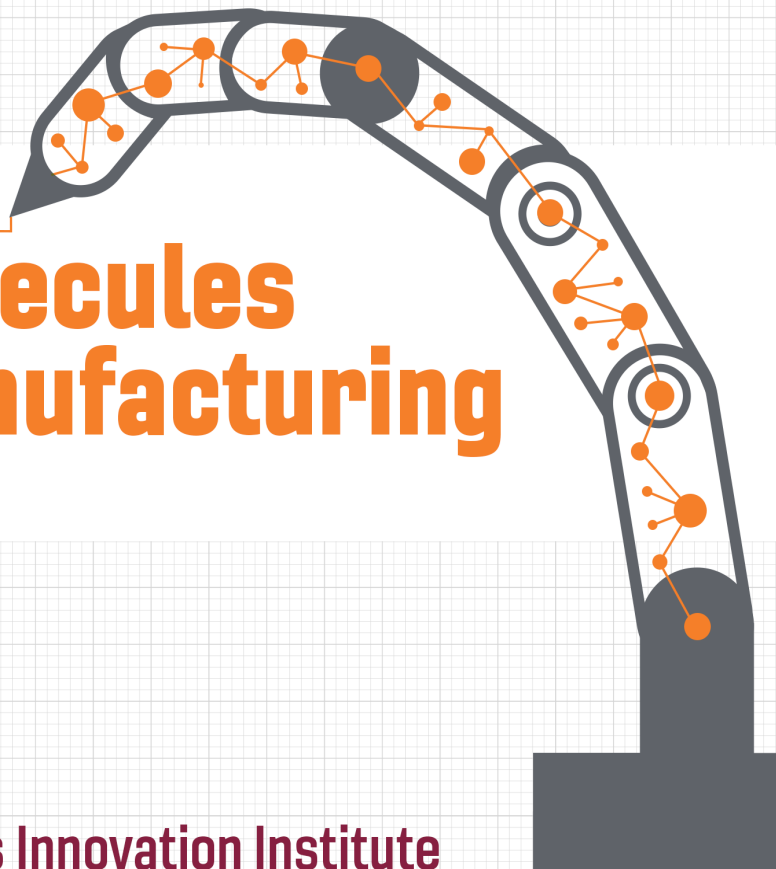


MII

Technical Conference & Review

2018



From **Molecules** To **Manufacturing**

Macromolecules Innovation Institute

April 16-18

Virginia Tech

The Inn at Virginia Tech and Skelton Conference Center

Blacksburg, Va.



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**MACROMOLECULES INNOVATION INSTITUTE
TECHNICAL CONFERENCE AND REVIEW**

2018

ABSTRACTS

**OF
ORAL AND POSTER PRESENTATIONS**

APRIL 16 - 18, 2018

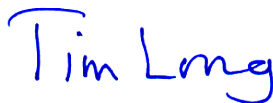
**THE INN AT VIRGINIA TECH AND SKELTON CONFERENCE CENTER
BLACKSBURG, VA**

PREFACE

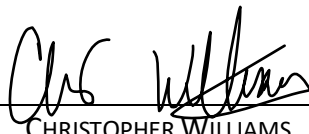
ON BEHALF OF THE FACULTY, STAFF, AND STUDENTS AT VIRGINIA TECH, WE WOULD LIKE TO PERSONALLY WELCOME YOU TO OUR CAMPUS. WE THINK THAT YOU WILL FIND THE TECHNICAL PROGRAM TO BE QUITE IMPRESSIVE. THE PARADIGM OF “MOLECULES TO MANUFACTURING” HAS PERCOLATED ACROSS THE GLOBE, WE ARE BOLDLY REDEFINING HOW INNOVATION OCCURS WITH A SYNERGY OF MOLECULAR UNDERSTANDING AND ALIGNMENT WITH ADVANCED MANUFACTURING. IT IS THIS SYNERGY THAT WILL ALLOW US TO CHANGE THE WORLD, ENSURING WE ARE TRANSLATING OUR DISCOVERIES TO SOCIETY. WE LOOK FORWARD TO SHOWCASING OUR VARIOUS RESEARCH, EDUCATIONAL, AND OUTREACH EFFORTS WITH YOU.

OUR GOAL IS TO ENSURE THAT VIRGINIA TECH EXCEEDS YOUR EXPECTATIONS FOR COLLABORATIONS. PLEASE DO NOT HESITATE TO CONTACT US FOR FURTHER INFORMATION REGARDING THE MACROMOLECULES INNOVATION INSTITUTE (MII) AT VIRGINIA TECH.

WITH OUR BEST REGARDS,



TIMOTHY E. LONG
DIRECTOR
MACROMOLECULES INNOVATION INSTITUTE




CHRISTOPHER WILLIAMS
ASSOCIATE DIRECTOR
MACROMOLECULES INNOVATION INSTITUTE

WELCOME TO THE MACROMOLECULES INNOVATION INSTITUTE (MII) AT VIRGINIA TECH!

I REMAIN PASSIONATE AND HONORED TO LEAD SUCH A VIBRANT GROUP OF FACULTY, STUDENTS, AND STAFF DEVOTED TO ADVANCING MACROMOLECULAR SCIENCE AND ENGINEERING. AS FACULTY, WE ARE ONLY AS GOOD AS OUR STUDENTS AND STAFF! THANK YOU FOR TRAVELING TO CAMPUS, AND I SINCERELY HOPE THAT YOU WILL BE IMPRESSED WITH THE CUTTING-EDGE RESEARCH AND EXPANDING FACILITIES AT MANY RAPIDLY EMERGING INTERSECTIONS OF SCIENCE AND ENGINEERING. OUR TECHNICAL CONFERENCE AND REVIEW CONSISTS OF OVER 110 POSTER PRESENTATIONS, 29 ORAL PRESENTATIONS, AND FIVE INVITED KEYNOTE SPEAKERS. THIS VOLUME OF SCHOLARLY OUTPUT SERVES AS A TESTAMENT TO OUR GENUINE EXCITEMENT AND IMMENSE VISION FOR MACROMOLECULAR SCIENCE AND ENGINEERING.

I WELCOME YOUR INPUT AS WE CONTINUE TO REFINE AND RESHAPE THE INSTITUTE, CONTINUALLY STRIVING TO REMAIN AS A TOP DESTINATION FOR MACROMOLECULAR SCIENCE AND ENGINEERING ACROSS THE GLOBE.

ENJOY OUR BEAUTIFUL CAMPUS, AND TO OUR ALUMS, WELCOME BACK!



TIMOTHY E. LONG
DIRECTOR
MACROMOLECULES INNOVATION INSTITUTE

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SCHEDULE OF EVENTS

Holtzman Alumni Center at Virginia Tech

MONDAY, April 16, 2018

10:00 AM–1:00 PM [Conference Check-In](#)

SESSION I: Polymer Processing and Advanced Manufacturing

Session Chair: Prof. Don Baird (Chemical Engineering)

1:00 PM–1:05 PM **Introductory Remarks** – Prof. Timothy E. Long, Director, MII

1:05 PM–1:10 PM **Welcome to Virginia Tech** – Dr. Stefan M. Duma, Director of Institute for Critical Technology and Applied Science (ICTAS)

1:10 PM–1:30 PM **MI – Year in review** – Prof. Timothy E. Long, Director, MII

1:30 PM–1:50 PM **Presentation of Garth L. Wilkes Interdisciplinary Scholar Awards** to Prof. Robert B. Moore (Chemistry) and Mr. Jacob J. Fallon, (Macromolecular Science & Engineering Student) for Prof. Michael Bortner (Chemical Engineering) – Prof. Timothy E. Long, Director, MII and Prof. Christopher B. Williams, Assoc. Director, MII

Recognition of MII Student Excellence – Prof. Timothy E. Long, Director, MII

1:50 PM–2:10 PM *“Model Analysis of Feedstock Behavior in Fused Filament Fabrication: Enabling Rapid Materials Screening,”* Prof. Michael J. Bortner (Chemical Engineering)

2:10 PM–2:15 PM **Introduction of Dr. Nancy Zhang, Carbon3D** – Prof. Timothy E. Long, Director, MII

2:15 PM–2:55 PM **Plenary Lecture:** *“Fabricating the Future of Material with Light in Additive Manufacturing,”* Dr. Nancy Zhang (Research Scientist; Carbon3D)

2:55 PM–3:05 PM **Break**

3:05 PM–3:30 PM *“Molecules to Manufacturing: Concurrent Design of Processes and Materials,”* Prof. Christopher B. Williams (Mechanical Engineering)

3:30 PM–3:55 PM *“Advanced Manufacturing of Ceramics for Extreme Applications,”* Prof. Carolina Tallon (Materials Science and Engineering)

3:55 PM–4:20 PM *“Achieving More With Less: Additive Manufacturing of Multi-Functional 3D Architected Metamaterials,”* Prof. Xiaoyu Rayne Zheng (Mechanical Engineering)

4:20 PM–4:45 PM *“From Fundamental Rheology to the Design of Novel Processes and Materials with Enhanced Properties,”* Prof. Don Baird (Chemical Engineering)

5:30 PM–7:00 PM **Poster / Reception / Best Poster Prizes** (Latham Ballroom – AB) – *(Dinner on your own)* – **Reception and Poster Prizes sponsored by The Dow Chemical Company**

TUESDAY, April 17, 2018

7:00 AM–8:00 AM [Conference Check-In](#) (*Breakfast on your own*)

8:00 AM–9:00 AM Tour of the Institute for Critical Technology and Applied Science II, Macromolecular Materials Discovery Center (MMDC), and the DREAMS Additive Manufacturing Facilities, Goodwin Hall, (Profs. Timothy E. Long, Christopher Williams, and Robert B. Moore)

SESSION II: Stimuli-Responsive Polymers: Designing Functional Polymers

Session Chair: Prof. John B. Matson (Chemistry)

9:15 AM–9:20 AM **Introductory Remarks** – Prof. Harry Gibson (Chemistry)

9:20 AM–9:45 AM *“Stereoselective Photoredox Ring-Opening Polymerization of Racemic O-Carboxyanhydrides,”* Prof. Rong Tong (Chemical Engineering)

9:45 AM–10:10 AM	<i>"Tapered Bottlebrush Polymers: A New Polymer Architecture,"</i> Prof. John B. Matson (Chemistry)
10:10 AM–10:35 AM	<i>"Host-Guest Templatation in Self-Assembly of Macromolecules,"</i> Prof. Harry Gibson (Chemistry)
10:35 AM–10:45 AM	Break
10:45 AM–11:10 AM	<i>"Renewable-Based, Self-Healing Hydrogels by Selective Polysaccharide Oxidation,"</i> Prof. Kevin J. Edgar (Sustainable Biomaterials)
11:10 AM–11:15 AM	Introduction of Dr. Bradley Lokitz (Oak Ridge National Laboratory) – Mr. Mingtao Chen (Chemistry Student)
11:15 AM–11:55 AM	Plenary Lecture: <i>"Probing Nanoscale Responses of Ionic Polymers to Applied Electric Fields,"</i> Dr. Bradley Lokitz (Research Scientist; Center for Nanophase Materials Science, Oak Ridge National Laboratory) (Posters up at 10 AM – Latham Ballroom – AB)
11:55 AM–2:00 PM	Lunch (on your own)

SESSION III: Polymer Structure – Property Relationships

Session Chair: Prof. Christopher B. Williams (Mechanical Engineering)

2:00 PM–2:05 PM	Introductory Remarks – Prof. David A. Dillard (Biomedical Engineering and Mechanics)
2:05 PM–2:30 PM	<i>"Block Copolymer Based Porous Carbon Fibers,"</i> Prof. Guoliang Liu (Chemistry)
2:30 PM–2:55 PM	<i>"Creating filled Nanocomposites from Industrially Relevant Polymers,"</i> Prof. Johan Foster (Materials Science and Engineering)
2:55 PM–3:05 PM	Break
3:05 PM–3:10 PM	Introduction of Dr. Sudhin Datta (ExxonMobil Chemical) – Prof. Michael J. Bortner (Chemical Engineering)
3:10 PM–3:50 PM	Plenary Lecture: <i>"meso Propylene – co-Ethylene Elastomers from ExxonMobil Chemical,"</i> Dr. Sudhin Datta (Sr. Research Scientist; ExxonMobil Chemical)
3:50 PM–4:15 PM	<i>"Advanced Composite Membranes Based on High-Aspect Ratio Nanoparticles"</i> Prof. Steve Martin (Chemical Engineering)
4:15 PM–4:40 PM	<i>"Toward Science-Based Manufacturing of Powder Bed Fusion Additive Manufacturing,"</i> Mr. Camden A. Chatham (Macromolecular Science & Engineering Student)
4:40 PM–5:05 PM	<i>"Characterizing Polymer Friction Anomalies and Reviewing Adhesion Scaling Laws,"</i> Prof. David A. Dillard (Biomedical Engineering and Mechanics)
5:05 PM–5:30 PM	<i>"Thermal Switching and Rectification in Polymers,"</i> Prof. Zhiting Tian (Mechanical Engineering)
5:30 PM–7:00 PM	Poster / Reception / Best Poster Prizes (Latham Ballroom – AB)
7:00 PM–9:00 PM	Conference Banquet (Latham Ballroom – AB) – Guest Speaker: Dr. Michael Hochella, University Distinguished Professor, Geosciences, Virginia Tech

WEDNESDAY, April 18, 2018

SESSION IV: Design and Computational Modeling of Complex Polymer Systems

Session Chair: Prof. Louis A. Madsen (Chemistry)

8:00 AM–8:05 AM	Introductory Remarks – Prof. Louis A. Madsen (Chemistry)
8:05 AM–8:30 AM	<i>"Designing Polymers to Improve Disease Treatments,"</i> Prof. Michael Schulz (Chemistry)
8:30 AM–8:55 AM	<i>"Photo-Activated, Simultaneous Chain Extension and Crosslinking for Lithographic 3D Printing of Siloxanes,"</i> Mr. Justin M. Serrine (Macromolecular Science & Engineering Student)
9:20 AM–9:45 AM	<i>"Multiscale Design of Carbon Nanotube Reinforced Piezoelectric Sensors and Actuators,"</i> Prof. Romesh Batra (Biomedical Engineering and Mechanics)
9:45 AM–9:55 AM	Break
9:55 AM–10:20 AM	<i>"Nature-Inspired Water Harvesting,"</i> Prof. Jonathan Boreyko (Biomedical Engineering and Mechanics)
10:20 AM–10:45 AM	<i>"Evaporation of Polymer and Colloidal Solutions,"</i> Prof. Shengfeng Cheng (Physics)

- 10:45 AM–10:50 AM **Introduction of Dr. Christopher Bowman (University of Colorado Boulder)** – Prof. Timothy E. Long (Director, MII)
- 10:50 AM–11:30 AM **Plenary Lecture:** *“Clicking Polymer Networks Together: Approaches to Form Smart, Functional Polymers Networks from Click Chemistry,”* Dr. Christopher Bowman (Clinical Professor of Restorative Dentistry; Chemical and Biological Engineering, University of Colorado Boulder)
- 12:00 PM–1:30 PM *Lunch (on your own)*
- 12:00 PM–1:30 PM **III External Advisory Board Meeting** (*lunch will be provided for Advisory Board – Preston's*)

SESSION V: Advances in Self-Assembly, Morphology, and Visualization

Session Chair: Prof. Robert B. Moore (Chemistry)

- 1:30 PM–1:35 PM **Introduction of Dr. Samuel Stupp (Northwestern University)** – Prof. John B. Matson (Chemistry)
- 1:35 PM–2:15 PM **Plenary Lecture:** *“Supramolecular Polymers and their Integration with Covalent Polymers,”* Dr. Samuel Stupp (Board of Trustees Professor of Materials Science, Chemistry, Medicine, and Biomedical Engineering; Northwestern University)
- 2:15 PM–2:40 PM *“Blocky Functionalization of Thermo-Reversible sPS and PEEK Gels,”* Prof. Robert B. Moore (Chemistry)
- 2:40 PM–3:05 PM *“Revealing Molecular Adversaries of Human Health,”* Prof. Deborah Kelly (VTCRI)
- 3:05 PM–3:30 PM *“Blocky Bromination of Poly(Ether Ether Ketone) in the Gel-State and Reactions Thereof,”* Ms. Lindsey Anderson (Chemistry Student)
- 3:30 PM–3:55 PM *“A Modular Ionic Material Platform Formed from a Double Helix Polyelectrolyte,”* Prof. Louis A. Madsen (Chemistry)
- 3:55 PM–4:20 PM *“Speaking Many Languages: A Synergy of Molecular Structure and Advanced Manufacturing for Emerging Technologies,”* Prof. Timothy E. Long (MII)
- 4:20 PM–4:30 PM **Concluding Remarks** – Prof. Timothy E. Long (Director, MII)

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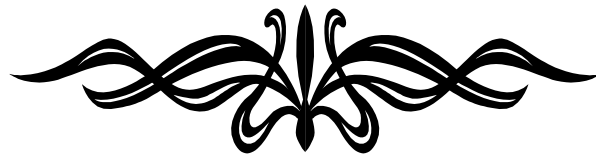
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ORAL PRESENTATION ABSTRACTS



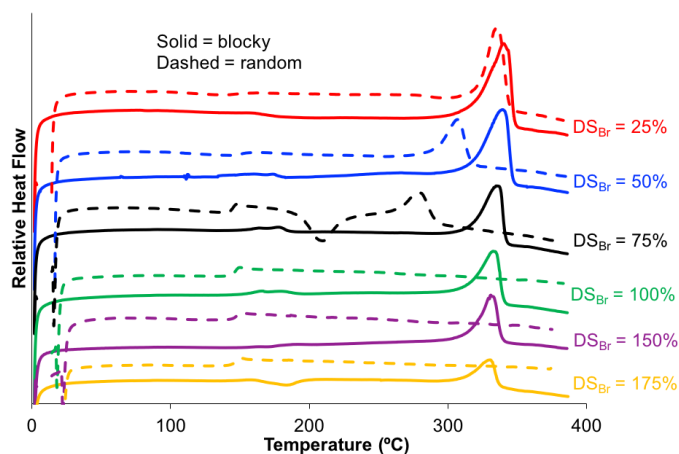
BLOCKY BROMINATION OF POLY(ETHER KETONE) IN THE GEL-STATE AND REACTIONS THEREOF

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Post-polymerization bromination is a useful technique to modify existing homopolymers and provide functional handles for further substitution. Most methods of bromination are performed in the homogeneous solution-state, thereby yielding random copolymers. Recently, however, functionalization in the semicrystalline gel-state has been shown to produce blocky copolymer architectures through selective functionalization of the amorphous domains.¹ In this work, the bromination of poly(ether ether ketone) (PEEK) using N-bromosuccinimide is explored and compared in the solution-state and the gel-state. The BrPEEK copolymers were fully characterized using NMR, FTIR, DSC, DMA, and SAXS to determine the influence of synthetic method and resultant architecture on crystallizability and morphology.

Following bromination, two further reactions were explored. First, Ullmann reactions were investigated to attach superacid side chains to the PEEK backbone. Second, the functionalization of blocky BrPEEK was investigated to produce blocky brominated, sulfonated PEEK copolymers. By utilizing the initial gel-state reaction, novel PEEK block copolymers are obtainable using facile post-polymerization techniques.



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FROM FUNDAMENTAL RHEOLOGY TO THE DESIGN OF NOVEL PROCESSES AND MATERIALS WITH ENHANCED PROPERTIES

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This presentation contains an overview of the use of polymer rheology in the design of novel processing operations for the purpose of delivering materials with improved properties. Existing research programs include:

- Modeling and simulation of injection molding of long fiber thermoplastic composites (H. Chen, G. Lambert, K. Boyce).
- The generation of novel wholly thermoplastic composite materials based on the use of higher melting liquid crystalline polymers to reinforce lower melting polymers for use in 3-D printing (C. Mansfield, M. Ansari, and T. Chen).
- Development of novel melt processing techniques based on replacing toxic solvents with benign plasticizers such as water and CO₂ (J. Yu).
- Generation of novel blends of widely different melting points and processing temperatures with biomedical applications (C. Mansfield)
- Designing processing operations for generating pipes with sufficient burst properties (J. Prefelt)

As an example we discuss the second program above concerned with the fabrication of continuously reinforced filaments using a thermotropic liquid crystalline polymer, TLCP, of higher melting point to reinforce a polymer of lower melting. TLCP's, are typically rod-like molecules based on highly aromatic polyesters or polyamides with high mechanical properties. Under extensional flow conditions, TLCP's become highly aligned leading to high modulus and strength values similar to those of carbon fiber. In this work, processing conditions were determined to design a device for blending TLCPs with a range of matrices such as ABS, a widely used polymer in Fused Filament Fabrication (FFF), PP, PET, and PPS. Rheological tests showed us the conditions at which we could combine the higher melting TLCP with the lower melting matrix to form strands reinforced with highly oriented micro-fibrils of the TLCP as shown below. Rheology was also used to establish the conditions the strands could be reprocessed without disrupting the highly oriented TLCP reinforcing fibrils.

The tensile properties of the filaments were also measured and found to reach a maximum modulus of around 20 GPa and a strength of 100 MPa at the composition of 46 wt.% TLCP in ABS. The filaments so produced can be processed in FFF below the melting point of the TLCP and above the melting point of matrix polymer, keeping the TLCP essentially solid. These filaments can also avoid nozzle clogging issues which occur at higher loading of other reinforcements, e.g. carbon fiber. The process has been extended to other polymer matrices such as polypropylene and polyphenylenesulphide (PPS). In the case of PPS, filaments with a modulus of 40 GPa and strength of 700 mPa have been generated and laid up in basic plaque geometries.

MULTISCALE DESIGN OF CARBON NANOTUBE REINFORCED PIEZOELECTRIC SENSORS AND ACTUATORS

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We first deduce values of material parameters of single-walled carbon nanotubes (CNTs) by studying their quasistatic infinitesimal deformations using molecular mechanics (MM) simulations, the freely available software, TINKER, and the MM3 potential. Subsequently, we employ a micromechanics approach to design piezoelectric sensor/actuator with CNT and piezoelectric (PZT) fibers aligned parallel to each other in an epoxy matrix. The volume fractions of the CNT and the PZT fibers are adjusted to get the desired value of the electro-mechanical coupling factor.

NATURE-INSPIRED WATER HARVESTING

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By 2025, it is expected that two-thirds of the world's population will lack sufficient access to fresh water.¹ Many natural organisms have ingenious tricks for harvesting water; here, we discuss how to mimic nature in order to invent novel and renewable methods of obtaining water. First, consider the mangrove tree, which can desalinate ocean water by virtue of its salt-excluding roots.² The large hydraulic pressure required to pump water across the root filters is achieved by the natural transpiration cycle, which generates a highly negative water pressure within the tree. By utilizing nanoporous media that mimic the tissue of mangrove leaves, it is shown that synthetic mangroves can be constructed capable of extracting and elevating water from the ground (Fig. 1a). Second, we discuss how organisms such as cacti or Bermuda grass are capable of efficiently harvesting fog from the air.³ Inspired by these plants, we design "fog harps" comprised of an array of parallel vertical wires (Fig. 1b,c), which harvest at least three times more fog compared to traditional engineered fog harvesters. Finally, desert beetles use bumpy patterns on their backs that selectively harvest water vapor from the air.⁴ We mimic this concept by laser-cutting micro-grooves along an aluminum surface, such that water selectively wicks and freezes along the grooves to keep the surrounding surface dry from dew and frost (Fig. 1d-f).

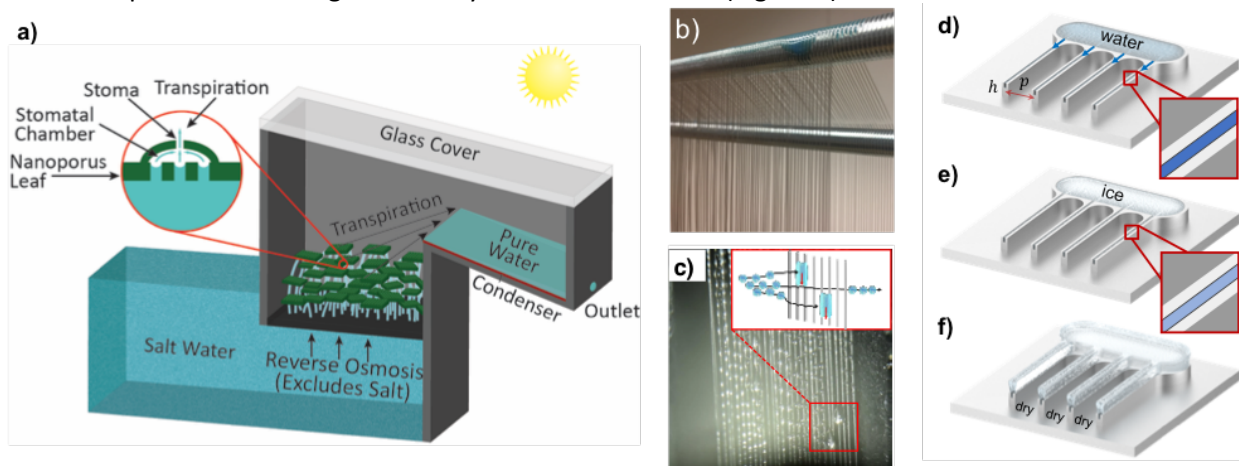


Figure 1: a) Mangrove-inspired water purification system. b,c) Cactus-inspired "fog harp", where harvesting droplets can efficiently slide down wires to a lower reservoir. d-f) Beetle-inspired anti-frosting surface, where elevated ridges harvest the ambient humidity to keep rest of surface dry from dew and frost.

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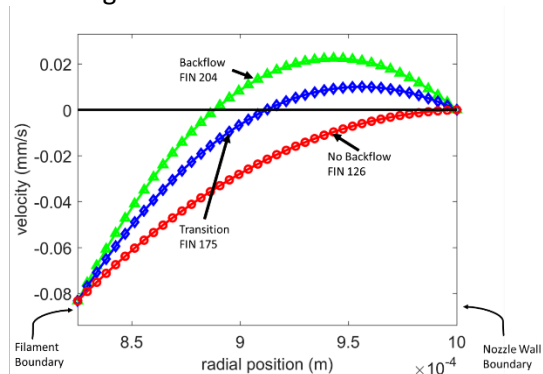
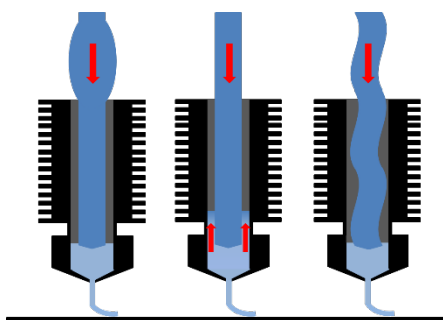
MODEL ANALYSIS OF FEEDSTOCK BEHAVIOR IN FUSED FILAMENT FABRICATION: ENABLING RAPID MATERIALS SCREENING

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Additive manufacturing (AM), a rapidly growing field, suffers from a small catalog of materials that can be successfully printed into robust geometries. A more diverse catalog is required to expand the applicability of AM to the end use market. The current methodology for the discovery of new materials is comprised of a trial and error processing tests. Since the material must be examined through multiple areas of the printing process including filament preparation, extrusion, and road deposition/interlayer bonding, the process of identifying new materials can be both time and material intensive.

To facilitate the discovery of new materials, we propose a rapid screening process to determine extrusion failure of polymer filaments in extrusion based AM as well as suggest optimal processing conditions for the polymer in Fused Filament Fabrication (FFF). The rapid screening process examines the two primary failure modes in FFF, annular backflow and filament buckling. Filament buckling was characterized using a previously developed model. Annular backflow was studied via the calculation of representative velocity profiles in the annular gap between an FFF feed block and the filament, and the subsequent normalized net flow magnitude. The characterization of the velocity profiles prompted the development of a non-dimensional number (Flow Identification Number, or FIN) that is able to predict the backflow potential of a polymeric material based on a rheological analysis and the system geometry. We empirically verified that both models accurately predict both the backflow and buckling behavior of multiple materials. From this work, we have determined that backflow potential, and by extension, extrusion failure, is most sensitive to system geometry and shear thinning behavior.



CLICKING POLYMER NETWORKS TOGETHER: APPROACHES TO FORM SMART, FUNCTIONAL POLYMER NETWORKS FROM CLICK CHEMISTRY

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A new paradigm encompassing several distinct chemical reactions and, more importantly, a generalized approach to molecular design and synthesis has been rapidly adopted in the fields of chemical synthesis, biotechnology, materials science, drug discovery, surface science, and polymer synthesis and modification. The *Click Chemistry* paradigm focuses on implementation of highly efficient reactions that achieve quantitative conversion under mild conditions. As such, these reactions represent ideal candidates for further development, understanding and implementation. In particular, the synergistic combination of these click chemistries with photochemical initiation and polymer formation has been used to afford 4D control of polymer formation, structure and patterned assembly. Here, we will focus on several vignettes related to our implementation of photoclickable polymer systems. The first of these focuses on the development of covalent adaptable networks (CANs) where the ability to controllably alter the network structure is used to alter topography and other material properties by forming materials which can be switched reversibly from elastic to plastic simply by exposure to light. Secondly, we will focus on the development of approaches to photoinitiate the Cu(I) catalyzed azide-alkyne cycloaddition (CuAAC) click reaction. Here, implementation of this reaction in surface modification, hydrogel formation, and lithography as well as in the development of a new class of photopolymerized polymer networks will be presented. Finally, we will discuss the implementation of click chemistry in the development of sequence controlled polymer structures, particularly click-based oligonucleotides that represent a novel class of DNA mimics.

TOWARD SCIENCE-BASED MANUFACTURING OF POWDER BED FUSION ADDITIVE MANUFACTURING

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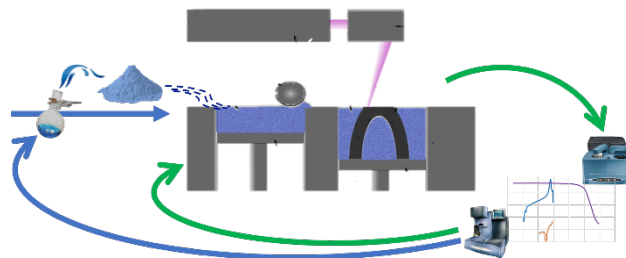
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The powder bed fusion (PBF) additive manufacturing (AM) technology exemplifies the industry-wide bottleneck caused by a lack of available materials. The technology has been around for around three decades, but close to 90% of the commercial materials market is within the polyamide family. To successfully expand the polymeric materials available for PBF the community needs to: i) understand the process physics details of the different AM processes, ii) identify the relevant polymer properties to each manufacturing process sub-function and their target ranges for successful manufacturing, and iii) synthesize polymers with fitting properties and appropriate form factor.

Currently, the PBF community relies on two primary framework interpretations of polymer thermal analysis during the material screening and manufacturing parameter selection process. These two frameworks, known as the energy melt ratio (EMR) and stable sintering region (SSR), begin to relate material properties to manufacturing parameters.^{1,2} However, they only utilize thermal properties and neglect other important property categories (e.g., optical and rheological). Part of the SSR framework states that a PBF suitable polymer should have a wide, observable separation



between the melting and recrystallization behavior when measured by differential scanning calorimetry (DSC). Poly(phenylene sulfide) (PPS) and other high performance polymers, however, do not exhibit this prescribed separation, but have been shown to be PBF printable. The current PBF guidelines were formulated by only studying polyamides, but the guidelines of the future must apply to a wider variety of polymer families.

This presentation will focus on how researchers have used a polymer science-based manufacturing approach in developing novel characterization methods and investigating how novel-to-PBF materials behave in the powder bed fusion process. We will cover the state of the art for PBF AM, before moving in depth on the next steps for improving the EMR through the inclusion of optical property measurements and selecting a synthetic strategy with powder particle feedstock in mind. The specific concerns of processing high-performance polymers, like PPS, on standard temperature PBF machines will also be addressed. We will conclude with a discussion on the universality of polymer research in PBF and future challenges to the industry as the community moves away from processing polyamides to other classes of polymeric materials.

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EVAPORATION OF POLYMER AND COLLOIDAL SOLUTIONS

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Evaporation is a ubiquitous process that plays an important role in many diverse fields including climate, environment, and industry and a frequently used tool in material fabrications. For example, controlled evaporation is used to make polymer thin films, polymeric particles, and nanocomposites,¹ and to assemble building blocks including particles into superstructures. We employ large-scale molecular dynamics simulations to study the evaporation of polymer and colloidal solutions with an explicit solvent.^{2,3} Our results show that the evaporation-induced nanoparticle assembly or dispersion (e.g, in a polymer matrix) can be controlled by tuning the evaporation rate and/or the polymer-nanoparticle interactions.² Our recent simulations show that in a drying solution suspended with a binary mixture of nanoparticles, the so called “small-on-top” stratification phenomenon can occur when the evaporation rate is high enough and the volume fraction of the smaller particles is in an appropriate window (Figure 1), consistent with the results in several recent studies.⁴⁻⁶ However, our results indicate that the solvent might develop temperature and density gradients during fast evaporation, which play an important role in controlling the distribution of the particles in the drying film. This finding calls for more studies to understand the stratification process in drying multidisperse particle suspensions. Our simulations also reveal several strategies to control the size-based stratification of particles in a drying film. Finally, our simulations of the evaporation of solutions containing charged polymer chains will be discussed.⁷

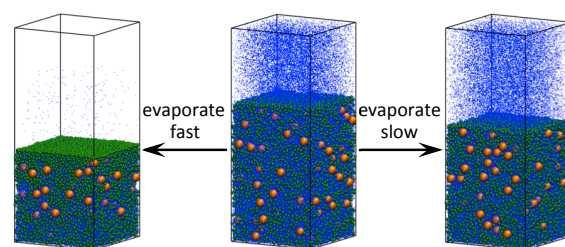


Figure 1: Distribution of polydisperse nanoparticles in a drying film depends on evaporation rate.

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MESO PROLYLENE – CO-ETHYLENE ELASTOMERS FROM EXXONMOBIL CHEMICAL

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Random propylene ethylene copolymers with predominant meso-propylene derived crystallinity with narrow composition and tacticity distributions are polyolefin elastomers. They have characteristic properties of complete and rapid recovery from tensile deformation while still being easily processed as thermoplastics. These polymers are made with a unique single site catalyst and offer a combination of properties and processing which are rare in polyolefins. They can be easily fabricated nonwoven webs, cast elastic films, multilayer structures, hot melt adhesives which are characteristic of thermoplastics yet retain the desirable elastomer properties of resilience, softness and recovery. As elastomers they can be compounded and vulcanized to rubbers with noteworthy strength. In common with other polyolefins they can form intimate physical blends with a variety of polyolefin oligomers and polymers which vastly extend the physical properties and thus utility of these polymers while still retaining most of the elastomeric properties. These unique dual attributes for a structurally precise propylene ethylene copolymer have led to the rapid commercial development of this elastomer as a replacement for thermoplastics to create elastic structures and fabrications. This large need for this unique polymer is being met by precise polymerization using advanced processes and catalysts.

CHARACTERIZING POLYMER FRICTION ANOMALIES AND REVIEWING ADHESION SCALING LAWS

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Understanding the frictional response of materials is a major and a practical topic of interest in the field of mechanical engineering. The well-known empirical Coulomb's friction law, which suggests no normal load dependence for the coefficient of friction (COF), has been successfully applied to many physical systems including metals and polymers. However, in some circumstances, Coulomb's friction law does not hold, resulting in a dependence of the COF on the normal force. In this study, the effect of normal force on the dynamic friction of two different elastomers, namely acrylic and silicone-based elastomers, was investigated. The dynamic coefficient of friction (COF) was quantified using an instrumented (with piezoelectric force sensors) pendulum setup to measure normal and friction forces exerted within the contact region between the elastomers and a macroscopically smooth poly(methyl methacrylate) (PMMA) substrate. Although both systems tended to obey Coulomb's friction law at higher loads, we found contradictory responses at very low normal forces, the COF of acrylic increased with increasing normal force, while that of the silicone decreased. The friction response of the silicone was consistent with the adhesion friction theory developed in the literature, whereas the acrylic response was the opposite of trends found in the literature.

Motivated by bio-inspired adhesive systems, a generalized scaling law for catastrophic adhesion failure has been proposed¹⁻³ suggesting that bond strength should scale with the square root of the ratio of contact area to the total system compliance ($\sqrt{A/C}$), and its validity has been successfully demonstrated for a broad range of biological and model systems. We have recently shown⁴ that this model appears to differ from the classic fracture mechanics concept, where bond strength should scale with the reciprocal square root of the derivative of the system compliance with respect to the bond area ($\sqrt{\partial A / \partial C}$). A revised generalized scaling law based on this latter approach was derived based on Volkersen's shear lag model. Experimental results suggested that the revised model agreed with the prior scaling law for very short bond lengths, when shear stresses are expected to be relatively uniform, but also accurately represented results for longer bond lengths where progressive failures occurred – a region not modeled by the original form. In this study, we continue this investigation into scaling law applicability to tensile loading of beam-like bond configurations. The flexible adherend is bonded to a rigid substrate, and modeled as a (short) beam on elastic foundation using Winkler's classic approach. Differences in predicted outcomes are presented based on the two scaling law approaches. Experimental results are anticipated to compare validity of the models.

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RENEWABLE-BASED, SELF-HEALING HYDROGELS BY SELECTIVE POLYSACCHARIDE OXIDATION

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Selective oxidation of polysaccharides has been restricted for the most part to oxidation of C-6 primary hydroxyls to carboxylic acids, forming uronic acids^{1, 2}. Oxidation of secondary alcohols to ketones is nearly unknown in polysaccharide synthetic chemistry. Yet oxidized polysaccharides have great value; for example, in our work on enhancing drug solubility and bioavailability by amorphous solid dispersion of drug in a polymer matrix^{3, 4}, we have demonstrated that carboxyl-bearing polysaccharides are frequently ideal polymers for such systems due to their pH-responsiveness and ability to participate in specific interactions with drug molecules. By creating reactive ketone moieties on polysaccharides, on the other hand, we can impart highly valuable functionality. Such functionality can include the ability to bind active molecules chemically and then release them slowly, and the ability to form valuable hydrogels.

We will describe new oxidation chemistry that permits selective creation of both carboxylic acid and ketone moieties on polysaccharides, and indicate some fascinating applications thereof, including in amorphous solid dispersion and in the preparation of benign, all-renewable, self-healing hydrogels that are promising for a wide range of biomedical and other applications.

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CREATING FILLED NANOCOMPOSITES FROM INDUSTRIALLY RELEVANT POLYMERS

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The incorporation of small amounts of high-stiffness, high-aspect-ratio nanometer-sized fillers into polymers is a design approach that has rapidly emerged as a broadly exploited framework for the creation of new materials with tailored mechanical properties. Crystalline cellulose nanocrystals (CNCs) are attracting significant interest in this context, mainly due to their intriguing mechanical properties and the abundance of cellulose in the biomass. These nanocomposites show dynamic mechanical

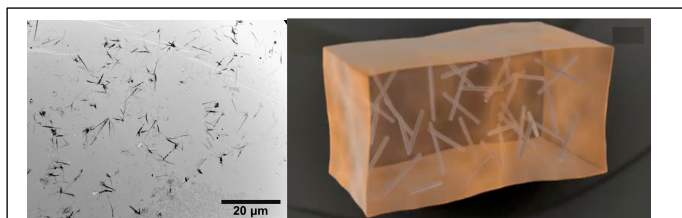


Figure: Left: showing transmission electron microscope image of a cryo-microtomed nanocomposite containing a soft polymer matrix and reinforcing cellulose nanocrystals. Right: showing a graphical representation of a polymer reinforced with rod shaped filler.

behaviour, which is achieved through regulation of the molecular interactions, and therewith the stress transfer, between adjacent nanocrystals. We will present our experimental research, targeting the design and processing of CNCs directly into industrially relevant polymers, without the use of surface functionalization. We investigated how different processing methods affect the morphology and mechanical properties of nanocomposites made from poly(vinyl acetate) (PVAc), nylon 12 or polyethylene and

cellulose nanocrystals (CNCs). Comparisons are made between traditionally made solution cast samples, and materials were post-processed by mixing in a roller blade mixer (RBM) or a twin-screw extruder (TSE) and subsequent compression molding.

HOST-GUEST TEMPLATING IN SELF-ASSEMBLY OF MACROMOLECULES

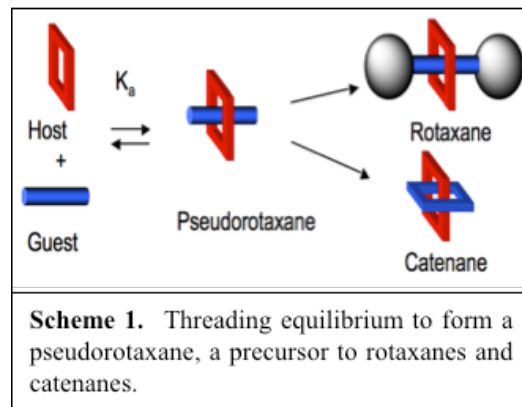
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Pseudorotaxane and rotaxane self-assembly (Scheme 1) have been used to alter and control the structures and properties of macromolecules.¹ Original efforts focused on bis(*p*-phenylene)-34-crown-10 and bis(*m*-phenylene)-32-crown-10 complexes of 4,4'-bipyridinium compounds ("paraquats" or "viologens") with association constants, K_a , of 500 to 1000 M⁻¹.²

In order to produce block, graft, brush and star polymers from host- and guest-functionalized components efficiently³ and supramolecular polymers with more than 100 pseudorotaxane linkages, high association constants ($K_a > 10^4$ M⁻¹) are required.⁴

Pyridino cryptands afford association constants in the range of 10⁴ to 10⁶ M⁻¹ with paraquats.⁵ Here we will report template-based methods for formation of the precursor crown ethers and the cryptands in high yields. In functionalized derivatives these powerful hosts enable new avenues to create supramolecular polymeric structures beginning with both functionalized polymers as well as monomeric species. These studies will be discussed along with characterization of the resultant novel materials.



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REVEALING MOLECULAR ADVERSARIES OF HUMAN HEALTH

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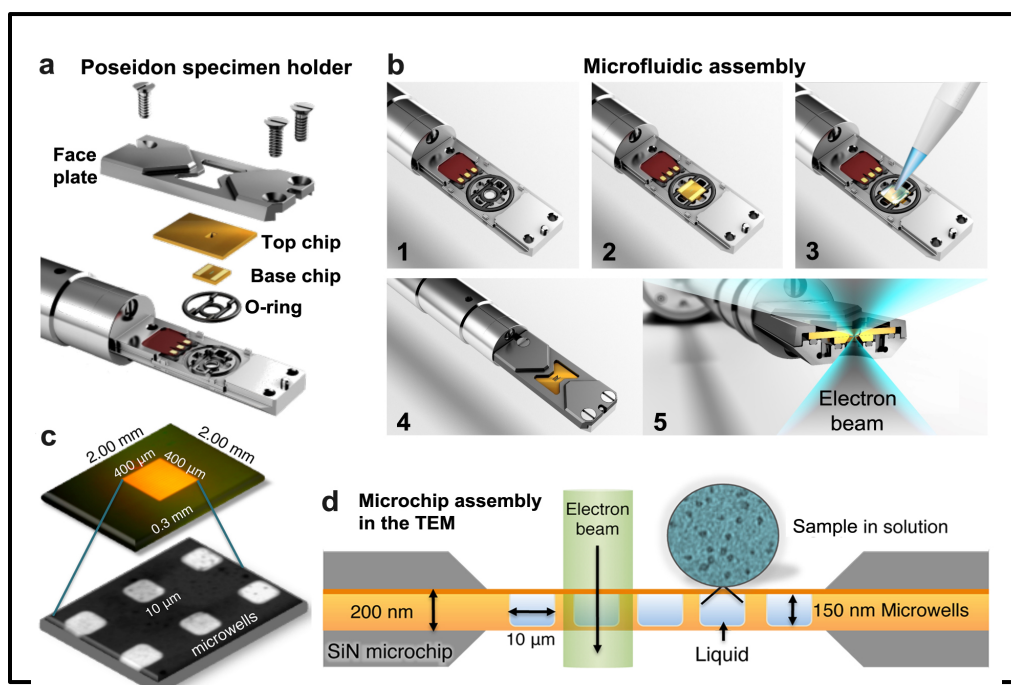
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Biomedical research improves our understanding of human health and disease through the development of new technologies. Cryo-Electron Microscopy (EM) is one technology that is transforming our view of the nanoworld—allowing us to study cells and molecules in exquisite detail. Structural information of dynamic components, however, reveals only a small part of their complex narrative. Recent advances in the production of materials such as graphene and silicon nitride provide new opportunities for EM imaging in real-time. We use these materials to create environmental chambers and perform experiments *in situ* or “inside” the EM column. Together, with microfluidic-based specimen holders, we can now view biological complexes in a native liquid environment at the nanoscale. Other recent applications of *in situ* imaging include real-time recordings of therapeutic nanoparticles interacting with brain tumor cells and changes in the molecular intricacies of viral pathogens. These results complement our cryo-EM studies on the breast cancer susceptibility protein (BRCA1) as we strive to analyse events with high spatial and temporal resolution.



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BLOCK COPOLYMER BASED POROUS CARBON FIBERS

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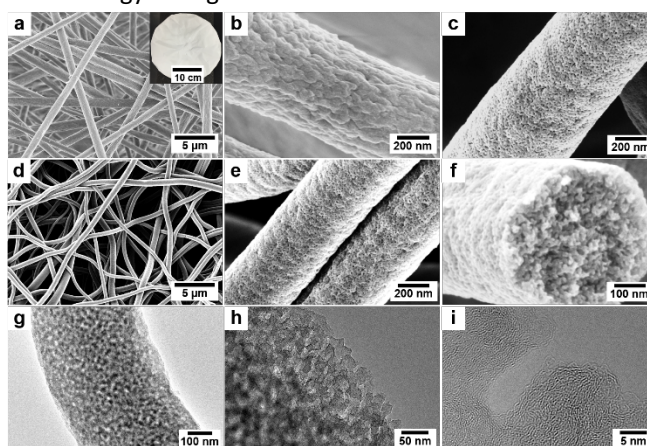
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Herein we describe a method for controlling the mesoporous nanostructures in block copolymers and their subsequently converted porous carbons. We systematically investigated the self-assembly behavior of polyacrylonitrile-block-polymethyl methacrylate (PAN-*b*-PMMA) after thermal and solvent annealing, as well as the pore size of mesoporous carbon thin films after pyrolysis. The as-spin-coated PAN-*b*-PMMA microphase-separated into globular nanostructures, and the globular nanostructures evolved into various morphologies after thermal or solvent annealing. Surprisingly, after thermal annealing and pyrolysis, the pore size and center-to-center spacing of the mesoporous carbon thin films increased significantly with the increasing annealing temperature, which differed from most block copolymers. In addition, the choice of solvent during solvent annealing strongly influenced the block copolymer nanostructures and the pore size of mesoporous carbon thin films.

Furthermore, we used the PAN-*b*-PMMA as a precursor for porous carbon fibers. Nanoporous carbon fibers possess high surface areas and rich surface functionalities for interacting with guest ions, molecules, and particulates. However, the control over the carbon fiber porosity, including pore size, pore size distribution, and pore position, has remained challenging. Conventional syntheses rely on blending polyacrylonitrile (PAN) with sacrificial additives, resulting in poorly-controlled pores due to macrophase separation. We utilize the microphase separation of poly(acrylonitrile-*block*-methyl methacrylate) (PAN-*b*-PMMA) block copolymer for synthesizing hierarchical porous carbon fibers with highly controlled mesopores (~9.3 nm) and micropores (~0.5 nm). Without infiltrating any additional carbon precursors or dopants, PAN-*b*-PMMA is directly converted to nitrogen and oxygen-doped porous carbon fibers. Owing to the highly optimized bimodal pores, interconnected diffusion network, and chemical composition, the block copolymer-based carbon fibers exhibit significantly reduced ion transport resistances and an ultrahigh surface-area normalized capacitance of $66 \mu\text{F cm}^{-2}$ (6.6 times that of activated carbon) as binder-free, conductive-additive-free electrodes in supercapacitors. The approach of utilizing block copolymers as a new precursor revolutionizes the fabrication of porous carbon fibers. In addition to the well-known mechanical strength, the significantly advanced electrochemical properties signify that the hierarchical porous carbon fibers represent an outstanding new platform material for electrochemical energy storage.



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PROBING NANOSCALE RESPONSES OF IONIC POLYMERS TO APPLIED ELECTRIC FIELDS

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The response of ionic polymers to an applied electric field is of significant interest to a variety of areas including energy storage, biomedical and industrial applications, as well as microelectronics. In order to better design electroresponsive polymeric systems, a more detailed understanding of how nanoscale interactions contribute to electromechanical responses is needed. The rational synthesis of electroresponsive polymers has the potential to achieve targeted responses by tuning conductivity, backbone rigidity, degree of deformation, or response times all through molecular design. This talk will detail the response of imidazolium based cationic diblock copolymer thin films containing either tetrafluoroborate (BF_4) or a bromide (Br) counter ions to an applied electric field. In situ neutron reflectometry measurements performed under applied electric fields provided nanoscale resolution of field-induced changes and showed that BF_4 counter ions drive film contraction while the films containing the same diblock copolymer with bromide counter ions exhibited film expansion under almost identical electric field strengths. Coarse-grained molecular dynamics simulations were used to develop a fundamental understanding of these responses and revealed a non-monotonic trend in film thickness change as a function of the electric field strength. The changes in the film thicknesses can be described as elastic responses of diblock copolymer chains to variations in interfacial tension of the polymeric interfaces, and the variations arise from the redistribution of counter ions in response to the applied electric field. The convergence of neutron reflectometry and computations at the nanoscale provide new insights into the important role counter ions can play in tuning the responses of ionic block copolymers to applied electric fields.

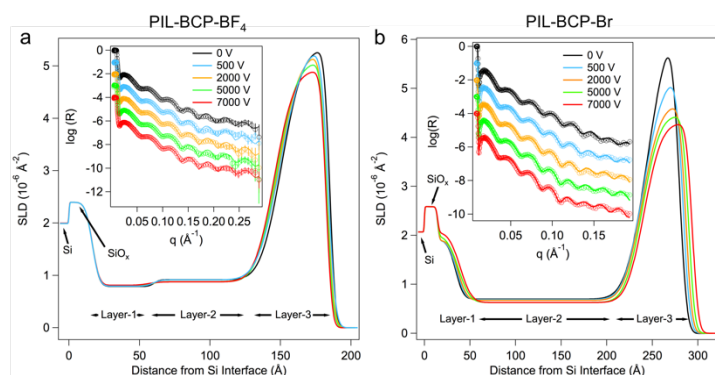


Figure 1 | Scattering length density (SLD) depth profiles. Profiles showing the SLD as a function of distance from the Si surface for the ionic diblock copolymers (PIL-BCP), PIL-BCP- BF_4 (**a**) and PIL-BCP-Br (**b**) systems at various applied potentials. The insets show reflectivity data (open symbols) and fits (solid lines). Reflectivity data and fits are offset for clarity

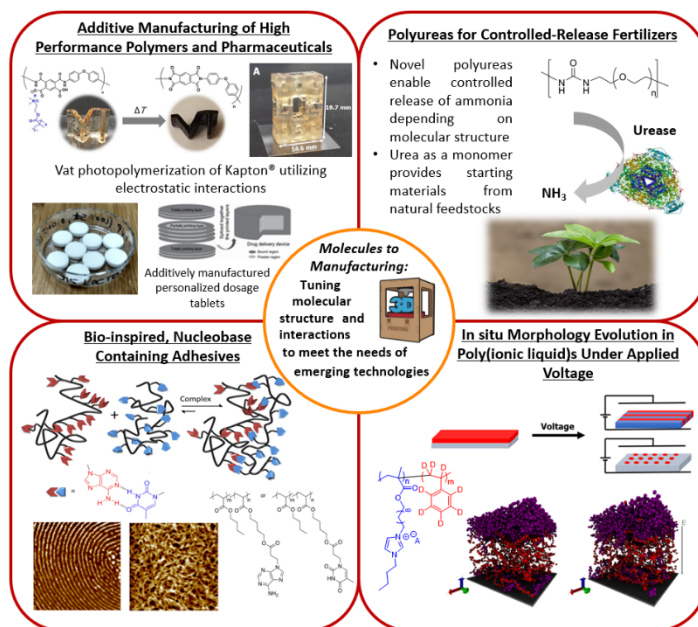
The Center for Nanophase Materials Sciences (CNMS) at Oak Ridge National Laboratory (ORNL) is one of five Department of Energy (DOE) Nanoscale Science Research Centers (NSRCs). The primary mission of the CNMS is to provide access to state-of-the-art nanoscience research capabilities, expertise, and equipment to a diverse user community in order to deliver cutting-edge nanoscience research that otherwise would not be possible. The scientists at the CNMS also drive a world class science program with emphasis in theory and simulation, nanofabrication, macromolecular synthesis and characterization, and understanding of structure, dynamics and functionality in nanostructured materials using scanning probe microscopy, neutron scattering, optical spectroscopy, and soft-matter electron and helium ion microscopy.

SPEAKING MANY LANGUAGES: A SYNERGY OF MOLECULAR STRUCTURE AND ADVANCED MANUFACTURING FOR EMERGING TECHNOLOGIES

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Our research group investigates structure-property-morphology-processing relationships of polymers, ranging from high performance thermoplastics and thermosets to biologically-derived/inspired macromolecules. In particular, the group focuses on the effect of noncovalent interactions on polymer properties, including hydrogen bonding and ionic aggregation. The design, performance, and societal implication of novel polymeric materials direct our research platforms, which focus on the following impactful technologies: (1) new materials for advanced manufacturing, (2) bio-inspired thermoplastics, (3) adhesive technology, and (4) charged polymers for actuators. Polymers featuring tailored monomer sequence and architecture afford microphase-separated structures that drive the performance of adhesives and 3D printing technology. Biologically derived monomers such as urea afford bio-degradable thermoplastics which release significant levels of ammonia. Alternatively, nucleobase-containing polymers afford sequence-controlled adhesives and microphase-separated morphologies. 3D printing platforms enable controlled polymer placement, enabling unprecedented architectures and part geometries. This lecture will highlight synthetic methods for unprecedented processing of polyimides and development of time-controlled dissolvable poly(ethylene glycol) (PEG)-based constructs. Lastly, structure-property relationship development of high-performance polymers such as polyesters, polysulfones, and polyimides offers opportunities to enhance processing, gas barrier, thermal stability, and mechanical properties.



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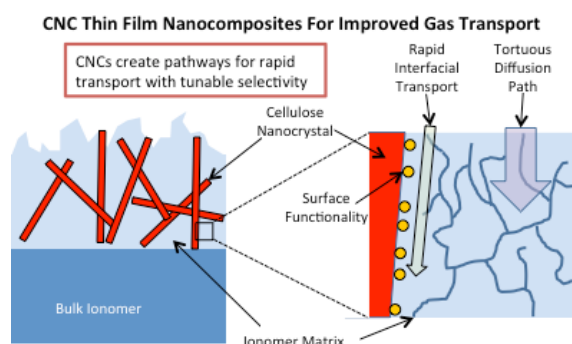
ADVANCED COMPOSITE MEMBRANES BASED ON HIGH-ASPECT RATIO NANOPARTICLES

Stephen M. Martin*

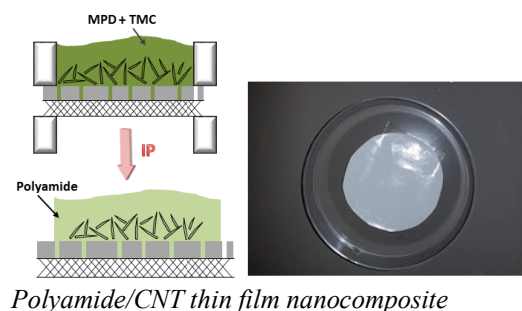
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Membrane separations are of significant interest due to their low energy requirements and ease of scalability. Our group is interested in using functional polymers and polymer nanocomposites to create novel membrane separation materials, including polymer membranes for gas phase separations (e.g. olefin/paraffin, CO₂) and porous and nanocomposite membranes for liquid phase separations (e.g. water desalination.) In this talk, I will discuss ongoing efforts in our group focused on using high-aspect ratio nanoparticles to create channels for rapid solute transport and impart desired functionality to membranes for water desalination.

Cost-effective purification and desalination of water is a global challenge. Reverse osmosis (RO), the current method of choice, is a membrane-based semipermeable process that separates salts from water, and it is limited by the intrinsic properties of the membranes used in the process. Biofilm fouling on the surface of the membranes is another critical problem in RO applications. We have utilized zwitterion functionalized carbon nanotubes (CNTs) incorporated in polyamide thin film composite membranes to improve membrane permselectivity and surface biofouling resistance for water desalination. The permeation flux was found to increase by approximately three-fold as the fraction of CNTs was increased from 0 to 20 wt% for all the salt solutions tested in our study. The steric hindrance to transport due to the zwitterionic functional groups prevents the permeation of the majority of ions through the CNT pores resulting in high salt rejection. The zwitterionic functionality also leads to decreased biofouling of the membrane.



Due to the high cost of CNTs, other nanoparticle additives are being explored as alternatives. Cellulose nanocrystals (CNCs) are of interest due to their lower cost and availability as well as their potential for functionalization. Results have shown that TEMPO-oxidized CNCs may increase the flux of the membranes by up to 40% while maintaining a reasonable salt rejection, prompting further study of CNCs as a thin film composite membrane additive. Finally, ongoing work is also focused on the inclusion of high-aspect ratio metal-organic framework (MOF) nanoparticles with tunable porosity, allowing multiple transport pathways (inside and outside the particles) to be exploited.



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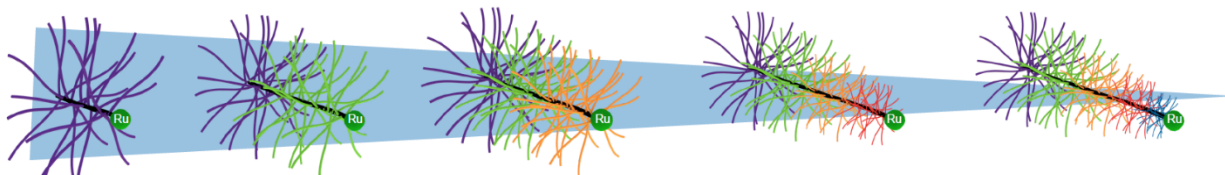
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TAPERED BOTTLEBRUSH POLYMERS: A NEW POLYMER ARCHITECTURE

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A new class of polymer topology termed tapered bottlebrush polymers will be discussed here. Traditional bottlebrush polymers are comprised of a linear polymer backbone with densely grafted side chain polymers of a single molecular weight. Tapered bottlebrush polymers are comprised of side chain polymers of systematically varied molecular weights, with side chain molecular weights ranging from 1–10 kg/mol. The synthetic method used to produce these polymers is termed sequential addition of macromonomers ring-opening metathesis polymerization (SAM-ROMP) and involves the addition of low dispersity macromonomers of varying molecular weights to a single living polymer chain. Synthetic methods and unique properties of these polymers will be discussed.



Schematic illustration of SAM-ROMP methodology.

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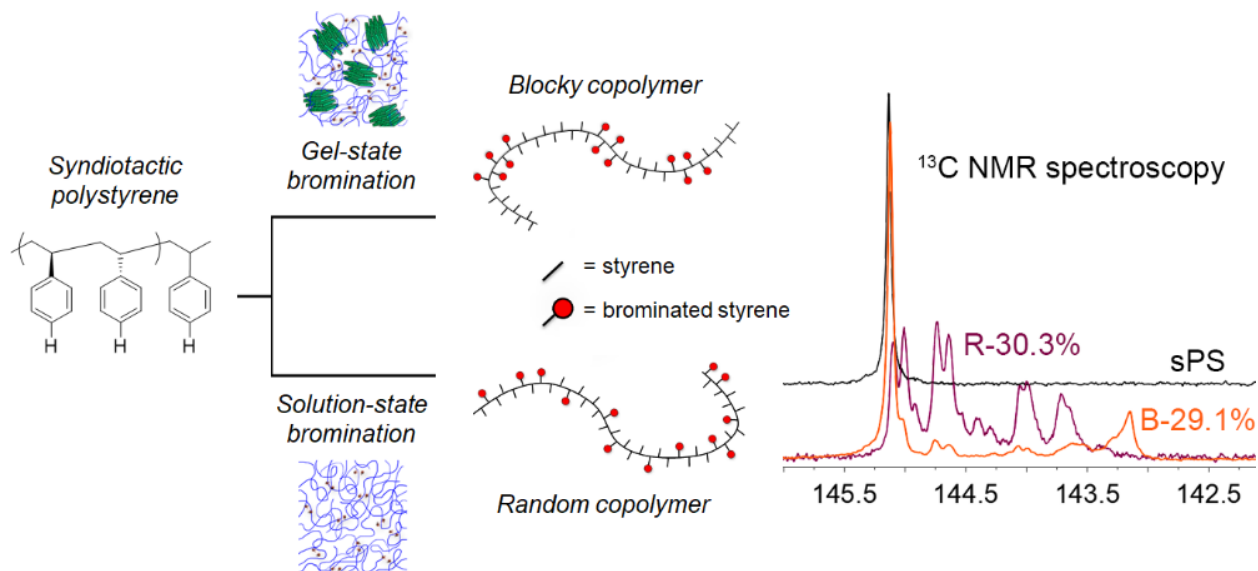
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BLOCKY FUNCTIONALIZATION OF THERMO-REVERSIBLE sPS AND PEEK GELS

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Recent findings from the ion-containing polymer membrane community have taught us the importance of controlled sequencing of ionic groups along polymer chains in the development of ordered polar domains for enhanced transport properties. When compared on an equal ion content basis, a blocked arrangement of ionic groups along polymer chains tends to produce more ordered nano-phase-separated domains while preserving the inherent properties of the unfunctionalized homopolymer over that of analogous random ionomers. Inspired by these demonstrated enhancements, we are exploring the impact of variable post-polymerization sulfonation and bromination reactions on the spatial distribution of functional groups in blocky copolymers. Very recently, we have discovered a non-functionalizing solvent for PEEK that allows for a homogeneous sulfonation reaction. Surprisingly, this new solvent also allows for the formation of a thermo-reversible gel. Following a method we previously developed to sulfonate syndiotactic polystyrene (sPS) in the gel state, we are now able to prepare a blocky form of sulfonated and brominated PEEK that has a high degree of functionalization and a high degree of crystallinity. A broader impact of this research involves the first development of PEEK hydrogels and aerogels with remarkable physical properties.



DESIGNING POLYMERS TO IMPROVE DISEASE TREATMENTS

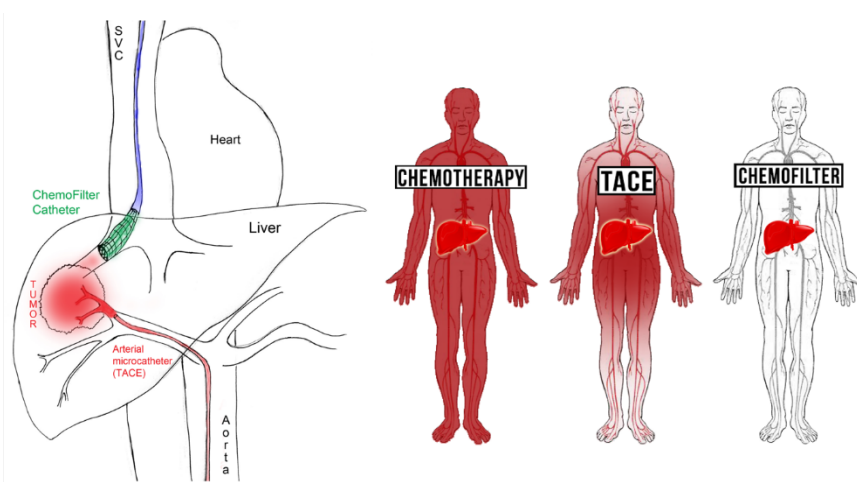
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At the interface between chemistry and medicine, the synthetic tools of polymer chemistry can be leveraged to overcome problems that arise in the clinic. In this talk, I will present a collection of vignettes that illustrate the application of a polymer chemistry-based approach to contemporary medical challenges.

In the first part I will discuss our recent work on developing materials capable of capturing chemotherapy agents from the bloodstream. The adverse side-effects of chemotherapy are a notorious problem in the treatment of cancer. One approach to mitigating this off-target damage, particularly in liver cancer, involves directly administering the chemotherapeutic agent to the tumor site via catheter, a procedure known as transarterial chemoembolization (TACE); however, excess drug still enters systemic circulation, leading to adverse side-effects.

We are developing a device, a “ChemoFilter”, that can be deployed downstream from the site of administration in order to capture this excess drug before it enters systemic circulation and causes off-target damage. Our initial studies explore methods of attaching genomic DNA to surfaces and evaluating the efficacy of the resulting materials at binding to doxorubicin, a common chemotherapeutic, in biologically relevant solutions.



Subsequently, I will give a brief overview of our work exploring antiviral polymers and elucidating the structure-property relationship between polymer architecture and viral inhibition. I will also describe our efforts to develop resins capable of sequestering toxins produced by *Clostridium difficile* in the large intestine. Each of these stories illustrates the value of bringing a chemical perspective to overcoming medical challenges.

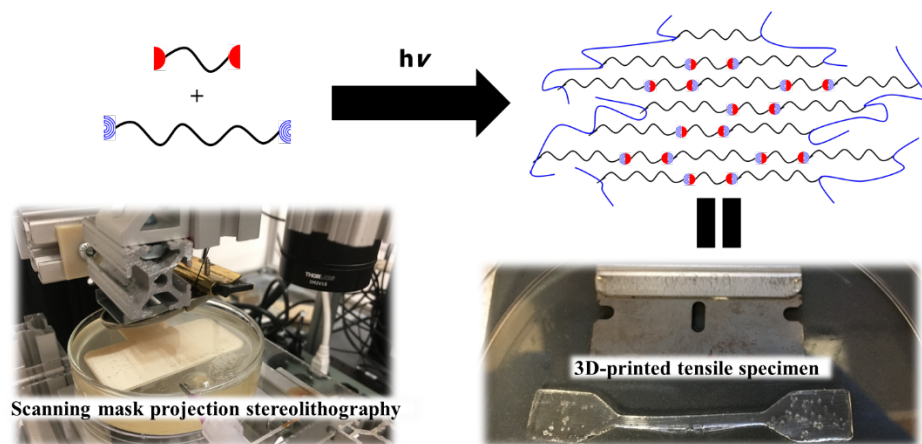
The ChemoFilter concept: Chemotherapy agents leaving the tumor are intercepted before entering systemic circulation, thus confining the toxicity to the target organ.

PHOTO-ACTIVATED, SIMULTANEOUS CHAIN EXTENSION AND CROSSLINKING FOR LITHOGRAPHIC 3D PRINTING OF SILOXANES

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Vat Photopolymerization (VPP) is a type of additive manufacturing (AM) or three-dimensional (3D) printing where a UV-curable liquid oligomer or polymer is photocured in a layer-by-layer fashion, producing a 3D object. Conventional photopolymer compositions ideally possess low viscosity and typically contain oligomeric or monomeric species. Photo-initiated crosslinking of these species often results in the formation of a brittle or rigid object, in part due to accompanying low molecular weight between crosslinks (M_c). The 3D fabrication of flexible and/or elastic objects requires high M_c , which carries a concomitant increase in the precursor photopolymer viscosity, resulting in prohibitively high layer recoat and print times. In this work, a novel, low viscosity, hybrid polydimethylsiloxane (PDMS) thiol-ene and conventional free radical photopolymer system is evaluated for simultaneous molecular weight growth and crosslinking upon UV irradiation. A model compound competition study with proton nuclear magnetic resonance (^1H NMR) spectroscopy confirmed that the thiol-ene chain extension product was preferred to polyacrylamide formation. Photorheology examined the gelation kinetics as a function of UV irradiation time and demonstrated adequate spatiotemporal control required for VPP. Preliminary 3D printing with VPP demonstrated adequate print speeds and high print resolution. Dynamic mechanical analysis (DMA) and tensile testing probed mechanical properties as a function of stoichiometry, revealing decreased plateau moduli and increased tensile strain at break with increasing levels of chain extension. This hybrid photopolymer system enables the fabrication of flexible and elastic objects without the use of co-solvents, reactive diluents, or heating of the photopolymer vat, preventing issues of shrinkage and low gel fraction associated with these other systems.



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SUPRAMOLECULAR POLYMERS AND THEIR INTEGRATION WITH COVALENT POLYMERS

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Supramolecular polymers with their energy-tunable noncovalent bonds among structural units have inherent potential as materials that are, reversibly responsive to external stimuli, highly dynamic, adaptable to environments, self-healing, or capable of integrating synergistic functions through weak interactions. The possibility of programming interactions in these systems through self-assembly also provides a good platform to design reversible hierarchical structures with novel physical properties. On the other hand, covalent polymers with their rich array of known architectures form mechanically robust soft materials but only with limited capacity to generate long range order and reversible short time scale dynamics. The integration of covalent and supramolecular polymers thus offers potential to design synthetic soft materials in which order, dynamics, and mechanics are optimized for novel functions. This lecture will provide examples of supramolecular polymers and also of systems that integrate these polymers with covalent macromolecules.

ADVANCED MANUFACTURING OF CERAMICS FOR EXTREME APPLICATIONS

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Hypersonic aircrafts and other extreme applications rely on the usage of Ultra High Temperature Ceramics (UHTCs) key components with a complex geometry and a variety of microstructures (dense, porous, composite, laminates, etc.) to target strategic properties (thermomechanical behavior, conductivity or oxidation resistance) that ensure their desired performance. The current state-of-the-art processing of these UHTCs relies on hot pressing to guarantee the densification at high temperatures, but the shaping capability and the versatility of the microstructure obtained remains a challenge. Near-Net-Shaping Techniques involving the colloidal processing of

UHTC powders can render near-net-shaped pieces, that can be sintered under pressureless conditions, with a range of microstructures.

This work will discuss how the colloidal processing approach for UHTCs can be employed for their manufacturing, by the



Figure 1. Examples of UHTCs components prepared by slip casting, freeze casting and gelcasting, and some of the combined microstructures that can be generated by colloidal processing

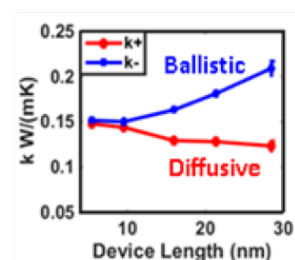
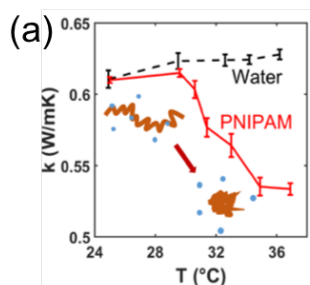
smart choice of suitable organic solvents, dispersants molecules and polymeric aids. In this approach, ceramic particles are suspended and dispersed in a solvent by a suitable stabilization mechanism (electric double layer, steric, electrosteric, depletion) to control the interparticle forces between ceramic particles and break powder agglomerates that can lead to defects and flaws. The ceramic suspensions are then shaped into a component using suitable consolidation techniques, and sintered to densify the particles into a final piece. This presentation will focus on two cases studies: i) new cost-effective manufacturing approaches for leading edges, using three consolidation mechanisms (filtration, freezing and chemical gelation) and, ii) the design of highly porous multi-scale porous materials for insulation packages and active cooling components, using polymeric sacrificial fillers with different sizes and morphologies. The promising results open the path to use this approaches in the next generation of advanced and additive manufacturing technologies and multi-material compositions.

THERMAL SWITCHING AND RECTIFICATION IN POLYMERS

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Could we control and manipulate heat just like electrons to have desired current flow on demand? This way we would have a full control of thermal energy flow for thermal engineering and energy utilization. To achieve this, the key is to discover and design functional thermal components that are analogous to electronic diodes and switches. Instead of the traditional approaches, we have been seeking answers to heat manipulations in polymers, a completely new territory to search for thermal diodes and switches. We demonstrated the unique thermal switching and rectification capability of polymers. For thermal switches, we take advantage of a second-order phase transition to achieve fast thermal conductivity change in thermoresponsive polymers. For thermal rectification, we discovered unusual and significant thermal rectification in a Christmas-tree-like macromolecule. Our work laid the groundwork for organic thermal switches and diodes, and can greatly impact dynamic building and space insulation, switchable thermal storage, smart textiles, and thermal computing.



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STEREOSELECTIVE PHOTOREDOX RING-OPENING POLYMERIZATION OF RACEMIC O-CARBOXYANHYDRIDES

Rong Tong,* and Quanyou Feng

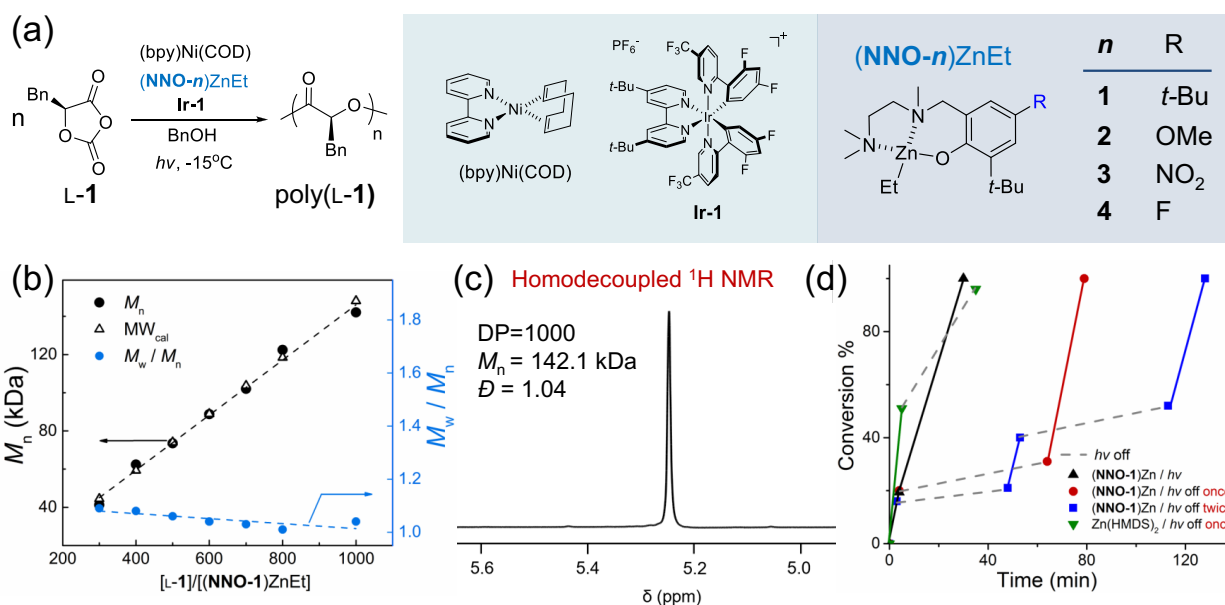
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Biodegradable polyesters with various tacticities have been synthesized by means of stereoselective ring-opening polymerization of racemic lactide and β -lactones but with limited side-chain groups. However, stereoselective synthesis of functional polyesters remains challenging from *O*-carboxyanhydrides that have abundant pendant side-chain functional groups. Herein we report a powerful strategy to synthesize stereoblock polyesters by stereoselective ring-opening polymerization of racemic *O*-carboxyanhydrides with the use of photoredox Ni / Ir catalysts and a selected Zn complex with an achiral ligand. The obtained stereoblock copolymers are highly isotactic with high molecular weights (>70 kDa) and narrow molecular weight distributions ($M_w/M_n < 1.1$), and they display distinct melting temperatures that are similar to their stereocomplex counterparts. Furthermore, in one-pot photoredox copolymerization of two different *O*-carboxyanhydrides, the use of such Zn complex mediates kinetic resolution of the co-monomers during enchainment and shows a chirality preference that allows for the synthesis of gradient copolymers. These results are significant because they offer new routes to polyesters with pendant side-chain functionalities and various microstructures, which could in turn result in the preparation of polymers with new physiochemical properties suitable for a wide range of applications.



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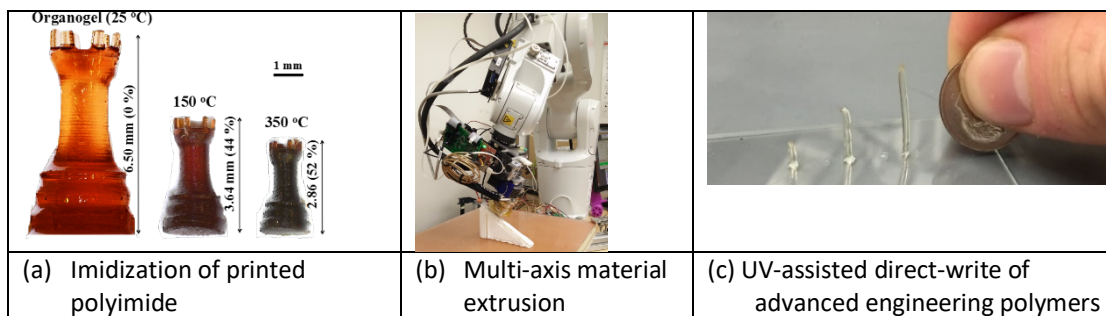
MOLECULES TO MANUFACTURING: CONCURRENT DESIGN OF PROCESSES AND MATERIALS

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Additive manufacturing (AM, also referred to as “3D Printing”) continues to be of significant interest due to its ability to (i) produce parts with complex, personalized geometries, (ii) provide democratized access to manufacturing, (iii) provide a means for deployable, on-site, and just-in-time fabrication, and (iv) fabricate components with tailored properties for application-specific use. However, the technologies’ adoption continues to be hindered due to a relatively limited selection of working materials. This limitation is due in part to industry-led efforts to apply existing materials, which were designed for traditional processing technologies (e.g., injection molding, casting, etc.), to these new technologies. In addition, there is a lack of fundamental understanding as to what intrinsic material properties define its “printability.”

In order to address this critical gap, MII scientists and engineers are conducting collaborative research within a “Molecules to Manufacturing” framework, in which polymeric materials are designed concurrently with advances in AM processing. Through this concurrent design, MII researchers have made new materials discoveries and contributions to the fundamental understanding of what defines a material’s printability. In this talk, some of these discoveries will be discussed, with emphasis placed on (i) new AM process capabilities that effectively expand the available chemistry that can be leveraged in AM, and (ii) the resultant redefined AM materials design guidelines.



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FABRICATING THE FUTURE OF MATERIAL WITH LIGHT IN ADDITIVE MANUFACTURING

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Additive manufacturing liberates the design space of objects through the creation of three-dimensional objects without the limitations of conventional injection molding. Although additive manufacturing was developed in the 1980s, polymeric materials used in this field has been largely limited to acrylate-based material used mainly in prototyping applications. However, in order to consider the additive manufacturing process in production cases, the materials currently available will need to be reimagined and redesigned with exceptional properties. At Carbon, engineering resins are produced for end-use applications to improve efficiency of the manufacturing process. This talk focuses on the Carbon-Adidas partnership that led to the creation of a 3D printed midsole that represents a breakthrough example of additive manufacturing in production. In elastomeric lattices, the overall final mechanical property is a combination of the bulk material properties and the geometric structure. Material science and computation are utilized to predict and explore these final lattice properties. As manufacturing continues to adopt the additive process, new opportunities in polymeric materials emerge for personalization and customization of products.

ACHIEVING MORE WITH LESS: ADDITIVE MANUFACTURING OF MULTI-FUNCTIONAL 3D ARCHITECTED METAMATERIALS

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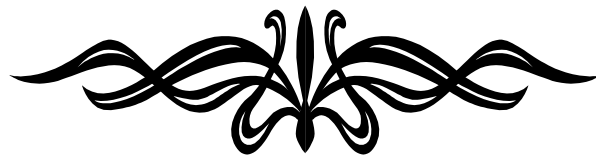
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Our knowledge of a material's property has been prescribed by its existing chemical composition and spatial arrangement of constituent elements inherent within. This fundamentally limits our desirable material property space when selecting materials for specific applications. For example, few solid materials exist considerably lighter than water. To decrease the density beyond this point, materials must have a porosity, which comes at the cost of a disproportional degradation of other desirable properties.

In this talk, we create a new class of materials with combinations of previously unachievable properties: 3D architected metamaterials. They utilize interconnected 3D hierarchical micro-structures and typologies, rather than relying on chemistry alone, to greatly expand the performance of a material. I will discuss a suite of scalable additive manufacturing technologies to enable fast manufacture of these ultralight metamaterials created with functional material feedstocks including polymer, metallic, ceramics and combinations thereof. Attention is focused on how rapid prototyping techniques are being evolved into a suite of novel manufacturing processes capable of creating traditionally unprocessable material building blocks, and proliferating them into macroscopic dimensions with hierarchical 3D features spanning from tens of nanometers, to micrometers, centimeters and above.

Next, we examine the potential to introduce designed-in attributes from disparate physical property space into metamaterials. These attributes include flexibility, fracture and high temperature resistance, sensing and actuation, which could transform our ability to design and tailor new properties and functionalities out of simple building block.

POSTER SESSION SCHEDULES



POSTER SESSION SCHEDULES

MONDAY – APRIL 16, 2018

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M	Alaboalirat, Mohammed	2	Synthesis and Characterization of Amphiphilic Bottlebrush Block Copolymers	J. Matson
M	Anderegg, David	3	In-Situ Monitoring of Extrusion Based Additive Manufacturing	M. Bortner
M	Baah-Dwomoh, Adwoa	7	Mechanical Analysis of the Uterosacral Ligament: Swine vs Human	R. De Vita
M	Bass, Lindsey	8	Tailored Fracture Energies at Multi-Material Interfaces of Material Jetting Parts	C. Williams
M	Blosch, Sarah E.	9	Effect of Ion Concentration on the Properties of Polyisoprene-Sodium Styrene Sulfonate Elastomeric Ionomers Prepared by Emulsion Polymerization	J. Matson
M	Cao, Ke	14	Tailoring the Tensile and Optical Properties of Telechelic Poly(Ether Imide)S by the End Groups	G. Liu
M	Chan, Kathleen J.	15	Alternative Methodology for Characterizing Tool-Ply Friction of Unidirectional Carbon Fiber Epoxy Prepregs at Various Processing Conditions	M. Bortner
M	Chartrain, Nicholas A.	16	Effects of Pore Size in 3D Printed Tissue Scaffolds on Mouse Fibroblast Proliferation	A. Whittington
M	Chatham, Camden A.	17	Material Extrusion Additive Manufacturing of Semi-Crystalline Poly(Ethylene Terephthalate) via Blending with Polypropylene	C. Williams
M	Chen, Hongyu	18	Modeling of Microstructure and Elastic Properties in Long-Fiber Injection-Molded Thermoplastics	D. Baird
M	Chen, Mingtao	20	Counter-Ion Effect on Radical Polymerization Kinetics of Ionic-Liquid Monomers	T. Long
M	Chen, Xi	23	Cytosine and Ureido-Cytosine Acrylic ABA Triblock Copolymers: Mechanical and Morphological Correlations	T. Long
M	Das, Arit	27	Crystallinity, Morphology and Thermal Properties of Blends of Polypropylene/Hydrocarbon Resin for Additive Manufacturing	M. Bortner
M	Dayal, Shreya	28	Self-Assembly of Actin-Like Filaments	S. Sheng
M	Fallon, Jacob J.	32	Influence of Processing on Additively Manufactured Mechanically Adaptive Cellulose Nanocrystal Polymer Composites	M. Bortner
M	Felice, Kristen	33	Evaluating Co-monomer Sequence Distribution in Brominated Syndiotactic Polystyrene Copolymers using ¹³ C NMR Spectroscopy	R. Moore

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M	Kasprzak, Christopher R.	50	Synthesis Of Poly(Phosphorus Ylide)s as Efficient Light Absorption Dyes	T. Long
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M	Kenaway, Hagar	53	Rolled Pcl/GelMA Composites as Scaffolds for Acl repair	A. Goldstein
M	Khan, Assad	54	Plasmonic Nanoparticles Sensitivity and Their Applications in Plasmonic Nanocomposites	G. Liu
M	Lambert, Gregory	58	Influence of Fiber Concentration on Fiber Orientation Evolution During Nonlubricated Squeeze Flow of Glass-Fiber-Reinforced Polypropylene	D. Baird
M	Liu, Jianzhao	60	Adsorption of Cationic Cellulose Derivatives onto a SAM-COOH Surface	A. Esker
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M	Nichols, Brittany	69	Amphiphilic Polysaccharide Schiff Base Delivery Vehicles for Controlled Release of Biologically Active Compounds	K. Edgar

Day	Author	Poster No.	Title	Advisor
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M	Sirrine, Justin M.	88	Melt-Stable Polyamides for Selective Laser Sintering Applications	T. Long
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M	Yang, Jier	107	Replacing Glass Fibers with Cellulosic Fibers While Enhancing the Bio-Composites' Mechanical Properties	D. Baird
M	Zanelotti, Curt J.	109	Battery Applications Utilizing a Tunable Stiff Solid Made from an Ionic Liquid and a Rigid-Rod Polyanion	L. Madsen

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TUESDAY – APRIL 17, 2018

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T	Arrington, Clay	5	Synthesis and Characterization of High Performance Polymers for Vat Photopolymerization: Polyamic Diacrylate Ester of PMDA-ODA	T. Long
T	Arrington, Kyle J.	6	Compatibilization of Polyolefins and Polysaccharides: Improving Properties of Sustainable Polymers	J. Matson
T	Bonnett, Brittany	10	Tunable Synthesis and Post-Synthesis Modification of a Porphyrinic Zirconium Metal-Organic Framework for Reverse Osmosis Membranes	A. Morris
T	Boyce, Kennedy	11	Predicting Stiffness of Injection Molded Long Fiber Reinforced Polymers	D. Baird
T	Brown, Chanelle	12	Design and Synthesis of Substituted Stilbene-Alt-Maleic Acid Copolymers with Fluorescence Properties	S. Turner
T	Burtner, Matthew	13	Mechanical Testing of Sulfonated Poly(Arylene Ether Sulfone) Random Copolymers for Water Electrolysis Applications	J. Lesko
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T	Chen, Mingtao	21	Block Copolymers Containing Pyridinium and Urea: A Unique Example of Charged Hydrogen Bonding Materials	T. Long
T	Chen, Tianran	22	Reuse And Recycling Of TLCP Reinforced Composites	D. Baird
T	Chen, Xi	24	Doubly-Charged Triblock Copolymers for Enhanced Physical Property and Self-Assembly	T. Long
T	Choudhury, Shreya R.	25	Structure-Property Relationships of Post Sulfonated Poly(Arylene Ether Sulfone) Membranes for Water Desalination	J. Riffle
T	Cornell, Hannah D.	26	Synthesis of Photodegradable Nano-Cages for Drug Delivery	A. Morris
T	DeButts, Barbara L.	29	Zinc Oxide (ZnO)-Free Synthetic Isoprene Rubber Vulcanizates Using Wheat Protein as an Activator	J. Barone
T	Donaldson, Kandace	30	Mechanical Properties of Rat Uterosacral Ligament	R. De Vita
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T	Frost, Brody	34	Polyurethane Composites for Annulus Fibrosus Scaffolds for the Correction of Disc Degeneration	E. Foster
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T	Hendren, Keith D.	45	Cellulose Nanocrystal Polyethylene Composites Mediated by Covalent Metallocene Attachment and Heterogeneous Polymerization	E. Foster
T	Herzberger, Jana	46	High Performance Polymers for Additive Manufacturing: 3d Printing of Kapton®	T. Long
T	Joseph, R. M.	48	A Comparison Between Two Post-Modification Approaches for Polybenzimidazoles with Improved Gas Permeability	J. Riffle
T	Ju, Lin	49	Phosphonated Poly(Ethylene Terephthalate) Ionomers as Compatibilizers in Polyester/Polyamide Blends for Packaging Applications	R. Moore
T	Kletetschka, Karel	55	3D Printed Flow Cells for Real-Time Geochemical Investigation of Ferric Hydroxyl-Sulfate Formation	F. Michel
T	Korovich, Andrew	56	Probing Multi-Scale Transport in Random Copolymer Membranes using NMR Diffusometry	L. Madsen
T	Kubalak, Joseph R.	57	Improving Mechanical Performance of Material Extrusion Parts using Multi-Axis Surface Reinforcement	C. Williams
T	Li, Xiuli	59	Investigating Block Copolymer Micelle Dynamics and Molecular Partitioning for Tunable Cargo Delivery	L. Madsen
T	Liu, Wei	61	Valorization of Hemicellulose Hydrolyzates into Eco-Friendly Surfactants	M. Roman
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T	Mukherjee, Ranit	67	Oil-Impregnated Hydrocarbon-Based Polymer Films	J. Boreyko
T	Murphy, Kevin	68	Droplet Bridging into Porous Media	J. Boreyko
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T	Rogers, Christian D.	81	The Effect of Carbon Fiber Characteristics on Ionic Polymer Carbon Composite Actuator Performance	R. Moore
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Day	Author	Poster No.	Title	Advisor
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T	Shi, Weiwei	86	Transpiration-Powered Pumps Using the Synthetic Tree	J. Boreyko
T	Smith, Ethan D.	89	Interfacial Transport in Nanocellulose-Based Nanocomposite Membranes for Improved Reverse Osmosis Performance	S. Martin
T	Stinson-Bagby, Kelly	90	Conductive Cellulose Nanocrystal For Transparent Films	E. Foster
T	Tian, Chixia	94	Designing Polymer Electrolytes Toward all Solid-State Lithium Batteries	T. Long
T	Titus-Glover, Kyle	95	A Molecular Dynamics Simulation Study of Interactions Between Sulfonated Polysulfone-Based Polymers and Water Molecules	J. Lesko
T	Venkatraman, Priya	96	A Novel Fabrication Technique of Electrospun Fiber Reinforced Gels	E. Foster
T	Vincent, Matthew	97	Investigation of the Isothermal and Non-Isothermal Crystallization Kinetics of Poly(Ethylene Oxide) (Peo) of Different Molar Masses Using Ultra-Fast Differential Scanning Calorimetry	H. Marand
T	Wen, Chengyuan	100	Evaporation of Solutions Containing Charged Polymers: a Molecular Dynamics Study	S. Cheng
T	White, B. Tyler	102	Michael Addition as a Means to Design Adhesives: Networks Based on Reactive Telechelic Oligomers	T. Long
T	Wilts, Emily M.	104	Isocyanate-Free Polyurethanes Based on Biocompatible Monomers	T. Long
T	Wolfgang, Josh D.	106	Improving Processability for High Performance Polyetherimides Using Long-Chain Branching	T. Long
T	Yu, Jianger	108	Study of Rheology and Stability Of Polyacrylonitrile-Based Copolymers with Various Plasticizers	D. Baird
T	Zawaski, Callie	110	Using Fillers to Improve Printability of Semi-Crystalline Materials for Material Extrusion Additive Manufacturing	C. Williams
T	Zhou, Mingjun	112	Thermoresponsive Dendritic Elastin-Like Peptides as Crosslinkers in Hyaluronic Acid Gels	J. Matson
T	Zornjak, Jennifer	113	Using Complementary Surface Analysis Techniques to Study the Interactions Between Novel Amphiphilic Cellulose Derivatives and Bile Salts	C. Fernandez-Fraguas

POSTER SESSION ABSTRACTS



PASSIVE ANTI-FROSTING SURFACES USING MICROSCOPIC ICE PATTERNS

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Despite exceptional advances in surface chemistry and micro/nanofabrication, no engineered surface has been able to passively suppress the in-plane growth of frost occurring in humid, subfreezing environments. Motivated by this, and inspired by the fact that ice itself can evaporate nearby liquid water droplets, we present a passive anti-frosting surface in which the majority of the surface remains dry indefinitely. We fabricated an aluminum surface exhibiting an array of small metallic fins, where a wicking micro-groove was laser-cut along the top of each fin to produce elevated water “stripes” that freeze into ice. As the saturation vapor pressure of ice is less than that of supercooled liquid water, the ice stripes serve as overlapping humidity sinks that siphon all nearby moisture from the air and prevent condensation and frost from forming anywhere else on the surface (Fig. 1). Our experimental results show that regions between stripes remain dry even after 24 hours of operation under humid and supercooled conditions. We believe that the presented anti-frosting technology has the potential to help solve the world's multi-billion dollar frosting problem that adversely affects transportation, power generation, and HVAC systems.

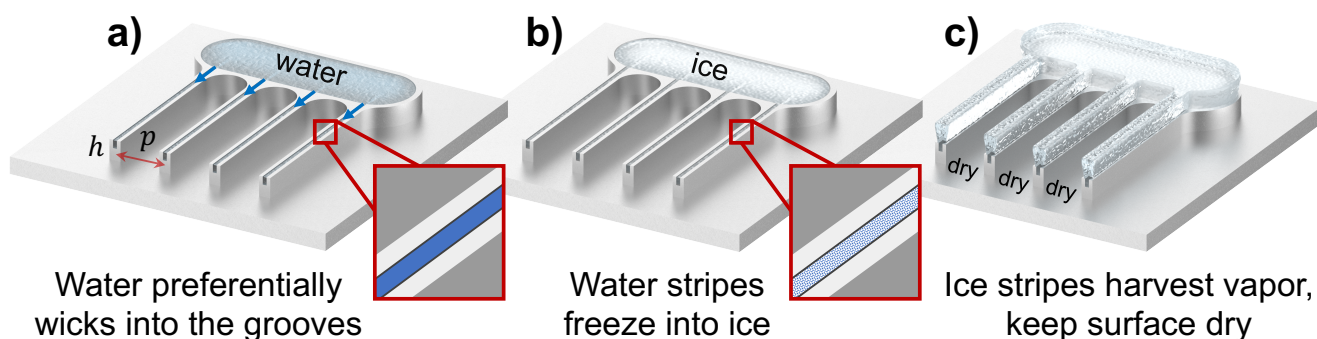


Fig. 1: Overlapping Dry Zones using macroscopic ice patterns. By machining micro-grooves along the top of each fin, water preferentially wicks along the tops of the fins (a). Upon freezing into ice in chilled conditions, these hygroscopic ice stripes siphon all nearby water vapor (b), keeping the rest of the finned surface completely dry from condensation and frost (c).

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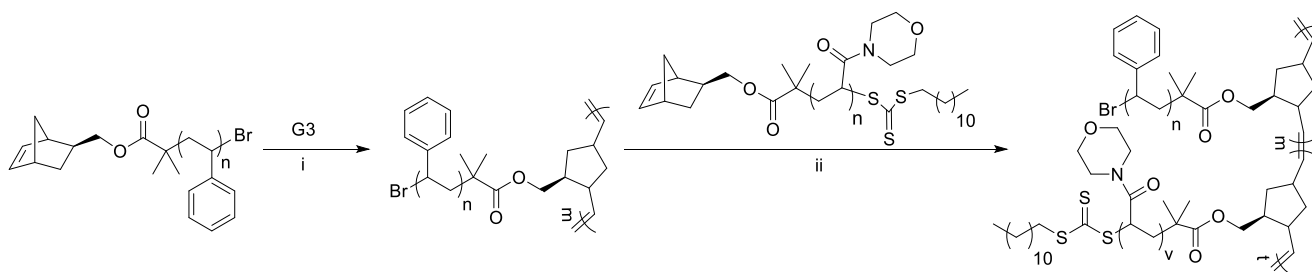
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SYNTHESIS AND CHARACTERIZATION OF AMPHIPHILIC BOTTLEBRUSH BLOCK COPOLYMERS

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Bottlebrush polymers contain a polymer backbone with densely grafted polymeric side chains, causing the backbone to have an extended chain conformation. This topology results in unusual rheological and mechanical properties, such as lower viscosity compared with linear polymers of similar molecular weights due to a smaller hydrodynamic radius and lack of chain entanglements. Despite evidence that bottlebrush block copolymer solution self-assembly behavior differs from their linear block copolymer counterpart, no large, systematic studies reporting phase diagrams of amphiphilic bottlebrush block copolymers have been published to date.^{1,2} This is surprising considering that amphiphilic bottlebrush block copolymers may have undiscovered potential in applications where traditional surfactants are currently used. In this work, we report the synthesis of a series of amphiphilic bottlebrush block copolymers with a poly(norbornene) backbone by sequential ring-opening metathesis polymerization (ROMP) of polystyrene and poly(4-acryloylmorpholine) macromonomers in a grafting-through approach. To accurately probe self-assembly behavior as a function of backbone degree of polymerization (DP), block length DP, and block ratio high precision is required in the synthesis of the necessary macromonomers. Synthesis of polystyrene macromonomers by atom-transfer radical polymerization (ATRP) (2.8 and 4.2 Kg/mol) as the hydrophobic polymeric sidechain block and poly(4-acryloylmorpholine) by photoiniferter polymerization (2.2 and 4.2 Kg/mol) as the hydrophilic polymeric sidechain block macromonomers gives a unique synthetic strategy which allows for a high degree of control over all pertinent parameters of the block copolymers. Small angle neutron scattering (SANS) and critical micelle concentration (CMC) measurements were used to evaluate and compare the self-assembled morphologies of bottlebrush block copolymers and linear block copolymers, which were synthesized as control, in aqueous solution.



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IN-SITU MONITORING OF EXTRUSION BASED ADDITIVE MANUFACTURING

*David Anderegg, Hunter Bryant, Devante Ruffin, Stephen Skrip,
Jake J. Fallon, Eric L. Gilmer, and Michael J. Bortner*

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Fused Filament Fabrication (FFF) has gained great popularity in both the academic and industrial spheres due to the low amount of material wasted during processing and the ability to create complicated geometries. Despite its vast potential, applications of FFF have been somewhat limited due to the lack of understanding of the actual conditions of the polymer melt in the extrusion nozzle, which has significant impacts on the nature of the deposited filament in terms of deposited road “shape” and adhesion to the underlying road. This is a result of the complexity of modeling the thermal and transport processes and lack of experimental data of conditions within the nozzles. Here we present a novel FFF nozzle design which is capable of measuring the temperature and pressure within FFF nozzles.

Testing was performed using ABS filament and a modified Monoprice Maker Select 3D printer equipped with thermocouple wire and a diaphragm based pressure transducer. Measurements were taken while idle and during extrusion at a constant flow rate of approximately 0.74 mm³/s. Thermocouple readings showed that the temperature within the nozzle is approximately 19 °C lower than the set temperature, suggesting significant deviation between actual and “setpoint” process conditions. Pressure readings ranging from 140-3578 kpa were recorded during an extrusion, though pressures as high as 6900 kpa were measured at higher flow rates. The pressure readings were within the uncertainty range of theoretical predictions. Additionally, it was discovered that poor PID calibration causes the temperature and pressure to fluctuate while idle, ranging from ± 2 °C and 14 kpa of the default settings of the printer and highlighting the need for high quality control systems to obtain quality printed parts. During printing, sharp drops in temperature (as high as 10 °C) are observed in the polymer melt, which dramatically impacts the resulting interlayer properties of the printed part. Our nozzle prototype succeeded in measuring internal conditions of FFF nozzles during extrusion for the first time, providing a number of important insights into the printing process vital to the development of new FFF filaments.

CONTINUOUSLY REINFORCED THERMOTROPIC LIQUID CRYSTALLINE POLYMER-THERMOPLASTIC COMPOSITE FILAMENTS FOR USE IN FUSED FILAMENT FABRICATION

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One of the major limitations in Fused Filament Fabrication (FFF), a form of additive manufacturing, is the lack of materials with superior mechanical properties. Traditional fibers such as carbon fiber and glass fiber are widely used to improve the mechanical properties of the filaments. The blending methods utilized to reinforce the filaments are known to break the fibers, preventing the production of continuously reinforced filaments essential for printing load-bearing components. This problem can be avoided by using *in-situ* composite filaments, where fibrils are generated during the processing stage [1]. These composites use thermotropic liquid crystalline polymers (TLCP's) to reinforce polymer matrices. The TLCP's possess high mechanical properties arising from the steric hindrance of their rod-like monomers which are aligned under extensional kinematics.

In this work, a unique dual extrusion technology is used to plasticate the resins in two different extruders at different temperatures [2]. Then a continuous stream of TLCP is injected below its melting temperature into the stream of the matrix polymer, following which the blend is passed through a series of static mixers, subdividing into fine streams. The composite stream is drawn to impart molecular orientation to the TLCP phase, following which the blend is cooled in a water bath and taken up on a winder. The composite filaments are processed in FFF above the melting temperature of the matrix polymer and below that of the TLCP. The temperature for the lay-down process is selected to avoid the relaxation of the orientation of the TLCP's using a solid state torsional test developed for this purpose.

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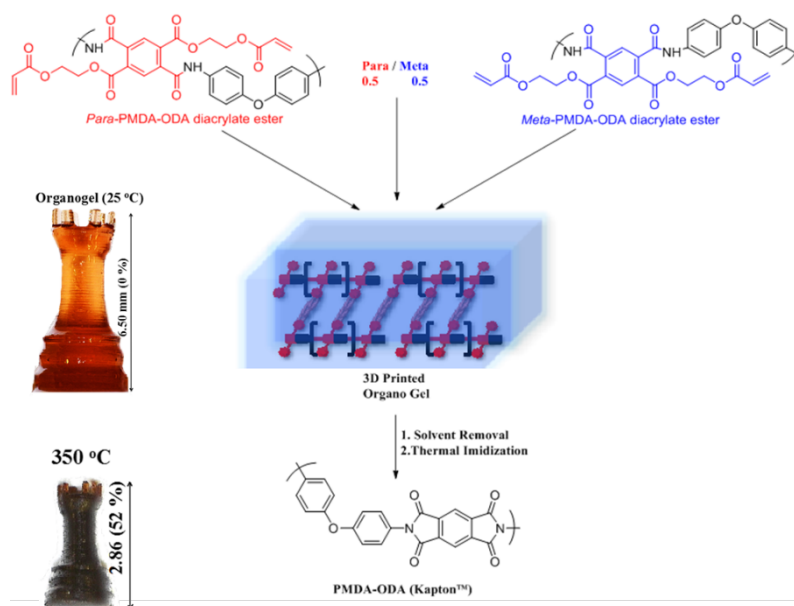
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SYNTHESIS AND CHARACTERIZATION OF HIGH PERFORMANCE POLYMERS FOR VAT PHOTOPOLYMERIZATION: POLYAMIC DIACRYLATE ESTER OF PMDA-ODA

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Currently, low T_g , thermally unstable elastomers dominate the catalog of vat photopolymerizable resins.^{1,2} Recently, Hegde *et al.* reported the unprecedented vat photopolymerization of the fully aromatic polyimide of pyromellitic anhydride (PMDA) and 4,4'-oxydianiline (ODA), Kapton™, via a soluble polyamic diacrylate ester (PADE) precursor.³ The ability to create 3D structures of PMDA-ODA with stereolithography (SLA) raises important questions regarding digital resolution and properties. When reacted with hydroxyethyl acrylate, pyromellitic dianhydride (PMDA) affords two isomeric products: para-PMDA-HEA and meta-PMDA-HEA. Separation of the isomers via multiple recrystallizations and subsequent polymerization with 4,4'-oxydianiline yields polyamic diacrylate esters which display variances in solubility and solution viscosity. Utilization of the isomeric polyamic diacrylate esters dissolved in N-methylpyrrolidinone (NMP) for 3D printing with SLA enables production of 3D structures with differences in part resolution and part fidelity. Likewise, thermal imidization of the printed isomeric polyamic esters produces polyimide parts that exhibit differences in morphology and mechanical properties primarily attributed to polymer chain alignment. Elucidation of these discrepancies with WAXS and SAXS aims to determine the impact of isomeric polyamic ester precursors on 3D polyimides prepared with SLA.



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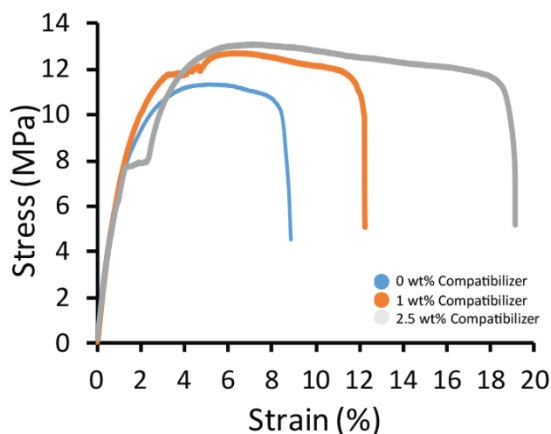
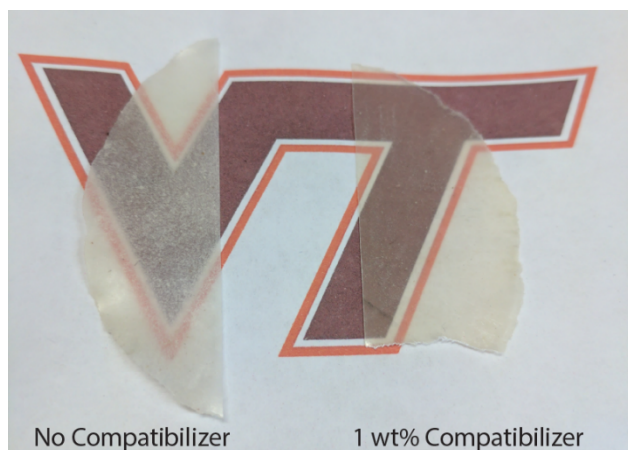
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COMPATIBILIZATION OF POLYOLEFINS AND POLYSACCHARIDES: IMPROVING PROPERTIES OF SUSTAINABLE POLYMERS

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Block copolymers can readily allow for tuned bulk mechanical properties; however, this method comes with added synthetic considerations and steps to develop the material. An easier method would be to simply blend homopolymers with two desired properties to make a new material. Sadly, this typically results in an immiscible and phase separated mixture with worse properties than either homopolymer. To overcome this problem, a compatibilizer can be added to decrease the interfacial tension between the two phases and improve the adhesion between the two phases.¹ This results in a material with properties similar to the respective block(y) copolymer at a lower price. Here, we have developed a novel synthetic method for developing polysaccharide and polyolefin compatibilizers. After three synthetic steps, compatibilizers can be synthesized using various polysaccharides and polyolefins. With as little as 1, 2.5, or 5 wt% addition of the compatibilizer the elongation at break, tensile strength, toughness, clarity, and modulus is drastically improved for the compatibilized blend.



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MECHANICAL ANALYSIS OF THE UTEROSACRAL LIGAMENT: SWINE VS HUMAN

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The uterosacral ligament (USL) is a major suspensory structure of the female pelvic floor, providing support to the cervix and/or upper vagina. It plays a pivotal role in surgical procedures for pelvic organ prolapse (POP), aimed at restoring apical support. Despite its important mechanical function, little is known about the mechanical properties of the USL due to the constraints associated with in vivo testing of human USL and the lack of validated large animal models that enable such investigations. In this study, we provide the first comparison of the mechanical properties of the swine and human USLs. Preconditioning and pre-creep data up to a 2 N load and creep data under a 2 N load over 1200 s were obtained on swine (n=9) and human (n=9) USL specimens by performing planar equi-biaxial tensile tests and using the digital image correlation (DIC) method. No differences in the peak strain during preconditioning tests, secant modulus of the pre-creep response, and strain at the end of creep tests were detected in the USLs from the two species along both axial loading directions (the main in vivo loading direction and the direction that is perpendicular to it). These findings suggest that the swine is an appropriate large animal model for studying the mechanical role of the USL in apical vaginal support and treatment of POP.

TAILORED FRACTURE ENERGIES AT MULTI-MATERIAL INTERFACES OF MATERIAL JETTING PARTS

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While the multi-material jetting additive manufacturing process has the opportunity to expand material selection for creating functional parts, not much consideration has been given to ensuring the robustness of the interface between different materials. From a design standpoint, it is important to ensure that the interface does not become a region for unexpected part failure. Additionally, the interfacial design could be used to control the mechanical response of the material. To understand interfacial behavior between a stiff material (VeroWhitePlus) and an elastomer-like material (TangoBlackPlus), fracture energies were characterized based on the double cantilever beam method with corrected beam theory. Specimens were created in a sandwich configuration with VeroWhitePlus representing the adherend on the outsides of the specimen and TangoBlackPlus acting as the inner adhesive. The specimens included regions of gradient layers to transition the VeroWhitePlus to TangoBlackPlus, and multiple print orientations were examined. Failures typically alternated between the VeroWhitePlus interfaces. However, specimens with larger gradient thicknesses experienced failures within the gradient layers. Even minor alterations to the direct VeroWhitePlus-TangoBlackPlus interface have been shown to increase fracture energy. This could lead to the implementation of algorithm adjustments in the additive system for tougher, multi-material parts. Future work could also aim to optimize gradient interfaces for desired fracture energy improvement. Knowledge about the materials' interfacial fracture behavior will inform strategies for designing for tunable mechanical behavior.

EFFECT OF ION CONCENTRATION ON THE PROPERTIES OF POLYISOPRENE-SODIUM STYRENE SULFONATE ELASTOMERIC IONOMERS PREPARED BY EMULSION POLYMERIZATION

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Ion containing polymers introduce intra- and intermolecular non-covalent bonding into a polymer system. Through the manipulation of the nature of the ions and the polymer backbone, scientists can tailor the properties of the polymer for use in specific applications.¹ Two ionomer functional groups that are commonly utilized are metal sulfonates and metal carboxylates attached to the polymer backbone via a styrene unit. Sulfonate ionomers allow much stronger ionic associations than carboxylate ionomers,² thus creating a more pronounced effect on the polymer properties. Ionomers are used in many applications including adhesives, thermoplastic elastomers, rheology modifiers, etc.³ Polymers containing low levels (< 10%) of ionic groups can exhibit properties that are dominated by the intra- and intermolecular noncovalent interactions of the ionic groups.

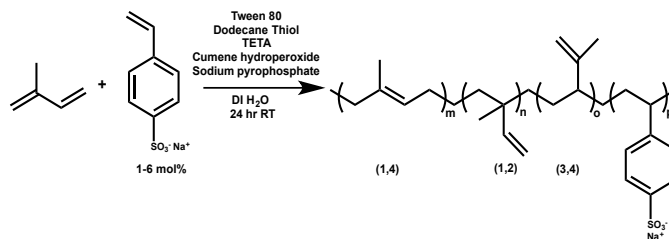


Figure 1: Reaction mechanism for the copolymerization of isoprene and sodium styrene sulfonate

One synthetic route to prepare ionomers is via direct copolymerization of an ion containing monomer (or protected ion containing monomer) with non-ion containing monomers. Our study is based on the emulsion copolymerization of sodium styrene sulfonate and isoprene to make poly(I-co-NaSS) (Figure 1). This system has been investigated previously,⁴⁻⁹ with a focus on chemical characterization and solubility. In this research a series of poly(I-co-NaSS) copolymers with systematically varied amounts of sodium styrene sulfonate ionomers was prepared with a focus on the structure-property behavior of the ionomers. Small angle X-ray scattering and thermal analysis indicate a lack of well-defined ionic aggregation, however, as the ion content increased the mechanical properties, including tensile, stress relaxation, and adhesion properties, improved. This study provides the fundamental interrelationships between chemical structure, morphology, and physical behavior of these ionomers.

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TUNABLE SYNTHESIS AND POST-SYNTHETIC MODIFICATION OF A PORPHYRINIC ZIRCONIUM METAL-ORGANIC FRAMEWORK FOR REVERSE OSMOSIS MEMBRANES

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Nanocomposite membranes for water purification by reverse osmosis (RO) have become a topic of growing interest due to their applications in a wide variety of industries including agriculture, manufacturing, energy production, and healthcare. However, current systems are limited by high energy costs and consumption, lack of membrane permselectivity, and fouling, reducing practicality for wide-scale industrial utilization. The incorporation of a porous and permselective material into the membrane would not only reduce operating pressures and therefore energy consumption, but would also result in enhanced desalination. Metal-organic frameworks (MOFs) are hopeful contenders for such material due to their porous nature, versatile application, and post-synthetic modification capability.

The synthesis of a porphyrinic zirconium MOF (MOF-545), was tuned such that the nanocrystals obtained comprised of distinct rod sizes for use in a cross-linked aromatic polyamide RO membrane. The crystallinity of the MOF nanorods was examined through powder X-ray diffraction (PXRD), and the particle sizes were confirmed with SEM and DLS. In addition, the structural stability of MOF-545 nanorods in solvents of various temperatures and pH was explored. Finally, post-synthetic modification of zirconium nodes through solvent-assisted ligand incorporation (SALI) was tested with stearic acid and characterized through NMR. The channel alignment, pore size, stability, and tunable synthesis of MOF-545 makes this framework a promising candidate for water filtration systems.

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PREDICTING STIFFNESS OF INJECTION MOLDED LONG FIBER REINFORCED POLYMERS

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Injection molded parts are commonly used in industry due to their low cost of production, the ability to make complex geometries, and the high speed of production. However, this process has limited material options. Composite materials provide the ability to produce plastic products with higher mechanical properties, such as modulus and strength, than polymers alone. This allows automotive manufacturers to create lightweight, high performance parts. When a composite piece is substituted for a heavier metal piece, then the car is lighter, therefore, increasing its fuel efficiency. As more manufacturers are finding better ways to utilize composites, cars are becoming increasingly more efficient, and therefore, decreasing overall emissions. Fiber length and orientation of the reinforcement have a direct effect on the mechanical properties of the final product. There are currently many challenges with predicting how these variables change during processing. Current research efforts are being made to predict and model the orientation and fiber length distributions, and these efforts will lead to being able to predict mechanical properties, such as strength and modulus. Some mechanical property modeling efforts have been made for short, rigid fibers. As fiber length increases, the fibers have a tendency to bend and become semi-flexible. In the case of glass fibers this state is reached at 1 mm. Due to this flexibility, the orientation can no longer be represented by a single vector¹. A two-vector Bead-Rod model is used to represent the fibers². It is predicted that using this Bead-Rod model will increase the accuracy of current modulus models³. The Bead-Rod model better represents the orientation of the long fibers by capturing their average flexed state, and the flexed fibers bear loads differently than rigid fibers. When conducting tensile tests on samples of injection molded polypropylene reinforced with 50 weight percent long glass fibers, it has been shown that the modulus and strength is higher than that for short glass fibers and agrees with literature values^{4,5}. Not only does fiber orientation effect the mechanical properties of the composite, but fiber length as well. The Bead-Rod model incorporates the fiber length, while the rigid-rod model does not. Future work will focus on collecting experimental orientation, fiber length, and tensile test data for end-gated plaques to test current stiffness models using the Bead-Rod model.

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DESIGN AND SYNTHESIS OF SUBSTITUTED STILBENE-*ALT*-MALEIC ACID COPOLYMERS WITH FLUORESCENCE PROPERTIES

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Fluorescent polymers have a wide range of applications including chemical and biochemical sensing, cell and protein imaging, organic light-emitting diodes, and Li-ion battery development.¹⁻² The structures of conventional fluorescent polymers often consist of rare-earth metals, conjugated polymer backbones, or fluorescent molecules attached to polymer backbones.² With conventional fluorescent polymer structures, the modifications necessary for fluorescence could significantly alter the physiochemical properties of the polymer, thereby limiting potential applications. The fluorescence properties of a series of non-conjugated, fluorophore-free, semi-rigid alternating copolymers were recently reported.³ Our current research focuses on the synthesis and characterization of new substituted stilbene-*alt*-maleic anhydride copolymers and the investigation of the effects of copolymer structure on fluorescence properties. The fluorescence properties of substituted stilbene-*alt*-maleic anhydride copolymers could make them suitable for various applications, including detergent-free visualization, isolation, and quantification of membrane proteins.⁴

Acknowledgements

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MECHANICAL TESTING OF SULFONATED POLY(ARYLENE ETHER SULFONE) RANDOM COPOLYMERS FOR WATER ELECTROLYSIS APPLICATIONS

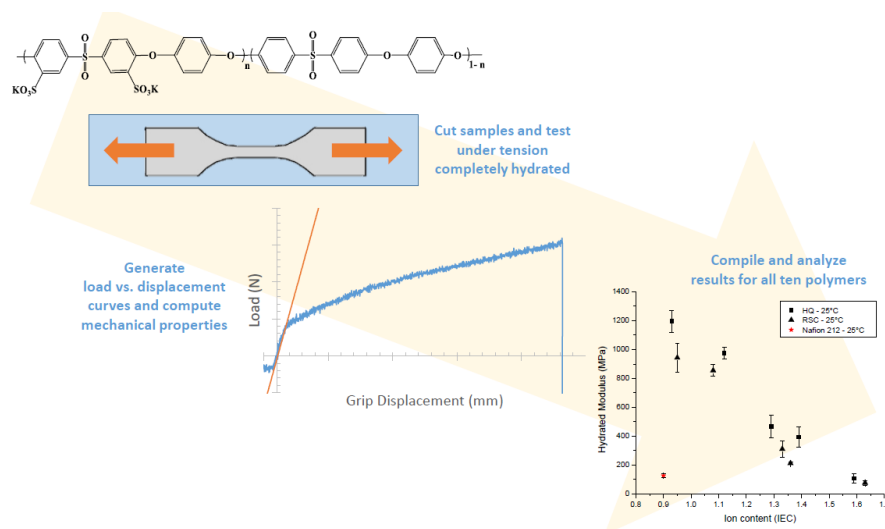
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Water electrolysis uses electricity to split water into hydrogen and oxygen. The hydrogen produced in this process is a viable green fuel source. A selective ionic polymer membrane isolates the hydrogen after it is split from water. The current industry standard polymer for this application is Nafion, which has poor mechanical properties particularly at higher temperatures. Since electrolysis is more efficient at higher temperatures, a more durable polymer is ideal.

For this research, two series of sulfonated poly(arylene ether sulfone) random copolymers were synthesized and solvent cast into films 25-65 μm thick. The polymer films were cut into dogbone shapes and tested under tension. Mechanical testing was conducted in fully hydrated conditions at 80°C and room temperature, as well as ambient atmospheric conditions. The elevated 80°C temperature hydrated tests simulated the most efficient operating conditions of a water electrolysis process.

Results show that as the ion contents of the polymers increase, the water uptakes increase, and the Young's moduli of the of the polymers decrease. At similar ion contents, the polymers had yield strengths two to five times and moduli five to ten times larger than those of Nafion. Some of the higher ion content polymers exhibited strains at break greater than 2.0. These polymers also exhibit noteworthy strain hardening; the stress at break typically reaches at least twice the magnitude of the yield stress. The significant increase in mechanical properties of the copolymer over Nafion shows potential for an improvement to the electrolysis process. The mechanical data will then be compared to classical models, especially effective medium theory, of solvent-polymer systems.



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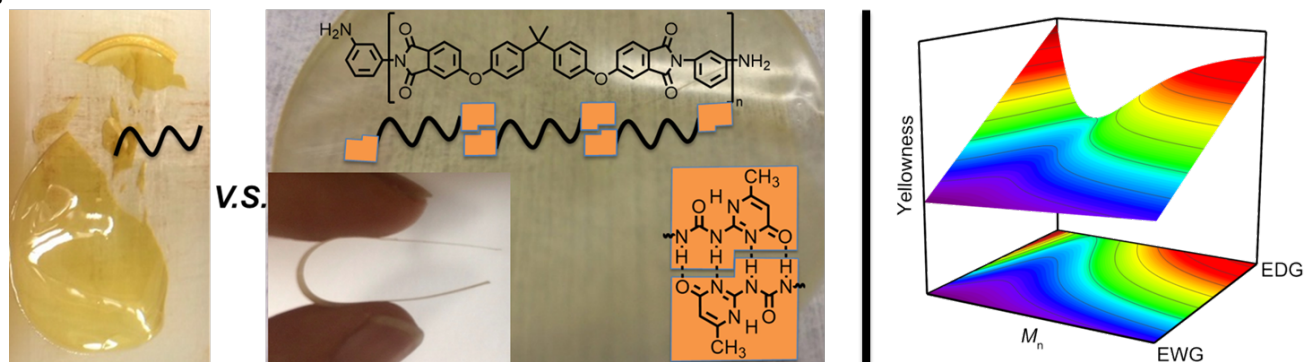
TAILORING THE TENSILE AND OPTICAL PROPERTIES OF TELECHELIC POLY(ETHER IMIDE)S BY THE END GROUPS

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Solution-processable poly(ether imide)s (PEIs) with ureidopyrimidinone (UPy) end groups were prepared by incorporating monoisocyanato-6-methylisocytosine into amine-terminated PEI oligomers. After functionalization with UPy end groups, PEI with a molecular weight as low as 8 kDa (8k-PEI-UPy) can be solution-cast to form films. Tensile tests revealed that 8k-PEI-UPy had an outstanding Young's modulus higher than those of state-of-the-art high-molecular-weight commercial PEIs. The tensile strength, maximum elongation, and Young's modulus of 8k-PEI-UPy were 87.2 ± 10.8 MPa, $3.10 \pm 0.39\%$, and $(3.20 \pm 0.14) \times 10^3$ MPa, respectively. The discovery herein significantly advances the chemistry of high-temperature PEI resins. UPy-based supramolecular chemistry is an effective and general strategy to achieve outstanding mechanical properties for PEI oligomers.¹

In addition to the tensile properties, the end groups affect the optical properties of PEIs. Therefore, we also investigated the effects of end group and molecular weight on the yellowness of telechelic PEI. Electron-withdrawing dianhydride end groups reduced the yellowness and increased the transparency of PEI regardless of the molecular weight. Electron-donating phenyl, amine, and phthalic end groups increased the yellowness of PEIs, but the effect depended on the molecular weight. As the molecular weight was increased, the yellowness of PEIs with electron-donating end groups initially decreased due to a decreasing end group density and then increased due to an increasing probability of charge-transfer complex formation. The systematic study reveals the correlations among yellowness, end group, and molecular weight of PEIs. The correlations can be used for designing highly transparent PEIs in applications of flexible displays, solar radiation protectors, and optical wave guides.²



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ALTERNATIVE METHODOLOGY FOR CHARACTERIZING TOOL-PLY FRICTION OF UNIDIRECTIONAL CARBON FIBER EPOXY PREPREGS AT VARIOUS PROCESSING CONDITIONS

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The quality of composite parts and structures depends strongly on the friction present during the composite forming process. The two major types of friction that cause deformations during this process are ply-ply friction and tool-ply friction. One of the challenges in the composite forming process is the occurrence of wrinkling and shape distortion of the fabric caused by the surface differences between the forming tool and surface of the laminate. Frictional measurements of composites can vary widely depending on processing parameters, measurement technique, and instruments used. The extent of interaction between the tool and surface of the laminate depends on the tooling height, and by extension, pressure, which cannot easily be monitored with traditional pull out test designs. In this study, a commercial rheometer was used to evaluate tool-ply friction of unidirectional carbon fiber epoxy prepreg at various contact pressures, temperatures and sliding velocities. Gap size and torque were monitored to provide information on the friction dependence on processing parameters. Preliminary results suggest this alternative methodology for measuring tool-ply friction produces similar trends as that seen in traditional pull-out tests. Further work must be done to confirm the applicability of the alternative methodology presented in this work.

EFFECTS OF PORE SIZE IN 3D PRINTED TISSUE SCAFFOLDS ON MOUSE FIBROBLAST PROLIFERATION

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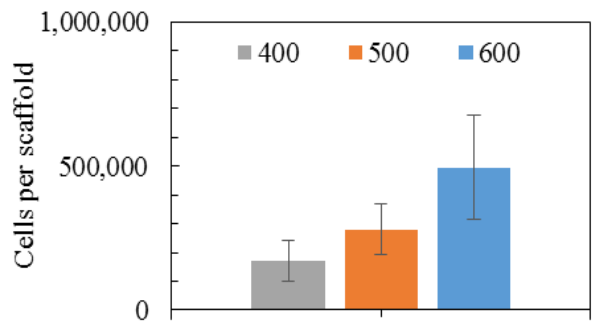
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Mask Projection Microstereolithography (MP μ SL) is an Additive Manufacturing (3D Printing) technique capable of fabricating complex geometries with micron-sized features. This makes MP μ SL well suited for the fabrication of tissue scaffolds for use in tissue engineering applications. Although there are few materials compatible with MP μ SL that are biocompatible and encourage cell attachment, recent work has been aimed at overcoming this challenge [1]. The coupling of a manufacturing technique with geometric flexibility not afforded by conventional scaffold fabrication techniques and new biocompatible materials permits the fabrication of scaffolds that will allow researchers to understand effects of scaffold geometry on cells. Scaffold pore size is an important parameter in cell viability and proliferation, but it is difficult to isolate the effects of pore size from those of pore shape, permeability, vascular networks, and other scaffold features. This work aims to isolate the effects of pore size on cell proliferation while maintaining constant other scaffold parameters (e.g. porosity, pore shape) by fabricating scaffolds with MP μ SL.

Print parameters for the resin were successfully developed and tissue scaffolds with 84% porosity and square pores were printed with three different pore sizes of 400, 500, and 600 μ m. After seven days of culture, the cell proliferation was found to be greatest on scaffolds with the largest pore size, despite their lower surface area. Additional work will include investigating a wide range of pore sizes.

Compression testing of scaffolds revealed that the scaffolds with 400 μ m pore sizes had the lowest modulus (635 kPa) while the moduli of the 500 and 600 μ m pore size scaffolds were higher (1.02 MPa and 1.04 MPa, respectively). Virtually no degradation was observed in scaffolds of any pore size after two weeks.

We have successfully used MP μ SL to fabricate tissue scaffolds with various pore sizes while maintaining constant porosity and pore geometry to evaluate pore size effects on fibroblast proliferation. The data suggest that a wider range of pore sizes is necessary to draw general conclusions, but that the techniques demonstrated can be used to evaluate the effects of not only pore size but also shape, porosity, permeability, and other scaffold design parameters.



Cell count on 3D printed scaffolds after seven days of culture. Proliferation was greatest on scaffolds with 600 μ m pores

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MATERIAL EXTRUSION ADDITIVE MANUFACTURING OF SEMI-CRYSTALLINE POLY(ETHYLENE TEREPHTHALATE) VIA BLENDING WITH POLYPROPYLENE

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Semi-crystalline polymers are widely used in molding manufacturing processes, but are difficult to process via filament material extrusion additive manufacturing (AM). The significant warping and shrinking that occurs during melt cooling and polymer crystallization often leads to build failure in FFF. Four material-centric methods enabling FFF processing with semi-crystalline polymers have previously been hypothesized in literature: i) adding micron-scale filler materials, ii) using copolymers to disrupt inherent crystallizability, iii) blending a secondary, immiscible polymer with the matrix polymer, and iv) using a semi-crystalline ionomer.^{1,2} All four methods direct morphology formation during solidification of the extruded melt. In this work, the authors present an investigation of approach (iii) by printing with a series of poly(ethylene terephthalate) (PET)/polypropylene (PP)/maleic anhydride-graft-polypropylene (MA-g-PP) polymer blends. It is shown that these blends can be extruded into a filament and then processed via filament material extrusion to form a printed structure.

Extrapolations from this demonstrated success indicate generalizable trends for target morphology in FFF. Choosing polymers with disparate peak melting temperatures, such as PET ($T_m = 255\text{ }^\circ\text{C}$) and PP ($T_m = 165\text{ }^\circ\text{C}$), allows for volumetric changes associated with crystallization to be spread out over a larger localized area and over a wider processing time. Maintaining a mobile PP phase while the PET phase crystallizes and holds the desired part shape enables manufacturing without reaching a level of critical distortion resulting in build failure. These conclusions suggest that blending polymers is one path to expanding the families of polymers processable via material extrusion AM, including looking toward capturing post-consumer waste streams for additive manufacturing feedstock.

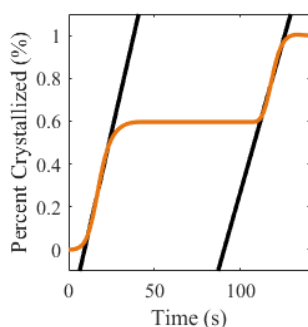
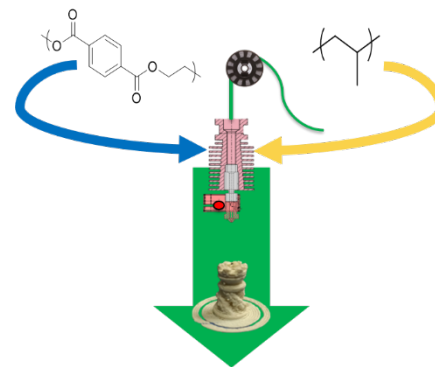


Figure 1. Graph depicting the linear fit corresponding to the rate of crystallization for both the PP and PET regions in a compatibilized PET/PP/PP-g-MA blend



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MODELING OF MICROSTRUCTURE AND ELASTIC PROPERTIES IN LONG-FIBER INJECTION-MOLDED THERMOPLASTICS

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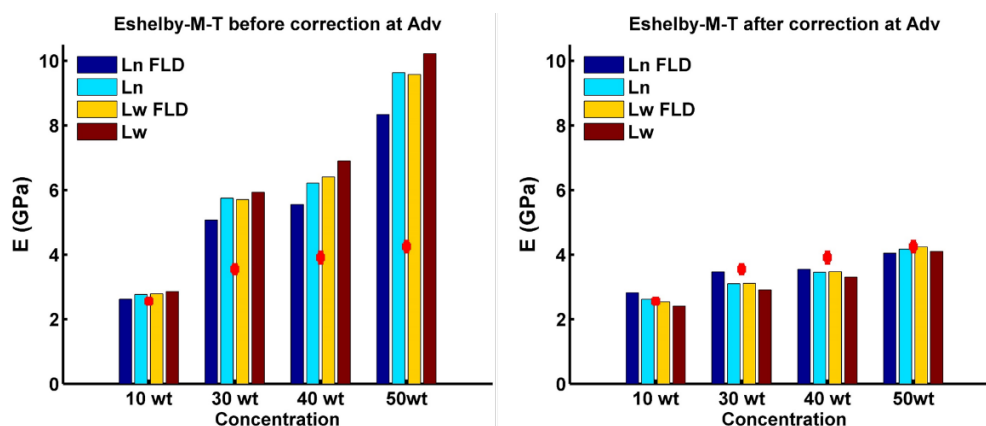
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Long-fiber (lengths > 1 mm) thermoplastic composites (LFTs) possess significant advantages over short fiber (< 1 mm) composites in terms of their mechanical properties while retaining their ability to be injection molded¹. Mechanical properties of LFTs are highly dependent on the microstructural variables imparted by the injection molding process including fiber orientation and fiber length distribution². Although LFTs have been commercially available for mostly twenty years and have been used in the automotive industry for more than fifteen years³, there exists little experimental and modeling work on these materials. This work focuses on the prediction of the elastic properties for a studied LFT system produced by injection molding. In the theories, well dispersion of fibers is assumed and single fiber diameter is used in modulus predictions⁴ which is not true within commercial fiber concentration range. Under high fiber concentration, fiber bundles existed which reduces the mechanical performances of the final injection-molded parts. We develops a methodology and empirical model to modify the fiber bundles' diameters. The stiffness of the actual as-formed composite was then determined from the stiffness of the modified bundles' diameter, the experimental fiber orientation and fiber length distributions. The methodology to predict the elastic properties of LFTS was validated via experimental verification of the moduli determined for long glass fiber injection-molded polypropylene specimens with 10 wt%, 30 wt%, 40 wt% and 50 wt% fiber concentrations. Our analysis shows that this empirical model significantly improved the stiffness predictions over high fiber concentrations. We also investigated the effects of various closure approximations of the 4th order fiber orientation tensor by comparing the as predicted stiffness results with that calculated from experimental obtained 4th order fiber orientation.



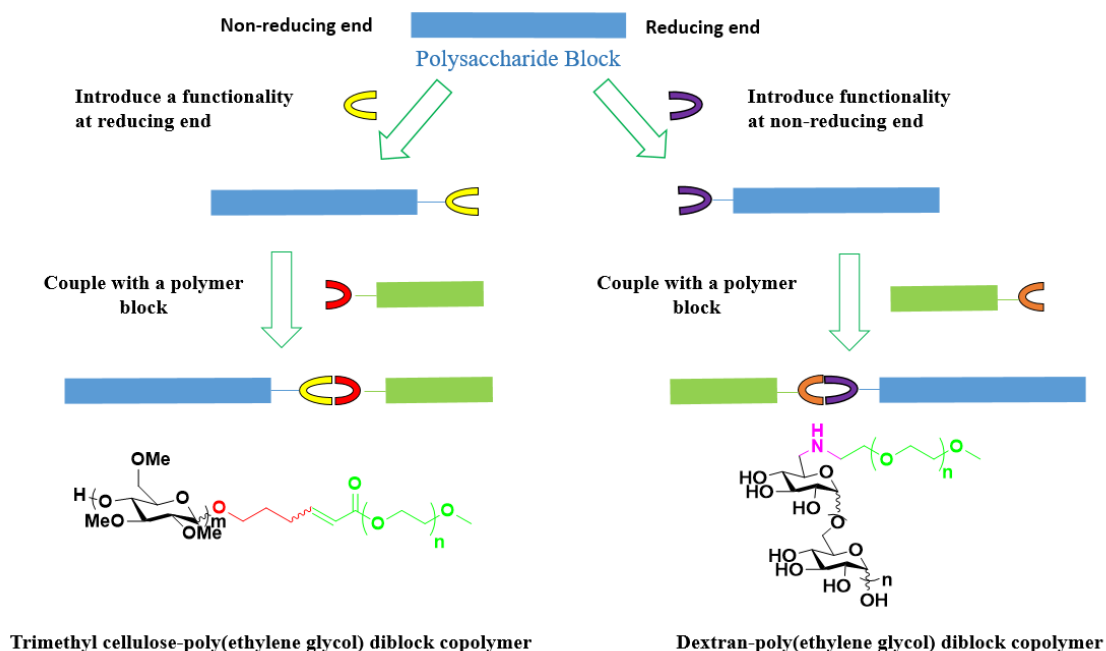
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NOVEL SYNTHETIC ROUTES TO POLYSACCHARIDE-BASED BLOCK COPOLYMERS

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Polysaccharide-based block copolymers are attractive materials which have potential to be used widely in many practical fields including biodegradable packaging and drug delivery. Micro-phase separation of block copolymers can afford specific morphologies, leading to extraordinary properties. Many polysaccharide derivatives, including cellulose, dextran and pullulan, are good candidates for block copolymer synthesis. In spite of this potential, however, only a limited number of approaches to polysaccharide-based block copolymers have been reported. The difficulty of polysaccharide regio-selective end group functionalization can explain the limited number of studies about this new block copolymer family. We have focused on developing synthetic strategies which can regioselectively modify the termini of polysaccharide derivatives, and from these selectively functionalized polysaccharides, build block copolymers. These approaches, including solvolysis, olefin cross-metathesis, amine alkylation and azide-alkyne cycloaddition, have generated a series of trimethyl cellulose- and dextran-based block copolymers. We will report insights into these interesting reactions, which will inform further design and synthesis of polysaccharide-based block copolymers.



COUNTER-ION EFFECT ON RADICAL POLYMERIZATION KINETICS OF IONIC-LIQUID MONOMERS

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Polyelectrolytes provide a library of unique properties that lead to applications ranging from battery membranes and electrolytes, gas purification to adhesives and antifouling coatings.¹⁻³ Despite the extensive studies on polyelectrolytes, the influence of ionic interactions on the polymerization kinetics is underexploited, especially in controlled radical polymerization (CRP). We successfully synthesized four imidazolium-containing ionic-liquid monomers with identical chemical structures except counter ions. *In-situ* FTIR monitored the corresponding radical polymerization kinetics of four different ionic-liquid monomers. The counter ions demonstrated minimum influence on polymerization kinetics in conventional radical polymerization, but showed drastic polymerization rate difference in reversible addition-fragmentation chain-transfer polymerization (RAFT) polymerization (**Figure 1**). RAFT polymerization of the same ionic-liquid monomer in different solvents also revealed kinetic differences. NMR diffusometry revealed limited difference in monomer diffusion rate and showed no ion aggregation under polymerization condition regardless of solvent and counter anion choices. Our simulation results based on Marcus theory shed light on the possible correlation between reorganization energy and the electron transfer rate during polymerization.

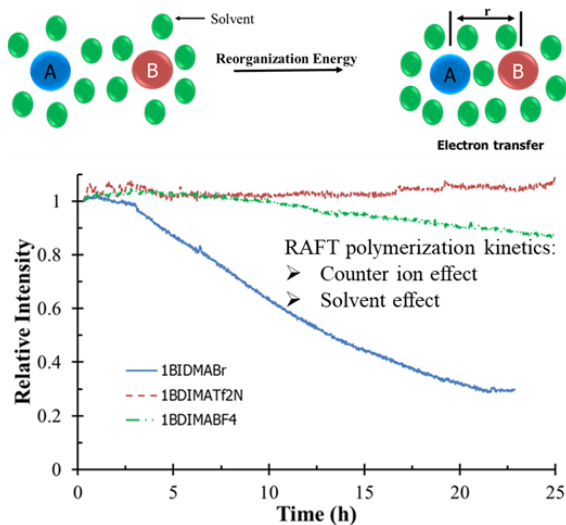


Figure 2 Polymerization kinetic differences in RAFT polymerization of ionic-liquid monomers with various counter anions.

energy and the electron transfer rate during polymerization.

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BLOCK COPOLYMERS CONTAINING PYRIDINIUM AND UREA: A UNIQUE EXAMPLE OF CHARGED HYDROGEN BONDING MATERIALS

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Non-covalent interactions in polymers provide a unique platform to introduce directional and/or reversible intra- and inter-molecular interactions which improve thermomechanical properties and promote micro-phase morphology. Extensive studies focused on the structure-property relationship of one specific type of secondary

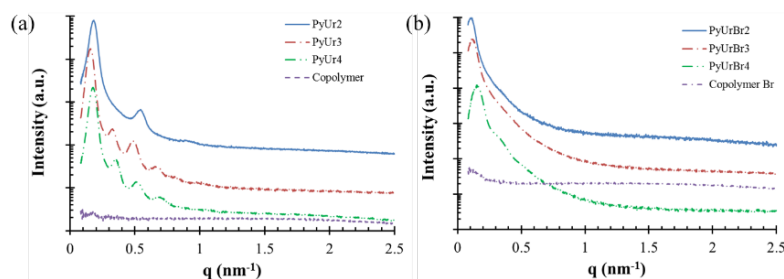


Figure 3 Small angle X-ray scattering of (a) neutral PyUr triblock copolymers and (b) charged PyUrBr triblock copolymers.

interaction in polymers, such as hydrogen bonding¹ and ionic interaction². However, current literature lacks fundamental understanding of block copolymers with different types of non-covalent interactions. Herein, we synthesized a series of ABA triblock copolymers with hydrogen bonding (urea) and electrostatic interactions (pyridinium) in the outer blocks. RAFT polymerization afforded the well-defined neutral triblock copolymers and post-

polymerization quaternization of the pendant pyridine sites allowed the synthesis of charged ABA triblock copolymers counterparts. Before quaternization, the neutral ABA triblock copolymers demonstrated extended plateau 70 °C above hard block T_g in dynamic mechanical analysis (DMA), indicative of ordered hydrogen bonding, which agreed with their lamellar morphology in small angle X-ray scattering (SAXS) (**Figure 1a**). Upon quaternization, electrostatic interactions served as additional physical crosslinkers to disrupt the ordered packing of hydrogen bonds (**Figure 1b**), resulting in lower flow temperature (T_{flow}) in DMA. However, electrostatic interaction improved the thermal stability and stress-relaxation of the charged block copolymers.

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REUSE AND RECYCLING OF TLCP REINFORCED COMPOSITES

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Interest in thermoplastic composites has been increasing rapidly, especially in aerospace and automobile applications. In their present form composite materials suffer from a number of limitations including long part fabrication times, high cost (when carbon fiber is used), adequate weight savings, and lack of recyclability. Thermotropic liquid crystalline polymers (TLCPs) reinforced thermoplastics as an alternative overcome these limitations and are potentially suitable for use in manufacture of automotive parts. TLCPs are wholly aromatic polymers which form rigid anisotropic units referred to as mesogen. Under extensional deformation, TLCPs as the minor components generate fibrillar structure to enhance mechanical properties of the matrix. These composites are easily produced by injection molding and the highest mechanical properties usually are generated by fiber spinning and strand extrusion with the tensile strengths over 1 GPa and tensile moduli up to 100 GPa. Even with the superior mechanical properties of TLCP reinforced composite, the high cost of raw TLCPs is an obstruction for wider range of application comparing to glass fiber.

The reuse and recycling of TLCP reinforced composites will be necessary to reduce the cost of their use. The first approach will be to study the influence of multiple recycling of TLCP reinforced thermoplastics by injection molding and regrinding. The tensile, impact and flexural tests will evaluate the mechanical properties of recycled TLCP composites. The morphology of the composites will be characterized with SEM and optical microscopy. The second strategy will be to generate TLCP fibrils of higher melting point within a matrix of lower melting point using a novel mixing approach developed in our laboratory and then assess their performance in various processing histories such as injection molding, thermo-forming, and compression molding. The advantage to this approach is the ability to generate high molecular orientation within the TLCP phase and hence higher reinforcing potential. The challenge will then be to devise recycling schemes for these materials. In the direct reuse of TLCPs, the composites are ground to small pieces and the polymer can be separated as a result of the difference in density. The alternative to the reuse of TLCP reinforced composites is selective dissolution and separation method, which select one solvent to dissolve only one polymer at a time. The undissolved TLCP will be filtered and the solution will undergo a devolatilization process to recover the TLCP.

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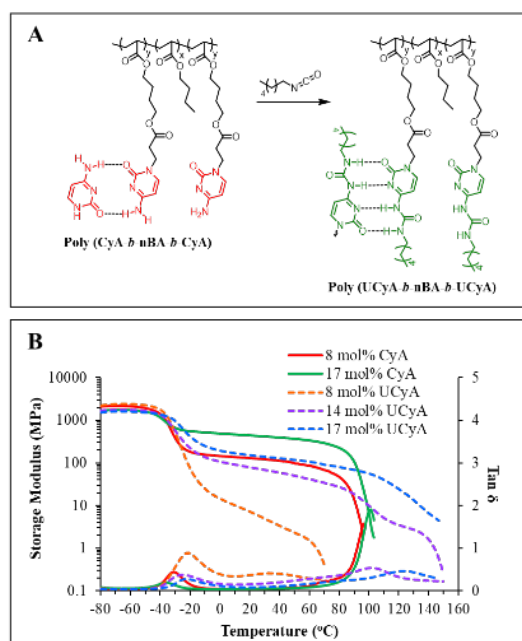
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CYTOSINE AND UREIDO-CYTOSINE ACRYLIC ABA TRIBLOCK COPOLYMERS: MECHANICAL AND MORPHOLOGICAL CORRELATIONS

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RAFT polymerization is a versatile and facile method to prepare triblock copolymers with controlled molecular weight and low polydispersity.¹ Poly(*n*-butyl acrylate) (PnBA) served as the central block, and chain extension with nucleobase-containing blocks, such as poly(cytosine acrylate) (poly(CyA)), produced an ABA triblock copolymers poly(CyA-*b*-nBA-*b*-CyA). The nucleobase external blocks and PnBA central block imparted structural integrity and flexibility. The flexible butylene linker in the cytosine acrylate segment facilitated intermolecular recognition and self-assembly.²⁻⁵ Moreover, hydrogen bonding between cytosine segments promoted physical crosslinking and enhanced mechanical performance. Post-functionalization with an isocyanate of cytosine-containing triblock copolymers afforded the corresponding ureido-cytosine acrylate (UCyA) block polymers poly(UCyA-*b*-nBA-*b*-UCyA)s with quadruple hydrogen bonding motifs, increasing the propensity for physical interactions. This thermally-reversible, noncovalent interaction also enabled melt processibility of ureido-cytosine polymers. Systematic comparison of the thermomechanical and morphological properties of cytosine and ureido-cytosine block copolymers revealed superior thermomechanical properties, extended modulus plateau regions, improved structural ordering, and excellent moisture resistance for the ureido-cytosine polymers. This enhanced performance verified the quadruple hydrogen bonding-dominated physical behavior. Hence, structure-property-morphology relationships illustrated key characteristics for novel thermoplastic elastomers.



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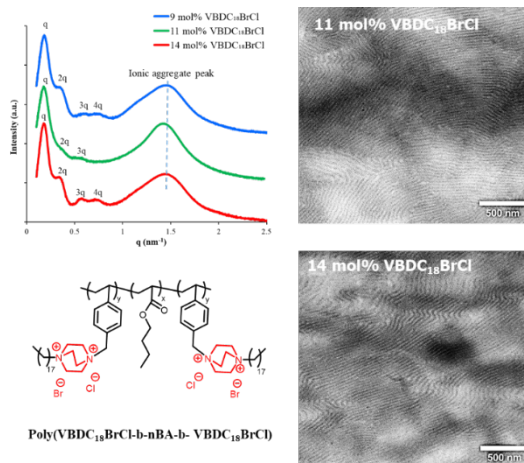
DOUBLY-CHARGED TRIBLOCK COPOLYMERS FOR ENHANCED PHYSICAL PROPERTY AND SELF-ASSEMBLY

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Ionomers represent a unique category of polymeric materials bearing <15 mol % of ionic units in the pendant groups. The non-directional Coulombic interactions induce the formation of ionic aggregates, resulting in significantly different physical properties compared to the nonionic analogs.^{1,2} The unique thermal, mechanical, and morphological properties of ionomers facilitate impacts in many fields, including energy storage, biomedicine, water treatment, and food processing.^{3–5}

Reversible addition-fragmentation chain-transfer polymerization (RAFT) afforded an unprecedented synthesis of doubly-charged DABCO salt-containing ABA triblock ionomers and the singly-charged analogs comprising a soft poly(*n*-butyl acrylate) (PnBA) center block and charged external hard blocks. Thermal analysis indicated the degradation of the DABCO salt-containing block copolymer followed closely to a reverse nucleophilic substitution pathway. Thermomechanical study revealed a much stronger ionic interaction and an extended service temperature window of DABCO salt-containing block copolymers comparing to their corresponding doubly-charged random copolymer and singly charged block copolymer controls, suggesting the formation of enhanced physical crosslinks. Morphological characterizations confirmed solution-cast DABCO block copolymers self-assembled into well-ordered lamellar microstructures. A unique three-phase morphology elucidated the structure-property-morphology relationships of the novel doubly-charged ionic block copolymers.



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STRUCTURE-PROPERTY RELATIONSHIPS OF POST SULFONATED POLY(ARYLENE ETHER SULFONE) MEMBRANES FOR WATER DESALINATION

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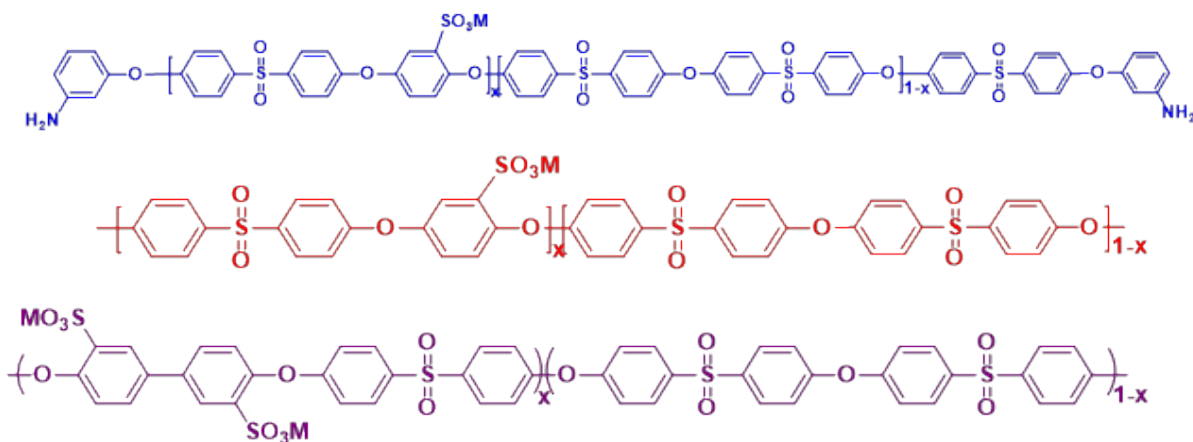
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Clean water is critical to the safety, security and survivability of humankind. Nearly 41% of the Earth's population lives in water-stressed areas, and the water scarcity will be exacerbated by an increasing population. Over 96% of the total water is saline and only 0.8% is accessible fresh water. Thus, saltwater desalination has emerged as the key to tackle the problem of water scarcity. Our current work deals with two membrane processes for desalination – Electrodialysis and Reverse Osmosis. Sulfonated polysulfones are a potential alternative to state of the art thin film polyamides. Synthesized by step growth polymerization, the polysulfone membranes have smooth surfaces and they are more chemically resistant relative to the polyamides.

Research in our group has suggested that monosulfonated polysulfone membranes have better transport properties than disulfonated polysulfone membranes. Post sulfonation of poly(arylene ether sulfone) is an effective way to strategically place the sulfonate ions along the backbone of the polymer chain. Rose and coworkers reported the controlled post-sulfonation of poly(arylene ether sulfones) that contained hydroquinone units¹. The sulfonation reaction proceeded only at the hydroquinone units because all of the other rings were deactivated toward electrophilic aromatic sulfonation by the electron withdrawing sulfone groups.

Novel hydroquinone based, amine terminated oligomers were synthesized with block molecular weights of 5000 and 10,000 g/mol. They were post-sulfonated under controlled conditions, then crosslinked at their termini with epoxy reagents. Linear polymers containing monosulfonation and disulfonation were also synthesized using post sulfonation.



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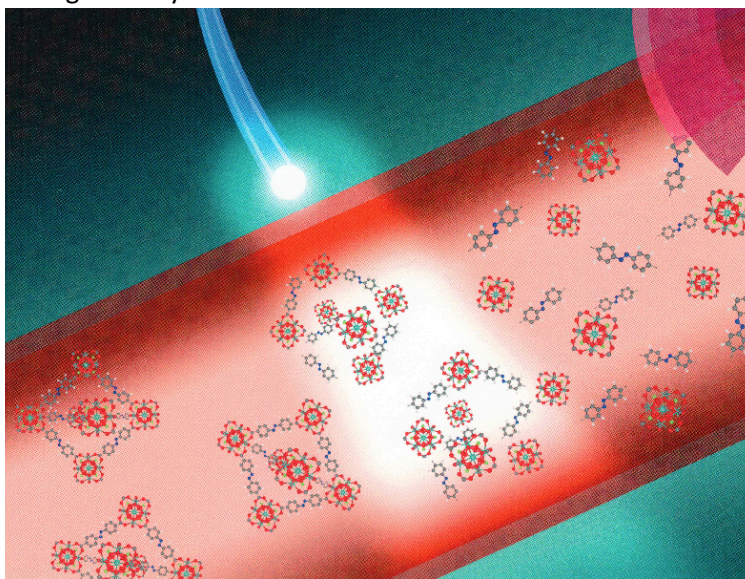
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SYNTHESIS OF PHOTODEGRADABLE NANO-CAGES FOR DRUG DELIVERY

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The development of controlled drug delivery systems is crucial for reducing toxicity and minimizing off target drug effects¹ for patients. A novel PEG functionalized nanoMOF containing an azobenzenedicarboxylate linker (UiO-AZB) has shown great promise as a potential nanocarrier². Nanoparticles were loaded with 5-fluorouracil (5-FU), an FDA approved therapeutic commonly used to treat cancer patients. PEGNH₂@5-FU-UiOAZB nanoparticles exhibit successful cellular uptake and enhanced biocompatibility after encapsulation with the PEG coating. Upon irradiation with light (340 nm), the AZB linkers isomerize, resulting in degradation of the nano-cages and controlled drug release. Preliminary in vitro studies have shown that only cells containing irradiated nanoparticles experienced cell death, which indicates that cell toxicity is induced by the release of 5-FU, not the presence of the nano-cage itself³. An additional benefit of nano-cages as drug delivery vehicles lies in their tunability. Future work aims to alter the identity of the photo-responsive linker and functionalize the polymer coatings in order to shift the therapeutic window and allow for selective targeting. These findings represent an exciting first step in the use of nanoMOFs for tailored drug delivery.



Photodegradable nano-cages² (Cover Art for Dalton Transactions, April 2017)

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CRYSTALLINITY, MORPHOLOGY AND THERMAL PROPERTIES OF BLENDS OF POLYPROPYLENE/HYDROCARBON RESIN FOR ADDITIVE MANUFACTURING

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Polypropylene (PP) has been used in a wide range of applications because of its remarkable physical, mechanical, chemical and optical properties¹. The crystallization behavior of PP is relatively fast which enables it to be processed using extrusion and injection molding processes with high effectiveness². However, it is of paramount importance to slow down the crystallization process in order to successfully 3D print materials using PP since it crystallizes relatively rapidly and traps the stresses in the additively manufactured parts, which in turn results in part warpage³. The addition of low molecular weight hydrocarbon compounds to PP shifts the onset of crystallization to lower temperatures, decreases the rate of crystallization and potentially reduces the overall amount of crystallinity when cooling it from the melt^{4,5}.

In this work, we have studied the effect of the variation in composition of two different hydrogenated resins on the thermal behavior, crystallization, and morphology of PP by performing differential scanning calorimetry (DSC) and hot-stage polarized optical microscopy (POM) of compression molded films. Compression molded films were observed through POM to examine the spherulite crystal structure. The thermal history of the PP/resin blends were recorded along with the isothermal crystallization profiles over the temperature range of 120-130°C with different cooling rates. The understanding of the thermal behavior and morphology of the blends at different temperatures plays a pivotal role in filament extrusion and subsequent extrusion based additive manufacturing, significantly impacting the mechanical properties of the parts generated using fused filament fabrication approaches.

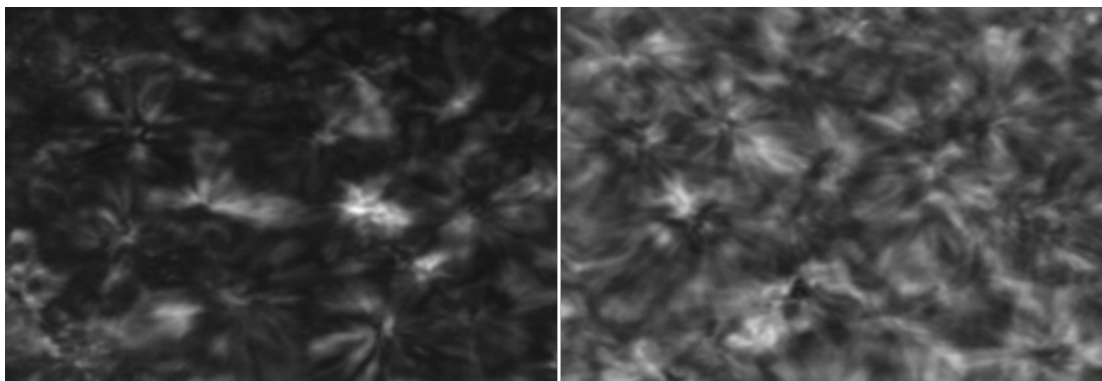


Figure 1: Polarized optical micrographs of films of pure polypropylene cooled at 120°C (left) and 130°C (right) at 50X.

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SELF-ASSEMBLY OF ACTIN-LIKE FILAMENTS

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Actin filaments (F-actins) are long, double-stranded, helical biopolymers that make up the cytoskeleton along with microtubules and intermediate filaments. In order to better understand the self-assembly process of actin filaments, a coarse-grained model to recreate their geometry was developed, which was motivated by the wedge model of microtubule self-assembly.^{1,2} The model monomer has the shape of a bent, twisted rod with binding sites on its lateral and top/bottom surfaces (Figure 1a). The longitudinal binding through the binding sites on the top/bottom surfaces of the rod allows the formation of strands, while the lateral binding between the rods enables the strands to adhere laterally to form double-stranded helical filaments (Figure 1b). Such a design captures the assembly behavior of G-actins into F-actins (Figure 1c). With molecular dynamics simulations, we explored the self-assembly of these bent-rod monomers. A variety of assembled phases were observed when the strengths of the binding interactions between monomers were varied. Our simulations indicate that only a narrow range of binding strengths yields double-stranded helical filaments resembling F-actins. Furthermore, the structure of the assembled filaments is much more robust and resistant to fluctuations and defects when the strength of the longitudinal binding interaction is stronger than that of the lateral binding between monomers.³ Finally, double-stranded filaments are found to be much more stable structurally than single-stranded ones. Our results reveal fresh insights into the fact that actin filaments are predominantly double-stranded.⁴

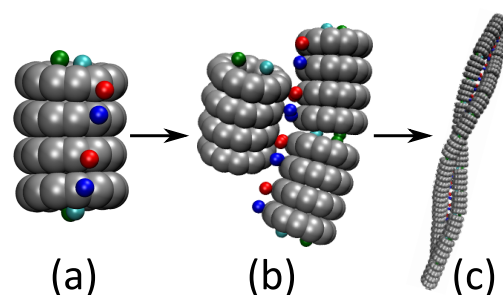


Figure 1: Bent-rod building block model of actin self-assembly.

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ZINC OXIDE (ZnO)-FREE SYNTHETIC ISOPRENE RUBBER VULCANIZATES USING WHEAT PROTEIN AS AN ACTIVATOR

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Trypsin hydrolyzed gliadin (THGd) from wheat gluten protein was used to activate the sulfur vulcanization of synthetic polyisoprene rubber (IR). THGd, a biobased and sustainable additive, was a replacement for zinc oxide (ZnO), which is expensive, high density, and ecotoxic.¹ The protein-activated vulcanizates were characterized using differential scanning calorimetry (DSC), tensile testing, swelling experiments, and Fourier transform infrared spectroscopy (FTIR). All protein-activated compounds were successfully crosslinked, as determined by swelling experiments. As the protein loading increased from 4 to 16 parts per hundred rubber (phr), the Young's modulus increased while the relative crosslink density decreased. This suggested that as protein loading increased, the effectiveness of the curing reaction decreased, and the additional protein served to reinforce the rubber. Reinforcement was attributed to the formation of β -sheet nanostructures in the protein phase during curing. By increasing the sulfur and accelerator loading, a crosslink density greater than the IR Control was achieved. The curing kinetics were evaluated by DSC and found to be slower in the THGd-activated vulcanizates, i.e. longer cure times were required to achieve a similar degree of cure to the control. This study showed that THGd protein could successfully activate the curing reaction of synthetic IR, while also serving as a reinforcing filler. Thus, the potential for a completely zinc-free rubber curing system exists.



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MECHANICAL PROPERTIES OF RAT UTEROSACRAL LIGAMENT

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The uterosacral ligament is one of the main structures that support the female pelvic floor organs. It connects distally to the cervix and proximally to the sacral spine. Pelvic floor disorders, which affect nearly 30 million people in the U.S., are associated with changes to the microstructures of these ligaments [1]. Treatments for pelvic floor disorders can have variable outcomes and may result in life-altering adverse events [1, 2]. Risk and ineffectiveness of these treatments results from inadequate understanding of the etiology and the mechanics of the pelvic tissues [1]. No studies on the mechanical properties of the rat uterosacral ligament have been conducted, despite the histological similarity between rats and humans [3]. Therefore, the objective of this study is to determine, for the first time, the stress-strain response of the rat uterosacral ligament. A novel method was developed for excising

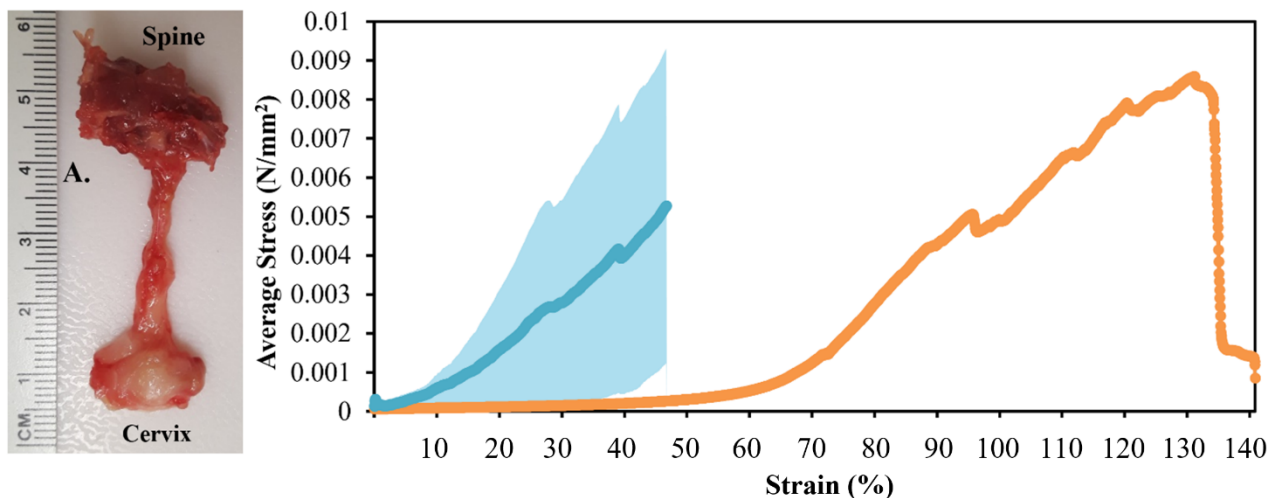


Fig. 2. A. Dissected rat uterosacral ligament with preserved spinal and cervical attachments. **B.** Toe region of average stress-strain curve with shading +/- standard error of the mean (blue), and a complete representative curve from one test (orange)

the rat uterosacral ligament from the pelvic floor, and stress/strain response was recorded while pulling uniaxially until failure.

Preliminary testing showed nonlinear behavior and high variability between specimens, which has also been observed for this ligament in swine and humans. This study lays the groundwork for further mechanical testing of the uterosacral ligament in the rat model that investigates its important roles in the development and treatment of pelvic floor disorders.

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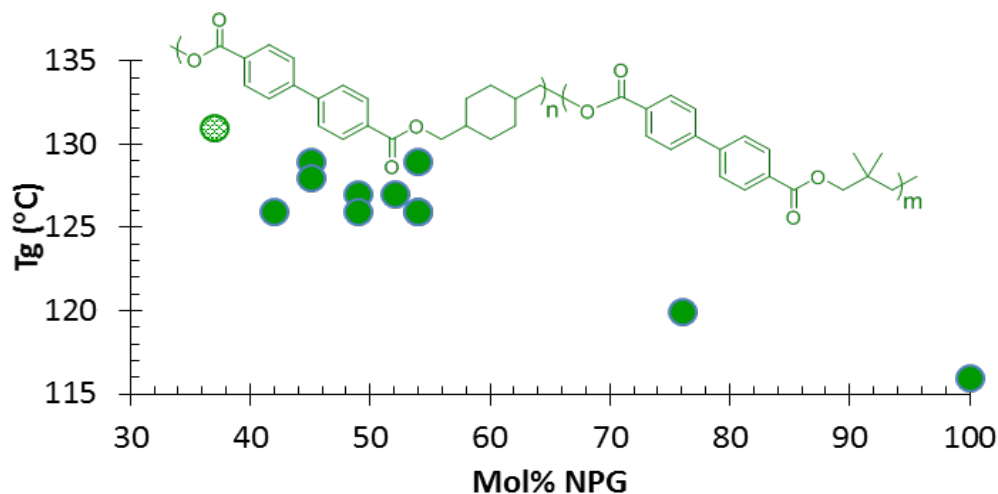
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COPOLYESTERS MODIFIED WITH NEOPENTYL GLYCOL

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Conventional polyesters are favored for industrial applications because they are inexpensive and have well established processing methods. Even though many commercial polyesters are based on diols and aromatic diacids, there are still many unexplored compositions capable of achieving improved thermal and mechanical properties relative to what is currently commercialized. Neopentyl glycol (NPG) has demonstrated good potential for disrupting crystallinity and improving thermal stability in copolyesters, however, it has received relatively little attention as a diol in copolyesters. In the past, bibenzoate structures have demonstrated excellent potential to increase the glass transition temperature (T_g) of copolyester compositions, but rapid crystallization, even when copolymerized, has largely prevented the synthesis of bibenzoate based amorphous materials.¹⁻³ This research investigates novel bibenzoate based copolyester compositions containing NPG and ethylene glycol or 1,4-cyclohexanedimethanol chosen to slow crystallization and produce high T_g materials that are amorphous under processing conditions.



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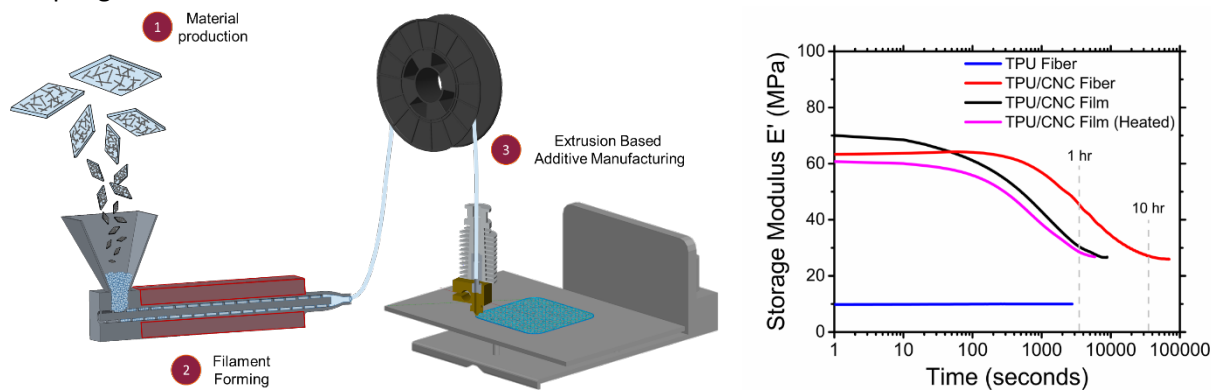
INFLUENCE OF PROCESSING ON ADDITIVELY MANUFACTURED MECHANICALLY ADAPTIVE CELLULOSE NANOCRYSTAL POLYMER COMPOSITES

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Cellulose nanocrystal (CNC) polymer composites have the potential to provide enhanced strength and impart mechanically adaptive behavior to a number of commercially available polymeric materials. We are currently investigating the potential to transition these unique characteristics from solvent cast polymer films to functional parts generated using extrusion based additive manufacturing (AM). The relationship between structure, process and properties of functional CNC polymer composites has not been explored when utilizing material extrusion based AM technologies. We are establishing relationships between key material properties such as mechanical strength, thermal transitions and morphology to aid in describing this complex relationship. Developing this understanding of the processing dependent material behavior will aid in developing novel CNC based materials for AM technologies.

We will present dynamic mechanical analysis (DMA) experiments conducted with a submersion chamber attachment, which allows for analysis of mechanical properties in both dry and water saturated environments. Preliminary DMA data indicate processing has a significant impact on dry mechanical properties of the CNC polymer nanocomposite cast films (385 MPa) and extruded fibers (63 MPa). Geometry also has a substantial impact on rate of diffusion and corresponding rate of mechanical switching, with thin film samples adapting in 350 seconds compared to 15 hours for a 1.75 mm diameter fiber. Small angle X-ray scattering is used to qualitatively analyze the degree of orientation induced by processing the cast film and fiber samples; despite machine direction orientation in an extruded fiber, we observe reduced dry state storage modulus compared to the unoriented solvent cast film. These results suggest the potential impact of thermal history on surface functionality of the CNCs. We deconvolute the separate, competing contributions of CNC orientation and thermal decomposition; the former is expected to substantially increase modulus, while the latter is expected to reduce coupling between CNC's.

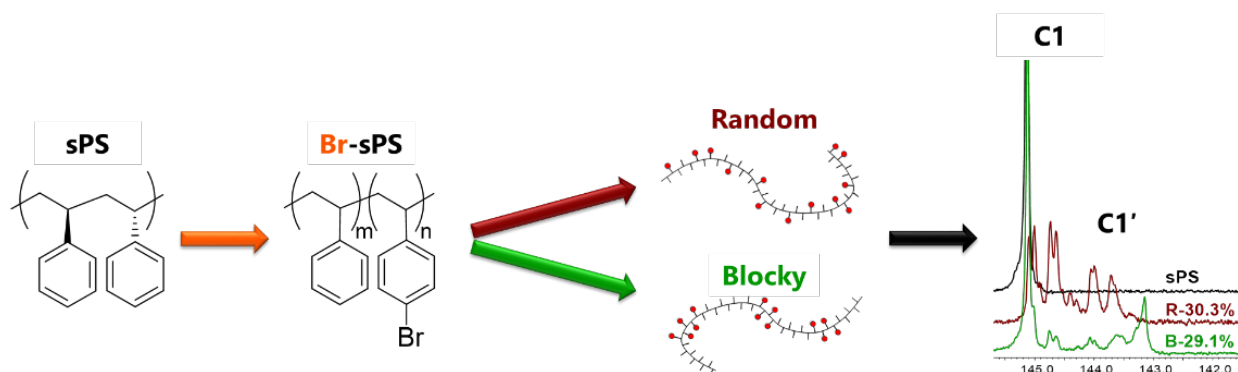


EVALUATING CO-MONOMER SEQUENCE DISTRIBUTION IN BROMINATED SYNDIOTACTIC POLYSTYRENE COPOLYMERS USING ^{13}C NMR SPECTROSCOPY

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^{13}C NMR spectroscopy has been used to evaluate co-monomer sequence distribution in brominated syndiotactic polystyrene (Br-sPS) copolymers prepared via a post-polymerization functionalization method carried out in solution and in a heterogeneous gel state. Bromination in solution produces Br-sPS copolymers with random architectures, while gel-state functionalization is expected to produce copolymers with blocky architectures through selective bromination of the amorphous polymer chain segments that interconnect the gel's crystalline domains. NMR spectroscopy experiments were used to characterize the microstructural differences between solution-state and gel-state Br-sPS copolymers, prepared in a matched set with degrees of bromination ranging from 6-30 mol% Br. Here, I will demonstrate assignment of the carbon resonance spectra of Random and Blocky Br-sPS copolymers to triad and pentad co-monomer sequences using 1D and 2D NMR spectroscopy experiments. Co-monomer sequence distributions were found to be in excellent agreement with 100 computer simulated random and blocky copolymers with 1442 monomer units (based on our sample, $M_w = 300\text{K}$, $\bar{D} = 2.0$).



Scheme: Schematic representation of the post-polymerization bromination of syndiotactic polystyrene to produce Random and Blocky copolymers with significantly different co-monomer sequence distributions, evaluated using ^{13}C NMR spectroscopy.

POLYURETHANE COMPOSITES FOR ANNULUS FIBROSUS SCAFFOLDS FOR THE CORRECTION OF DISC DEGENERATION

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Spinal disc degeneration is a very prevalent problem in today's society, effecting anywhere from 12% to 35% of a given population, and when severe enough, can cause bulging and herniation of the intervertebral disc.^{1,2} This can cause immense lower back pain in individual's stricken with this disease, and in the US, medical costs associated with lower back pain to exceed \$100 billion.³ This research study suggests a new method for creating an artificial annulus fibrosus scaffold, similar to that of the natural intervertebral disc, for the correction of disc degeneration in the spine. Because the system will be *in vivo*, the materials used were all characterized as biocompatible; a polyurethane (PU) currently being used in medical devices and implants, and the cellulose nanocrystals (CNCs) coming from natural cellulose in sources such as wood and plants. Solvent casting using N,N-dimethylformamide and melt pressing techniques were recruited for the processing of the polymer

composites for multiple different compositions (100/0, 90/10, 80/20, and 70/30 wt% PU/CNC). Once thin films were obtained from melt pressing, they were cut into ribbons for swell, tension, and creep testing, and wound into ringed structures, of lengths 500 and 650 mm, similar to the natural annulus fibrosus for compression and relaxation testing, **Figure 1**. Swell testing revealed a maximum water uptake after 48 hours, leading to significant softening of the material. Due to the stiffness of the dry samples however, only swelled samples were used for mechanical testing. Tension testing utilizing DMA resulted in Young's moduli of 17.1, 24.4, 32.3 and 33.4 MPa, respectively, three within the ideal range of 18-45 MPa for the natural annulus fibrosus.⁴ Creep, relaxation, and compression tests were all performed

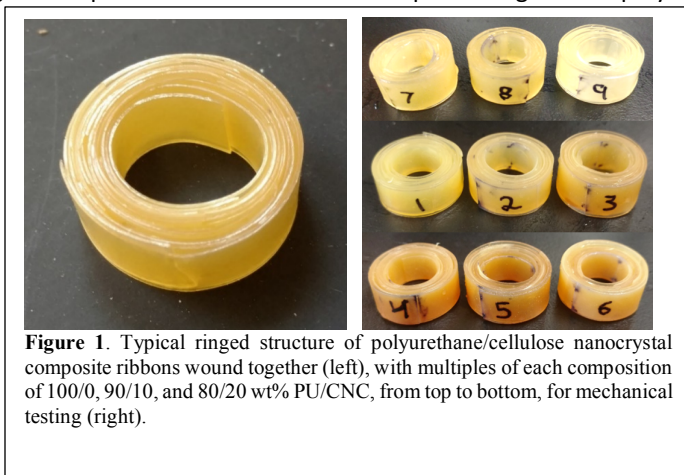


Figure 1. Typical ringed structure of polyurethane/cellulose nanocrystal composite ribbons wound together (left), with multiples of each composition of 100/0, 90/10, and 80/20 wt% PU/CNC, from top to bottom, for mechanical testing (right).

using a tensile tester, showing varying results for mechanical properties for each composition and each length of total ringed structure. Compression tests of 500 mm ringed samples resulted in bulk moduli of 5.9, 9.1, and 14.1 MPa for compositions of 100/0 – 80/20 wt% PU/CNC, and bulk moduli of 10.5, 13.8, and 18.8 MPa for the 650 mm ringed samples of the same compositions. This shows the tunability of the system, and although an ideal bulk modulus of around 4.2 MPa is desired,⁴ future work looks at improving the durability and integration of the system for *in vivo* applications.

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BMP-2 MODIFIED FIBERS FOR SOFT GRAFT-BONE INTEGRATION DURING LIGAMENT RECONSTRUCTION

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After the reconstruction of a damaged anterior cruciate ligament, strong integration between the bone ends and the transplanted graft is essential. Existing reconstruction practices, that avoid invasive bone-tendon-bone tissue harvest, commonly compromise integration and directly fix the soft tissue graft to the native bone risking mechanical instability and pullout of the graft. Scaffolds with transition regions involving multiple phases have been engineered [1], yet the gradients developed over extremely small-scales complicate the structures and introduce fabrication challenges. In view of this, new simple scaffolds that provide functional regeneration with a smooth transition between the two tissues are needed. With the goal of developing so, this work focuses on the fabrication of bone-forming scaffolds. Electrospun fiber scaffolds are presented with bone morphogenic protein (BMP-2) to make up graft ends that can fit into native bone tunnels. With the tunnels treated as broken bones, tunnel healing with the contacting bone-forming scaffold will allow functional graft-bone integration, thus decreasing graft failure rates and patient rehabilitation time.

Polycaprolactone (PCL) and a 1:99 w/w heparin/PCL blend were dissolved in tetrafluoroethanol to give 8 wt% solutions. Solutions were electrospun into 300 μm thick meshes for the analysis of BMP-2 conjugation, or onto 1.8 cm^2 circular glass coverslips ($\sim 100 \mu\text{m}$ thickness) for *in vitro* studies. Fibers were modified with BMP-2 through adsorption and covalent conjugation by incubating with 250 ng/ml BMP-2 solutions. Immobilized BMP-2 was quantified with ELISA and values normalized per unit mass of fiber mesh. Cell viability and proliferation studies, involved seeding 4×10^4 mesenchymal stem cells (MSCs) the electrospun fibers and cultured for 3, 7 and 14 days. Viability was analyzed with Live/Dead cell staining and proliferation by DNA quantification using PicoGreen kit. Alkaline phosphatase (ALP) activity was determined using *p*-nitrophenyl phosphate as a colorimetric substrate and normalized to cell number.

The concentrations of BMP-2 on the fiber surfaces ranged from 1 to 12 μg BMP-2 per gram of fibers for both immobilization techniques (Figure 1A). The highest BMP-2 was on the covalent attachment on the heparin/PCL surface due to the introduction of carboxylic acid groups on heparin that facilitate conjugation [2]. At the same time, enhanced BMP-2 adsorption to heparin/PCL meshes suggests ionic interactions between anionic heparin and cations on BMP-2. Cell studies on BMP-2 displaying fibers show that cells attach and remain viable on both PCL and heparin/PCL meshes (Figure 1B). Osteoblastic differentiation studies on BMP-2 conjugated heparin/PCL of ALP activity in the presence of covalently conjugated BMP-2 was 0.55 pmol/(cell.min) compared to 0.38 pmol/(cell.min) without BMP-2, indicating the bioactivity of BMP-2 and its guidance towards the osteogenic differentiation of MSCs.

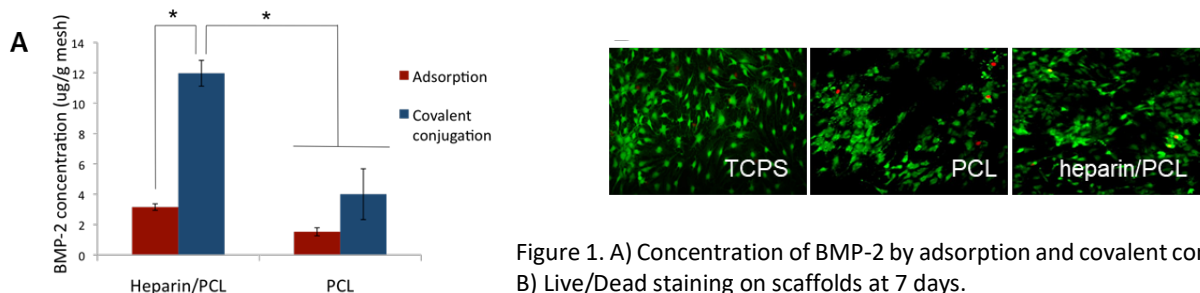


Figure 1. A) Concentration of BMP-2 by adsorption and covalent conjugation B) Live/Dead staining on scaffolds at 7 days.

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SYNTHESIZING A HEPARIN MIMIC MATERIAL DERIVED FROM CELLULOSE NANOCRYSTALS

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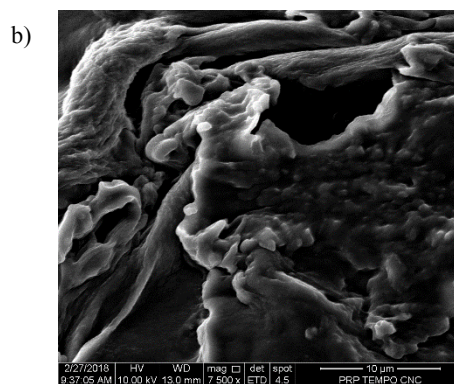
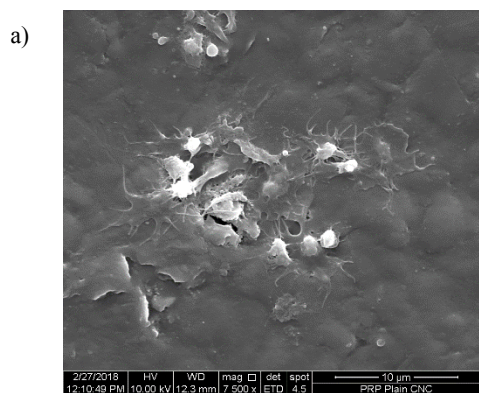
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To prevent clotting during dialysis, heparin is used to line the tubing which blood flows through. Unfortunately, many side effects arise from taking heparin, especially when it's used for an extended period of time. As such, long term exposure for individuals undergoing dialysis every day is unavoidable. To prevent the solubilized heparin from entering the bloodstream, we are investigating a material, instead of a small molecule, to reduce coagulation and long-term effects of heparin.

Cellulose nanocrystals (CNCs) contain the same backbone structure as heparin along with desirable mechanical properties, like high stiffness and anisotropic shape. By altering the functionalization on the surface of CNCs to closely mirror that of heparin, it should be possible to make a material that counteracts blood clotting, while not introducing soluble small molecule anti-coagulants into the body. Through blood assays and platelet fixing analysis we have been able to show that this change in functionalization does reduce coagulation. Surface chemistry of CNCs were modified from 'plain' CNCs (70 mmol SO³-/kg residual from hydrolysis) to 500 mmol COO⁻/kg (TEMPO oxidized) and 330 mmol SO³-/kg CNC (sulfonated CNCs). We will show that by utilizing CNCs reactive functional groups and incredible mechanical properties we are able to create a material that reduces clotting while maintaining the tubing's mechanical strength, all while eliminating all heparin induced side effects.



(a) 30 wt% 'plain' CNC/polyurethane film that shows platelet growth after platelet fixing (b) 30 wt% TEMPO oxidized CNC/polyurethane film

REGIOSELECTIVE CHLORINATION OF CELLULOSE ESTERS BY METHANESULFONYL CHLORIDE

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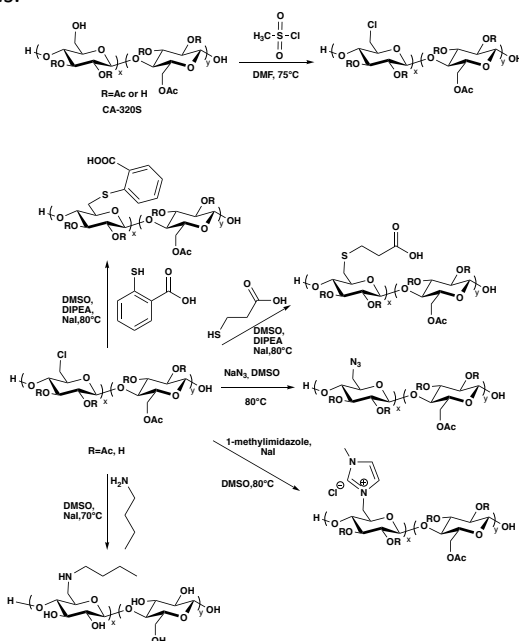
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Cellulose is an attractive material due to its abundance in nature, low toxicity and renewability.^{1,2} However, wider applications of cellulose are impeded by its poor solubility in common solvents and lack of thermoplasticity. Our group is using chemical modification to tailor cellulose physicochemical properties and append new functional groups, thereby enabling new applications.

Here we develop a method for chlorination of cellulose esters using methanesulfonyl chloride (MsCl) (**Scheme 1**). This chlorination reaction is chemo- and regioselective, despite in the presence of esters groups, with negligible side reactions (mesylation, formation of formate groups), while preserving DP. We also demonstrate that the chlorinated cellulose esters are useful intermediates for appending new functional groups by nucleophilic substitution reactions. We use azide, amines and thiols as model nucleophiles to test the reactivity of 6-Cl with nucleophiles. Chlorinated cellulose can undergo quantitative displacement with strong nucleophiles but is much less reactive towards weaker nucleophiles. We further explore a strategy to improve the conversion of chlorinated cellulose esters with weak nucleophiles by adding sodium iodide (NaI). This chlorination method has strong potential for practical preparation of a wide variety of cellulose esters derivatives, including cationic and anionic derivatives.



Scheme 1. Regioselective chlorination of CA320S and subsequent displacement by azide, amines and thiols.

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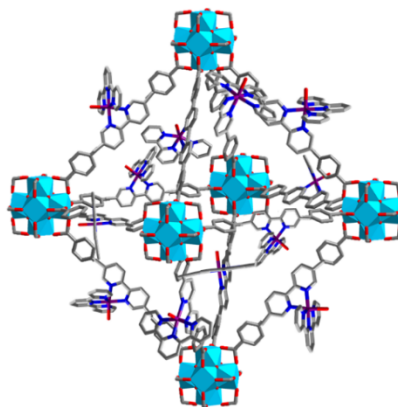
A CATALYST LOADED MOF FOR ELECTROCHEMICAL WATER OXIDATION

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As global energy demand continues to rise, there is an increased demand for alternative, renewable energy sources. One of the most promising renewable sources is solar energy, which provides enough energy in an hour and a half to meet the global energy demands for an entire year.¹ One way to harness this energy is the development of artificial photosynthetic devices. These devices would capture solar energy, water and carbon dioxide and produce carbon-based fuels that can be used with our current energy infrastructure. The most significant bottleneck in these artificial photosynthetic devices is the water splitting reaction, and as a result development of catalysts for water oxidation is essential.² Many new water oxidation catalysts are homogeneous, and suffer from typical drawbacks in homogeneous catalysis such as degradation and lack of recyclability. A new area of interest has been in developing materials that can incorporate homogenous catalysts into a heterogeneous system, while retaining the catalytic properties of the catalyst in solution.

Metal-Organic Frameworks (MOFs) are highly tunable 1D, 2D or 3D materials composed of metal nodes and organic linkers with high internal surface area.³ Zirconium based MOFs are a subset of MOFs with extreme thermal and chemical stability. Because of their high stability and large internal surface areas Zr-based MOFs have been investigated as potential hosts for homogeneous catalysts. Here the synthesis, characterization and catalytic testing of a new Zr-based MOF with $[\text{Ru}(\text{tpy})(\text{BPDB})\text{OH}_2]^{2+}$ (tpy = 2,2':6',2''-terpyridine, BPDB = 2,2'-bipyridine-5,5'-dibenzoic acid) as the water oxidation catalyst is reported. The new MOF was grown as a film on conductive fluorine-doped tin oxide (FTO) and tested for electrochemical water oxidation. The films have been shown to be active for water oxidation over the course of multiple catalytic runs.



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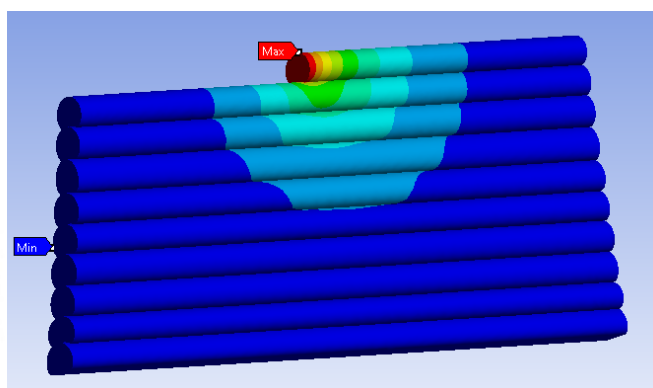
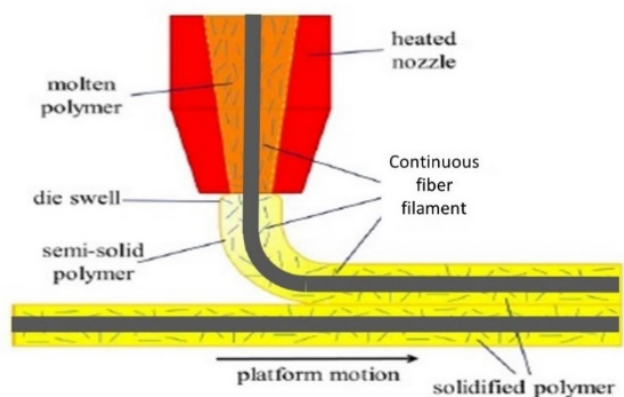
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CHARACTERIZATION OF POLY(ETHER IMIDE) TOWARDS THE DEVELOPMENT OF A FUSED FILAMENT FABRICATION PROCESS MODEL

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To better understand the evolution of part strength during the FFF process, we are developing a model to describe the self-healing phenomenon that couples the complex thermal and geometric profiles with diffusion at the layer interface as well as incorporating a continuous carbon fiber reinforcement material. This model is strongly dependent on the transient behavior of the polymer governed by the processing and environmental conditions present during the printing process. Our preliminary work analyzes the viscosity of the neat polymer, combined with characterizing the complete re-entanglement time of the neat polymer to quantify the extent of self-healing as a function of temperature. The corresponding mechanical strength is driven by interlayer adhesion and can be characterized as a function of processing conditions. Our preliminary rheological findings of a poly(ether imide) amorphous thermoplastic indicate that times for substantial self-diffusion are longer than the time at processing temperature currently implemented in FFF processing. This limits the amount of chain re-entanglement at the layer interface and corresponding bond strength between layers of a printed part, and suggests that a modified printing process to create stronger parts with this material is required to produce parts with increased mechanical properties. Furthermore, the inclusion of the continuous carbon fiber reinforcement material introduces an anisotropic thermal conductance that will modify the thermal transport during the cooling and consolidation process.



THERMAL AND MORPHOLOGICAL CHARACTERIZATION OF VIRGIN AND RECYCLED PET/PP BLENDS FOR MATERIAL EXTRUSION ADDITIVE MANUFACTURING

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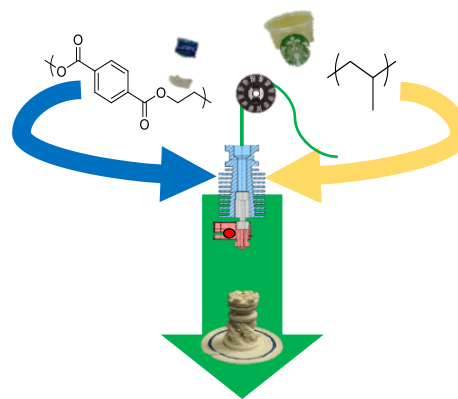
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Poly(ethylene terephthalate) (PET) and polypropylene (PP) are two semi-crystalline polymers that are widely available and recyclable. PET and PP account for 18 and 55 million tons of plastic production per year, respectively.¹ Currently, only 31% and 1% of all post-consumer PET and PP, respectively, are recycled.^{2, 3} Unrecycled, post-consumer PET and PP are abundant and are widely applicable in consumer and industrial settings, making them ideal candidates for cheap and useful feed material for additive manufacturing (AM) processes, specifically fused filament fabrication (FFF), a form of the material extrusion technology. However, printing semi-crystalline materials such as PET and PP is challenging given that as the extrudate cools and crystallizes, the printed layer shrinks and warps, which renders it unusable. One potential solution to successfully printing semi-crystalline materials is to create and print polymer blends. Virgin PET and PP blends, compatibilized with maleic-anhydride-graft-polypropylene, has been successfully fabricated into complex structures via FFF. In this work, the authors highlight differences between the virgin polymeric materials and selected post-consumer waste stream counterparts and discuss such differences with respect to their influence on FFF printability.



Virgin PET and PP pellets were blended with PP-g-MA in a twin-screw extruder to reduce the rate of crystallinity for fused filament fabrication (FFF) additive manufacturing applications. This blend was then extruded into print filament using a Filabot EX2 extruder and printed using a custom-built FFF printer. Next, the recycled PET (rPET), Aquafina water bottles, and recycled PP (rPP), Starbucks cold drink cups, were blended using a twin-screw extruder with PP-g-MA to explore possible applications for semi-crystalline recycled polymer blends in FFF. Thermal and rheological characterization of both virgin and recycled blends compared material properties in pursuit of science-based manufacturing. Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and rheological characterization points to differences in key properties. Polarized light micrographs (PLM) show varying morphological structures between the blends accentuating their differences. Predicted solutions to successfully printing the rPET/rPP blend are posed based on characterization comparisons with the previously successful blend of virgin polymers.

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FILLER-FREE BIOMIMETIC HYDROGELS WITH HIGH YIELD STRESS AND CONTROLLABLE MODULUS FOR BIOPRINTING OF NEURAL TISSUES

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Additive manufacturing (AM) using cell-laden hydrogels, also referred to as bio-inks, underlies various emerging applications in regenerative medicine, drug discovery, and fundamental study of microphysiological systems. Bio-inks should exhibit chemical and mechanical properties found in native extracellular matrix (ECM) as well as rheological properties that support AM of high quality tissues, such as shear thinning and high yield stress characteristics that enable low shear stress and formation of free-standing structures, respectively. Furthermore, it is also desirable that bio-inks exhibit material properties that enable in situ monitoring capabilities. However, the current state-of-the-art bio-inks are based on heterogeneous mixtures of structural polymers that provide mimicry of native ECM, such as gelatin methacrylate or alginic acid, with rheological modifiers (e.g., fillers), such as nanocellulose or clay nanoparticles, that improve bio-ink processability. Although such bio-ink formulations enable the fabrication of high modulus tissues (e.g., connective tissue), they impede the production of low modulus tissues (e.g., neural tissues). Furthermore, fillers lead to highly opaque bio-inks, which impedes the use of optical-based sensing techniques. Here, we show a biomimetic filler-free bio-ink which exhibits native ECM components, low modulus, high yield stress, optical transparency, and photopolymerizable moieties for selective tuning of tissue modulus. Pluronic F-127, which forms a gel with Herschel-Bulkley properties above the critical micelle concentration, was thiolated and mixed with dopamine functionalized gelatin (Gel-DA) and hyaluronic acid (HA-DA) to form a lightly crosslinked network. Gelatin conjugated with both dopamine and methacrylate (Gel-DA-MA) was incorporated to facilitate additional tuning of neural tissue modulus via photopolymerization. Ultimately, this bio-ink provides a step toward quality-controlled AM and in situ monitoring of biomimetic microphysiological neural systems and scaffolds for nerve regeneration.

MINIMIZATION OF INTERFACIAL STRESS IN 3D PRINTED FIBER REINFORCED POLYMER (FRP) COMPOSITES USING META-HEURISTIC OPTIMIZATION

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The layer-by-layer nature of many additive manufacturing (AM) processes yields a final component with complex states of residual stress and many weak interfaces. This is especially true of multi-material AM processes, which have multiple dissimilar interfaces, requiring some interfacial adhesion. Given a specific geometry and a well-defined loading condition (or set of loading conditions), it is of interest to design a material distribution which sufficiently minimizes stress concentrations, particularly at weak interfaces, while simultaneously maximizing another variable (e.g. stiffness).

This study is focused on the optimization of fiber direction in multiple layers of a fiber reinforced composite. The composites are fabricated using a MarkForged Mark II 3D Printer (Boston, MA), which allows for design of arbitrary fiber orientation in any print layer. Using a combination of finite element models and a meta-heuristic search algorithm, the optimal fiber distribution can be determined for a particular scenario. In order to validate results from optimization, mechanical experiments will be conducted on both control and optimized samples. Digital image correlation (DIC) will be used to quantify local stress and strain distributions (in-situ), and ex-situ X-ray tomography may be used to characterize internal composite damage.

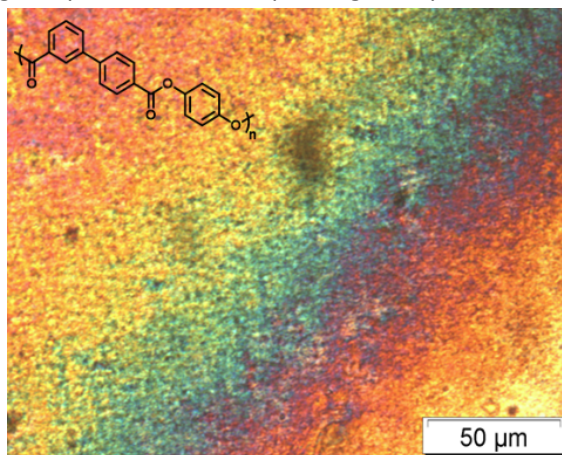
SYNTHESIS OF A NOVEL FULLY AROMATIC LIQUID CRYSTALLINE POLYESTER UTILIZING A KINKED 3,4' BIBENZOATE MONOMER

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Fully aromatic thermotropic polymers comprise a wide range of high performance applications resulting from their uniquely beneficial shear thinning and orientational properties when processing in the mesophase. Vectra and Xydar comprise the most commonly utilized commercial materials in this field exhibiting nematic liquid crystalline mesophases and melting temperatures > 330 °C. The use of linear aromatic backbones often results in polymers with melting temperatures higher than the polymer degradation temperature making them improcessable.¹ Liquid crystalline polymers (LCPs), like Vectra, utilize random copolymerization with secondary linear monomers to disrupt chain packing and lower processing temperatures. Chain packing disruption can also occur through the use of flexible diol spacers, but these polymers often exhibit smectic rather than nematic mesophases.²⁻⁴

In previous studies, the use of kinked aromatic monomers, such as isophthalate, has only demonstrated a loss of LC properties and a resulting semi-crystalline or amorphous polymer. This work focuses on the synthesis and characterization of a liquid crystalline polyester, poly(hydroquinone-3,4'-bibenzoate), based on the novel kinked monomer, dimethyl 3,4'-bibenzoate. Acidolysis polymerization with acetylated or pivilated hydroquinone and biphenyl-3,4'-dicarboxylic acid afforded tan or white polymers respectively. Differential scanning calorimetry (DSC) and polarized optical microscopy (POM) elucidated that the longer kinked structure of 3,4'BB disrupted crystallization while maintaining LC properties. This novel nematic glass polymer provides a wide temperature range for processing and further (co)polymerization with common diacids demonstrated tunable thermal and mechanical properties.



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TAILORING THE MESOPHASE RANGE OF THERMOTROPIC POLYESTERS THROUGH COPOLYMERIZATION OF 4,4'-BIBENZOATE AND KINKED ISOMER

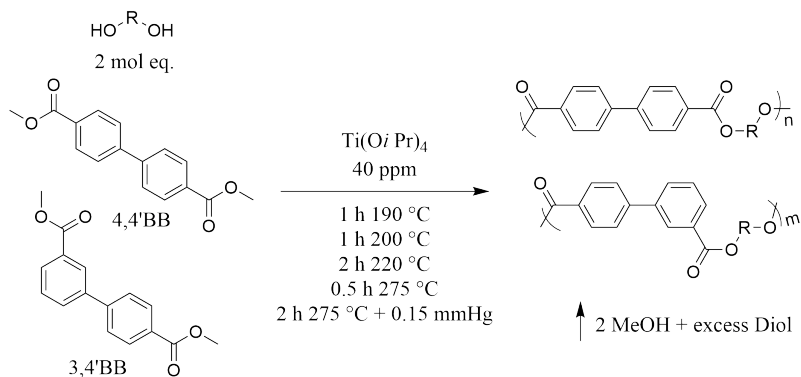
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High performance fibers and coatings for electronics are just a few of the many applications that utilize liquid crystalline polyesters. Vectra and Xydar make up the most commonly used forms of LCPs in industry and containing fully aromatic back bones comprised of a variety of aromatic monomers such as hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid. These polyesters exhibit nematic LC mesophases, melting temperatures > 330 °C, and incredible solvent resistance generating high performance materials able to withstand a large variety of conditions. While these polymers are incredibly industrially relevant, their solvent and thermal resistance makes in depth characterization of these polymers challenging. One common method used to lower the processing temperatures of these materials is to incorporate a variety of flexible aliphatic diols in between a rigid mesogenic monomer thereby breaking up the chain packing. Using diol spacers with only methylene units, smectic CA and smectic A LCPs can be developed that have processing temperatures < 300 °C.¹

The incorporation of kinked aromatic diesters also produces the same effect of lowering processing temperatures. Unfortunately previous studies have demonstrated short kinked monomers, such as isophthalate, disrupt LC properties at low

mol % incorporation into LC polymers.² This work will focus on the synthesis and characterization of two series of semi-aromatic LC (co)polyesters (poly(butylene-4,4' bibenzoate) and poly(diethylene glycol- 4,4' bibenzoate)) utilizing a novel biphenyl kinked monomer, dimethyl 3,4'-bibenzoate. In each series, the linear dimethyl-4,4' bibenzoate (4,4'BB) was systematically exchanged with its kinked isomer, dimethyl-3,4' bibenzoate (3,4'BB). These polymers series were synthesized using melt transesterification at temperatures ranging from 190 – 275 °C. Differential scanning calorimetry (DSC), wide angle X-ray scattering (WAXS), and polarized optical microscopy (POM) elucidated that the kinked structure of 3,4'BB disrupted crystallization at low incorporations, significantly lowered the melting transition temperature (> 50 °C) in each series. The LC properties were less impacted due to the biphenyl structure resulting in LC glasses with wide mesogenic windows. Dynamic mechanical analysis (DMA) further demonstrated the tunable nature of the thermomechanical properties resulting from the (co)polymerization of these isomers.



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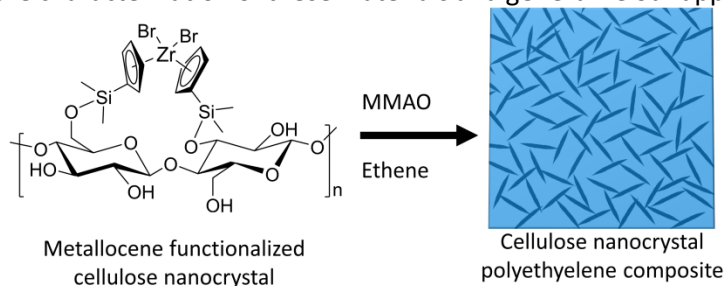
CELLULOSE NANOCRYSTAL POLYETHYLENE COMPOSITES MEDIATED BY COVALENT METALLOCENE ATTACHMENT AND HETEROGENEOUS POLYMERIZATION

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Wood based cellulose nanocrystals (CNCs) are an ideal filler material due to their high aspect ratio, high elastic modulus, and abundance of source material. Cellulose nanocrystals have been previously shown to increase the storage modulus of low density polyethylene (LDPE) by up to 340%¹ at a critical volume concentration. Given that polyethylene is the world's most-used polymer and that the demand for nanofilled polyethylene is increasing,² methods to incorporate CNCs into other polyethylene grades, especially HDPE, remain an important challenge.

The functionalized metallocene catalyst 1,1'-bis(bromodimethylsilyl)zirconocene dibromide³ was covalently bound to the surface of the hydroxyl-rich CNC. Polymerization ensued with an excess of alumoxane co-catalyst showing reasonable productivity. Leaching studies showed that the catalyst remained surface-bound. AFM micrographs showed no evidence of aggregation. Optical transparency indicated that the CNCs were well dispersed. Importantly, mechanical testing showed substantial reinforcement – a threefold increase was observed in the storage modulus relative to unfilled commercial ultra-high molecular weight polyethylene. Work is underway to complete the characterization of these materials and generalize our approach to other polyolefins.



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HIGH PERFORMANCE POLYMERS FOR ADDITIVE MANUFACTURING: 3D PRINTING OF KAPTON®

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Poly(4,4'-oxydiphenylene pyromellitimide) (PMDA-ODA PI), commonly known by the trademark Kapton®, is a high performance polymer with exceptional thermal and thermomechanical properties from -260 °C to 400 °C. Unfortunately, an all-aromatic structure results in insolubility, prohibiting traditional manufacturing processes. This limits commercial Kapton® products mainly to films and coatings, which are processed in a 2-step procedure. The advent of additive manufacturing (or 3D printing) revolutionized modern manufacturing and motivated reinvestigation into overcoming the processing challenges of Kapton®.

We will present a facile chemical modification of PMDA-ODA PI, which allowed for the development of Kapton® into 3D shapes.¹⁻² In particular, attaching (meth)acrylate moieties to soluble ODA-PMDA precursors enabled their processing using vat photopolymerization (VP). VP utilizes UV light to photo-crosslink the polymeric precursors layer-by-layer resulting in 3D objects.³ Subsequent thermal treatment yielded 3D parts consisting solely of PMDA-ODA PI (Figure 1). This processing strategy expands Kapton® products from films to complex 3D objects, thus opening the door to create previously unimaginable parts for applications including spacecrafts/satellites, electronics and automotive.

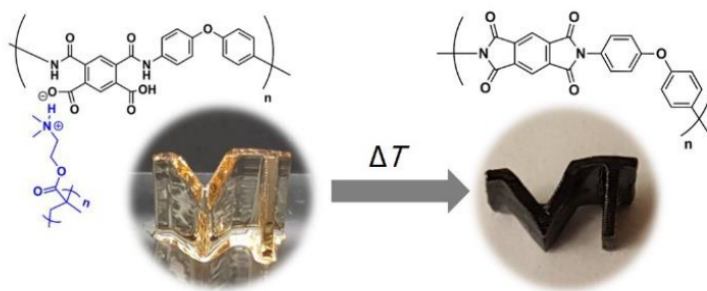


Figure 4. Thermal imidization of crosslinked organogel renders fully aromatic PMDA-ODA PI.

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TAKING A SMALL MOLECULE SEMICONDUCTOR FROM THE ELECTRONICS INDUSTRY TO SUCCESSFUL VISUALIZATION IN NANOMEDICINE

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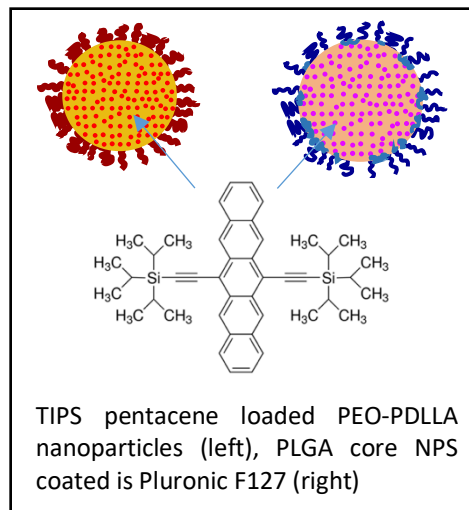
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The use of nanoparticles in drug delivery can address many of the difficulties faced by traditional methods such as systemic toxicity, transport limitations, and drug solubility. By loading drugs into biocompatible polymeric nanoparticles, we can increase the bioavailability of drugs that may previously have been deemed unusable. However, the visualization of particle biodistribution is essential in characterization of a drug carrier's efficacy as a future treatment option and its path toward the clinic.

6,13-Bis(triisopropylsilylethynyl)pentacene (TIPS pentacene) is a small molecule organic semiconductor that has been primarily used in transistors, LEDs and solar cells. [1, 2] However, its high quantum yield and photostability make it a promising candidate as a fluorescent imaging agent for biomedical applications. Due to its highly hydrophobic nature, this pentacene derivative has been successfully encapsulated into both poly(lactic acid) and poly(lactic-co-glycolic acid) based polymer nanoparticles and used in 3 distinct biological studies and shown to be non-immunogenic. The particles were imaged by fluorescence microscopy, confocal microscopy and imaging cytometry and even at just 1 wt% loading were readily visible. TIPS pentacene labeled particles have been used to study cell uptake in M1 versus M2 macrophages [3], ensure cell internalization for plasmid loaded NPs, and attached to the surface of bacteria as a potential tumor therapy. This presentation will give an overview of these different applications where TIPS pentacene has been applied in the field of nanomedicine.



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A COMPARISON BETWEEN TWO POST-MODIFICATION APPROACHES FOR POLYBENZIMIDAZOLES WITH IMPROVED GAS PERMEABILITY

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Polybenzimidazoles (PBI) are a promising material for gas separation membranes at elevated temperatures due to their excellent chemical and thermal stability and high glass transition temperature. Their properties make them useful for gas separation of H₂ and CO₂ from pre-combustion syngas, which requires operating temperatures of 150-300 °C to improve selectivity towards H₂. PBIs based on the Celazole® structure exhibit poor permeability and solubility due to chain rigidity and high packing efficiency. Previous work involved synthesizing PBI polymers with a sulfonyl-containing tetraamine, which resulted in improved PBI solubility as compared to the commercial standard, Celazole®.

The focus of this work was to try and improve gas permeability without sacrificing selectivity and mechanical properties of the membrane. Low molecular weight poly(ethylene oxide) (PEO) or poly(propylene carbonate) (PPC) were incorporated as thermally labile grafts or blends, respectively. The concept was if the low molecular weight sacrificial components were removed via a controlled heat treatment process, they would then introduce “nanovoids” in the polymer membrane, improving gas permeability. Gas transport measurements for 7 and 11 wt% PPC blends, and a 13 wt% PEO graft copolymer were conducted before and after heat treatment. The 13 wt% PEO graft copolymer exhibited the largest increase in permeability and selectivity, however, it had the largest decrease in mechanical properties. The 7 wt% PPC blend exhibited an increase in both permeability and selectivity, in addition to retaining mechanical properties comparable to the PBI homopolymer after the PPC component was removed.

PHOSPHONATED POLY(ETHYLENE TEREPHTHALATE) IONOMERS AS COMPATIBILIZERS IN POLYESTER/POLYAMIDE BLENDS FOR PACKAGING APPLICATIONS

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Poly(ethylene terephthalate) (PET) is widely used in the packaging industry. The oxygen barrier properties of PET are acceptable for many food and beverage products, but do not meet the stringent requirements for packaging highly oxygen-sensitive products. Blending PET with aromatic polyamides, such as MXD6, reduces the inherent oxygen permeability of the polyester matrix. However, due to the immiscibility of these two parent polymers, a compatibilizer is necessary to achieve efficient and stable mixing. Herein, we present the influence of phosphonated polyester ionomers (PPET) as a minor-component compatibilizer on the morphology and properties of polyester/MXD6 blends prepared in melt blending methods. Using scanning electron microscope (SEM), we demonstrated decreased phase size of the dispersed MXD6 component in polyester matrix as a result of added PPET. Haze value measurements indicated decreased haze value with increasing the amounts of ionic groups, which is attributed to the decreased MXD6 particle dimensions. Thermal analysis showed increased nucleation effect of MXD6 on PET crystallization and inhibited crystallization of MXD6 in compatibilized blends. Blends containing polyester ionomer were demonstrated to exhibit comparable mechanical properties compared to blends without compatibilizer. Gas barrier properties were examined by oxygen permeability tests. Consistent with previous literature results, this compatibilization behavior is attributed to specific interactions between the ionic functionality and the amide units of MXD6, which lowers the interfacial tension and leads to a reduction in phase dimensions.

SYNTHESIS OF POLY(PHOSPHORUS YLIDE)S AS EFFICIENT LIGHT ABSORPTION DYES

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Phosphonium-containing polymers exhibit superior thermal and chemical stability,¹ as well as enhanced ion conductivity,²⁻³ in comparison to ammonium-containing analogs. However, the application of phosphonium-containing polymers in light absorption is underexplored. In this work, we report the synthesis and characterization of a novel class of polymers, poly(phosphorus ylide)s.

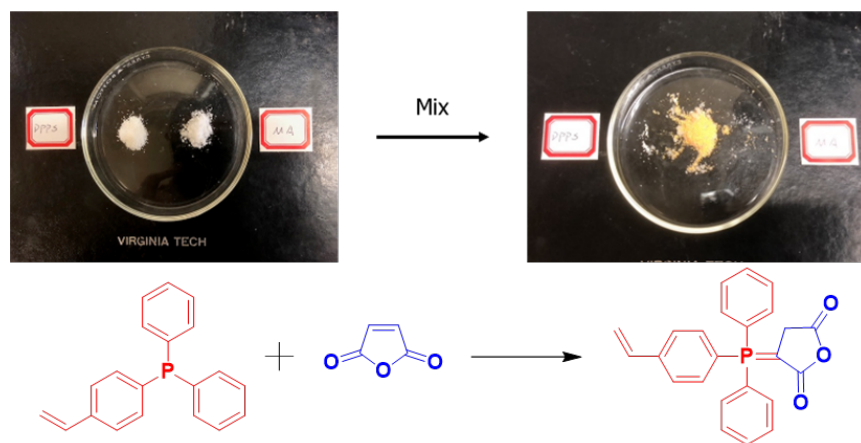


Figure 5 Solid-state charge transfer between DPPS and MA.

Facile reaction between 4-(diphenylphosphino)styrene (DPPS) and maleic anhydride (MA), in either solution or solid state, produced polymerizable phosphorus ylide monomers (Figure 1). Time-of-flight mass spectrometry, ¹³C NMR, ³¹P NMR and ¹H NMR spectroscopy confirmed the structure of

phosphorus ylide monomers. ¹H NMR spectroscopy confirmed control of different DPPS/MA product ratios through reaction stoichiometry. Conventional free radical polymerization of phosphorus ylide monomers yields poly(phosphorus ylide) homopolymers. Post-polymerization modification of poly(DPPS) homopolymers with MA, in either solution or solid state reactions, also yields poly(phosphorus ylide)s. Solutions created from these materials demonstrate promising light absorption properties. Poly(phosphorus ylide)s showed tunable UV-Vis absorption peaks from 360-420 nm depending on different DPPS/MA ratios. Both monomers and polymers exhibited strong fluorescence with maximum emission wavelengths ranging from 510-545 nm. Differential scanning calorimetry (DSC) demonstrated no glass transition temperature (T_g) before thermal degradation in poly(phosphorus ylide)s. The combination of thermal and air stability, as well as optical properties, of poly(phosphorus ylide)s demonstrate their potential as light absorption dyes in various applications, such as dye-sensitized solar cells.

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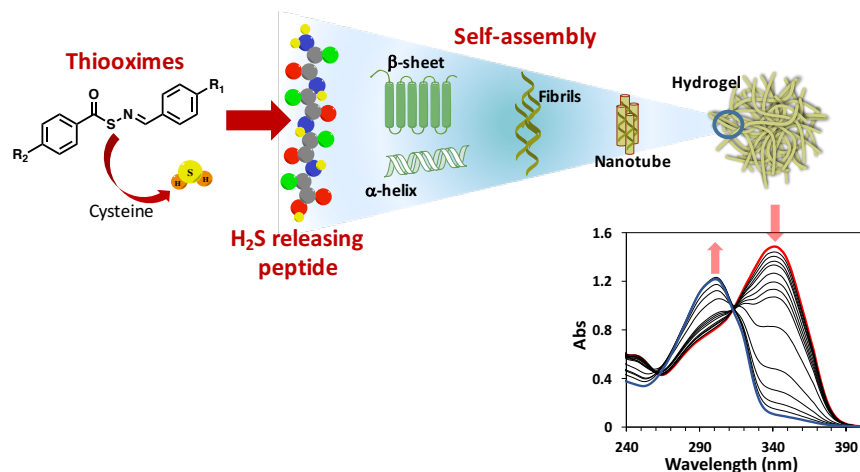
H₂S RELEASING PEPTIDE HYDROGELS: AN INSIGHT INTO STABILITY AND SELF-ASSEMBLY

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H₂S-releasing donors, with sustained H₂S release, are often employed to study its role in regulating various physiological processes. Thiooximes are cysteine triggered H₂S-releasing donors with structure dependent H₂S release but lack water solubility and localized delivery.¹ The localized H₂S delivery is required to maintain high local H₂S concentrations for better understanding in the therapeutic models like wound healing and SMC proliferation. As a result, the thiooximes were appended onto an aromatic peptide amphiphile, which formed hydrogels with Ca²⁺.² However, it was observed that the low hydrolytic stability of the resulting peptide limited the sustained H₂S release as the hydrolyzed peptide loses its mechanical properties.

Herein, we show how structural modification of the peptide components can affect its hydrolytic stability and self-assembly. We changed the linker segment (one of the four components of APAs) to include electron withdrawing groups, electron donating groups and groups with extended conjugation. Hydrolysis of the peptides was followed using UV-Vis spectroscopy at a range of different pH values and exhibited pseudo first-order kinetics. Changing the linker also affected the self-assembling properties of the peptides and the robustness of the hydrogel which was studied using rheology and optical imaging.



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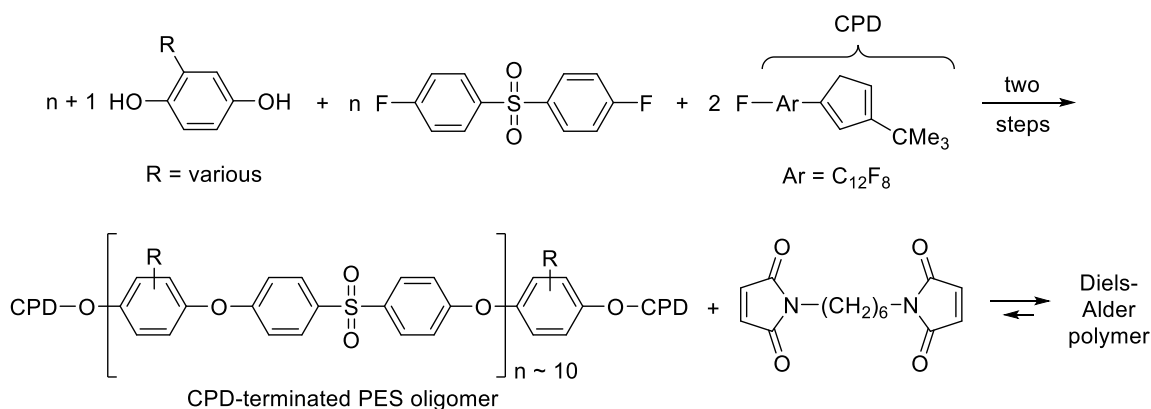
APPROACHES TO SELF-HEALING MATERIALS USING SEGMENTED POLY(ETHER SULFONE)S CONTAINING THERMALLY REVERSIBLE LINKAGES

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Our group is working on synthetic approaches to linear polymers that are propagated through Diels-Alder (DA) reactions of cyclopentadienes and maleimides (CPD+MI). We want to make film-forming materials that have self-healing capability owing to the thermally reversible linkages within the polymer.

Our approach is shown in the accompanying scheme. Substituted hydroquinones were oligomerized with bis(4-fluorophenyl)sulfone, end-capped with CPD functionality, and then polymerized with bis(MI) monomers. The resulting segmented polymers show good solubility and film-forming characteristics. Hydroquinone substituents were selected to adjust the T_g of the PES segments to match the temperature at which we expect thermal self-healing to occur. This approach allows us to test self-healing properties just above the T_g , minimizing other mechanisms such as bulk flow. This poster describes the details of our synthetic methods and the results of our physical testing.



ROLLED PCL/GelMA COMPOSITES AS SCAFFOLDS FOR ACL REPAIR

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Approximately 200,000 anterior cruciate ligament (ACL) injuries occur each year with 50-75% of these requiring surgical repair¹. Autografts are commonly used for ACL replacement, yet suffer from limited tissue availability and donor site morbidity. Allografts are another option, yet risk disease transmission². Engineered ligament tissues that consist of cells and a degradable fibrous scaffold hold promise as an alternative treatment³. Electrospinning can be used to fabricate fibrous scaffolds but results in thin meshes with small pores that inhibit cell infiltration and proliferation. We propose that 3D cylindrical composites can be made by combining electrospun fiber meshes with a gelatin methacrylate (GelMA) hydrogel. By combining GelMA with electrospun PCL/PEGDA (polycaprolactone/polyethylene glycol diacrylate) fibers, GelMA would fill the pores and crosslink with the electrospun fibers. Furthermore, the mechanical properties of the composite as well as the rate of cell infiltration are expected to depend on the GelMA properties. Therefore, the objectives of this project are to determine how different concentrations of GelMA affect 1) the mechanical properties of GelMA hydrogels 2) migration of bone marrow stromal cells (BMSCs) into hydrogels, and 3) the mechanical properties of rolled electrospun PCL/PEGDA fiber meshes.

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PLASMONIC NANOPARTICLES SENSITIVITY AND THEIR APPLICATIONS IN PLASMONIC NANOCOMPOSITES

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Plasmonics is the study of coherent oscillations of conduction electrons in metal nanoparticles excited by certain incident frequencies of electromagnetic radiations. The localized surface plasmon resonance wavelength (λ_{LSPR}) of these nanoparticles are sensitive to minute changes in refractive index of the medium around them and can therefore detect trace amounts of chemicals, biomolecules, and environmental pollutants. Sensitivity, which is the ratio of shift in λ_{LSPR} to change in refractive ($S = \Delta \lambda_{\text{LSPR}} / \Delta n$), is the key criterion that determines the performance of nanoparticles for such applications. Herein we have conducted the most detailed and compressive study of the plasmonic sensitivity as a function of various nanoparticle parameters including shape, size, composition, cross-sectional area, initial plasmonic resonance frequency, and aspect ratio. Through this comprehensive study, we have found that the correlation between shape and sensitivity is much weaker than that between aspect ratio and sensitivity.¹ Based on the sensitivity plot we selected the most sensitive 2D plasmonic nanoparticles in visible light range and utilized them as analytical sensors to probe the kinetics of polymer brush formation.

The 2D nanoparticles, having intrinsically flat surfaces, are ideal models for investigating the polymer brush formation. Moreover, the unique plasmonic properties possessed by the 2D nanoparticles enable to determine the amount of polymers near the nanoparticle surfaces *in situ*. As the amount of polymers increases near the surfaces, the nanoparticle characteristic λ_{LSPR} redshifts, and the shift amount corresponds linearly to the polymer density near the nanoparticle surfaces. By functionalizing the nanoparticles in solutions of thiolated polyethylene glycol (PEG-SH) with and without PEG disulfide (PEG-S-S-PEG), the three regime kinetics of polymer brush formation was confirmed. Importantly, this study revealed that the fast adsorption and slow chain rearrangement in the first regime are the causes of the latent regime. In the latent regime, the adsorbed polymer chains rearrange to anchor their ends onto the surface and contract to liberate space for other polymer chains to further graft onto the surface until saturation.²

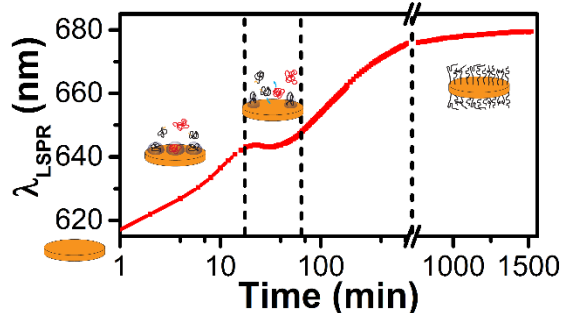


Figure: λ_{LSPR} as a function of time for Ag 2D nanoparticles functionalized with a mixture of PEG-SH and PEG-S-S-PEG.

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3D PRINTED FLOW CELLS FOR REAL-TIME GEOCHEMICAL INVESTIGATION OF FERRIC HYDROXYL-SULFATE FORMATION

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Real-time characterization of mineral nucleation and growth phenomena is becoming increasingly necessary for investigating how materials nucleate, grow, transform, and interact with their surrounding environments. For geochemical conditions in particular, real-time methods are vital for observing the often fleeting, metastable stages of formation. For example, the formation pathways of iron oxyhydroxide sulfates such as schwertmannite are poorly understood, and since these materials are known to co-precipitate and adsorb toxic contaminants, the details of their growth have important implications for quantifying biogeochemical transport of toxic species. However, studying these complex formation mechanisms in the laboratory requires intricate, custom experimental setups. To that end, we are fabricating custom reactors and flow cells for geochemical experiments by 3D printing stereolithography (SLA). Coupled with in-line analytical techniques such as small angle x-ray scattering (SAXS), we can employ these 3D printed devices to obtain novel mechanistic information via *in-situ* characterization.

Before we can comfortably deploy our 3D printed devices, it is necessary to know if the material, a methacrylate-based photopolymer, is compatible with the relevant geochemical conditions. Accordingly, we are performing tests at various post-processing stages of our material and assessing if the custom reactors are stable at a range of pH (0-12) conditions. The role of post-curing processes in facilitating more solvent resistance polymers is being investigated as well. The stability of the material is being evaluated by thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA) which provide thermal degradation patterns and mechanical properties, respectively.

Early *in-situ* SAXS experiments applying the material in 3D printed flow cells then allowed us to observe the evolution of ferric hydroxide nanoparticles as they advance towards schwertmannite or goethite, depending on pH. Preliminary results indicate that at low pH (1.8-3.5), the primary particle size remains the same as the system proceeds toward schwertmannite; at higher pH (5.6-6.5), however, particles of the same starting size grow linearly as the system evolves towards goethite. These early experiments suggest that initial FeO(OH)-like particles are rapidly coated by the negatively charged sulfate anions at low pH, inhibiting growth. As the pH increases, -OH group can more easily displace the sulfate groups and the system advances towards goethite. In order to obtain further mechanistic insight, we will couple our custom reactors with in-line analytical techniques across a variety of experimental conditions. With these methods we aim to elucidate the often transient phases of crystallization, improve experimental design versatility, and reduce costs associated with laboratory-based geochemical research.

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PROBING MULTI-SCALE TRANSPORT IN RANDOM COPOLYMER MEMBRANES USING NMR DIFFUSOMETRY

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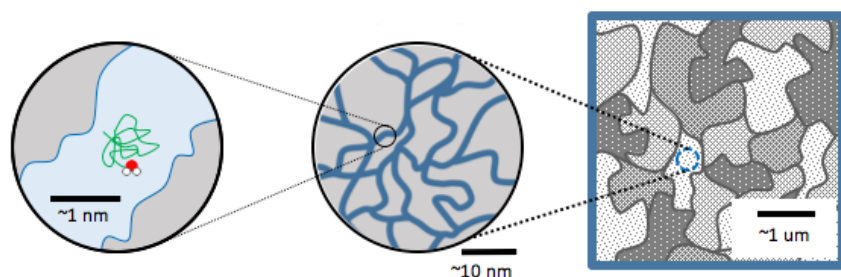
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Transport of small molecules and ions through a polymer matrix is not only dependent on the local (nanometer scale) intermolecular interactions these molecules experience, but in many cases also the micrometer scale morphology of the matrix itself.^{1,2} We will present investigations using NMR diffusometry and molecular dynamics simulations in order to better understand water transport through polymer membranes at multiple length scales.

In order to understand the effects of polymer chain dynamics on water transport, studies on two neutral random copolymer membranes based on polyhydroxyethylacrylate-co-ethylacrylate (poly(HEA-co-EA)), with $T_g < \text{room temperature}$ (rubbery dynamics), and polyhydroxymethylmethacrylate-co-methylmethacrylate (poly(HEMA-co-MMA)), with $T_g > \text{room temperature}$ (glassy dynamics). We measure water diffusion as a function of polymer composition and diffusion encoding time, revealing micron-scale heterogeneity in these polymers. We introduce the quantitative separation of material tortuosity into two regimes for the first time, averaged over the nm-bulk and μm -bulk ranges. This allows for separation of the influences on the bulk transport of water due to morphology over multiple length scales. Comparison of these two tortuosity ranges with bulk water and salt measurements reveal that nm-scale interactions contribute greatly to the differences in permeability and water-salt selectivity seen between the two membranes.

We are also studying activation energy E_a of water/ion diffusion in ionic polymers with both NMR diffusometry and molecular dynamics simulations. Valuable information regarding the local molecular environment of the diffusing species and geometric confinement of the polymer matrix is contained in the diffusive E_a .² The study of E_a probes nanoscale intermolecular interactions and provides new understanding of transport in polymer membranes.



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IMPROVING MECHANICAL PERFORMANCE OF MATERIAL EXTRUSION PARTS USING MULTI-AXIS SURFACE REINFORCEMENT

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The typical material extrusion (ME) additive manufacturing process operates through the sequential deposition of XY-planar layers stacked along the Z-axis [1]. This layer stacking introduces layer interfaces that, due to weak interlayer bond strength, weaken the part along the build axis [2]. These weak interfaces are the result of the material cooling rapidly upon deposition. The material is only above its glass transition temperature for a short window of time, limiting molecular diffusion and therefore the degree of bonding between layers [3]. To a lesser extent, this same phenomenon occurs within the layers themselves, between adjacent depositions. The mechanical performance of ME parts is therefore anisotropic, dependent on both the part orientation and road directions within each layer [2, 4]. Often, these anisotropic mechanical properties require compromises in part design either through the addition of material in critical areas, reducing end-use loads, or forgoing ME as a manufacturing option.

To address this limitation of ME, the authors propose a multi-axis deposition strategy that deposits material conformal to a part's surface to improve mechanical performance. Specifically, a custom six degree of freedom (DoF) ME system, based on a robotic arm, is used to create a surface-reinforcing 'skin', inspired by the composite layup process [5], in a single manufacturing step. As a demonstration of the deposition strategy, vertical tensile bars were fabricated through stacked XY-planar layers followed by the conformal deposition of material directly onto the printed surface (Figure 6) to evaluate the effect of the skinning approach on mechanical properties. Considering a skin pattern at 45° to the applied load, the surface-reinforced specimens demonstrated a 59% increase in yield strength as compared to geometrically similar, unreinforced, XY-planar specimens [6].

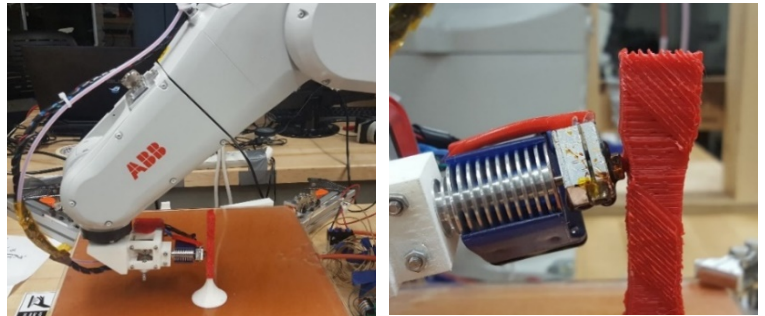


Figure 6. Skinned tensile specimen fabrication

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INFLUENCE OF FIBER CONCENTRATION ON FIBER ORIENTATION EVOLUTION DURING NONLUBRICATED SQUEEZE FLOW OF GLASS-FIBER-REINFORCED POLYPROPYLENE

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In order to meet with increasingly stringent limits on vehicle emissions and fuel efficiency being implemented over the world, auto manufacturers have implemented a strategy known as “lightweighting”. Components made of dense materials (i.e. metal) in the vehicle are replaced with fiber-reinforced plastics such as polyamides and polypropylene. These materials blend the relatively easy processing of thermoplastics with mechanical properties (e.g. Young’s modulus, strength) that meet or exceed safety standards.

The primary variables governing the mechanical properties of the parts are the fiber length and fiber orientation distributions throughout the parts. In order to create parts with complex shapes, manufacturers must use injection molding, which causes severe fiber breakage and results in a non-uniform fiber orientation state throughout the part. Modeling how the fiber length and orientation distributions change during the injection molding process is crucial for determining the processing conditions that result in parts with optimal mechanical properties. This work focuses on predicting the fiber orientation evolution.

Several models for predicting fiber orientation are available, but all of these models rely on empirical parameters, and no independent test for obtaining those parameters exists. Manufacturers thus rely on an iterative design methodology which is limited by time, funding, and material. Rheological tests seem especially suited for obtaining these parameters, as the deformation profiles for shear, extension, etc. are well-defined. Orientation model parameters have been obtained by fitting to orientation as a function of shear strain during the startup of steady shear for polymer-glass fiber systems¹ and the parameters thus obtained make reasonable predictions for the fiber orientation in a simple injection-molded geometry (the center-gated disk)², but make very poor predictions for more complex geometries like the end-gated plaque³.

Non-lubricated squeeze flow (NLSF) has been proposed as an alternative test for a number of theoretical and practical reasons. Previous work⁴ investigated how shorter glass fibers orient during NLSF, and this work extends the analysis to longer glass fibers at several fiber concentrations. Furthermore, several fiber orientation models are fit to the orientation data to demonstrate what effect fiber concentration has on the orientation evolution and the corresponding model parameters. This work will ultimately be used to predict the fiber orientation throughout injection molded parts.

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INVESTIGATING BLOCK COPOLYMER MICELLE DYNAMICS AND MOLECULAR PARTITIONING FOR TUNABLE CARGO DELIVERY

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Block-copolymer micelles (BCMs) self-assemble from amphiphilic copolymers that can be tailored to form nm-scale vessels suited for targeted drug delivery or tunable “nanoreactors”. Our group is using NMR spectroscopy and diffusometry methods in combination with neutron scattering to study molecular dynamics of BCMs in order to enhance understanding of these systems.¹⁻²

Here we study a diblock poly (ethylene oxide)-poly (ϵ -caprolactone) (PEO_{5k}-b-PCL_{8k}) that forms spherical micelles at 1 % (w/v) in mixed solvents (D₂O/THF-d₈). We quantify the populations and diffusion coefficients of coexisting micelles and free unimers over a range of temperatures and solvent compositions by NMR diffusometry. We present evidence for dominance of the insertion-expulsion mechanism of unimer exchange in BCMs, and map a micelle-unimer phase diagram versus temperature and solvent composition (**Figure 1**).

We have developed a technique involving simple T_1 measurements versus time after mixing solutions for unimer exchange. Also, we can quantify cargo (e.g., hydrophobic drugs) partitioning in PEO₉₉-PPO₆₉-PEO₉₉ BCMs, and we observe that more hydrophobic cargos have a higher partition fraction. In summary, our NMR studies shed light on how intermolecular interactions fundamentally affect cargo partitioning and release, unimer exchange, and the tuning of micelle structure and dynamics.

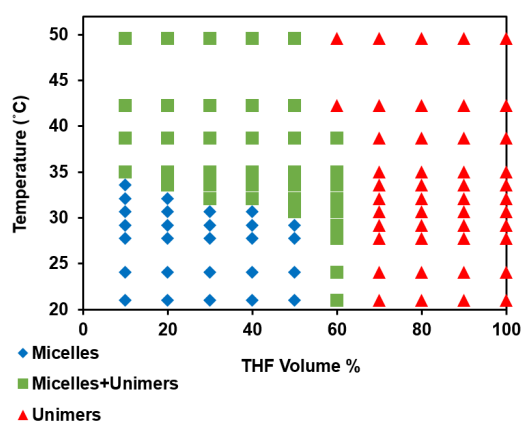


Figure 1. PEO-PCL micelle-unimer phase diagram by tuning solvent composition and temperature.

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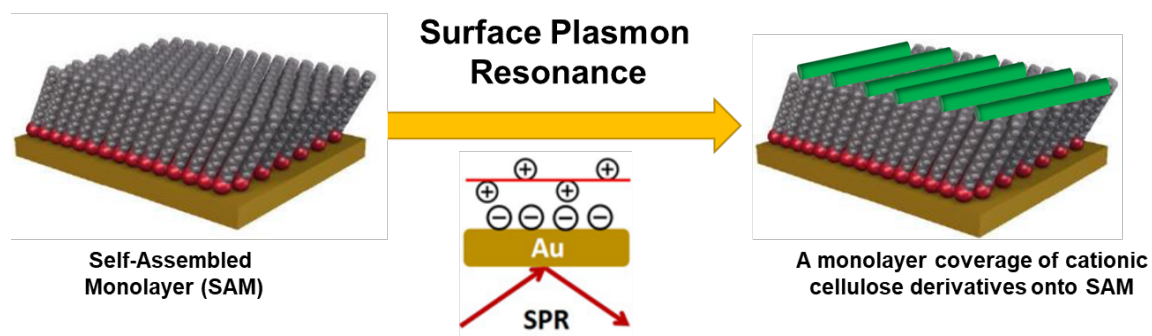
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ADSORPTION OF CATIONIC CELLULOSE DERIVATIVES ONTO A SAM-COOH SURFACE

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Cationic polymers are widely used in industry. Among different varieties of cationic polymers, cationic cellulose derivatives are of special interest, not only because of their bio-renewability¹ in natural resources, but also their biodegradability.² In this study, the potential of cationic cellulose derivatives acting as carriers in controlled drug delivery systems is examined by using surface plasmon resonance (SPR) to monitor the adsorption of cationic cellulose derivatives onto a carboxylic acid terminated, anionic self-assembled monolayer (SAM-COOH). The SPR results quantitatively suggest that a monolayer or multilayers of cationic cellulose derivatives can be formed onto the anionic SAM-COOH surface. Thus, cationic cellulose derivatives are promising vehicles to deliver controlled amount of drug to the negatively charged sites. This study will shed light on the investigation of the interactions between the cationic cellulose derivatives and biomolecules such as nucleic acids or certain anionic proteins for drug delivery applications.^{3,4}



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VALORIZATION OF HEMICELLULOSE HYDROLYZATES INTO ECO-FRIENDLY SURFACTANTS

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Biorefining refers to the process of converting renewable raw materials into biobased chemicals and fuels. First generation biorefineries, focusing only on ethanol or related biofuel production, have limited opportunities for profitability. To achieve commercial viability, biorefineries have to integrate the production of low value fuel with that of high-value chemicals. Various pretreatment technologies that prepare biomass for further downstream processing within a biorefinery have been developed. However, most commercially viable pretreatment technologies suffer from significant cross-contamination. To enable profitable next-generation biorefineries, pretreatment must evolve into fractionation processes that fully separate lignocellulosic biopolymers in the yield and purity needed for the parallel production of both fuels and chemicals. Numerous uses and conversion processes exist for the cellulose fraction and the lignin fraction is receiving increasing attention. This study focuses on valorizing the hemicellulose fraction. Hemicellulose hydrolyzates will be a complex mixture of sugars and impurities. Here we will present our current efforts to analyze sugar mixtures and valorize hemicellulose hydrolyzates into high-value eco-friendly surfactants.

USE OF THE CO-EXTRUSION PROCESS FOR PRODUCTION OF A NOVEL COMPOSITE OF ULTRA-HIGH MOLECULAR WEIGHT POLY(ETHYLENE OXIDE) AND A POLYARYLSULFONE FOR APPLICATIONS IN NEONATAL CYTAPHERESIS OF LEUKOCYTES

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Cytapheresis is an effective means for the removal of cells from the blood of a patient. Separation is often achieved using either a centrifuge¹ or a polymer membrane filter pack². The polymer membranes used for cytapheresis contain a hydrophobic structural component and an ultra-high molecular weight hydrophilic surface component to adsorb the desired cells. The high molecular weight of the hydrophilic component prevents it from dissolving into the mobile aqueous phase of assembled packs in use, but makes processing of the polymer considerably more difficult. These membranes are industrially produced via a process called gel spinning, wherein a dilute solution of high molecular weight polymers is passed through a spinneret and precipitated from solution as a porous, small diameter filament or tube. While useful for producing cytapheresis membranes, gel spinning typically requires the use of toxic solvents, which introduce a high overhead cost to ensure all solvent is recaptured.

The research conducted sought to overcome the limitations of gel spinning for the production of cytapheresis filter packs by eliminating the need for a solvent with a melt based process, co-extrusion. Co-extrusion is a process wherein two polymer streams are plasticated separately and combined in a mixing head, called a phase distributor, immediately prior to exiting the system via a nozzle or spinneret³. Two principle challenges arose when implementing co-extrusion: plasticating and processing an ultra-high molecular weight polymer and minimizing degradation due to mismatched melt processing temperature requirements. The ultra-high molecular weight hydrophilic polymer was poly(ethylene oxide) (UHMW PEO) and the hydrophobic support polymer was a polyarylsulfone (PAS). The first challenge was addressed by using a low molecular weight poly(ethylene oxide) (LMW PEO) to carry and disperse the UHMW PEO. The LMW PEO was then washed from the resulting composite filaments prior to use. To address the second challenge, the degradation of PEO was investigated using a novel combination of rheometric tests to characterize the rheology of the PEO during processing and predict changes to the molecular weight. Processing parameters for producing the composite filaments were selected to minimize the degradation within the constraints of the system. The resulting composite filaments were tested in vitro with animal model blood and compared to an industry gold standard. It was found that the filaments produced via co-extrusion retained up to 35 times the number of eosinophils relative to the industry gold standard. The significant increase in co-extruded filament effectiveness is particularly advantageous for potential future applications requiring miniaturization of cytapheresis devices, such as treating neonatal leukemia patients.

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HIGH-TEMPERATURE VAT-PHOTOPOLYMERIZATION

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Using high-molecular weight polymers for part fabrication via vat-photopolymerization results in enhanced mechanical properties. However, as molecular weight of the polymers increases, the viscosity and thus the inertial forces acting on the cured geometry also increases. This limits the achievable aspect ratio and feature sizes of the printed parts. While hydrogen-bonding systems^{1,2}, organo-gel systems³ and simultaneous chain-extension and crosslinking systems have shown enhanced mechanical properties, they also reach critical viscosity values with increase in polymer concentration and increase in molecular weight.

To mitigate the problems associated with VP of high-viscosity photopolymers, the authors have invented a high-temperature vat-photopolymerization system with the capability of reaching temperatures up to 200 °C. High-temperature processing lowers the operating viscosity of the photopolymer resin, therefore providing the opportunity to increase the molecular weight and the polymer loading concentration to enhance the mechanical performance of the printed parts. The designed high-temperature VP apparatus is coupled with a high-torque rotary recoating system which further pushes the threshold limit⁴ of the photopolymer viscosity from 3 Pa.s to 25 Pa.s at 200 °C. In this work, the authors begin by discussing the material selection, design and construction of the high-temperature VP system. The authors then present the results from the additive manufacturing of urea monoacrylate, a solid photopolymer at room temperature, using the developed high-temperature VP apparatus. Finally, a brief discussion regarding the effects of high-temperature processing on the printing parameters such as cure depth and dosing energy is presented. With the designed high-temperature VP system, enhancement of mechanical properties can be achieved via simple modifications to molecular weight and polymer loading concentrations. The high-temperature VP system unlocks the possibility of using temperature-modulated polymerization strategies for additive manufacturing of high-performance polymers, accelerating the use of vat-photopolymerization for the fabrication of end-use performance components.

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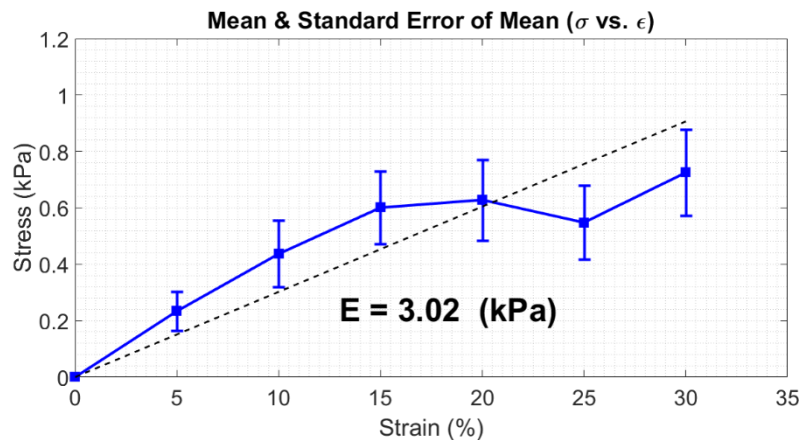
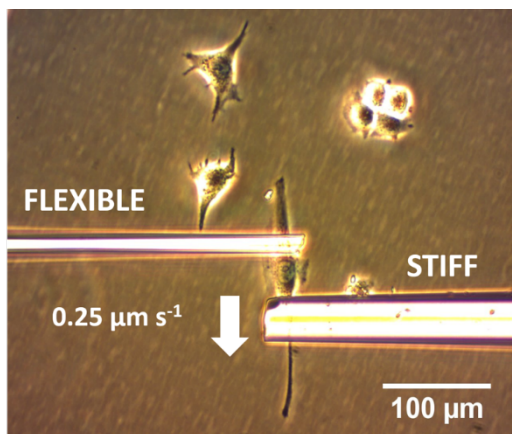
MECHANICAL PROPERTIES OF SINGLE VAGINAL SMOOTH MUSCLE CELLS

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Pelvic organ prolapse (POP) affects up to half of parous women in the United States. The etiology of POP is unknown and likely multifactorial but, without doubt, alterations in the mechanical properties of the pelvic organs and their supportive muscles and connective tissues play a critical role in the development of POP. Several studies have shown that the vaginal tissue and surrounding endo-pelvic structures of women with POP contain a lower ratio of smooth muscle cells (SMCs). This decrease in SMC content may alter the overall mechanical properties of the pelvic tissue possibly leading to POP [1]. In order to determine the mechanical properties of SMCs and better understand the etiology of POP, this study focuses on establishing the experimental protocols for testing single vaginal SMCs. Toward this end, cells were enzymatically isolated from vaginal wall biopsies of freshly sacrificed, nulliparous Long Evans rats and they were cultured using well-established methods [2]. For each test, two micropipettes were custom built and coated in cellular adhesive to clamp the cells. In the experimental setup, a very flexible pipet was used as a cantilever-type load cell, while a much stiffer pipet was controlled by a piezoelectric actuator to stretch the cells at $0.25 \mu\text{m s}^{-1}$. Image data were collected by keeping the cell under a microscope and were then used to measure the deflection of the flexible pipet to calculate force and the resulting cell deformation.

Assuming the SMCs have a circular cross-section and that they are linearly elastic, stress-strain data of ($n=14$) single cells were collected. Data collection was terminated when adhesion between one of the pipettes and the cell failed, resulting in a mean (\pm SD) elastic modulus of $3.02 (\pm 0.36)$ kPa. While several studies exist that characterize the mechanical properties of vaginal tissues, this study offers unprecedented results on the mechanics of single vaginal SMCs. With the current experimental setup, future work will investigate alterations in the mechanical behavior of SMCs of the vaginal wall and endo-pelvic structures determined by POP using cells from human biopsies. The long-term goal of this research is to offer guidelines in the development of effective prevention and treatments methods for POP.



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EXTENSION OF THE LAURITZEN-HOFFMAN CRYSTAL GROWTH THEORY FOR COPOLYMERS WITH SHORT CHAIN BRANCHES

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Metallocene linear low density polyethylenes (m-LLDPEs) are copolymers synthesized from ethylene and small amounts of α -olefins in the presence of a homogenous catalyst.¹ When the α -olefin is a 1-butene or larger comonomer, it introduces short branches in the otherwise linear ethylene backbone and cannot enter the polyethylene crystal structure, hence, leads to a decrease in crystallinity and stiffness, compared to pure polyethylene.² While the presence of randomly distributed, non-crystallizable comonomers was carefully considered in the thermodynamics of copolymer crystallization by Flory, it has been mostly ignored in the analysis of crystal growth rate data.³⁻⁵ In this work, we proposed an extension of the Lauritzen-Hoffman secondary nucleation theory for the crystal growth process of random copolymers of crystallizable and non-crystallizable units. We followed Flory's approach, concentrating on crystallizable sequences of various lengths instead of focusing on the whole polymer chain.³

Our model was evaluated through studies of the effect of crystallization temperature on the melting temperature and the isothermal spherulite growth rate for an m-LLDPE sample (ExxonMobil Exceed™ 3518CB). Using optical microscopy, spherulite growth rates were measured at different crystallization temperatures. At similar undercoolings, the spherulite growth rates of the m-LLDPE sample were lower than that of polyethylene, in agreement with model predictions. The melting temperature and degree of crystallinity were measured as a function of crystallization temperature and time using a Mettler-Toledo Flash™ DSC1. The melting temperatures of initial lamellae formed at different temperatures were determined at different heating rates (1000 - 10,000 K/s) and extrapolated to zero heating rate to yield zero-entropy production melting temperatures. Extrapolation to zero-heating rate allowed for the elimination of non-equilibrium effects (melting kinetics and thermal lag) from the melting behavior. In the vicinity of the equilibrium melting temperature, the initial melting temperatures increased steadily with the crystallization temperature (Figure 1), which agrees with the models predictions.

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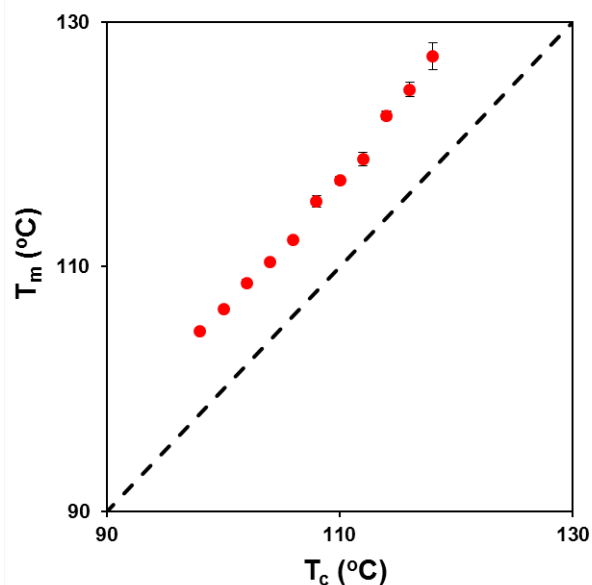


Figure 7. Melting temperature vs. crystallization temperature for the m-LLDPE sample. The dashed line is the $T_m = T_c$ line.

ANALYSIS OF THE CRYSTALLIZATION TEMPERATURE AND CHAIN LENGTH DEPENDENCES OF THE SPHERULITE GROWTH RATE OF LINEAR POLYETHYLENE AND POLY(ETHYLENE OXIDE) FRACTIONS

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Equilibrium melting temperatures, T_m^{eq} , of three linear polyethylene (LPE) and four poly(ethylene oxide) (PEO) fractions were estimated using the non-linear Hoffman-Weeks treatment. In the case of LPE, the resulting T_m^{eq} s are about 4°C lower than those predicted by the Flory-Vrij equation¹ and are within experimental error indistinguishable from the values reported by Wunderlich et al.² and Okada et al.³ for the melting of extended chain crystals. Using the Huggins equation to model the dependence of T_m^{eq} on n , the average number of repeat units per chain, we found a limiting equilibrium melting temperature for the infinite chain length LPE, $T_m^{eq,\infty} = 141.4 \pm 0.8^\circ\text{C}$. The same analysis leads to $T_m^{eq,\infty} = 81.9 \pm 1.0^\circ\text{C}$ for PEO, about 12°C higher than predicted by Buckley and Kovacs.⁴

The chain length dependence of T_m^{eq} was then used to analyze spherulite growth rate, G , vs. crystallization temperature data for 26 LPE and 14 PEO fractions with intermediate molecular weights and narrow molar mass distributions. The Lauritzen-Hoffman secondary nucleation theory was modified to account for stem length fluctuations during crystal growth and for the temperature dependence of the lateral surface free energy. At constant undercooling in regimes I and II, $G_{PE} \propto n^{-1.7}$ and $G_{PEO} \propto n^{-1}$. For both polymers, the undercooling at the I \rightarrow II regime transition and the nucleation constants K_{gI}^o , in regime I, and K_{gII}^o , in regime II, are independent of n . The ratio of K_{gI}^o/K_{gII}^o is equal to two. The configurational path degeneracy and the magnitude of the stem length fluctuations, y , exhibit strong chain length dependence. For LPE, the magnitude of y increases with n while for PEO the opposite behavior is observed, Figure 1. We attribute this phenomenon to opposite dependencies of the chain dimensions on the crystallization temperature in LPE and PEO. The apparent friction coefficient of the crystallizing chain, ξ , is proportional to $n^{1.9}$ for both LPE and PEO. The observed power dependence of the friction coefficient of the crystallizing chain on chain length is much stronger than that ($\xi \sim n^1$) predicted by Hoffman and Miller⁵ for forced reptation in the Rouse regime. Our analysis supports Hikosaka's speculation⁶ that other mechanisms, such as sliding diffusion of crystallizing chains on the growth front, may play an important role during crystal growth of LPE and PEO.

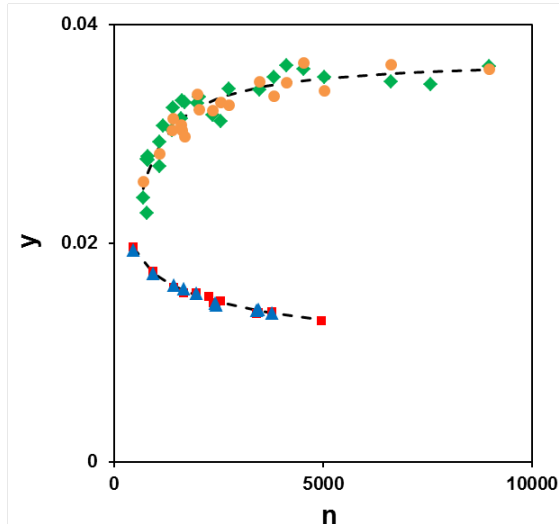


Figure 8 y vs. n at the regime I to regime II transition temperature: LPE regime I (\blacklozenge), LPE regime II (\bullet), PEO regime I (\blacktriangle) and PEO regime II (\blacksquare). The dashed lines are the best fit to the experimental data.

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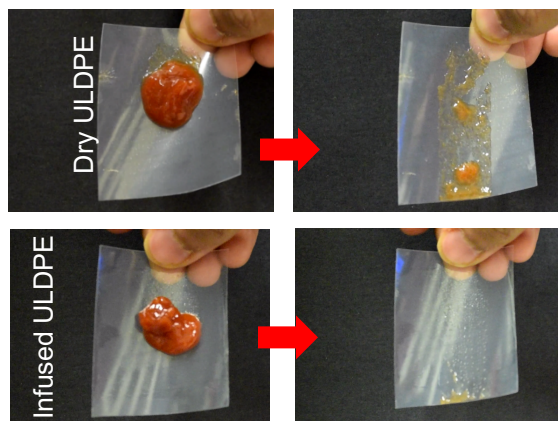
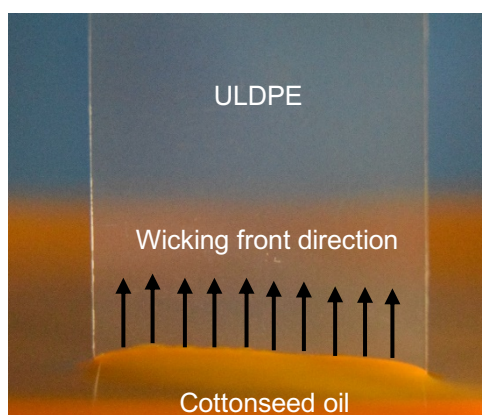
OIL-IMPREGNATED HYDROCARBON-BASED POLYMER FILMS

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Slippery liquid-infused porous surfaces (SLIPS) minimize the contact angle hysteresis of a wide range of liquids and aqueous food products. Although hydrophobic polymers are often used as the porous substrate for SLIPS, the choice of polymer has been limited to silicone-based or fluorine-based materials. Also, in most cases, a certain degree of chemical and/or physical surface modification is required to achieve a stable lubricant layer over the substrate.

Hydrocarbon-based polymers, such as polyethylene, are cost effective and widely used in food packaging applications where SLIPS would be highly desirable. However, to date there have been no reports on using polyethylene as a SLIPS substrate. Here, we show that thin films of low-density polyethylene can be stably impregnated with carbon-based oils without requiring any surface modification. A compatible oil (e.g. cottonseed oil) wicks within the intermolecular spaces of the polymer to create a stable layer which is shown by Washburn equation. The nanometric effective pore size of the polyethylene does result in a very low wicking speed, but by using micro-thin films and a drawdown coater, impregnation can still be completed in under one second. The oil-impregnated polyethylene films promoted ultra-slippery behavior for water, ketchup, and yogurt while remaining durable even after being submerged in ketchup for over one month.



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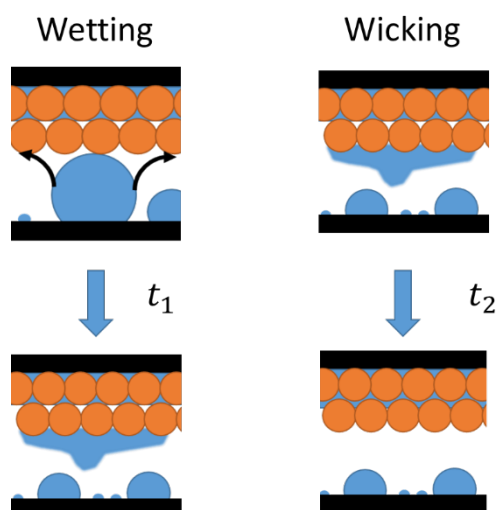
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DROPLET BRIDGING INTO POROUS MEDIA

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When the top of a sessile droplet is brought into contact with an opposing surface, the droplet can transfer to the new surface. Previous reports have characterized the extent and speed of droplet transfer as a function of the surface and droplet properties; however, the two surfaces have always been impermeable [1]. What if the surface receiving the liquid was porous instead? Here, we use side-view high-speed imaging to capture the transfer of liquid from a solid substrate to an opposing porous surface. Variables to consider include the wettability of the donor surface, the porosity and pore size of the receiving surface, and the droplet's volume, viscosity, and surface tension. Generally, the transfer process is split into two regimes: the wetting transition, similar to the wetting of the receiving solid surface in a solid-to-solid transfer, and the wicking transition, where the liquid is pulled into the porous surface. The wetting transition scales with the capillary-inertial velocity for low viscosity fluids and a varying power law for viscous fluids, while the wicking transition scales with Darcy's Law.



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AMPHIPHILIC POLYSACCHARIDE SCHIFF BASE DELIVERY VEHICLES FOR CONTROLLED RELEASE OF BIOLOGICALLY ACTIVE COMPOUNDS

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Aqueous solubility and controllable release are essential for bioactive compounds. In the case of oral drug delivery, the poor aqueous solubility of a drug leads to low bioavailability.¹ Thus, higher dosages of the drug are required to achieve a therapeutic effect in systemic circulation which can increase undesired side effects. The aqueous solubility and release rate of a bioactive molecule can be improved with the conjugation of a carrier molecule, to form a pro-active delivery system.² Polysaccharides have great potential as carriers since they are biodegradable, nontoxic, and sustainable.^{3,4} We have utilized a strategic and economical synthetic route to give amphiphilic derivatives of cellulose and dextran as carrier molecules for delivery of bioactive molecules. The secondary alcohols of hydroxypropyl substituents are selectively oxidized with sodium hypochlorite and reacted with primary amines to form a Schiff base imine bond with model drugs. Schiff bases hydrolyze under acidic conditions which can be advantageous for the lysosomotropic delivery of antibiotics as well as for targeted delivery in tumors. Here we report the synthesis, characterization and physical properties of amphiphilic cellulose and dextran Schiff base delivery systems with successful drug conjugation confirmed with FTIR, ¹H and ¹³C NMR spectroscopy. We also evaluate and quantify the pH triggered release of active compound with HPLC.

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DESIGN OF SYNERGISTIC DRUG CRYSTALLIZATION INHIBITORS VIA OLEFIN CROSS-METATHESIS OF HYDROPHILIC CELLULOSE ETHERS AND BILE ACID DERIVATIVES

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Poor aqueous solubility is a major hurdle in the pipeline of developing new drugs. This lowers drug effectiveness and results in limited drug bioavailability. Crystallization inhibitors have been employed as excipients in amorphous solid dispersions in order to form metastable, supersaturated drug formulations with enhanced solubility.¹ Olefin cross-metathesis has successfully provided an array of new and multifunctional cellulose-based derivatives for amorphous solid dispersion polymer matrices.²⁻⁶ Several of these derivatives, as well as endogenous bile salts, effectively extend nucleation induction times of hydrophobic therapeutics in physiologically similar settings.⁷ In this study, cellulose ether derivatives are appended to bile salt mimics to yield conjugates that may act synergistically as drug-crystallization inhibitors while also increasing drug solubility. Conjugate hydrophilicity is enhanced via selective modification of bile salt mimics and by choice of cellulosic backbones (hydroxypropyl and hydroxyethyl cellulose). Increased hydrophilicity enhances the ability of these conjugates to achieve supersaturation.⁴ Here we report, the synthesis of these novel conjugates and characterization by NMR spectroscopy, DSC, and FTIR. Amorphous solid dispersion candidacy is evaluated via aqueous stability, solubility, and retention of amorphous properties of these novel candidates, as well as induction time studies in biologically relevant conditions.

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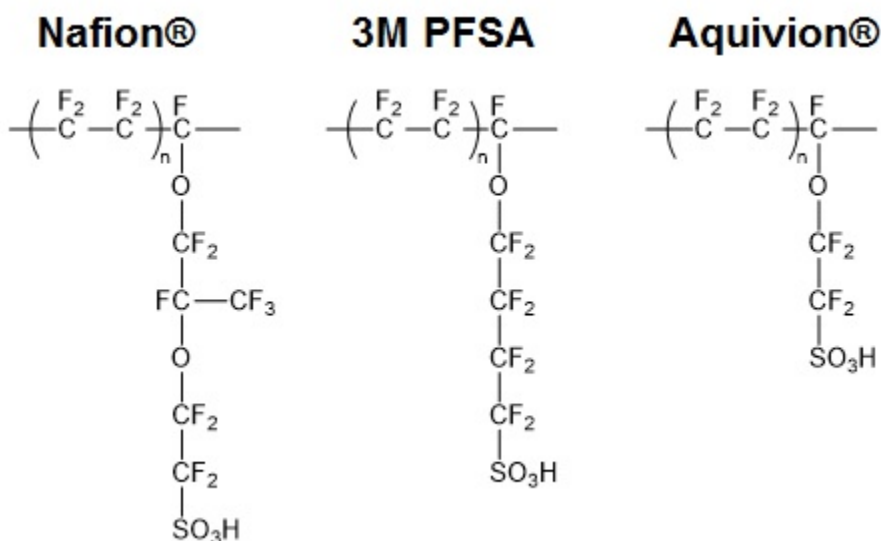
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DYNAMIC MECHANICAL RELAXATIONS OF PERFLUOROSULFONIC ACID MEMBRANES

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Evaluating the transport and mechanical properties of perfluorosulfonic acid (PFSA) membranes is crucial for applications in polymer electrolyte membrane (PEM) fuel cells. Increasing the ionic content of PFSA improves proton conductivity, but also decreases crystallizability and water swelling sensitivity. Previous studies using dynamic mechanical analysis (DMA) found that the α -relaxation was due to the onset of long-range mobility of the ionomer main chains and side chains via a thermally activated destabilization of the electrostatic interactions, yielding a dynamic network involving significant ion-hopping processes. Segmental motions of backbone chains within the static network is thought to be the molecular origin of the β -transition. Understanding changes in the α - and β -relaxations with membrane ionic content is needed to develop tailored processing conditions to produce high-performing membranes for PEM fuel cells. This study used DMA to examine the α - and β -relaxations of PFSA membranes of different equivalent weights. Ion-exchanged membranes were subjected to the same analysis to elucidate the relationship between relaxation temperature and strength of electrostatic interactions in the ionic domains. Membrane morphology was investigated with small- and wide-angle X-ray scattering.



PROBING THE THERMAL TRANSITIONS, DYNAMIC MECHANICAL RELAXATIONS, AND MORPHOLOGY OF PERFLUORINATED IONOMERS

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Perfluorosulfonic acid ionomers (PFSAs) are the benchmark materials used as proton-exchange membranes (PEMs) in fuel cells. Typical PFSA membranes have a chemical structure consisting of a PTFE backbone with perfluoroether side chains containing a pendant sulfonic acid group. The complex, phase-separated morphology of PFSAs has been the focus of many investigations aimed at exploring the effect of processing conditions and sidechain structure on the morphology and thermomechanical transitions of these ionomers. In this study, we aim to investigate the effect of an additional acidic site in the sidechain on the morphology and properties of perfluoroimide acid ionomers (PFIA). Utilizing alkylammonium counterions allows for systematic control of ionic interactions within PFIA according to the chain length of the ions, which can be probed by applying techniques such as dynamic mechanical analysis (DMA). Morphology and thermal transitions of multi-acid PFIA compared to single-acid PFSA are also investigated by small angle x-ray scattering (SAXS) and differential scanning calorimetry (DSC) to determine the dependence of sidechain structure on the morphology and properties of perfluorinated ionomers.

POLYMER ELECTROLYTES FOR SOLID-STATE LITHIUM METAL BATTERIES

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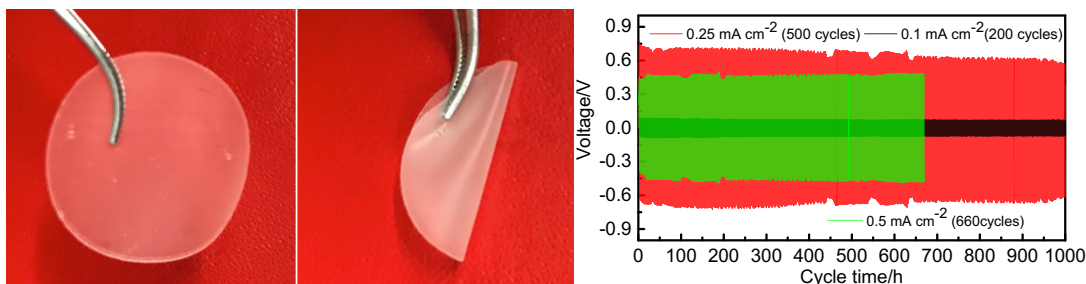
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The large and growing lithium-ion battery market (recently projected to reach \$46.21 billion by 2022) provides strong incentives to continue development, especially as new opportunities in vehicular applications and large-scale energy storage emerge. Solid-state batteries, in particular those utilizing the lithium metal anode (specific capacity of 3,829 mAh/g and 2,061 mAh/cm³, electrochemical potential of -3.04 V vs the standard hydrogen electrode), are considered the “Holy Grail” of the battery future and are intensively studied for the next-generation battery technology.¹ However, solid-state batteries encounter significant fundamental challenges related to the lithium metal anode, including lithium dendritic growth, low Coulombic efficiency, and high interfacial impedance at the lithium–solid electrolyte interface. Current secondary lithium ion batteries contain flammable organic liquid electrolytes and fail to address the fundamental challenges of the lithium metal anode. In recent years, we have witnessed a huge wave of research activities in developing solid-state electrolytes to resolve these outstanding fundamental challenges.²

Our group specializes in developing electrode and electrolyte materials for solid-state lithium metal and sodium metal batteries. In this presentation, we showcase our recent progress in composite polymer electrolytes in lithium metal batteries. Room temperature ionic liquids (RTILs) are used as plasticizers for gel polymer electrolytes because of their non-volatility, inflammability, wide electrochemical windows, and high ionic conductivity, and excellent thermal stability. Specifically, we describe an ionic liquid gel polymer electrolyte (ILGPE) based on a robust, flexible, and elastic PVDF-HFP polymer and ionic liquid [N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide]. The resulting composite polymer exhibits a high ionic conductivity (1.3×10^{-3} S cm⁻¹) at room temperature, a high lithium ion transference (0.66), a wide electrochemical window (5.0 V) and excellent thermal stability up to 200 °C. These excellent properties allow us to design solid-state lithium metal batteries that show good compatibility with high-energy cathode materials, such as LiFePO₄ and LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂. Finally, we will discuss how we make use of advanced synchrotron X-ray spectroscopy to tackle scientific questions related to electrolyte–electrolyte interphases in these new battery systems.



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MELT PROCESSING OF ULTRA-HIGH MOLECULAR WEIGHT POLYMERS

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Ultra-High molecular weight polymers (UHMWP) are polymers with molecular weight above 1 million g/mol. Due to their high molecular weight, UHMWP offer many high-performance properties and have found successful applications in many industrial and bio medical sectors. Current work is concerned with melt processing of Polyethylene Oxide (PEO) which is nonionic, semi-crystalline, and a water soluble polymer. Due to its biocompatibility, it has gained recent interest in biomedical applications. Ultra-high molecular weight Polyethylene Oxide (UHMWPEO) is traditionally processed in solution to lower the viscosity. This process suffers from low throughput and inherently difficult solvent sequestration. Melt processing offers a unique solution to this problem but it has its own challenges. For example, it is extremely difficult to melt process due to its high viscosity and susceptibility to degradation.

Previous efforts within our group have examined use of low molecular weight polyethylene oxide (LMWPEO) as a processing aide to melt process UHMWPEO. Current work will focus on using supercritical CO₂ as a plasticizer to melt process HMWPEO. To optimize the process, solubility of ScCO₂ will be first determined using a gravimetric method and then further characterized using a rotational rheometer and a slit die rheometer to determine when and to what extent degradation took place.

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THERAPEUTIC DELIVERY OF H₂S VIA COS: SMALL MOLECULE AND POLYMERIC DONORS WITH BENIGN BYPRODUCTS

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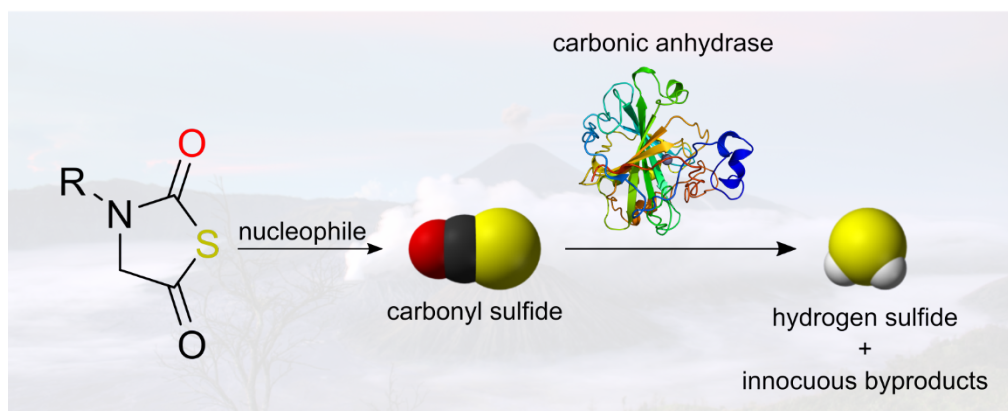
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Carbonyl sulfide (COS) is a gas that may play important roles in mammalian and bacterial biology, but its study is limited by a lack of suitable donor molecules. We report here the use of *N*-thiocarboxyanhydrides (NTAs) as COS donors that release the gas in a sustained manner under biologically relevant conditions with innocuous peptide byproducts. Carbonic anhydrase converts COS into H₂S, allowing NTAs to serve as either COS or H₂S donors, depending on the availability of the enzyme. Analysis of the pseudo-first order H₂S release rate under biologically relevant conditions revealed a release half-life of 75 min for the small molecule NTA under investigation. A polynorbornene bearing pendant NTAs made by ring-opening metathesis polymerization was also synthesized to generate a polymeric COS/H₂S donor. A half-life of 280 min was measured for the polymeric donor. Endothelial cell proliferation studies revealed an enhanced rate of proliferation for cells treated with the NTA over untreated controls.



BIDIRECTIONAL SHIFTING TO ESTABLISH ACCELERATED CONDITIONS OF HDPE PIPES TESTING

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A common requirement for High-density polyethylene (HDPE) pipes is that they last 50 years or more once they have been installed. When subjected only to the stresses that arise from a fluid flowing through the pipe, creep will be the expected failure mechanism. Creep is the continued deformation of a material under a constant stress even at stresses lower than those that would cause instant failure of a material. Current tests to characterize the performance of pipes are expensive and time consuming. Tests that quickly determine the performance of a pipe are desirable. In this work, pipes are characterized through viscoelastic testing. Dynamic mechanical analysis (DMA) shows that conventional time temperature superposition (TTSP) is not applicable and two sets of shift factors are required to build viscoelastic properties master curves. Creep testing allows a way to test the shift factors in an independently measured viscoelastic property. The activation energies obtained suggest that one hour of testing at 80°C is equivalent to four months of testing at 25°C. This work presents first steps into shifting short-term test data for HDPE pipes into predictions of their service lifetime.

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DEVELOPMENT OF NANOPARTICLE ALIGNMENT REGIMES IN DRYING CELLULOSE NANOCRYSTAL DROPLET SUSPENSIONS FOR ADDITIVE MANUFACTURING

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Nanoparticle suspensions are of interest for many applications, particularly when deposited in droplet form and subsequently dried via evaporation of the suspending agent. The drying process often results in deposition of ring patterns, typically referred to as the coffee ring effect. When drying picoliter-sized, aqueous, cellulose nanocrystal droplet suspensions, we observe alignment of these rod-like nanoparticles in multiple orientations within the resulting dried droplet. A radial alignment is formed near the center of the droplet, and tangential orientation is observed in the particles along the circumference of the droplet. Tuning particle orientation enables unique opportunities for control of nanocomposite structure required for next generation optical and electronic materials, specifically when considering droplet based additive manufacturing techniques. To successfully control the nanoparticle orientation during the drying process, a fundamental understanding of the alignment mechanism is necessary.

We have developed a 3-dimensional, continuum-based, finite element model implementing a deforming mesh to understand the impact of shear induced alignment driven by evaporative flow. Simulations of a single-phase, sessile water droplet suggest a relationship between velocity profile, shear stress, and particle orientation. We have explored the coupled effects of Marangoni flows, air convection, heat transport, and concentration dependent viscosity models on evaporation of single-phase picoliter-sized droplets leading to new insights into particle orientation in the evaporation of colloidal droplets. Velocity and shear stress profiles indicate the development of radial flows enacting shear stresses on the fluid driving the alignment of rod-like nanoparticles in the flow direction which varies with location in the confined flow field.

LIGHTWEIGHT ORIGAMI-CORE SANDWICH STRUCTURES FOR IMPROVED BLAST RESISTANCE

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The response of single (Figure 1) and two-core (Figure 2) elastic-plastic Miura-ori core sandwich plates to high-intensity dynamic loads is numerically studied using the commercial finite element software ABAQUS/ Explicit. The facesheets and the core are assumed to be made of a high strength material modeled as an isotropic material that obeys the von Mises yield criterion with linear strain hardening. Exploratory design studies have been conducted to (i) determine the influence of the unit cell parameters of the Miura-ori pattern (Figure 3) on the energy dissipated by the core through plastic deformations, and (ii) compare performances of Miura-ori and square honeycomb cores of equal areal density.

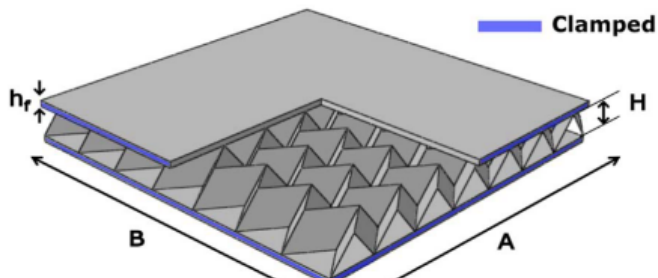


Figure 10 Single-core Miura-ori sandwich plate

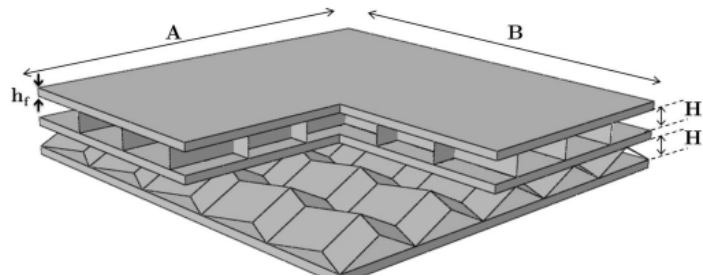


Figure 9 Hybrid "Honeycomb-Miura" sandwich plate

For single-core sandwich plates, it is found that up to moderate load intensities, the Miura-ori core outperforms the corresponding honeycomb core in terms of energy dissipated (by as much as 68%) and centroidal deflections of the facesheets.

Four different two-core sandwich plates obtained by varying locations of the Miura-ori and the honeycomb cores have been considered. It is found that using a Miura-ori core beneath the topmost facesheet dissipates more energy for moderate blast loads, while a combination of a honeycomb and a Miura-ori core has the least facesheet deflections.

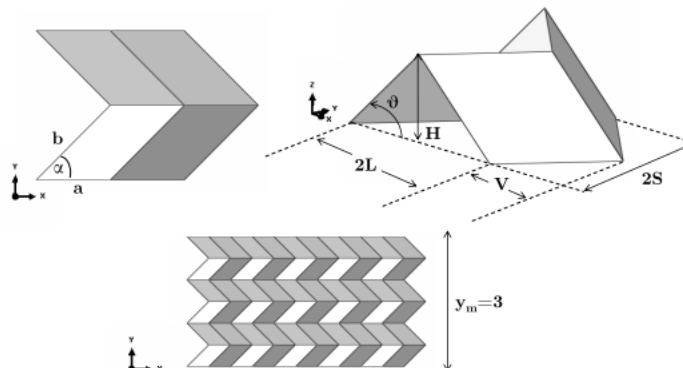


Figure 11 Geometric parameters of a Miura-ori unit cell

SELF-ASSEMBLED DIPEPTIDE HYDROGELS FOR SIGNALING GAS DELIVERY

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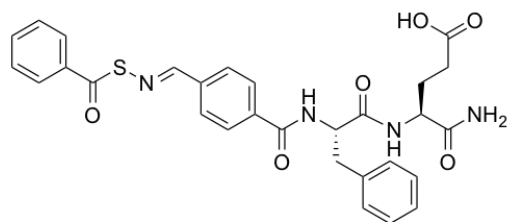
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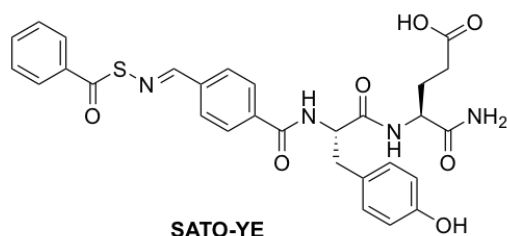
Signaling gases are small gas molecules such as NO, CO, and H₂S, which produced exogenously or endogenously in mammalian¹. They play important roles in many biological functions and regulation physiological functions. H₂S, as one of the gastransmitters, has shown its therapeutic applications in treating cardiovascular diseases, diabetes, wound, and even cancer. However, the delivery of H₂S is the bottleneck to utilize the H₂S as a therapeutic factor².

To solve the issue, in this study, self-assembled dipeptide Phe-Glu (FE) and Try-Glu (YE) were used to form hydrogels and provided localized delivery of H₂S. S-Aroylthiohydroxylamine (SATO) was chosen to conjugated to peptide as the H₂S donor, because it specially responses thiol triggers to release H₂S. The resulted SATO-FE and SATO-YE dipeptides self-assembled into nanoribbons with lengths in μm and widths about 20 nm. β -sheet was found in the self-assembled structure, as well as aromatic stacking interaction.

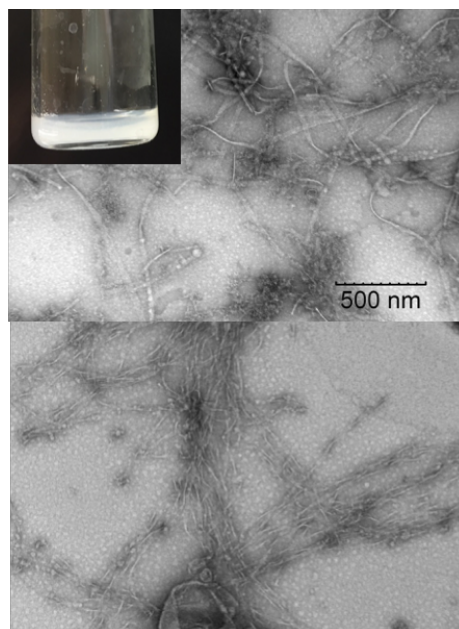
H₂S was released instantaneously from SATO-FE and SATO-YE when cysteine was added. For 0.1 mM SATO-FE and SATO-YE solutions with 10 eqv. of cysteine, H₂S release half-lives were 24 and 22 min. Hydrogels were formed when pH around 6.5, and providing a longer release of H₂S. The storage modulus of SATO-FE and SATO-YE gels were around 300-500 Pa, making them useful hydrogels for bioengineering applications.



SATO-FE



SATO-YE



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USING ULTRAVIOLET-ASSISTED DIRECT INK WRITE TO ADDITIVELY MANUFACTURE 3D ALL-AROMATIC POLYIMIDE PARTS

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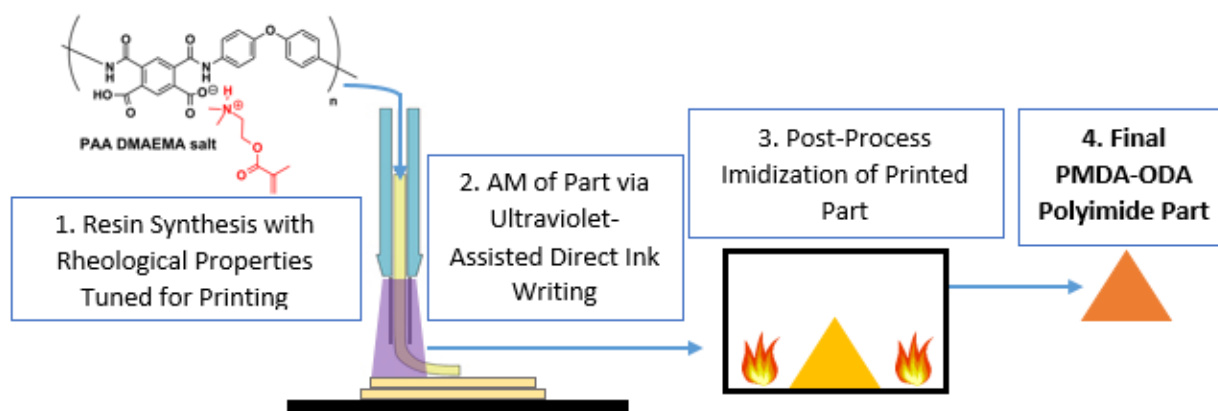
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PMDA-ODA polyimide (PI), also known by the trademark Kapton[®], is a high-performance engineering polymer which possesses remarkable thermomechanical properties from -269 °C to 400 °C, exhibits a degradation temperature above 550 °C and is electrically insulating¹⁻². These properties make PMDA-ODA PI suitable for a wide range of uses, including aerospace and electronics packaging applications. Due to a glass transition temperature above 350 °C and insolubility in common solvents, it is impossible to process PMDA-ODA PI into 3D parts using traditional processing techniques³. Here, we address the need of manufacturing PMDA-ODA PI in complex three-dimensional shapes using Additive Manufacturing (AM, also known as 3D Printing). In particular, the facile addition of an amino-functional methacrylate (DMAEMA) to the soluble precursor of PMDA-ODA PI allowed for 3D printing using UV-assisted direct ink writing (UV-DIW). UV-DIW enables processing of complex object geometries, requires only small amounts of material and makes multi-material printing possible. Careful synthesis rendered photocurable resins that possessed suitable viscosities for UV-DIW. Extrusion and immediate UV-curing afforded organogels, which possessed mechanical integrity. Subsequent solvent removal, imidization and pyrolysis of the sacrificial crosslinkers yielded fully-aromatic PMDA-ODA PI. The detailed processing procedure is illustrated in the Scheme below.



Most important, UV-DIW allowed for facile fabrication of PMDA-ODA PI in three dimensional shapes, required little amounts of material and enabled printing of large parts (> 160 mm) and structures with high aspect ratios.

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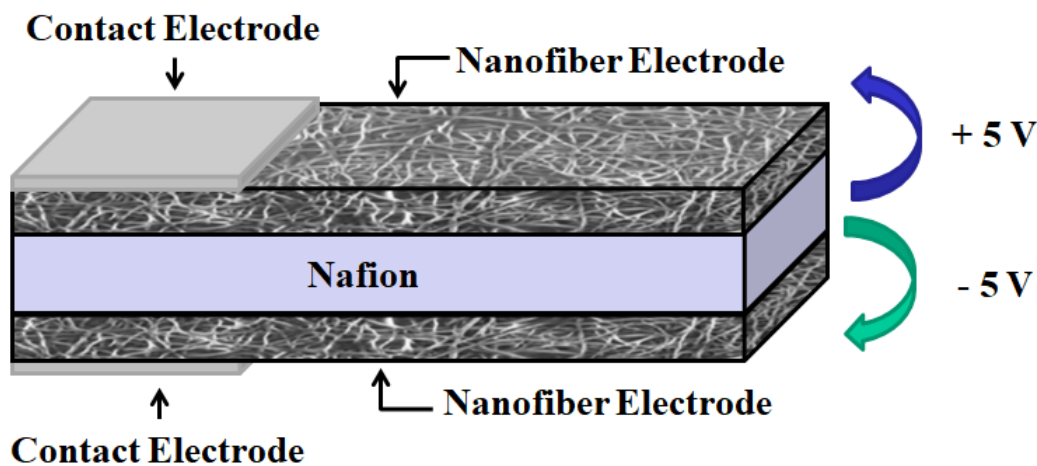
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THE EFFECT OF CARBON FIBER CHARACTERISTICS ON IONIC POLYMER CARBON COMPOSITE ACTUATOR PERFORMANCE

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In this research, the effects of the physical properties of carbon nanofiber mats on the performance of ionic polymer carbon composite electrodes were investigated. The effect of fiber diameter on conductivity was examined by electrospinning polyacrylonitrile solutions at 10, 12, and 15 wt%, where fiber diameter increases with increased concentration. Previous work in the Moore Research Group demonstrated that the orientation of the polymer component of an ionic polymer metal composite (IPMC) actuator affects the orientation of the actuator under an applied electric field. With the development of the carbon fiber based actuator, this work will investigate the orientation of actuator motion with oriented and non-oriented carbon fibers. Finally, increasing the temperature in the carbonization step has been shown to increase the degree of graphitization of carbon fibers. Here, we will examine the effect of increasing graphitization on electrode conductivity and ultimately actuator performance¹.



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JOINTED-TUBE MODEL OF CARBON NANOTUBES AND ITS APPLICATIONS IN POLYMER NANOCOMPOSITES

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Bead-spring models of polymer chains have been widely adopted to study mechanical and thermal properties of polymers. For nanocomposites containing carbon nanotubes (CNTs), it is thus desirable to develop similar models for CNTs [1,2]. However, a bead-spring representation of a CNT suffers from the corrugation nature of a bead-spring chain, which makes the model incapable of correctly capturing the load transfer, friction, and adhesion at the interface between the CNT and other components in the nanocomposite. To overcome the corrugation issue, we have developed a jointed-tube model of CNTs in which each bond connecting two neighboring beads in a usual bead-spring chain is replaced by a tube. Each tube is capped with two half spheres at its ends. The diameter of the tubes and spheres are set by the CNT diameter. Each segment thus appears as a capsule (Figure 1). We have confirmed that in the jointed-tube model the potential experienced by a bead sliding over the surface of a CNT is smooth and does not show corrugation any more. We use the jointed-tube model to study the adhesion and friction between CNTs and the mechanical properties of nanocomposites consisting of a polymer matrix with dispersed CNTs and/or CNT bundles.

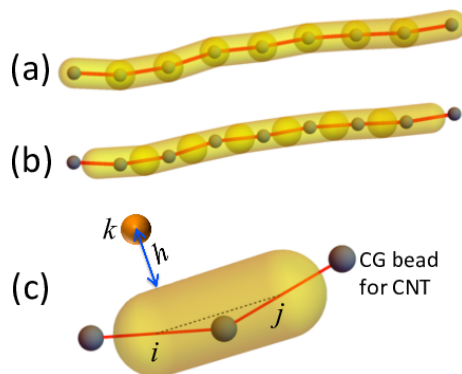


Figure 1: Jointed tube model of a CNT represented as a bead-spring chain (a) without dihedral interactions and (b) with dihedral interactions to capture its twist rigidity. (c) Interactions between a tube (yellow) and either a polymer or CNT bead (orange). Here the tube has a central axis which connects the centers (i and j) of two consecutive CG bonds as in (b). h is the distance from the center of the orange bead to the surface of the tube.

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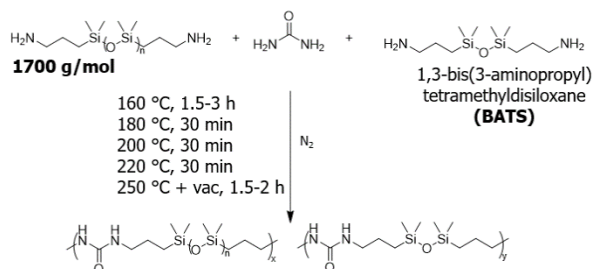
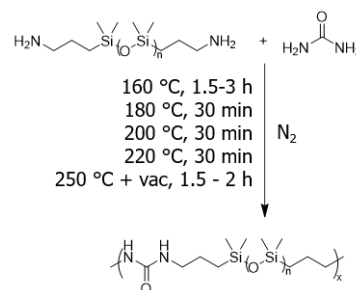
UREA AS A MONOMER FOR THE DESIGN OF ISOCYANATE-FREE POLY(DIMETHYL SILOXANE)-CONTAINING POLYUREAS AS ANTIFOULING COATINGS AND ELASTOMERIC SEALANTS

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Due to the health and safety concerns surrounding isocyanates, alternative methods to produce isocyanate-free polyurethanes and polyureas are gaining popularity¹. In-situ generated isocyanic acid yields urea linkages in the absence of isocyanate reagents, while products maintain the characteristics of isocyanate produced polyureas. This process creates an inherently safer and industrially relevant bio-based reaction process. Melt polymerization of oligomeric or monomeric diamines in the presence of urea proceeds in the absence of solvent or catalyst, only requiring heat^{2, 3} and form optically clear, freestanding films at room temperature.

These poly(dimethylsiloxane)- (PDMS-) based elastomers enabled a wide service window, limited only by potential PDMS melting for crystallizable systems and the elastomer flow temperature. Melt polymerization in the presence of PDMS oligomers leveraged the low glass transition temperature (T_g) and nonpolarity of PDMS, enabling highly phase-separated thermoplastic elastomers isolated directly from the melt. Melt polymerization afforded polyureas from diamines and urea, while stoichiometric excess of diamine ensured the desired 1,3-dialkylurea linkage and avoided formation of side products. Melt homogeneity was ensured in the beginning stages of the reaction, and transureaization under vacuum and at higher temperatures drove the reaction to high molecular weight. Polymerization in the presence of short-chain diamines yielded multiblock copolymers, potentially lending mechanical property improvements. Synthesis of PDMS-based elastomers with the addition of a PDMS-soluble 1,3-bis(3-aminopropyl)tetramethyldisiloxane (BATS) chain extender facilitated homogeneity in the melt and enabled a novel family of high molecular weight, linear polyurea copolymers.



Melt rheology confirmed thermal stability and probed viscoelastic properties. Thermomechanical analysis measured mechanical properties and glass transitions as a function of temperature, and tensile testing determined mechanical properties of the freestanding films. Adhesion to these silicone polyureas will also be probed with a variety of techniques and is relevant to their applications in biomaterials, microfluidics, or antifouling coatings.

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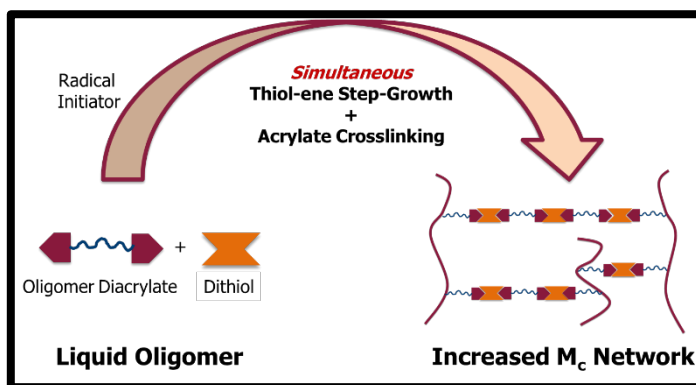
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3D PRINTABLE POLYBUTADIENE ELASTOMERS VIA SIMULTANEOUS CHAIN EXTENSION AND CROSSLINKING OF FUNCTIONAL OLIGOMERS

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Vat Photopolymerization (VP) Additive manufacturing, a leading form of 3D printing, enables the reproducible fabrication of complex architectures with unprecedented precision.¹⁻² However, the current library of photopolymers limits the commercial capability of 3D printing and necessitates the development of novel 3D printable systems. The design and synthesis of photopolymers for 3D printing with stereolithography (SLA) is crucial in the innovation and development of advanced technologies. Specifically, the synthetic design of novel strategies to provide a crosslinking network with high molecular weight between crosslinks (M_c) from low viscosity precursors is imperative to improving the strain and elastic performance lacking in many VP materials.



A unique synthetic approach involving simultaneous thiol-ene step growth chain extension and acrylate crosslinking during 3D printing overcomes traditional SLA material challenges.³ This novel approach combines the processing advantages of low molecular weight systems with the tunable (thermo)mechanical performance similar to high molecular weight polymer networks. With addition of photo-initiator, the liquid polybutadiene oligomer/ dithiol resin cures selectively under UV exposure to form uniquely high-strain, elastic parts in comparison to neat diacrylate systems. In concert with mask-projection micro-stereolithography (MP μ SLA), the fabrication of well-defined elastomers is possible. Photo-DSC and photo-rheology elucidates curing behavior as a function of resin composition and UV intensity, while optical microscopy and SEM reveals quality and resolution. As a result, this work expands the capability of additive manufacturing by developing a solvent-free resin with the processability of an oligomer and the elastic properties of a higher molecular weight polymer.

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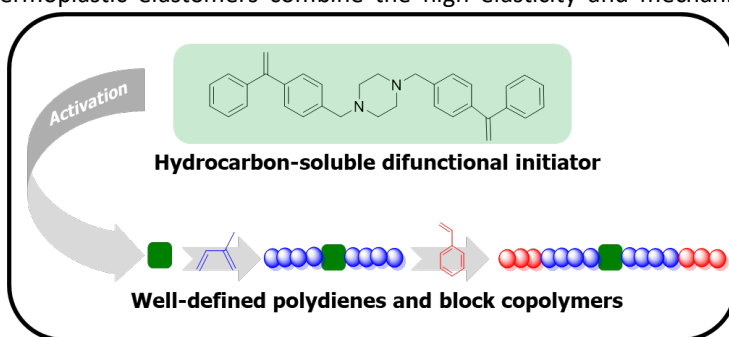
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HYDROCARBON-SOLUBLE PIPERAZINE-CONTAINING DILITHIUM ANIONIC INITIATOR FOR HIGH CIS-1,4 ISOPRENE POLYMERIZATION

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Difunctional initiation is a well-studied strategy for the facile synthesis of triblock block copolymers.¹ It is especially important for the synthesis of ABA triblock copolymers of monomers that present challenges with crossover in both directions. A premier application of ABA triblock copolymers, thermoplastic elastomers combine the high elasticity and mechanical performance of thermoset rubbers with the facile processing and recyclability of thermoplastics. Anionic polymerization remains a leading technique for the polymerization of well-defined block copolymers. For the synthesis thermoplastic elastomers from diene monomers (butadiene, isoprene, etc.), hydrocarbon-soluble difunctional initiators are necessary to maintain control of the repeat unit microstructure and ensure high ideal cis-1,4 content necessary for the elastic performance of the low T_g , polydiene inner block. Development of these initiators that provide high solubility in nonpolar solvents while providing precise control of molecular weight, polydispersity, and microstructure remains a highly pursued synthetic challenge.²⁻³



The synthesis of 1,4-bis[4-(1-phenylethenyl)benzyl] piperazine and subsequent reaction with *sec*-butyllithium enables a novel piperazine-containing difunctional organolithium initiator for the living anionic polymerization of isoprene.⁴ Piperazine provides a polar unit within the difunctional initiator, promoting ion dissociation and solubility in hydrocarbon solvents, and enabling the formation of well-defined polyisoprene homopolymers with predictable molecular weights and controlled microstructure. In situ Fourier transform infrared spectroscopy monitors the dilithium initiator formation and the anionic polymerization of isoprene, revealing kinetic insight into this synthetic method. Furthermore, sequential monomer addition with styrene affords symmetric poly(styrene-block-isoprene-block-styrene) ABA triblock copolymers with controlled molecular weight and narrow polydispersity (PDI). This novel initiator facilitates the synthesis of thermoplastic elastomers with desired high cis-1,4 microstructure in the inner, polydiene block that exhibit high mechanical performance under tensile loading.

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TRANSPIRATION-POWERED PUMPS USING THE SYNTHETIC TREE

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In nature, the plants utilize the transpiring leaf to serve as the water pump to lift water and sap by water evaporating from leaf pores [1-3], which results in concave liquid-air menisci that generate a highly negative Laplace pressure ($P_{\text{leaf}} \approx -6\text{MPa}$). Here, we show a synthetic tree utilizes a nanoporous ceramic disk with pore diameters of 160 nm and 19 tubes to act as the xylem. This synthetic tree could lift water from the reservoir to the porous disk which pumped due to the pressure produced by transpiration of the leaf. When the tree working at different humidity, it has a better transpiration rate for 85% comparing to 75%. It demonstrates that for high ambient humidities (i.e. 85%), the porous leaf significantly enhances the evaporation rate, presumably by virtue of the sharp curvature and three-dimensional surface area of the water menisci. At low humidities (i.e. 50%) the water menisci cannot achieve a local equilibrium, due to the mismatch in water activity across the interface outcompeting the negative Laplace pressure. As a result, the menisci retreat partway into the leaf, which increases the local humidity directly above the menisci until equilibrium is reached. Using a ceramic disk with pore diameters of 160 nm, we find the surprising result that the synthetic tree exposed to an ambient relative humidity of 85% has a higher evaporate rate than it exposed to 75% humidity, due to the long and tortuous vapor pathway.

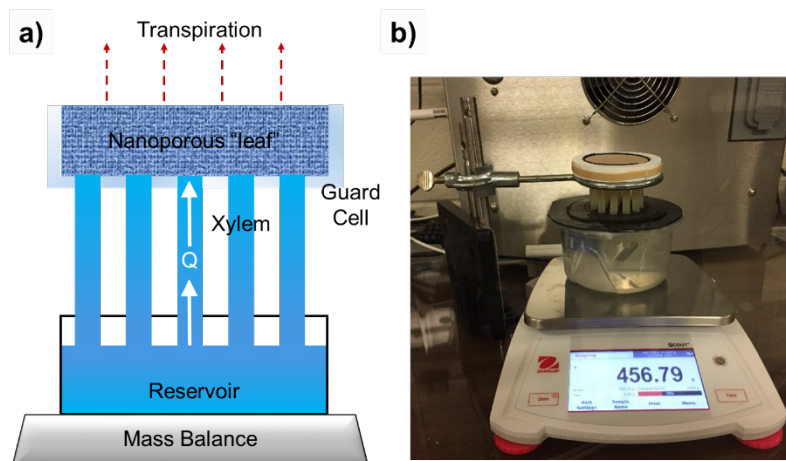


Figure 12 a) The schematic of the synthetic tree; b) The setup of the synthetic tree with 19 tubes

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ELECTRO-MECHANICAL RESPONSE OF POLYMER BONDED SURROGATE ENERGETIC MATERIALS WITH CARBON NANOTUBE SENSING NETWORKS FOR STRUCTURAL HEALTH MONITORING APPLICATIONS

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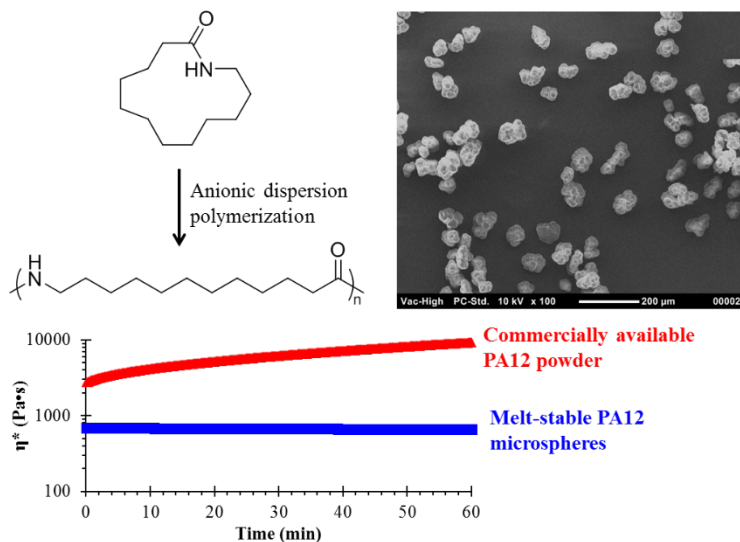
The addition of carbon nanotubes throughout the binder phase of energetic particulate composites is investigated in an effort to develop real-time embedded sensing networks for detection of small-scale damage in polymer bonded explosives undergoing mechanical load. The experimental effort herein focuses on the exploration of multi-walled carbon nanotube (MWCNT) concentration in energetic composite material; the fabrication of such specimen include the substitution of sugar as a mock energetic for the crystal particulate Ammonium Perchlorate (AP), an oxidizer most often used in solid rocket propellants. Further explored was the particulate embedded into a binder of PDMS, a polymeric silicone, as well as the addition of aluminum powder, a common combustive fuel in solid propellants, in the particulate. Electrical and mechanical properties of neat (no MWCNTs) energetics and MWCNT hybrid energetics were quantitatively evaluated under monotonic compression, and tension to failure. Noteworthy electro-mechanical response was obtained for these MWCNT AP hybrid energetics, justifying further study of CNT binder network formation for real-time electro-mechanical sensing in an effort for structural health monitoring (SHM) in energetics.

MELT-STABLE POLYAMIDES FOR SELECTIVE LASER SINTERING APPLICATIONS

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Polyamide 12 (PA12), or nylon 12, is a workhorse semicrystalline polymer employed for selective laser sintering (SLS), otherwise known as polymer powder bed fusion (PBF). PBF is an additive manufacturing (AM) technique that selectively melts micron-sized polymer particles together in a layer-by-layer fashion to produce a 3D object. Due to the fact that an object is printed within a cube of powder, most of the powder bed is not employed for production of a 3D object and remains in powder form after the PBF process. Powder recyclability is thus an issue with PBF, which is thought to be affected by molecular weight changes in unmelted PA12 powder near the sintered object, likely caused by reaction of polymer chain ends at elevated temperatures. In this work, novel and melt-stable PA12 molecular architectures are explored through use of an anionic dispersion polymerization. This reaction is based in the literature and directly produces polymer microparticles with minimal purification after polymerization. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) probe thermal transitions in these PA12 microparticles. Finally, melt rheology demonstrates melt stability over PBF-relevant time scales, and scanning electron microscopy (SEM) and particle size analysis via laser light scattering probe particle shape and size as a function of polymerization conditions.



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INTERFACIAL TRANSPORT IN NANOCELLULOSE-BASED NANOCOMPOSITE MEMBRANES FOR IMPROVED REVERSE OSMOSIS PERFORMANCE

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Improvement of current reverse osmosis membranes poses an intricate challenge that, if solved, could affect global access to clean water. Thin film composite (TFC) membranes are used commonly in industrial desalination processes, relying on a thin polyamide skin layer for selectivity. Recent studies in our research group involving the addition of nanoparticles to the selective polymer layer of existing TFC membranes have shown promising results, yielding higher water permeance (flux), improved chemical resistance, anti-biofouling properties, and mechanical property enhancement[1]. It is desired to understand how the addition of nanoparticles to the polyamide skin layer influences polymer formation, thereby altering the transport properties of the overall membrane. In addition, these thin film nanocomposite (TFN) membranes are often cost-ineffective, prompting the search for an economically viable alternative. Nanocellulose has become a popular field of study given that it is produced on large scales globally in many different varieties. In this study, cellulose nanocrystals (CNCs) of varying lengths are explored as additives to TFN membranes. The high aspect ratios of the CNCs may assist the formation of transport pathways for water molecules, as well as improve the mechanical properties of the membranes. CNCs were deposited in situ during polyamide skin layer formation in various amounts and the resulting transport properties of the membranes were observed. Inclusion of CNCs has been shown to increase flux by 20% while maintaining acceptable levels of salt rejection, however, developing a consistent deposition method remains a challenge.

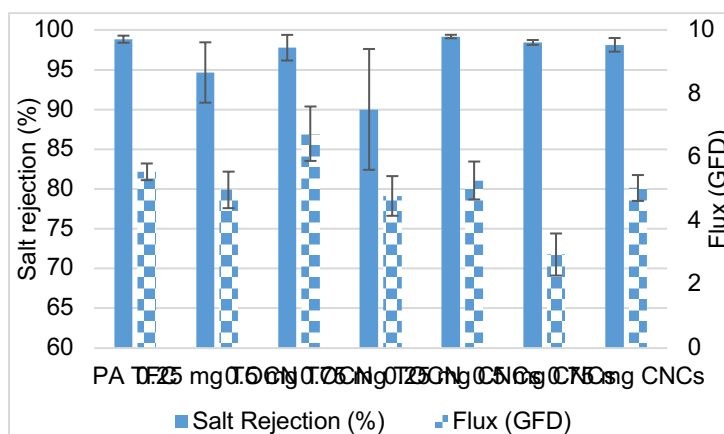


Figure 13. Comparison of TFN membrane performance between control (PA TFC) and various loading amounts of TEMPO-oxidized CNCs (TOCNs) and CNCs as obtained. The best performance was observed at a loading of 0.5 mg TOCNs.

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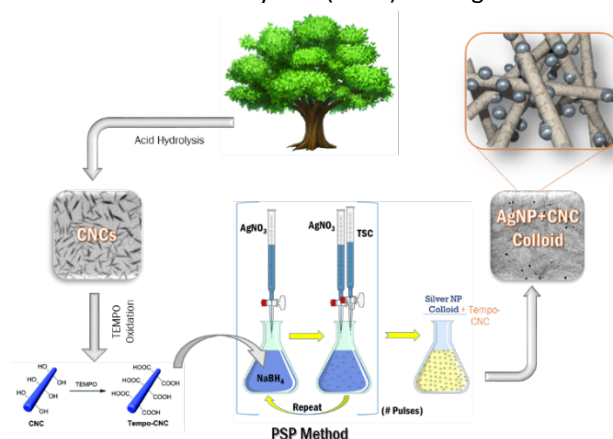
CONDUCTIVE CELLULOSE NANOCRYSTAL FOR TRANSPARENT FILMS

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Optically transparent, electrically conductive films are essential for many of today's "smart" electronics and aerospace applications. Most of these transparent conductive films are made from doped metal oxides such as indium tin oxide (ITO) and fluorine tin oxide (FTO). An emerging alternative is conductive cellulose nanocrystals (CNCs) coatings. This work focuses on the adsorption and growth mechanisms of silver nanoparticles (AgNP) on CNCs using the pulsed synthesis process (PSP) and correlating to the structure properties of the resulting transparent conductive, conformal coating. Key to this is obtaining an understanding of the interfacial mechanisms of the CNC with the NP and the resulting structure-property relationships with the conformal film.

Pulsed synthesis processing (PSP) was used to produce a AgNP/CNC aqueous colloid by the alternated addition of AgNO₃ to NaBH₄ and AgNO₃ plus TSC to NaBH₄. The trisodium citrate (TSC) is used as a capping agent to hinder the growth of the AgNPs with the goal of producing particles smaller than the CNCs (<100nm) to ensure opportunity for multiple AgNPs can attach to the CNCs without competition due to dimensional constraints. Additionally, the PSP method provides a means to perpetuate nucleating seed particles and increase the opportunity for AgNPs to adsorb and grow on the CNCs. To encourage AgNP attachment, the CNCs were functionalized to add carboxyl groups on the surface through TEMPO oxidation. Variations of the PSP method, reactant ratios, and comparisons with and without CNCs were conducted to study the impact of these process parameters. Films were prepared using the layer-by-layer (LBL) technique.



The results of this work showed the preparation of size-limited silver nanoparticles with the PSP method, effects of control parameters within the PSP method, and effects of the in situ addition of cellulose nanocrystals resulting in the attachment of silver nanoparticles. These findings were discovered through the use of dynamic light scattering (DLS) and transmission electron microscopy (TEM). Complementary analysis was done as needed with conductimetric titration, scanning electron microscopy (SEM), and zeta potential.

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MULTISCALE INVESTIGATION OF PIEZORESISTIVE SENSING OF NANOCOMPOSITE BONDED EXPLOSIVES (NCBXS)

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Polymer Bonded Explosives (PBXs) are extremely dangerous substances which have several civilian and military applications. They are composites composed of explosives grains such as HMX or RDX which are bound together by a polymer medium such as estane or epoxy. Generally the polymer binder comes in very low weight concentrations. PBXs are extremely susceptible to accidental initiation due to thermal or shock induced stimuli. As such, monitoring the strain and damage states of these materials is crucial for safe handling and transportation. The ability of CNTs to provide a piezoresistive effect when dispersed within a polymer medium is leveraged. This work will focus on the computational modeling and analysis of the derived piezoresistive effect due to the presence of the CNTs within the polymer binder surrounding the explosive grain substances. This new composite with the original pristine polymer binder replaced with the nanocomposite of polymer binder plus the CNTs together is given the term Nanocomposite Bonded Explosives (NCBXs). Microscale level RVEs are generated from actual experimental specimens with the help of SEM micrographs and modeling is done with the help of an in house 2D finite element code. The averaged microscale piezoresistive effect is quantified with the help of a gage factor and this measure is analyzed as the properties of the grain, the nanocomposite binder, the interface between the explosive grain and nanocomposite binder and the amount of CNTs is varied.

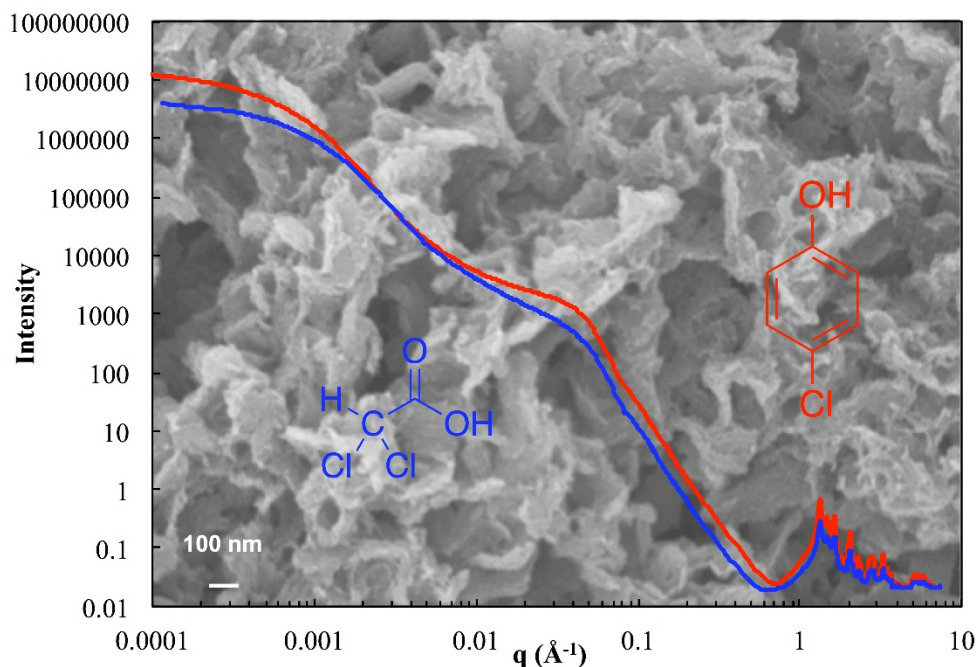
The presence of CNTs within the polymer binder and analysis of the derived piezoresistivity is an inherent multiscale problem. The piezoresistive effect is generally derived from lower scale level phenomena traversing higher up in scales and manifesting itself in the observable macroscale. One of these phenomena includes the electron hopping or tunneling effect observed at nanoscale level length scales. Computational modeling of nanoscale level RVEs is conducted with the help of the same in house 2D finite element code but with the Simmon's model for electron tunneling active within the polymer binder. An averaged nanoscale gage factor will be used to quantify the piezoresistive effect derived from this phenomenon. The variation in this gage factor is studied by varying the weight concentration of CNTs as well as their alignment. Finally, these nanoscale level gage factors are used in the microscale level simulation of the NCBXs, thus forming a hierarchical multiscale framework to analyze the piezoresistive sensing of the NCBX materials subjected to variation due to changes in nanoscale and microscale level features.

SOLVENT, TEMPERATURE, AND CONCENTRATION EFFECTS ON THE GELATION OF POLY(ETHER ETHER KETONE)

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Poly(ether ether ketone) (PEEK) is of particular interest as an engineering thermoplastic due to its high temperature thermal transitions, high crystallizability, mechanical strength, and low chemical reactivity. The effort to find new solvents capable of dissolving PEEK has produced relatively few solvent options, and, only recently, solvents in which PEEK will form stable gels, hydrogels, and aerogels following solvent exchange. In this report, small angle x-ray scattering and scanning electron microscopy are utilized as complementary techniques to characterize the hierarchical nanostructure of PEEK gels. The form and spatial distribution of the morphological features are correlated to processing conditions such as solvent selection, gelation temperature, drying technique (freeze-drying versus supercritical CO₂ extraction), and gel concentration.

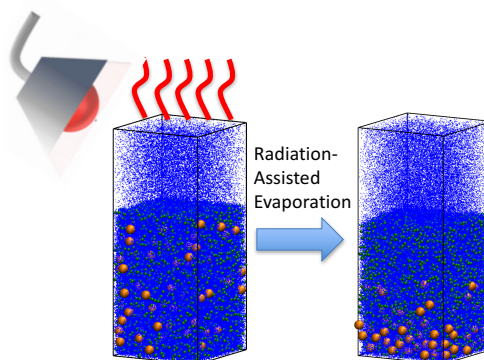


CONTROLLING STRATIFICATION OF POLYDISPERSE NANOPARTICLES DURING SOLVENT EVAPORATION

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Evaporation is a ubiquitous process that is widely utilized in material fabrication. For example, controlled evaporation is used to make polymer thin films, polymeric particles, and nanocomposites. Recently, it is found that films generated by drying suspensions of a bidisperse mixture of particles of different sizes can have various distributions of particles that depend on drying conditions and volume fractions of particles [1]. For very fast evaporation, the smaller particles are found to accumulate near the top of the dry film (i.e., small-on-top stratification) while for slow evaporation, the distribution of particles in the film is uniform. At intermediate evaporation rates, the larger particles can concentrate on top of the smaller ones in the final film, which is called large-on-top stratification. These findings point to useful techniques of fabricating multifunctional film materials. However, the underlying physical mechanisms leading to stratification remain elusive. We performed large-scale molecular dynamics (MD) simulations of the drying of suspensions containing a binary mixture of nanoparticles of two different radii, with an explicit solvent model, and mapped out a state diagram of stratifying outcome [2]. Our results show that current theoretical models tend to overestimate stratification as these models usually overlook the backflow in the solvent induced by particle migration and the possible density and temperature gradients that can emerge in the solvent during very fast evaporation because of evaporative cooling of the liquid-vapor interface. These gradients can strongly suppress the predicted “small-on-top” stratification at high evaporation rates of the solvent.



More recently, our interest turns to the control of the stratified distribution of nanoparticles in the dry film. We find that this goal can be achieved by controlling the temperature and density gradients of the solvent during evaporation. For example, if the gas phase is heated up during evaporation to induce a positive temperature gradient and an associated negative density gradient in the solvent toward the liquid-vapor interface, then “small-on-top” stratification can be strongly promoted as the larger particles are driven strongly toward the bottom of the drying film via solvophoresis (see Figure). This strategy leads to a strongly stratified dry film with the smaller particle in the top region of the film, even when the solvent evaporates slowly. By varying the direction of the temperature and density gradients, “large-on-top” stratification can also be produced. Our results thus reveal possible techniques to tune the stratified structure of drying nanoparticle or colloidal films.

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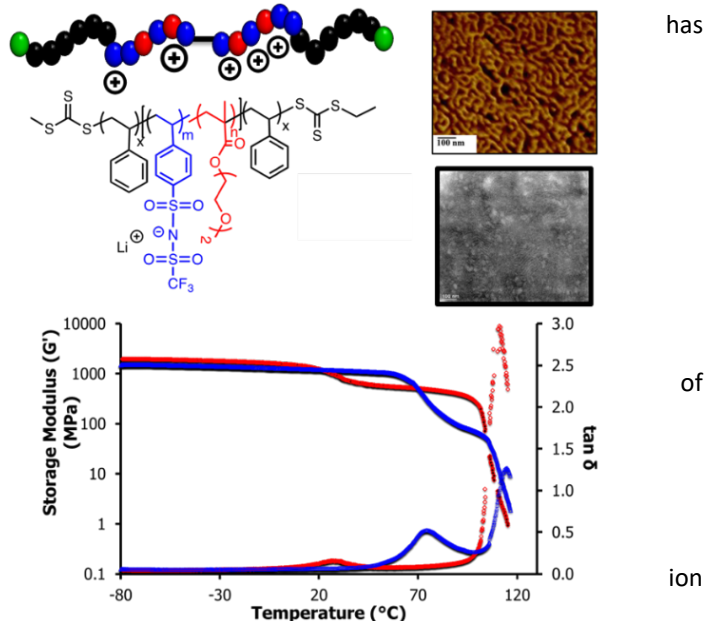
DESIGNING POLYMER ELECTROLYTES TOWARD ALL SOLID-STATE LITHIUM BATTERIES

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Commercially available electrolytes in lithium ion batteries are nearly exclusively based on lithium salts dissolved in polar aprotic organic solvents, such as ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethylmethyl carbonate (EMC).¹ The optimized liquid electrolyte exhibits a high ionic conductivity (5-10 mS/cm at room temperature), a wide electrochemical stability window, and capability of forming stable solid-electrolyte interphases (SEIs) on the anode side. However, the high flammability and lithium dendrite formation have been obstacles to achieve high safety, mechanical strength, and compatibility. The enthusiasm in developing solid state batteries with high energy densities has been overwhelming. Besides inorganic ion conductors, polymers have also been actively investigated as an important alternative due to their excellent manufacturability.²

To achieve high ionic conductivity and maintain mechanical strength simultaneously, the polymer chain segmental motion should be independent from the ion movement. One approach is to synthesize block copolymer, where the two conflicting properties can be tackled separately. In this work, we will present synthesis well-defined ionomeric A-BC-A triblock copolymers, poly[Sty-b-(StyTf2N-Li-co-DEGMEMA)-b-Sty] using the reversible addition-fragmentation chain transfer (RAFT) polymerization technique. The resulted polymer, with a microphase-separated morphology, enables a combination of excellent mechanical properties and high transport.^{3,4} Finally, we will report the properties of the resulting polymer electrolyte for shaping cathode/polymer electrolyte interfaces and improving the performance of lithium ion batteries.



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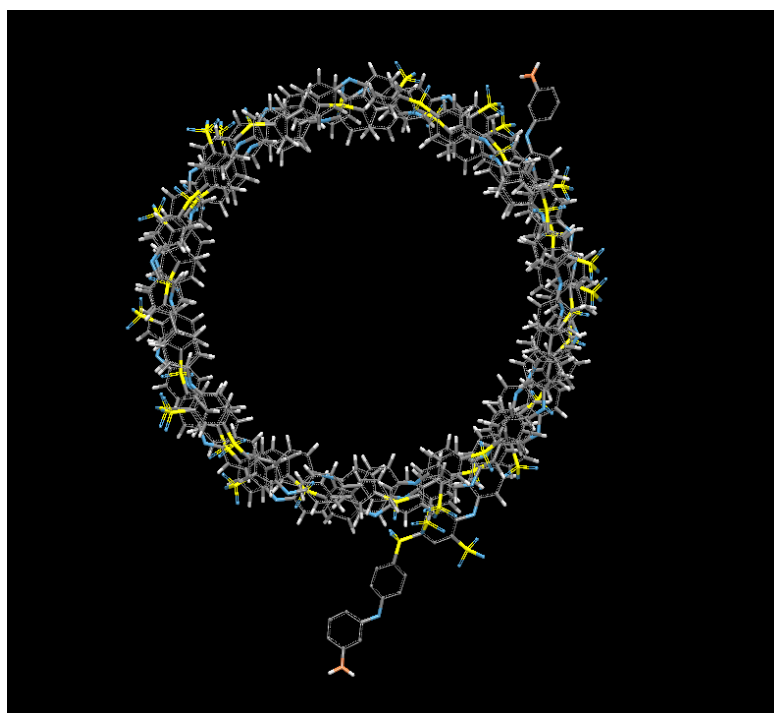
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A MOLECULAR DYNAMICS SIMULATION STUDY OF INTERACTIONS BETWEEN SULFONATED POLYSULFONE-BASED POLYMERS AND WATER MOLECULES

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Universal accessibility to safe drinking water is a feat humanity has yet to accomplish. Roughly 1 in 10 people worldwide do not have access to potable water. One approach to solving this issue is driving down the cost of water purification. The distillation of water is a very energy intensive process. Common methods of water purification, such as Reverse Osmosis (RO) and electrodialysis, require polymeric thin film membranes with optimal properties to separate unwanted solutes. Many scientists, particularly chemists, have synthesized novel ionic polymer membranes to increase the efficiency of purification processes. However, there continues to be a lack of consensus and understanding concerning how both water molecules and solvated ionic species interact with these polymer backbones on a molecular level. This study investigates the effects of divalent ions on the conformation and dynamic behavior of sulfonated polymers using Molecular Dynamics (MD).



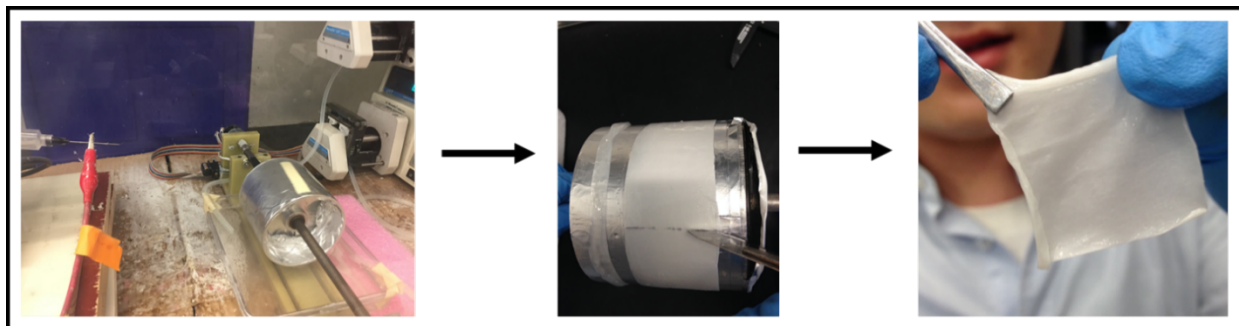
Using the GROMACS and LAMMPS MD software packages, we generate atomistic models of sulfonated polysulfone-based monomers, oligomers, and polymers in an aqueous solution. The membrane environment is simulated using both implicit and explicit solvation. Implicit solvation models are generated with OPLS-AA force fields and known dielectric properties of the polymer and water. In the simulation, the interactions between the water molecules, the mobile ions, and the charged polymers are observed and analyzed. Results indicate that in the presence of water, the polar sulfone groups in the polymer backbone play a role in mediating the interactions of mobile ions and polymer-based ionic groups. This result highlights the importance of polymer backbone chemistry for ionic polymer membranes used in desalination processes.

A NOVEL FABRICATION TECHNIQUE OF ELECTROSPUN FIBER REINFORCED GELS

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We report a novel, one-step process for fabricating electrospun fiber reinforced hydrogel composites for skin regeneration. This work describes the development of a method to accomplish a homogeneous distribution of micro-fibers throughout a hydrogel phase. An innovative apparatus and process was developed to deposit electrospun micro-fibers into slowly growing gelatin film producing a composite matrix of electrospun polycaprolactone (PCL) fibers and gelatin. The process was designed to achieve a continuous hydrogel phase with sufficient mechanical properties to encourage cell infiltration and support handling and application as a skin scaffold. Deposition of gelation around the mandrel occurred for gelatin concentrations ≥ 2.75 % w/v. These electrospun fiber reinforced gels (EFRGs) exhibited promising mechanical properties for wound dressing applications to facilitate skin repair. PCL was concurrently electrospun onto the rotating drum at different rates to achieve composites with 7 to 18% w/w PCL fibers and Young's moduli of 0.03 to 0.36 MPa. Overall, the data validate a novel and practical method to fabricate fiber reinforced composite films with mechanical properties suitable for wound dressings that facilitate skin regeneration.



INVESTIGATION OF THE ISOTHERMAL AND NON-ISOTHERMAL CRYSTALLIZATION KINETICS OF POLY(ETHYLENE OXIDE) (PEO) OF DIFFERENT MOLAR MASSES USING ULTRA-FAST DIFFERENTIAL SCANNING CALORIMETRY

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The Mettler-Toledo Flash™ DSC 1 has a very low time constant, several milliseconds, and can reach cooling rates, as high as $2 \times 10^3 \text{ K.s}^{-1}$, making it very useful for investigating rapid thermal transitions over a large temperature range. Specifically, the Flash™ DSC 1 can be used to study non-isothermal crystallization at cooling rates that mimic processing conditions and isothermal crystallization at real processing temperatures. The crystallization process of four narrow molecular weight distribution poly(ethylene oxide) (PEO) samples was monitored using the Mettler-Toledo Flash™ DSC 1 under both isothermal and non-isothermal conditions. For non-isothermal conditions, crystallization took place during cooling at a constant rate ranging from 5 to 800 K.s^{-1} , with no observable crystallization at cooling rates greater than 10^3 K.s^{-1} . For crystallization under isothermal conditions, the peak time of the crystallization exotherm, τ_{peak} , was recorded over a 90°C temperature range extending to the glass transition. A bimodal distribution of τ_{peak} vs. crystallization temperature was observed and related to a change from heterogeneous nucleation at high temperatures to homogeneous nucleation at low temperatures (Figure 1). Neither the low nor the high crystallization temperature regions show a clear trend with respect to molecular weight. The degree of crystallinity monotonically increased over the entire range of crystallization temperatures, but showed no clear molecular weight dependence over the range of temperatures ($T_x < 35^\circ\text{C}$) investigated in this study.

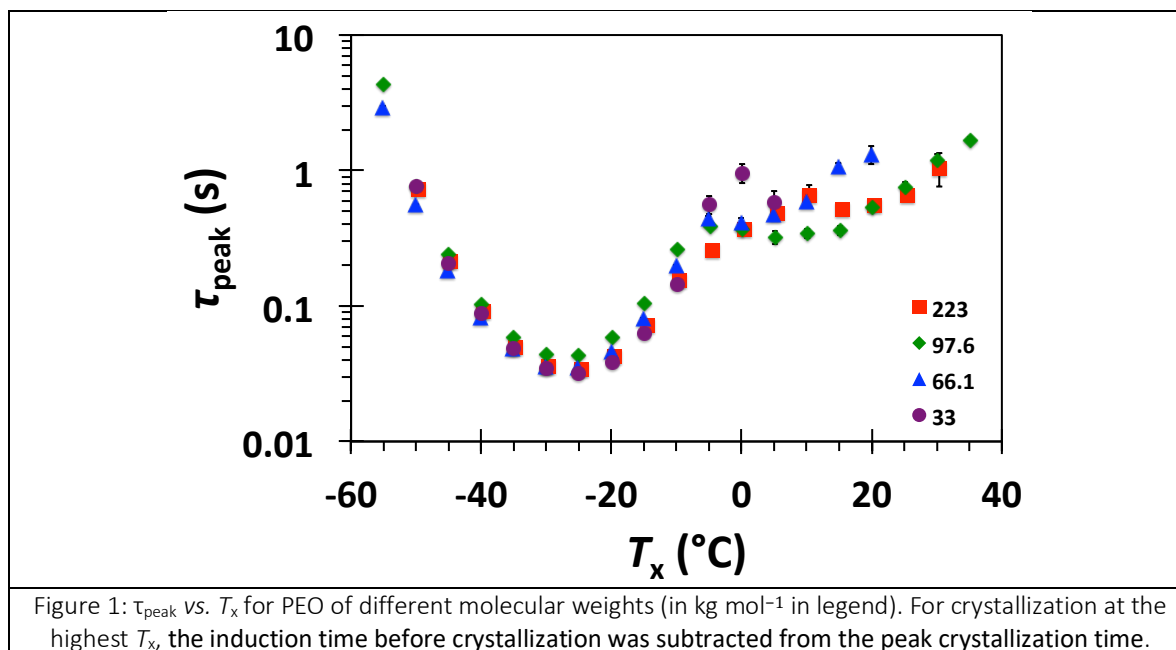


Figure 1: τ_{peak} vs. T_x for PEO of different molecular weights (in kg mol^{-1} in legend). For crystallization at the highest T_x , the induction time before crystallization was subtracted from the peak crystallization time.

THE RELATIONSHIPS BETWEEN MECHANICAL BEHAVIOUR AND WATER INTERACTIONS IN SULFONATED POLYSULFONES FOR DESALINATION MEMBRANE APPLICATIONS

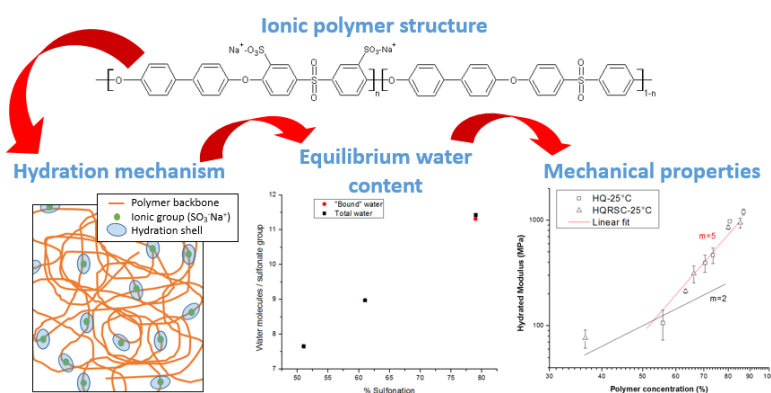
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Electrodialysis desalination (ED) systems require ionic polymer membranes that have high ion conductivity, low electrical resistance, and are mechanically robust. Industrial ED membranes are prepared with a thick non-ionic polymer fiber reinforcement in order to achieve adequate handleability and durability. This method leads to membranes with a low content of ionic polymer and a high total thickness. The development of more mechanically robust ionic polymers would decrease the amount of reinforcement needed, which would decrease the thickness of the membrane and increase the overall efficiency of the ED cell.

Since ionic polymers inherently interact with water and the membranes will be fully immersed in the ED cell, it is important to study the properties of these polymers when they are in equilibrium with liquid water. For this research, polysulfone random copolymer backbones are post-sulfonated in order to produce ionic polymers.[1] The chemical structures are varied in a controlled way in order to probe the effect of the location of the ionic groups along the backbone. The location of the ionic groups impacts the equilibrium water uptake of the polymers, which in turn governs the mechanical properties.

Presented here are the equilibrium water uptakes of the polymers as well as the tensile properties in the water-immersed state. The tensile modulus of the polymers is found to be related to water uptake via a power law.[2] Water melting analysis is also conducted using DSC in order to probe the specific interactions of the water molecules with the ionic groups and shed light on the molecular origins of hydration.[3] There are 3 “states” of water molecules in ionic polymers: bound, interacting, and free. Based on this analysis, the polymers with the best mechanical and ion transport properties contain only bound water molecules.



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EFFECT OF HIGHLY-ALIGNED NANOSCALE SURFACE STRUCTURES ON MICROBIAL ADHESION

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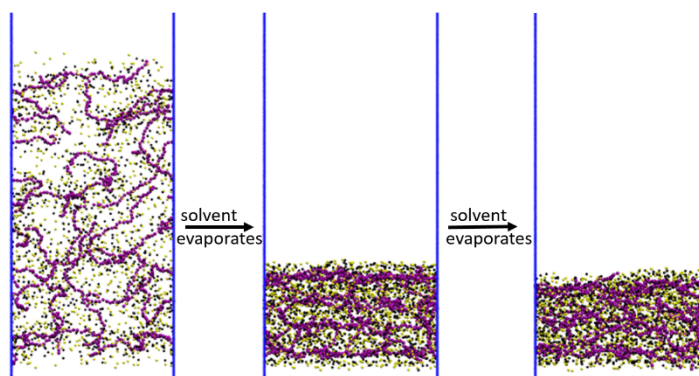
Microbial adhesion and biofilm formation are prevalent in many natural and industrial settings and can be contextually beneficial or detrimental. Microbial biofilm formation on implantable medical devices and biomaterials is an intractable problem since it causes up to 70% of hospital-acquired infections, leading to an estimated additional \$28-45 billion healthcare costs per year in the U.S. alone. Previous works done by our lab and others have shown that microbial retention on surfaces is strongly dependent on the surface micro/nano-scale topographical features, and that there exists an optimal set of parameters (topographical feature size, shape, spacing, and configuration) which can yield minimum microbial attachment density. In this work, we investigate the role of aligned nanofiber-coating on retention of two uropathogenic model organisms -- *Escherichia coli* and *Candida albicans*. Surface architectures were varied by changing nanofiber diameter and spacing. Short-term and long-term effects of the introduction of an anti-adhesion chemical coating were also studied. Dynamic retention assays were carried out and microbial attachment density on engineered surfaces was compared to the unmodified polystyrene surfaces, using fluorescent microscopy and image processing. This work culminates in determining the role of surface topography and chemical coating in long-term mitigation of microbial attachment on urological devices.

EVAPORATION OF SOLUTIONS CONTAINING CHARGED POLYMERS: A MOLECULAR DYNAMICS STUDY

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Polyelectrolyte solutions show rich physical behavior different from that of solutions of neutral polymers. For example, in a solution of both polycations and polyanions the complexation of oppositely charged chains can lead to complex coacervates that contain most of the two polymers. Such equilibrium phenomena have been studied for many decades. However, other nonequilibrium processes such as the evaporation of polyelectrolyte solutions have received less attention. We use molecular dynamics simulations to study the evaporation of solutions containing both polycations and polyanions. The polymers are represented by MARTINI-type bead-spring chains. Water is used as the solvent and modeled with a model taking into account polarization effects. Counterions and salts are explicitly included as mobile single beads. The solution of only polyanions and of a mixture of polycations and polyanions are studied. The effects of polymer concentrations, charge ratio, and evaporation rates on the structure of the final polymer film are clarified. The connections of the film structure to the complexation behavior of polyelectrolytes prior to evaporation are elucidated. Our results reveal potential new strategies of fabricating polyelectrolyte films with controlled structures.



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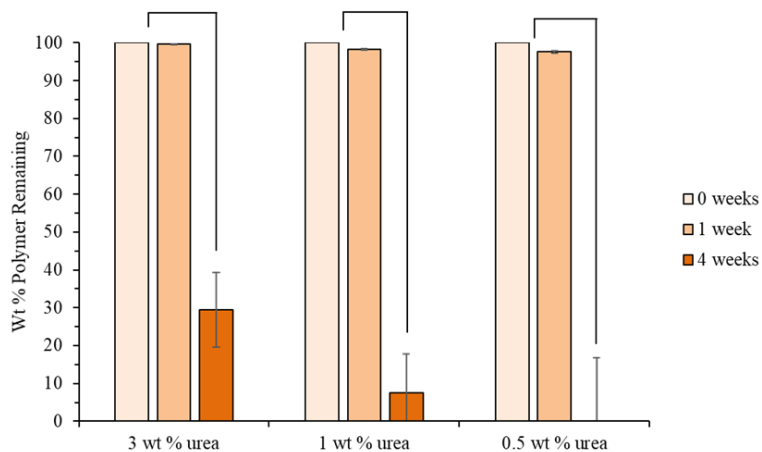
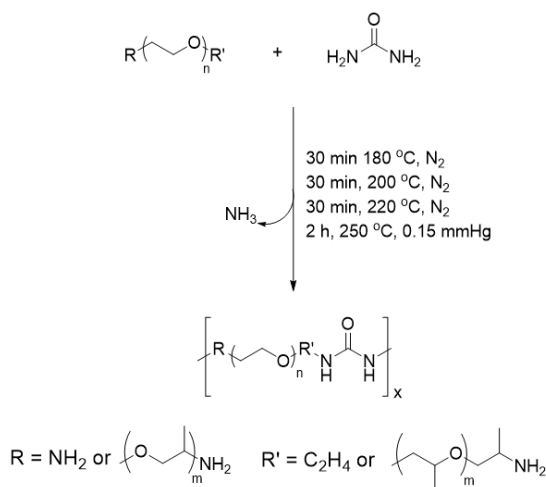
BIOLOGICALLY-DERIVED, WATER-SOLUBLE POLY(ETHER UREA)S AS NITROGEN SOURCES FOR PLANTS

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The synthesis of polyureas commonly requires the use of isocyanates and toxic catalysts. However, the melt polycondensation of diamines with urea presents a less toxic and bio-sourced method to produce high molecular weight polyureas. Poly(ether urea)s synthesized from poly(ethylene glycol) (PEG) diamines or Jeffamine® with urea exhibited complete water solubility in under 30 min at concentrations of 1 mg/mL. Thermal analysis revealed low melting points (< 60 °C) in the poly(ether urea)s, demonstrating their potential as melt-processable materials. Rheological analysis further determined that the viscosities of the poly(ether urea)s were suitable for melt extrusion based processes.

Melt pressed films of these materials exhibit thermoplastic behavior with strains at break as high as 600%. Variable temperature Fourier transformed infrared spectroscopy confirmed the presence of urea hydrogen bonding, which accounts for these mechanical properties. Rheological analysis determined that the viscosities of the poly(ether urea)s were suitable for melt processing. Additionally, poly(ether urea)s synthesized from urea degrade in the presence of urease to release ammonia on time scales of < 1 month. This represents the potential use of the polymers as controlled-release nitrogen delivery vehicles to plants.



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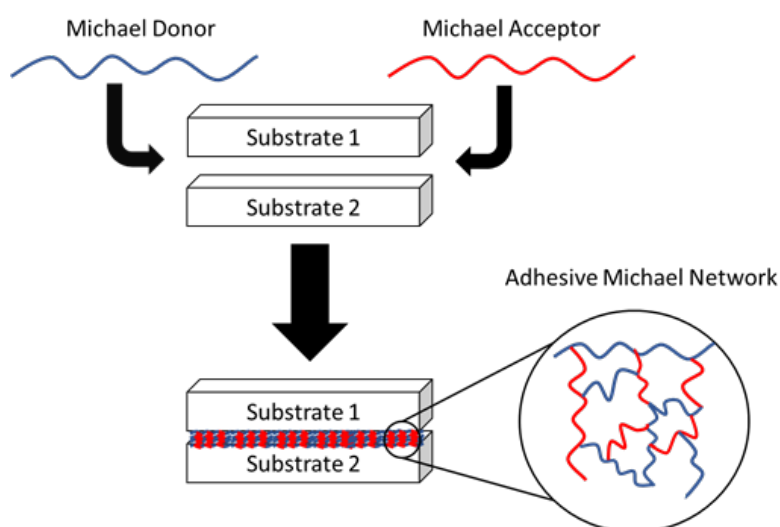
MICHAEL ADDITION AS A MEANS TO DESIGN ADHESIVES: NETWORKS BASED ON REACTIVE TELECHELIC OLIGOMERS

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Many industrial solvents are polymer solutions which require a drying process for adhesive hardening. However, adhesive hardening is slow in polymer solutions due to low viscosity. We propose a novel, fast hardening adhesive based on reactive telechelic oligomers. Two facile reactions of a telechelic diol allowed for the successful synthesis of a Michael donor and Michael acceptor with identical oligomeric backbones. The bulk Michael addition of the telechelic oligomers resulted in a crosslinked adhesive network. DBU was chosen as an organic base over an inorganic base in order to keep the reaction homogeneous. The molecular weight and functionality of the Michael acceptor was also varied to determine how the crosslinking kinetics were affected.

Rheology revealed that the crosslinking kinetics increased significantly with increasing wt% of catalyst. The kinetic also slowed as a function of decreasing cure temperature from 50 °C to -20 °C. Peel tests performed at 90° determined the maximum load the adhesive achieved before failure upon addition to three types of industrial rubber. The addition of tackifier enhanced the adhesion strength of the network and increased the crosslinking time. The oligomer-based networks showed maximum loads in peel testing which were comparable or greater than that of a neoprene-based control adhesive. This method provides a novel crosslinked adhesive with excellent adhesion properties formed entirely in the bulk.



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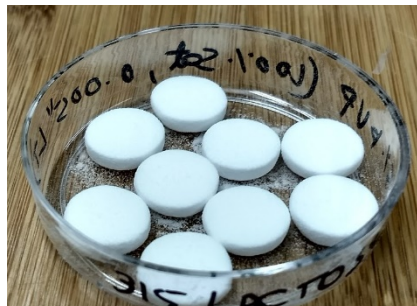
POLYMER DESIGN FOR DRUG DELIVERY SYSTEMS: FROM ACID CLEAVAGE NETWORK SCAFFOLDS TO WATER-SOLUBLE 3D PRINTED POLYMERS

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Water-soluble polymers are the most common materials applied for drug delivery systems, enabling drug encapsulation and slow release on-demand. The advent of 3D printing allows to customize drug carriers for patient's needs; for example, 3D printed oral drug delivery tablets enable personal dosage, which will help minimize drug side effects. In addition, one can imagine designing degradable medical devices or cell scaffolds, which exhibit a complex geometry and tailored dissolution to improve drug release.

Here, we present different polymeric structures suitable for 3D printing. Each 3D printing technique requires tailored polymer properties to maximize success. We developed polyethylene glycol polymers to generate degradable drug delivery vehicles. These polymers are suitable

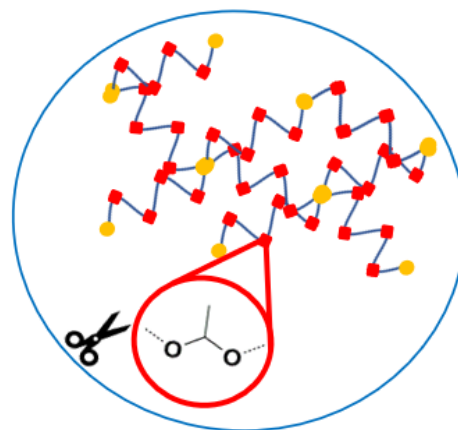


Personalized dosage tablet made using additive manufacturing.

for 3D printing techniques utilizing UV-light, e.g. stereolithography. UV-

crosslinking leads to hydrogels, which are stable at physiological conditions and degrade at slightly acidic pH. These structures are promising to implant in tumor tissue, providing slow release of anti-tumor drugs.

Further, we developed water-based binders with poly(2-oxazoline)s and poly(vinyl pyrrolidone) to bind lactose and starch to 3D print personalized dosage tablets through binder-jetting. Binder jetting is a powder bed-based system where a binder is deposited onto a powder surface to make layers. It is the most popular method of 3D printing for tablets because of inexpensive materials and the ability to use excipients already used in compression molding tablet processes.



Schematic of acid cleavage hydrogels for drug delivery applications.

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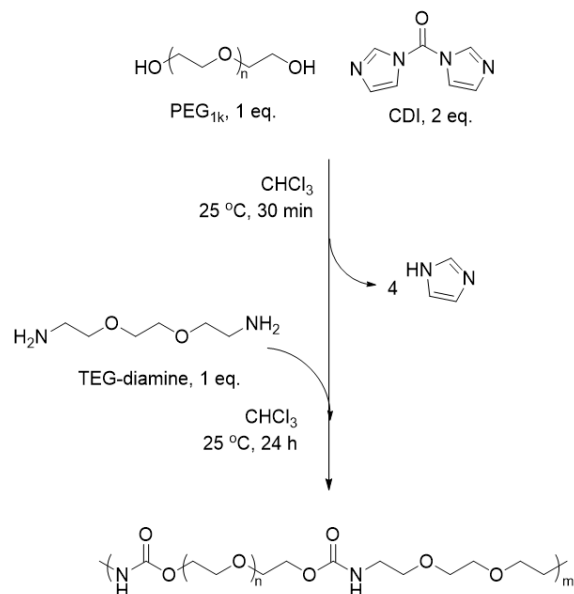
ISOCYANATE-FREE POLYURETHANES BASED ON BIOCOMPATIBLE MONOMERS

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Polyurethanes remain a commercially-viable solution for many common applications, most notably in the formation of polyurethane foams or in biomedical applications. While the method and applications of polyurethanes are well preceded, novel polyurethanes, such as ion-containing polyurethanes, pique the interest of many scientists. Typical polymerization to form polyurethanes requires an isocyanate coupled between a soft segment diol and a chain extender urethane to form a hard segment. However, isocyanates require the use of dry solvent and heavy metal catalyst and pose health risks for employees responsible for polyurethane polymerizations. The movement away from isocyanates in the formation of polyurethanes poses a great scientific challenge to ensure safety for employees while also yielding high molecular weight polymer suitable for target applications.

Conventional polyurethane polymerization includes highly toxic diisocyanate monomers, which limits its application in biological settings. The production of isocyanate-free polyurethanes begins with end-capping reactions of diols with carbonyl diimidazole, providing a favorable leaving group. Upon the addition of diamines in stoichiometric amounts, the polymerization proceeds to produce polyurethanes with imidazole by-products. The control of hard and soft segments relies entirely on monomer manipulation and dispersity, as this synthetic route avoids the chain-extension reaction to produce polydisperse segments. This reaction enables the addition of functional groups along polymer backbones, due to its selectivity to primary amines and alcohols. Precisely-tuned polymer structure tailored for a specific biological application to match the biochemistry, cell type, and tissue modulus of a target application.



Synthetic scheme of isocyanate-free polyurethanes

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ICE WICKING

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The mechanism of liquids wicking through porous media, while widely characterized for many materials, has never been studied for ice. Liquid-ice interactions are becoming increasingly relevant for many applications including hydraulic fracturing, arctic drilling, and oil-infused surfaces. Here, we observe oil as it wicks up sheets of frost grown on aluminum surfaces of varying wettability: superhydrophilic, hydrophilic, hydrophobic, and superhydrophobic. The frost was grown and maintained at varying thicknesses in a humidity chamber, and a bath of fluorescent silicone oil was raised until the bottom of the frost sheet was submerged in the oil. Length vs time data was recorded for each trial and compared across surface wettability. It was found that the superhydrophilic and hydrophilic surfaces promoted wicking with a power law time slope of $1/3$. The discrete droplet distribution in the non-wetting surfaces resulted in lower time slopes, with $1/4$ for the hydrophobic surface, and essentially 0 for the superhydrophobic surface, where almost no wicking was observed. Using a modified version of the classical Washburn equation, the length vs time data can give insight into the morphology of frost by estimating the effective pore radius of the frost. Additionally, this research shows that the spreading rate of a liquid through frost can be controlled by tuning the wettability of the underlying surface.

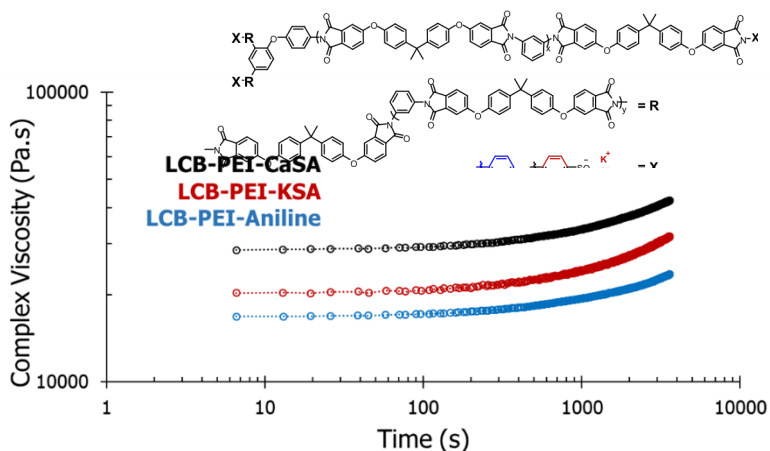
IMPROVING PROCESSABILITY FOR HIGH PERFORMANCE POLYETHERIMIDES USING LONG-CHAIN BRANCHING

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Polyetherimides, PEIs, are thermally stable thermoplastics with uses in engineering, industrial, and medical fields. Their high mechanical strength, chemical resistance, and heat resistance are desirable qualities for a range of demanding applications. However, high T_g polymers are known to have lower melt flow properties. When branching is utilized in small percentages, branching improves polymer processability by lowering the melt viscosity while maintaining bulk mechanical properties.¹⁻³ Low branching concentration means that there are long-chain branches, which increase restrictions on the mobility of each polymer chain.

We synthesized multiple long-chain branched polyetherimides (LCB-PEIs) using low percentages of trisamine monomers, in conjunction with a diamine monomer. We also introduced ionic end-groups onto branched polyetherimides to develop an understanding of the role of ionic interactions at elevated temperatures. We investigated the melt processability of the LCB-PEIs with rheology to understand the effect of long-chain branching and ionic interactions. The LCB-PEIs showed significant differences in melt viscosities while their thermal stability remained similar to that of linear polyetherimides. Glass transition temperatures remained unchanged for branched polyetherimides with ionic end-groups while their melt viscosities changed significantly. Finally, a variety of analytical techniques, including differential scanning calorimetry, dynamic mechanical analysis, and size-exclusion chromatography, provided an in-depth understanding of structure-property relationships.



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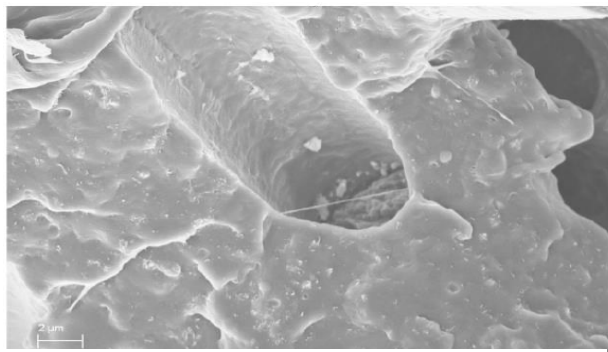
REPLACING GLASS FIBERS WITH CELLULOSIC FIBERS WHILE ENHANCING THE BIO-COMPOSITES' MECHANICAL PROPERTIES

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The proposed research addresses several challenges of using cellulosic fiber to replace glass fiber in high modulus and high strength composites. One challenge is the variable properties (density, strength, and modulus) of raw bio-fiber, which cause unsteady composite mechanical properties. Another challenge is that the low modulus and strength of raw cellulosic fiber causes low composite mechanical properties relative to the glass fiber reinforcement. The low strength of raw cellulosic fiber, compared to glass fiber, results in easier fiber breakage, and, therefore, it is more difficult to maintain fiber length during injection molding. Injection molding is preferred to wet lay due to its lower cost. In particular, this research is concerned with the processing (injection molding) of hemp derived cellulosic fiber (HDCF) reinforced thermoplastic composites, and the development of multi-scale composites (MSCs) with cellulose nano-crystals (CNCs).

Preliminary work was performed on MSCs based on the addition of carbon nano-tubes (CNTs) to carbon fiber (CF) reinforced composites of either polypropylene (PP) or polyetheretherketone (PEEK). A 1 wt% CNT addition to a 30wt% CF/PP composite lead to a 19% increase (11.6 GPa to 13.8 GPa) in modulus, and a 1 wt% CNT addition to a 30wt% CF/PEEK composite lead to a 54% increase (17.5 GPa to 27.0 GPa) in modulus [1, 2]. CNCs are possibly able to enhance the modulus of cellulosic fiber MSCs due to the compatibility. Mechanical properties results from previous studies, transmission electron microcopy (TEM), and scanning electron microcopy (SEM) will be used to understand the origin of the modulus enhancement in order to extend the approach to other systems. Cellulosic fiber reinforced MSCs have a possibility of competing with glass fiber reinforced composites for mechanical properties and low weight. Therefore, cellulosic fiber may possibly replace glass fiber, with significant applications in the automotive and aerospace industries. Processability and recyclability are also motivations for the proposed research efforts in the development of cellulosic fiber reinforced MSCs with CNCs.



Fracture surface for flow direction 40 wt% CF/ 1 wt% 10X CNT

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STUDY OF RHEOLOGY AND STABILITY OF POLYACRYLONITRILE-BASED COPOLYMERS WITH VIRIOUS PLASTICIZERS

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Polyacrylonitrile (PAN) fiber is currently one of the most important synthetic fibers and approximately 90% of carbon fiber is made from PAN fibers as a precursor [1]. PAN-based carbon fiber plays a significant role in many modern industries, such as the aerospace and automobile industries, because it has low density, high thermal stability, high tensile strength and high tensile modulus. However, due to the limitations of the current PAN spinning processes (solution spinning), the cost is relatively high and the relevant solvents are environmental unfriendly. The development of PAN melt spinning has the potential to significantly reduce the cost of carbon fiber.

The melting point of PAN polymer is as high as 320°C, but PAN starts to suffer a cyclization reaction around 180°C (the reaction becomes rapid and spontaneous at 220°C) [2]. This degradation reaction is undesirable in the spinning process (but desirable in the carbon fiber conversion process). In this case, the major challenge of PAN melt spinning is to decrease the melting point of PAN to avoid degradation reaction during the melt spinning process. Coxe[3] first discovered that by adding water into PAN as a plasticizer, the melting point of PAN could be significantly reduced to below 200°C, which made PAN melt spinning technically feasible. Later, further research had been performed and more potential plasticizers has been discovered. BASF [4] claimed in their patent that a mixture of water and acetonitrile(AC) could be used as a plasticizer for the PAN melt spinning. This process has been proved to be very effective, and it can produce a decent quality fiber. However, due to economic considerations, the melt spinning PAN process has not been commercialized yet.

Several chemicals, including water and acetonitrile, and their mixture, are considered as potential plasticizers in this study. The relevant rheological and stability behavior of PAN with those plasticizers is reported. The steady-shear rheological data shows the presence of acetonitrile can further decrease the processing temperature of PAN melt spinning. The time-dependent rheological stability data show that PAN could hold its viscosity stable without significant degradation for a sufficient period of time below 180°C.

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BATTERY APPLICATIONS UTILIZING A TUNABLE STIFF SOLID MADE FROM AN IONIC LIQUID AND A RIGID-ROD POLYANION

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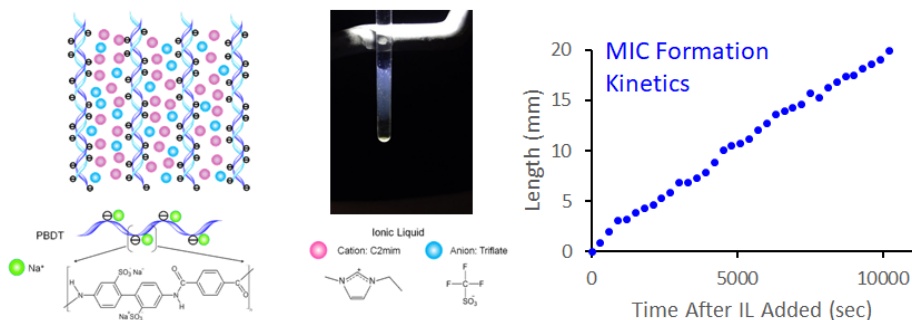
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Batteries play an important role among various energy storage technologies. However, safety risks (flammability) and limited storage capacity are still challenges for battery application and development. Here we present a new class of solid materials formed from a rigid-rod polyanion and an ionic liquid. This “molecular ionic composite” (MIC) behaves mechanically as a solid, but contains ions that move nearly as in a neat liquid.¹ Prototypical MICs are based on solutions of the rigid-rod polyelectrolyte poly(2,2'-disulfonyl-4,4'-benzidene terephthalamide) (PBBDT) combined with a range of ionic liquids (ILs). This composite exhibits an unprecedented combination of properties: ionic conductivity up to 8 mS/cm, tunable elastic modulus from 0.03-3 GPa, and thermal stability up to 300 deg. C.² The MIC systems remain highly tunable with amount of PBBDT used in an aqueous seed solution as well as the type of IL and volume of IL to the seed solution. The kinetics of composite formation can be easily measured by the MICs fluorescence property under the exposure to white light. These composite systems show promise as candidates for replacing flammable and volatile liquid electrolytes in rechargeable batteries especially when loaded with, e.g., lithium or sodium salts. When loading MICs with 4 M lithium, the composite forms a locally ordered polymer-IL matrix with a mixture of nano-scale crystalline structures, as shown in wide-line solid state NMR, X-ray diffraction, and small angle X-ray scattering experiments. This electrolyte has shown long-term cycling in a Li-Li symmetric cell, thus demonstrating its promise for use in Li batteries.

Molecular Ion Composite



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USING FILLERS TO IMPROVE PRINTABILITY OF SEMI-CRYSTALLINE MATERIALS FOR MATERIAL EXTRUSION ADDITIVE MANUFACTURING

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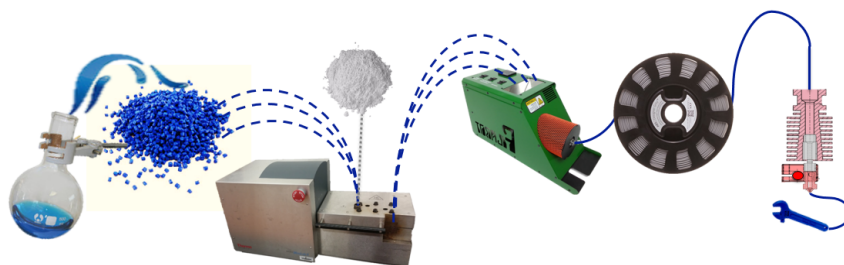
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Additive manufacturing (AM) allows for rapid prototyping, customization of parts, and is cost effective for low production volumes parts, affecting industry sectors such as aerospace, biomedical applications, startups manufacturing companies, and personalized medicine. AM applications are currently constrained by the limited selection of process-able materials. For example, printable soluble materials are of interest for AM as the technology's design freedom would allow printing personalized medicines with tailored dissolution profiles.¹ The author's have previously investigated the influence of divalent counter-ions on sulfonated poly(ethylene glycol) (PEG). These polymers were evaluated based on the criteria of (i) dissolving quickly, and (ii) manufacturability via fused filament fabrication at low temperatures (< 100 °C) to allow for the incorporation of active ingredients.² However, the ion exchange following the synthesis of the sulfonated PEG is expensive in production scale-up.

To circumvent this limitation, this work explores the use of filler materials in the sulfonated PEG sodium ion containing polymer, poly(PEG_{8k}-co-NaSIP), to achieve the desired properties enabling fused filament fabrication. Adding different fillers is common practice in sheet molding compounds to achieve the required material properties for manufacturing.³ This technique was applied to the sulfonated PEG with the sodium counter ion with different filler particles (calcium chloride, silica, and starch) and the material properties were measured. Changes in the viscosity, crystallinity, and crystal structure, show positive results to enable processing via material extrusion.



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CONTROLLED PHOTOREDOX RING-OPENING POLYMERIZATION OF O-CARBOXYANHYDRIDES

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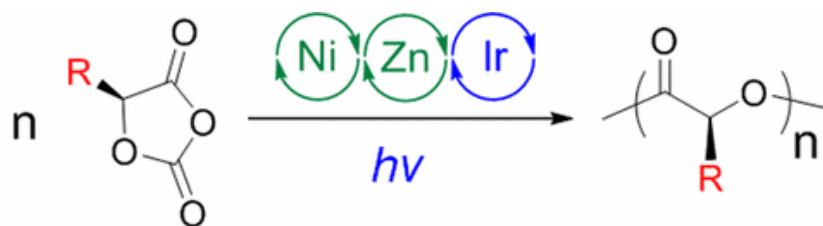
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Poly(α -hydroxy acids) are important biodegradable polymers with wide applications. Attempts to synthesize them from O-carboxyanhydrides with pendant functional groups by various methods, including methods involving organocatalysts or organometallics, have been plagued by uncontrolled polymerization, including epimerization for some monomers, which hampers the preparation of stereoregular high-molecular-weight polymers. Herein we describe an effective protocol that combines photoredox Ni/ Ir catalysis with the use of a Zn-alkoxide for efficient ringopening polymerization, allowing for the synthesis of isotactic polyesters with expected molecular weights (>140 kDa) and narrow molecular weight distributions ($M_w/M_n < 1.1$). Mechanistic studies indicate that the use of a low temperature ($-20\text{ }^\circ\text{C}$) and photoredox Ni/Ir catalysis synergistically accelerates ring-opening and decarboxylation of the monomer for chain propagation while avoiding the formation of the undesired Ni-carbonyl complex.



- ✓ High molecular-weight polymer (> 140 kDa)
- ✓ Controlled living polymerization ($\mathcal{D} < 1.1$)
- ✓ No epimerization
- ✓ Polyester with pendant functional groups

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THERMORESPONSIVE DENDRITIC ELASTIN-LIKE PEPTIDES AS CROSSLINKERS IN HYALURONIC ACID GELS

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Hydrogels that mimic the native extracellular matrix were investigated using dendritic elastin-like peptides (denELPs) of generations 1, 2, and 3 as crosslinking units. The denELPs, which contained structural segments based on the repeating GLPGL pentamer, were covalently crosslinked with hyaluronic acid (HA). The physical properties of the hydrogels were investigated by rheology, scanning electron microscopy, swelling tests, and model drug loading and release assays. Combined results from these characterization methods revealed that hydrogels with higher generation denELPs were stiffer, more turbid, had smaller pore sizes, swelled less in water, and absorbed more of a model drug while releasing it more slowly. We attribute these differences primarily to additional physical crosslinking, caused by aggregation of the higher generation number dendrimers during hydrogel formation, which is a result of the dendrimer crossing its transition temperature (T_t). These denELP clusters disassembled over the course of 4 d at 4 °C (below the T_t of the denELP component), indicating that the hydrogels retained the thermoresponsive character of the denELPs, although response time was substantially slower in the gel state than for free denELPs in solution. These findings provide important insights into the behavior of ELP-based hydrogels, in which physical crosslinking of the ELP domains can be controlled to tune mechanical properties, highlighting the potential of HA_denELP hydrogels as biomaterials.^{1,2}

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USING COMPLEMENTARY SURFACE ANALYSIS TECHNIQUES TO STUDY THE INTERACTIONS BETWEEN NOVEL AMPHIPHILIC CELLULOSE DERIVATIVES AND BILE SALTS

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Cellulose derivatives are surface-active biopolymers used in foods as emulsifier and thickener agents [1]. They are considered dietary fibers because they can neither be absorbed nor metabolized in the human body, thus providing positive health benefits, like lowering blood cholesterol levels. One of the proposed mechanisms behind the cholesterol-lowering effect of soluble fiber is its ability to modulate lipid digestion and absorption through interactions with bile salts (BS) in the duodenum [2]. BS are a mixture of steroid acid conjugates with surfactant properties that prepare the oil-water interface in emulsions for the adsorption of enzymes that

hydrolyze lipids. We have previously observed that some commercial cellulose derivatives containing hydroxypropyl groups adsorb onto the surface of emulsified lipid droplets hindering adsorption of low concentrations of BS. However, those cellulose networks were not strong enough to protect the lipid surface at BS concentrations relevant to physiological conditions within the duodenum [3]. Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D) and Surface Plasmon Resonance (SPR) are surface analysis techniques that provide real-time, label free measurements of molecular interactions. They are widely used in applications ranging from biomedical to electrochemical studies but there are limited studies that have used these techniques to characterize interactions between cellulose derivatives and BS. In order to investigate the potential of novel Hydroxypropylcellulose (HPC) derivatives to modulate lipid digestion at high physiological BS concentrations, the objective of this work was to study the interactions between these two surface active species using both acoustic (QCM-D) and optical (SPR) surface techniques.

Amphiphilic derivatives of HPC have been prepared through novel, mild, versatile olefin cross-metathesis chemistry [4]. QCM-D and SPR were used to study the interactions between HPC derivatives and two BS with different degrees of hydrophobicity, sodium taurocholate (NaTC) and sodium taurodeoxycholate (NaTDC), at different BS concentrations. QCM-D and SPR provided complementary information in terms of adsorbed mass and thickness of the HPC layer as the adsorption of BS progressed. Results showed that the novel amphiphilic HPC derivatives are more resistant to BS displacement at a high BS concentration than the commercial HPC for both NaTC and NaTDC. Both BS types showed similar adsorption trends onto the commercial HPC layer, but the more hydrophobic BS (NaTDC) showed a greater displacement of HPC from the surface than NaTC. These findings will provide valuable information on how commercial cellulose derivatives can be tailored and exploited into both novel food and pharmaceutical matrices to control blood cholesterol levels.

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