



**THE 2022 APPLIED POLYMER
TECHNOLOGY EXTENSION CONSORTIUM**

NOVEMBER 9TH, 2022

HILTON CAPITOL CENTER

201 LAFAYETTE STREET, BATON ROUGE



EVENT PROGRAM:

REGISTRATION & BREAKFAST - STUDENTS AND SPONSORS SET UP TABLE AND POSTERS

8:30-9:00AM

INTRODUCTORY REMARKS: DR. DANIEL MCCARTHY

9:00-9:15AM

HEADLINER : DR. MARC HILLMYER

9:15-10:00AM

BREAK FOR STUDENTS AND SPONSORS TO SET UP POSTERS AND TABLES

10:00-10:15AM

ORAL PRESENTATIONS SESSION ONE

10:15-11:15AM

POSTER SESSION 1

11:00-12:15PM

LUNCH

12:15-1PM

KEYNOTE SPEAKER: DR. URARA HASEGAWA

1:00-1:45PM

POSTER SESSION 2:

1:45-2:45PM

BREAK

2:45-3:00PM

ORAL PRESENTATIONS SESSION TWO

3:00-3:45PM

CAREER PANEL

3:45-5:00PM

NETWORKING AND FINAL REMARKS

5:00-6:00PM

HEADLINERS:

DR. MARC HILLMYER - UNIVERSITY OF MINNESOTA

McKnight Presidential Endowed Chair, Distinguished University Teaching Professor, Director of NSF Center for Sustainable Polymers, Department of Chemistry. Will be presenting his research on Polyester block polymers as sustainable high-performance thermoplastic elastomers.

Aliphatic polyester block polymers that behave as thermoplastic elastomers can be prepared from straightforward sequential ring-opening transesterification polymerizations of cyclic esters. Poly(lactide) is an attractive hard block for these materials because of its ready availability, renewable origins, relatively high glass transition temperature, ability to crystallize in the isotactic form, and the capacity to be industrially composted. We have focused our work on the development of suitable low glass transition temperature, non-crystalline, soft midblocks that can also be synthesized from renewable resources and that are compostable. To that end, we have focused our attention on poly(4-methyl caprolactone). The monomer, 4-methyl caprolactone, can be prepared from cresols, which in turn can come from renewable lignin, in an economical manner, and the corresponding polymer is industrially compostable. In this presentation I will discuss our recent efforts to prepare block polymers from these hard and soft components and focus on architecture control (e.g., triblocks, star blocks, and graft blocks), the influence of tacticity in the poly(lactide) segments, the ultimate properties of these thermoplastic elastomers, and the environmental fate in soils and compost.

DR. URARA HASEGAWA- PENN STATE UNIVERSITY

Dr. Hasegawa's research focuses on the development of polymeric nanomaterials for controlled delivery of drug and bioactive signaling molecules. She received the NSF career award in and the Kansas State University Warren and Gisela Keystone Research Scholar Award. Will be presenting her research on Redox Biology-Inspired Biomaterial Design.

ABSTRACT:

Small reactive species such as reactive oxygen, nitrogen and sulfur species (RONSS), which are produced in almost all tissues in the human body, serve as key regulators in various physiological and pathological processes. These molecules include hydrogen peroxide (H₂O₂), hydroxyl radical (HO•), nitric oxide (NO), and hydrogen sulfide (H₂S). RONSS exert regulatory functions in the cardiovascular, nervous, and immune systems by mediating a series of redox signal transductions. In addition, accumulating evidence suggests that unregulated RONSS production in tissues leads to initiation and progression of various pathological conditions such as cancer and cardiac dysfunction. My group is interested in the biological significance of RONSS and has sought to engineer polymeric materials that generate, scavenge or respond to those reactive species. In this presentation, I will discuss how polymeric material design impact delivery of H₂S and NO as well as their biological functions in cardiomyocytes and vascular endothelial cells. I will also present our strategy to use reactive oxygen species as a biological trigger to induce site-specific drug release from polymeric micelles in cancer tissue.

ORAL TALKS SCHEDULE

SESSION ONE:

1) Ronard Herrera, Dr. Megan Robertson - 10:15-10:30AM

Tunable functionalization and upcycling of polyolefins to polyurethanes:

By 2050 the accumulation of plastic waste is projected to reach 12,000 Mt, where 18% are recycled, 24% incinerated, and the remaining 58% are either landfilled or enters the natural environment (In the US, only 9% is recycled). The main contributors to this waste are polyolefins, which constitute roughly 45% of all plastic waste (76% at the U.S. level). Momentum has shifted towards looking for a solution for polyolefin waste and moving to a circular economy. Post-polymerization modification has shown promising results to upcycle polyolefins, removing the limitation of inertness, and improving the final physical properties of the material. Subsequently, this modified polyolefin can be repurposed in a wide variety of applications including polyurethanes, foams, coatings, and films, among others. In this work, polypropylene (PP) was functionalized and upcycled to polyurethanes. First, hydroxylated PP (PPOH) was synthesized through the hydroxylation of maleic anhydride-grafted PP. Then, the polyurethane (PU) was synthesized by the reaction of PPOH with a diisocyanate in solution and in the melt. Melt processing was enabled by using a blocked isocyanate that delayed the crosslinking reaction for easy processability. The presence of PU crosslinks and PP strands in the network were confirmed with spectroscopy. At a low level of maleation and hydroxylation, the PP thermal properties (glass transition, melting, and crystallization temperatures) were unaffected by functionalization, PP crystallization was still observed in the PU network that contained PP segments.

2) Bernard Whajah, Dr. Kerry M. Dooley -10:30-10:45AM

Zeolite Supported Pt for Depolymerization of Low-Density Polyethylene by Induction Heating:

The development of plastics over the past half century has led to rapid technological advances. Nonetheless, long-term negative environmental impacts of these materials compel new upcycling strategies. Worldwide production of polymers in 2015 reached 380 MMT. Despite the substantial amounts of polymers potentially available for reutilization, it has been estimated that of all synthetic polymers produced since 1950, only 7% have been recycled, compared to 60% which have been discarded (lifetimes > 20 yr). Currently, reconstituting these polymers into chemical products often requires high-temperature pyrolysis yielding unattractive product distributions. This work aims to address this issue by converting plastic waste into useful alkanes/alkenes oligomers, using rationally designed heterogeneous catalysts suitable for use in radio frequency (RF)-based induction heating.

Pt(0), either alone or in alloy form, is widely used for hydrocracking catalysis due to its high dehydrogenation activity leading to high rates of carbon-carbon cleavage of adsorbed alkene moieties. Four types of zeolites, decorated with Pt, were chosen to elucidate the role of crystal size, pore structure and acidity (as quantified, e.g., as Si/Al molar ratio). Zeolite-supported Pt catalysts mixed with Fe₃O₄ were inductively heated under inert atmospheres (no H₂) to depolymerize low density polyethylene. The depolymerization showed high concentrations of alkene/alkane hydrocarbons with a narrow product distribution that could be tuned between light gases to C₁₄ hydrocarbons based on the zeolite structure. The addition of Sn as a promoter was found to increase activity with a preference for heavier products, and to reduce the coke formation. LDPE conversions up to 95% with minimal coke and light gas formation were obtained with Pt/LTL or SSZ-13 at 375°C estimated surface temperature and 2 h reaction time. Reaction kinetics show that the depolymerization process is diffusion limited across moderate temperature ranges (~280-500 C).

3) Jacob Schekman, Dr. Yoan C. Simon, and Dr. Sergei Nazarenko-

10:45- 11:00AM

Investigating solvent effects on thiol-ene network formation:

Quick reaction kinetics under atmospheric conditions and low energy-cost of fabrication have made thiol-ene networks a popular material choice for research on protective coatings and films. Physical properties of thiol-ene materials produced from bulk monomer have been widely explored, though solubility issues may arise in situations which require a solid monomer or filler. Because thiol-ene materials are often fabricated in the bulk, the effect of solvent on network formation remains unknown. Interestingly, we have found thiol-ene films fabricated through photopolymerization exhibit higher glass transition temperatures (T_g) when processed in good solvents vs in the bulk. To investigate this phenomenon, we fabricated networks by combining tetrafunctional tetramethylolpropanetetra(3-mercaptopropionate) (4T) and trifunctional 1,3,5-triallyl-1,3,5-triazine-2,4,6-trione (TTT) in a 1:1 thiol:alkene ratio (adding 20 wt% of good solvent when needed) and curing under UV light (λ = 340 nm). Our results show solvent-processed films to exhibit higher T_g than bulk processed-films, as determined through differential scanning calorimetry, dynamic mechanical analysis, and thermomechanical analysis. Additionally, our 4T-TTT films fabricated in good solvents have shown greater thermal dilation and lower storage moduli than their bulk-processed counterparts, deviating from trends in literature which typically show thermomechanical values increase for materials with higher glass transition temperatures. We have looked for chemical differences between our bulk- and solvent-processed thiol-ene networks, but through IR spectroscopy have found all systems reach >99% functional group conversion. Continuing structural investigations through positron annihilation lifetime spectroscopy will elucidate on the differences in free hole volume and connectivity between bulk- and solvent-processed networks together these results highlight the importance of photopolymerization processing conditions and demonstrate their ability to lead to vastly

different network connectivity and physical properties, further expanding the modularity of thiol-ene-based materials.

4) Weiliang Sun, Dr. Samuel Snow, Dr. Xiuping Zhu- 11:00- 11:15AM

Electric field stimulates hydrogels for desalination:

Hydrogels are frequently used as draw agent during forward osmosis (FO) desalination, and here we explore the feasibility of utilizing electro-responsive hydrogels as direct mediators for desalination. We added highly conductive graphene to the conventional conductive hydrogel P(AMPS-co-AM). The water absorption, and electrical conductivity of the new hydrogels were tested. The swollen hydrogel exhibits extremely strong electrical responsiveness, shrinking and expanding reversibly with the switching of the electric field in the electrode contact system. The magnitude of hydrogel de-swelling increases with the degree of swelling and the applied voltage. This dehydration phenomenon is caused by the reduced hydration capacity of the micro-counterions due to the interaction of water electrolysis with the electrodes. The hydrogel was shown to have nearly 100% water recovery and 80% salt rejection in the second and subsequent cycling experiments. And it has stable performance in four cycle experiments.

SESSION TWO:

1) Paraskevi (Evi) Flouda , Dr. Vladimir V. Tsukruk 3:00-3:15

Mechanically Robust Ionogels with Hyperbranched Ionic Polymers for Enhanced Ion-Conduction and Energy Storage:

Mechanically robust and flexible gel electrolytes offer enhanced energy storage capabilities and safety in batteries and supercapacitors. The challenge, though, is that ion-conduction and mechanical robustness come at a trade-off for these materials. Here, we suggest that the utilization of hyperbranched ionic polymers (PILs) in nanocellulose-based ionogels will lead to both enhanced ion-conduction and mechanical performance due to the PILs' ionically conductive bearing groups and complementary interfacial interactions. More specifically, we investigate the effect of hyperbranched PILs with imidazolium counterions and carboxylate terminal groups with various ionic group densities on the properties of ionogels composed of co-assembled cellulose nanofibers (CNFs) and cellulose nanocrystals (CNCs). By harnessing hydrogen bonding interactions between PILs and the CNFs/CNCs "frame", highly interconnected open porous, lightweight, and shape-persistent ionogels are formed. Multi-fold improvements in ionic conductivity and Young's modulus, tensile strength, and toughness are achieved. Lastly, corresponding thin-film gel supercapacitors possess enhanced electrochemical cycling stability upon repeated bending (85% capacitance retention after 10,000 cycles), promising new insight in the development simultaneously mechanically robust and conductive gel electrolytes.

2) Nduka Ogbonna , Dr. Jimmy Lawrence 3:15-3:30

Precision bottlebrush polymers: Elucidating the impact of macromonomer dispersity on polymerization kinetic:

Bottlebrush polymers are inherently disperse and chemically heterogeneous because they are prepared by polymerizing a disperse mixture of macromonomers. We describe the systematic investigation of the impact of macromonomer (side chain) dispersity on the polymerization kinetics and overall structure of bottlebrush polymers. We also show the synthesis of fully

discrete ($\mathcal{D} = 1.0$) bottlebrush polymers using discrete building blocks. Our results suggest that dispersity could result in erroneous estimation of structural parameters that may impact theoretical studies. Overall, our results highlight the importance of precision building blocks in advancing structure-property relationship studies and the development of precision polymer platforms.

3) **Anthony Engler , Dr. Paul Kohl 3:30-3:45**

Synthesis, Applications, and Depolymerization of Polyaldehydes:

Polyaldehydes have great potential as plastics that can be chemically recycled back to their high-value monomers, a capability made possible through their favorable polymerization thermodynamics. Although this class of materials was studied in the 1960's-70's, commercial applications were not found due to their instability at room temperature and tendency to depolymerize. The means to room temperature stability has recently been found and current research has been focused on taking advantage of their ability to rapidly depolymerize upon triggering. These characteristics makes polyaldehydes well suited as a chemically recyclable polymer, sacrificial materials for semiconductor manufacturing, or fabricating stimuli-responsive devices.

POSTER PRESENTATIONS

1) **Daniel Hicks, Dr. Paul Russo**

Compact, multi-angle, multicorrelator static & dynamic light scattering instrument:

We report a SLS/DLS device that can measure most samples of interest to researchers in the polymer, particle and colloid communities. At a cost comparable to commercial single-angle DLS gear, an old 18-angle SLS instrument bound for the surplus pile was upcycled by outfitting it with a modern multichannel autocorrelator and 8 avalanche photodiode detectors. The result is 8 angles of simultaneously acquired DLS data, providing accurate hydrodynamic radii, plus 16 angles of simultaneously acquired SLS data, providing accurate radii of gyration. In the same time normally required for a single-angle DLS measurement, a user can obtain multiple-angle data and avoid inaccuracies associated with nonuniform size, molecular rotation and (for very large polymers) internal motions. The resulting R_h value can be compared with R_g to yield information about shape. Besides speed and simplicity, other attributes of the instrument include compact size, stability of alignment, portability, and safety (users do not require laser safety training). The system can use everyday scintillation vials, which usually arrive free of dust and other particulates and therefore do not require pre-cleaning. The system uses an open-source, visually intensive data analysis package written in Microsoft Excel and Excel VBA to collect data from the autocorrelators and/or perform independent fitting. This software is readily adaptable to the output structure of other correlator manufacturers.

2) **Siamalan Krishnathas, Dr. Christopher Kloxin**

Validating Protein Characterization Techniques for a Novel Peptide System:

Over millions of years, nature has optimized proteins through evolution to perform specific functions very efficiently. Many essential proteins such as keratin, SNARE complex and Influenza HA, have a subdomain called a coiled-coil that is critical to the robust structures and functions of these proteins. To capture the unique structures and functions found in proteins in a synthetic environment it is advantageous to only use the coiled-coil motif as it is responsible for the desirable properties found in many proteins. To do this, peptides (short proteins, 10-30 amino

acids) that were computationally designed to self-assemble into homotetrameric coiled-coils (termed bundlemers) in water or aqueous solution, are used. These bundlemers have great potential as building blocks for hybrid materials such as hydrogels and metal-peptide hybrids due to their biocompatibility, molecular monodispersity, and their predictable structure based on computational design. Given the vast range of potential applications for bundlemers, it is vital to have the ability to accurately characterize these peptides in various solution conditions. In this work, three commonly used characterization techniques for proteins, UV-vis spectroscopy, NMR, and SDS-PAGE, were optimized for this peptide system. UV-vis and NMR measurements were used to develop a protocol for accurate determination of peptide concentration where traditional protein techniques may not give the accuracy required for desired applications. To further explore the solution phase behavior and oligomerization states of bundlemers, native SDS-PAGE was implemented to allow for the characterization of both positive and negatively charged peptides at the same time under non-denaturing conditions. This was done by varying amounts of denaturing agent to determine a concentration that would not denature the coiled-coil, but would still mask its charge; enabling one to run both positively and negatively charged peptides down the same gel.

3) Dr. James Cho, Shaoyang Liu, Pixiang Wang, Martin Bouldo
Green Biochemical Synthesis of Silver Nanoparticle with Hydrophilic proteins/peptides-rich aqueous extract of American Giant Millipede, *Narceus americanus*:

In nature, living organisms usually provide versatile shape controlling tools (in nanometer scale) for organic/inorganic materials. There have been many researches, performed on plants, bacteria, virus, and marine organisms, but not many on arthropods. This research is based on extraction and purification of certain useful hydrophilic polypeptides and proteins (in arthropods) to be a peptide or protein-based biotemplate for nanomaterial synthesis. Additionally, arthropods are invertebrate animals. It means that the research is animal regulation-free, yet meaningful research for bionanotechnology and green chemical studies. In this research, silver nanoparticles (AgNPs) were successfully synthesized by a green biochemical method in aqueous American giant millipede (*Narceus americanus*) extract (AAGME) solution. Hydrophilic biological molecules (such as hydrophilic proteins and polypeptides) were acted as reducing and stabilizing agents for AgNP formation.

4) Samuel Owoso, Dr. Donghui Zhang
Ring-opening polymerization induced crystallization-driven self-assembly of poly (N-Methyl glycine)-block- poly (N-Decyl glycine):

Polypeptoids are structural biomimetics of peptides whose backbone is N-substituted polyglycine. Unlike polypeptides, there are no stereogenic centers and extensive hydrogen bond interactions along the main chains, giving peptoids favorable advantages. Studies on solution self-assembly of amphiphilic block co-polypeptoids into 1D, 2D, and 3D nano- and microstructures are justified because of their potential biotechnological applications such as smart coatings, drug, and gene delivery, and bioseparation. Despite the level of control offered by living crystallization-driven self-assembly (CDSA), it is a multi-step post-polymerization technique carried out at very low concentrations (~1% solids w/w) limiting the scale that is essential to explore possible applications of these structures. Herein we report the extension of ring opening polymerization-induced crystallization-driven self-assembly (ROPI-CDSA) to access 1D and 2D nanostructures of Poly (N-Methyl glycine)-block-Poly (N-Decyl glycine) block copolymers, having a scaled-up advantage for self-assembled nano and microstructures at higher concentrations

(5–15% w/w solids). Transmission electron microscopy (TEM) images from these experiments show mainly nanofibers and nanosheets as the metastable structure and revealed the morphological evolution of the system as the decyl NCA monomer is consumed. These experiments demonstrate that ROPI-CDSA is a promising and scalable solution self-assembly method for block co-polypeptidoids.

5) Ashley Miles, Dr. Scott Grayson

Linear-Dendritic Comb Polymers via Thiol-yne Click Chemistry:

AB₂ Polymers have various topologies and architectures such as linear, dendritic, and hyperbranched. However with an AB linear polymer once can have long flexible chains that can easily move past one another and entangle. While dendrimers are a monodispersed branched polymer that starts from the core and monomers array through protection and deprotection steps to expand the polymer to different generations. Due to the architecture of dendrimers, the functional groups are mostly on the periphery and significantly decreases entanglement. As a result, the miscibility is enhanced. The AB linear and AB₂ dendrimer properties can often be combined by forming Linear-Dendritic (LD) copolymers. LD copolymers are typically synthesized by compatible chain ends or branched functional groups on linear polymer and a dendron to form a block, star, or brush-like architecture. There are few reports of LD copolymers that have dendrimers and linear polymers alternating uniformly. A new synthetic strategy was designed to develop a new LD copolymer with alternating linear dithiol spacers and a 2,2'-bis(hydroxymethyl)propionic acid (Bis-MPA) dendrimer through thiol-yne “click” chemistry. Assorted studies were completed to optimize the synthetic strategy such as time studies to determine reaction completion, how dendron generations react with various dithiol linkers, and stoichiometric variations. As a result, this reaction produced high molecular weight uniform alternating LD polymers in 30-90 minutes for the larger dithiol linkers (1,6 hexane dithiol and 1,10 decane dithiol) with the G1, G2, G3 propargyl dendron generations. The optimization polymer studies were characterized by gel permeation chromatography and each structure was identified through nuclear magnetic resonance (NMR), and Matrix-Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry (MALDI-ToF MS)

6) Mahi Ahmad, Dr. Scott Grayson

Ring opening polymerization of ethylene brassylate:

Several researchers have done ring-opening polymerization (ROP) of polyester, but in most cases, small cyclic (six to eight-membered ring) molecules such as ϵ -caprolactone, γ -valerolactone, lactide, etc., were used as a monomer. Not much work has been done regarding macrocyclic monomer like ethylene brassylate (seventeen membered ring). In this project, ethylene brassylate was polymerized as a monomer since the use of macrocyclic monomers is less explored, and the cost is cheaper than other monomers. In 2014 Mecerreyes and coworkers successfully synthesized the fast linear poly(ethylene brassylate) (PEB) with different organocatalysts while using benzyl alcohol as an initiator. Out of a wide range of acidic and basic organocatalysts 5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) was the most effective. In our project, linear poly(ethylene brassylate) was synthesized in the presence of TBD as a catalyst while using propargyl alcohol as an initiator. Nuclear Magnetic Resonance (NMR), Gel Permeation Chromatography (GPC), and Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry (MALDI-ToF MS) support the formation of the linear PEB. 3480 Da molecular weight PEB with 1.58 polydispersity was obtained according to GPC. In addition, the major product is linear PEB with end groups as

hydroxide alkyne. MALDI also shows the presence of two minor linear polymers with different end groups, one with two alcohol and another with two alkynes. This two polymers were generated because of the breakdown of both ester bonds in ethylene brassylate. In the process, the ethane 1,2 diol group was freed, which acted as initiator afterward.

7) **Zhaoxian Zhang**

Zero-angle depolarized dynamic light scattering for characterization of cellulose nanomaterials:

The size and uniformity of cellulose nanocrystals (CNCs) are important considerations in many applications. Vendors and customers alike require accurate and precise size distributions, but present methods such as electron microscopy and asymmetric field flow fractionation can be tedious and expensive. They may require highly trained personnel too. Zero-angle depolarized scattering (ZADS) can be used instead. ZADS measures the rotational diffusion coefficient, which is much more sensitive to differences in size than the translational diffusion coefficient reported by conventional dynamic light scattering. We show that CNCs produce strong ZADS signals for rapid measurements (~1 minute) with good precision. The simple instrument requires little training. Billions or trillions of particles are measured in just minutes. Prospects for miniaturization of the ZADS apparatus for quality control labs are considered and compared to alternatives for QC work.

8) **Amman Nadeem, Dr. Scott Grayson**

Synthesis of linear poly(hydroxypivalic acid):

Polymers are macromolecules which can be synthesized with different morphologies and architectures depending upon the reaction conditions. 2,2-Bis(methylol propionic acid) (bis-MPA) is one of the very common AB₂ type monomers to be used to form a polyester with various polymer frameworks. The useful thing about bisMPA is that it has two hydroxy groups so that one can synthesize a dendrimer (perfectly branched) with a number of reactions, or one can get a hyperbranched polymer with just one reaction. With a growing interest in dendrimers and hyperbranched polymers, it is useful to shed light on a related linear polymer, for example, 2,2-dimethyl-3-hydroxypropionic acid (HPA) which is an AB type monomer and has mostly been studied as a co-polymer. Herein, linear poly(HPA) was formed via condensation polymerization in bulk using acid as a catalyst. The majority of the product was linear poly(HPA), however, some of the product also consisted of cyclic structures. In addition, poly(bisMPA-co-HPA) with different equivalents of ratios for bisMPA:HPA were also synthesized. The products were then characterized by nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), fourier transform infrared spectroscopy (FTIR) and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-ToF MS).

9) **Moustafa Zagho, Dr. Sergei Nazarenko**

Polyvinylidene Fluoride Microfiltration Membranes with Enhanced Oil Fouling Resistance through Incorporation of Mussel Inspired Polydopamine-Based Composites for Water/Oil Separations:

A new oil fouling-resistant coating based on polydopamine (PDA) was designed by codeposition on the surface of polyvinylidene fluoride (PVDF) microfiltration membranes. The physicochemical properties of the surface-modified PVDF membranes were investigated by attenuated total reflectance-fourier transform infrared (ATR-FTIR) spectroscopy and atomic force microscopy

(AFM). The performance of the modified membranes was evaluated with respect to the water flux and rejection properties. The PDA-based modified PVDF membranes displayed significant enhancement in separating oil from water in tight emulsions while demonstrating remarkably high resistance to fouling in comparison to the unmodified PVDF membranes. This work offered a promising strategy for enhancing the stability of PDA-based coatings for PVDF membranes. The reported functionalized microfiltration membranes can be recommended for water/oil separations.

10) Weiliang Sun , Dr. Samuel Snow and Dr. Xiuping Zhu

A New and Effective Dewatering Method for Hydrogels by Ammonia Gas:

Hydrogels were extensively used for water adsorption attributed to their strong swelling ability. Facile and effective dewatering methods are crucial to recover water from swollen hydrogels and recycle the hydrogels. However, traditional dewatering methods, such as mechanical squeezing, heating, and solar evaporation, have low water recovery and consume a lot of energy. Here, a new method by using ammonia gas (NH₃) was tested to dewater poly (acrylic acid-co-acrylamide) (PAAM) hydrogels for desalination, and impressive results are obtained. When PAAM hydrogels were used to absorb water from 1 g/L NaCl solution and then NH₃ was introduced to dewater the hydrogels, the water recovery was nearly 100% with a salt rejection of 43%. Even for actual seawater (~ 30 g/L NaCl), the water recovery could reach about 100% with a salt rejection of 20%. More notably, the system was extremely stable. During over 100 cycles (100 days), no obvious changes in water recovery and salt rejection were observed for 1 g/L, 15 g/L NaCl solutions, and actual seawater. Through physicochemical characterizations and Density Functional Theory (DFT) calculations, it is speculated that the excellent dewatering performance of NH₃ was mainly because NH₃ can form a more stable hydrogen bond with hydrogels than water and thus the bonded water can be released from the hydrogels.

11) Samantha Daymon , Dr. Sergei Nazarenko

A Comparative Study of Hydrogen Bond Organization Between three generations of dendrimers based on bis-MPA:

The physical properties of hyperbranched polymers (HBPs) based on 2,2-bis(hydroxymethyl) propionic acid (bis-MPA), a polyester monomer with a high concentration of hydroxyl groups, have been widely studied for their propensity to form hydrogen bonds (H-bonds). Similar studies and characterization have not yet been extended to bis-MPA based dendrimers due to the added synthetic efforts required. Despite these additional efforts, filling this intellectual gap is crucial to understanding the effects H-bonds have on the physical properties of these systems. Herein, hydrogen bond organization and interrelated structural order formation of a bis-MPA based dendrimers of the first through third generation (D1-3) were investigated via NMR, FTIR and WAXS. H-bond associations were found to decrease in strength as generation number increased (D1>D2>D3), while simultaneously, lower generations showed the highest propensity for OH-OH H-bonds as opposed to OH-CO H-bonds. Since hydroxyls are capable of participating in either a donor or acceptor role, OH-OH H-bonds are capable of forming 'chain-like' associations of multiple H-bonds, carbonyls on the other hand are only capable of filling an acceptor role, limiting them to a single H-bond association. Molecular dynamics (MD) simulations were also used to predict the WAXS spectra and reveal these 'chain-like' associations of H-bonds. Dendrimers make a good candidate for simulations due to their uniform molecular distributions and lack of

entanglements. Overall, computational results for these systems agree well with experimental data previously obtained for density, glass transition temperature and WAXS validating these systems.

12) Khang Pham, Dr. Donghui Zhang

Ring-Opening Random Copolymerization of N-(3-tert-butoxy-3-oxopropyl) glycine derived N-Carboxyanhydrides and N-butyl glycine derived N-Carboxyanhydrides:

Polypeptoids are structural mimetics of polypeptides with N-substituted polyglycine backbones. In 2017, Guseva and coworkers¹ proposed that the chemistry-to-biology (CTB) transition might occur through foldable polymers under certain external conditions that carry random distribution of hydrophobic and polar monomers and exhibiting some catalytic activities. To evaluate this hypothesis, a hydrophobic-polar (HP) polypeptoid random copolymer model was constructed by random copolymerizing two glycine-derived N-carboxyanhydride (NCA) monomers, namely, N-(3-tert-butoxy-3-oxopropyl) glycine derived N-Carboxyanhydride (tBuO₂Pr-NCA) and N-Butyl N-Carboxyanhydride (Bu-NCA) using benzylamine as initiator. Towards this end, poly(N-(3-tert-butoxy-3-oxopropyl) glycine)-random-poly(N-butyl glycine) was synthesized with monomer-to-initiator ratios ([M1]₀ : [M2]₀ : [I]₀ = 50 : 50 : 1 and 70 : 30 : 1), molecular weights (M_n) of 6000 Da and 3700 Da and narrow molecular weight distribution (PDI = 1.002 and 1.012), respectively. Investigating the HP random polymer model could help in understanding their folding and association in aqueous solution and autocatalytic behavior that leads to long chains of sequence-defined protein-like molecules.

13) Neha Sherif, Dr. Megan Robertson

Epoxidation and Curing of Bio-Renewable para-Coumaric Acid:

Sustainability has never been more important than now as we continue to accumulate waste in our landfills. Numerous amounts of waste are due to the imperishable nature of certain chemical compounds. Therefore, it is necessary to find degradable compounds to substitute them. One such compound is epoxy resin.

Epoxy resin is a thermoset polymer made from epoxy monomers combined with a curing agent. It is commonly used as an adhesive in the construction of chemicals and for composite lamination, amongst other applications. It is also used for products that require rigidity and durability (like windmill blades). Most epoxy resins are not biodegradable as they are produced from crude oil refinements. It is very effective for such uses however, once it becomes waste, this class of polymer can't be recycled with traditional methods and also is highly resistant to breaking down in the environment. This yields a significant amount of landfill waste, or it must be incinerated which has a high energy usage. Therefore, it is of interest to replace nonrenewable starting materials such as petroleum with a renewable feedstock.

One such substance from which epoxy monomers can be derived from is lignin, which is a complex organic polymer that is found in the cell walls of plants (mainly wood and bark). In the paper industry, it is a by-product of creating paper, as the lignin produces a dark color and oxidizes easily so it weakens the paper. There are few applications that use lignin, it is often just a waste product of the paper industry and incinerated. Under the right conditions, lignin can be broken down or depolymerized into a mixture of small molecules that have rigid aromatic rings,

which are potentially useful for making rigid polymer materials. Their rigidity makes them a promising starting material for synthesizing epoxy resins.

This project focused on a small molecule of the complex lignin structure called para-coumaric acid. The aim of this project was to epoxidize the para-coumaric acid and characterize this new structure. This was done using a two-step synthesis to convert para-Coumaric acid into an epoxy monomer. First, the para-coumaric acid was allylated using allyl bromide. Once the allylated compound was verified using NMR, the double bond in the allylated coumaric acid was epoxidized with meta-chloroperoxy benzoic acid to get epoxy groups. NMR was once again used to characterize the new epoxidized para-coumaric acid. This novel monomer was then cured with an anhydride curing agent to create epoxy resin which was then tested to find its thermal properties.

14) Brooke Parker, Dr. James Cho

Green Biochemical Synthesis of Nanomaterials With Aqueous Field Cricket

Extract Solution:

This research is based on extraction, purification, and the utilization of useful proteins present in the field cricket. In nature, living organisms such as insects are a source of various organic and inorganic materials. There are many examples of research performed on other living organisms such as plants, bacteria, and marine organisms, though there is a glaring lack of research involving insects. Insects, such as the field cricket utilized in this research project, are an excellent source of proteins. Hydrophilic surfaced proteins contained within this insect can be utilized for many functions in the field of biochemistry, provided that they are chemically or biologically modified. Other proteins may serve as a biotemplate, given their affinity for interacting with metal ions, such as gold and silver, and as such may be utilized to synthesize nanoparticles useful for enhanced drug delivery, electronic components, and even cancer treatment. Over the course of this study, signs of SPR have been observed in the field cricket extract solutions, which is a solid indication of the presence of nanomaterial. The benefit of performing such research on an invertebrate animal such as insects is that biomolecules can be observed in a higher form of life than, for example, bacteria, without the added complication of animal-based regulations in the research sphere.

15) Michael Dearman, Dr. Jimmy Lawrence

Elucidating the Impact of Side Chain Dispersity in Thin Films of Bottlebrush

Polymers:

Surface pressure isotherm measurements of bottlebrush polymers with discrete side chains and their thin film dynamics are reported. Monolayer thin films of bottlebrushes with discrete side chains have higher packing density and distinct phase transitions when compared to disperse counterparts. These insights advance fundamental knowledge of structure-property relationships of branched polymers and their theoretical self-assembly.

16) Mateen Jangda, Dr. Paul Russo

Particle Sizing Comparison: Particle Tracking, DDM, DLS:

Characterization of the size of particles in complex liquids has many vital applications in a broad range of sciences. Multiple sizing techniques are widely used, including Dynamic Light Scattering,

Differential Dynamic Microscopy, Particle Tracking, etc. In this experiment, the three aforementioned techniques are analyzed to determine the correct applications of each in order to determine their strengths and weaknesses. The Brownian motion of seven different latex particles was recorded under a microscope and analyzed using the three techniques. The recordings were made at 20x and 100x. The results of the experiment showed that Dynamic Light Scattering has a difficult time with large particles (> 500nm); otherwise, in simple suspensions, it is the easiest technique. Differential Dynamic Microscopy and particle tracking work better in complex environments, while Differential Dynamic Microscopy is less finicky than PT due to less demanding parameters.

17) Anuja Thapa, Dr. Donghui Zhang

Synthesis and Characterization of Polypeptide and Polypeptoid Polyelectrolyte Complexes:

Peptides are the class of biochemicals that have the side chains attached to the α -carbon while peptoids or poly-N-substituted glycines are the peptidomimetic synthetic molecules that have side chains attached to the amide nitrogen. Peptide and Peptoid based biomaterials are ideal for biomedical and biotechnological applications due to their low cytotoxicity and highly tunable properties such as net electrostatic charge, hydrophobicity, hydrophilicity, and side chain. They are widely used in drug/gene delivery systems, sensors, and medical imaging. This work is mainly focused on the synthesis and characterization of polypeptides synthesized by controlled ring-opening polymerization (ROP) of glutamic acid and lysine derived N-carboxyanhydride (NCA) monomers using nucleophilic initiators followed by the deprotection of the protecting groups. A diblock, triblock, and multiblock peptide based polyampholytes along with the N-substituted analogs were synthesized. Charged polymers, can undergo liquid-liquid phase separation to form a dense coacervate phase and a dilute supernatant phase and thus the future direction of this project would be to study the self-coacervation phenomena of the resulting polyampholytes along with the salt and pH effect on coacervation formation.

18) James Dyess, Dr. Sanichiro Yoshida, Dr. Sita Aggarwal

Ultraviolet-Induced Optical Degradation of Aqueous BSA Solutions:

Bovine serum albumin (BSA) is a monomeric, water-soluble protein and important plasma transporter. Disruption of its native structure, due to denaturation and/or misfolding (conformation change), can lead to a variety of physiological disorders. Several factors, including temperature, pH change, ionic strength, and radiation exposure, can cause conformation change. Understanding the underlying mechanisms of conformation change is therefore a useful tool for determining a protein's function. This research aims to understand the effect of UV radiation on conformation change of BSA via absorption spectroscopy. The absorption spectrum of the UV-radiated sample relative to the one obtained before the radiation reveals that the absorption peak at $\lambda \approx 250$ nm increases with the radiation time (up to 20 min with an increment of 5 min). This peak is not visible in the absolute absorption spectrum, indicating that it may represent some absorption mechanism resulting from UV radiation. Attempts are being made to identify the absorption mechanism via analyses of the second order derivative of the absolute absorption spectra. Preliminary results from secondary differentiation of absorption spectra show evidence of a UV-induced conformational change in the microenvironment of BSA.

Keywords: Serum albumins, Bovine serum albumins, UV-vis spectroscopy, radiation

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