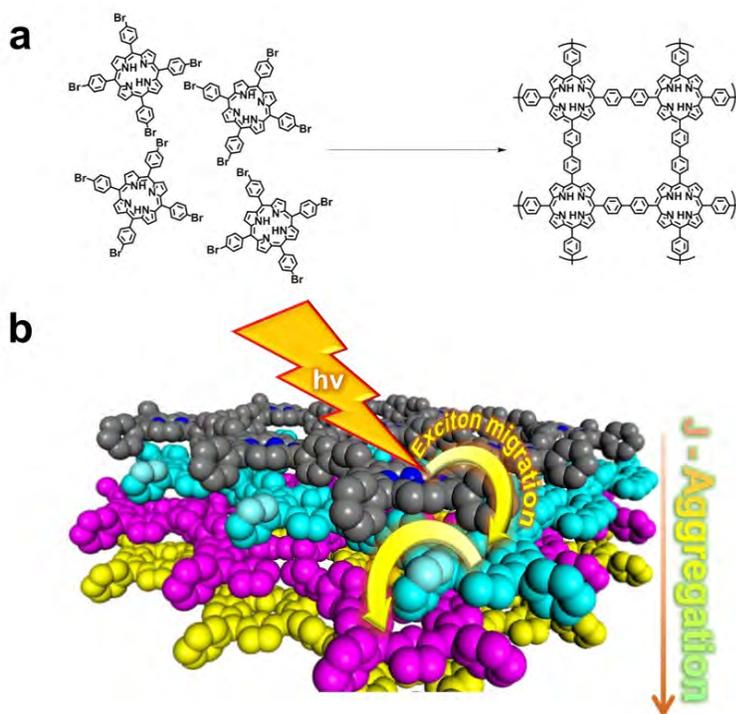
Supramolecular polymers, assembled from low molecular weight monomers via noncovalent interactions, such as hydrogen bonding, metal coordination as well as host-guest interactions, have demonstrated traditional polymeric properties and become an important source for the development of stimuli-responsive dynamic materials. We are interested in the fabrication of supramolecular polymers based on host-guest molecular recognition motifs. Self-sorting organization of two AB-type heteroditopic monomers led to the formation of linear supramolecular alternating copolymers driven by host-guest noncovalent interactions based on the bis(p-phenylene)-34-crown-10/paraquat derivative and dibenzo-24-crown-8/dibenzylammonium salt recognition motifs. By utilization of host-guest and metal-ligand noncovalent recognitions motifs, different topologies of supramolecular polymers, such as linear and crosslinked species, can be reversibly interconverted by external stimuli. Based on the dibenzo-24-crown-8/1,2-bis(pyridinium)ethane recognition motif, a hyperbranched mechanically interlocked polymer was prepared by polyesterification of an easily available dynamic trifunctional AB<sub>2</sub> pseudorotaxane monomer. By utilization of a crown ether-based host-guest recognitions motif, a supramolecular polymer gel constructed from a low molecular weight A-B monomer shows thermo- and pH-induced reversible gel-sol transitions. The thermal- and pH-responsive gel-sol transitions were successfully employed in the controlled release of Rhodamine B.



## POLY 496: Energy transfer relay upon panchromatic light absorption by two-dimensional porphyrin covalent arrays

**Hwa Seob Choi**, *cchs1990@kaist.ac.kr*, Jeung Ku Kang. KAIST, Daejeon, Korea (the Republic of)

A porphyrin array in the antenna pigments of natural light-harvesting complexes, including chlorophyll, which absorbs photons from light and then enables an energy transfer relay of photon-excited excitons to a reaction centre, is of great importance for light harvesting in nature. Herein, a 2-dimensional porphyrin covalent array with J-J, J-H and H-H aggregated stacking configurations of transition dipoles was synthesised and verified experimentally using X-ray diffraction and photophysical measurements combined with first-principles calculations of the structures. The ordered array of light-sensitizing porphyrins with J-J and J-H configurations serves as a funnel to transport excitons via both Forster and Dexter energy transfer mechanisms, thereby enabling the rapid and long-range transfer of excitons to the exciton-accepting reaction centre upon panchromatic photon absorptions. This enhanced transfer boosts the collection of photons to the reaction centre by approximately 20-fold, far exceeding the absorbed light energy in the single porphyrin unit. Additionally, the covalent bonds between porphyrins, resulting in the formation of channels for excitons, exhibited chemical stability even in a strongly acidic solution, in addition to thermal stability up to a high temperature in air.

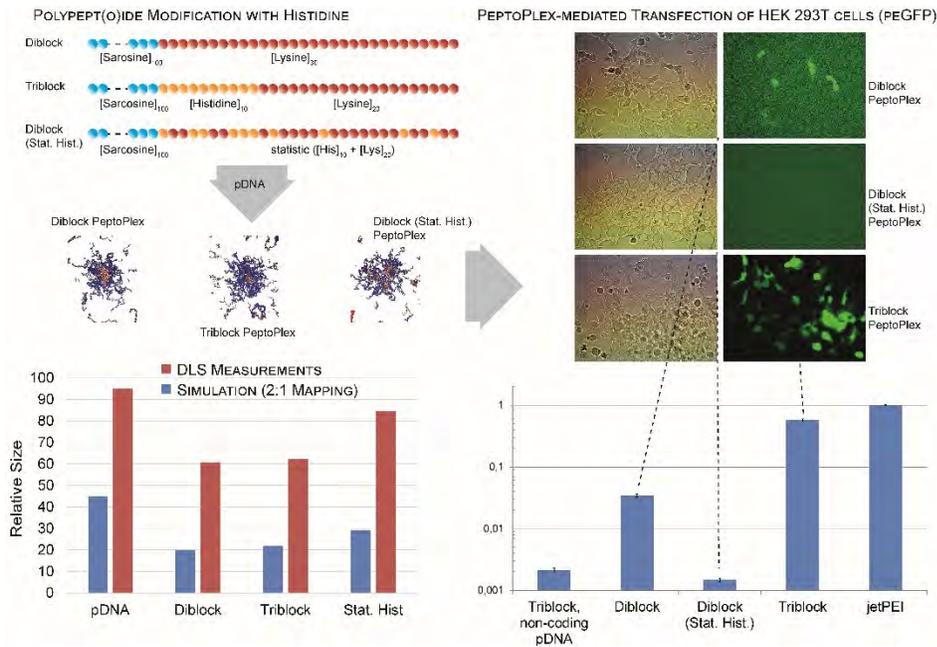


(a) Synthetic pathway for H2P PON (b) Schematic of J-aggregated stacking structures and exciton migration through the stacking of H2P PON.

## POLY 497: Controlling polyplex properties by polymer microstructure

**Philipp S. Heller<sup>1</sup>**, heller@uni-mainz.de, Benjamin Weber<sup>1</sup>, Jiajia Zhou<sup>3</sup>, Dominika Hobernik<sup>4</sup>, Matthias Barz<sup>2</sup>. (1) Institute of Organic Chemistry, Johannes Gutenberg University, Mainz, Germany (2) Institute of Organic Chemistry, Johannes Gutenberg University Mainz, Mainz, Germany (3) Institute of Physics, Johannes Gutenberg University, Mainz, Germany (4) Department of Dermatology, University Medical Center, Mainz, Germany

Histidinylated is a well-known method to enhance polymer transfection efficiency. Experimental investigations and simulations on histidine-bearing multiblock copolypept(o)ides with different block sequences reveal a clear impact of spatial histidine arrangement on complexation behavior and transfection efficiency, underlining the importance of microstructure design in block copolymer-based transfection reagents.

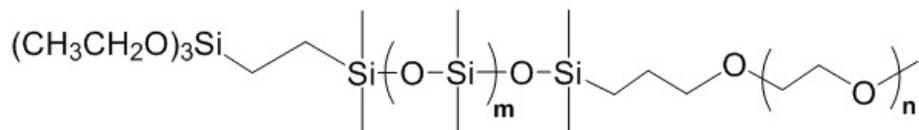


Effect of spatial histidine residue arrangement on DNA complexation properties and transfection efficiency of block copolypept(o)ides.

## POLY 498: Anti-fouling amphiphilic silicones: Efficacy against marine biofouling

**Melissa Grunlan**<sup>1</sup>, [mgrunlan@tamu.edu](mailto:mgrunlan@tamu.edu), *Melissa Hawkins*<sup>1</sup>, *Marc A. Rufin*<sup>1</sup>, *Shane Stafslie*<sup>2</sup>, *Isabelle Linossier*<sup>3</sup>. (1) Texas AM University, College Station, Texas, United States (2) Center for Nanoscale Science & Engineering, North Dakota State University, Fargo, North Dakota, United States (3) University of South Brittany, Lorient, France

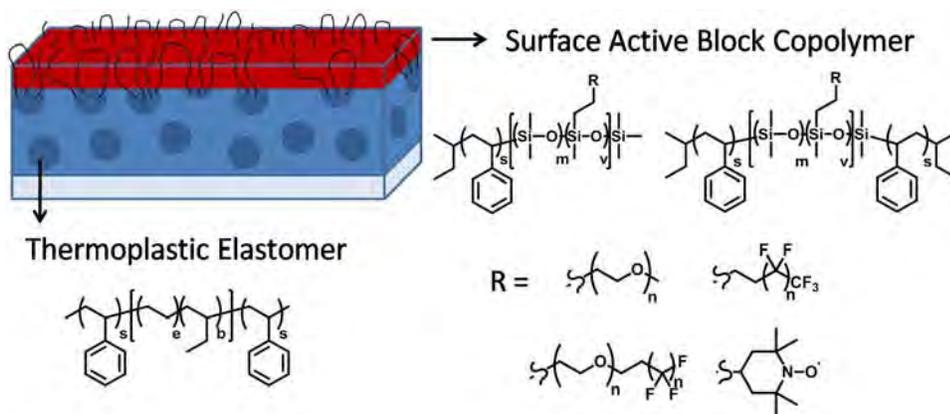
Silicone foul-release (FR) coatings represent a non-toxic alternative to ablative marine coatings. However, the efficacy of silicones to broadly control biofouling is limited. Based on the limitation of silicone FR coatings, amphiphilic antifouling coating systems have emerged as a potentially effective alternative way to resist fouling by multiple organisms. In this work, silicones were modified with PEO-silane amphiphiles which act as highly efficient surface-modifying additives, enabling the rapid water-driven formation of a PEO-enriched surface highly resistant to biofouling. Temporal, water-driven surface hydrophilicity and the resulting control of marine biofouling are described.



## POLY 499: Controlling surface composition and structure of antifouling coatings using functionalized siloxane block copolymers

**Brandon Wenning**<sup>2</sup>, [bmw97@cornell.edu](mailto:bmw97@cornell.edu), Christian Pester<sup>4</sup>, John A. Finlay<sup>5</sup>, Nicholas Aldred<sup>5</sup>, Tony Clare<sup>5</sup>, Edward J. Kramer<sup>3</sup>, Christopher K. Ober<sup>1</sup>. (1) Cornell Univ, Ithaca, New York, United States (2) Cornell University, Ithaca, New York, United States (3) Univ of Cali at Santa Barbara, Santa Barbara, California, United States (4) UC Santa Barbara, Santa Barbara, California, United States (5) Newcastle University, Newcastle, United Kingdom

Settlement and adhesion of marine fouling organisms can be effectively controlled using environmentally benign siloxane based coatings. Di- and triblock copolymers of PS-*b*-P(DMS-*r*-VMS) and PS-*b*-P(DMS-*r*-VMS)-*b*-PS were designed as hydrophobic, low surface energy backbone materials capable of being functionalized via thiol-ene “click” chemistry. This backbone provides a highly customizable platform for screening a wide array of functional groups for antifouling performance. Thiols of hydrophilic chemical groups such as PEG as well as fluoroalkyl and stable radical groups can be synthesized and attached to the polymer to control surface chemistry and antifouling performance. Amphiphilic block copolymers, combining both hydrophilic and hydrophobic components, have been shown to be very effective in reducing settlement of marine organisms. Additionally, stable radical groups may disrupt settlement and adhesion of a broad range of organisms. Block copolymer design can control the surface chemistry and was studied using multiple X-ray spectroscopy methods. Stratification and self-ordering of these films was examined under water using Neutron Reflectivity. Because of the dynamic nature of these surfaces, the kinetics of surface rearrangement in aqueous environments can be studied by bubble contact angle under water. The antifouling performance of these materials was investigated through study of settlement, attachment, and removal of fouling organisms such as algae, diatoms, and barnacles. Highly effecting coatings can be developed by correlating polymer structure, surface chemistry, surface rearrangement characteristics, and antifouling performance.



## POLY 500: Multilayered perfluorinated ionomeric reactive coating for abatement of organic pollutant

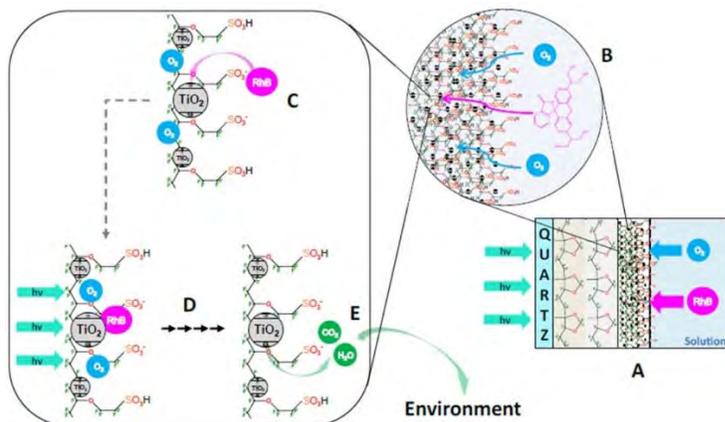
**Maurizio Sansotera**, *maurizio.sansotera@polimi.it*, **Federico Persico**, **Luca Magagnin**, **Walter Navarrini**. *Dip-CMIC, Politecnico di Milano, Milan, Italy*

A multilayered perfluorinated ionomeric matrix with embedded  $\text{TiO}_2$  has been developed as Photoactive Coating (PAC) for abatement of organic pollutants in liquid phase.[1] The immobilization of  $\text{TiO}_2$  into a polymeric matrix has overcome the drawback of slurry  $\text{TiO}_2$  due to catalyst recovery costs that limit the industrial applications. PAC degradative activity has been studied and its photocatalytic efficiency has been evaluated on both clear and turbid aqueous polluted solutions. The properties of perfluorinated ionomeric polymers, such as high chemical resistance, high UV transparency, good wettability and good permeability to  $\text{O}_2$  and water vapor, has been employed for the preparation of a reactive coating that promotes the reaction between polluted solutions and a UV-activated catalyst.[2,3]

The perfluorinated multilayered coating has been applied directly on the UV source and it has been based on a double-layer of tetrafluoroethylene(TFE)/perfluorodioxole copolymer, acting as primer, and an outer photoactive layer of the ionomeric TFE/perfluorosulphonylvinylether copolymer with dispersed  $\text{TiO}_2$ .[4] The strong acidity of the ionomeric side chains confers hydrophilicity to the coating, allowing a good interaction with the polluted aqueous solutions. Rhodamine B-base and Crystal Violet have been used as organic hydrosoluble pollutant and their concentrations have been monitored by UV-Vis and HPLC-MS.

Photodegradation tests shows that PAC allows higher rates of pollutant photoabatement than slurry  $\text{TiO}_2$ , even at low pollutant concentration. Further tests in presence of dispersed solids show good performances of PAC even in turbid suspensions. Indeed,  $\text{TiO}_2$  activation and pollutant diffusion takes place at the opposite sides of the coating and, moreover, any costly catalyst separation from purified water is required because of catalyst immobilization in the polymeric matrix.

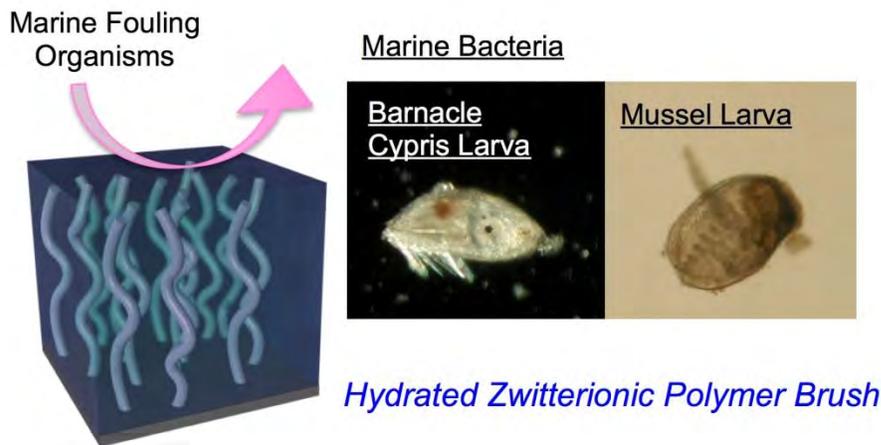
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## POLY 501: Anti-fouling characteristics of superhydrophilic polyelectrolyte brushes

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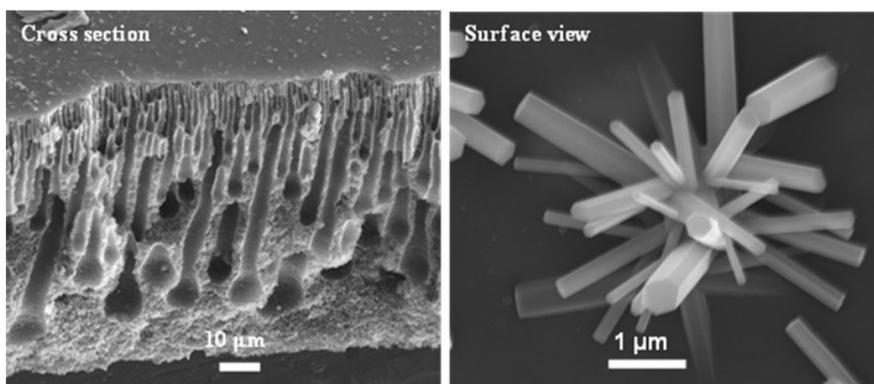
Various high-density polyelectrolyte brushes were prepared on initiator immobilized Si-particle, initiator immobilized Si-wafer and macroinitiator-modified polypropylene sheet by surface-initiated ATRP (SI-ATRP). Chain conformation of polymer brushes at water/solid interfaces were characterized by neutron reflectivity. Wettability of polymer brushes was improved by the introduction of zwitter ionic group in the side chain group. The anti-fouling characteristics of high-density zwitterionic polyelectrolyte brushes for various marine fouling organisms was demonstrated by settlement tests for barnacle cypris larvae and mussel larvae in an adhesion period, and a marine bacteria colonization test. The zwitterionic poly(phosphobetaine) brushes and poly(sulfobetaine) brushes exhibit excellent anti-fouling characteristics for macro- and micro-organisms, whereas poly(quaternary ammonium cation) brushes allow mussel larvae settlement and bacterial adhesion. Regardless of the surface free energy and chain dynamics, all hydrophobic polymer brushes showed poor anti-fouling character for the marine organisms. The outstanding universal anti-fouling character of the zwitterionic polyelectrolyte brushes is attributed to the neutral charge, high swelling and chain dynamics in a saline seawater environment, and the weakly bound water layer around the zwitterionic interfaces.



## **POLY 502: Modification of blended polyethersulfone membranes by in-situ growth of zinc oxide nanostructures for prevention of biofouling during water treatment**

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Pure polymeric membranes are facing challenges of biofouling and bacteria induced degradation which reduces their life time and cost effectiveness in water treatment. Mixed matrix membranes composed of a polyethersulfone as base polymer and zinc oxide (ZnO) nanostructures as modifiers were synthesized to control the chemical surface properties and pore size of the membrane and consequently the membrane performance and antimicrobial properties. Water contact angle measurements on the membranes show an increase in hydrophilicity of the ZnO nanoparticles (ZnO-np)-modified membranes. Surface charge of the membranes was controlled by modifying the ZnO content and the size of zinc oxide nanorods (ZnO-nr) grown in the membranes using a simple hydrothermal process. Antibacterial activity of the membranes was tested using E-coli and it was found that ZnO-np and ZnO-nr reduce the bacterial growth at the membrane surface by up to 70% compared to the unmodified polyethersulfone membranes. Reducing the bacterial growth at the modified membrane surface by growing the ZnO nanorods can offer useful solutions to increase the life time of the membrane and maintain the performance in water treatment plants.



Scanning electron micrograph of ZnO-nR modified polyethersulfone membrane cross section (left) and surface view (right)

## POLY 503: Partially hydrolyzed poly(2-oxazoline)s and poly(2-oxazine)s as additives for the preparation of self-disinfectant surfaces

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The usage of antimicrobially active polymers as additives in commodity materials enables the preparation of self-disinfectant surfaces for sanitary applications. Based on a study of the use of partially hydrolyzed poly(2-oxazoline)s as contact biocides [1], novel antimicrobially active polymers have been developed, namely partially hydrolyzed poly(2-oxazoline)s and poly(2-oxazine) with reduced water solubility. Cell membrane potential assays showed that non-hydrolyzed poly(2-nonyl-2-oxazoline) could not cause cell damage in *E. coli* strains. Poly(2-nonyl-2-oxazoline)s with hydrolysis degrees of 80 and 100%, however, killed about 50/80% of *E. coli*.

For the reduction of the water solubility of the polymer-based biocides, two approaches have been pursued, the synthesis and partial hydrolysis of higher homologues of poly(2-oxazoline)s, in particular poly(2-oxazine)s, as well as crosslinking of copoly(2-oxazoline)s by means of the UV-induced thiol-ene reaction [2]. Various poly(2-oxazoline)s and poly(2-oxazine)s with hydrolysis degrees of 0 and 50% were tested as 2.5 wt.-% additive in polypropylene compounds against the four germs *E. coli*, *S. aureus*, *P. aeruginosa*, and *C. albicans*.

The surfaces of compounds with partially hydrolyzed poly(2-phenyl-2-oxazine) exhibited high antimicrobial activity against all four germs (Figure 1). With the exception of *P. aeruginosa*, also partially hydrolyzed poly(2-phenyl-2-oxazoline) proved to be an antimicrobially active additive; nonetheless, partially hydrolyzed poly(2-phenyl-2-oxazine) always showed a more pronounced antimicrobial action.

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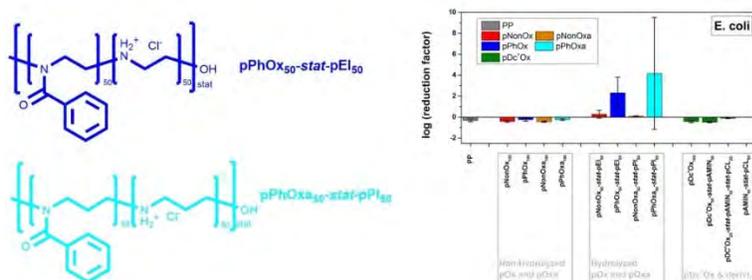
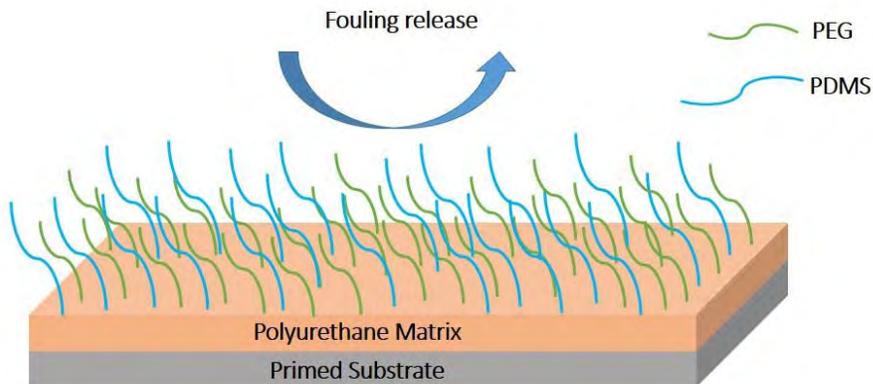


Figure 1: Left: Structure of two antimicrobially active additives based on partially hydrolyzed poly(2-phenyl-2-oxazoline) and partially hydrolyzed poly(2-phenyl-2-oxazine). Right: Antimicrobial activity of PP compounds (with 2.5 wt.-% of the additive) against *E. coli*, represented by the logarithmic reduction factor.

## POLY 504: Poly(ethylene) glycol modified amphiphilic siloxane polyurethane coatings and their performance as effective fouling release surfaces

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A series of isocyanate pre-polymer compositions modified with poly(ethylene) glycol (PEG) and poly(dimethyl) siloxane (PDMS) were synthesized and utilized to prepare siloxane-polyurethane fouling release (FR) coatings. The pre-polymer composition was confirmed by Fourier Transform Infrared spectroscopy (FTIR) and isocyanate titrations. Attenuated Total Reflectance FTIR (ATR-FTIR) and contact angle measurements suggest that both siloxane and PEG are pre-dominant on the surface after water aging, which indicates that the coating surfaces have an amphiphilic character. Several of the coating compositions displayed excellent fouling release performance against a broad spectrum of representative marine organisms during laboratory biological assays with similar performance to leading commercial FR coatings. Using PEG and PDMS modified isocyanate pre-polymers considerably improved the fouling release performance of the coating system towards bacteria (*Cellulophaga lytica*), diatoms (*Navicula incerta*) and green algae (*Ulva linza*). Therefore PEG-modified amphiphilic siloxane polyurethane coatings are a viable approach towards a non-toxic tough fouling release solution.



Amphiphilic Siloxane-Polyurethane Coating

## POLY 505: Self-healing perfluoropolymer brushes as highly polymer-repellent coatings

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Fouling of surfaces has been studied extensively for the fouling by proteins and biological materials in water. However, the fouling of surfaces by organic polymers in organic media has barely been touched upon yet, even though it is a problem of significant and increasing importance (e.g. for the resolution of 3D printing, and for a variety of issues in the processing industry). In the current presentation we discuss that this fouling of surfaces by organic polymers can even on a flat silicon Si(111) surface be strongly reduced by covalently bound monolayers with a single F atom, or by applying a well-defined, 75 nm thick, covalently bound perfluorinated PMAF17 polymer brush (synthesized using SI-ATRP) (see Figure 1a).

In the former case we demonstrate that a mono-F monolayer is often better than both a non-fluorinated or a per-fluorinated monolayer, and provide an explanation for this highly surprising behavior. In the latter case of the polymer brush, this strong reduction can be repaired, even more than 10 times, after the polymer brush has been damaged (e.g. by strong base) (see Figure 1b). This self-repairing character of these brushes occurs via molecular reorganization at the surface-air interface at slightly elevated temperatures.

Using the information derived from these two coatings we outline the chemical factors that are important for the generation of antifouling layers, and which can be complemented with properties of the underlying substrate (e.g. structuring on micro and nanoscale) to obtain surfaces that repel organic polymer fouling nearly completely.

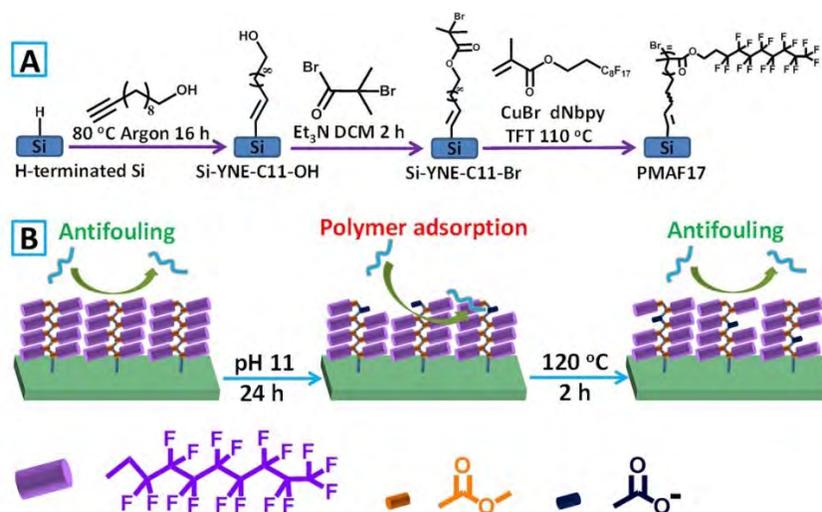


Figure 1. A) Preparation of the perfluoropolymer brush on Si(111). Bottom: B) Schematic illustration of the anti-fouling behavior of the original, damaged and repaired PMAF17 brush upon immersion into the polymer solution.

## **POLY 506: Controlled release of phytochemical-based antimicrobial coating for sustained disinfection**

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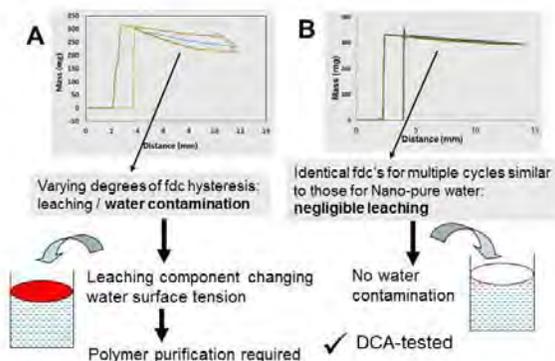
In recent years, increasing concerns have been raised to indoor air quality problems. Humans stay indoor over half of their lifetime. With frequent exposure to poor indoor air, the presence of harmful substances like biological contaminants, respirable particulates and radon would increase our risk of getting allergies, airway or surface infections and cancers. Essential oils derived from natural plants contain different phytochemicals that possess pesticide, bactericide, and fungicide properties. Thus, our works aim to investigate the possible use of essential oils with coating materials for sustained disinfection via encapsulation and controlled release mechanism. In the research, thyme oil was chosen as the major disinfecting agent because of its low minimum inhibitory concentration against different microorganisms. The composition was reformulated to optimize bactericidal efficiency and durability. Long term release and bactericidal tests were launched on glass medium, which showed that the coating can remain 2 log reduction over a month whilst challenging with *S. aureus*. The coating was also applied to HEPA filters incorporated with air purifiers for air disinfection. Corresponding field tests were conducted at the HKUST office and clinic, as well as Haven of Hope Hospital where results revealed efficient antimicrobial properties possessed by the modified filters.

## POLY 507: Dynamic contact angles (the Wilhelmy plate method) and zeta potentials: Uncommon methods for characterization of antimicrobial / cytocompatible coatings

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Biomaterials applications often involve immersion in an aqueous environment for extended time periods. Seemingly mild conditions such as contact with bodily fluids at 38 °C may constitute a harsh environment for a coating due to protein adsorption, biofilm formation, ion exchange, hydrolysis or enzymatic biodegradation. For applications where immersion of a polymer in an aqueous environment may result in leaching of polymer constituents, an adaptation of dynamic contact angle instrumentation can provide a sensitive detection method. This test comprises immersion of the target polymer in water, removal, and testing surface tension of the post-sample water with a clean (flamed) glass slide. Figure 1A shows post-sample test water for an as-received biomedical polyurethane. The force distance curves (fdc's) change with each immersion and removal of the glass slide. These fdc's are characteristic of leached contaminants concentrating on the water surface and changing  $\gamma_L$ , water surface tension. The mass pickup is of leached substances on the glass coverslip accounts for sequential increases in mass. Purification of the polyurethane followed by the DCA test shows superposed fdc's characteristic of the glass-water interface alones (Figure 1B).

An “electrokinetic potential” or “zeta potential” develops during flow of electrolyte over a solid (e.g., a polymer coating). This phenomenon is attributed to an electrical double layer formed at the interface. This method is seldom used for coatings, but we have found that zeta potentials, which can be converted to charge density, facilitate understanding of antimicrobial surfaces having polycation functionality. In particular, the stability of charge density upon immersion in an aqueous environment is readily assessed.



Dynamic contact force distance curves for detection of leaching

## POLY 508: Block copolypept(o)ides: Combining polypeptides with polypeptoids

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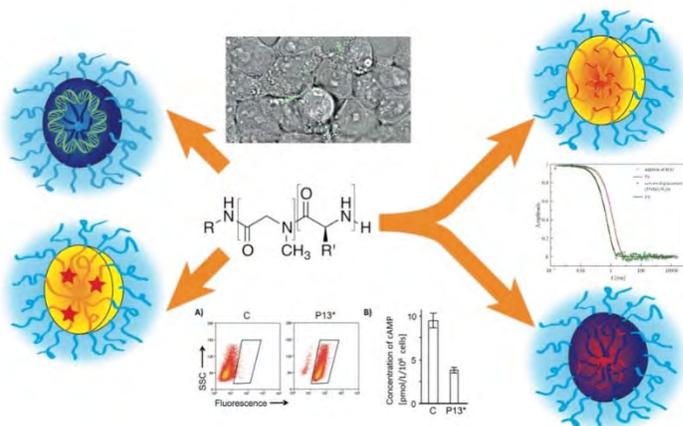
Nanomedicines bear the enormous potential to adjust pharmacokinetics of the incorporated drugs, combine different bioactive agents and deliver them simultaneously or separately to improve therapeutic or diagnostic tools.[1] In respect to an application *in vivo*, the material needs to fulfill basic requirements, such as biocompatibility, non-immunogenicity and the ability to be excreted or even better metabolized within the body.[2]

One remarkable polymeric material fulfilling these needs are polypept(o)ides (polypeptide-block-polypeptoid copolymers). The most versatile pathway to both classes of polymers is the sequential polymerization of  $\alpha$ -amino acid-*N*-carboxyanhydrides (NCAs).[3,4] Although this technique cannot provide sequence control it allows to adjust polymer size, architecture, solubility, functionality and immunogenic properties to a specific need and include functionalities beyond nature's possibilities.

Surprisingly this class of block copolymers has been almost completely overlooked in polymer science. With the intention to change this fact, we have developed various polypept(o)ide architectures based on different natural and non-natural amino acids by NCA polymerization having molecular weights from 10 – 50 kDa and a dispersity index below 1.1.[5-7]

We report the synthesis and biomedical application of polypept(o)ides in PeptoMicelles, PeptoPlexes, PeptoNanoGels and PeptoColloids. [8-10]

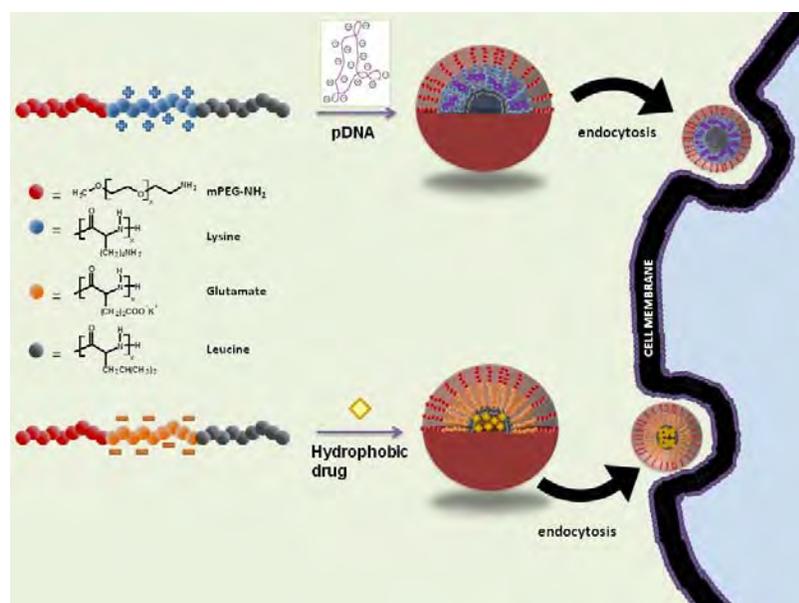
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## POLY 509: Synthesis and utilization of cationic and anionic PEGylated poly(amino acid)s for gene and drug delivery

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Synthetic biopolymers have been shown to exhibit physical and chemical properties that can be widely utilized for biologically therapeutic purposes. Amphiphilic block and random copolymers consisting poly(ethylene glycol) (PEG) and poly(amino acid) (PAA) segments allow for the construction of biomedically applicable delivery systems for both drug and gene therapies. Within PEG-PAA copolymers, PEG provides biocompatibility while PAAs permit tunable hydrophilic, ionic (cationic and anionic), and hydrophobic characteristics within the polymer constructs when using specific amino acid moieties. By using amino acids with ionic side chains, amphiphilicity and solubility of PEG-PAA copolymers can be regulated, allowing for nanoparticle formation with biologically active small molecules and plasmid DNA in aqueous solutions. PEGylated PAAs are synthesized using an amino-terminated PEG as the macroinitiator for ring opening polymerization of amino acid N-carboxyanhydrides. The self-assembly of block and random copolymers comprised of PEG and p(L-Glutamate) or p(L-Lysine) and p(L-Leucine) will be discussed. Due to cationic charge provided by p(L-Lys) blocks, PEGylated-p(L-Lysine)-p(L-Leucine) copolymers were examined for their capability of complexing with DNA and forming small polyplexes for gene transfections. Results such as dynamic light scattering, Dnase protection, and transfection will be discussed. PEGylated PAA copolymers containing p(L-Glutamate) and p(L-Leucine) were studied for their ability to properly encapsulate hydrophobic drugs, such as indomethacin and doxorubicin hydrochloride, and increased their solubility in aqueous systems.



## POLY 510: Polymer materials to fold and activate functional DNA and peptides

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Proper folding and assembling are essential for biopolymers to exhibit their inherent biological activities. In living system, molecular chaperones support precise folding of proteins and nucleic acids. We have designed ionic graft copolymers consisting of a polyion backbone and hydrophilic graft chains to engineer folding and assembling of biopolymers such as DNA and peptides having opposite ionic charges. The cationic copolymer formed soluble inter-polyelectrolyte complex with DNA and acidic peptides. The copolymers significantly facilitate DNA assembly including DNA duplex, triplex and quadruplex formations and exhibit nucleic acid chaperone-like activity. The activity of the copolymer was applied to DNA analysis including genotyping methods and DNA nanotechnology. We recently showed that the copolymer enhanced activity of DNA enzyme (DNAzyme) over a wide temperature range under multiple-turnover conditions (1). Activity of an allosteric DNAzyme, MNAzyme, was also increased by the copolymer (2).

The cationic graft copolymers effectively induced random-to-helix transition of an acidic peptide, E5, having membrane-disrupting activity. The copolymer/peptide mixture showed stronger membrane disrupting activity than peptide alone at acidic pH. Of interest, the copolymer is capable of activating the peptide at neutral pH, where the peptide also is inactive (Fig. 1) (3). These findings would be crucial to design functional liposomes and delivery tools to cytosols.

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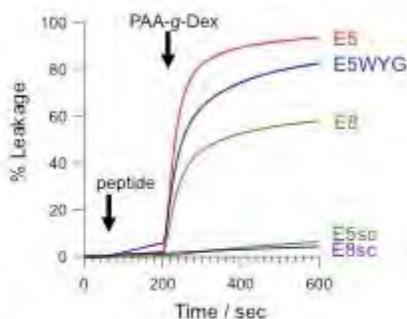
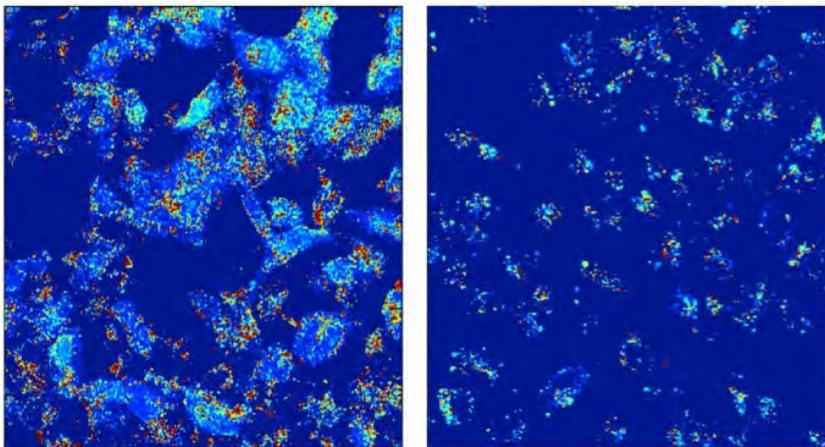


Fig. 1 Liposome membrane disruption activity of peptides induced by cationic graft copolymer, PAA-g-Dex.

## POLY 511: Endosomal escape and nuclear permeability triggered by membrane intercalation of linear poly(ethylenimine) drives gene expression

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A FRET oligonucleotide molecular beacon (OMB) designed to indicate the intactness of intracellular DNA was employed to investigate which polyplex transport pathway(s) lead to expression and which pathway(s) lead to degraded DNA. Polyplexes formed using both linear poly(ethyleneimine) (L-PEI) and generation five poly(amidoamine) (G5 PAMAM) dendrimer exhibited a similar level of uptake into HEK 293A cells that belied the > 10-fold better protein expression obtained from L-PEI. The OMB indicated that G5 PAMAM maintained a higher level of *intact* DNA in the cell than did L-PEI, which further belied the greater protein expression obtained from L-PEI. Similar levels of *intact* OMB transport to endoplasmic reticulum (60-70%) and Golgi apparatus (40%) were observed for both vectors. The level of gene expression was related to the release of *intact* OMB into the cytosol (jetPEI >> G5 PAMAM). Moreover, the gene expression obtained for G5 PAMAM polyplex was increased by ~ 10-fold by adding L-PEI before, along with, or after adding the G5 PAMAM polyplexes to the cells. For the L-PEI polyplexes and for all three mixed G5 PAMAM/L-PEI polyplexes, a diffuse, *intact* OMB distribution combined with a fluorescence signal in the nucleus was then observed. We hypothesize that L-PEI saturated into the cell plasma membrane is exchanged with internal cellular membranes, including endosomal membranes, and is therefore active for the release of DNA into the cytosol regardless of whether or not it is present in the initial vector/DNA polyplex and therefore the polyplex material internalized into endosomes. These studies provide a new mechanistic hypothesis for previous experiments highlighting the role of free vector in bringing about gene expression. The membrane intercalation hypothesis outlined herein provides an alternative to the proton sponge hypothesis that can inform further development of cationic vectors for gene delivery.



Intact beacon locations after delivery by L-PEI (left) and G5 PAMAM (right) polyplexes.

## POLY 512: Cationic nanohydrogel particles as carriers for therapeutic oligonucleotide delivery

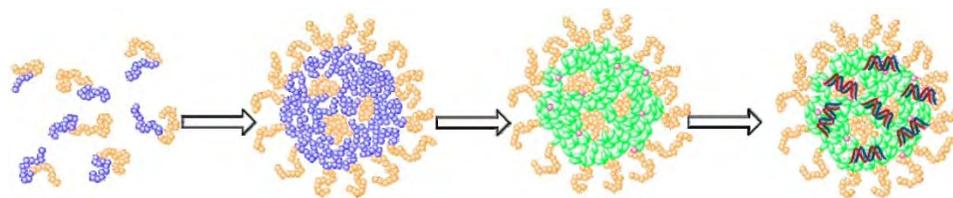
Lutz Nuhn, Nadine Leber, **Rudolf W. Zentel**, zentel@uni-mainz.de. Univ Mainz Dept of Chem, Mainz, Germany

Pharmaceutically active oligonucleotides (e.g siRNA) require adequate carriers for targeted and safe transport through the body, crossing membrane barriers and controlled release of their payload at the site of action. In contrast to lipoplex or polyplex formulations, cationic nanogels can serve as alternative oligonucleotide carriers. Usually they have pre-adjusted superstructures independent from their polyanionic cargo and show great stability, especially in presence of further polyanionic competitors. To this respect, we developed a novel concept for synthesizing polymeric cationic nanohydrogels,[1] which provides a safe and stable environment for siRNA, avoids carrier aggregation under physiologically relevant conditions and promotes size-dependent gene silencing *in vitro*. Via RAFT polymerization well-defined block copolymers of pentafluorophenyl methacrylate and tri(ethylene glycol) methyl ether methacrylate were synthesized that self-assemble in polar aprotic solvents (e.g. DMSO) into nm-sized polymer micelles. The resulting superstructures were used to generate cationic nanohydrogel particles by covalently cross-linking the reactive ester cores with spermine providing cationic moieties for stable siRNA complexation. Interestingly, the synthetic process offers possibilities to synthesize nanohydrogels of various sizes, which show a size-dependent gene silencing potential *in vitro*. Presently, we are working on the introduction of groups for active targetting and degradable cross-linkers for stimuli-responsive siRNA release.[2] Looking ahead, these novel cationic nanohydrogel particles can also serve as platform for advanced therapeutic oligonucleotide delivery strategies in the field of cancer immunotherapy.[3]

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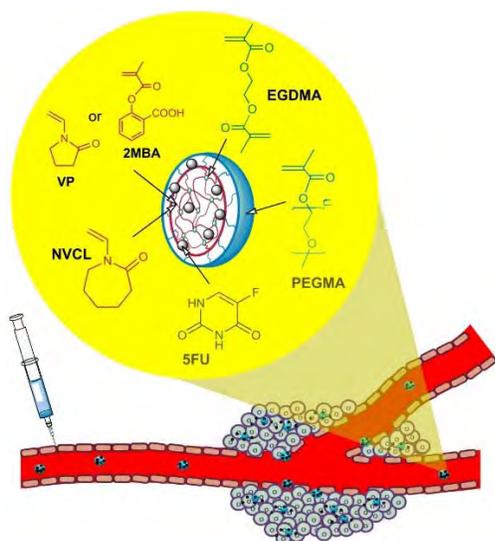


Scheme for hydrogel synthesis and loading

## POLY 513: Pegylated smart nanogels for drug delivery

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Nanogels are nanometric sized cross-linked polymers that show properties typical for hydrogels but also of colloidal polymers due to its small size. For example in the case of stimuli-responsive materials, the response time for nanogels is expected to be much faster than its macroscopic counterparts. Nanogels are typically prepared by emulsion polymerization, a well-known and robust polymerization process that has the disadvantage of needing a great amount of surfactant to control the size of the polymeric materials prepared. For biomedical applications, remaining surfactant can be toxic or usually interferes with the stimuli-responsive property desired for the product. In this contribution a variation of the classical emulsion polymerization, called surfactant-free emulsion polymerization (SFEP) is presented as a method of choice for the preparation of stimuli-responsive nanogels envisioned for biomedical applications. This methodology makes use of a specific type of macromers: methacrylate functionalized polyethyleneglycol (PEG-MA) with two goals in mind: to stabilize the emulsion process and to provide the nanogels with a PEGylated shell chemically attached to the crosslinked core. This methodology has been exploited to prepare temperature responsive and dual temperature and pH-responsive nanogels. The proper choice of synthetic parameters allows for controlling the size and the response temperature in the case of temperature responsive nanogels. Poly(*N*-isopropylacrylamide) containing, temperature responsive nanogels, were loaded with doxorubicin, poly(*N*-vinylcaprolactam) (PNVCL) containing, temperature responsive nanogels were loaded with 5-fluorouracil (5-FU). Results showed that this tailor made nanogels are excellent candidates for delivery of the selected antineoplastic drugs into tumors.

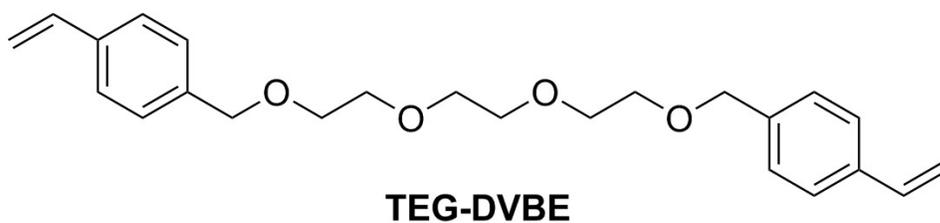


PEGylated PNVCL temperature responsive nanogels acting as drug delivery vehicle for 5-FU into tumors

## POLY 514: Rapid photo-copolymerization of styrene and methacrylate derivatives

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Copolymers of styrene derivatives and methacrylate derivatives have broad applications in automobile coating, electronic devices and medical devices because of their excellent light transparency and anti-weathering properties. However, slow polymerization rate and low degree of vinyl conversion (DC) limit their usage. Our group has recently developed a new polymerization approach that, upon 20 s visible light irradiation, may yield DC as high as 90 %. In this study, styrene derivatives, triethyleneglycol divinylbenzylether (TEG-DVBE), and urethane dimethacrylate (UDMA) were copolymerized in the presence of the visible light initiators, camphorquinone (CQ)/ 4-*N,N*-dimethylaminobenzoate (4E). The DC and the compositions of TEG-DVBE and UDMA in monomer mixtures and in copolymers were evaluated by FTIR, NMR and Raman micro-spectroscopy. The latter was also used to study photo-copolymerization kinetics. TEG-DVBE and UDMA monomer reactivity analysis suggested an alternating copolymerization mechanism, and an azeotropic composition at the equimolar monomer ratio. As a result, a sequence-controlled resin network may be achieved, and the structure and properties of the resins may be precisely controlled through adjusting the chemical structure of the feeding monomers. Our rapid photo-polymerization approach yielded highly cured copolymers with alternating styrene-methacrylate repeating units. This approach opens many new capabilities in material design and development. This research is supported by NIH U01DE023752.

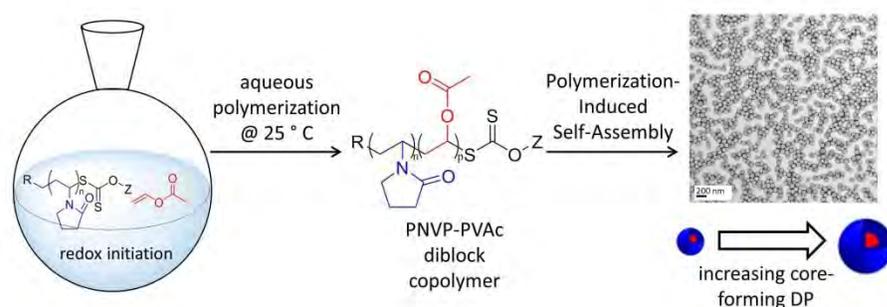


## POLY 515: Diblock copolymer nanoparticles via RAFT aqueous emulsion polymerization of less activated monomers

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Polymerization-induced self-assembly (PISA) presents a robust strategy to produce well-defined copolymer nanoparticles in a wide range of solvents at high solids<sup>1–3</sup> and is therefore potentially amenable to industrial-scale production. In principle, the polymerization of less activated monomers (LAMs) can be achieved using reversible addition-fragmentation chain transfer (RAFT) polymerization.<sup>4</sup> Here we present the well-controlled RAFT solution polymerization of *N*-vinyl pyrrolidone (NVP) using a xanthate-based chain transfer agent (CTA), followed by the RAFT aqueous emulsion polymerization of vinyl acetate (VAc) at ambient temperature. The PNVP homopolymer is used as a water-soluble macro-CTA to form sterically-stabilized PNVP-PVAc diblock copolymer nanoparticles of tunable size via PISA. Selective deprotection of PVAc to afford poly(vinyl alcohol) (PVA) leads to the production of double-hydrophilic PNVP-PVA diblock copolymers.

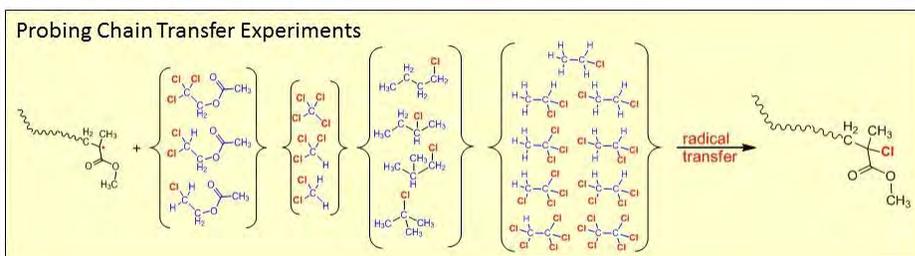
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## POLY 516: Polymerization of mono-, di- and trichloroethyl methacrylates: A study in chain transfer

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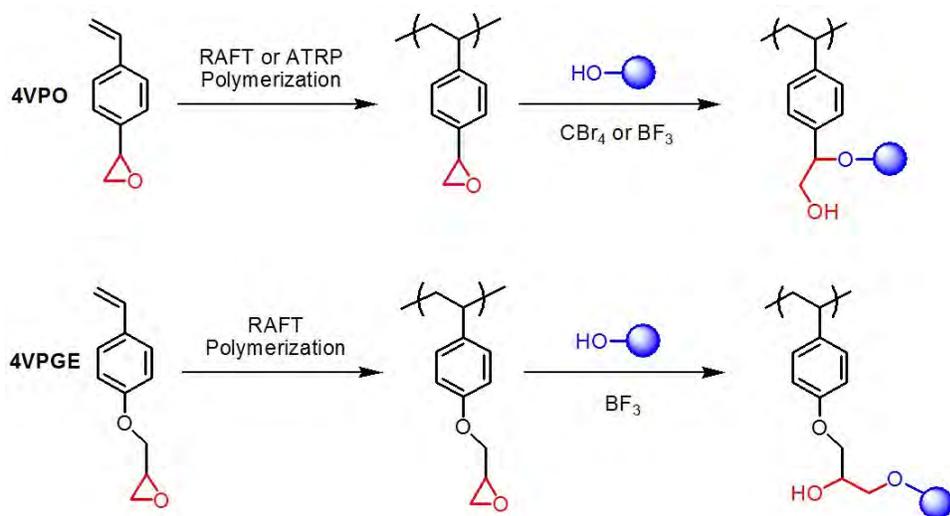
The incorporation of chloroalkyl substituents in well-behaved bulk free radical polymerization systems has significant potential to impact optical fiber and lens applications via its associated refractive index and homogeneous blend forming characteristics. To employ such properties this polymer must be prepared and processed under optically clean conditions. The benchmark optical polymer poly(methyl methacrylate) can be prepared as a monomer-polymerized casting with >99% monomer conversion and with molecular weight control for melt viscosity adjustment in subsequent processing at 230°C. The objective of this work was to analogously prepare and characterize polymers from the monomer series  $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_2\text{CH}_3\text{Cl}_n$ ,  $n = 1, 2, 3$ . An unexpected finding was that each member produces a crosslinked polymer under bulk polymerization conditions. Their crosslink densities correlate with the quantity of added chain transfer agent and with the degree of chlorine substitution in the respective monomer ( $n=1 > n=2 > n=3$ ). This latter effect is further quantified by chain transfer measurements on the pendant group model compound series  $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}_3\text{Cl}_n$ ,  $n = 0, 1, 2, 3$  in a methyl methacrylate polymerization with a parallel finding for the order of the transfer constants ( $n=1 > n=2 > n=3 > n=0$ ). An understanding of this result is further probed by chain transfer measurements on three series of chloroalkane compounds as depicted below. Key results are the low chain transfer activity associated with the  $-\text{CCl}_3$  moiety and the high transfer activity of the *t*-butyl chloride isomer. The crosslinking during polymerization can be eliminated by using an excessive quantity of mercaptan chain transfer agent or by diluting with an inert solvent (benzene) to a monomer concentration of  $\leq 10\%$  by volume. In the former case the molecular weight is depressed below that useful for melt processing. In the latter the molecular weight distribution becomes quite broad (dispersity  $> 8$ ) which is a significant issue in molecular weight control for melt processing.



## POLY 517: Synthesis of well-defined, epoxide-containing styrenic polymers and their functionalization with alcohols

**David McLeod**, *xerocooldown@hotmail.com*, *Nicolay V. Tsarevsky*. *Chemistry, Southern Methodist University, Garland, Texas, United States*

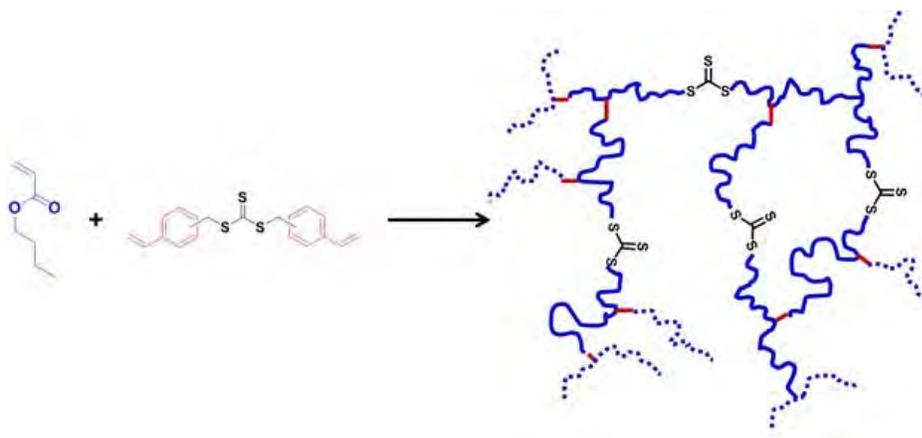
Epoxide-containing polymers can be readily modified with a wide variety of nucleophiles to produce useful functional materials. Two epoxide-containing styrenic monomers, 4-vinylphenyloxirane (4VPO) and 4-vinylphenyl glycidyl ether (4VPGE), were efficiently synthesized and then polymerized in a well-controlled manner under low-catalyst-concentration atom transfer radical polymerization or reversible addition-fragmentation chain-transfer polymerization conditions. The pendant epoxide groups were modified with a structurally-diverse library of alcohols and phenols using either  $\text{CBr}_4$  or  $\text{BF}_3$  as the acid catalyst with minimal cross-linking/branching side reactions. The structures and macromolecular characteristics of the resulting well-defined  $\beta$ -hydroxy ether-functionalized polymers were determined using size exclusion chromatography,  $^1\text{H}$  NMR spectroscopy, IR spectroscopy, and thermal gravimetric analysis.



## POLY 518: Covalently cross-linked poly(*n*-butyl acrylate) networks prepared with a dual reversible addition fragmentation chain transfer/crosslinking agent

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3,4-divinylbenzyl trithiocarbonate (DVBTC) was successfully synthesized via a one-pot reaction and used as a dual chain transfer and crosslinking agent to prepare poly(*n*-butyl acrylate) (PBA) networks at target crosslink densities from 1.5 to 307.8 mol/m<sup>3</sup> via reversible addition fragmentation chain transfer (RAFT) polymerization. The cross-link density of PBAs were measured by swelling and through the Flory-Rehner equation and oscillatory shear rheology from the plateau modulus. A monotonic increase in the crosslink density with RAFT agent concentration was observed. The role of interchain radical transfer during crosslinking to produce branched chains and more complex viscoelastic behavior will be discussed.



## POLY 519: Thermodynamic and kinetic syntheses of conjugated ladder polymers

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Fully conjugated ladder polymers with coplanar,  $sp^2$  atom-rich backbones represent a captivating class of macromolecules, on account of their well-defined rigid structures, intriguing syntheses, and promising potential in materials applications. Combining the superior materials performance of fused-ring carbon materials and solution processability of conventional polymer materials, ladder polymers emerge as promising candidates for the next-generation synthetic organic materials with breakthrough performances (Figure). To explore efficient synthesis of this class of polymers, kinetic and thermodynamic controlled methods were employed to construct well-defined ladder polymers derived from quinacridone and carbazole units, respectively. Their structural feature and functionality were carefully designed to allow for excellent solubility and solution-processability. Solution-phase and solid-state characterization were conducted extensively, setting the stage for their applications in the forms of thin film, fiber, or hybrid materials.

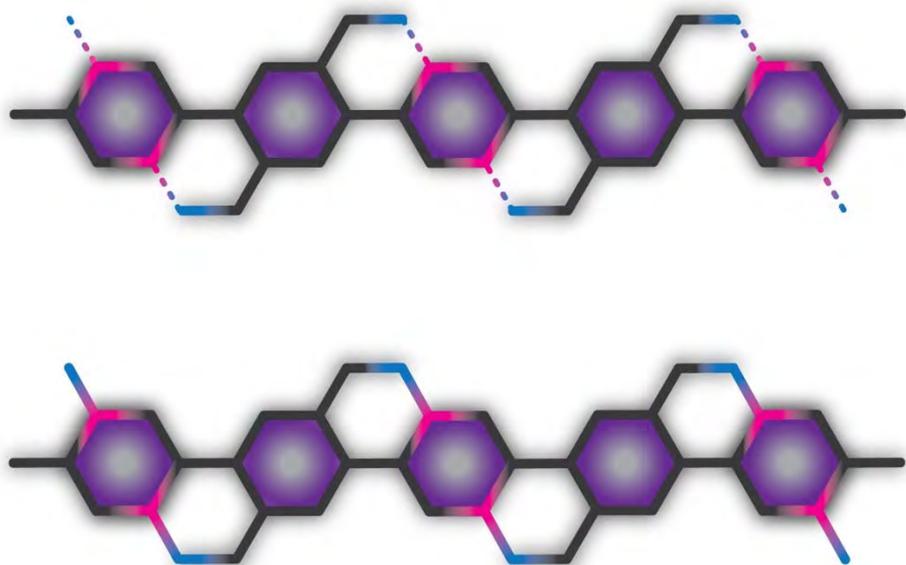


Figure. Graphic representation of coplanar ladder polymers bridged by dynamic non-covalent bonds (top) and kinetically stable covalent bonds (bottom).

## POLY 520: Simple bench top approach to polymer brush nanostructures using visible light mediated metal-free atom transfer radical polymerization

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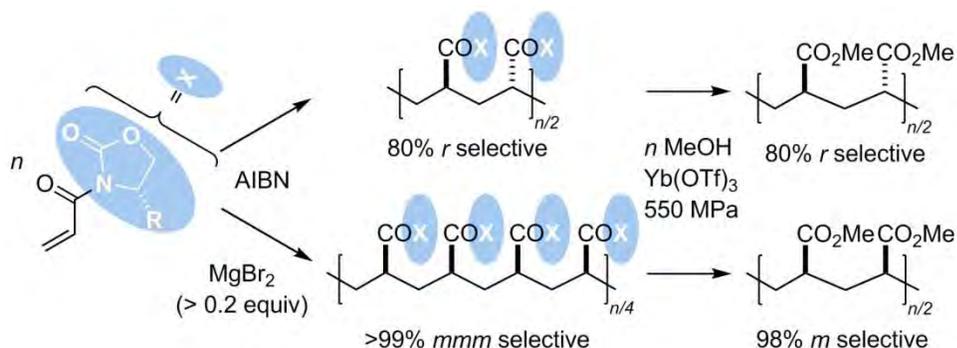
The development of an operationally simple, metal-free surface-initiated atom transfer radical polymerization (SI-ATRP) is reported. The facile nature of this process enables the fabrication of well-defined polymer brushes from surfaces using a novel “bench top” set-up that can be easily scaled to 4 inch wafers. This approach circumvents the requirement of stringent air-free environments (i.e. glovebox), and mediation by visible light, allows for manipulation of brush thicknesses as well as spatial control on the nanoscale, with complex 3-dimensional patterns achieved in a single step. This robust approach leads to unprecedented access to brush architectures on a variety of substrates for non-experts.



## POLY 521: Lewis acid-mediated stereospecific radical polymerization of acrylamides

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Lewis acid-catalyzed radical polymerization of acrylamides bearing chiral oxazolidinones gave highly isotactic polyacrylamides with up to >99% meso tetrad (*mmm*) selectivity. Polymerization in the absence of Lewis acid gave atactic polymers with 80% racemo diad (*r*) selectivity; the selectivity was deliberately tuned from 80% *r* to >99% *mmm* by varying the polymerization conditions. The polyacrylamide was quantitatively converted to corresponding polyacrylates while preserving the stereoregularity, thus providing a general method for the synthesis of atactic to isotactic polyacrylates.

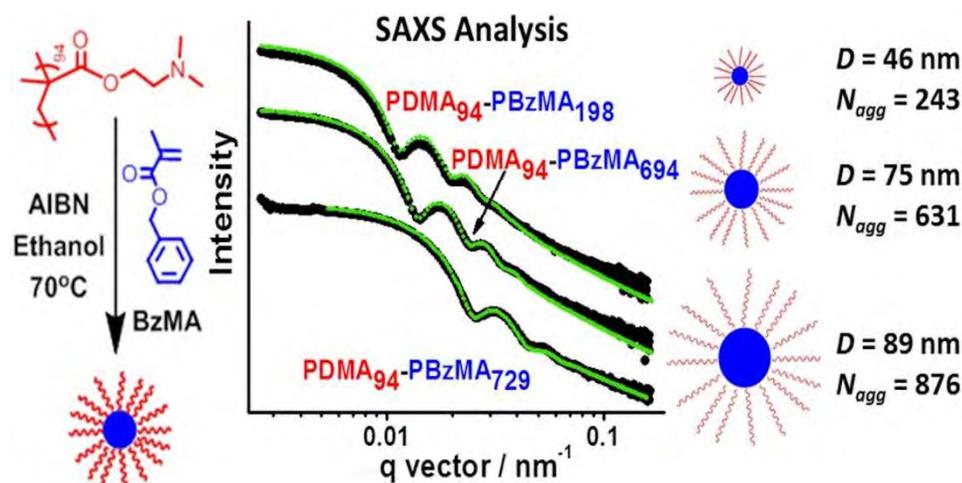


Stereospecific polymerization of acrylamides

## POLY 522: How do spherical diblock copolymer nanoparticles grow during RAFT alcoholic dispersion polymerization?

**Elizabeth Jones**<sup>2</sup>, [cha07erj@sheffield.ac.uk](mailto:cha07erj@sheffield.ac.uk), **Oleksandr Mykhaylyk**<sup>2</sup>, **Mona Semsarilar**<sup>2</sup>, **Mark Boerakker**<sup>2</sup>, **Paul Wyman**<sup>2</sup>, **Steven P. Armes**<sup>1</sup>. (1) Univ of Sheffield Dept of Chem, Sheffield, United Kingdom (2) The University of Sheffield, Sheffield, United Kingdom

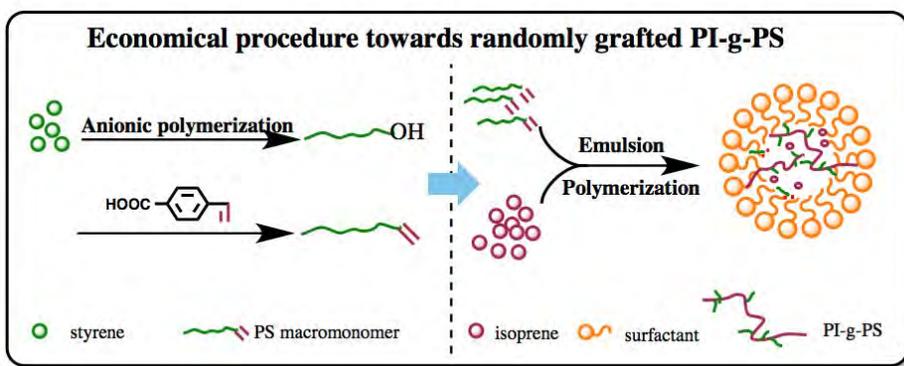
A poly(2-(dimethylamino)ethyl methacrylate) (PDMA) chain transfer agent (CTA) was used for the reversible addition-fragmentation chain transfer (RAFT) alcoholic dispersion polymerization of benzyl methacrylate (BzMA) in ethanol at 70°C. THF GPC analysis indicated a well-controlled polymerization (molecular weight increasing linearly with conversion) and also showed good blocking efficiency with no homopolymer contamination apparent, and all  $M_w/M_n$  less than 1.35. <sup>1</sup>H NMR confirmed greater than 98% BzMA conversion for a target PBzMA degree of polymerization (DP) of up to 600. The PBzMA block becomes insoluble as it grows, leading to the *in situ* formation of sterically-stabilized diblock copolymer nanoparticles *via* polymerization-induced self-assembly (PISA). Fixing the mean DP of the PDMA stabilizer block at 94 units and varying the DP of the PBzMA block enabled a series of spherical nanoparticles of tunable diameter to be obtained. These nanoparticles were characterized by TEM, DLS, MALLS and SAXS, with mean diameters ranging from 35 to 100 nm. The latter technique was particularly informative: data fits to a micelle model enabled calculation of the core diameter, surface area occupied per copolymer chain and the mean aggregation number ( $N_{agg}$ ). The scaling exponent derived from a double logarithmic plot of core diameter vs PBzMA DP suggests that the conformation of the PBzMA chains is intermediate between the collapsed and fully extended state. This is in good agreement with <sup>1</sup>H NMR studies, which suggest a relatively low degree of solvation for the PBzMA core-forming chains (5-13 %). The  $N_{agg}$  values calculated from SAXS and MALLS are similar and scale approximately linearly with PBzMA DP. This suggests that spherical micelles grow in size not only as a result of the increase in copolymer molecular weight during the PISA synthesis, but also by exchange of individual copolymer chains between micelles and/or by sphere-sphere fusion events.



## POLY 523: Synthesis and characterization of graft thermoplastic elastomers polyisoprene-g-polystyrene (PI-g-PS) through anionic and emulsion polymerization

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Thermoplastic elastomers (TPEs) are biphasic materials consisting of a continuous rubbery matrix reinforced by glassy physically crosslinking. Compared with conventional synthetic rubber SBR (styrene-butadiene rubber), TPEs exhibit competitive mechanical properties with improved processibility and recyclability. Tetrafunctional multigrafted copolymer with 22% polystyrene (PS) and 10 regularly spaced branch points exhibited almost twice the strain at break than that observed for commercial Kraton<sup>®</sup> linear triblock TPEs (20%PS). However, these graft copolymers were synthesized by combining living anionic polymerization (LAP) with chlorosilane coupling reaction under high vacuum condition, which was not suitable for large scale production. Here we presented synthesis and characterization of randomly grafted copolymers polyisoprene-g-polystyrene(PI-g-PS) by combining LAP with low cost emulsion polymerization. PS macromonomers was synthesized by LAP then copolymerized with isoprene in emulsion polymerization. The range of Mw for multigraft copolymers was from 200 to 700 kg/mol. Glass transition temperatures of PS and PI were observed at 80°C and -47.6 °C respectively. Decomposition temperature of 5% weight loss was 328°C. Our work is different from previous work on PI-g-PS in the following aspects. First, styrene was used as cosolvent, instead of toluene, to help to disperse macromonomers, which increase conversion of macromonomer drastically. Further, long chain branching analysis will be investigated by SEC with online viscometer detector. Also, mechanical properties will be evaluated by dynamic mechanical analysis and tensile test. Additionally, morphological characterization will be carried out with transmission electron microscopy and small angle x-ray scattering in order to correlate structure-property relationship.

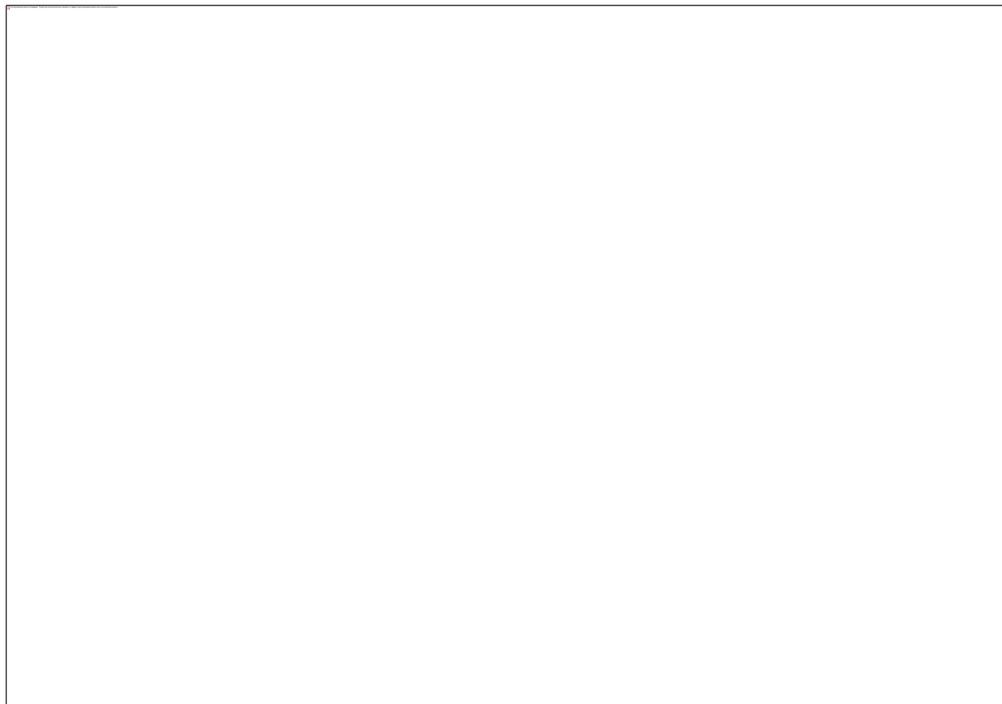


Synthetic scheme of PI-g-PS random graft copolymers

**POLY 524: Ultrahigh molecular weight linear block copolymers: Rapid access by reversible-deactivation radical polymerization and self-assembly into large domain nanostructures**

*Jose Kenneth D. Mapas, josekenn@buffalo.edu, Javid Rzayev. Chemistry, Natural Science Complex, SUNY Buffalo, Buffalo, New York, United States*

High molecular weight block copolymers ( $M_n \geq 1 \times 10^6$  g/mol), which grant access to periodic nanostructures with large domain spacings, afford the fabrication of materials with interesting properties and enable a variety of applications. However, the phase behavior and other physical properties of high molecular weight linear block copolymers remain largely unexplored due to their highly entangled conformations. Furthermore, the production of these copolymers requires challenging synthetic protocols, which limits the availability of these materials for non-synthetic experts and diminishes their potential impact. In this work, we report a “user-friendly” RDRP method for the rapid synthesis of ultrahigh molecular weight linear diblock copolymer using a combination of ATRP and RAFT polymerization to generate block copolymers that can self-assemble into ordered nanostructures with domain spacings exceeding 100 nm.





## POLY 526: Click chemistry tools for delivering cisplatin to cancer cells

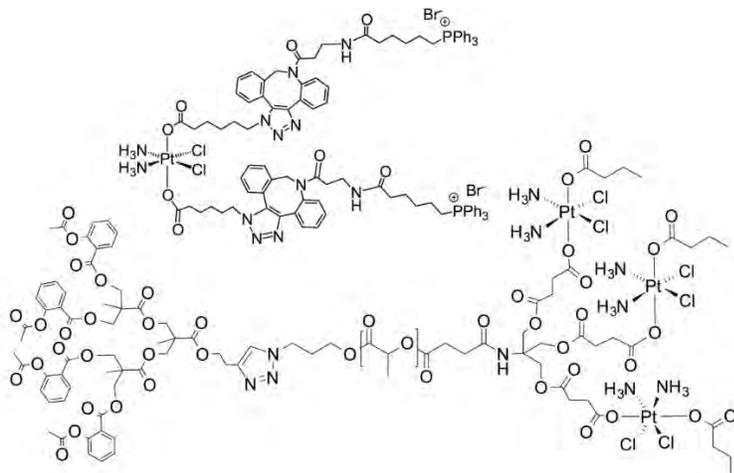
**Shanta Dhar**, *shanta@uga.edu*. Chemistry, University of Georgia, Athens, Georgia, United States

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Mitochondria play significant roles in carcinogenesis process due to their active participation in energy production and maintenance of cellular apoptosis. The genome, which resides inside the mitochondrial lumen, mitochondrial DNA (mtDNA), is important in cell death and drives tumor towards a more metastatic stage. The most widely used nuclear DNA (nDNA) damaging agent cisplatin is highly effective in many cancers, however several types of malignant cells become resistant to cisplatin-based therapy. This resistance often results from accelerated nDNA repair by the nucleotide excision repair (NER) machinery. The lack of NER in the mitochondria and highly mutated mtDNA in aggressive cancers indicated that directing cisplatin in the form of a prodrug to the mitochondrial lumen can be beneficial to overcome resistance. Here, we describe a click chemistry based methodology to construct prodrugs for cisplatin with mitochondrial association properties, incorporation of these prodrugs in biodegradable polymeric nanoparticles, *in vitro*, and *in vivo* properties of this system. In another approach, we will describe the use of click chemistry to construct new polymers for delivery of a cocktail of cisplatin and anti-inflammatory agents.

### Reference:

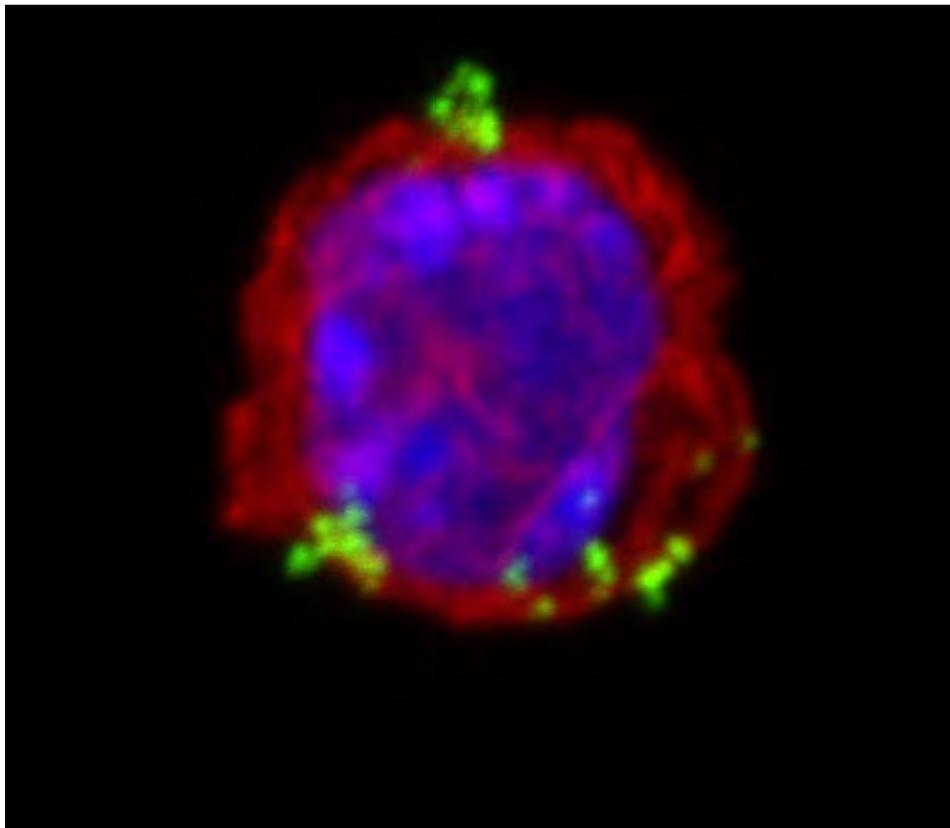
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## POLY 527: Engineering cell surfaces with synthetic polymers

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

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



**POLY 528: Poly(lactic-co-glycolic acid)-based clickable polymersynthesis and blending of magneto-responsive colloidal polymers: Observation of mesoscopic phase separation**

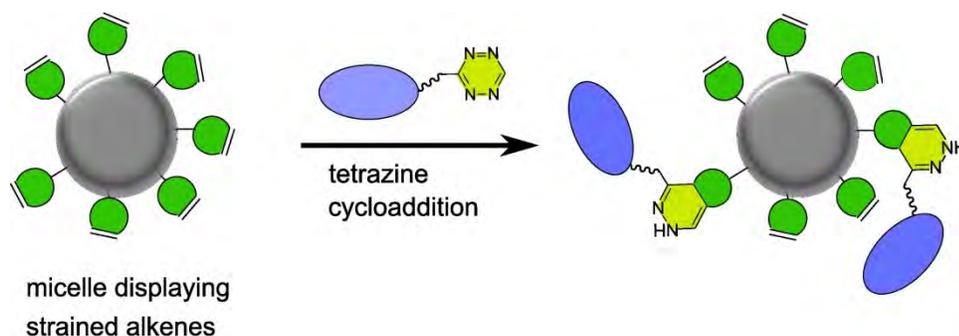
**Jason Olejniczak**<sup>1</sup>, [jolejnic@ucsd.edu](mailto:jolejnic@ucsd.edu), Adah Almutairi<sup>3</sup>, Viet Anh Nguyen Huu<sup>1</sup>, Sangeun Lee<sup>1</sup>, Minnie Chan<sup>2</sup>, Guillaume Collet<sup>1</sup>. (1) University of California San Diego, San Diego, California, United States (2) PSB 2186, University of California San Diego, La Jolla, California, United States (3) Pharmaceutical Sciences MC 0600, University of California San Diego, La Jolla, California, United States

We have prepared a biodegradable polymer inspired by the backbone of Poly(lactic-co-glycolic acid) with pendant azide groups built into the structure. These pendant azides provide an ideal platform for further modification of the polymer. We have worked to modify the polymer directly using copper catalyzed click chemistry to test its ability to act as a polymer prodrug conjugate. We have also formulated the polymer into polymeric nanoparticles. These particles are shown<sup>2</sup> to be capable of functionalization with copper free cyclooctyne based click strategies with model dyes. This novel material has great potential for targeted drug delivery applications.

## POLY 529: Bioorthogonal labeling of micellar nanoparticles

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Previous work in the Gianneschi lab has demonstrated that enzyme-responsive micellar nanoparticles are capable of a targeted accumulation and retention within tumor tissue in response to overexpressed matrix metalloproteinases. It has also been shown that small molecule therapeutics that were covalently bound to the nanoparticle scaffold could selectively be delivered to the site of disease. This targeted delivery method is, however, only applicable to molecules that can be conjugated to the polymer without altering the resulting overall micellar structure. We have developed an approach that enables the bioorthogonal conjugation of molecules onto micellar nanoparticles by the means of a tetrazine cycloaddition reaction. The synthesis of the polymer amphiphiles is facilitated by ring-opening metathesis polymerization (ROMP) followed by the conjugation of either a strained alkene or a tetrazine moiety. After the formulation of the polymers into spherical micelles, molecules of different sizes were successfully conjugated by the cycloaddition reaction onto the micelles. With this approach we aim to facilitate the *in vivo* labeling of assembled nanomaterials with any large molecule or therapeutic.



Labeling of spherical micelles using the tetrazine cycloaddition reaction.

## **POLY 530: Diffusion-controlled interfacial bioorthogonal polymerization**

**Xinqiao Jia**, *xjia@udel.edu. Univ Delaware, Newark, Delaware, United States*

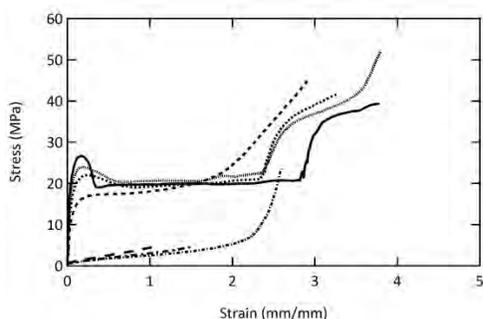
Tetrazine ligation, the cycloaddition of *s*-tetrazine (TET) with *trans*-cyclooctene (TCO) derivatives, has been employed for biomaterials synthesis owing to its biocompatibility, bioorthogonality and exceptional reaction kinetics. Hyaluronic acid (HA)-based hydrogels with spatial gradients of stiffness and ligand density have been prepared via a diffusion-controlled interfacial crosslinking process through the instantaneous reaction between TET and TCO functionalized precursors at the gel/liquid interface. A new cell invasion platform was created where cancer cells were attached to a HA gel with parallel stripes of ECM signals or crosslinking gradients normal to the gel surface. The invasion speed and pattern were found to directly correlate to the metastatic potential of the cancer cells. Tetrazine ligation has also enable the direct production of high molecular weight multiblock copolymers, as robust polymer fibers, via interfacial bioorthogonal polymerization employing TET and TCO-functionalized precursors at the oil/water interface. When cell-adhesive peptide is incorporated in the TET monomer, the resulting protein-mimetic polymer fibers provide guidance cues for cell attachment and elongation. Replacing the bisTCO monomer with a trisTCO crosslinker resulted in the production of PEG-based crosslinked hydrogel fibers. Overall, the modular approaches allow facile substitution of the constituent building blocks to fine-tune the materials properties for applications in tissue engineering and drug delivery.

## POLY 531: Ultra-tough aliphatic thiol-isocyanate elastomers achieved through thiol-click reactions

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Thiol click chemistry has seen increased attention due to its versatility in producing polymers from a wide range of reactants such as alkenes, acrylates, isocyanates, and other reactive groups under either radical or anionic conditions. These reactions tend to be efficient, fast, free from oxygen or water inhibition, and produce little to no byproducts in solvent-free conditions. Thiol-ene polymers are by far the most well studied thiol chemistry, having been investigated for use in biomedical and optical industries, as dental restorative resins, and in other areas. Thiol-ene networks photopolymerize quickly under a radical mediated, step growth mechanism, have high network uniformity, and low cure stresses. However, they lack the mechanical toughness required to serve well for industries where robust materials are desirable such as aerospace, rapid prototyping, and protective coatings. New chemistries such as thiol-isocyanate click reactions may be needed to produce highly tough photocurable polymers.

This work describes the synthesis and physical properties of tough thiol-isocyanate thermoplastics and thermosets cured via a UV initiated amineimide photobase, reacted without the use of pre-polymerization or solvent. The thiol-isocyanate elastomers form unique semi-crystalline morphology that can be controlled by both thermal treatment and monomer choice. Glass transition temperatures are as low as 7 °C and are easily increased through altering the monomers used. The thermomechanical properties of the polymers are shown to be dependent on both crystallinity and crosslink density. The material shows toughness roughly an order of magnitude higher than previously described thiol-click systems, reaching up to 100 MJ/m<sup>3</sup>. Tensile strengths approach 50 MPa, and failure strains exceed 380 %. This exceptional toughness combined with rapid photo-curing opens the door to applications such as fused filament fabrication and stereolithographic 3D printing.



Tensile behavior of UV-cured thiol-isocyanate elastomers

## POLY 532: Oxidation of thiol-ene networks for post-polymerization modification of thermomechanical properties

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Thiol-ene chemistries have recently seen a surge in use for broad applications such as optical holograms<sup>[1]</sup> and microenvironments for cell culture<sup>[2]</sup>. In these and many other examples, the underlying thiol-ene systems are elastomeric above ambient temperatures due to the flexible thioether linkage resulting from the ‘click’-reaction between the thiol and alkene moieties. While monomers exist that can enable vitreous thiol-ene networks at higher temperatures (up to 100°C)<sup>[3]</sup>, the monomers tend to form solutions that are highly viscous and difficult to process. In this work, we explore a post-polymerization modification of low glass transition temperature ( $T_g$ ) thiol-ene networks through an oxidation procedure involving 30% hydrogen peroxide ( $H_2O_2$ ). Using a base system comprising the stoichiometric balance of the thiol Tricyclodecanedithiol (TCDDT) and the alkene 1,2,4-Trivinylcyclohexane (TVCH), 1mm thick films were synthesized and studied for thermomechanical characteristics using dynamic mechanical analysis. Results show a  $T_g$  of 34.4°C as denoted by the peak in tangent delta, with oxidation raising the  $T_g$  to 152.3°C denoting the appearance of the rotationally-inflexible sulfone groups in the backbone of the network, substituting the previously flexible thioether linkages. This post-polymerization modification is currently being explored for elevating transition temperatures of 3D-printed thiol-ene elastomers for the stereolithographic (SLA) printing of load-bearing thiol-ene parts.

[1] Nair, Devatha P., et al. *Adv. Funct. Mat.* 22.7 (2012): 1502-1510.

[2] DeForest, Cole A., et al. *Nat. Mat.* 8.8 (2009): 659-664.

[3] Carioscia, Jacquelyn A., et al. *JOPS Part A: Poly. Chem.* 45.23 (2007): 5686-5696.

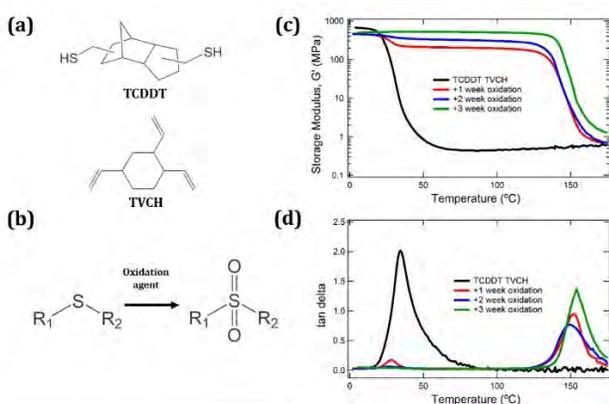
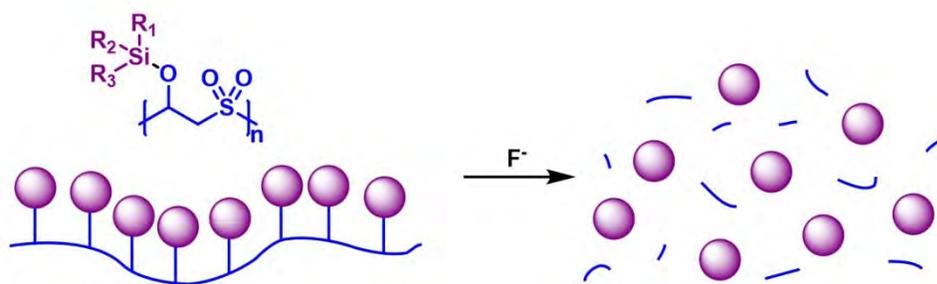


Figure 1: (a) Monomers used in compositions for oxidizing thiol-ene networks via the introduction of (b) sulfone groups along the backbone of the thiol-ene network post-polymerization. The change in (c) modulus as a function of temperature and (d) the corresponding viscoelastic behavior are shown for various degrees of network oxidation.

## POLY 533: Rapid fluoride-triggered depolymerization of poly(olefin sulfone)s

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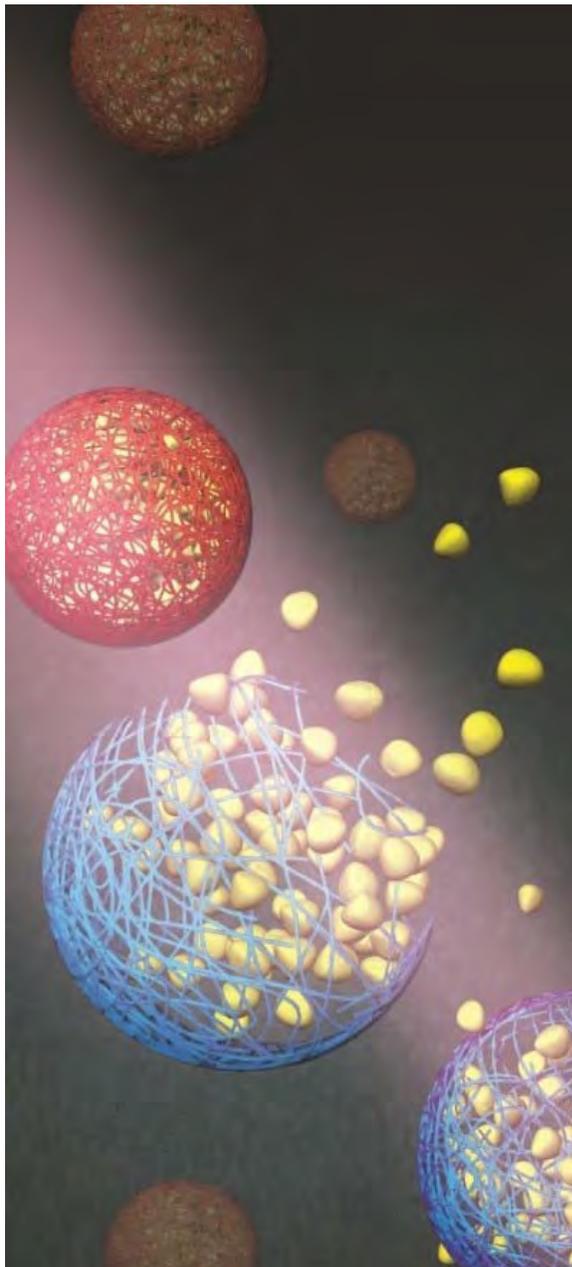
The ability to efficiently control the depolymerization of materials through stimuli has applications in many fields such as encapsulation and transient electronic devices. Poly(olefin sulfone)s (POSs) represent an interesting class of polymers that have been shown to depolymerize through thermolysis, radiolysis and hydrolysis with base. Our previous work with poly(vinyl *tert*-butyl carbonate sulfone) has demonstrated that depolymerization of this material can be triggered through removal of the side group. With this insight, we have designed fluoride sensitive POSs through the incorporation of silyl ether functional groups along the polymer backbone. These polymers are synthesized through free radical polymerization of silyl enol ether monomers and sulfur dioxide. Variation of the silyl group of these poly(silyl enol ether sulfones) (PSEESs) will result in polymers with a range of susceptibility to fluoride-mediated deprotection and subsequent depolymerization. This work will discuss the synthesis of PSEESs, their characterization and their application as fluoride-sensitive materials for rapid degradation.



## **POLY 534: Light-triggered chemical amplification to accelerate degradation and release from polymeric particles**

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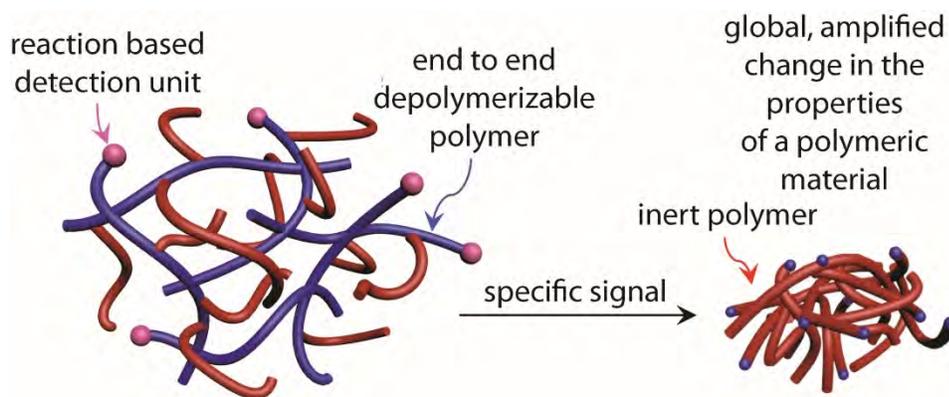
We describe a means of chemical amplification to accelerate triggered degradation of a polymer and particles composed thereof. We designed a light-degradable copolymer containing carboxylic acids masked by photolabile groups and ketals. Photolysis allows the unmasked acidic groups in the polymer backbone to accelerate ketal hydrolysis even at neutral pH.



## POLY 535: Design, synthesis, and applications of new self-immolative and low ceiling temperature polymers

**Scott T. Phillips**, *sphillips@psu.edu*. Pennsylvania State University, University Park, Pennsylvania, United States

This presentation will describe new classes of self-immolative and low ceiling temperature polymers that depolymerize from end to end continuously and completely in response to specific stimuli. Various stimuli-responsive materials made from these polymers will be described as well, with a focus on achieving depolymerization in the solid state.

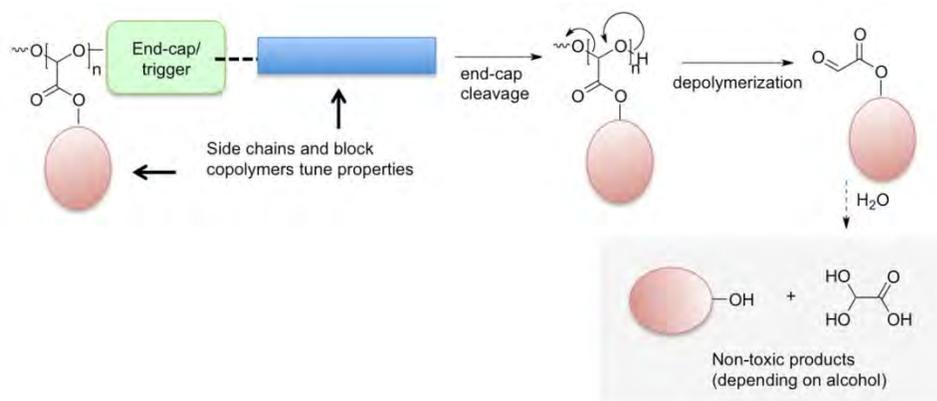


## POLY 536: Self-immolative polyglyoxylates: Towards functional backbones and assemblies

**Elizabeth R. Gillies**<sup>1,2</sup>, [egillie@uwo.ca](mailto:egillie@uwo.ca), Bo Fan<sup>2</sup>, Rebecca Yardley<sup>1</sup>, John Trant<sup>1</sup>. (1) Chemistry, The University of Western Ontario, London, Ontario, Canada (2) Chemical and Biochemical Engineering, The University of Western Ontario, London, Ontario, Canada

Self-immolative polymers are a class of materials that degrade by an end-to-end depolymerization mechanism in response to a stimulus-mediated cleavage of a stabilizing end-cap from the polymer terminus (1, 2). Relative to conventional stimuli-responsive or biodegradable polymers, they exhibit several unique properties including a degradation time dependent on the degree of polymerization and the ability to change their responsiveness to stimuli by simply changing the end-cap. These aspects make them of increasing interest for a wide variety of applications including sensors and controlled drug release. This presentation will describe our group's progress toward the development of self-immolative polyglyoxylates (Figure 1) (3). End-capping strategies that enable these polymers to depolymerize in response to an array of different stimuli while at the same time providing linkers for the synthesis of block copolymers will be described. The self-assembly of such block copolymers in aqueous solution enables the development of stimuli-responsive assemblies such as micelles and vesicles that can encapsulate and release drugs in a controlled manner. Furthermore, the incorporation of glyoxylate monomers with functional groups will allow the conjugation of molecules to the polymer backbone to introduce new functions and properties. Polyglyoxylates are particularly attractive for applications as they depolymerize to afford glyoxylic acid hydrate, a metabolic intermediate in the glyoxylic acid cycle, which has been demonstrated to be non-toxic in mammalian models and in the environment (4).

1. Wong, A. D.; DeWit, M. A.; Gillies, E. R. *Adv. Drug Delivery Rev.* 2012, *64*, 1031.
2. Phillips, S. T.; DiLauro, A. M. *ACS Macro Lett.* 2014, *3*, 298.
3. Fan, B.; Trant, J. F.; Wong, A. D.; Gillies, E. R. *J. Am. Chem. Soc.* 2014, *136*, 10116.
4. Belloncle, B.; Bunel, C.; Menu-Bouaouiche, L.; Lesouhaitier, O.; Burel, F. *J. Polym. Environ.* 2012, *20*, 726.

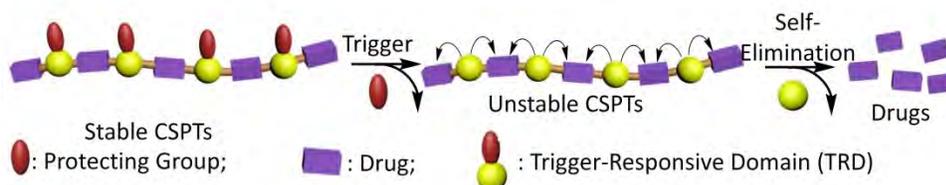


**Figure 1.** Schematic of the design of a stimuli-responsive polyglyoxylate.

## POLY 537: Polymer-drug conjugates capable of on-demand burst release via controlled depolymerization

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We designed 2,6-bis(hydroxymethyl)anilines 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 chain-shattering polymers (CSP) bearing trigger-responsive domains controlling the CSP degradation. Application of triggers to remove the protecting group of CSPs resulted in elimination reactions at each repeating unit by means of a chain-shattering mechanism rather than by the propagated, stepwise mechanism observed for self-immolative polymers. We used CSPs to prepare dye- and drug-containing nanoparticles from which the encapsulated cargos can be rapidly released upon trigger-induced degradation. We also used similar concept to design UV- and redox-responsive chain-shattering polymer-therapeutics conjugates for controlled, complete release of the built-in therapeutics in a chain-shattering manner upon exposure of external triggers.

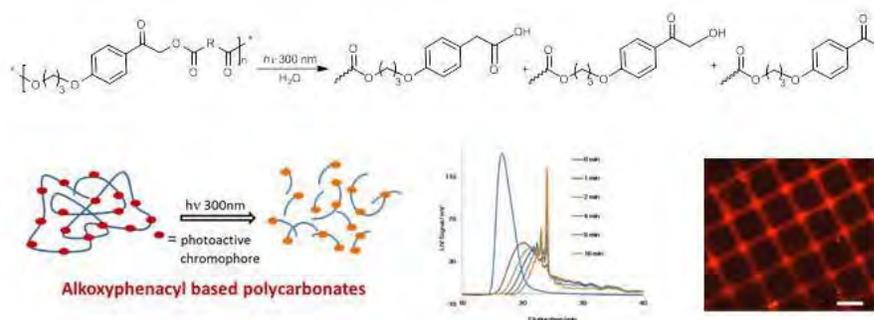


Chain-shattering polymeric therapeutics

## POLY 538: Photodegradable and biodegradable alkoxyphenacyl polyesters

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Polymer Science, The University of Akron, Akron, Ohio, United States

Photoresponsive materials are advantageous in numerous applications due to the temporal and spatial control they provide. Our lab is interested in the design of functional photoresponsive polymers for biomedical and engineering applications. In this regard we have developed photoresponsive alkoxyphenacyl polyesters and polycarbonates. When irradiated at 300 nm, these polymers undergo controlled polymer chain scission (ACS Macro Letters, 2012; Photochem. Photobiol. Sci. 2014). The mechanism of chain scission closely follows that observed for alkoxyphenacyl phototriggers and have been characterized by NMR and mass spectroscopy. The photoresponsive behavior of the above polymers enables the fabrication of micropatterned thin films, controlled release matrices and reversible engineering plastics. During this presentation we will illustrate the photochemical behavior of these polymers and their advantages for several applications.



## **POLY 539: Living polymerizations on different length scales**

**Ian Manners**, *Ian.Manners@bristol.ac.uk*. Univ of Bristol Sch of Chemist, Bristol, United Kingdom

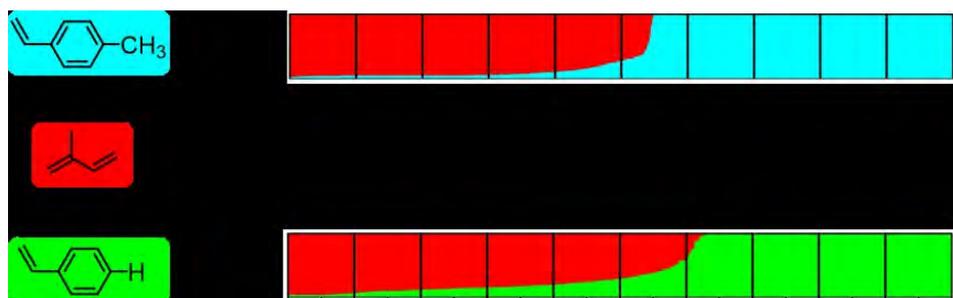
In this talk the extension of the classic “living polymerization” concept to a allow access to well-defined 1D and 2D supramolecular materials of controlled shape, size, and structural hierarchy on a length scale from 10 nm – 100 microns will be described. The approach used has been termed “living crystallization-driven living self-assembly” (CDSA) and was discovered as a result of an investigation of the solution self-assembly behavior of block copolymers with crystallizable polyferrocenylsilane (PFS) metalloblocks. These materials are available via the living anionic polymerization of strained, silicon-bridged [1]ferrocenophanes. Living CDSA offers a versatile new route to monodisperse cylindrical micelles and 2D platelets, block comicelles with segmented non-equilibrium structures, and complex, hierarchical materials with controlled dimensions and a variety of potential applications.[1]

[1] Recent work: H. Qiu et al *Science* 2015, 347,1329; X. Li, Y. Gao et al *Nature Comm.* 2015, 6, 8127; O. Gould, H. Qiu et al *Nature Comm.* 2015, in press;

## POLY 540: Watching polymer chains grow by in-situ monitoring of living copolymerisations: From gradient assessment to one-step block copolymer synthesis

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Since the fundamental discovery of the living polymerization in 1956 by Michael Szwarc, carbanionic polymerization has been employed for the generation of an immense variety of precise macromolecular architectures, commonly based on sequential addition of monomers to achieve segmented chain structures, i. e., block copolymers, stars and more complex polymer architectures. This has paved the way to unprecedented polymer materials. In contrast, direct living copolymerization of different vinyl monomers in one step has only been studied to a limited extent. However, this strategy is important with respect to formation of gradient type architectures. The nature of the gradient plays a key role for nanosegregation and resulting materials properties. Detailed understanding of the comonomer distribution in carbanionic copolymerizations can be achieved by online NMR-monitoring of the monomer consumption. This method was developed in our group for copolymerizations carried out in apolar solvents, due to the slow polymerization kinetics in this case. Obtaining detailed knowledge of the changing monomer concentration in stock during the reaction, this technique permits to determine the incorporation probability for each comonomer at every position of the polymer chain formed with unprecedented precision, leading to a precise assessment of the comonomer drift. As an example, for the comonomer system isoprene/*p*-methylstyrene (*l/p*-MS) extremely divergent copolymerization parameters are obtained (i.e.,  $r_1=140$  for *l* and  $r_2=0.02$  for *p*-MS), which enable a one-step block copolymer synthesis with a very narrow gradient between both blocks. Perspectives for the convenient synthesis of multiblock and multigradient architectures will be discussed.

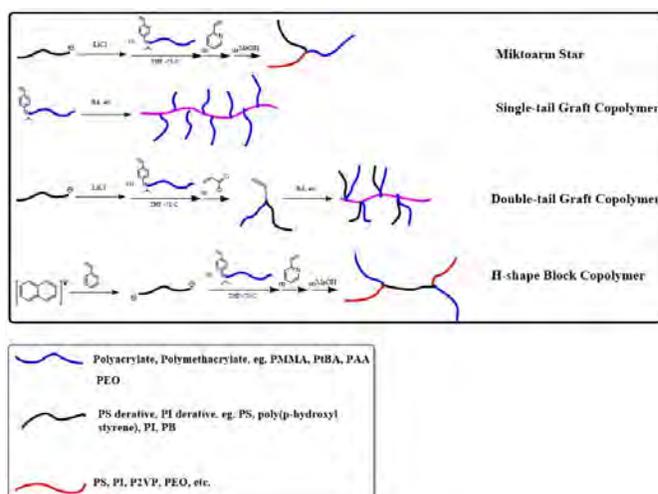


Schematic image of comonomer distribution from in-situ NMR in copolymers of isoprene/*p*-methyl styrene (top) and isoprene/styrene (bottom), respectively (copolymerization in cyclohexane)

## POLY 541: N-isopropyl-4-vinylbenzylamine: A novel initiator to build various polymer architecture through anionic polymerization

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Polymer with complex architectures including miktoarm stars, graft/multi graft copolymers, etc., have been widely investigated. Compared to linear chains, their smaller hydrodynamic radii, lower melt and solution viscosities, lower glass transition temperature, lower crystallinity and higher solubility endow them in many cases with improved rheological behavior (such as strain and hardening) and improved processability. Furthermore, block copolymers with miktoarm star architectures and graft/multigraft architectures allow additional capacity to tune morphology and long range order. Most current approaches to build these complex architectures require post-modification of living polymer chains using linking agent or macromonomer/initiator. These approaches have limitations including complex operation, low conversion or long linking reaction time. In this study, a novel styrenic initiator-- N-isopropyl-4-vinylbenzylamine (PVBA), provides us with the routine to make macromonomer or marolinking agent with 100% conversion and short reaction time through living anionic polymerization. PVBA was easily synthesized by the alkylation of isopropylamine by 4-vinylbenzyl chloride. After being activated by sec-BuLi or potassium naphthalenide, it can initiate (methyl)acrylate or ethylene oxide in THF at -78 °C, with the styrenic vinyl group intact. To prepare graft/multigraft copolymers, this intact vinyl group was used as the macromonomer and copolymerized with butylacrylate or isoprene by radical polymerization, which leads to thermoplastic elastomers with promising mechanical performance. To make miktoarm stars, the living polystyrene was linked with the styrenic vinyl group, with further anionic polymerization of the third arm like poly(2-vinyl pyridine). Furthermore, more complex architectures were also attempted, like H-shape copolymers, by the introduction of linking agent or living polystyrene initiated by potassium naphthalenide.

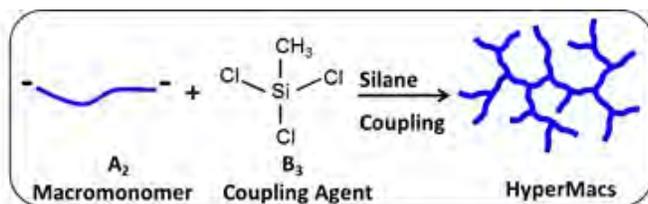
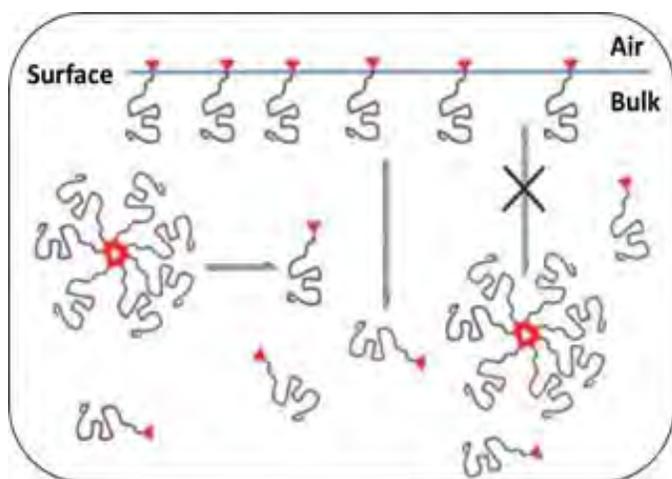


N-isopropyl-4-vinylbenzylamine—A Novel Initiator to Build Various Polymer Architecture through Anionic Polymerization

## POLY 542: Anionic polymerization: Versatile technique for end functionalized and branched polymers

**Norazilawati Muhamad Sarih**<sup>1</sup>, nmsarih@um.edu.my, Lian R. Hutchings<sup>2</sup>, Fatem Hamime<sup>1</sup>, Richard L. Thompson<sup>2</sup>. (1) Chemistry Department, University of Malaya, Kuala Lumpur, Wilayah Persekutuan, Malaysia (2) Chemistry Department, Durham University, Durham, United Kingdom

Anionic polymerization permits the development of various sort of polymeric materials with well-defined molecular weight, polydispersity composition and molecular architecture comprising homopolymers, block copolymers, end functionalized and branched polymers with various architectures. In our work, we have prepared a series of multi-end functionalized polystyrene and polyisoprene additives within a wide range of molecular weights, carrying 1 to 3 fluoroalkyl groups by end capping the living chain ends of polymers via anionic polymerization<sup>1</sup>. The resulting polymers were used as additives in an attempt to render the surface of polymer films hydrophobic/lipophobic which have promoted the interesting surface modifying properties where the properties at polymer surfaces are differed from the bulk, while retaining the advantageous properties of the bulk polymer. Moreover, by exploiting the inherent of no termination of anionic polymerization, the ongoing work has been carried out by developing facile new route to synthesize the hierarchically branched polymers, HyperMacs<sup>2</sup> via macromonomer coupling strategy.



## **POLY 543: From retarded to activated anionic polymerization: A focus on magnesium and aluminum derivatives**

**Stephane Carlotti**<sup>1,2</sup>, [carlotti@enscbp.fr](mailto:carlotti@enscbp.fr). (1) *Bordeaux University, Bordeaux, France* (2) *Bordeaux INP, Pesac, France*

This lecture will focus on the role of magnesium and aluminum compounds as additives to alkali metal, onium salts, or simple alcohols to either retard the living polymerization of styrene and dienes or activate the anionic ring-opening polymerization of cyclic ethers.

To produce economically polystyrene-based materials via an anionic route, and therefore to compete with a free radical process, bulk and high temperatures experimental conditions are required. The addition of Lewis acids such as magnesium or aluminum alkyls to an anionic initiator (Li or Na derivatives) permits to adjust the reactivity of the active centers and to control the copolymerization of styrene and dienes with peculiar issues in terms of reactivity ratios and microstructure.

A similar and unique approach was then applied to different cyclic ether monomers. The addition of Lewis acids such as trialkylaluminum to alkali metal alkoxides or onium salts showed a strong increase of the polymerization rates of epoxides and glycidyl ethers as well as a consequent decrease of transfer reactions allowing the controlled synthesis of (co)polymers with various molar masses. A specific focus will be given to simple Grignard reagents and dialkylmagnesium, in the presence of protic compounds, for the polymerization of epoxides and the synthesis of polyethers.

## **POLY 544: Novel and straightforward route to polycarbonates and its copolymers**

*Dongyue Zhang, Hefeng Zhang, Yahya Alzahrany, Nikos Hadjichristidis, **Xiaoshuang Feng**, xiaoshuang.feng@kaust.edu.sa, **Yves Gnanou**, yves.gnanou@kaust.edu.sa. Physical Sciences and Engineering, King Abdullah University of Science and Techn, Thuwal, Saudi Arabia*

Carbon dioxide (CO<sub>2</sub>) is a thermodynamically and kinetically stable compound that leaves little option but to resort to organometallic complexes for promoting reactions such as its copolymerization with epoxides. These organometallic complexes function by coordination-insertion of CO<sub>2</sub> for the mechanism of their (co)polymerization with epoxides and involve generally either transition metals (mainly Cr, Co, Zn) or earth-abundant main group metals (Al, Mg).

In this study a non-coordinating route is investigated based on the use of mere alkoxydes for the initiation of the copolymerization of CO<sub>2</sub> and epoxides and on alkyl aluminum for the activation of epoxides. This anionically-driven copolymerization of CO<sub>2</sub> and epoxides is versatile enough to allow not only the straightforward synthesis of perfectly alternating polycarbonates but also the easy derivation of poly(ether-co-carbonate)s of different compositions or the facile preparation of block copolymers of polystyrene-*b*- polycarbonate type by sequential polymerization.

## POLY 545: Anionic polymerization of BioFene (*trans*- $\beta$ -farnesene) and their physical properties

**Taejun Yoo**<sup>2</sup>, [taejun.yoo@total.com](mailto:taejun.yoo@total.com), **Tomas Trnka**<sup>2</sup>, **Steven K. Henning**<sup>2</sup>, **Derek J. McPhee**<sup>1</sup>. (1) Amyris, Emeryville, California, United States (2) Total Cray Valley, Exton, Pennsylvania, United States

During the last 60 years, commercially relevant monomers used in anionic polymerization technology are limited to dienes (butadiene and isoprene) and vinyl aromatics (styrene), and industrial manufacturers are still largely limited to these monomers when introducing new products to the market. Even though there have been many academic studies evaluating new monomer systems which may produce value in anionic polymerization, it has been a challenge to commercialize new monomers for industrially because the monomers are not commercially available.

Recently Amyris developed a new molecule, *trans*- $\beta$ -farnesene (farnesene, or BioFene™) using a biotechnology platform which is a sustainable alternative to a broad range of petroleum-sourced feeds, and its conjugated diene structure has been shown to be a drop-in monomer for a range of polymerization chemistries, including anionic polymerization. Total Cray Valley has partnered with Amyris to developed farnesene-based anionic polymers, including mono- and di-functionalized oligomers. Due to the highly branched structure, farnesene-based polymer show interesting rheological properties compared with linear analogs.

The anionic polymerization of *trans*- $\beta$ -farnesene, the functionalization and modification of the oligomers, and the resulting physical properties will be discussed. Potential applications which take advantage of the new structure-property relationships will be included.

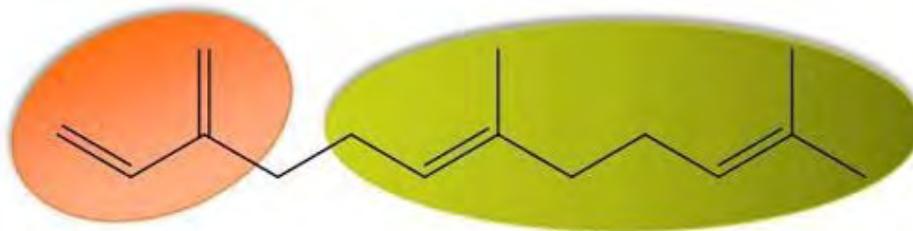
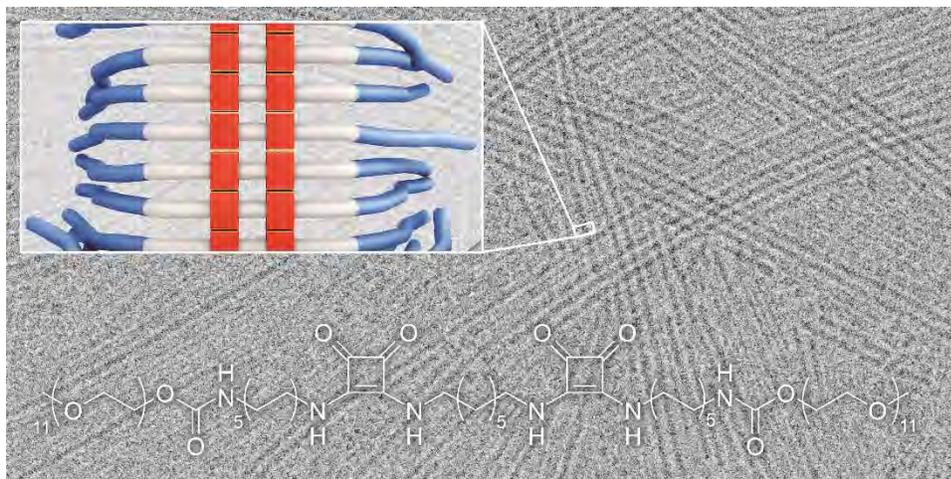


Figure 1: Structure of *trans*- $\beta$ -farnesene

## POLY 546: Synergy between aromatic gain and hydrogen-bonding in a supramolecular polymer

**Roxanne Kieltyka**, *r.e.kieltyka@chem.leidenuniv.nl*. Leiden University, Leiden, Netherlands

The relationship between aromaticity and hydrogen bonding in the self-assembly of a supramolecular polymer is examined. Partially aromatic bis(squaramide) bolaamphiphiles were designed to self-assemble through a combination of hydrophobic, hydrogen-bonding and aromatic effects into long fibrillar architectures. Electronic and geometric changes within the squaramide ring indicative of strong hydrogen bonding and aromatic gain of the monomer units were observed using IR and UV-vis spectroscopy. Greater aromatic character upon polymerization, at least 30 percent of the interaction energy in a pentamer, was determined computationally using nucleus-independent chemical shift (NICS) and harmonic oscillator model of aromaticity (HOMA) indices. A significant increase in thermodynamic stability and a striking difference in the morphology of the self-assembled bis(squaramide) bolamphiphiles was observed in comparison to isosteres that cannot access the aromatic gain-hydrogen bonding effect.



## POLY 547: Synthesis and characterization of supramolecular self-healing polymers designed for application in lithium-ion batteries

**Jeffrey Lopez**<sup>3</sup>, [jlopez12@stanford.edu](mailto:jlopez12@stanford.edu), Allen Pei<sup>1</sup>, Zheng Chen<sup>3</sup>, Yi Cui<sup>1</sup>, Zhenan Bao<sup>2</sup>. (1) Stanford Univ McCullough Bldg, Stanford, California, United States (2) Chemical Engr Dept MC 5025, Stanford University, Stanford, California, United States (3) Chemical Engineering, Stanford University, Stanford, California, United States

Our group has demonstrated the use of a supramolecular, self-healing polymer (SHP) to enable high capacity anode materials for lithium ion batteries (LIBs). While promising, the SHP used in these prior studies was not specifically designed for batteries. Here we present the synthesis and characterization of new supramolecular self-healing polymers with different backbone structures designed for improved performance in LIBs. Synthesized by simple condensation reactions, the branched polymers associate via urea and amide hydrogen bonding groups to form a supramolecular network. This work characterizes the Li-ion conduction, adhesive properties, and self-healing capability of the polymers. We will also discuss the effects of backbone chemistry on their performance in LIBs. By controlling the mechanical properties and electrolyte interaction, we are able to influence the cycling stability of the electrode materials and contribute toward a better understanding of the requirements for polymers in LIBs. This will lead toward the eventual systematic design of LIB binder materials and allow for the realization of high capacity anodes.

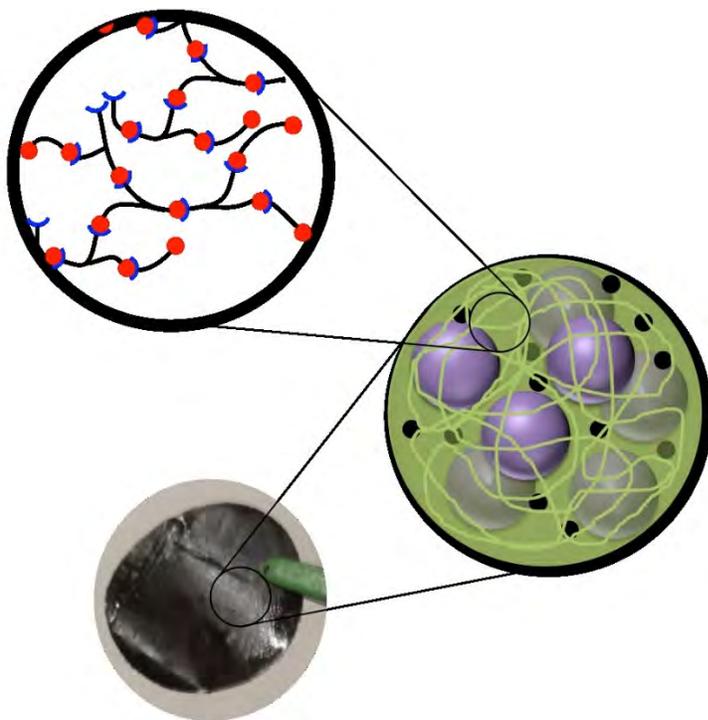


Photo of a Si electrode with supramolecular binder and representation of the self-healing polymer/carbon black/Si composite.

## POLY 548: Nanoscale chemical and topological imaging of block copolymers with photo-induced force microscopy

**Derek Nowak**<sup>2</sup>, [derek.b.nowak@gmail.com](mailto:derek.b.nowak@gmail.com), William Morrison<sup>2</sup>, Sung Park<sup>2</sup>, kristin Schmidt<sup>1</sup>, Jane E. Frommer<sup>1</sup>, Dan Sanders<sup>1</sup>. (1) IBM Almaden Research Center, San Jose, California, United States (2) Molecular Vista, San Jose, California, United States

Supramolecular self-assembly provides a powerful and low-cost way to achieve nanoscale materials synthesis and pattern formation for applications in advanced lithography, nanophotonics, photovoltaics, therapeutics, and related areas. The chemical and structural morphology of these materials ranges in size from 5 – 100 nm, which is not easily interrogated in real space via existing instruments based on optics (insufficient spatial resolution arising from the diffraction limit) or electrons (limited contrast between materials and the possibility of sample damage).

Infrared Photo-induced Force Microscopy (IR PiFM) is based on an atomic force microscopy (AFM) platform that is coupled to a widely tunable mid-IR laser. PiFM measures the dipole induced on a sample by an excitation light source, then detecting the dipole-dipole force that exists between the sample and a metallic AFM tip. This interaction is strongly affected by the optical absorption spectrum of the sample, thereby providing a significant spectral contrast mechanism, which can be used to differentiate between chemical species. Due to the steep dipole-dipole force dependence on the tip-sample gap distance, PiFM spectral images surpass topographical spatial resolution, showcasing sub 10 nm spatial resolution despite the typical tip radius of metal-coated tips.

PiFM studies on various self-assembled block copolymer systems will be presented. The results consist of PiFM spectral images associated with several absorption bands of different blocks along with broad spectra associated with nano-spots on sample surfaces. Images of fingerprint patterns (figure 1) of poly (styrene-*b*-methyl methacrylate) and polystyrene and parallel lamellae (prepared via directed self-assembly) for both poly (styrene-*b*-methyl methacrylate) and poly (styrene-*b*-2-vinylpyridine) show a clear spectral contrast between the two blocks of each material system. For poly (styrene-*b*-2-vinylpyridine), PiFM contrast between blocks was far greater than is generally available by scanning electron microscopy without staining. By enabling imaging at the nm-scale with chemical specificity, PiFM provides a new analytical method for deepening our understanding of nanomaterials.

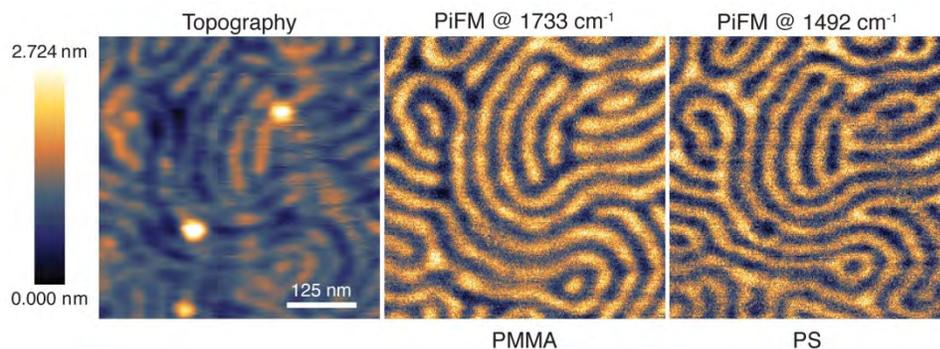


Figure 1. Chemical imaging of BCP composed of PMMA and PS.

## POLY 549: Mechanical activation of mechanophore enhanced by strong hydrogen bonding interactions

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Engineering, Xiamen University, XIAMEN, Fujian, China

Polymer mechanochemistry studies how exogenous force drives chemical reactions of force-sensitive moieties (mechanophores) and has been applied to reveal new chemical reactivities, fabricate stress-responsive materials, and aid mechanistic study of polymer fracture. Despite the fruitful developments, the mechanical activation of polymer-linked mechanophores is less well understood to date. Herein we for the first time demonstrate that the mechanical activation of mechanophores in the bulk can be enhanced by supramolecular interactions.

As shown in Figure 1, a mechanically active spiropyran (SP) mechanophore is incorporated into the backbone of prepolymer which is further end-capped with ureidopyrimidinone (UPy) or urethane. The prepolymers form long chain supramolecular polymers through the association of the self-complementary UPy motifs. As we have expected, strong mechanochromic reaction of SP arises in the bulk films of UPy containing materials whereas much weaker activation occurs in urethane containing counterparts, coincident with their stress-strain responses. The difference in the magnitudes of supramolecular interactions leads to different degrees of chain orientation and strain induced crystallization (SIC) in the bulk and consequently distinct capabilities to transfer the load to the mechanophores. Moreover, we discovered a physical picture of sequential activation of liable units under loads: first the break of the UPy stacks, followed by the dissociation of UPy motifs, and eventually the mechanical activation of SP. We hope the study may open a new way to create novel mechanoresponsive polymers whose responsiveness can be controlled by tailoring the supramolecular interactions of the system.

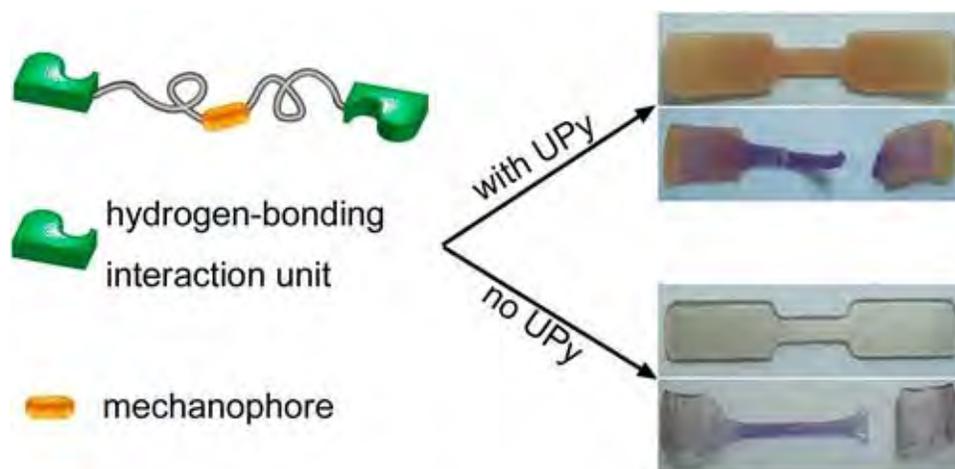


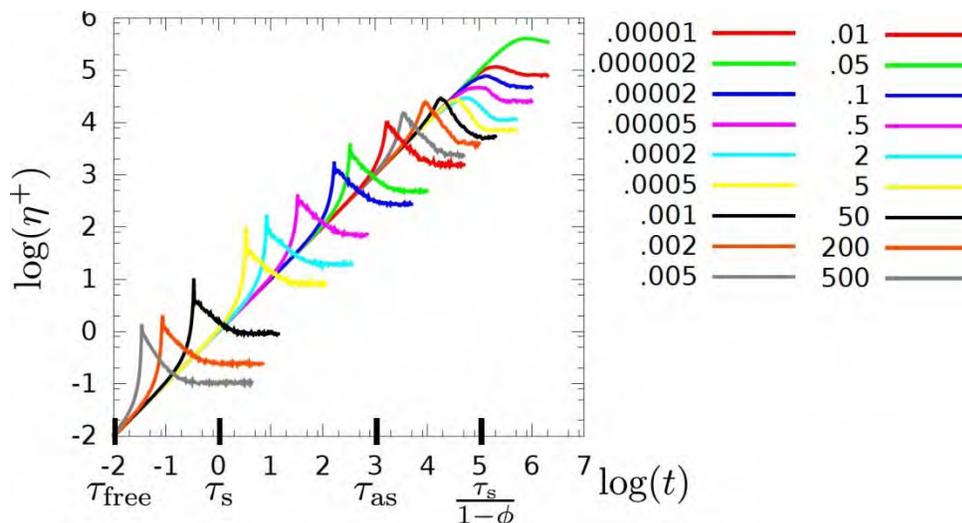
Figure 1. Enhancing the mechanical activation of SP mechanophore through the introduction of hydrogen bonding UPy motifs at the two termini of a macromolecule.

## POLY 550: Simplified tube models for entangled telechelic star polymers

**Daniel Read**, *d.j.read@leeds.ac.uk*, Victor Boudara. *Mathematics, University of Leeds, Leeds, United Kingdom*

This presentation describes current efforts investigating and understanding non-linear rheology of entangled, supramolecular polymeric materials. In order to illustrate the interplay between timescales of relaxation of supramolecular groups and motion in an entangled environment, we have developed a simple "toy" model for the rheology of entangled telechelic star polymers. This is based on a pre-averaged orientation tensor, a stretch equation, and stretch-dependant probability of detachment of the sticker. The attachment and detachment dynamics are handled stochastically, with different attachment and detachment histories for different star arms. In both linear and non-linear regimes, we produce maps of the whole parameter space, indicating the parameter values for which qualitative changes in response to flow are predicted - such maps are useful for understanding how changes in temperature or supramolecular association will affect flow and processing. Results in the linear rheology regime are consistent with previous more detailed models (van Ruymbeke et al. *Macromolecules*, 43, 4401-4411, 2010) and are in qualitative agreement with experimental data. We also detail a "pre-averaged" version of the model, which closely approximates the stochastic model, but which is suitable for flow computation and investigation of flow instabilities.

The work leading to these results has received funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme (FP7/2007-2013) under REA grant agreement no. 607937 (SUPOLEN)



Transient viscosity during start-up shear flow of toy model for telechelic stars, in region of diagram where the stretch relaxation time  $\tau_s$  of a free arm is intermediate between the typical time a sticker remains free  $\tau_{\text{free}}$  and the typical time a sticker remains associated  $\tau_{\text{as}}$ .

## POLY 551: Structure-property relationships for polyelectrolytes: Thermal stability, film morphology and supramolecular assembly with conjugated polyelectrolytes

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A series of polyelectrolytes modified with hydrophobic octyloxy groups as side chains and different spacers between charged units were prepared to study the influence of chain flexibility on properties. The thermal stability as assessed by thermogravimetric analysis depends on the side chains and spacer length. Differential scanning calorimetry and X-ray powder diffraction indicated a significant dependence of crystallinity and phase transition on side chain composition and spacer as well. Obvious structure-film morphology relationships were observed both in dip cast polycation films and in the films made via layer-by-layer (LbL) deposition of polycations with anionic polythiophene derivatives. The size and incidence of pores (see Figure) in films can be controlled both by structural modification of the polyelectrolytes and by exposure to ambient humidity or water in the casting solvent.

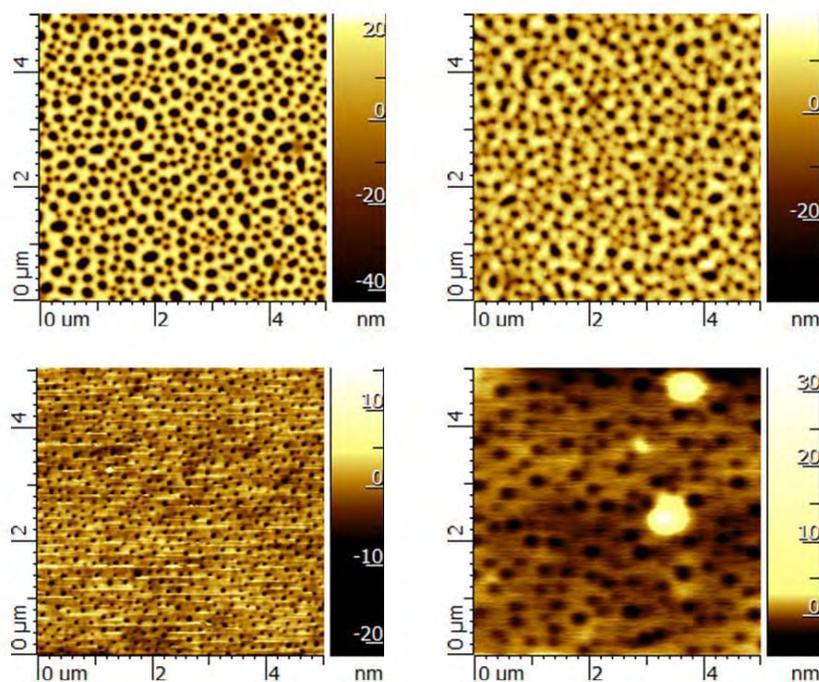


Figure 1. AFM 2D-height images ( $5\ \mu\text{m}\times 5\ \mu\text{m}$ ) of dip-cast films of polyelectrolyte cast from  $\text{CHCl}_3$  and  $\text{CHCl}_3/\text{CH}_3\text{CN}$  under various conditions showing the ability to control incidence and size of pores

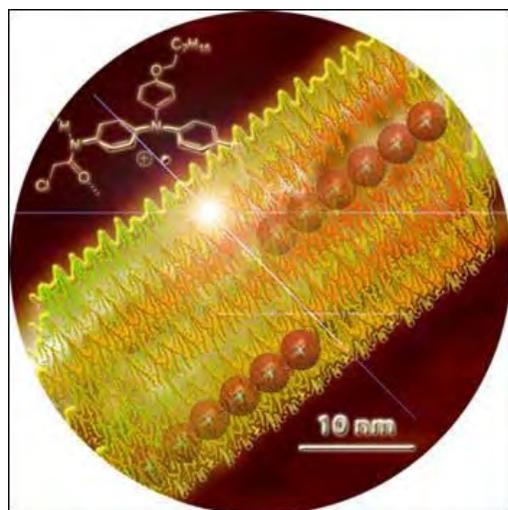
## POLY 552: Supramolecular triarylamine self-assemblies as functional nanomaterials

**Emilie Moulin**, [emoulin@unistra.fr](mailto:emoulin@unistra.fr), Nicolas Giuseppone. SAMS Research Group icFRC, CNRS, Strasbourg, France

Supramolecular organic electronics rests on the use of bottom-up chemical self-assembly processes in order to design conducting components at the 5–100 nm scale. Challenges in this field are both the construction of 1D-nanostructures displaying optimized transport properties and their precise connections to electrodes. By externally controlling light-responsive supramolecular polymerization processes of some triarylamine molecules,<sup>1</sup> and by using appropriate methods of orientation, we have now demonstrated that it becomes possible to pre-determine the accurate positioning of organic interconnects within patterned nano-circuitry.<sup>2</sup> Along this main line, we will describe the detailed mechanism of this very original self-assembly process.<sup>3</sup> We will also discuss the optical and electronic properties of these supramolecular polymers which reveal metallic signatures; the nature of their through-space conduction will be described.<sup>4</sup> Furthermore, the supramolecular dynamics of these assemblies allows for the creation of novel soft materials not accessible with conducting conjugated polymers. In particular, we will show that some triarylamine-based nanofibers demonstrate a mechanism of defect repair driven by polaron diffusion through their supramolecular stacks.<sup>4</sup> Finally we will show that this light-triggered self-assembly process can be extended to a number of advanced triarylamine derivatives for the production of various nanostructures.

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## POLY 553: Preparation of amylose supramolecular materials by vine-twinning polymerization

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Amylose, which is a linear natural polysaccharide, plays a host compound that forms inclusion complexes with relatively lower molecular weight guest compounds. However, little has been reported regarding the formation of inclusion complexes between amylose and polymeric compounds. The main difficulty in the complexation of amylose with polymeric guests is owing to that the driving force for the binding is only caused by hydrophobic interactions. Amylose, therefore, does not have sufficient ability to include the long polymeric chains. The author has developed a new method of the polymerization system for the formation of well-defined amylose supramolecules, that is, amylose–polymer inclusion complexes. The method was achieved by the phosphorylase-catalyzed enzymatic polymerization of  $\alpha$ -D-glucose 1-phosphate monomer from maltoheptaose primer to produce amylose in the presence of hydrophobic synthetic guest polymers. Because the image of this polymerization system is the similar as the way that the vines of a plant grow twining around a rod, it has been named ‘vine-twinning polymerization’ (Figure 1). By means of this method, we have prepared hierarchically controlled supramolecular network materials.

For example, the author performed the preparation of supramolecular network materials by the vine-twinning polymerization using poly( $\gamma$ -glutamic acid-*graft*- $\epsilon$ -caprolactone) as a new guest polymer. A supramolecular network hydrogel was obtained with the progress of the vine-twinning polymerization. Macroscopic interfacial healing was achieved by the formation of inclusion complexes at interface between two hydrogel pieces through the enzymatic polymerization. A porous cryogel was further obtained by lyophilization of a hydrogel. Ion gels were also fabricated by soaking the hydrogels in an ionic liquid, 1-butyl-3-methylimidazolium chloride.

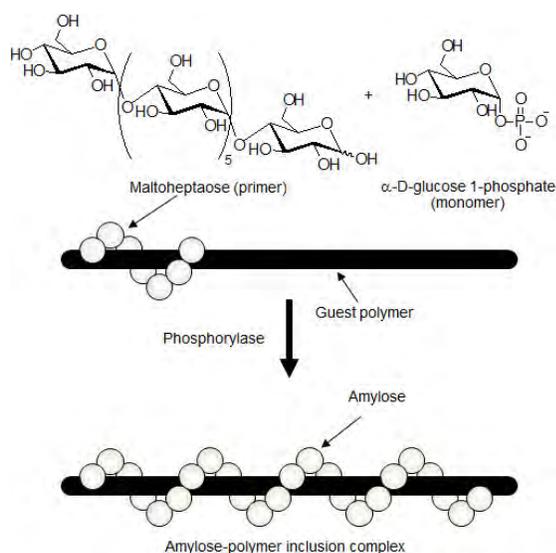


Figure 1. Image of vine-twinning polymerization.

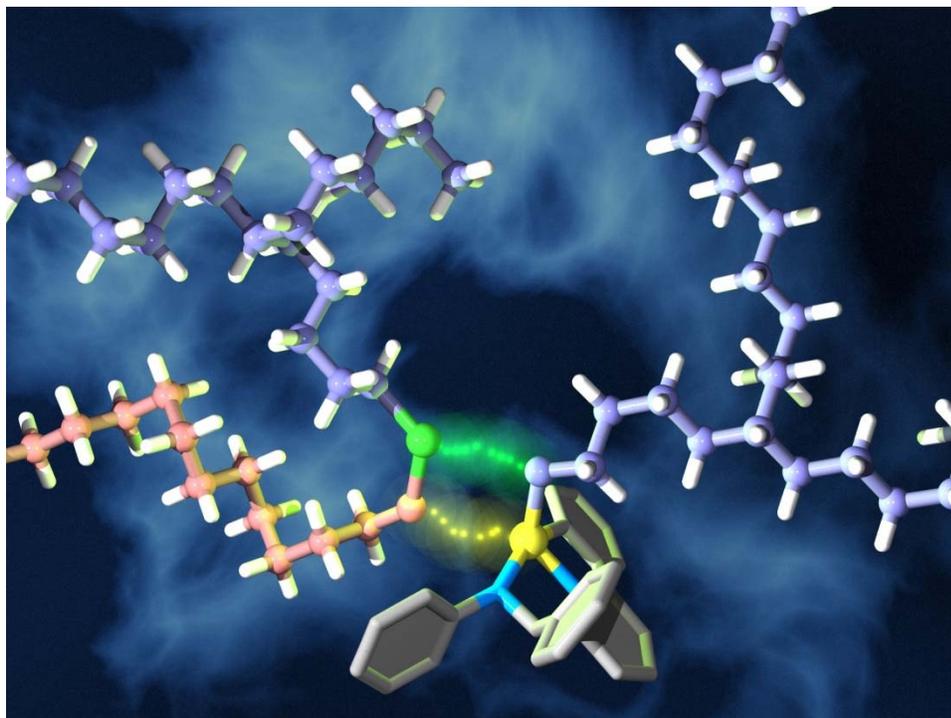
## POLY 554: Innovation in a mature field: The commercialization of olefin block copolymers

**Edmund Carnahan**, [EMCarnahan@dow.com](mailto:EMCarnahan@dow.com). The Dow Chemical Company, Freeport, Texas, United States

Carbon and hydrogen, organized appropriately, have generated a massive global industry with products touching most aspects of modern life. Three quarters of a century later, scientists are still able to extract additional performance from these diminutive polymer chains. Our search for ways to craft polyethylene with a better balance of flexibility and heat resistance led to some fascinating discoveries in catalysis and polymer materials science. Along the way, The Dow Chemical Company commercialized INFUSE™ Olefin Block Copolymers and INTUNE™ Olefin Block Copolymers. The path from “interesting science” to “valuable products” will be explored, with real-world examples of what it can take to commercialize new technology in a seemingly-mature field.

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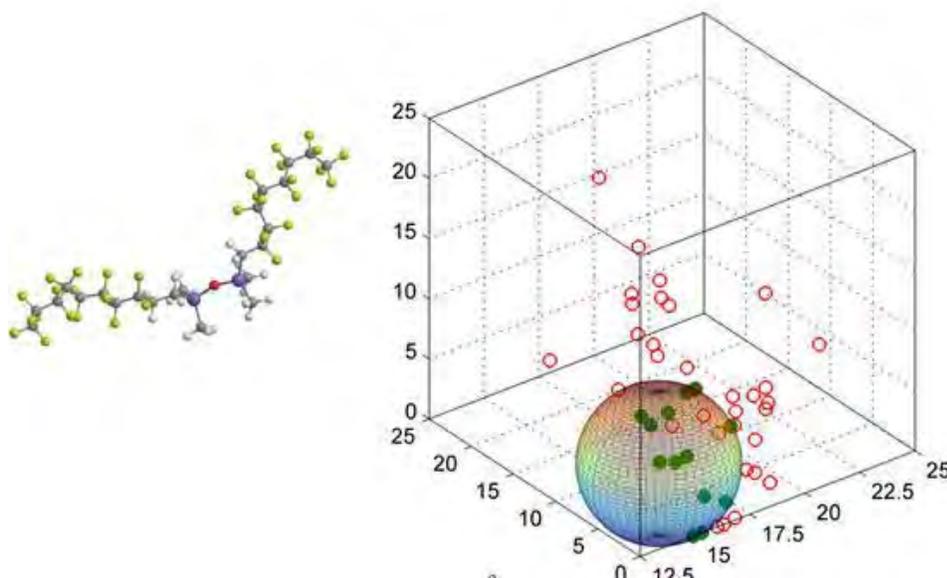
™Trademark of The Dow Chemical Company



## POLY 555: Insights into surface structure and performance of fluorinated silicates from cohesive energy studies

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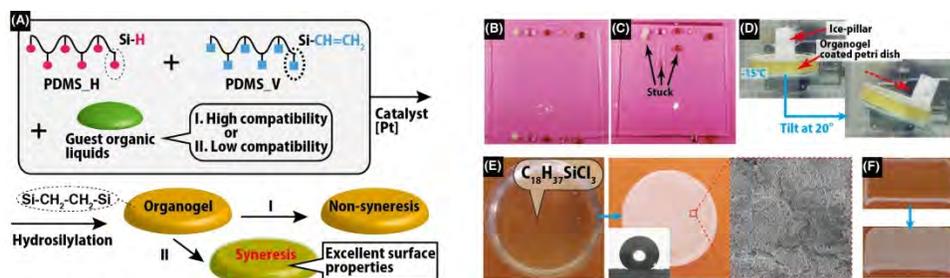
Despite the fact that the building blocks of fluorosilicates (such as highly fluorinated alkanes and siloxanes) are typically expected to have low surface energies (around 20 mN/m), the measured surface energies of fluorosilicates vary widely (from <10 mN/m to > 30 mN/m). These variations indicate the importance of the molecular architecture of fluorosilicate compounds in determining their surface properties. In order to better understand how the architecture of fluorosilicates impacts surface characteristics, data from a number of theoretical and experimental sources have been collected and analyzed. Among the many interesting sources of insightful data are cohesive energy density parameters. These parameters, which we report for a number of different fluorosilicates, indicate the presence of features such as dipoles formed at the junctions of chemical moieties, that influence the surface energy in important ways. Insights from these studies form a key basis for the design and development of fluorosilicates with extremely low surface energies.



## POLY 556: Anti-stick coatings using self-lubricating organogels (SLUGs)

**Chihiro Urata**, *chihiro-urata@aist.go.jp*, Gary Dunderdale, Matt England, Atsushi Hozumi. AIST, Nagoya, Japan

Functional coatings with exceptional surface properties, such as liquid-repellency and low-friction/adhesion, have been commonly prepared by combining textured surfaces with long-chain perfluorinated compounds. However, unfortunately, the chemical and physical effects of the LPFCs on human health and environment have been viewed lately with concern. In addition, once such artificial surfaces are physically and chemically damaged, they permanently lose their surface properties. In contrast, some living things maintain their surface properties through secretion of plant waxes and mucus. Here, we report on novel coatings inspired by such biological systems. To realize long-lasting surface properties, we have particularly focused on the syneresis of organogels, which were prepared by hydrosilylation of 2 types of silicones, and several guest organic liquids (Fig.A). As compatibility between guest liquids and polymer matrixes (cross-linked polydimethylsiloxane) is decreased to a certain critical point which is induced by the chemical and/or physical effects, the guest liquids begins to gradually leach out to the outmost organogel surface. Thanks to this self-lubricating property, adhesion of various objects was effectively reduced, resulting in the excellent anti-sticking properties. Viscous liquids flowed on the syneretic organogel surface more freely than that of non-syneretic organogel surface (Fig. B and C). For the purpose of anti-icing applications, we tuned the critical incompatibility point our organogels, which possess reversible thermo-responsive secretion nature (Fig. D). In this case, the syneresis gradually starts when the temperature is cooled ( $< 0^{\circ}\text{C}$ ) and the syneresis liquids returns back into the organogel again by heating to room temperature. Thanks to this smart surface property, an ice-pillar formed on the organogel at  $-15^{\circ}\text{C}$  easily slid off without any additional force. Furthermore, we have successfully demonstrated regeneration of superhydrophobicity artificially mimicking lotus leaves using n-octadecyltrichlorosilane as an active guest liquid (Fig. E and F). Our technique, demonstrated here, undoubtedly shows great potential for application in dynamic, multifunctional, and self-recovering coatings.

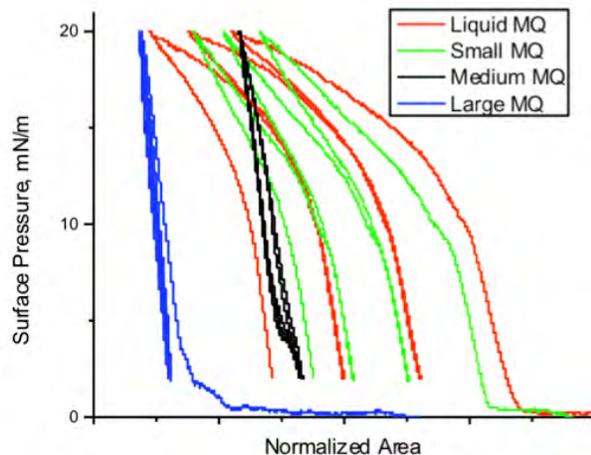


(A) Conceptual image of this study. (B-F) Organogels and their surface properties. Anti-stick behavior of viscous liquids (mayonnaise, liquid glue, ketchup, honey, and worcester sauce) on (B) a syneretic and (C) a non-syneretic organogel sheets. (D) Sliding motion of an ice-pillar at  $-15^{\circ}\text{C}$  on the thermo-responsive organogel coated petri dish. (E) Spontaneously formed superhydrophobic surface on the organogel. (Inset images are a water droplet on the organogel surface and SEM image of superhydrophobitized organogel). (F) Cross-sections of the organogels after the superhydrophobization and regeneration of the superhydrophobic surface on the cross-sectional surface

## POLY 557: MQ silicones at interfaces

**Daniel H. Flagg**, *dflagg21@mail.pse.umass.edu*, **Thomas J. McCarthy**, *Univ of Massachusetts, Amherst, Massachusetts, United States*

MQ silicone resins synthesized using a two-step sol gel reaction exhibit interfacial properties that are functions of their molecular size. After initial observations of emulsion formation in oil-water mixtures, we studied the behavior of MQ resins at the air-water interface, at the oil-water interface, and on solid surfaces. The behavior at these interfaces depends on the size of the molecule. At the air-water interface, pressure-area isotherms show a transition from compressible to solid-like behavior as molecular size increases. At the oil-water interface, MQ resins behave similar to nanoparticle solutions but show little size dependence. MQ resins on solids surfaces show increases in thickness and contact angle hysteresis as the size increases. These resins primarily contain hydrophobic methyl organic functionality with only traces of residual silanols or ethoxy groups to provide hydrophilicity. Due to their condensed, silica-like structure we propose that MQ resins act as liquid nanoparticles which adsorb at the interface.

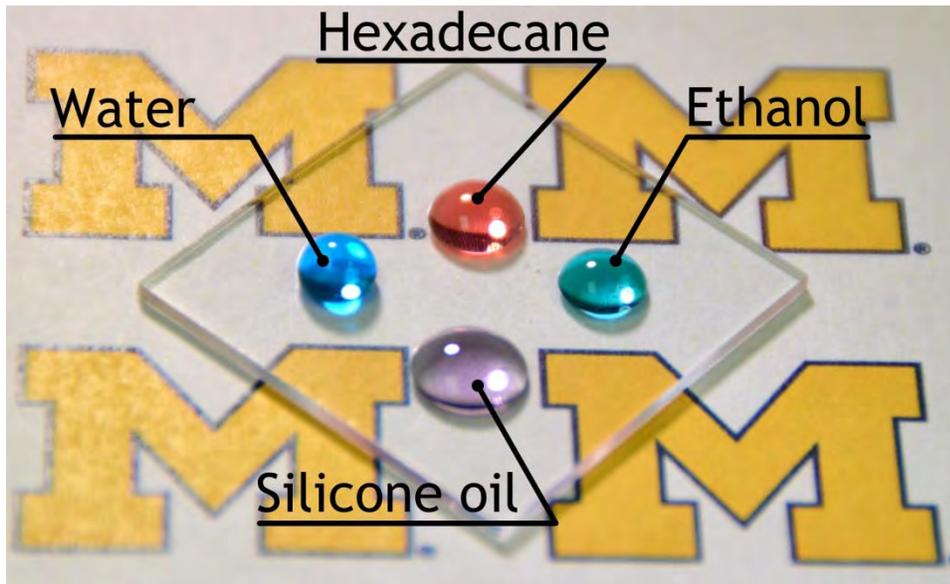


High Pressure Collapse of MQ Silicone at the air-water interface.

## POLY 558: Smooth, all-solid, omniphobic surfaces

**Mathew Boban**<sup>3</sup>, mboban@umich.edu, Joseph M. Mabry<sup>1</sup>, Anish Tuteja<sup>2</sup>. (1) AFRL/RZSM, Air Force Research Laboratory, Edwards AFB, California, United States (2) Dept. of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States (3) Dept. of Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States

Surfaces that are resistant to wetting by a broad variety of liquids are relevant for numerous industrial applications. Omniphobic surfaces, i.e. surfaces that resist wetting by virtually all liquids, are capable of self-cleaning, chemical protection, corrosion reduction, and biofouling prevention. Such surfaces may be useful in fields ranging from enhancement of phase-change heat transfer, prevention of contamination of medical devices by biological agents, and manipulation of sub-microliter volumes of liquids. Typical non-wetting surfaces rely on one of three approaches: incorporation of re-entrant texture to entrap air beneath the liquid, incorporation of an immiscible non-volatile liquid impregnated into surface texture, or surface modification with a reactive, low surface energy molecule. These approaches each have potential drawbacks, which limit their long-term stability, durability, scalability to industrial applications, or generalizability to a wide range of substrates. In this study we have developed a novel, all-solid, omniphobic coating that can be applied on to a variety of substrate materials, rendering them repellent to most liquids. Liquids including water, hexadecane, toluene, ethanol, and silicone oil all exhibit low contact angle hysteresis ( $<10^\circ$ ) on these surfaces and can easily slide off without leaving a trail.



## **POLY 559: Ultralow wear fluoropolymer composites: Nanoscale functionality from microscale fillers**

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Over the last decade, several research groups have explored an intriguing set of materials based on Teflon® PTFE 7C (a granular molding resin) and certain alumina “nanoparticles.” These materials are exceptional because small amounts of alumina additive (often less than 5 wt.%) improve the wear performance of the PTFE composite by over four orders of magnitude. It is believed that the “nano” sized alumina somehow shuts down the flaky wear mechanism of the PTFE, and stabilizes the formation of a persistent transfer film.

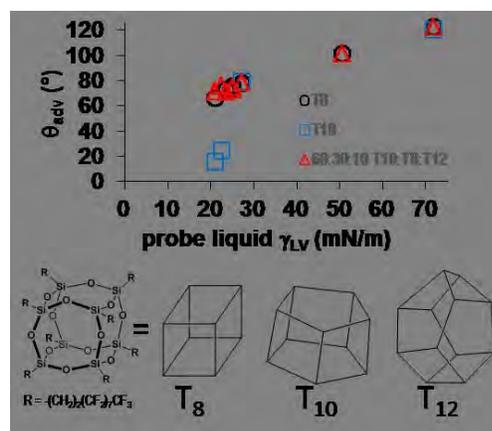
We have now elucidated the chemical mechanism behind the mechanochemistry which allows generation of a robust thin transfer film on the metal surface, and running film on the polymer surface. This talk will describe this unique chemistry, the role it plays during fluoropolymer sliding wear against a metal countersurface, as well as the critical importance of the filler size, shape, friability and surface chemistry.

## POLY 560: Elucidating the low surface energy of cubic fluoroPOSS compounds through the synthesis and surface characterization of fluoroPOSS cage mixtures

**Raymond Campos**<sup>4,3</sup>, [raymond.campos.32@gmail.com](mailto:raymond.campos.32@gmail.com), Timothy S. Haddad<sup>4</sup>, Bruce M. Novak<sup>2</sup>, Joseph M. Mabry<sup>1</sup>. (1) Aerospace Systems Directorate, Air Force Research Laboratory, Edwards AFB, California, United States (2) School of Natural Sciences Mathematics, University of Texas at Dallas, Richardson, Texas, United States (3) Chemistry, University Of Texas At Dallas, Dallas, Texas, United States (4) Aerospace Systems Directorate, Air Force Research Laboratory, ERC, Inc., Edwards AFB, California, United States

The self-assembly and liquid repellence of polymeric materials possessing n-fluoroalkyl substituents is heavily influenced by the spatial arrangement of substituents and the symmetry of the underlying macromolecular framework (e.g. single or dendritic substituents, as either end-groups or side-chains on linear polymers, have significantly different surface energy values). The 3-D structure and high symmetry of fluoroalkyl-substituted cubic silsesquioxanes, or  $T_8-O_h$  fluoroPOSS compounds, imbues enhanced surface crystallinity and liquid repellency compared to linear or cyclic silicates, approaching the theoretical minimum when the n-perfluoroalkyl chain length is  $\geq 8$  carbons.

The synthesis, surface assembly, and liquid repellency of fluoroPOSS compounds with mixed-cage structures will be presented for the first time revealing the influence of purity and symmetry on the oleophobicity of fluoroPOSS compounds. The structural features that imbue  $T_8-O_h$  fluorodecyl POSS with its champion oleophobic properties has been further elucidated from this study and will be presented along with potential design strategies for producing oleophobic materials without long-chain fluoroalkyl substituents that bio-accumulate. Base-catalyzed redistribution of  $T_8-O_h$  fluorodecyl POSS produced mixed-cage samples whose compositions were determined by <sup>29</sup>Si NMR spectroscopy and MALDI-TOF mass spectrometry. The surface assembly and liquid repellency of the following four samples were characterized by grazing-incidence X-ray diffraction experiments and dynamic contact angle analysis: pure  $T_8-O_h$  ( $T_8$ ), pure  $T_{10}-D_{5h}$  ( $T_{10}$ ), a 60:30:10 mixture of  $T_{10}-D_{5h}$ : $T_8-O_h$ : $T_{12}-D_{2d}$  ( $T_{10}$ : $T_8$ : $T_{12}$ ), and an ill-defined sample possessing multiple cage sizes and significant amounts of resinous material ( $T_n$ ).



Advancing contact angle vs. probing liquid surface energy for three fluorodecyl POSS samples.

## POLY 561: Permanently grafted abrasion resistant nanocomposites for anti-icing applications

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(1) Univ of Georgia Riverbend Rsch, Athens, Georgia, United States (2) Chemistry, University of Georgia, Athens, Georgia, United States

In this work, we have investigated copolymer/silica nanocomposites for anti-icing applications that can be covalently grafted to any substrate containing C-H bonds. The copolymers of interest consists of benzophenone, hexafluorobutyl and a variety of other comonomers that under mild UV irradiation, generates a densely cross-linked network that includes immobilizing well-dispersed nanoparticles to a substrate. Investigations into substituent effects lead to important discrimination between cross-linking reactions and chain scission reactions. The iso-butyl acrylate comonomer promotes photoreaction efficiency in terms of kinetic and network robustness leading to films that can sustain high shear forces and abrasion. The anti-icing capability of the composite was investigated using the impact of super-cooled water on the substrate. The composite maintains its icephobicity after Taber testing with multiple abrasion cycles using a 300 g load, demonstrating excellent mechanical resistance. In addition, this study has led to a rational design of polymers that can maximize permanent attachment of different surface functionalities in terms of grafting density and reaction kinetics.



(A) Optical images taken after the icing experiment that demonstrates the anti-icing properties of a p(BP/F/iBA)/nanoparticle composite coated substrate after abrasion.

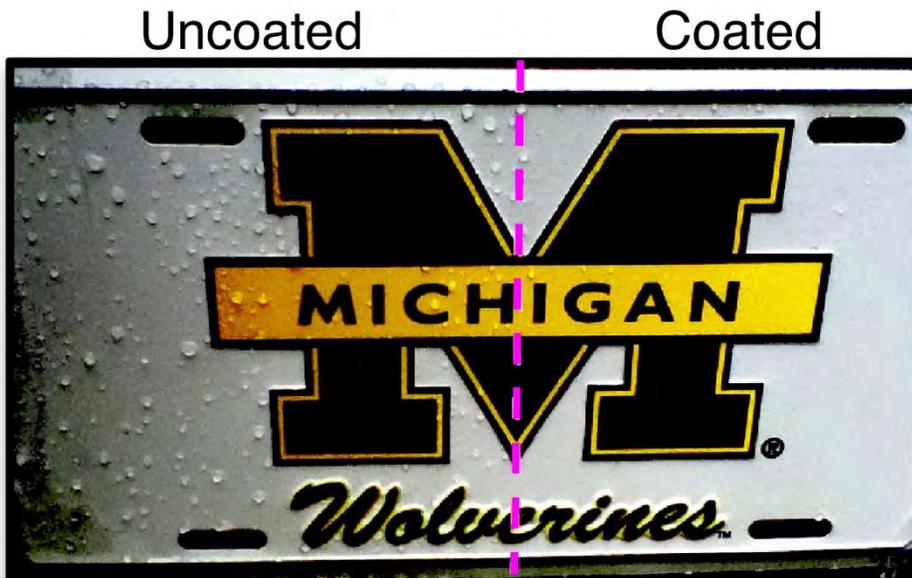
(B) Side view image of a cross section of p(BP/F/iBA)/nanoparticle coated silicon wafer.

(C) Covalent attachment of copolymer/nanoparticle composite to C-H alkyl containing surfaces.

## POLY 562: Designing durable icephobic surfaces

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Ice accretion and its subsequent removal is a safety hazard for aircrafts, power lines, motor vehicles, marine structures, communication towers and wind turbines. Icephobic surfaces are typically defined as having an ice adhesion strength,  $t_{ice} < 100$  kPa. In comparison, most structural materials like aluminum or steel have extremely high  $t_{ice}$ , around 1600 and 1400 kPa, respectively. Polymers such as Teflon possess a much lower ice-adhesion strength ( $\sim 240$  kPa). However, different applications including airplane wings ( $t_{ice} < 80$  kPa), power lines or boat hulls ( $t_{ice} < 20$  kPa), require much lower values of  $t_{ice}$  to enable the passive removal of ice. In this work we discuss two universal parameters that enable the systematic design of icephobic surfaces from a range of different material chemistries. The coatings developed in our work display some of the lowest ice-adhesion strength ever reported ( $t_{ice} < 1$  kPa). In addition, the developed coatings are some of the most durable icephobic coatings produced. Some of the coatings developed in our work maintain an ice adhesion strength  $< 10$  kPa even after severe Taber® abrasion (ASTM D4060), acid/base exposure, accelerated corrosion (ASTM B117), thermal cycling, peel testing (ASTM D3359), accelerated corrosion, and exposure to Michigan wintery conditions over several months.



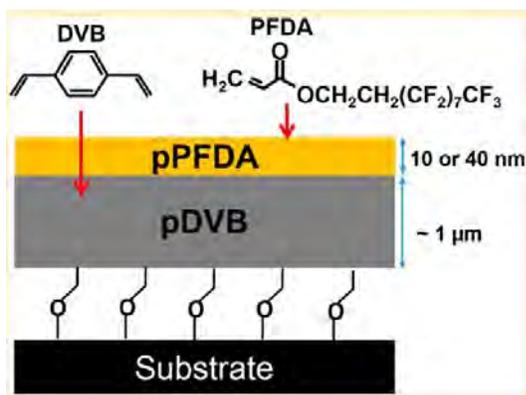
A license plate half-coated with one of our icephobic coatings during outdoor winter 2013 testing. After an ice / snow storm, the uncoated side showed significant ice accretion, whereas all accreted ice sheared off from the coated side due to the shear from the prevailing wind.

## POLY 563: Scalable and durable polymeric ice-phobic and hydrate-phobic coatings

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Blockage of pipelines by formation and accumulation of clathrate hydrates of natural gases can compromise project safety and economics in oil and gas operations, particularly at high pressures and low temperatures such as those found in subsea or arctic environments. Here, durable and mechanically-robust bilayer poly-divinyl benzene (pDVB)/poly(perfluorodecylacrylate) (pPFDA) coatings are developed using initiated chemical vapor deposition (iCVD) to reduce the adhesion strength of ice/hydrates to underlying substrates (silicon and steel). Utilizing a highly cross-linked polymer (pDVB) underneath a very thin fluorine-rich polymer (pPFDA) in designed inherently rough bilayer polymer films deposited on rough steel substrates, results in surfaces which exhibit receding water contact angle (WCA) higher than 150° and WCA hysteresis as low as 4°.

The strength of ice adhesion is reduced more than six-fold when the surfaces are coated with the iCVD bilayer polymer films. Both water miscible and water immiscible hydrates are studied. Tetrahydrofuran (THF) is used to study the formation and adhesion of the water miscible hydrates. The strength of THF hydrate adhesion experiences a ten-fold reduction when substrates are coated with these iCVD polymers: from 1050 ± 250 kPa on bare silicon to 128 ± 100 kPa on coated silicon and from 1130 ± 185 kPa on bare steel to 153 ± 86 kPa on coated steel. To study water immiscible hydrates, cyclopentane (CyC5) is used as the guest molecule. The adhesion strength of the CyC5 hydrate deposits is reduced from 220 ± 45 kPa on rough steel substrates to 20 ± 17 kPa on the polymer-coated steel substrates. The measured strength of ice/hydrate adhesion is found to correlate very well with the work of adhesion between the liquid droplets (water, THF-water mixture, CyC5-in-water emulsion) used to form the ice/hydrate and the underlying substrates.

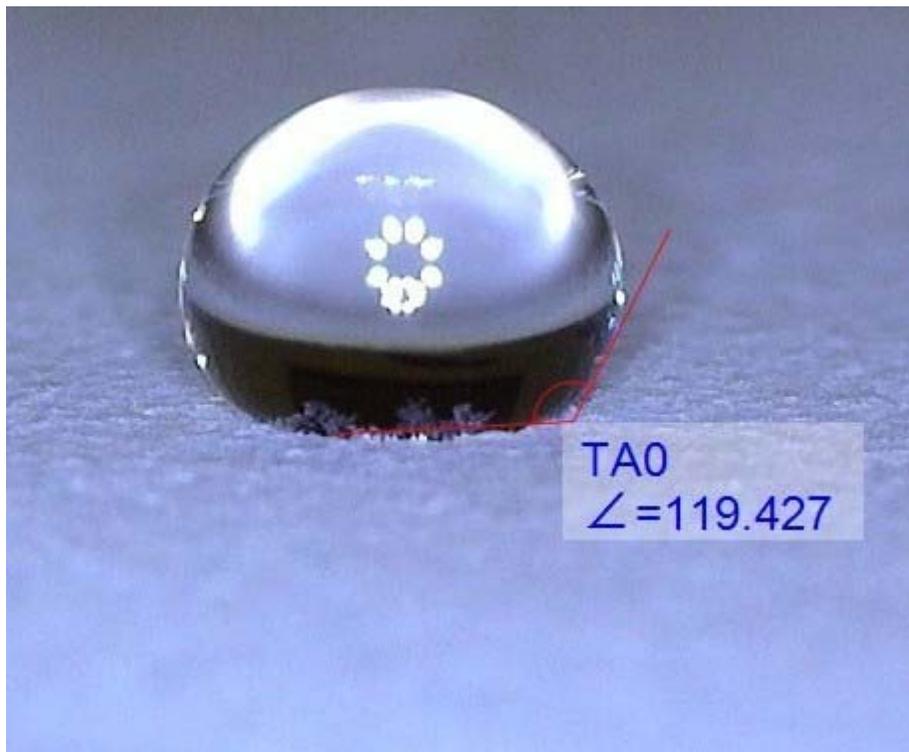


Schematic of a mechanically-robust and hydrate-phobic bilayer polymer film

## POLY 564: Moving anti-ice coatings from the lab to the field: Key issues to overcome

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Development of Ice-phobic coatings has been an interest among research communities and industries in past decade. Similar to marine anti-fouling, and self-cleaning surfaces, the typical strategy involves controlling wettability through combined material choice and roughness to create a superhydrophobic surface. However development of long lasting, exterior environmental resistance, abrasion resistance, thermal resistance, can be challenging, especially in a commercially viable cost-effective package. Especially when products like air conditioners, heat exchangers, wind turbines, transformers and transmission line products are exposed to exterior environmental conditions and wide variability in temperature. In this work, we have focused to design and develop an ice-phobic coating composition with an eye towards actual use. We will present the key parameters affecting performance as well as comparison to semi-commercial products.



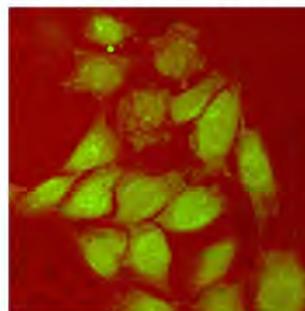
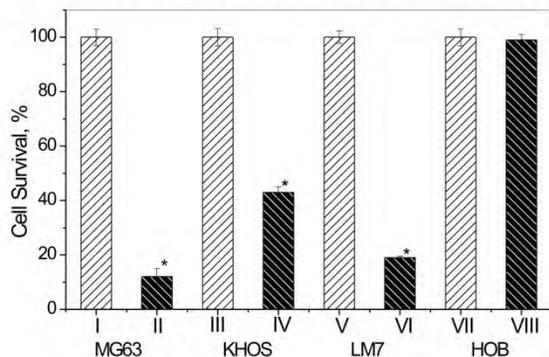
## POLY 565: Responsive polymer-mediated targeted delivery of curcumin to osteosarcoma cells

**Andriy S. Voronov**, *andrevoronov@hotmail.com*. *Coatings and Polymeric Materials, North Dakota State University, Fargo, North Dakota, United States*

Osteosarcoma is the most common type of malignant bone tumor in children and young adults, and it is the sixth leading cancer in children under 15 years of age. The prognosis for osteosarcoma is often poor, as 30% of patients with that diagnosis eventually develop lung metastases. The standard clinical treatment consists of presurgical (neoadjuvant) chemotherapy, followed by surgical resection of the primary tumor after the second or third cycle of the year-long chemotherapy regimen. Curcumin is a phytochemical agent that occurs naturally in plants. It is the principle curcuminoid constituent of the spice turmeric, has been investigated for its therapeutic effects on several cell types, including osteosarcoma and other cancers. However, the therapeutic dose and the intracellular uptake are not fully known yet. Curcumin application is currently limited due to its low bioavailability and poor solubility in aqueous medium (11 ng/ml). One possible way to enhance curcumin aqueous solubility and bioavailability is to conjugate its molecules with polymers.

Synthesized in our group amphiphilic invertible polymers (AIPs) can rapidly self-assemble into micellar nanostructures by changing their concentration in aqueous media, reversibly change their macromolecular conformation in response to a changing environment (e.g. polarity), and effectively incorporate (solubilize) curcumin molecules. The effect of responsive AIPs-mediated curcumin delivery on osteosarcoma cells survival was investigated at different concentrations of loaded assemblies using MTS assays. The obtained results show that presence of micellar curcumin essentially reduces cell survival in human osteosarcoma cell lines MG63 (treated with different concentrations of micellar curcumin), KHOS, and LM7. Remarkably, no effect of polymer micelles tested at the same concentrations, on normal cells survival has been observed. The data show that micellar assemblies effectively deliver curcumin and target three different bone cancer cells (MG63, KHOS, and LM7) but not normal primary human osteoblasts (HOBs).

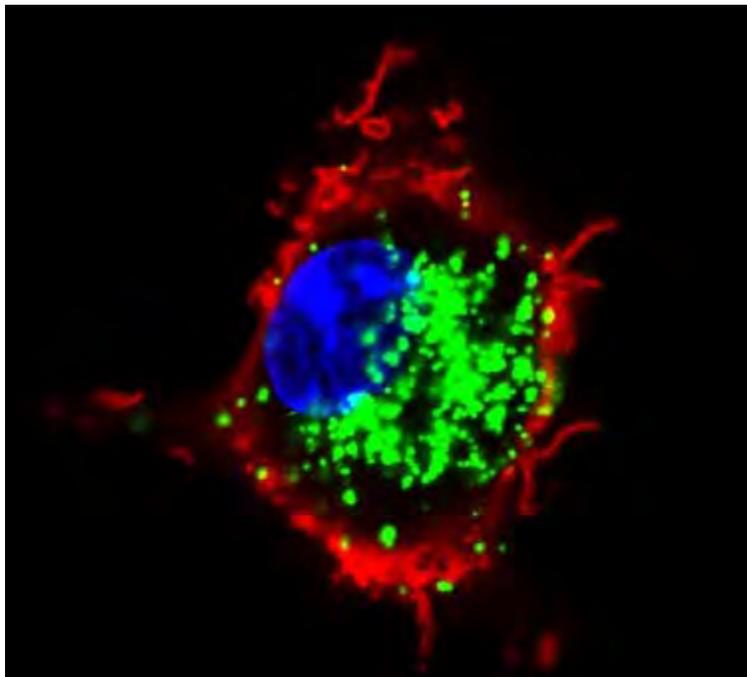
Polymer-Mediated Targeted Delivery of Curcumin to Osteosarcoma cells



## POLY 566: Engineering polymer hydrogel nanoparticles for lymph node targeted vaccine delivery

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The induction of an antigen-specific adaptive immune response exclusively occurs in lymphoid organs. As a consequence, the efficacy with which vaccines reach these immune-inducing sites strongly affects the protective efficacy of the vaccine. Here, we report the design of redox-sensitive polymer hydrogel nanoparticles that efficiently target multiple immune cell subsets in the draining lymph nodes. Nanoparticles are fabricated by infiltrating mesoporous silica particles (~200 nm) with poly(methacrylic acid) followed by disulfide-based crosslinking and template removal. PEGylation of these nanoparticles does not affect their cellular association *in vitro*, but dramatically improves their lymphatic drainage *in vivo*, as elucidated by flow cytometry and confocal fluorescence microscopy. The functional relevance of these observations is further illustrated by the increased priming of antigen-specific T cells. Our findings highlight the potential of engineered hydrogel nanoparticles for the lymphatic delivery of antigens and immune-modulating compounds.



## POLY 567: Biodegradable injectable polymer systems forming covalent hydrogel in response to temperature

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Biodegradable polymers exhibiting temperature-responsive sol-gel transition between room temperature and body temperature are expected to be applied as injectable polymer (IP) systems in biomedical applications. IP solution containing drugs or living cells can be injected by simple syringe injection at the target site in the body to form a hydrogel acting as sustained drug releasing depots or scaffolds for tissue regeneration. For example, Lee *et al.* reported ABA-type triblock copolymer of poly(lactide-co-glycolide) and poly(ethylene glycol) (PEG) as biodegradable injectable polymer [1]. We also reported several biodegradable IP systems using block copolymers of aliphatic polyesters and branched PEG [2-4]. However, such IP systems forming physically cross-linked hydrogel are likely to dissociate to sol state under highly wet condition such as intra-peritoneal space. To overcome the problems, we developed an injectable polymer formulation forming chemically cross-linked hydrogel in response to temperature change. We synthesized poly(caprolactone-co-glycolic acid)-*b*-poly(ethylene glycol)-*b*-poly(caprolactone-co-glycolic acid) (PCGA-*b*-PEG-*b*-PCGA) triblock copolymer bearing succinimidyl groups on its termini (CP-OSu). The copolymer was mixed with water-soluble polymer bearing amine groups, such as poly-L-Lysine (PLys), which can form covalent bonds with the functional groups on the triblock copolymer termini. The mixture solution showed irreversible sol-to-gel transition and covalent bond formation in response to temperature change (Figure 1). The obtained hydrogel showed longer duration time of the gel state in aqueous solution.

1. D. S. Lee *et al.*, *Macromol. Rapid Commun.*, 22, 587 (2001).
2. Y. Ohya *et al.*, *Adv. Funct. Mater.*, 18, 1220 (2008).
3. K. Nagahama, A. Takahashi, Y. Ohya, *React. Funct. Polym.*, 73, 979 (2013).
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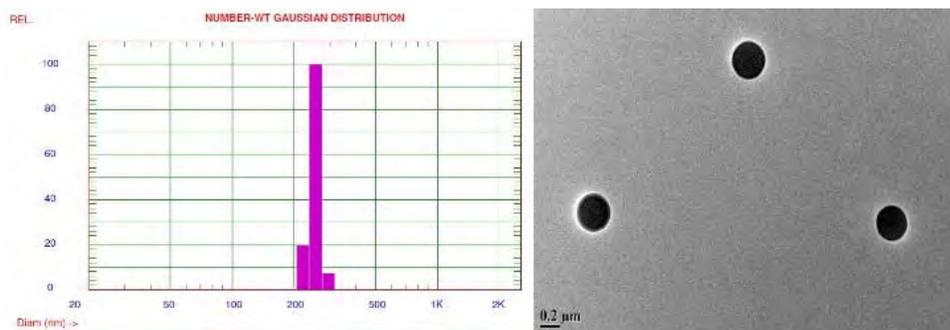
Figure 1. Irreversible sol-gel transition of CP-OSu/PLys solution in response to temperature changes.

## POLY 568: Synthesis and characterization of stable polypyrrole nanospheres

**Oksana Zholobko**, *oksana.zholobko@ndsu.edu*, **Andriy S. Voronov**, *Coatings and Polymeric Materials, North Dakota State University, Fargo, North Dakota, United States*

Conducting polymers, especially nanoparticles or nanospheres, find their use in in the biomedical field such as in biosensors, tissue engineering (include cardiac, bone and neural), neural probes and drug delivery, etc. The potentially valuable properties of nanoparticulate materials result from their behavior as independent particles. When left alone for a while, nanoparticles typically settle and clump together into a glob that no longer retains the beneficial nanoproperties. Polypyrrole is a biocompatible material, which is promising for advanced biomedical and biotechnological applications, particularly when this polymer is in the form of nanoparticles.

Developed at NDSU methodology results in polypyrrole nanospheres (PPNs) that remain in suspension almost indefinitely, and when they settled, were re-suspended in seconds. This non-agglomerating feature means the PPNs might retain their beneficial properties in production and handling situations that can be expected during production, shipping, and use by a customer. Stable PPNs with a size of 70 - 200 nm, were synthesized using pyrrole, water and ozone as an oxidizing agent. The obtained PPNs were characterized using Fourier transform infrared (FTIR) spectroscopy characterization to provide the absorption peaks of infrared spectra that correspond to the frequencies of vibration between the bonds of atom comprising the nanospheres. X-Ray photoelectron spectroscopy (XPS) and zeta-potential measurements were used to determine chemical identity and mechanism of nanospheres formation. UV-Vis spectroscopy was employed to confirm the presence of polarons and bipolarons through electron excitation from the ground state to an excited state and to determine conductivity properties of PPNs. Dynamic light scattering measurements (DLS) and transmission electron microscopy (TEM) were used to confirm PPNs morphology, as well as particles size and size distribution.



## **POLY 569: Materials construction through peptide design and solution assembly**

**Darrin J. Pochan**, *pochan@udel.edu*. Univ of Delaware, Newark, Delaware, United States

Self-assembly of molecules is an attractive materials construction strategy due to its simplicity in application. By considering peptidic molecules in the bottom-up materials self-assembly design process, one can take advantage of inherently biomolecular attributes; intramolecular folding events, secondary structure, and electrostatic interactions; in addition to more traditional self-assembling molecular attributes such as amphiphilicity, to define hierarchical material structure and consequent properties. These self-assembled materials range from hydrogels for biomaterials to nanostructures with defined morphology and chemistry display for inorganic materials templating. The local nano- and overall network structure, and resultant viscoelastic and cell-level biological properties, of hydrogels that are formed via beta-hairpin self-assembly will be presented. These peptide hydrogels are potentially excellent scaffolds for tissue repair and regeneration due to inherent cytocompatibility, porous morphology, and shear-thinning but instant recovery viscoelastic properties. Slight design variations of the peptide sequence allow for tunability of the self-assembly/hydrogelation kinetics as well as the tunability of the local peptide nanostructure and hierarchical network structure. In turn, by controlling hydrogel self-assembly kinetics, one dictates the ultimate stiffness of the resultant network and the kinetics through which gelation occurs. During assembly and gelation, desired components can be encapsulated within the hydrogel network such as drug compounds and/or living cells. The system can shear thin but immediately reheal to preshear stiffness on the cessation of the shear stress. Studies revealing an advantageous drug release profile after weeks in vitro will be discussed. In addition, peptide nanostructures can be used to template the growth of inorganic materials as well as the assembly of inorganic nanoparticles. Finally, theory and simulation are critical tools for the prediction of new molecules with which one can form new peptide nanostructures in solution. Recent results from the theory-driven work will be presented.

## POLY 570: Effect of post-drawing on the macromolecular and functional properties of polymer nanofibers

David Brennan, **Vince Z. Beachley**, beachley@rowan.edu. Biomedical Engineering, Rowan University, Glassboro, New Jersey, United States

Conventional polymer fibers are manufactured by mechanical extrusion and a secondary post-drawing step that stretches the fiber to several times its original length to induce molecular alignment and impart strength. Unfortunately, nanofiber materials are not compatible with conventional post-drawing processes because of their small size and delicate mechanical properties. As a result, electrospun nanofibers are mechanically weaker than their conventional microfiber counterparts, contrary to the theoretical expectation of increased strength with decreasing fiber diameter. We have developed new methods to post-draw thousands of individual electrospun nanofibers within a continuous manufacturing/processing system (**Fig. 1**). This will allow an unprecedented ability to systematically examine the mechanisms associated with nanofiber post-drawing. Polymer nanofiber macromolecular arrangement, crystallinity, crystalline alignment and mechanical strength are assessed with FTIR, DSC, X-ray, and mechanical analysis (**Fig. 2**). The effect of drawing conditions on these properties are analyzed and mechanisms are proposed.

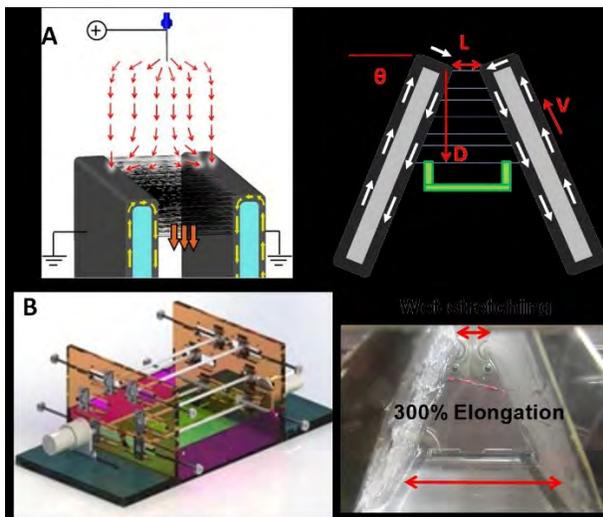


Figure 1A: Previous Electrospinning Configuration B: Prototype Clamped Bearing Design C: Variable track diagram D: Wet Stretching to 300% elongation.

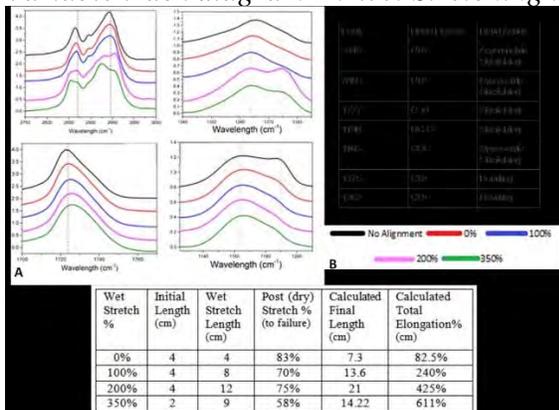


Figure 2A: FTIR analysis for fibers at varying stretching elongations. B: Peak and Associated Bond/Bond Action. C: Mechanical testing data.

## POLY 571: Osmotic behavior of proteoglycan assemblies

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Cartilage is a complex tissue that has many biological functions. In cartilage the largest and most abundant proteoglycan is the bottlebrush shaped aggrecan that possesses more than 100 chondroitin sulfate and keratan sulfate chains. Aggrecan interacts with hyaluronic acid (HA) to form large aggregates. Each aggregate is composed of a central filament of HA with many aggrecan molecules attached to it non-covalently. The interaction between the aggrecan core protein and the HA molecule is stabilized by the presence of a link protein that interacts with both the aggrecan and HA. In cartilage the aggrecan-HA complexes are interspersed in the network of collagen fibrils. Both the high anionic charge on the individual aggrecan molecules due to the sulfated glycosaminoglycan chains and the localization of the aggrecan-HA complexes in the collagen matrix are essential for the load bearing function of cartilage. The aggrecan-HA aggregates exhibit high osmotic swelling pressure, which gives cartilage its ability to resist compressive loading.

We made swelling pressure measurements and rheological measurements to quantify the effect of complex formation on the osmotic modulus of aggrecan-HA complexes. The changes in the supramolecular organization of aggrecan assemblies were studied by small-angle neutron scattering and small-angle X-ray scattering. These techniques probe the structure and interactions over a broad range of length scales. The dynamic response of the systems was determined by dynamic light scattering and neutron spin-echo measurements.

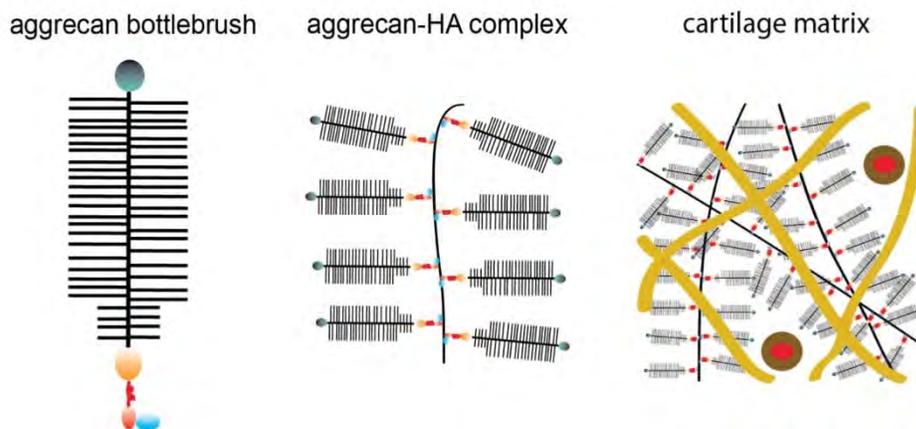
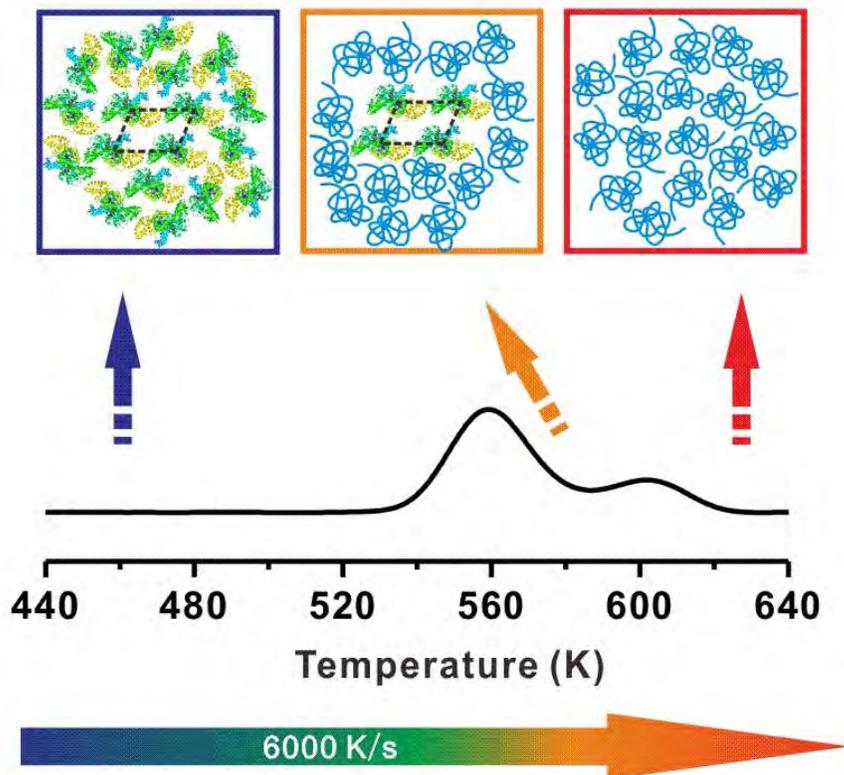


Figure 1. Hierarchical organization of cartilage extracellular matrix.

## POLY 572: Fast-scan DSC characterization of bulk bovine serum albumin

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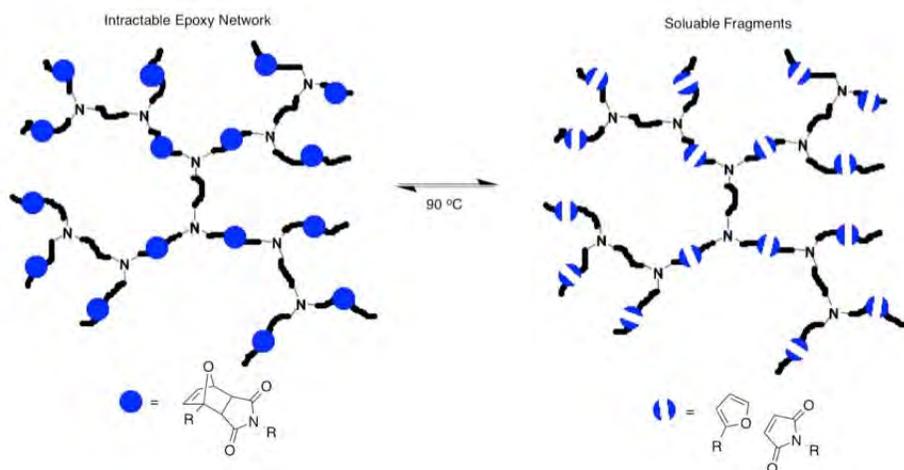
We employed chip-calorimeter for differential scanning calorimetry (DSC) measurement of unfolding enthalpies of native bovine serum albumin (BSA) in their solution-cultivated single crystal, lyophilized amorphous and vacuum-dried semi-crystalline states. By comparing the unfolding enthalpies between crystalline and amorphous BSA, we obtained the fusion enthalpy. In addition, fast-scan benefits the separation of two unfolding peaks of crystalline and amorphous fractions in semi-crystalline BSA, and allows us to obtain a precise crystallinity.



## POLY 573: Thermally re-workable epoxy adhesives for use in artifact repair

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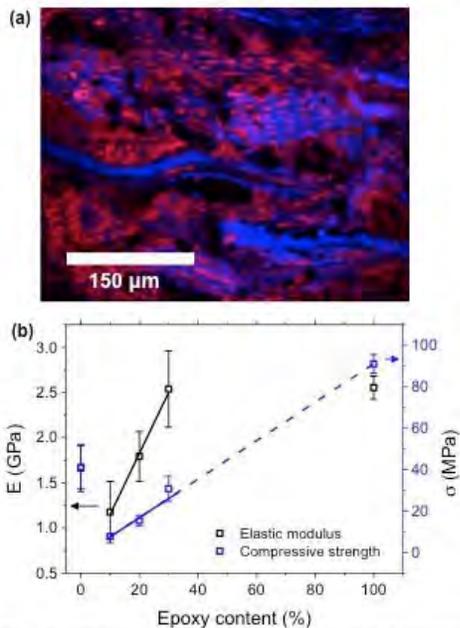
Polymeric adhesives such as acrylics and epoxies are commonly used for the reconstruction and repair of ceramic and glass artifacts. Currently used epoxies have superior strength but are non-reversible after they have cured, making any important structural artifact corrections impossible. Thermally reversible epoxies with Diels Alder cycloadduct weak links have been previously reported but generally utilize solid epoxy precursors. In this work we have prepared a liquid bis-epoxy precursor with two maleimide-furan cycloadducts in the bridging group. The cycloadducts, while unaffected by the epoxy curing reactions, undergo a retro [4 + 2] cycloaddition when heated above 90 °C that results in the liquefaction of the resin. At this point, the resin can be removed from the artifact or allowed to reform the cycloadduct bonds to reform the thermoset. Adhesive bond strength of the new adhesive was determined using lap shear testing. The reworkability of the resin was determined by heat treating lap shear samples until the thermoset was liquefied, then resetting and cooling the sample to reform the bond. We found that the thermally reversible adhesive could be reworked four or five times before the adhesive strength degraded. Through such tests we were able to show that these adhesives can be easily re-worked and act as a useful new tool for object conservation.



## POLY 574: Moldable plant biomass by cross-linking thermoset polymer and lignocellulose

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From stover to woody materials, lignocellulosic biomass is characterized by cellular structures, comprised of 3 types of biopolymers, cellulose, hemicellulose, and lignin. Cell wall possesses superior mechanical properties because of a unique arrangement in its components. Although lignocellulosic biomass is the closest natural alternative to plastics, it cannot be molded or extruded like plastics. This powdery and highly porous material is made into a bulk-like and moldable structure by blending lignocellulose with plastics and they are typically known as Wood plastic composites (WPCs). Despite synergistic advantages of its components, the stiffness and strength of WPCs are still significantly lower than lignocellulose due to weak adhesion between its constituents. The present work demonstrates a high biomass content (i.e., up to 90% by weight) and moldable material known as thermoset-cross-linked lignocellulose (TCL). It is prepared by controlled covalent cross-linking of lignocellulosic particles by an epoxy thermoset using epoxide-hydroxyl reactions. Compression tests reveal, at 30% thermoset content TCL has superior mechanical properties over a commercial WPC while comparable stiffness and strength to bulk epoxy and wood, respectively. Macroscopic to molecular scale interactions of the thermoset with the lignocellulose are attributed to the improved mechanical properties. These interactions have been revealed using scanning fluorescence microscopy and vibrational spectroscopy. The capillary action of biomass cellular network as well as applied pressure in the processing of TCL results in impregnation of the resin in the matrix of lignocellulose forming thermoset microrods. We also infer permeation of the thermoset into the cell walls from the reaction of epoxides with the hydroxyls of the lignin.



**Figure 1:** a) Fluorescence micrograph obtained by overlay of emissions from epoxy (stained with Rhodamine B) and Eastern reedcedar (ERC) domains for a 30% epoxy TCL sample. The applied force in the molding/pressing stage is in the vertical direction with respect to the micrographs. Hence, elongation of ERC particles and cells occurs effectively in the perpendicular direction (horizontal). b) Increase in modulus and strength of the TCL samples with epoxy content and comparison with bulk ERC and epoxy.

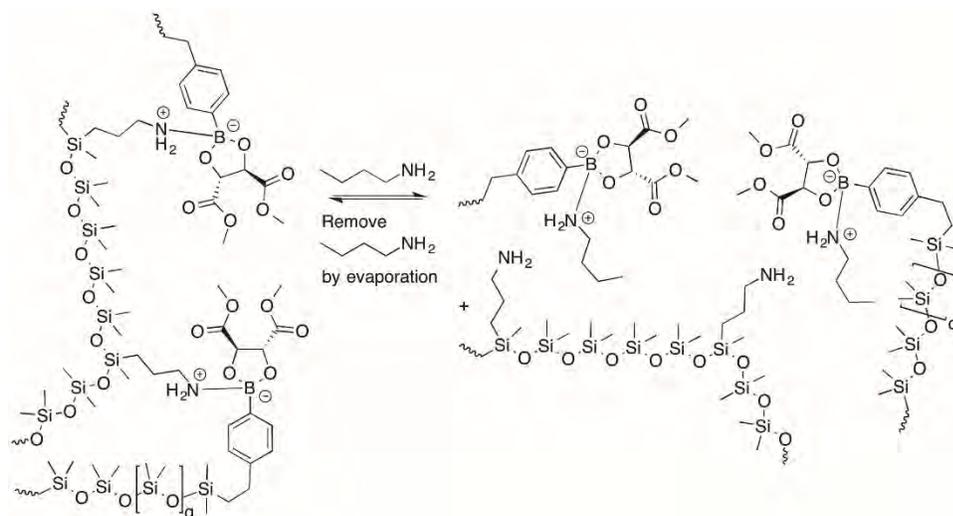
## POLY 575: Lewis acidic silicone polymers: Creating stable, reversible elastomers

**Laura Zepeda-Velazquez**<sup>1</sup>, [lauracathzpeda@gmail.com](mailto:lauracathzpeda@gmail.com), Benjamin Macphail<sup>2</sup>, Michael A. Brook<sup>1</sup>. (1) Chemistry and Chemical Biology, McMaster University, Mississauga, Ontario, Canada (2) Chemistry and Chemical Biology, McMaster University, Hamilton, Ontario, Canada

Traditional routes to silicone-based materials involve irreversible covalent crosslinking to produce robust materials with properties that can be tailored much like any other network, using fillers or by varying the crosslink density. One of the major drawbacks to these methods is that the resulting elastomers cannot be reshaped or manipulated after curing: they are non-recyclable thermosets. Recently, we demonstrated that boronic acid-modified silicones<sup>1</sup> could strongly associate with amine-functionalized silicones to produce elastomeric networks.<sup>2</sup> The properties of the elastomer are controlled by network topology arising from both silicone-boronates and amino-partners: materials, normally transparent, ranging from soft gels to almost brittle glasses could be produced. The polymers are thermoplastic. Depolymerization could be induced thermally. Samples stored under compression overnight mostly recovered their shape after the compressive force was removed, but no such recovery occurred with samples heated at 60 °C. Complete depolymerization could reversibly be induced by adding a mono-amine. After solvation, elastomers became viscous liquids/gels but formed a new elastomer after the amine was removed via evaporation. The impact of structure on reversible elastomeric properties will be discussed.

### References

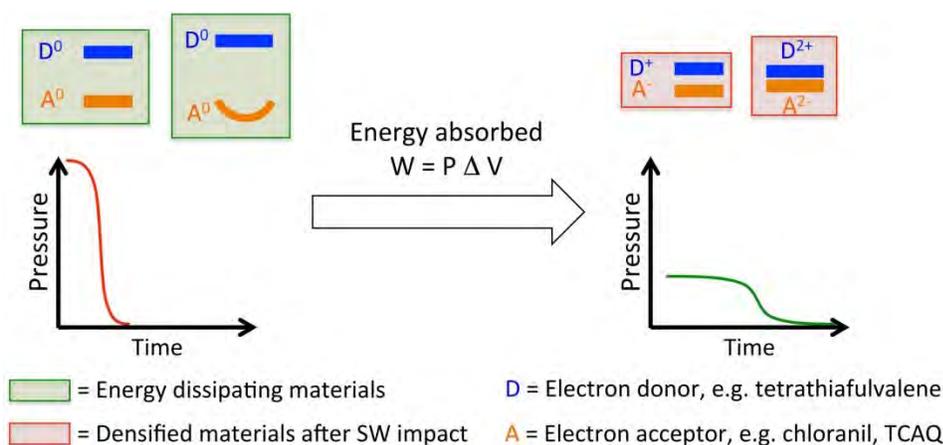
1. M. A. Brook, L. Dodge, Y. Chen, F. Gonzaga, H. Amarne, *Chem. Commun.* 2013, 49, 1392.
2. L. Dodge, Y. Chen, M. A. Brook, *Chem. Eu. J.* 2014, 20, 9349.



## POLY 576: Development of organic charge transfer complexes for shock wave energy dissipation (SWED)

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Dissipating shock wave energy using mechanochemically active compounds is a hypothetical concept under investigation for protecting personnel and machinery from hazardous detonations. We envision materials capable of volume collapse upon external compression transforming the kinetic energy of a shock wave into chemical energy, which attenuates the shock wave impact. A series of charge-transfer complexes (CTCs) that undergo pressure-induced neutral-to-ionic phase transitions (NIPT) are tested with laser-driven flyer plates as a new class of energy dissipators. Compared to polyurea, the current state-of-the-art energy dissipator, CTCs comprised of tetrathiafulvalene-chloranil cocrystals exhibit improved performance in energy dissipation at various impact levels. To further enhance SWED performance, we prepared a series of CTCs with butterfly-shaped tetracyano-anthraquino-dimethane (TCAQ) motifs, which exhibit large structural change upon accepting two electrons. We also incorporated tetrathiafulvalene and TCAQ moieties into polymers to improve processability. The feasibility of butterfly-shaped CTCs and their polymeric analogs to undergo pressure-induced NIPT will be discussed.

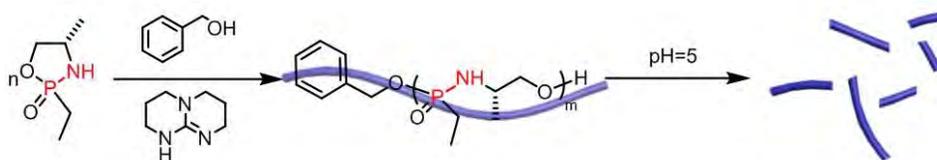


Mechanochemically active charge transfer complexes capable of volume collapse upon shock wave impact as energy dissipators.

## POLY 577: Facile synthesis of highly pH-responsive and water-soluble polyphosphonamidates

**Hai Wang**, wanghaihp@gmail.com, Richen Li, Jingwei Fan, Lu Su, Fuwu Zhang, Karen L. Wooley. 3255 TAMU, Texas AM University, College Station, Texas, United States

The direct and facile synthesis of a highly pH-responsive and water-soluble polyphosphonamidate (PPNA) by organobase-catalyzed ring-opening polymerization was developed and acid-assisted cleavage of the phosphonamidate bonds along the backbone of the PPNA was studied. Introducing pH-responsive linkages, such as hydrazones, acetals/ketals, phosphonamidates along the polymer backbone can lead to rapid degradation of the whole polymer and quick release of preloaded therapeutics, which holds great promise for biomedical applications, such as the selective delivery of therapeutics to tumor and inflammatory tissues by taking advantage of their relatively low extracellular pH values. Nevertheless, current methods suffer from synthetic challenges and most of the achieved polymers are not well-defined with only mild pH-responsiveness. The fast organobase-catalyzed ring-opening polymerization of a cyclic phosphonamidate monomer initiated by benzyl alcohol allowed for the preparation of well-defined PPNAs, which have phosphonamidate acid-labile along the backbone, with predictable molecular weights, narrow molecular weight distributions ( $PDI < 1.20$ ), and well-defined chain ends. Cleavage of the acid-labile phosphonamidate bonds on the PPNA repeat units was evaluated under acidic conditions over a pH range of 4–6, and highly enhanced hydrolytic degradation was observed compare to neutral pH.

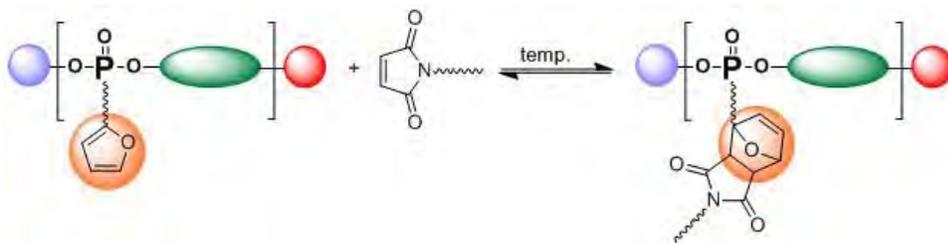


## POLY 578: Click and unclick: A furfuryl group as a versatile tool in Poly(phosphoester)s

**Greta Becker**<sup>1,2</sup>, [beckergr@uni-mainz.de](mailto:beckergr@uni-mainz.de), **Frederik Wurm**<sup>1</sup>. (1) Max Planck Institut für Polymerforschung, Mainz, Germany (2) Graduate School Material Science in Mainz, Mainz, Germany

Poly(phosphoester)s (PPEs) are a very interesting, yet rather neglected class of polymers. The chemical structure of PPEs is highly modular, they are degradable and their hydrophilicity can be precisely adjusted. At the same time, the thermoreversible furan/maleimide Diels-Alder reaction is a versatile tool in macromolecular synthesis e.g. opening the way to recyclable networks or self-healing materials.

Herein, we present novel PPEs bearing furfuryl groups which can be easily modified after polymerization. Small molecules or functional groups can be introduced which may not be tolerated by the catalyst or conditions for polymerization reactions. Moreover, the hydrophilicity can reversibly switched.



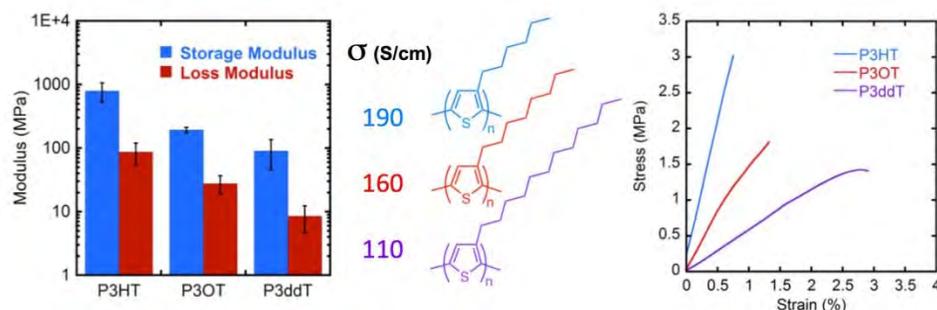
Schematic view of Diels-Alder reaction between functionalized PPE and maleimide

## POLY 579: Enhancing the mechanical and electronic properties of poly(3-alkylthiophenes) through random copolymerization

**Stefanie A. Sydlik**, [ssydlik@mit.edu](mailto:ssydlik@mit.edu), Zachary Smith, Zoe Wright, Anne Arnold.  
Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States

Conductive polymers promise to serve as lightweight, flexible electronic devices. We envision that such devices could be accessed via convenient solution processing methods and rolled or folded for ease of storage. However, the mechanical demands of rolling or folding are actually quite great, and require a material that is tough and deforms elastically, even after many cycles of deformation. Unfortunately, little work has been done to actually understand the mechanical properties of these materials, even in well-characterized conductive polymers such as the ubiquitous poly(3-hexylthiophene) (P3HT). Recently, some work has been done to address this chasm. Researchers have estimated the modulus of regioregular P3HT through various extrapolation methods, and the result is a stiff, but brittle material. In reality, most conductive polymers are highly ordered and crystalline, which gives rise to good electronic properties, but would not allow the flexible devices envisioned.

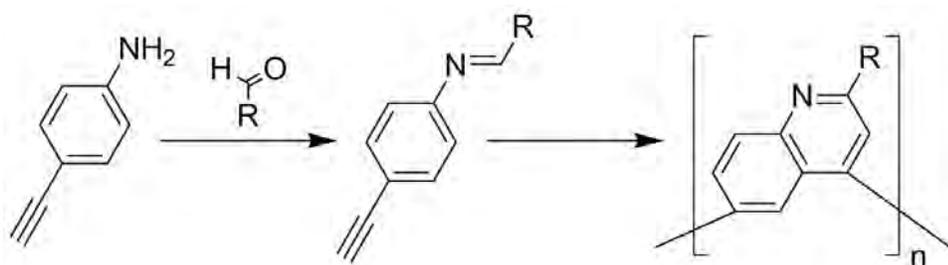
Here, we report the bulk mechanical properties of regioregular poly-3(alkylthiophenes) (P3ATs) as measured at room temperature by dynamic mechanical analysis (DMA). We find that as side chain length increases, polymer ductility increases, but conductivity, mobility, and stiffness decrease. In search of a conductive polymer with superior electronic and mechanical properties, we synthesized a series of random copolymers of P3ATs and unsubstituted thiophene, incorporating thiophene monomers in a 3:1 and 1:1 ratio. The unsubstituted thiophene should enhance the electronic properties, as well as the stiffness of the material, and its random incorporation should increase disorder, making the semi-crystalline material more amorphous, hopefully increasing its toughness. The 3:1 random copolymers were found to have increased conductivity (150, 400, and 300 S/cm, respectively for 3:1 P3HT, P3OT, and P3ddT) and mobilities on par with that of P3HT (0.07 cm<sup>2</sup>/Vs). Remarkably, these polymers are more ductile and also 620, 760, and 430% tougher than their respective homopolymers. This is an interesting example of how introducing competing molecular factors can allow us to engineer a conductive polymer with superior mechanical and electronic properties.



## POLY 580: Aza-Diels-Alder route to polyquinolines

**Mehran Umerani**, *Mumerani@uci.edu*, David J. Dibble, Amir Mazaheripour, Young S. Park, Joseph W. Ziller, Alon A. Gorodetsky. 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 581: Hexaphenylbenzene and hexabenzocoronene-based porous polymers for selective adsorption of volatile organic compounds

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Toxic volatile organic compounds (VOCs) such as BTEXs (i.e., benzene, toluene, ethylbenzene, and xylenes), formaldehydes and chlorinated hydrocarbons, emitted from industrial chemical processes and outdoor or indoor chemical applications are harmful to environment and threat to human health. Removal and recovery of VOCs from air with porous adsorbents like zeolites, activated carbon and its derivatives, and MOFs has been widely studied and confirmed as an effective technique. However, porous organic polymers (POPs) which gain much interest during last decade as an alternative stable material for gas adsorption/separation is rarely studied with VOCs. Herein, we have designed and synthesized Hexaphenylbenzene (HPB) and Hexabenzocoronene (HBC)-based POPs and studied their adsorption of organic vapors. Our HPB-based POP selectively adsorbs aromatic vapors with a superior capacity (99.9 wt. %) whereas HBC-based POP shows simultaneous high adsorption capacities towards both aliphatic and aromatic vapors (51.7 and 53.0 wt. %).

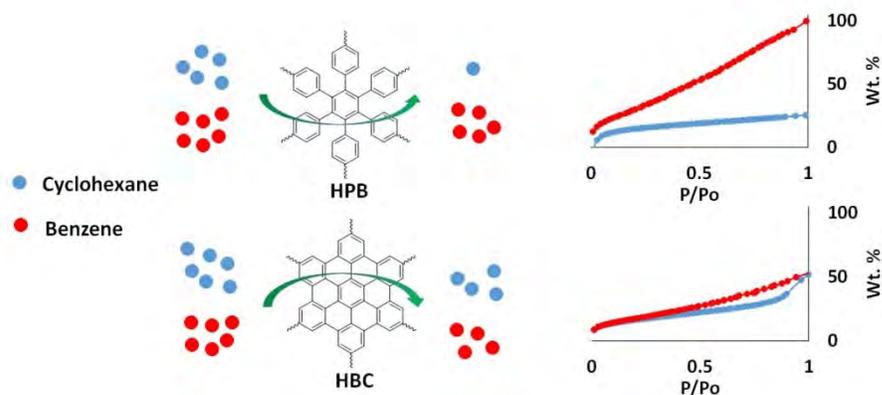
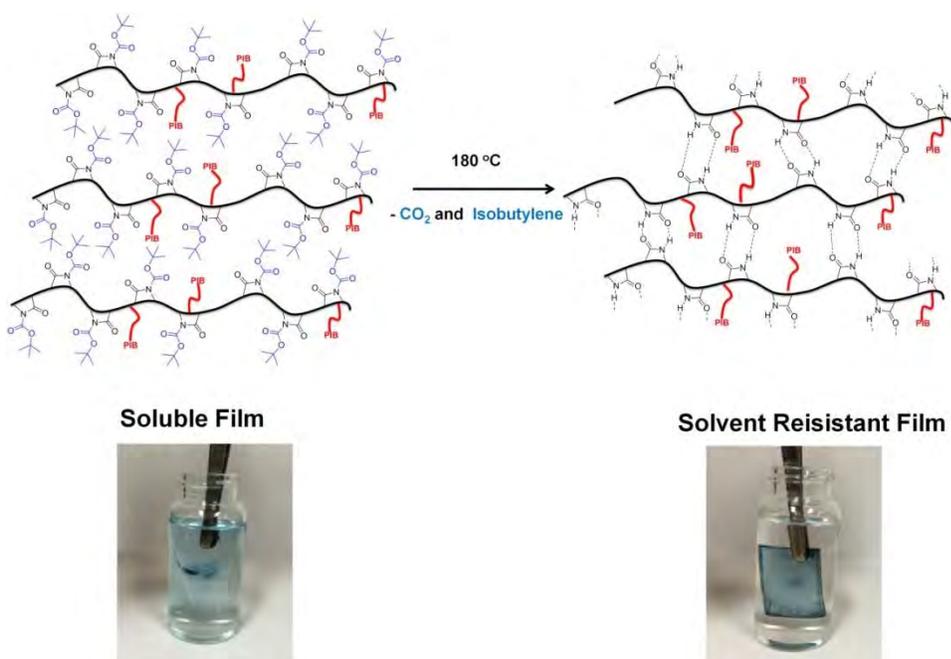


Figure: Organic vapour adsorption by HPB and HBC-based POPs

## POLY 582: Cleavable side-chain promoted interesting chemistry

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Functional polymers can be decorated with cleavable solubilizing groups that can be removed by post-treatment such as heat, light, pH changing, etc. The chemical and physical properties of the polymers can be changed dramatically after such side-chain cleavage. Here, two different systems bearing cleavable side-chains were investigated. First, thermal cleavable *tert*-butyloxycarbonyl (*t*-Boc) group was installed to a series of isoindigo based random copolymers, in which polyisobutylene (PIB) groups were incorporated as solubilizing side-chain. These polymers showed distinguished physical properties, especially solubility, before and after the post thermal treatment. However, the charge carrier property maintained well, measured through organic field-effect transistor (OFET) devices. This unique property makes these materials a great potential for solvent resistant material for organic electronics. The second example involves polylactic acid (PLA) as cleavable side-chain which could be removed by heat or pH changing. Alkyne group and different length PLA were introduced into polythiophene (PT) backbone. These functionalized PT polymers could be cross-linked by alkyne-alkyne Glaser coupling reaction into bulky materials. The expecting conjugated porous polymer network (cPPN) could be easily achieved by removing the PLA side-chain. In addition, the porosity of cPPN is determined by the length of PLA.



## POLY 583: Novel functional conjugated polymers derived from a common set of enediyne building blocks

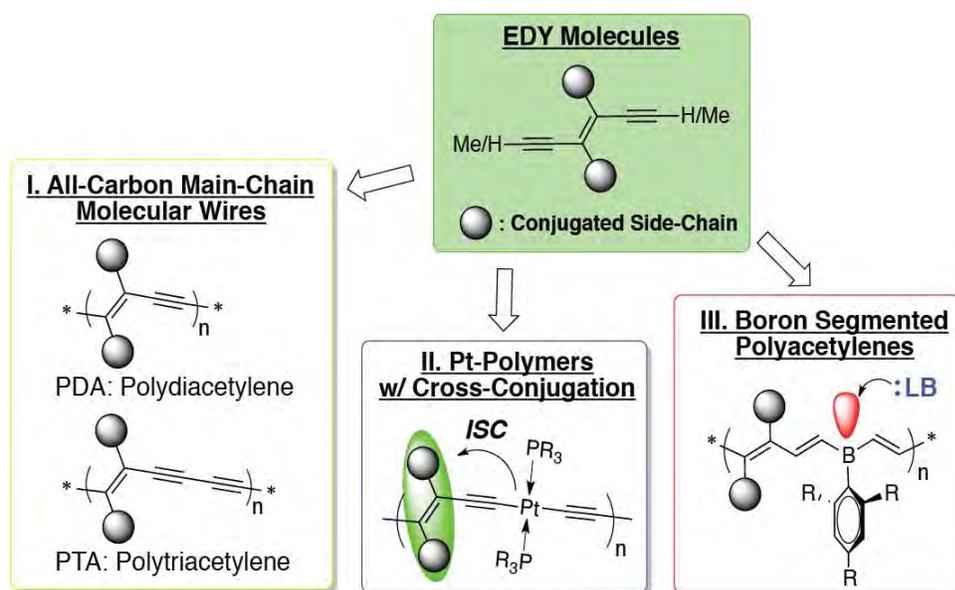
**Yang Qin**, qinshou314@gmail.com. University of New Mexico, Albuquerque, New Mexico, United States

Organic conjugated materials, including small molecule dyes, conjugated polymers and allotropes of carbon, have found widespread applications in modern electronic devices such as biological sensors, transistors, memory devices, lasers, and solar cells. Each application places unique and sometimes stringent requirements on the properties of the materials applied. Discoveries of new materials and properties can enhance performance of existing devices and lead to emerging applications. Thus, new synthetic methodologies for novel materials and basic understanding on the structure-property relationships are greatly sought after.

We have developed facile synthetic methodologies for a set of *trans*-enediyne (EDY) molecules containing various aromatic moieties directly attached to the central double bonds. These EDYs can serve as versatile building blocks for a variety of functional conjugated polymers and we discuss our efforts in the following areas: (i) the first solution synthesis of polydiacetylenes (PDAs) using a newly developed acyclic enediyne metathesis (AEDMET) polymerization technique;<sup>1</sup> (ii) the first examples of polytriacetylenes (PTAs) that contain aromatic groups directly attached to the polymer main-chains, through Glaser-Hay and Pd-catalyzed oxidative coupling reactions; (iii) Pt-segmented PDAs that contain cross-conjugated chromophores, differing from conventional Pt-bisacetylenide polymers;<sup>2</sup> and (iv) boron-segmented polyacetylenes (BPAs), representing the first main-chain boron-containing conjugated polymers without aromatic groups.

1. Hu, K.; Yang, H.; Zhang, W.\*; Qin, Y.\* *Chem. Sci.* 2013, 4, 3649.

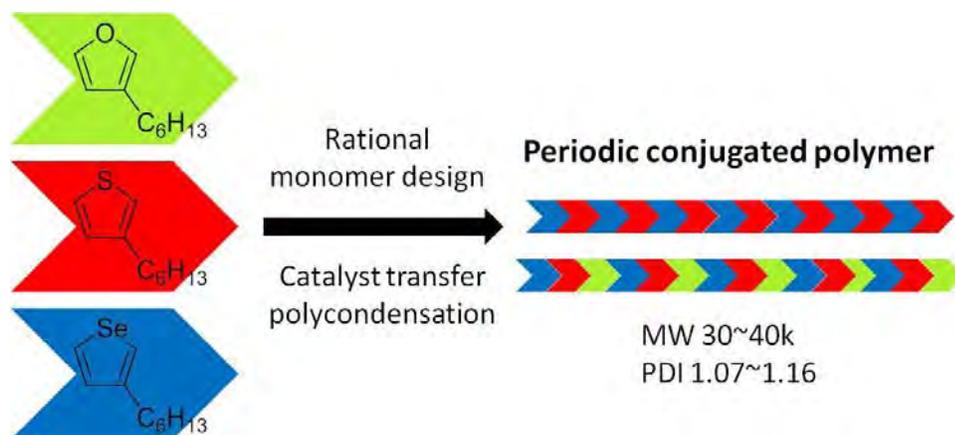
2. Hu, K.; Pandres, E.; Qin, Y.\* *J. Polym. Sci. A Polym. Chem.* 2014, 52, 2662.



## POLY 584: Periodic conjugated polymers: The group 16 dance

**Chia-Hua Tsai**<sup>1</sup>, [chiahuat@andrew.cmu.edu](mailto:chiahuat@andrew.cmu.edu), Andria Fortney<sup>1</sup>, Yunyan Qiu<sup>4</sup>, Tomasz Kowalewski<sup>2</sup>, Kevin J. Noonan<sup>3</sup>. (1) Carnegie Mellon University, Pittsburgh, Pennsylvania, United States (2) Dept of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States (3) Box 63, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States (4) Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States

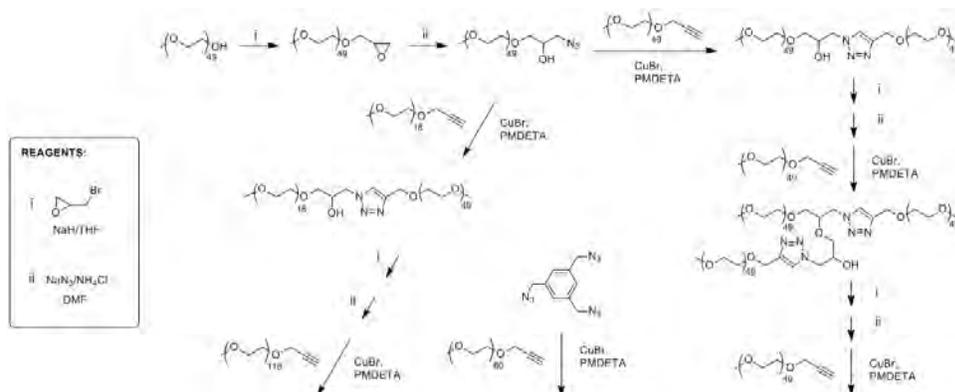
Biopolymers composed of well-defined sequences of amino acids are capable of performing complex chemical functions and these materials have inspired researchers to investigate sequence manipulation as a means to tune synthetic macromolecules. Applying sequence control to conjugated polymers can help in tuning the electronic and photophysical properties of semiconducting systems. Combining rational monomer design with catalyst transfer polycondensation (CTP) will allow for investigation of “sequence control” and “living polymerization” together. This will afford access to low dispersity p-conjugated polymer materials with periodic structure. In this presentation, several periodic polymers based on group 16 heterocycles (furan, thiophene and selenophene) have been synthesized using CTP. High molecular weight (30~40k) and low polydispersity (1.07~1.16) materials can be obtained; the AFM images of polymers show uniform fibrillar structures. Properties of these systems show the tunability that can be achieved by manipulating monomer sequence.



## POLY 585: Use of click chemistry to construct complex, yet well-defined architectures

**Scott M. Grayson**, *sgrayson@tulane.edu*. Tulane Univ, New Orleans, Louisiana, United States

The use of click chemistry had become an important tool in the conjugation of polymeric materials owing to the high efficiency of the coupling reactions as well as reasonable functional group tolerance. These synthetic tools have lowered the synthetic barrier to preparing and studying polymer materials of complex architecture. Among these click reactions, the copper-catalyzed azide-alkyne cycloaddition remains one of the more frequently used due to its broad compatibility. The extremely rapid coupling reaction has enabled the synthesis of architectures that have traditionally proved difficult to prepare in high purity, including cyclic polymers, star polymers, graft polymers, etc. A particularly attractive feature of this chemistry is the ability to use solid phase resins to click scavenge excess reagent, and therefore isolate materials of exceptional purity. One demonstration of this technique is the synthesis of PEG mikto-arm star polymers that exhibit arms of different molecular weight radiating from the same core. This exotic library has also enabled a comparison of their characterization using traditional viscometry techniques and ion mobility spectrometry.

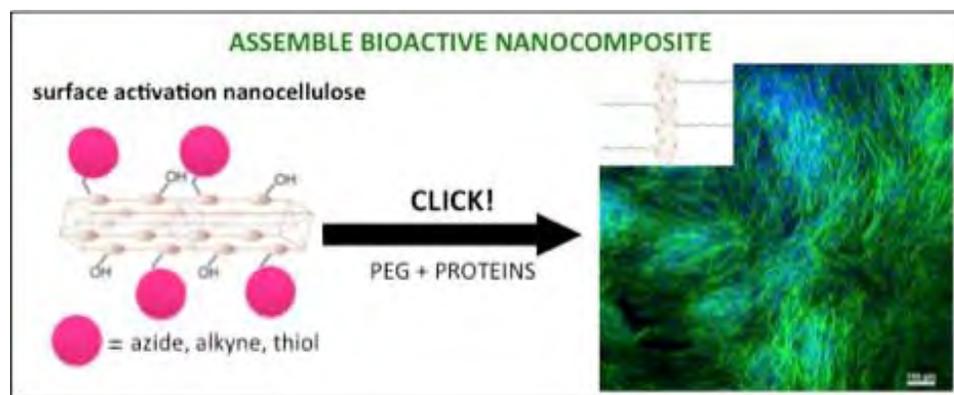


Synthesis of PEG mikto-arm star polymers

## POLY 586: Utilizing click chemistry to assemble nanocellulose, polymers and proteins into bioactive nanocomposites

Ethan Marrow<sup>3</sup>, Kyle A. DiVito<sup>1</sup>, Scott Walper<sup>1</sup>, **Michael A. Daniele**<sup>2,3</sup>, michaelangelo.daniele@gmail.com. (1) Center for Bio/Molecular Science & Engineering, US Naval Research Laboratory, Washington, District of Columbia, United States (2) Electrical & Computer Engineering, North Carolina State University, Raleigh, North Carolina, United States (3) Joint Department of Biomedical Engineering, North Carolina State University / University of North Carolina-Chapel Hill, Raleigh, North Carolina, United States

Cellulose nanomaterials are ideally suited for biomedical applications because of their unique chemical and physical properties. Cellulose nanomaterials are biologically benign hydrogels (some gels exhibit >99% water content) with uniquely tunable surface chemistry. The simple addition of protein and polymer ligands can result in new nanocomposites with both high-strength and benign bioactivity, a rare characteristic of biomaterials. To assemble these nanocomposites, we exploit the regular availability of hydroxyl groups at the surface of the cellulose nanocrystal or nanofiber. The moieties are dealt for common substitution reactions that generate cellulose ethers and esters, which are in turn converted to alkyne, azide, and thiol moieties with primary reactivity at the C-6 hydroxyl group. Using these new “chemical handles,” we use both copper catalyzed azide-alkyne cycloaddition and photo-initiated thiol-based click chemistries to attach poly(ethylene glycol) and gelatin ligands. By utilizing attaching these moieties via click chemistry, a library of nanocomposite biomaterials have been rapidly and easily generated which display high-strength and high cell adhesion. Continued efforts are characterizing the utility of these nanocomposites as a toolbox of easily modified scaffolds for directing tissue growth.



## POLY 587: Stimuli-responsive switchable networks: Click and un-click reaction of furanyl-functionalized (co)poly(2-oxazoline)s with bis(maleimide)

**Sarah Schiller**<sup>1,2</sup>, sarah.schiller@pccl.at, Franz Stelzer<sup>2</sup>, Frank Wiesbrock<sup>1</sup>. (1) Polymer Competence Center Leoben, Leoben, Styria, Austria (2) Institute for Chemistry and Technology of Materials, University of Technology, Graz, Styria, Austria

(Co)poly(2-oxazoline)s have been thoroughly investigated due to their multifaceted properties that can be varied and manipulated by the incorporation of dedicatedly substituted repetition units [1]. The crosslinking of functionalized copoly(2-oxazoline)s can be performed either in polymeranalogous fashion or in situ during the polymerization [2].

In order to find new synthetic routes for 'switchable' self-healing networks, the monomer 2-furanyl-2-oxazoline has been synthesized according to the Witte-Seeliger reaction protocol from the reaction of 2-furonitrile and ethanol amine. This monomer can undergo microwave-assisted cationic ring-opening polymerizations, and the poly(2-furanyl-2-oxazoline)s as well as corresponding copoly(2-oxazoline)s can be crosslinked by UV-induced Diels-Alder click-reaction of the furan moiety with (at least) bisfunctional maleimides (Figure 1) [3].

The crosslinking reaction may be subjected to click-unclick cycles involving the so-called retro-Diels-Alder reaction, namely the cleavage of the crosslinked bonds in the course of increased temperatures. The density of the networks can be quantified by swelling degrees: dense networks have comparably low swelling degrees. Hence, this type of switchable copoly(2-oxazoline)-based networks can be applied as sensors if dyes or other tracers are included in the network, which are released upon a temperature stimulus.

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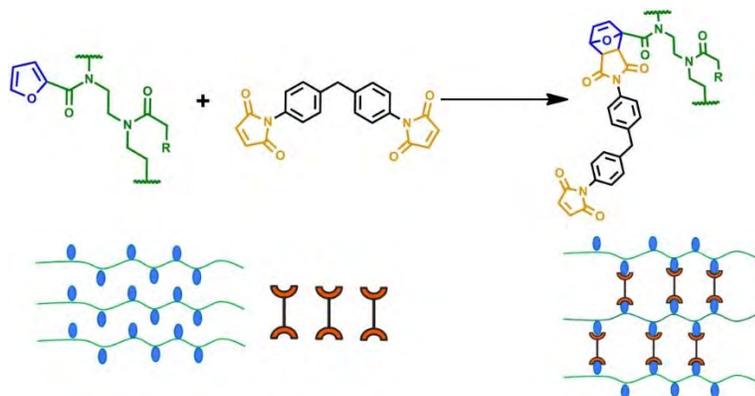
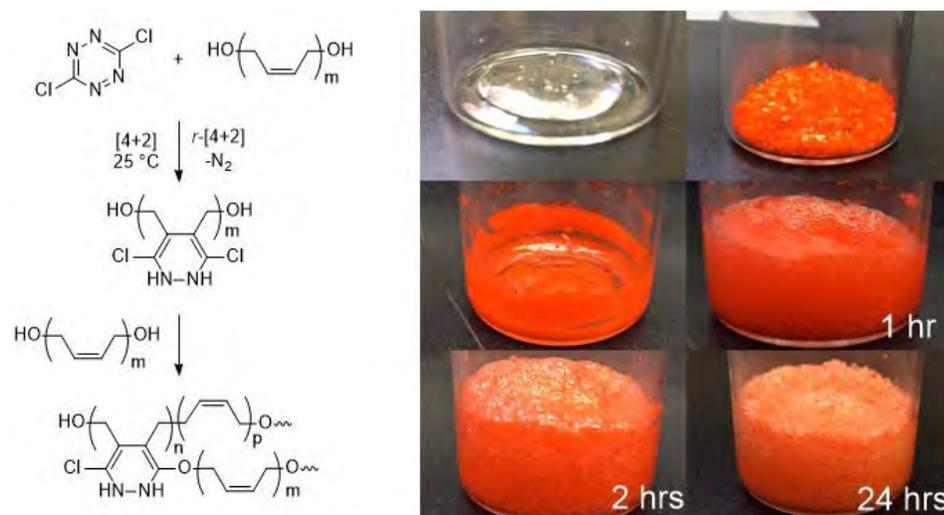


Figure 1: Copoly(2-oxazoline)s comprising the repetition unit poly(2-furanyl-2-oxazoline) can be crosslinked with bis-(4-maleinimido-phenyl)-methane (stimulus: UV irradiation).

## POLY 588: Tetrazines as polydiene modifiers and blowing agents

**Robb E. Bagge**<sup>3</sup>, [rbagge@email.arizona.edu](mailto:rbagge@email.arizona.edu), Dylan Boday<sup>1</sup>, Douglas A. Loy<sup>2</sup>. (1) IBM, Tucson, Arizona, United States (2) Materials Science and Engineering, The University of Arizona, Tucson, Arizona, United States (3) Chemistry, University of Arizona, Tucson, Arizona, United States

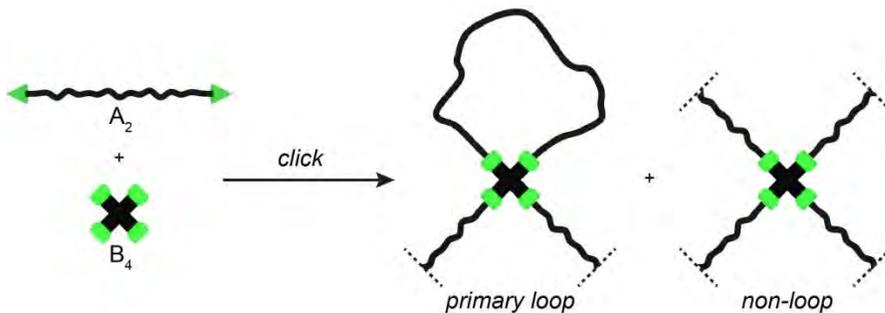
Polymeric foams can be generated using physical or chemical blowing agents. Polyurethanes for example, can be foamed by adding sufficient water to hydrolyze isocyanate groups to give off carbon dioxide as a blowing agent and a reactive amine group to help build the polymer. In this paper, we will present our discovery that 3,6-disubstituted-1,2,4,5-tetrazines could be used as new polymer modifiers and blowing agents for polydienes. The deep orange tetrazines react at room temperature with neat liquid polybutadiene through a cycloaddition reaction, followed by a cheletropic elimination of nitrogen gas. Depending on the stoichiometry of the tetrazine and the nature of the tetrazine substituents the product can be an elastomeric, a thermoplastic or a thermoset foam. The latter forming with the reaction of 3,6-dichlorotetrazine with hydroxyterminated polybutadiene where crosslinking occurs when the hydroxyl end groups crosslink react with the chloride substituents. As the tetrazines react, their intense color fades providing a colorimetric indicator for the cycloaddition reaction. The structure of the cycloaddition product depends on the tetrazine used, but most appear to oxidize to pyridazine groups giving rise to a strong blue fluorescence with UV.



## POLY 589: Cyclic defects and elasticity in click hydrogels

Ken Kawamoto<sup>3</sup>, Mingjiang Zhong<sup>2</sup>, Rui Wang<sup>1</sup>, Bradley D. Olsen<sup>1</sup>, **Jeremiah A. Johnson<sup>3</sup>**, jaj2109@mit.edu. (1) Chemical Engineering, MIT, Cambridge, Massachusetts, United States (2) Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (3) MIT, Massachusetts Institute of Technology, Boston, Massachusetts, United States

This talk will describe our recent efforts to quantify cyclic defects in  $A_2 + B_3$  and  $A_2 + B_4$  model hydrogels derived from copper-catalyzed azide-alkyne cycloaddition. Through a combination of rheometry and network disassembly spectrometry we have quantitatively assessed the role of elastically ineffective network defects on shear modulus. These studies have allowed us to address longstanding discrepancies between affine and phantom network theories of non-entangled networks.



## POLY 590: Copoly(2-oxazoline)-based photoresists from renewable resources

Klaus P. Luef<sup>1,2</sup>, Charlotte Petit<sup>3</sup>, Bruno Grassl<sup>3</sup>, Stéphanie Reynaud<sup>3</sup>, **Frank Wiesbrock<sup>1</sup>**, frank.wiesbrock@pccl.at. (1) Polymer Competence Center Leoben, Leoben, Austria (2) ICTM, Graz University of Technology, Graz, Austria (3) UPPA, Pau, France

Facing the challenges of the on-going trend to high-technology applications with decreased feature sizes, the development of novel photoresists has become a major factor within this area of research. Negative photoresists reproduce geometric patterns commonly by the crosslinking of polymers, yielding insoluble 2.5-dimensional surface structures. Proceeding our work on the formulation of a water-developable photoresist<sup>1,2</sup>, we hereby present the latest addition of our toolbox of 2-oxazoline-based photoresists by a photoresist derived from renewable resources<sup>3</sup>. The monomers to be used for the microwave-assisted synthesis of the copolymer were synthesized from undecenoic acid (castor oil) and decanoic acid (coconut oil) and ethanol amine in one-step solvent-free reactions. The copolymerization itself was performed in consideration of energy efficiency at a scale of 300 g under microwave irradiation in ionic liquids. The copolymer precipitated upon cooling, enabling for the fast recovery of the product and the ionic liquid with yields over 95%. The photoresist could be formulated (and developed) in ethyl lactate (Figure 1). Crosslinking of the copolymer was realized by UV-induced thiol-ene reactions of the polymer and a tetrathiol, providing resolutions of 1  $\mu\text{m}$  at a film height of 100 nm.

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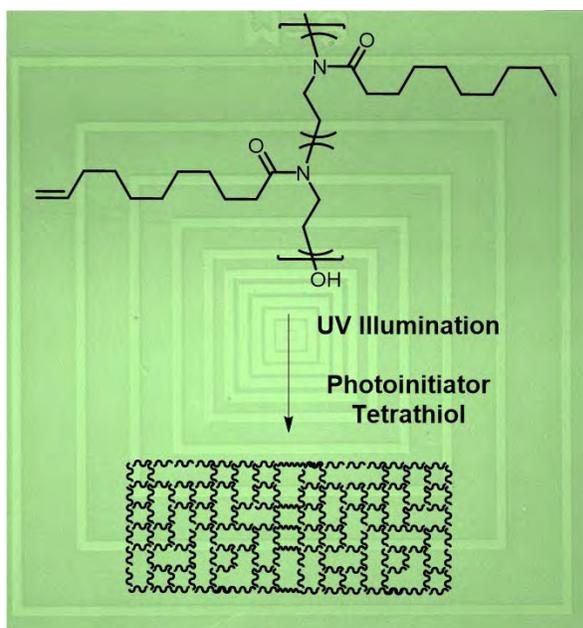


Figure 1. Schematic representation of the UV-induced crosslinking of a poly(2-oxazoline)-based copolymer with a tetrathiol.

## POLY 591: Click chemistry-mediated synthesis of polyester-*stat*-poly(2-oxazoline) drug reservoirs

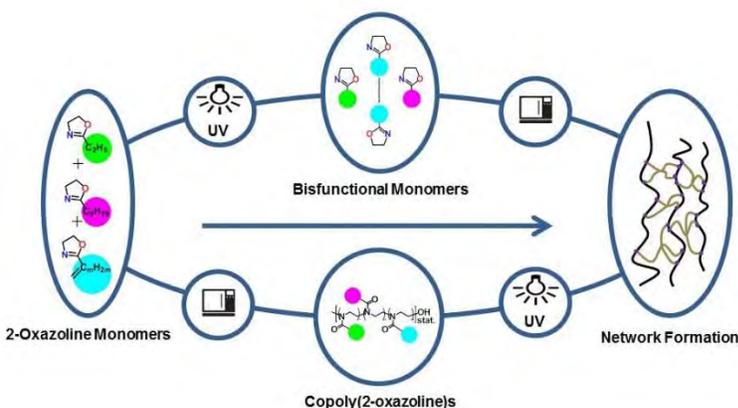
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Novel dosage forms for active pharmaceutical ingredients, especially implantable polymer-based drug depots, have become a topic of high interest in the past years. Biocompatible and biodegradable polyesters such as poly(hydroxy alkananoate)s [1] often exhibit bottlenecks in terms of degradation rates. By designing copolymers that comprise two polymer classes, degradation of the network favorably might follow zero-order kinetics. Proceeding our study of poly(2-oxazoline)s for medical applications [2], we here present polyester-*stat*-poly(2-oxazoline) networks. Thiol-ene click chemistry provides a powerful tool for the syntheses of these copolymers; it enables space-resolved reactions that pave the way for the formation of defined polymer networks [3]. By employing thiol-ene click in two different strategies (in-situ and polymer-analogous crosslinking), an 80-membered network library as well as crosslinked copoly(2-oxazoline)s of defined shapes could be synthesized in straightforward manner. These novel hydro-, lipo- and amphigels were characterized by their capability of swelling in different media, by thermal properties such as glass-transition temperatures, and by studies of drug inclusion and network degradation. Within the degradation studies, the chemically induced degradation of the gel networks in alkaline and acidic media was investigated as well as the enzymatic degradation of the same.

[1] K.P. Luef, F. Stelzer, F. Wiesbrock, *Chem. Biochem. Eng. Q.* 2015, 29, 287-297.

[2] V. Schenk, E. Rossegger, C. Ebner, F. Bangerl, K. Reichmann, B. Hoffmann, M. Höpfner, F. Wiesbrock, *Polymers* 2014, 6, 264-279.

[3] C. Petit, K.P. Luef, M. Edler, T. Griesser, J.M. Kremsner, A. Stadler, B. Grassl, S. Reynaud and F. Wiesbrock, *ChemSusChem* 2015. doi: 10.1002/cssc.201500847

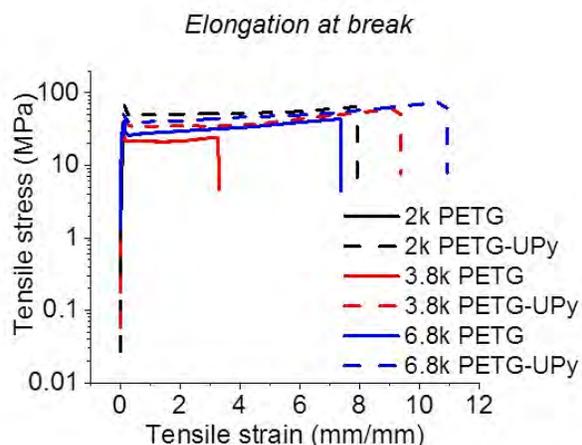


**Figure 1:** Synthesis of hydrogels by thiol-ene click reactions.

## POLY 592: Endgroup functionalization of poly(ethylene terephthalate) derivatives with ureidopyrimidinone

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The structure-property relationships of end-functionalized glycol-modified poly(ethylene terephthalate) (PETG) of various molecular weights was investigated using the quadruple hydrogen bonding ureidopyrimidinone (UPy) group. The UPy group has been extensively used to end-functionalize low molecular weight polymers with low glass transition temperatures to create supramolecular materials with improved tensile properties and thermoreversibility. While the effect of the UPy endgroup has been investigated on many aliphatic materials, the effect of these groups has not been broadly investigated for high performance, aromatic polyesters. While high molecular weight engineering plastics have excellent mechanical properties, they can be difficult to process. By end-functionalizing low molecular weight engineering polymers with the UPy moiety, issues involving processability could be overcome while maintaining the overall robust properties of the high molecular weight polymer. The terminal functionalization of low molecular weight PETG derivatives with the UPy moiety was performed via isocyanate-hydroxyl reactions employing different diisocyanate linkers. The subsequent structure-property relationships were studied, and select mechanical properties, such as strain at break and storage modulus, were enhanced after end-functionalization. Ultimately, this study shows that endgroup functionalization with supramolecular moieties provides a promising route to improving the properties of low molecular weight engineering plastics.



The strain at break of PETG of various molecular weights is significantly improved after UPy functionalization. The numbers in the key refer to the molecular weight of the polymer in kg/mol. "PETG" represents the virgin polymer and "PETG-UPy" refers to the UPy functionalized polymer. The strain at break of the PETG-UPy of 2000 g/mol ("2k PETG-UPy") is comparable to a polymer greater than 3 times its molecular weight, 6.8k PETG.

## **POLY 593: Thermocleavable side chains: A gateway to new processing routes for semiconducting polymers**

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Solubilising side chains are an essential part of semiconducting polymers and their engineering has shifted into focus over the last couple of years. The solution processability of conjugated polymers is one of the major advantages over silicon based semiconductors and would not be possible without the use of solubilising side chains. However with ongoing research, it became apparent that by careful side chain engineering certain properties of the conjugated backbone could be enhanced or suppressed depending on the application. Nowadays side chain design is crucial to achieve high performing organic field effect transistors (OFET) and often significant synthetic efforts are taken to balance the semiconducting properties of conjugated polymers by means of side chain engineering. Despite their importance, side chains do not actively contribute to the semiconducting properties of the polymer. Their electrically insulating character could actually hinder charge transport between adjacent polymer chains and if poorly designed disrupt the solid state packing in the material.

To circumvent these problems, we developed thermocleavable side chains. This allows us to deposit the polymer from conventional organic solvents and to remove the side chains by post-deposition thermal annealing. Once the side-chains are removed from the conjugated backbone, the polymer chains are able to form strong interchain hydrogen-bonding interactions, which will not only alter the materials solubility, but also the semiconducting properties. By taking this two-step approach, we are able to maintain the advantages of solution processability, but at the same time allow the polymer chains to pack closely to achieve superior charge transport characteristics. Furthermore, stripping the polymer of its side chains significantly alters its solubility, making the use of orthogonal solvents for subsequent layer unnecessary, thus opening-up new and potentially “greener” processing routes.

## POLY 594: Induction of CD and CPL to non-chiral fluorescent dyes in chiral nano-pocket created by L-glutamide-based helical nano-assemblies

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Circularly polarized luminescence (CPL) properties have been gathering considerable attentions because of their possible applicability for advanced optical management technique. Various CPL materials have been reported based on chiral molecules such as helical polymers, chiral fluorophores and so on. In this paper, we propose a new strategy for induction of large CPL by incorporation of non-functionalized, non-chiral fluorescent dyes into chiral nano-pocket created by L-glutamide-based helical nano-assemblies.

An amphiphilic L-glutamide derivative (*g*-Py<sup>+</sup>) was selected for creating nano-pockets in an aqueous system because it can form bilayer membrane-based helical and tubular aggregates.<sup>1)</sup> When anthracene was mixed with *g*-Py<sup>+</sup> in chloroform and dried at 60 °C, the obtained powders were dissolved in water at 90 °C to produce a clear solution. In fluorescence spectroscopy, the *g*-Py<sup>+</sup>/anthracene mixture showed no significant difference from that in anthracene alone system, but provided a distinct Cotton effect around the absorption band of anthracene in CD spectroscopy. This indicates that the *g*-Py<sup>+</sup> assemblies provide chiral microenvironment to the incorporated anthracene to bring induced chirality. Furthermore, large CPL was induced to anthracene in the presence of *g*-Py<sup>+</sup> assemblies. The  $g_{lum}$  value, indicating the magnitude of CPL, reached  $-1.39 \times 10^{-2}$ , which is the maximum level in a solution system. On the other hands, in the cases of 9-phenylanthracene and 9,10-diphenylanthracene instead of anthracene, a little lower ( $g_{lum} = -0.47 \times 10^{-2}$ ) and almost no CPL signals were observed, respectively. These results indicate that the chiral nano-pocket of *g*-Py<sup>+</sup> fits the molecular sizes of anthracene and 9-phenylanthracene, but not for bulky diphenylanthracene.

1) Y. Okazaki, H. Jintoku, M. Takafuji, R. Oda, H. Ihara, *RSC Adv.*, 2014, 4, 33194-33197.

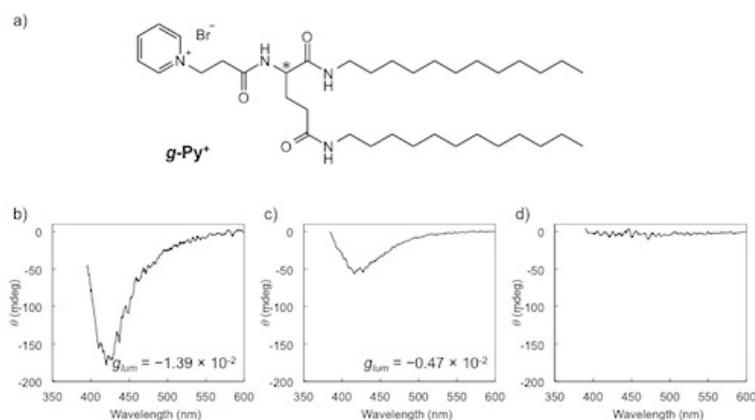
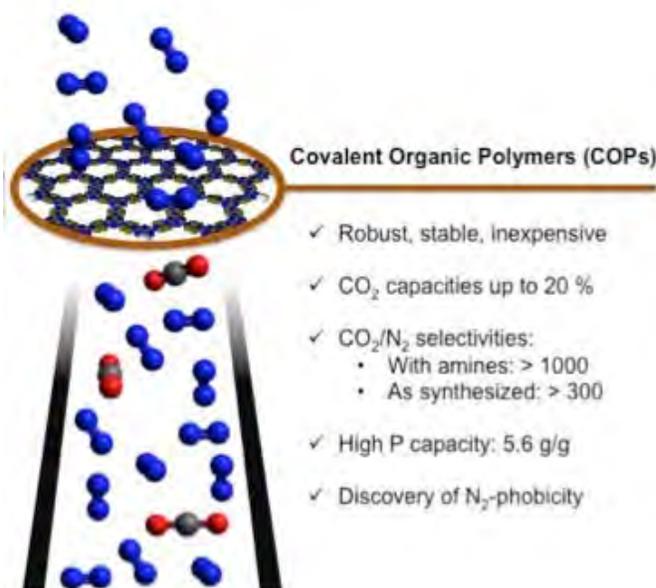


Fig. 1 (a) Chemical structure of amphiphilic L-glutamide derivative for creating chiral nano-pocket. CPL and fluorescence spectra of (b) anthracene, (c) 9-phenylanthracene and (d) 9,10-diphenylanthracene in the presence of *g*-Py<sup>+</sup> in aqueous systems.

## POLY 595: Chemistry in the confined spaces of porous polymers

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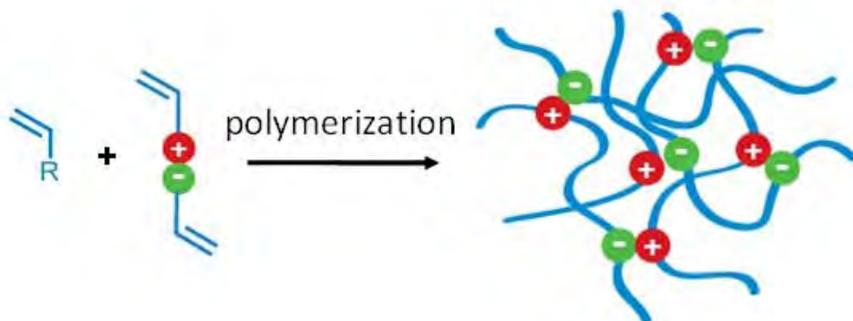
Porous polymers with robust organic structures through a covalent backbone feature permanent voids that can be used for chemical activities. We have developed a family of nanoporous (pore size < 100 nm) covalent organic polymers (COPs), which show significant capacities and selectivities for carbon dioxide. Surprisingly, azo (N=N) bearing COPs show lack of N<sub>2</sub>-philicity by increasing temperature, in other words N<sub>2</sub>-phobicity, leading to very high CO<sub>2</sub>/N<sub>2</sub> selectivities. Under high pressures COP-1 shows a record high capacity of 5.6 g/g CO<sub>2</sub> uptake at 200 bar and 45 °C. COP-83 has a capacity of 5 mmol/g at 298 K and 1 bar, and COP-97 shows an uptake of 8 % (w/w) CO<sub>2</sub> in 2 minutes from a simulated flue gas mixture (CO<sub>2</sub> 15%, H<sub>2</sub>O 3.8%, He 81.2%, 40 oC, flow rate: 80 mL/min). More recently we established the first direct introduction of ethylene diamines on the walls of COPs through bromination intermediates. CO<sub>2</sub> uptake capacities multiply with the nitrogen content, up to an unprecedented four times of the starting porous polymer in dry flue gas conditions. In an attempt to use the basic heteroatoms like nitrogens found in the pores of porous polymers as catalysts, we tested base catalyzed reactions such as Strecker synthesis and discovered high activity by benzoxazole COPs without the need for metals. Morphology control is another subject of interest and we made hollow spheres of COP-122 with nitrile pendant groups for further grafting chemistry. Our results point to a great potential in porous polymers for chemical conversions in their confined spaces since they are highly porous, inexpensive, physisorptive solids, which can be chemically modified with chemisorptive functionalities.



## POLY 596: Synthesis and characterization of ionically crosslinked polymer networks

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In polymer materials, dynamic bonding is a useful approach to generate structurally dynamic, supramolecular polymer networks leading to stimuli-responsive materials, such as self-healing and shape memory polymers. This talk will discuss the synthesis and characterization of ion-containing polymer networks. In one example, hydrophobic polyampholyte ionomer networks were prepared through the free radical copolymerization of a hydrophobic, non-ionic monomer and an ion-pair comonomer. Ion pair comonomers were synthesized through metathesis ion-exchange of an anionic (e.g. sodium styrene sulfonate) and a cationic monomer (e.g. vinyl benzyl tri-*n*-octylammonium chloride) to produce an ion-pair with two vinyl groups. Under conditions where ion-pairs are formed, the ion-pair comonomer acts as a dynamic crosslinker that can reversibly dissociate/associate. Measurements to characterize the thermo-mechanical behavior of these systems will be presented and discussed in terms of the structure of the polymer network and chemical structure of the ion-pair crosslink.



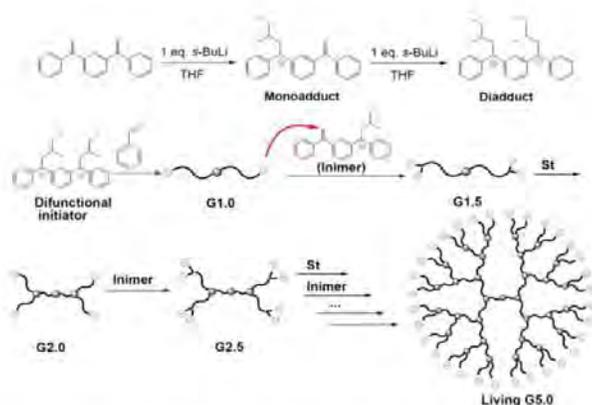
## POLY 597: Extending the capability of living anionic polymerization: From architecture to microstructure of polymers

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The control of polymer structures on different levels by the same polymerization is a long-standing goal of polymer chemistry. Anionic polymerization is a truly living polymerization system and has been widely used to tailor polymer structure. Recently, we have made efforts to control polymer architecture using 1,1-diphenylethylene chemistry, and to control polymer chain microstructure, such as regiospecificity and sequence, using disubstituted 1,3-butadiene.

Syntheses of a series of star, hyperbranched, cylindrical brush-like and dendrimer-like polymers were achieved by using an anionic inimer derived from the monoaddition between carbanion and 1,3-bis(1-phenylvinyl)benzene (MDDPE). Monoaddition occurred almost exclusively in polar solvent such as THF. Star-like polymers were prepared by sequential monoaddition of a living polymer to MDDPE, followed by anionic polymerization. Hyperbranched polymers were prepared by self-condensing copolymerization of styrene and the inimer. Dendrimer-like polymers were prepared through a continuous iterative process employing the anionic inimer as the branching agent (Scheme 1). Cylindrical brush-like polymer with dendritic side chains was prepared by iterative grafting of living polymer chains to the main chain.

Regio-specific and sequence-specific polymers were prepared through living anionic polymerization of 2,3-disubstituted-1,3-butadienes as template monomers. The template monomers were synthesized through Wittig reaction or Kumada coupling. The butadiene derivatives were subsequently undergo living anionic polymerization initiated by secondary butyllithium. The polymerization proceeded through almost exclusively 1,4-addition due to the steric hindrance at 2,3-position. The resulting products were subject to further hydrogenation and dehydrogenation, respectively, to prepare saturated and pi-conjugated polymers of regio- and sequence-specificity with identical and different side groups.

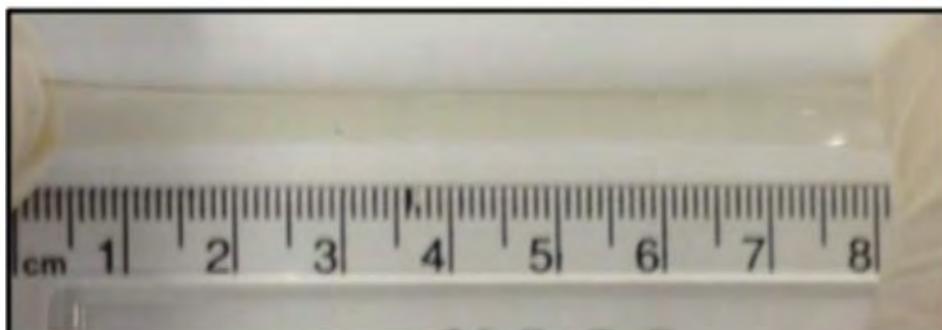


**Scheme 1.** Continuous synthesis of dendrimer-like star living polystyrene in a divergent process.

## POLY 598: Multigraft copolymer superelastomers

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Multigraft copolymers with a rubbery backbone and glassy side chains represent a new class of thermoplastic elastomers (TPEs) with superior elongation at break and low residual strains as compared to conventional TPEs, so-called "Superelastomers". This presentation summarizes our efforts on the development of multigraft copolymer superelastomers. One of our focuses includes the synthesis of well-defined multigraft copolymers having an acrylic backbone with polystyrene (PS) side chains. Use of living anionic polymerization to synthesize PS macromonomers enabled a facile free radical copolymerization with acrylate (e.g. n-butyl acrylate), yielding multigraft copolymers with regularly spaced PS side chains. Furthermore, PS block was lightly sulfonated to enhance the mechanical properties. The structure-property relationships of the synthesized superelastomers especially in morphology and TPE properties will be discussed.



## POLY 599: Novel catechol-containing vinyl monomers for carbanionic Polymerization: *In Situ* monitoring of the formation of poly(styrene-co-vinyl catechol) copolymers by carbanionic living copolymerization

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Catechol containing polymers have become an attractive field of research in materials science, because of their strong attachment to a variety of surfaces, which is promising for a large variety of surface applications.<sup>1</sup> Multiple catechol functionalities at a polymer chain will lead to considerably stronger attachment than a single anchoring moiety. We present a strategy to obtain well-defined polystyrene derivatives bearing multiple catechol moieties via carbanionic polymerization. This polymerization method demands particular protecting groups to prevent proton abstraction or cleavage under harsh alkaline conditions.<sup>2</sup>

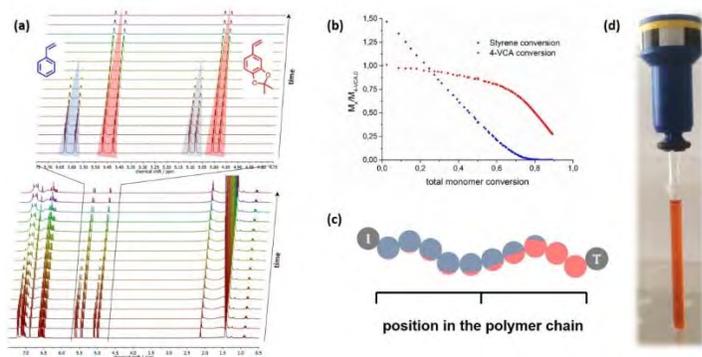
The newly developed catechol containing vinyl monomers 4-vinyl catechol acetonide (4-VCA) and 3-vinyl catechol acetonide (3-VCA) were synthesized in several steps. The monomers can be polymerized via carbanionic polymerization to obtain poly(vinyl catechol acetonide)s in a wide molecular weight range from 2,500 to 80,000 g/mol with PDIs below 1.10. The key advantage of these polymer structures is the quantitative removal of the acetonide protecting groups under mild acidic conditions.

A precise method to investigate monomer reactivity in copolymerizations is the *in-situ* monitoring via real-time <sup>1</sup>H NMR kinetics.<sup>3</sup> The living anionic polymerization is monitored by measuring proton NMR spectra during chain growth, enabling an exact determination of the copolymers' microstructure (see figure). The new monomers enable us to control the microstructure of catechol containing copolymers in a concurrent copolymerization. The resulting polymers are highly promising for surface or interface modification and tailoring.

[1] H. Lee, Y. Lee, A. R. Statz, J. Rho, T. G. Park, P. B. Messersmith, *Adv. Mater.* 2008, 20, 1619.

[2] A. Hirao, S. Loykulnant, T. Ishizone, *Prog. Polym. Sci.* 2002, 27, 1399.

[3] A. Natalello, M. Werre, A. Alkan, H. Frey, *Macromolecules* 2013, 46, 8467.



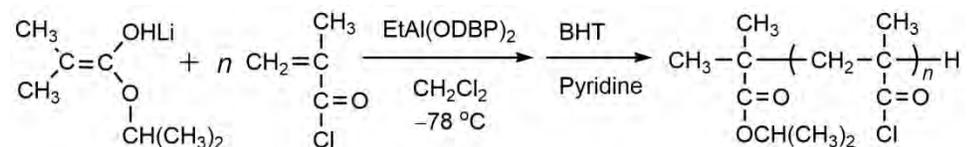
(a) Online <sup>1</sup>H NMR copolymerization kinetics of styrene (blue) and 4-VCA (red). (b) Residual monomer concentrations vs. total monomer conversion. (c) Corresponding visualization of the polymer chain. (d) Picture of the living anionic polymerization in the NMR tube.

## POLY 600: Anionic polymerization of methacryloyl chloride

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Methacryloyl chloride (MACI) is known to undergo radical polymerization to afford a reactive polymer, poly(methacryloyl chloride) (PMACI) [Otsu, T.; Tajima, T. *Kobunshi Ronbunshu*, 1974, 31, 181; Stroehriegl, P. *Makromol. Chem.* 1993, 194, 363.], but the controlled polymerization of MACI has never been achieved. Judging from its large positive  $e$  value (1.75) in Q-e scheme, the vinylidene group of MACI is potentially feasible against nucleophilic attack of anionic species and thus expected to be anionically polymerizable. However, acid chlorides generally function as an acylating agent against nucleophiles and, in fact, anionic polymerization of MACI has never been reported. We have found that methacrylic anhydride, also a potential acylating agent, could be anionically polymerized in the presence of bulky aluminum Lewis acid, ethylaluminum bis(2,6-di-*tert*-butylphenoxide) [EtAl(ODBP)<sub>2</sub>], to form soluble linear polymers of cyclized units through cyclization polymerization [Kitaura, T.; Moroi, N.; Kitayama, T. *Polymer* 2013, 54, 1987.]. Encouraged by this finding, we examined anionic polymerization of MACI by using the aluminum Lewis acids and succeeded for the first time in preparing PMACI anionically; the polymerization of MACI with isopropyl  $\alpha$ -lithioisobutyrate (Li-*i*PrIB) in the presence of EtAl(ODBP)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> at -78 °C completed within 5 min, though the initiator efficiency was low (ca. 0.5) and livingness of the polymerization was poor.

In an attempted copolymerization of MACI with methyl methacrylate (MMA) at the ratio of 1:1, only MACI was consumed in a slower rate. The retarding effect of MMA on the polymerization of MACI was effective even at such a low content as [MACI]/[MMA]/[EtAl(ODBP)<sub>2</sub>]/[Li-*i*PrIB]=10/2/1/0.2, and afforded a polymer with a smaller molar-mass dispersity of 1.1 with an improved initiator efficiency (0.8). Moreover, livingness of the polymerization was confirmed by a monomer-addition experiment. The role of ester compounds on the control of anionic polymerization of MACI will be discussed.



## **POLY 601: Kraton performance polymers: 50 years of experience with commercial scale anionic polymerization**

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The emergence of anionic, living polymerization in the 1950s enabled the synthesis of polymers with controlled structures. A key consequence of controlled molecular architecture was the distinct phase separation and self-assembling morphologies of polymers containing discrete blocks of styrene and isoprene or butadiene. The self-reinforcing nature of such styrenic block copolymers was recognized for its broad commercial potential as a new class of polymers; styrenic thermoplastic elastomers (TPE-S).

More than fifty years after the commercial introduction of styrenic block copolymers, the annual global consumption is significant and includes scores of different polymer structures tailored to meet the specific needs in numerous markets and applications. Applications as diverse as the roads we drive on, the cars in which we drive, the shoes we wear and the personal hygiene items we use are all enhanced by the properties of styrenic block copolymer TPEs. New styrenic block copolymers continue to be developed and commercialized as a result of the robust chemistry leading to novel performance features.

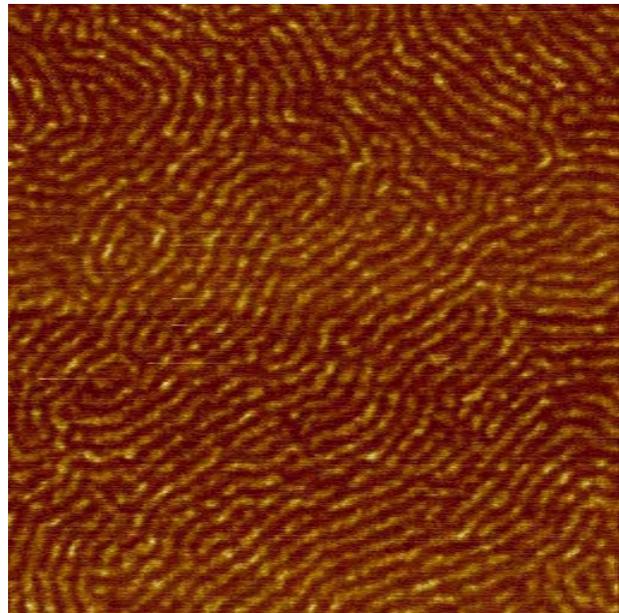
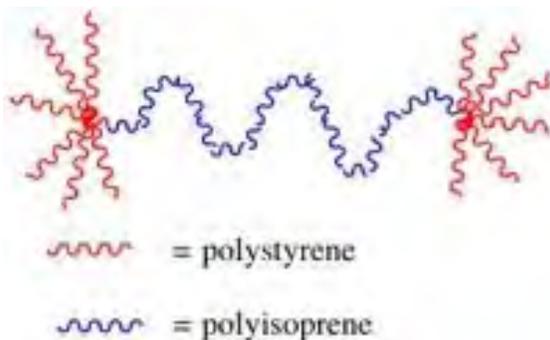
This presentation will present the versatility of styrene, butadiene and isoprene, combined in block copolymer architectures, as well as new developments.



## POLY 602: Thermoplastic elastomers with complex architecture by sequential addition

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(2) Colorado State University, Fort Collins, Colorado, United States (3) Chemistry,  
Colorado School of Mines, Golden, Colorado, United States*

Triblock copolymers of polystyrene-*b*-polyisoprene-*b*-polystyrene are produced with controlled branching in the polystyrene component. The polymers are prepared by the sequential addition of monomers and coupling agents in a living anionic polymerization. Polystyrene is first synthesized with a living chain end and then coupled with 4-(chlorodimethylsilyl)styrene to form a polystyrene star with a single living chain end at the core. Isoprene is then polymerized from the polystyrene star to yield a (star-polystyrene)-*b*-polyisoprene diblock. The living diblock is subsequently coupled in order to make the resulting triblock thermoplastic elastomers. The progression of the synthesis was followed by gel permeation chromatography to characterize the length of the polystyrene chain, the number of arms in the polystyrene star, and the diblock and triblock molecular weights. Copolymers were made with varying polystyrene to polyisoprene composition while also varying the length of the polystyrene chains and the number of arms in the star. Samples were made in order to study the effect of the branching on the resulting phase morphology. The morphology was investigated for as cast and annealed samples by atomic force microscopy and small angle xray scattering.



## **POLY 603: Generating complex self-assemblies from block polymers: Triply-periodic structures from anionic polymerization**

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Block polymers (BPs), and their ability to self-assemble into a variety of nanoscale structures with tailored chemical and physical properties, have motivated extensive research investigations for many emerging nanotechnologies such as nanotemplates, analytical separation membranes, and electrical and ionic conductors. In many cases, the utility of BPs for the above applications is predicated on the ability to generate well-controlled macromolecules. In the Epps group, we have focused on two major aspects related to the generation of well-defined macromolecules *via* anionic polymerization techniques. In the first area, we are generating complex nanoscale networks through the combination of anionic polymerization with judicious polymer blending and hydrogenation procedures. This approach is allowing us to assess the stability of triply-periodic nanostructures in triblock terpolymers. In the second area, we are manipulating polymer synthesis feeds through the use of programmable syringe pumps to introduce tapered profiles into diblock copolymer and triblock terpolymer interfaces. These synthetic interfacial modifications allow us to tune thermal and mechanical properties independent of molecular weight without eliminating complex network structures such as the double gyroid.

