ABSTRACTS
2025 INTERNATIONAL SYMPOSIUM ON STIMULI-RESPONSIVE MATERIALS

SUNDAY PM SESSION

FRONTIERS IN FUNCTIONAL RESPONSIVENESS: ENZYME CONTROL TO SOFT ACTUATORS

4:00 - 4:10 **Introductions**, **Cécile Chazot**, Northwestern University

4:10 - 4:40 **Turning Enzymes On-Off for Visible Signal Amplification**, **Krzysztof Matyjaszewski,** Carnegie Mellon University, Pittsburgh, PA, 15213, USA

The synthesis and application of artificial zymogens using protein−polymer hybrids to mimic the controlled enzyme activation observed in natural zymogens was explored. Protrypsin (pro-TR) and pro-chymotrypsin (pro-CT) hybrids were engineered by modifying the surfaces of trypsin (TR) and chymotrypsin (CT) with cleavable peptide inhibitors utilizing surface-initiated atom transfer radical polymerization. These hybrids exhibited reductions in catalytic efficiency for pro-TR and pro-CT, respectively, due to the inhibitory effect of the grafted peptide inhibitors. The activation of pro-TR by CT and pro-CT by TR resulted in several-fold increases in enzymatic activity. Furthermore, the activated hybrids triggered an enzyme activation cascade, enabling amplification of activity through a dual pro-protease hybrid system. This highlights the potential of artificial zymogens for therapeutic interventions and biodetection platforms by harnessing enzyme activation cascades for precise control of catalytic activity.

4:40 - 5:10 **Stimuli Responsive and AI/ML in Additive Manufacturing and Advanced Polymer Materials**, **Rigoberto Advincula**, University of Tennessee, Oak Ridge National Laboratory, USA

Creating and curating new data appends the way we approach materials science. In additive manufacturing (AM), the fabrication of parts and objects with high complexity and high performance is advantageous over other methods. Using nanocomposites enables highly improved properties even with “commodity polymers” that do not need to undergo high-temperature processes or extensive reformulation. With artificial intelligence and machine learning (AI/ML), optimizing the formulation and manufacturing methods is possible. Using sensors capable of a feedback loop mechanism and the ability to use simulation to create digital twins, optimizing properties in record time is possible. Statistical and logic-derived design, including regression analysis, are starting points for designing experiments (DOE) or principal component analysis(PCA) in optimization and analysis vs trial-and-error approaches when working with polymer materials. In this talk, we demonstrate the approaches toward understanding Nanostructuring in composites, stimuli responsive materials, and hierarchical approaches in optimization via AI/ML and other training/learning sets for specific properties and applications, such as 3D printing and flow chemistry reactions. Introducing more sensors (monitoring instruments) in AM processes and realtime ML with online monitoring allows a feedback loop and deep learning (DL) for autonomous fabrication and data analytics.

5:10 - 5:40 **On "life-inspired" light-driven soft actuators and moving polymer films, Arri Priimagi,** Tampere University, Finland

Molecular photoswitches have multiple faces as building blocks for photonic soft matter. On the one hand, their reversible photoisomerization powers life-like soft actuators, particularly in liquid crystal networks and hydrogels, where light acts as a remote trigger for adaptive, responsive, and bioinspired motions. Importantly, these photochemical processes often also generate significant photothermal heating, further boosting actuation. On the other hand, molecular photoswitches, azobenzenes in particular, can drive photoinduced mass migration in thin polymer films, producing well-defined surface relief patterns in response to laser interference irradiation, with applications ranging from cell-instructive substrates to diffractive optical elements in AR/VR technologies. This presentation will address these two manifestations of photomechanics, "life-inspired" actuation and surface patterning, pointing the way toward light-driven multifunctional soft systems across scales.

MONDAY AM SESSION

RESPONSIVE SOFT MATTER: NETWORKS, GELS, AND MESOSCALE DYNAMICS

8:30 - 8:40 **Introductions**, **Neil Dolinski**, **Columbia** University

8:40 - 9:10 **Kinetics of chain exchange in concentrated block copolymer sphere phases**, **Timothy Lodge,** University of Minnesota, USA

The process of chain exchange, whereby an individual block copolymer spontaneously escapes from one micelle and subsequently re-inserts into another, can be followed quantitatively by time-resolved small-angle neutron scattering (TR-SANS). A great deal is now known about the dependence of the escape time on core and corona block lengths, for diblock and triblock micelles in dilute solution. However, performing such measurements at higher concentrations, in the ordered state, is more challenging. I will describe recent measurements of exchange in polystyrene-block-poly(ethylene-alt-propylene) (PS-PEP) diblocks and triblocks in squalane, up to concentrations as high as 50%, where the individual micelles pack onto a BCC lattice. The triblock case allows, for the first time, direct comparison of the timescales for chain pullout and macroscopic flow in thermoplastic elastomers as model reversible networks.

9:10 - 9:40 **Propagating Phase Transitions: Stimuli-Responsive Signals in Lipid Membranes and Polyelectrolyte Gels**, **Matan Mussel,** University of Haifa, Israel

A phase transition represents a sharp change in a material's properties in response to an external stimulus, enabling highly sensitive and dynamic responses to environmental changes. Motivated by biological electric nerve signaling, I will describe the properties of two biomimetic phenomena: (1) divalent-monovalent cation exchange, which creates a propagating phase boundary in negatively charged polyelectrolyte gels, and (2) longitudinal pulses that induce a reversible phase change in lipid membranes and share many similarities with action potentials.

9:40 - 10:10 **Stimuli-Responsive Conductive Hydrogels**, **Laure Kayser,** University of Delaware, USA

Electronically-conductive hydrogels, composites of crosslinked and water-swollen polymers with a conducting material (polymer or inorganic nanoparticles) can address the mechanical and electronic mismatch between electronic devices and biological systems. While several methods have been reported to prepare these conductive hydrogels, several issues have to be addressed to enable their translation in bioelectronics. These issues include: (1) the increase in elastic modulus at high loading of conducting material, (2) the irreversibility of the gelation mechanism, which complicates the delivery and potential removal of the conductive hydrogel in vivo, and (3) the difficulty in controlling the micro- and macro-structure of the conductive hydrogels for applications in tissue engineering and wearable electronics. In this talk, I will share our progress towards addressing these issues with stimuli-responsive polyelectrolytes. The first part will be focused on achieving spatiotemporal control by using photo-active polymers to simultaneously photo-catalyze the polymerization of a conducting polymer and photo-crosslink its supporting matrix. This approach allows for printing conductive hydrogels with high resolution. In the second part, I will discuss the use of thermo-responsive polyelectrolyte block copolymers to achieve a reversible sol-gel transition close to body temperature in conductive systems. The materials hold promise in injectable bioelectronics for their mechanical and electronic properties and biocompatibility.

10:10 - 10:30 COFFEE BREAK

REACTIVITY-DRIVEN DESIGN: TRANSDUCTION, SULFUR POLYMERS, & CIRCULAR CHEMISTRY

10:30 - 10:40 **Introductions**, **S. Eileen Seo**, Arizona State University, USA

10:40 - 11:10 **Grayscale Transduction of Mechanical and Swelling-induced Forces into Chemical Reactivity**, **Stephen Craig,** Duke University, USA

This talk will present extrinsic mechanical force and internal tension generated by swelling as a stimulus that can be used to systematically tune the catalytic response of a polymer network. A long-standing vision of top-down atomic manipulation is to push or pull molecules in a way that changes their function, such as catalysis. The forces in a stretched polymer distort molecular conformation in ways that couple to reactivity, but to date the use of this type of polymer mechanochemistry to bias the outcome of a reaction has been limited to stoichiometric reactions whose products are covalently tethered to the polymer. In collaboration with Ross Widenhoefer and Roman Boulatov, we have demonstrated that the selectivity of an active catalytic site can be manipulated by straining an elastomeric support within which the catalyst is covalently bound. Specifically, the enantiomeric ratio of the products of the hydrogenation of a series of 2-acetamidoacrylates by a bisphosphine Rh catalyst increases with macroscopic strain, in one case reaching up to twice its initial value when the support is compressed by approximately 73% in a single dimension. Reactivity reverts to the original state upon relaxing the support. Qualitatively similar effects are achieved when tension is generated by swelling rather than mechanical distortion. Control experiments, structure-activity studies using strained macrocycles, and computations support mechanochemical coupling as the interpretational framework for the observed reactivity and suggest that even larger effects are possible with advances in the control of molecular topology of the supporting network.

11:10 - 11:40 Polymerizations with Elemental Sulfur and Sulfenyl Chlorides: A Novel Route to High-Performance Commodity Polymers, **Jeffrey Pyun,** University of Arizona, USA

An incredible surfeit of elemental sulfur (nearly 7 million tons annually) is generated via refining of fossil fuels to suppress hazardous emissions from gasoline. Furthermore, there are very limited uses for this waste sulfur in the chemical industry for various chemical, or material applications, the exception being sulfuric acid production. Hence, to address this important environmental and chemical challenge, we have developed new chemical synthetic and processing methods for the utilization of elemental sulfur to form polymeric materials. We recently demonstrated the use of liquid sulfur as the reaction medium for the synthesis of chemically stable and processable copolymer materials using a methodology, termed, inverse vulcanization. We discuss the significance of the “excess sulfur problem” along with new synthetic and polymerization methods that we have developed that directly utilize elemental sulfur and commodity sulfur chemicals as chemical feedstocks for polymeric materials. We will discuss the useful properties and applications derived from sulfur based plastics in the areas of optics, energy and defense.

Related Reviews on these topics:

1. “Polymerizations with Elemental Sulfur: A Novel Route to High Sulfur Content Polymers for Sustainability, Energy and Defense,” Griebel, J.J.; Glass, R.S.; Char, K.; Pyun, J. Prog. Polym. Sci. 2016, 58, 90-125
2. “100th Anniversary of Macromolecular Science Viewpoint: High Refractive Index Polymers from Elemental Sulfur for Infrared Thermal Imaging and Optics,” Kleine, T.K.; Glass, R.S.; Lichtenberger, D.L.; Mackay, M.E; Char, K.; Norwood, R.; Pyun, J. ACS Macro Lett. 2020, 9, 245-259.
3. “Polymerizations with Elemental Sulfur: From Petroleum Refining to Polymeric Materials,” Lee, T.; Dirlam, P.D. Njardarson, J.T.; Glass, R.S.; Pyun J. JACS 2022, 144, 5-22

11:40 - 12:10 Advanced Recycling – Selective Depolymerization of Heteroatom Containing Polymers – Thermoplastics and Thermosets, **Thomas Epps,** University of Delaware, USA

Approaches that valorize biomass and plastics waste have continued to emerge in recent years. One common strategy is deconstruction/depolymerization, whereby polymers are degraded into smaller molecules by various reaction pathways. The dynamics of these complex systems of molecules, with evolving molecular weights and molecular weight distributions that span the range from monomer up to commodity polymer, are a strong function of process technology. Hence, efficient development of deconstruction technologies benefits from simple and descriptive models that link material characteristics and process parameters to physical properties and product distributions. We have applied these models and learnings to both biobased and petroleum-based macromolecules. As one example, we have recently achieved the chemical recycling and upcycling of laboratory-based and commercial, heteroatom-containing polymers demonstrating the ability to chemically depolymerize both thermoplastics and thermosets back to monomers that can be repolymerized to generate new or upgraded polymeric materials. Moreover, we have developed approaches that allow us to separately trigger the depolymerization/deconstruction of various polymeric linkages to unlock the sequential depolymerization and separation of mixed polymer waste streams to significantly reduce the costs, solvent usage, and energy demands associated with these advanced recycling processes. Overall, this work offers new pathways to 'closing the loop' on the life cycle for higher-performance polymer systems.

12:10 PM LUNCH BUFFET

1:10 PM- OPEN AFTERNOON – On your own

TUESDAY AM SESSION

MOLECULAR PROGRAMMING FOR ADAPTIVE BEHAVIOR

8:30 - 8:40 Introductions, **Amal Narayanan**, University of Florida, USA

8:40 - 9:10 Development of Light-Responsive Soft Materials, **Javier Read de Alaniz**, UC Santa Barbara, USA

Photons have multiple enabling advantages to control chemical reactions, processes and stimuli-responsive materials. In this seminar, I will discuss our groups effort to design and develop novel photochromic molecules, their incorporation into liquid crystal elastomers and subsequent effort to unlock their potential to create photoresponsive materials.

9:10 - 9:40 Unraveling Mechanisms of Viscoelasticity in Dynamic Covalent Networks, **Alexei Sokolov**, University of Tennessee and Oak Ridge National Laboratory, USA

Dynamic Covalent Networks (DCNs) containing reversible covalent bonds might provide a solution for polymers recyclable by design. Reversible bonds make DCNs not only recyclable, but also enable unique properties such as self-healing, shape memory, time programmable behavior and extreme toughness [1-3]. This talk overviews studies of dynamics and viscoelastic properties of model DCNs emphasizing many current misconceptions [4,5] which should be avoided in analysis of these materials. Our results clearly demonstrate that metathesis often claimed as associative bond exchange mechanism is not observed even at the highest temperatures [5,6], revealing multiple misinterpretations in literature. Our studies discovered the important role of the so-called steric factor in the viscoelastic properties of DCNs [6,7]. This factor can be expressed as a significant entropic barrier and is completely neglected in DCNs literature. This entropic barrier leads to strong slowing down of the bond rearrangement time despite rather low enthalpic barrier [7].
Based on a broad range of experimental data, we suggest two regimes controlling terminal relaxation and viscoelasticity of DCNs [7]: reaction-rate limited regime at high temperatures that appear to be not sensitive to the polymer segmental dynamics, and diffusion-controlled regime at temperatures approaching glass transition where segmental relaxation plays critical role. At the end we propose a general model describing unique viscoelastic properties of DCNs and emphasize several puzzling results that remain unexplained.

References

1. S. Samanta, et al., J. Phys. Chem. B 125, 9389 (2021).
2. J. Luo, et al., Matter 5, 1391 (2022).
3. B. Li, et al., Chemical Reviews 123, 701 (2023).
4. M. Martins, et al. Macromolecules 56, 8688 (2023).
5. G. P. Carden, et al., Macromolecules 57, 8621 (2024).
6. S. J. Rukmani, et al., Macromolecules 57, 11020 (2024).
7. G. P. Carden, et al.; Macromolecules 58, 5494 (2025).

9:40 - 10:10 **Unraveling Sequence–Structure–Dynamics–Function Relationships in Responsive Macromolecules, Abigail Knight**, The University of North Carolina at Chapel Hill, USA

Encoding dynamic behavior in synthetic polymers requires drawing connections between polymer sequence, structure, dynamics, and function. Our recent work focuses on uncovering how molecular sequence encodes conformational preferences, dynamic fluctuations, and emergent functions in synthetic macromolecules. By linking sequence to structure, structure to dynamics, and dynamics to function, we aim to establish general design rules for “smart” materials capable of selective interactions, adaptive assembly, and environmentally triggered transformations. This framework integrates synthesis, characterization, and modeling to reveal fundamental principles for engineering responsive polymer systems.

References:

Bogen, M.P.; Swofford, W.M.; Chittari, S.S.; Knight, A.S. Structure-Function Relationships in Sequence-Controlled Copolymers for Rare Earth Element Chelation. 2025. J. Am. Chem. Soc. ASAP. DOI: https://doi.org/10.1021/jacs.5c07853

Chittari, S.S.; Dykeman-Bermingham, P.A.; Bogen, M.P.; Knight, A.S.; Structure-Function Insights into Thermoresponsive Copolymers as Lanthanide Precipitants. 2024. J. Am. Chem. Soc. 146, 33499-33508. DOI: 10.1021/jacs.4c10427

Dykeman-Bermingham, P.A.; Stingaciu, L.R.; Do, C.; Knight, A.S.; Dynamic Implications of Noncovalent Interactions in Single-Chain Polymer Nanoparticles. 2024. ACS Macro Lett. 13, 889-895. DOI: 10.1021/acsmacrolett.4c00269

10:10 - 10:30 COFFEE BREAK

MECHANICS AND ASSEMBLY AT THE BIOINTERFACE

10:30 - 10:40 Introductions, Tetsu Ouchi, Louisiana State University

10:40 - 11:10 Controlling Non-Equilibrium Self-Assembly and the Mechanics of Nanorobots, Henry Hess, Columbia University, USA

Non-equilibrium flows occur in chemical reactions, materials assembly, machines, engines, and electronic circuits, as the system evolves from a high energy non-equilibrium state towards the equilibrium state. Controlling the rate of flow is critical to the performance of the system. Conversely, external effects on the rate of flow can be used to sense these effects. External control of a flow (switching) is different from initiating the flow by placing the system in a non-equilibrium state (powering) to initiate the flow. While the rate of flow is dependent on the thermodynamic driving forces, a switch does not act on the thermodynamic driving force. Many demonstrations of control over non-equilibrium flows rely on moving the system towards a non-equilibrium state, that is the equivalent of charging the battery in a simple circuit. In contrast, a switch regulates the flow by altering the resistance of the system to the flow for a given thermodynamic driving force. Switching a flow off requires work. Larger switches typically require more work to operate, and some switches require more work than others to achieve the same amount of alteration. Our theoretical analysis aims to determine the minimal amount of work necessary to reduce a flow, and then aims to apply this result to a variety of processes in chemistry, physics, materials assembly, and sensing.

Secondly, aspects of the mechanics of biohybrid nanorobots will be discussed. Mechanical failure of biological nanostructures, such as microtubules and actin filaments, due to sustained force application has been studied in great detail and explained with the principles of mechanochemistry. In contrast, fatigue failure arising from repeated application of subcritical stresses has received little attention despite its prominent role in engineering and also in biology. Taxol-stabilized microtubules have been bent up to 256 times into sinusoidal shapes of varying wavelength and the frequency of breaking events has been observed. These experiments allow the calculation of fatigue life parameters for microtubules. Repeated buckling due to 12.5% compression – equal to the compression level experienced by microtubules in contracting cardiomyocytes – results in failure after in average 5 million cycles, whereas at 20% compression failure occurs after in average one thousand cycles. The fatigue strength (Basquin) exponent B is estimated as -0.06.

References

Y. Zhang and H. Hess*: “Converting microscale linear to rotary motion in kinesin-powered systems”. Supramolecular Materials, 1, 1000022 (2022)

S. Tsitkov†, J.B. Rodriguez III†, N.M. Bassir Kazeruni†, M. Sweet, T. Nitta and H. Hess*: “The rate of microtubule breaking increases exponentially with curvature”, Scientific Reports, 12, 20899 (2022)

S.R. Nasrin‡, N.M. Bassir Kazeruni‡, J.B. Rodriguez III, S. Tsitkov, A. Kakugo*, H. Hess*: “Mechanical Fatigue in Microtubules”, Scientific Reports 14, 26336 (2024)

11:10 - 11:40 Stimuli-Responsive, Bioinspired Glycopolymers for Selective Heavy Metal and Rare Earth Element Capture, **Cassandra Callmann**, University of Texas at Austin, USA

Selective metal sequestration from water is essential for advancing sustainable technologies in both environmental remediation (e.g., heavy metal removal) and energy-critical resource recovery (e.g., rare earth element capture). In this presentation, we report a class of bioinspired, stimuli-responsive glycopolymers capable of targeted, reversible ion capture via pH-tunable binding mechanisms. These materials, synthesized through ring-opening metathesis polymerization (ROMP), feature amphiphilic glucuronate sidechains that selectively bind heavy metal cations, including cadmium and lead, in complex aqueous environments. At neutral pH, the glycopolymers achieve >99% metal ion removal within minutes, and acidification induces metal release, enabling recyclability without loss of capture efficiency. These glycopolymers also demonstrate selectivity for middle rare earth elements (MREEs), which are challenging to isolate due to similar ionic radii. By tuning the charge density and degree of polymerization within the glycopolymer scaffold, we achieve distinct size-dependent selectivity, allowing effective separation of MREEs from light and heavy REEs in mixed solutions. This dual capability for heavy metal and REE separation highlights the versatility of these glycopolymers as stimuli-responsive materials, positioning them as promising candidates for applications in water remediation and resource recovery.

11:40 - 12:10 Tuning Oligomer Composition to Modulate Protein Functions, **Adrian Figg,** Virginia Tech, USA

Synthetic polymers are widely used in high-performance materials because of the scalability and chemical diversity, yet they are largely underexplored for protein recognition. We synthesized random hetero oligomers (RHOs) using reversible-deactivation radical polymerization (RDRP) based on the average surface chemistry of GFP. Affinity HPLC showed that there is a privileged subset of strong-binding RHOs resulting from a single RDRP. Experimental and computational analyses confirmed that RHOs are forming a supramolecular complex with GFP. For example, well-tempered metadynamics simulations identified 6 distinct binding locations on the GFP surface from strongly binding RHOs (which agrees with experimental measurements). High-throughput polymer synthesis and binding assays elucidated key RHO–GFP interactions, where pH played a significant role in binding. This pH-dependent interaction introduces a new class of stimuli-responsive materials, where the RHO serves as a responsive unit for both protein binding/unbinding and functional modulation.

12:10 PM LUNCH BUFFET

TUESDAY PM SESSION

BOND DYNAMICS AND MOLECULAR ADAPTABILITY

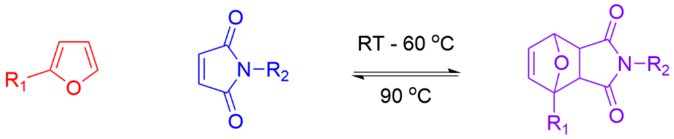
1:30 - 1:40 **Introductions,** **Anthony Engler**, Louisiana State University, USA

1:40 - 2:10 **Weak Bonds: a Strong Case to Stimulate Function,** **Yoan Simon**, Arizona State University, USA

Nature leverages non-covalent interactions and has perfected multiple reversible systems to accomplish complex functions such as repair, plasticity, or haptic perception. It is also able to construct and deconstruct molecules with a set of building blocks. Drawing inspiration from these abilities, we have created a series of polymeric materials that include weak links capable of reporting on mechanical activation and/or to achieve reprocessability. First, we will look into remoldable polymeric chains and networks. Specifically, we will focus on unravelling the governing principles of supramolecular interactions in zwitterionic systems and associative dynamic exchanges by modulating the chemistry of uncatalyzed exchanges in diketoenamines and diketoxime structures by utilizing orthogonal thiol-ene photopolymerization. Specifically, we will broach the topics of chemical exchange and chain dynamics and their overall impact on the rheological properties of the materials. Additionally, we will discuss our latest finding in mechanochemistry that could help transform our understanding of how shockwaves are dissipated in materials at high velocity. Time permitting, we will also discuss some of our findings with respect to network formation and characterization as well as shape transformation of complex architected molecules. We believe that these findings can have huge influence on understanding impact mitigation, transport properties, and reprocessability of such systems.

2:10 - 2:40 **Expanding the Color Wheel of Diels-Alder Chemistry**, **Philip Costanzo**, California Polytechnic State University, USA

Diels-Alder (DA) chemistry has been studied extensively, and the chemical reaction mechanisms are well understood. In a DA reaction, a dienophile and a diene undergo a [4+2] cycloaddition to form a six-membered ring. It is mostly commonly demonstrated by a reaction with a furan (red) and maleimide (blue) to yield a DA adduct (purple). By employing different dienes and dienophiles, different adducts can be prepared with tunable retro-DA temperatures. New work with nucleophile-induced retro-DA reactions will be described, as well as the development of preparation of debondable adhesives.



2:40 - 3:10 **Controlling Dynamics of Polymer Materials and Blends with Rearranging Bonds,** **Charles Sing**, University of Illinois Urbana-Champaign, USA

Dynamic bonds, which can break and reform or undergo exchange, have long been a key motif in polymer science. Their role in controlling the mechanical properties of polymer networks has been historically important in the context of rubber, and as a route to tune or control the viscoelastic properties in both melt networks and swollen gels. There has recently been a dramatic increase in chemistries – and consequently applications – available to polymer scientists as they realize the possibilities of this class of materials. These advances have benefited from progress in polymer physics, where molecular-level physical insights can guide molecular-level design of dynamic networks.

This talk will highlight examples from our recent research where computational and theoretical polymer physics is used to understand both dynamic and thermodynamic phenomena in dynamic networks, in close collaboration with several experimental and theoretical colleagues. We show how the kinetic and mechanistic attributes of dynamic bonds can be engineered to control material dynamics. In the glassy state, we show how activated segmental motions couple to molecular bond exchange events. In the rubbery state, we show how bond exchange motifs can be harnessed to stabilize polymer blends, by coupling polymer dynamics to slow bond-exchange kinetics. Finally, we can predict how competition between bond exchange mechanisms can be used to engineer stimuli-responsive molecular rearrangements. These examples highlight not only the promise of this important class of materials, but the abundance of scientific questions that remain to be addressed in our understanding of these fascinating systems.

3:10 - 3:30 **COFFEE BREAK**

MACROSCOPIC RESPONSE AND PREDICTIVE MODELING

3:30 - 3:40 **Introductions,** **Ariana Tamura**, University of Florida, USA

3:40 - 4:10 **Coarse-Grained Modeling of Crystallization, Melting, and Degradation of Stimuli-Responsive Polymeric Materials,** **Olga Kuksenok**, Clemson University, USA

Controlling degradation of polymer materials can introduce a means to tailor materials properties or to enhance recyclability of these materials. Incorporating degradable ester groups into the polyethylene backbone can offer a means to enhance recyclability while maintaining targeted properties suitable for a range of applications. We recently introduced coarse-grained molecular dynamics simulations to characterize the effect of ester functionalization on crystallization and melting processes in polyethylene mimics (Suhail et al, ACS Appl. Polym. Mater, 7, 12, 7976, (2025)). The model is based on the united monomer model for polyethylene, which reproduces crystallization upon cooling from the melt state. We demonstrate an increase in density and a decrease in crystallinity for polyethylene mimics with an increase in the ester-to-methylene ratio. We track the fraction of esters contributing to the crystalline and amorphous regions during the cooling process and demonstrate uniform partitioning of ester groups between these regions throughout the cooling processes. This uniform partitioning of ester beads results in an approximately linear decrease in melting and crystallization temperatures with an increase in ester fraction. Further, we focus on the effect of the length of the sidechain and placement of ester groups on the crystallization and melting processes. Our model captures the key trends observed in experiments and contributes to the understanding of the crystallization and melting processes in linear and branched polyethylene functionalized with esters. Further, we recently developed a mesoscale framework to model degradation of polyethylene melts at a range of high temperatures. We characterize the fragmentation process by tracking the time evolution of the distribution of degrees of polymerization of chain fragments. As a next step we model crosslinking of polymer fragments received during the degradation. Our modeling approaches are validated with respect to concurrent collaborative experimental studies. Understanding thermal degradation of polyolefins on the mesoscale can result in the development of alternative strategies for recycling a range of thermoplastics.

4:10 - 4:40 **Stretch-Responsive and Impact-Damping Constructs from Multi-Layers of Thermoplastic Elastomers and Unvulcanized Rubbers,** **Gary Wnek**, Zachary Baeirl, Andrew Ko, Austin Mills and Kathryn Daltorio, Case Western Reserve University, USA

There is significant interest in adding value to existing high-volume polymeric materials, commodity polyolefins through engineering plastics and elastomers. One attractive possibility is via scalable processing approaches. Of particular interest is the development of multi-layer constructs of rubbery materials systems that exhibit multi-functionality, including low gas permeability, improved tactile properties, and unique mechanical responses. Toward that end, we discuss work on construction and tension-and-release properties of simple bilayers of vulcanized and unvulcanized rubbers which necessarily have different viscoelastic responses, namely vulcanized rubber exhibiting classical neo-Hookean behavior (for example, styrenic thermoplastic elastomers), with the unvulcanized counterpart, such as poly(isobutylene), being dominated by viscous and thus permanent deformation. Also of interest is energy absorption behavior, with unvulcanized rubber layers acting to dissipate energy via viscous damping. We note that these multi-layers offer a nice visual platform to complement introductory studies of viscoelasticity.

4:40 - 5:10 **Photochemical Uncaging of Frustrated Lewis Pairs in Polymeric Matrices, Nathan Romero**, UC San Diego, USA

Frustrated Lewis Pairs (FLPs) consist of sterically encumbered Lewis acids (LAs) and Lewis bases (LBs) that cannot form classical LA-LB adducts, rendering FLPs highly reactive towards covalent adduct formation with a variety of molecular functionalities. The reversible nature of these molecule-FLP adducts can be leveraged to create dynamic, stimuli-responsive polymeric materials, but the potent reactivity of free FLPs poses severe synthetic limitations in accessing polymeric FLPs. Our work has focused on the development of novel synthetic approaches for controllable installation of latent FLP functionality and stimuli-responsive release of FLPs in polymeric matrices. This presentation will highlight recent efforts in our group to prepare “caged” FLP-containing polymers by vinyl addition (VA) polymerization and Ring-Opening Metathesis Polymerization (ROMP) and to study their stimuli-responsive FLP “uncaging” behavior. Notably, we discovered that covalent adducts between alkenes and vicinal FLPs are photochemically reactive, fragmenting to release an alkene and a free FLP. Our work towards harnessing the photo-uncaged FLP-containing materials in catalytic applications will be discussed.

5:10 - 5:15 **Closing Remarks** **Marek W. Urban, Brent S. Sumerlin, Ying Yang**

5:30 - 7:00 **POSTER SESSION AND WINE SOCIAL**

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