



Book of Abstracts

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- 6) Soft responsive materials from block copolymer hydrogels, **R. B. Grubbs**
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- 6) Design of stimulus-sensitive polymeric micelles for tumor targeting and drug sensitization, **L. Zhu**
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- 9) Understanding the stability of PLCL implants used for treating rotator-cuff injuries, **A. Kumar**

- 10) Synthetic linear antioxidant polymers for corrosion protection of steel substrates, **H. Hlushko**
- 11) Quantitative and qualitative analysis of shape memory polyurethane foam biodegradation, **L. Graul**
- 12) A comb-type thermoresponsive 'self-cleaning' membrane to house an optical glucose sensing assay, **P. Dong**
- 13) Engineering an exosome-based co-delivery platform via lipid-hybridization and polymer layer-by-layer deposition for cancer therapy, **Y-Yu Jhan**
- 14) Evaluating the thromboresistance of silicones modified with PEO-silane amphiphiles, **B. K. D. Ngo**
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- 19) Degradable polyphosphoester-based nanoparticles carrying silver-based antimicrobials for the treatment of bacterial infections, **F. Zhang**
- 20) Poly(D-glucose carbonate)-based crosslinked networks designed for renewable and degradable coatings in challenging situations, **Y. Shen**

Synthesis and Sustainability

Invited

- 1) Designing for degradation: Utilizing topology, architecture and stoichiometry to control polymer degradation in vivo, **M. L. Becker**
- 2) Stereochemically-directed elastomer properties, **A. P. Dove**
- 3) Investigating new sources for and applications of cellulose nanocrystals, **S. Rowan**
- 4) Polyisobutylene and BASF's commitment to sustainability, **J.S. Zigmund**
- 5) Accelerated hydrolytic degradation of ester-containing biobased epoxy resins, **M. Robertson**
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- 8) Metal-organic light initiated radical (MILRad) polymerization, **E. Harth**
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- 2) Removal of heavy metals from water using pressure-stable, imprinted polymers, **A. Mueller**
- 3) Intertwining polymers with control, **Z. A. Page**
- 4) The best of both worlds: High-throughput multidetector UPLC, **C. Schindler**
- 5) Rational design and synthesis of electrochemically stable and processable PANI-like polymers, **C. Scott**

- 6) Fluorogenic controlled polymerization amplification strategies for detection of biological analytes, **C. B. Cooley**
- 7) Synthesis of well-defined polymeric adhesives: Chemical functionalities and crosslinking effect on properties, **H. Chung**
- 8) Modulating particle-polymer interaction via particle morphology, **D. Qiu**
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- 17) Incorporation of functionalized rhenium(i) bipyridine catalysts into polycarbonates via chain transfer chemistry, **G. A. Bhat**
- 18) An engineering approach to find the possible path to polypeptides in the prebiotic world, **S.-S. Yu**
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- 20) Organic radical polymer-electrolyte interactions from Flory-Huggins theory, **A. D. Easley**
- 21) Emergent properties of sequence-defined conjugated oligomers, **H. Yu**
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- 23) Naturally-sourced, degradable polycarbonates for the reduction of plastic waste accumulation in the natural environment, **A. A. Jahnke**
- 24) Controlling phase change sologel mechanics via polymer-crosslinker bond dynamics, **P. Karimineghlani**
- 25) Water-based nanocoatings for flame retardant wood, **T. J. Kolibaba**
- 26) An efficient and mild synthesis for polyurethanes using a glucose-derived biorenewable co-monomer, **C. H. Komatsu**
- 27) Extreme heat shielding by clay/chitosan nanobrick wall on flexible foam, **S. Lazar**
- 28) Enhanced ordering in lamellar PS-b-PMMA polymer using ionic Liquid, **A. Masud**
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- 33) Rapid ordering of block copolymer films by utilizing the effect of as cast nucleation, **M. Singh**
- 34) Catalyst-controlled stereoselective polymerization to form polar, vinyl ether-based thermoplastics, **A. Teator**

- 35) Sustainable hydrogel-base materials for capture and storage of excessive liquid water through ring-opening copolymerization with bio-based materials and carbon dioxide, **D. K. Tran**
- 36) An automated platform for controlled polymer synthesis, **D. J. Walsh**
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- 38) Solvent induced switchable phase separation of polymer-grafted nanoparticle blends, **W. Wu**
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- 40) Self-assembly of block copolymers with ionic liquid crystals in thin films, **C. Yuan**
- 41) Functionalization of graphene oxide with multi-hydroxy-containing phosphoramidate: Preparation and flame-retardation on epoxy resin, **B. Zhao**
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- 44) APO-BMI and the two-tone billet: A material investigation into polymorphism, **A. P. Sanders**

Energy and Electronics

Invited

- 1) Synthesis and applications of semiconducting polymers. **T. M. Swager**
- 2) Pyrrole-based organic semiconducting materials for organic electronics applications, **M C. Stefan**
- 3) Materials for transient electronics, **J. A. Rogers**
- 4) Pickering emulsions stabilized by 2D particle surfactants and their applications, **E. Pentzer**
- 5) Ultra-thin conformal coating for spin-on doping applications, **P. Trefonas**
- 6) Dendrimeric Pi-conjugated polymer hybrids and electrochemically molecularly imprinted polymer (E-MIP)s sensors, **R. Advincula**
- 7) Chromophore-catalyst assemblies for solar fuels, **K. Schanze**
- 8) Three-dimensional morphological analysis of polymer blends through combined ToF-SIMS/AFM, **R. Verduzco**
- 9) Influence of distortions and defects in soft matter crystals for metamaterials and energy storage, **E. L. Thomas**

Contributed

- 1) The Crawford group: At the interface of sensors and soft materials, **K. E. Crawford**
- 2) Bridging the gaps with nitrogen, silicone and sulfur for efficient BJH solar cells, **C. Chang**
- 3) Heating, curing, and welding of 3D printed carbon nanotube-polymer systems by locally induced RF heating, **C. B. Sweeney (M. J. Green)**
- 4) Turning the tables: from polymer insulator to heat conductor, **Y. Xu**
- 5) Ambient temperature waterborne polymer/reduced graphene oxide nanocomposite films: Effect of reduced graphene oxide distribution on electrical conductivity, **Y. Fadil**

- 6) Nature-inspired structural supercapacitor electrodes based on dopamine functionalized graphene oxide, **P. Flouda**
- 7) A tale of redox-active organic radical polypeptides as electrode materials: From full organic batteries to electron transfer kinetics, **T. P. Nguyen**
- 8) Thermoelectric performance improvement of polymer nanocomposites by selective thermal degradation, **D. L. Stevens**
- 9) Topological design of a hole transporting molecular bottlebrush system for highly anisotropic alignment in solution-processed thin films, **N. Kang**
- 10) Tannic acid: A potential small molecule binder for silicon electrodes in lithium-ion batteries, **K. Sarang**
- 11) Extreme deformation and extraordinary energy absorption of MWCNT mats under ballistic impact, **E. L. Thomas**
- 12) Core-shell inverse amphiphilic molecular polymer bottlebrush additives to increase lubricity in lubricants, **M. Vazquez**

Program

Polymers for Advanced Technologies (PAT2019 <http://pat2019.tamhsc.edu>), Texas A&M University, College Station, Texas
 August 8-10, 2019, held @ **The George Hotel <https://www.thegeorgetexas.com>**
August 7, 2019 (Wednesday): Arrival and Registration 6-7 PM; August 8, 2019 (Thursday): Registration 08:00-08:30 am

Thursday August 8, 2019 (Day-1)				
Start	The Statesman (The George)			Finish
8:30	Opening Ceremony: Introduction (<i>Ravi Majeti, Karen Wooley</i>), PAT Award Presentations (<i>Avi Domb</i>), Awardee speeches			9:00
9:05	Keynote-1 Krzysztof Matyjaszewski (Carnegie Mellon) "Advanced polymers by ATRP" (<i>Session Chairs: Avi Domb and Stan Slomkowski</i>)			10:05
10:10	Keynote-2 Robert Grubbs (Caltech) "Synthesis of controlled polymeric structures" (<i>Session Chair: Karen Wooley</i>)			11:10
11:10	Break			11:40
	Session I (Life & Health) The Statesman (The George)	Session II (Synthesis & Sustainability) The Statesman (The George)	Session III (Energy and & Electronics) Cavalry Court (Stables II)	
	<i>Session Chairs: Corey Bishop and Stan Slomkowski</i>	<i>Session Chairs: Quentin Michaudel and Colleen Scott</i>	<i>Session Chairs: Christina Cooley and Zachariah Page</i>	
11:45	Samir Mitrangotri (Harvard University) "Polymer-based biohybrid drug delivery systems"	Matthew Becker (Duke University) "Designing for degradation: Utilizing topology, architecture and stoichiometry to control polymer degradation in vivo"	Timothy Swager (MIT) "Synthesis and applications of semiconducting polymers"	12:15
12:15	Lunch (The Statesman-The George) & Poster presentations (Cavalry Court)			1:55
	Session I (Life & Health) The Statesman	Session II (Synthesis & Sustainability) The Statesman	Session III (Energy and & Electronics) Cavalry Court	
2:00	Darrell Irvine (MIT) "Materials to enable next-generation vaccines and cancer immunotherapies"	Andrew Dove (Univ Birmingham, UK) "Stereochemically-directed elastomer properties"	Mihaela Stefan (UT Dallas) "Pyrrole-based organic semiconducting materials for organic electronics applications"	2:30
2:35	Eugenia Kharlampieva (UAB) "Theranostic microcapsules for imaging and ultrasound-triggered drug delivery"	Stuart Rowan (U Chicago) "Investigating new sources for and applications of cellulose nanocrystals"	John Rogers (Northwestern) "Materials for transient electronics"	3:05
3:10	Avi Domb (The Hebrew University of Jerusalem), Israel "Cyclopropenium-based Polymers"	Jennifer Summerhill Zigmund (BASF) "Polyisobutylene and BASF's commitment to sustainability"	Emily Pentzer (Texas A&M University) "Pickering emulsions stabilized by 2D particles and their applications"	3:40
3:40	Break			4:15
	Session I (Life & Health) The Statesman (The George)	Session II (Synthesis & Sustainability) The Statesman (The George)	Session III (Energy and & Electronics) Cavalry Court (Stables II)	
	<i>Session Chair: Kevin McHugh</i>	<i>Session Chair: Micah Green</i>	<i>Session Chair: Kaitlyn Crawford</i>	
4:20	Bradley Olsen (MIT) "Engineering protein-polyelectrolyte interactions for novel biosensing devices"	Megan Robertson (Univ Houston) "Accelerated hydrolytic degradation of ester-containing biobased epoxy resins"	Peter Trefonas (Dow) "Ultra-thin conformal coating for spin-on doping applications"	4:50

4:55	Barney Grubbs (Stony Brook Univ) “Soft responsive materials from block copolymer hydrogels”	Christopher Bowman (Univ Colorado Boulder) “Novel applications and developments utilizing photopolymerizations”	Rigoberto Advincula (Case Western) “Dendrimeric Pi-conjugated polymer hybrids and electrochemically molecularly imprinted polymer (E-MIP)s sensors”	5:25
6:30-10:00 Banquet Dinner (The Statesman-The George)				
8:00	Keynote-3 (<i>Dinner Speech</i>) Joseph DeSimone (Univ North Carolina/Carbon3d) “Digital light synthesis to drive additive manufacturing: Convergence of hardware, software, and molecular science” (Session Chair: Mark A Barteau)			9:00
Friday August 9, 2019 (Day-2)				
Start	The Statesman (The George)			Finish
9:00	Keynote-4 Grant Willson (UT Austin) “Materials for high resolution imaging applications” (Session Chair: Jodie Lutkenhaus)			10:00
10:05	Keynote-5 Zhenan Bao , (Stanford University) “Designer polymers for skin-like electronics” (Session Chair: Melissa Grunlan)			11:05
	Session I (Life & Health) The Statesman (The George)	Session II (Synthesis & Sustainability) The Statesman (The George)	Session III (Energy and & Electronics) Cavalry Court (Stables II)	
	Session Chair: Lin Zhu	Session Chair: T. H. Ware	Session Chair: Anja Mueller	
11:15	David Oupicky (Univ Nebraska) “Development of pharmacologically active polymers”	Rachel O'Reilly (Univ. Birmingham, UK) “Precision polymer nanoparticles”	Kirk Schanze (UT San Antonio) “Chromophore-catalyst assemblies for solar fuels”	11:45
11:45	Lunch (The Statesman-The George) & Poster presentations (Cavalry Court)		PAT Editorial Board Meeting ~12:00-1:00 PM (Cavalry Court)	1:40
01:45	Selected Contributed Abstracts for oral Presentations 10 min each			5:45
Saturday August 10, 2019 (Day-3)				
Start	The Statesman (The George)			Finish
9:30	Keynote-6 Brigitte Voit (Institute of Macromolecular Chemistry, Germany) “Glycodendrimers as therapeutics, bioconjugates and polyplexes” (Session Chair: Svetlana Sukhishvili)			10:30
	Session I (Life & Health) The Statesman (The George)	Session II (Synthesis & Sustainability) The Statesman (The George)	Session III (Energy and & Electronics) Cavalry Court (The George)	
	Session Chair: Veronika Kozlovskaya	Session Chair: Hoyong Chung	Session Chair: A. C. Weems	
10:35	Theresa Reineke (Univ Minnesota) “Enabling Functional Biomaterials Through Controlled Polymer Synthesis”	Eva Harth (UH) “Metal-organic light initiated radical (MILRad) polymerization”	Rafael Verduzco (Rice Univ) “Three-dimensional morphological analysis of polymer blends through combined ToF-SIMS/AFM”	11:05
11:10	Eric R. Molina (Rice Univ) “Modeling Divergent Clinical Phenotypes in Osteosarcoma with Mechanically Tunable 3D Polymeric Microenvironments”	Hawker Craig (UCSB) “Studies at the interface of organic synthesis and polymer chemistry: Role of macromolecular isomers”	Edwin L. (Ned) Thomas (Rice Univ) “Influence of distortions and defects in soft matter crystals for metamaterials and energy storage”	11:40
Lunch (The Statesman-The George) and Departure				

Contributed Abstracts, **Oral presentations (10 min each)**

August 9, 2019					
	Start	<i>Session Chairs: Lin Zhu; Dongin Kim; Corey Bishop; Kevin McHugh</i>	<i>Session Chairs: Lei Fang; Macro Giles; Kai Qi and Adriana Pavia Sanders</i>	<i>Session Chairs: Yanfei Xu; Emily Pentzer; Yunxiang Gao</i>	Finish
		Session-1 (The Statesman-The George)	Session-2 (The Statesman-The George)	Session-3 (Cavalry Court-Stables II)	
1	1:45	4D Printable biocompatible photopolymers for adipose tissue engineering, A. C. Weems	Polystyrene/polyglycidol homo and copolymers and their self-assembly into functional nano- and microparticles, S. Slomkowski	The Crawford group: At the interface of sensors and soft materials, K. E. Crawford	1:55
2	2:00	A UV-curable, theranostic, core-shell polybubble vaccine platform formed via phase separation, S. A. Kumar	Removal of heavy metals from water using pressure-stable, imprinted polymers, A. Mueller	Bridging the gaps with nitrogen, silicone and sulfur for efficient BJH solar cells, C. Chang	2:10
3	2:15	Polymersome drug nanocarriers from temperature-sensitive block copolymers, V. Kozlovskaya	Intertwining polymers with control, Z. A. Page	Heating, curing, and welding of 3D printed carbon nanotube-polymer systems by locally induced RF heating, M. J. Green	2:25
4	2:30	Polymerized high internal phase emulsions for porous shape memory polymer scaffolds, G. K. Fletcher	The best of both worlds: High-throughput multidetector UPLC, C. Schindler	Turning the tables: from polymer insulator to heat conductor, Y. Xu	2:40
	2:40	Tea Break			3:00
5	3:05	Preventing surface colonization with layer-by-layer coatings of fluorinated polyphosphazenes and antibiotics, V. Albright	Rational design and synthesis of electrochemically stable and processable PANI- like polymers, C. Scott	Ambient temperature waterborne polymer/reduced graphene oxide nanocomposite films: Effect of reduced graphene oxide distribution on electrical conductivity, Y. Fadil	3:15
6	3:20	Design of stimulus-sensitive polymeric micelles for tumor targeting and drug sensitization, L. Zhu	Fluorogenic controlled polymerization amplification strategies for detection of biological analytes, C. B. Cooley	Nature-inspired structural supercapacitor electrodes based on dopamine functionalized graphene oxide, P. Flouda	3:30
7	3:35	Thermoresponsive polycaprolactones for drug delivery applications, E.L. Calubaquib	Synthesis of well-defined polymeric adhesives: Chemical functionalities and crosslinking effect on properties, H. Chung	A tale of redox-active organic radical polypeptides as electrode materials: From full organic batteries to electron transfer kinetics, T. P. Nguyen	3:45
8	3:50	"Self-Fitting" CMF Bone Scaffolds with Highly Tunable Degradation Profiles, M. R. Pfau	Modulating particle-polymer interaction via particle morphology, D. Qiu	Thermoelectric performance improvement of polymer nanocomposites by selective thermal degradation, D. L. Stevens	4:00
9	4:05	Understanding the stability of PLCL implants used for treating rotator-cuff injuries, A. Kumar	Modern organic reactions as tools to access unique polymer architectures, Q. Michaudel	Topological design of a hole transporting molecular bottlebrush system for highly anisotropic alignment in solution-processed thin films, N. Kang	4:15

10	4:20	Synthetic linear antioxidant polymers for corrosion protection of steel substrates, H. Hlushko	Intelligence, both living and non-living, in shape-morphing polymers, T. H. Ware	Tannic acid: A potential small molecule binder for silicon electrodes in lithium-ion batteries, K. Sarang	4:30
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12	4:50	A comb-type thermoresponsive 'self-cleaning' membrane to house an optical glucose sensing assay, P. Dong	Polymeric clickase accelerate the copper click reaction of small molecules, proteins, and cells, J. Chen	Incorporation of functionalized rhenium(i) bipyridine catalysts into polycarbonates via chain transfer chemistry, G. A. Bhat	5:00
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Posters *Displayed on 8 and will be viewed on August 8 and 9 during lunch break (Cavalry Court). Please remove the posters on August 9 after lunch or before the end of the day without fail.*

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Keynote Speakers

Advanced polymers by ATRP

Krzysztof Matyjaszewski

Center for Macromolecular Engineering
Carnegie Mellon University, Pittsburgh, PA, 15213, USA

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Precise macromolecular engineering has been enabled by many controlled radical polymerization procedures. Copper-based ATRP (atom transfer radical polymerization) catalytic systems with polydentate nitrogen ligands are among most efficient controlled/living radical polymerization systems. By applying new initiating/catalytic systems, Cu level in ATRP was reduced to a few ppm. The activators are regenerated by light, reducing agents, electrical current or mechanical forces. By employing these systems, ATRP of acrylates, methacrylates, styrenes, acrylamides, acrylonitrile and other vinyl monomers was employed for macromolecular engineering of polymers with precisely controlled molecular weights, tuned dispersities, designed shape, composition and functionality. Examples of polymers for advances technologies, including block, graft, star, hyperbranched, gradient and periodic copolymers, molecular brushes and various hybrid materials and bioconjugates prepared with high precision will be presented. Special emphasis will be on nanostructured multifunctional materials for application related to biomedicine, environment, energy and catalysis.

Synthesis of controlled polymeric structures

Robert H. Grubbs

Division of Chemistry and Chemical Engineering
California Institute of Technology

Ruthenium based initiators of ring opening metathesis polymerization (ROMP) allow the controlled polymerization of a cyclic olefins. Strained olefins can be polymerized in a controlled fashion to provide high molecular weight polymers of controlled dispersity. Over the past several years, these initiators have been used to prepare brush-block polymers of extremely high molecular weight. Block systems spontaneously phase separate into well-ordered structures. At sufficient molecular weights, the systems are photonic crystals that reflect into the IR. The systems are robust enough to make multiblock systems. These systems allow the control of the structure to yield materials with precisely designed structures for numerous applications and to study structure function relationships. Recent advances have been made in the study of the role of brush density of structure and in the synthesis of cyclic polyolefins.

**Digital light synthesis to drive additive manufacturing:
Convergence of hardware, software, and molecular science**

Joseph M. DeSimone

Carbon, Inc.
Redwood City, California
and
Department of Chemistry
University of North Carolina at Chapel Hill
and
Department of Chemical and Biomolecular Engineering
North Carolina State University

In many ways, manufacturing processes define what's possible in society. Opportunities to make things that can improve the health and well being of society are central to our interests to develop scalable methods that can make complex structures more economically than in the past. This lecture will describe a new advance in additive manufacturing, referred to as Digital Light Synthesis (DLS), which is rapid, uses materials that have the requisite properties to yield final parts, and is economically competitive. Our approach promises to advance industry beyond basic prototyping, which is what 3D printing has primarily been limited to, to truly enable 3D manufacturing. DLS harnesses light and oxygen to continuously grow objects from a pool of resin instead of printing them layer-by-layer. DLS capitalizes on the fundamental principle of oxygen inhibited photopolymerization to generate a continual liquid-interface of uncured resin between the growing part and the exposure window. The DLS technology raises the state-of-the-art in additive manufacturing in three ways:

- GAME-CHANGING SPEED: 25-100 times faster than conventional 3D printing
- COMMERCIAL QUALITY: produces objects with consistent mechanical properties
- MATERIAL CHOICE: enables a broad range of polymeric materials

The combination of performance and speed has enabled many important use cases to emerge including large scale manufacture of running shoes by Adidas (FutureCraft 4D), mass-customized dental products, and numerous parts in the automotive, consumer electronics, aerospace and medical fields.

Materials for high resolution imaging applications

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During the past several decades, there has been a continuing and nearly frantic effort on the part of the microelectronics manufacturers to make ever smaller devices. The rate of device scaling is described by the famous “Moore’s Law”. Companies that cannot keep pace with Moore’s Law quickly disappear from the market place and sadly, many with famous names like Siemens, Motorola, Sony and TI have fallen by the wayside. For many years, we have participated in efforts to continue improving the resolution of photolithography, the key process that has enabled the production of all of today’s microelectronic devices. Unfortunately, this process has now reached physical limits. Efforts to push that technology to provide still higher resolution by the historical paths of exposure wavelength reduction, increasing the numerical aperture of the projection lens and reduction in the Raleigh constant have been abandoned. Is this the end? Can device scaling continue?? No more Moore??

We are striving to develop new materials and new processes that offer an opportunity to continue this scaling. We will describe one of our approaches to the design of new material solutions that generate very small structures. We are attempting to exploit block co-polymer chemistry to generate very small patterns of the sort that are useful for lithography. This so-called, “Directed Self Assembly” approach to patterning has now afforded well-formed 50-angstrom wide lines and spaces with very low defect density. These tiny, defect free structures offer hope for still more Moore!

Designer polymers for skin-like electronics**Zhenan Bao**

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Skin is the body's largest organ and is responsible for the transduction of a vast amount of information. This conformable, stretchable, self-healable and biodegradable material simultaneously collects signals from external stimuli that translate into information such as pressure, pain, and temperature. The development of electronic materials, inspired by the complexity of this organ is a tremendous, unrealized materials challenge. However, the advent of organic-based electronic materials may offer a potential solution to this longstanding problem. In this talk, I will describe the design of organic electronic materials to mimic skin functions. These new materials enabled new functions in medical devices, robotics and new manufacturing methods through the use of self-healing materials.

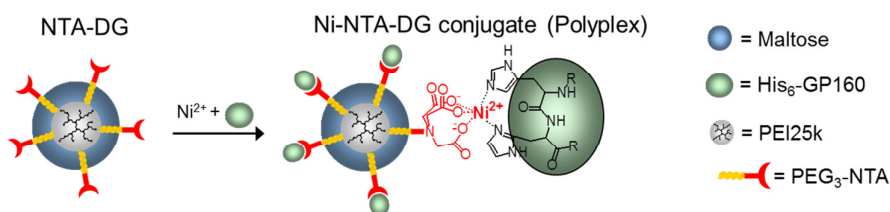
Glycodendrimers in bioconjugates, polyplexes and as therapeutics

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The use of linear and dendritic glycopolymers is steadily growing up in the field of life sciences and nanotechnology. Especially, the multifunctional features of the sugar moieties such as non-covalent interactions, molecular recognition, tailoring of biological processes, enhancing biocompatibility and many others are of importance for the development of polymeric therapeutics and in diagnostics. Our main research interest is the fundamental understanding of complexation and stabilization properties of dendritic glycopolymers towards drugs and bio(macro)molecules, the cellular uptake of dendritic glycopolymers, the formation of drug@glycopolymer associates, and their bio-interactions with different biological materials and systems for finally being able to tailoring the biohybrid materials for in-vitro and in-vivo experiments in the field of (bio-)medical applications. Here, we present recent examples which concern the potential use of dendritic glycopolymers as polymeric therapeutics, e.g. as non-toxic antiamyloidogenic agents in Alzheimer's disease, treatment of chronic lymphocytic leukemia, ligand-mediated endocytosis, uptake of peptides in immature/mature DC by Ni-NTA-His-tagged conjugation, conjugation in polyplexes with si-RNA for cancer- and immunotherapies, and for diagnostics (e.g. prion strains typing).



Schematic representation of glycodendrimer-peptides conjugates for immunotherapy

Life and Health

Polymer-based biohybrid drug delivery systems

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Polymer-based drug delivery systems are widely explored to improve the biological outcome of encapsulated drugs. However, poor vascular circulation, limited targeting and the inability to negotiate many biological barriers are key hurdles in their clinical translation. Biology has provided many examples of successful “carriers” in the form of circulatory cells, which routinely overcome the hurdles faced by synthetic nanoparticle systems. Our laboratory has developed polymeric systems that leverage the abilities of circulatory cells for better therapeutic outcome. We have explored “cellular hitchhiking” which involves combining polymeric particles with circulatory cells to drastically alter their in vivo fate. I will provide an overview of the principles and capabilities of these polymeric drug delivery systems.

Materials to enable next-generation vaccines and cancer immunotherapies

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Our laboratory focuses on the use of materials chemistry to control the timing, dose, and location of delivery of immunostimulatory cues to enhance immunity induced by vaccines and cancer immunotherapies. Two examples of our recent work will be discussed:

In infectious disease vaccines, the kinetics of antigen availability following immunization impact follicular helper T cell priming, germinal center responses, and ultimate antibody production, but clinically-relevant methods to control the duration of antigen delivery to lymph nodes in subunit vaccines are lacking. We conjugated antigens derived from the gp140 HIV envelope trimer with a phosphoserine (pSer) peptide that binds tightly to the most common clinical adjuvant, aluminum hydroxide (Alhydrogel, or alum). Site specific modification of an engineered outer domain (eOD) gp120 or stabilized SOSIP trimer immunogen with varying numbers of pSer groups allowed self-assembly of these antigens on the surfaces of alum particles to be tuned and alum-bound antigens were presented from alum particle surfaces with a defined orientation. Tight binding to alum converted alum itself into a nanoparticle delivery vehicle, as alum nanocrystals released from the injection site trafficked to lymph nodes and were taken up by antigen-specific B cells. Ultimately, a 30-fold increase in germinal center responses and antibody titer relative to the unmodified protein was observed four weeks after primary immunization with both pSer-eOD and pSer-SOSIP conjugates, and long-lived plasma cells in bone marrow were doubled by immunization with pSer-modified immunogens. Overall, pSer-antigen conjugates elicited significant increases in antibody titers and altered specificity of the humoral response through controlling the display of antigen on the surface of alum.

In a second area of research, we recently developed a strategy to target peptide vaccines to lymph nodes, by linking peptide antigens to albumin-binding phospholipid-polymers. Small peptides are normally rapidly dispersed in the bloodstream following parenteral injection, but binding of amphiphile-peptides to endogenous albumin, which constitutively traffics from blood to lymph, retargeted these molecules to lymph nodes. However, these lipid-polymer conjugates bind to albumin with a relatively low affinity, and these molecules can also partition into cell membranes. We hypothesized that by attaching a small molecule, peptide, or protein ligand for a chimeric antigen receptor (CAR) to the same polymer-lipid tail (forming an “amph-vax” molecule), CAR ligands could be delivered efficiently to lymph nodes by albumin and subsequently partition into membranes of resident antigen presenting cells (APCs), thereby co-displaying a CAR T cell ligand from the cell surface together with native cytokine/receptor costimulation. In syngeneic mouse models of adoptive cell therapy, we demonstrated that this approach effectively concentrates CAR T ligands on the surfaces of dendritic cells in lymph nodes, leading to profound expansion of amph-vax-boosted CAR T cells *in vivo*. Amph-vax boosting safely increased the polyfunctionality of CAR T cells in parallel with T cell expansion, and dramatically enhanced the efficacy of CAR T cell therapy in solid tumors. This concept provides a strategy to regulate the expansion and function of CAR T cells directly *in vivo* to enhance adoptive cell therapy of cancer.

Theranostic microcapsules for imaging and ultrasound-triggered drug delivery**Eugenia Kharlampieva**

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The ability to track drug carriers in their administered environment in real time and to release the drug in a controlled, minimally invasive manner are hallmarks of an advanced drug delivery system. This talk focuses on ultrasound-sensitive multilayer capsules as efficient contrast-enhanced imaging agents utilizing ultrasound, magnetic resonance imaging (MRI), and positron emission tomography (PET) imaging modalities. These capsules are composed of hydrogen-bonded polymers and capable of delivering biological and synthetic molecules upon low-power ($\sim 100 \text{ mW/cm}^2$) diagnostic or high-power ($>10 \text{ W/cm}^2$) therapeutic ultrasound irradiation. We will also discuss the capsule efficacy in modulating the redox state that can influence immune responses for prolong circulation in the blood. The ability of this material to conjugate metalloporphyrin to further enhance immunomodulatory potential by dissipation of free radicals will be also presented. Owing to the active contrast, long circulation, customizable size, shape, composition, and precise delivery of high payload concentrations, these materials present a powerful and safe platform for imaging-guided precision drug delivery.

Cyclopropenium-based Polymers

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Cationic polymers offer a wide range of potential biomedical applications, and so their continued development is of paramount importance. We describe here the synthesis and characterization of a series of novel polymers bearing cationic cyclopropenium either along a polyester backbone, both linear and crosslinked, or as a tri-functional crosslinker of secondary amine-containing polymers. Polymers containing cyclopropenium along the polymer backbone are synthesized stepwise via the reaction between diol-functionalized tris(amino)-cyclopropenium (TAC) monomers and diacyl chlorides. Incorporation of cyclopropenium as a chemical crosslinker of secondary amine-containing polymers was performed in a rapid one-step crosslinking reaction that requires no subsequent purification. When dispersed in aqueous media, polymers form spherical nanoparticles with highly positive charge that is maintained even in alkaline conditions. Biodegradable cyclopropenium polymers undergo hydrolytic degradation and swell significantly, displaying an important framework for the drug-delivery capabilities of a hydrolytically degradable cationic polyester. One polymer displayed potent antimicrobial activity against *Staphylococcus epidermidis*, and one displayed improved transfection capabilities compared to poly(ethylene imine). These synthetic strategies will enable the incorporation of cyclopropenium into a wide variety of macromolecules.

Engineering protein-polyelectrolyte interactions for novel biosensing devices

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Coacervation of proteins and polyelectrolytes enables proteins to be encapsulated and stabilized, promising advantages for a wide range of applications in biosensing, biocatalysis, and the delivery of active proteins. When block copolymers containing charged and uncharged blocks are used, the charged proteins interact preferentially with the charged polymer domains, providing a potential method for protein nanopatterning and control over nanostructure in both solution and solid-state materials. Here, dynamic light scattering and turbidity are used to show how charge distribution on the protein affects the way that the protein interacts with a polyelectrolyte polymer, providing an important handle for engineering interactions. When a protein is nearly charge neutral but has the charge distributed in a Janus pattern, it is capable of strong interaction and coacervation. However, when the charge is uniformly spread across the protein surface, coacervation is not observed. This allows estimation of a critical charge patch size for protein coacervation. Control over protein charge is then used to incorporate proteins into solid-state block copolymers as immobilized enzymes for biosensing applications. Self-assembly in the solid films is studied as a function of the casting conditions and charge ratios between protein and block copolymer to fundamentally understand the film formation process, and films are then applied for the selective detection of heavy metals within ionic mixtures. The results show the ability of these immobilized films to stabilize enzymes and provide for sensitive and selective detection even in complex mixtures and environmental samples.

Soft responsive materials from block copolymer hydrogels**Robert Bernard Grubbs**

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Soft materials that can respond to different stimuli are of interest in a range of applications. We have investigated the preparation of block copolymers that are capable of forming hydrogels that respond to temperature, magnetic fields, or pH. Aspects of the synthesis and characterization of these polymers, in particular responsive block copolymers that form micelle-based gels and polyacetal copolymers that form acid-sensitive gels, and their gelation will be discussed.

Development of pharmacologically active polymers**David Oupicky**

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Chemokine networks control cell movement to specific locations throughout the body as part of normal homeostasis and during pathological processes such as cancer, inflammation, and fibrogenesis. In tumors, a complex chemokine network controls cell trafficking into and out of the tumor microenvironment. The tumor chemokine network also participates in angiogenesis and generation of the fibroblast stroma. Importantly, chemokine networks are directly involved in the molecular control of metastasis and govern organ-specific homing of metastatic cells, which makes them promising targets for the development of antimetastatic therapies. The CXCR4 axis is also involved in mediating the infiltration and migration of inflammatory cells during pulmonary fibrosis. I will present our progress in the development of polymer drugs that target chemokine receptor CXCR4 as part of combination therapies in the treatment of metastatic pancreatic cancer and pulmonary fibrosis.

Enabling functional biomaterials through controlled polymer synthesis

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Multifunctional macromolecules have a tremendous impact on a multitude of applications. For example, the development of polymer excipients can improve the solubility and bioavailability of intractable drugs, nucleic acid delivery vehicles have promise to promote selective genome editing, and materials from sustainable monomers may lower the environmental impact of plastics. While the materials function is diverse across these fields, the polymer chemistry is similar and should be readily tunable for each specific application while remaining biologically and environmentally benign. Bio-based feedstocks such as carbohydrates and their derivatives offer great promise for tailoring materials development for a multitude of uses due to their rich functionality (high heteroatom content and stereochemistry), renewable production on an impressive scale, low toxicity, and the potential for triggered degradation. In addition, renewable feedstocks offer high glass transition temperatures, the ability to modulate solubility through chemical modification, and the utility to target delivery to selective tissue types. Indeed, the chemical, physical, mechanical, and morphological properties of polymers containing sustainable and biologically-friendly monomers can be tuned based on chemistry, sequence, and composition to yield diverse function and properties. Herein, the design and development of tailored polymers using a variety of synthetic pathways will be presented. Their application in the development of sustainable polymers, improvement of oral pharmaceutical bioavailability, and design of nucleic acid delivery vehicles for genome editing applications will be presented.

Modeling divergent clinical phenotypes in osteosarcoma with mechanically tunable 3D polymeric microenvironments

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Repeated failures of clinical trials to confirm potential therapeutics highlight the need for more accurate preclinical testing which currently relies heavily on monolayer culture and xenograft systems. While a host of osteosarcoma *ex vivo* models exists, most are not engineered to control the mechanical properties of the tumor microenvironment and thus may not accurately reflect the effects of mechanotransduction on tumor biology. To elucidate what sarcoma cells may “sense” as their mechanical environment, our work distinguishes the role of bulk mechanical properties from surface properties in engineered bone-like polymeric substrates. Utilizing coaxial electrospinning of poly(ϵ -caprolactone) and gelatin, we have built a highly porous, mechanically tunable model system that highlights key elements of the mechanical microenvironment in osteosarcoma. We determine the effects of coaxial polymeric fiber stiffness and culture architecture on therapeutic response and osteosarcoma cell phenotype with respect to the mechanosensitive Hippo and IGF-1/mTOR pathways. We then confirm that our mechanically tunable polymeric models generate clinically relevant phenotypic shifts in osteosarcoma cells by correlating phenotypes observed in our models with tumor biopsies from 37 osteosarcoma patients and determining the relationship between generated phenotypes and known patient outcomes. Thus, our models highlight the need for incorporation of complex biophysical cues in preclinical cancer studies and provide a versatile, mechanically tunable platform for the study of the osteosarcoma microenvironment.

4D Printable biocompatible photopolymers for adipose tissue engineering

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4D printable biomaterials offer tissue engineering the combination of accessing otherwise unobtainable geometries and surface features compared to traditional manufacturing as well as minimally invasive therapeutics. Taking advantage of this concept, we have developed a series of 4D polycarbonate resin inks (PCResinks) materials which can be 3D printed but additionally possess the ability to change their shape in response to an external stimulus. We demonstrate the versatility of the PCResink platform through characterization of tunable thermomechanical, degradation, and shape memory behaviors. More importantly for adipose tissue engineering, the PCResinks platform is capable of large void filling behaviors without exerting substantial expansion forces which would distort soft tissues. Cytocompatibility was demonstrated in 2D and 3D by in vitro cell studies; printed 3D scaffolds were used to demonstrate that morphology, including surface topology and pore size in porous materials, did not impact cellular proliferation. Building upon these results, in vivo subcutaneous rodent studies examined biocompatibility over 4 months. The presented PCResink system is used to demonstrate that minimally invasive tissue scaffolds possessing tunable thermomechanical properties and degradation behaviors are now possible to rapidly and reproducibly manufacture. In vivo studies confirm that the translational potential of this technology, indicating the promise of these functional 4D printable materials in medical applications.

A UV-curable, theranostic, core-shell polybubble vaccine platform formed via phase separation

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Around 1.5 million children die worldwide every year from vaccine preventable diseases. Access to life-saving vaccines is often limited due to inefficient transportation and storage facilities. There is thus a need for novel vaccine delivery platform that can potentially reduce the need for constant cold chain transport. Single-injection vaccines can potentially deliver multiple doses of vaccine while preserving its functionality with reduced need for constant refrigeration. We have developed a single-injection vaccine (“polybubble”) that can cater a novel delayed burst release of the cargo. We successfully formed polyester-based polybubbles with centered cargo and were able to achieve delayed burst release. For example, poly(lactic-co-glycolic acid) diacrylate (PLGADA) polybubbles incubated at 37 °C resulted in burst cargo release on day 19. To further enable on-demand control of release extracorporeally and to track the polybubbles in an *in vivo* context, theranostic gold nanorods (AuNR)s are encapsulated within the shell of the polybubble. We were able to show that cargo release could be expedited with intermittent near infrared laser (NIR) activation of the polybubbles. Delayed burst release of the cargo with laser activation of PLGADA polybubbles occurred on day 12 compared to release on day 19 without laser activation. We were also able to show that the polybubbles can be NIR activated multiple times with a constant temperature change of 10 ± 3.0 °C before and after laser activation while preserving the shape of the AuNRs. We also conducted *in vivo* studies where polybubbles were injected into a melanoma tumor in balb-c mice and were laser activated for 3 minutes. The temperature change in the mice with polybubbles was significantly higher when compared to that of control mice. Currently, there are on-going release studies with cargo-encapsulated nanoparticles in the middle to achieve delayed sustained release.

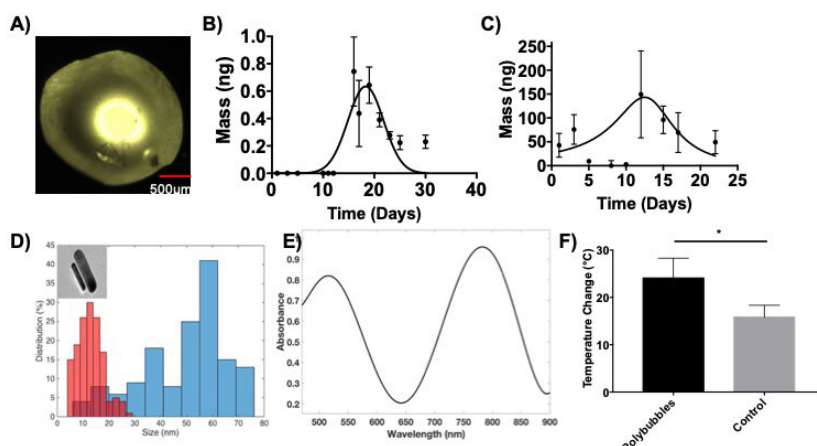


Figure 1: **A)** Centered cargo in the PLGADA polybubble, **B)** delayed burst release without laser activation, **C)** delayed burst release with laser activation, **D)** size distribution and **E)** absorbance spectra of AuNRs, **F)** temperature change in mice injected with and without polybubbles

Polymersome drug nanocarriers from temperature-sensitive block copolymers

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Naturally occurring self-assembled biological carriers (e.g., cell membranes, exosomes) that provide a nanometer-thin hydrophobic barrier to protect and transport cargo have inspired the development of new nanosized polymeric vesicles (polymersomes) for advancing the field of precision therapy. Polymersomes have demonstrated increased mechanical stability, efficient drug entrapment, and controllable stimuli-triggered delivery of cargo. Herein, we present synthesis and assembly of polymersomes from thermally responsive poly(N-vinylcaprolactam)-*block*-poly(N-vinylpyrrolidone), poly(N-vinylpyrrolidone)-*block*-poly(3-methyl-N-vinylcaprolactam), and poly(N-vinylcaprolactam)-*block*-poly(dimethylsiloxane)-*block*-poly(N-vinylcaprolactam) block copolymers and explore their biomedical potential. The poly(N-vinylcaprolactam)_n-*block*-poly(N-vinylpyrrolidone)_m polymersomes are synthesized by stabilizing the vesicular morphology of the diblock copolymers via hydrogen bonding with an antioxidant, tannic acid (TA), at 48 °C. The size of the TA-locked (PVCL₁₇₉-PVPON_m) polymersomes is controlled by the PVPON chain length and TA:PVPON molar unit ratio. These TA-locked polymersomes can encapsulate and store the anticancer drug doxorubicin (DOX) and higher molecular weight rigid molecules (e.g., dextran). Encapsulated DOX can be released in the nuclei of tumor cells after 6-h incubation via biodegradation of the TA shell. For PVCL-PDMS-PVCL triblock copolymer polymersomes, increasing the temperature above the LCST of PVCL results in gradual vesicle shrinkage leading to sustained drug release. *In vivo* transthoracic electrocardiography of mice injected with the DOX-loaded PMVC-*block*-PVPON polymersomes and liposomes followed by necropsy analysis revealed that while free DOX was toxic to the mice at low and high doses after 14 days, and showed detrimental effects to the heart left ventricle, neither liposomal or polymersomal DOX showed direct evidence of cardiotoxicity at low DOX dose. However, both analyses revealed the detrimental effects of liposomal DOX at a higher DOX dose unlike that for DOX-(PMVC-*block*-PVPON) polymersomes. Our results provide the evidence for superior stability of synthetic polymersomes *in vivo* and show a great promise for development of the next generation of advanced therapeutics carriers with minimal side effects.

Polymerized high internal phase emulsions for porous shape memory polymer scaffolds

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Polymerized high internal phase emulsions (polyHIPEs) are polymeric emulsions comprised of at least 74% internal phase. These low-density scaffolds have been investigated for a variety of biomedical applications, including tissue engineering and drug delivery. Our lab has demonstrated the potential utility of porous shape memory polymer (SMP) materials as embolic devices because they can be crimped to low diameters to enable delivery via catheter, have high volume-filling properties, and promote blood clotting. Fabrication of a porous scaffold from a thermoplastic polyurethane (TPU) SMP material capable of post-process crosslinking developed by our lab will further expand this material's utility in biomedical applications. The primary goals in translating the emulsion-templated porous polymer approach to the TPU material system are to achieve scaffolds with smaller pore sizes and improved pore uniformity relative to the traditional thermoset SMP foams.

PolyHIPEs offer many advantages to the current gas-blown thermoset foams used in embolic devices. The current lower limit for the thermoset foam pore size is 200 microns, but polyHIPEs enable pore sizes in the range of 1-100 microns. PolyHIPEs will be synthesized with calcium chloride in the aqueous internal phase to suppress Ostwald ripening and to attain less coalescence in the emulsion and therefore, more uniform pore sizes. The pilot polyHIPEs synthesized show promise due to high gel fractions and dry T_g in the desired range, but further optimization is needed to reach appropriate density and morphology.

Preventing surface colonization with layer-by-layer coatings of fluorinated polyphosphazenes and antibiotics

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Preventing bacterial colonization of biomedical surfaces, ranging from skin grafts to hip implants, is highly desirable. Such a goal can be achieved by coating materials with biocompatible, polymeric layers that release antibiotics in response to a trigger that occurs at the onset of infection, such as locally induced acidification. Here, we explore pH-responsive coatings constructed with ionic fluorinated polyphosphazenes (PPzs). PPzs are promising building blocks for biomaterials due their known biocompatibility and unique structure of the repeat unit, which enables control over charge density, hydrophobicity, and biodegradation rate. Fluorinated PPzs enabled unique, not possible with common polyelectrolytes, direct layer-by-layer assembly with cationic antibiotics. The amount of antibiotics bound in the coatings could be tuned by the degree of fluorination of PPzs and/or film thickness. Importantly, coatings did not elute antibiotics at pH 7.4, but released antibiotics in response to presence of bacteria, with doses highly tunable *via* PPz fluorination degree and/or film thickness. The coatings were able to prevent the onset of bacterial growth in solution *via* antibiotic release and were also highly surface active. Importantly, by tuning the PPz fluorination degree, coatings with unprecedentedly low hemolytic activity and cytotoxicity could be developed.

Design of stimulus-sensitive polymeric micelles for tumor targeting and drug sensitization

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Low cancer specificity and multidrug resistance (MDR) are two major challenges of anticancer drugs. Matrix metalloproteinase 2 (MMP2), a major extracellular enzyme involving in cancer initiation, growth and metastasis, is upregulated in numerous cancers. In this study, MMP2 was used as a tumor microenvironmental stimulus for developing the MMP2-sensitive polymeric micelles for tumor targeting and drug sensitization. A series of MMP2-sensitive amphiphilic polymers (PEG-pp-PE) were synthesized and evaluated. Among them, the PEG2k-pp-PE was used as an example to construct the micellar nanoparticles. Both the chemotherapy and molecularly targeted therapy drugs were used as the model drugs. The cellular uptake, tissue penetration, and cytotoxicity of the drugs in the presence of the PEG2k-pp-PE polymers or loaded into the PEG2k-pp-PE micelles were evaluated in cancer cells and their 3D multicellular spheroids. The *in vivo* biodistribution, tumor targeting, and anticancer activity of the PEG2k-pp-PE micelles were evaluated in the 4T1 tumor-bearing mice.

In vitro, the PEG2k-pp-PE micelles enhanced the cellular uptake and tissue penetration of anticancer drugs and sensitized the drug treatments, compared to their nonsensitive counterpart, the PEG2k-PE micelles. The PEG2k-pp-PE's efflux inhibitory capability was comparable to those of the well-known P-glycoprotein inhibitors, verapamil and D- α -tocopherol PEG1k succinate (TPGS). *In vivo*, the PEG2k-pp-PE micelles could specifically and effectively deliver the loaded cargoes to the tumor site, as evidenced by the enhanced drug accumulation and prolonged drug retention in the tumor tissue, resulting in the improved anticancer activity. The results suggested that the PEG2k-pp-PE assembled micelles might have great potential to be a simple but multifunctional nanocarrier for tumor-targeted drug delivery and drug sensitization.

Thermoresponsive polycaprolactones for drug delivery applications

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Thermoresponsive polymers are very important in the biomedical field due to their wide range of applications including drug delivery, tissue engineering, and gene delivery. These polymers exhibit temperature-dependent and reversible volume phase transition allowing them to release the incorporated drug. Polymers having a lower critical solution temperature (LCST) become insoluble upon heating, while those having upper critical solution temperature (UCST) become soluble upon heating. The most studied thermoresponsive polymers, poly(N-isopropylacrylamide) exhibits an LCST at 32°C, which can be shifted to body temperature with the addition of surfactants and additives. However, its applications are limited due to its non-biodegradability. . Herein, we report the synthesis of thermoresponsive polycaprolactones (PCLs) having LCST close to physiological temperature with the added advantage of biocompatibility and biodegradability. Homopolymers of di-, tri-, and tetra-oligoethylene-substituted caprolactones - poly(γ -2-(2-methoxyethoxy)ethoxy- ϵ -caprolactone) [PMEECL], poly(γ -2(2-(2-methoxyethoxy)ethoxy)ethoxy- ϵ -caprolactone) [PMEEEECL], and poly(γ -2(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)ethoxy- ϵ -caprolactone) [PMEEEEEL] - of varying molecular weight were synthesized and characterized. Sharp transitions were observed with LCSTs ranging from 37 to 80 °C. Block copolymers of hydrophobic γ -benzyl polycaprolactone and hydrophilic PMEEEEEL with varying ratios of each block gave LCSTs between 40 and 50 °C. These block copolymers also exhibit critical micellar concentration in the range of 10^{-4} to 10^{-3} g/L.

“Self-fitting” CMF bone scaffolds with highly tunable degradation profiles

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We have proposed “self-fitting” scaffolds, based on poly(ϵ -caprolactone)-diacrylate (PCL-DA) shape memory polymers (SMPs), as a potential tissue engineering (TE) strategy to better treat craniomaxillofacial (CMF) bone defects. Autografting is limited by the difficulty in fitting rigid bone grafts into defects with complex geometries, resulting in graft resorption. The “self-fitting” SMP scaffolds become malleable with mere exposure to warm saline ($T \sim 55^\circ\text{C}$) and can be easily press-fitted into irregular-shaped CMF bone defects, thereby promoting osseointegration and improved healing. PCL-DA scaffolds were shown to have high shape fixity/recovery, robust (non-brittle) mechanical properties, and highly interconnected pores. However, PCL is known to degrade relatively slow *in vivo* ($\sim 1\text{-}2$ years), compared to bone neotissue formation ($\sim 3\text{-}12$ weeks). More recently, we incorporated thermoplastic poly(L-lactic acid) (PLLA) of a single molecular weight ($M_n \sim 15$ kDa) into the PCL-DA network to produce semi-interpenetrating networks (semi-IPNs). Semi-IPNs exhibited accelerated degradation with increasing PLLA content. To better understand this behavior and to achieve superior control over scaffold degradation profiles, this current work explores the impact of varying thermoplastic polymer microstructure (e.g. M_n , hydrophilicity, and crystallinity) in PCL-DA/PLA semi-IPNs. A variety of degradation rates were achieved, without compromising other properties, and were shown to be primarily linked to polymer miscibility. Partially miscible systems displayed accelerated degradation rates compared to immiscible, or phase separated systems and fully miscible systems. Control over polymer miscibility in PCL-DA/PLA semi-IPNs can potentially be used as a tool to fine tune the degradation profile of “self-fitting” CMF bone scaffolds.

Understanding the stability of PLCL implants used for treating rotator-cuff injuries

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Biodegradable poly(l-lactide-co- ϵ -caprolactone) (PLCL) balloon implants are used in treating rotator-cuff injuries. These implants act as a temporary spacer for tissues, while reducing pain and allowing rehabilitation after surgery. From the biotechnological point of view, we focused on analyzing the vital molecular properties of the PLCL material after sterilization, and storage by examining the changes in polymer crystallinity, molecular weight distributions (Mw, Mn and PDI), inherent viscosity (η), optical activity [α] and thermal properties. Both *in vitro* and *in vivo* degradation behavior of the implants was examined for one year, and the information obtained was used to correlate its reliability under different storage conditions. We also examined the limits of the mechanical stability of the balloons under prolonged pressure, to be able to predict their physical stability *in vivo*. Overall, the data disclose that the PLCL balloons could retain their molecular and physical integrity under long-term degradation conditions. Further, the implants did not show any variation from reference samples, and they exhibited a constant stability profile even after shelf-storage of more than a year. This approach offers an absolute assurance that balloon failures will not occur after implantation.

Synthetic linear antioxidant polymers for corrosion protection of steel substrates

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We have explored the capability of a linear synthetic polyphenol, poly(N-(3,4,5-trihydroxybenzyl) methacrylamide (P3HMA), to provide corrosion protection of steel substrates. First, the capability of P3HMA to form complexes with Fe^{3+} ions, which are formed as a result of steel corrosion, was studied. As demonstrated by FTIR and UV-vis spectroscopies, P3HMA formed complexes with metal ions, and easily oxidized in the presence of oxygen. Second, the protective properties of P3HMA were explored in layer-by-layer assemblies of this polymer with several partners, including polyethylene oxide (PEO), polyethylene amine (BPEI) and polyvinyl caprolactam (PVCL). While all the films were stable and did not demonstrate thickness loss after exposure to 0.6 NaCl solutions for at least 30 days, the effect of FeCl_3 on film integrity was strongly dependent on the strength of interpolymer binding. While strongly associated, linearly growing P3HMA/BPEI and P3HMA/PVCL films exhibited no chemical or physical changes upon exposure to Fe^{3+} ions, as indicated by FTIR and ellipsometry, respectively, exponentially growing P3HMA/PEO films underwent oxidation of polyphenol functional groups and degradation upon exposure to FeCl_3 . The effect of Fe^{3+} ions on film integrity correlated with the degrees of film swelling and was lower for the less swollen P3HMA-BPEI and P3HMA-PVCL films. Moreover, potentiodynamic polarization experiments revealed that ultrathin P3HMA-BPEI and P3HMA-PVCL films significantly reduced the corrosion current of bare steel substrates. This fact, taken together with high resistance of the latter films to the attack by iron (III) ions, makes them promising candidates for counteracting the degradation of steel substrates.

Quantitative and qualitative analysis of shape memory polyurethane foam biodegradation

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Our laboratory has developed biodegradable shape memory polyurethane (SMP) foam vascular occlusion devices. Measuring the mass loss and mass loss rate of our devices is critical in evaluating the systemic release rates of degradation products. Currently, degradation-induced mass loss is evaluated by removing the tissue from the explanted device and performing gravimetric analysis. This precludes the ability for simultaneous histological evaluation of the tissue-device explant. While some histological methods exist for characterizing degradation, none quantify a mass loss rate. From pathological analysis, it has been determined that the degradation along the edges of the material is quantifiable through trans-sectional area measurements. We have developed a method to use the measured area loss in histological slides to predict the volumetric mass loss of the whole device. This method allows for simultaneous analysis of the foreign body response and biodegradation both qualitatively and quantitatively across different time points. This presentation will demonstrate the rationale behind histologically-based degradation evaluation, the approach that we developed, and the results produced from the method that have been used in FDA 510(k) submissions. Additionally, we have begun to validate and refine the method through virtually simulated histological analysis of a computationally modeled foam structure with degradation. This will establish a relative error associated with the number of trans-sectional evaluations performed for one explant and offer future guidance for sectional analysis of polymeric biodegradation. Future work will include benchtop validation of the measurement method in chemical and cell-mediated degradation studies, as well as the development of a mass loss kinetics model for our SMP foams in homogeneous and heterogeneous degradation conditions.

A comb-type thermoresponsive ‘self-cleaning’ membrane to house an optical glucose sensing assay

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Towards the development of a fully implantable continuous glucose monitor (i-CGM) with long-term functionality, we described the development of a ‘self-cleaning’ membrane, which is able to house an optical glucose sensing assay while reducing biofouling. These membranes are based on thermoresponsive hydrogels, whose thermally-driven cyclical deswelling/reswelling (activated by local temperature changes in the subcutaneous tissue) would lead to the detachment of adhered cells. In our study, double network (DN) hydrogels were formed with poly[*N*-isopropylacrylamide-*co*-(2-acrylamido-2-methylpropane sulfonic acid)] [P(NIPAAm-*co*-AMPS)] and PNIPAAm as 1st and 2nd networks, respectively. A membrane was prepared as a hollow cylinder and used to house a liquid optical assay solution comprised of PEGylated concanavalin A (mPEG-TRITC-ConA, Ø~30 nm) and APTS-mannotetraose (APTS-MT, Ø~3 nm). The membrane itself exhibited a high degree of biocompatibility and was mechanically robust. However, the membrane was unable to prevent the leaching of the optical assay solution contained within its cavity. This was attributed to the relatively high mesh size of the membrane (~7-10 nm) versus that of the assay components. Thus, membrane analogues with comb architectures were prepared to reduce the mesh size to below that of the size of APTS-MT. These combs were based on methacrylate oligo(AMPS) and were incorporated at varying concentrations into the 1st network. A mesh size of <3 nm was achieved to limit the leaching issue of APTS-MT while still permitting glucose (Ø~1 nm) diffusion. Furthermore, we demonstrated that the comb length, concentration and charge would impact the ability to control membrane mesh size.

Engineering an exosome-based co-delivery platform via lipid-hybridization and polymer Layer-by-Layer deposition for cancer therapy

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Combination therapies of siRNA-mediated gene silencing and small molecule drugs have the potential to be a powerful synergistic strategy for cancer treatment. A remaining challenge, however, is the co-delivery of anionic nucleic acids and hydrophobic anti-cancer drugs in a nanocarrier system, because of their vastly different physicochemical properties. Here, we report a simple and low-cost approach to develop an engineered exosome (eEVs)-based system that is capable of encapsulating siRNA and combines polyelectrolytes via layer-by-layer (LbL) assembly. In this multi-functional platform, the siRNA-loaded eEVs served as a core; small molecule drugs such as doxorubicin (DOX) could be incorporated into the shell assembly of polyelectrolytes via hydrophobic interactions (**Figure 1A**). To explore the physicochemical properties of LbL-eEVs, particle size and zeta potential were characterized via a ZetaSizer (Malvern). To validate the functionality of vesicles, RNA interference (RNAi) efficacy and drug dose effects were investigated using human lung adenocarcinoma (A549). The particle size of eEV reached a final size of 140.2 ± 9.0 nm diameter following LbL deposition (**Figure 1B**). A reversal of surface charge was observed with the deposition of alternate polyelectrolyte layers (range: -15.7 ± 5.9 mV to $+22.1 \pm 0.5$ mV) (**Figure 1C**). The RNAi assay demonstrated the knockdown efficiency of the LbL-eEV was comparable to the commercial Lipofectamine RNAiMax (**Figure 1D**). The LbL assembled eEVs with DOX showed a higher antitumor efficacy in terms of reduced inhibitory concentration (IC) values (10^{11} eEV concentration and ~ 0.12 μ g/ml DOX concentration) in the cells compared to that of free DOX. These studies demonstrate a multi-layered co-delivery platform can be established by eEVs via lipid hybridization and LbL deposition. Future work will involve investigating synergistic effects on cancer cells.

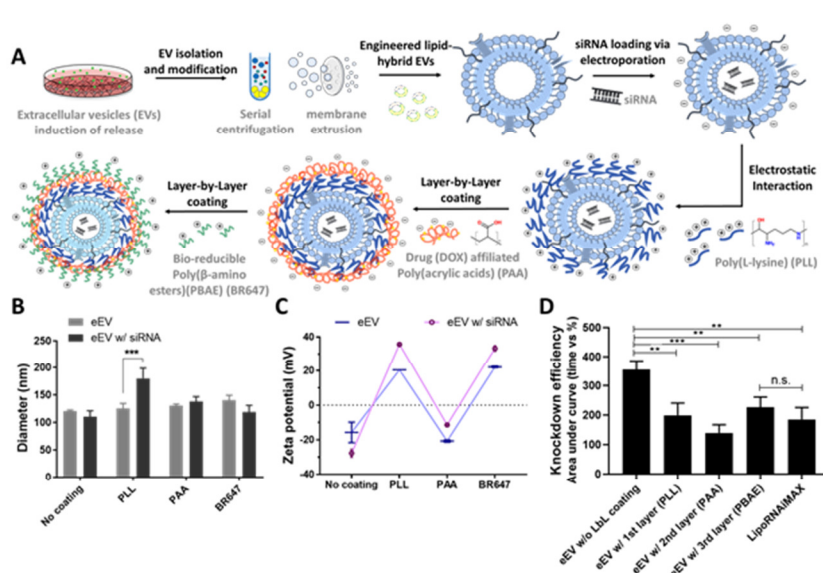


Figure 1. (A) Diagram illustrating the preparation for layer-by-layer coated extracellular vesicles containing drug/siRNA complexes (B) Diameters of the eEVs (without siRNA or with siRNA) at each of the layered stages showing a continual slight increase; (C) the zeta potential of eEVs with and without siRNA at each of the layered stages of the eEVs, showing a continual reversal; (D) siRNA-mediated GFP knockdown quantified by area under curve over time in human lung adenocarcinoma cells (A549) by Cytation 5.

Evaluating the thromboresistance of silicones modified with PEO-silane amphiphiles

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Silicone is commonly used in blood-contacting devices, but its hydrophobicity leads to non-specific protein adsorption and subsequent thrombosis. Hydrophilic poly(ethylene oxide) (PEO) is known to impart exceptional protein resistance when grafted to a model substrate (e.g. gold). In silicones, PEO is an ineffective surface-modifying additive due to its inability to migrate to the surface-biological interface. Alternatively, we have reported PEO-silane amphiphiles that, when blended into a condensation cure silicone, can undergo water-driven surface restructuring to form a hydrophilic, protein resistant surface that is maintained following aqueous conditioning. This amphiphile is composed of a crosslinkable triethoxysilane (TEOS), a hydrophobic oligo(dimethyl siloxane) (ODMS) tether, and a hydrophilic PEO segment: $\alpha\text{-(EtO)}_3\text{Si-(CH}_2\text{)}_2\text{-ODMS}_m\text{-}b\text{-PEO}_8\text{-OCH}_3$. In this study, silicones modified with PEO-silane amphiphiles (0-50 $\mu\text{mol/g}$ silicone) were further evaluated using human blood. Both the aforementioned crosslinkable, TEOS-terminated amphiphile (XL diblock, $m=13$; XL13) and a non-crosslinkable silane-terminated amphiphile (Diblock, $m=30$; DB30) were assessed. These were prepared as films in 96-well plates and evaluated statically with human blood pre-treated with fluorescently labelled platelets and human fibrinogen (HF). Fluorescent imaging was used to assess platelet adhesion (488 nm) and HF adsorption (647 nm), where sample fluorescence intensity was calculated using ImageJ and compared to the unmodified control. For both the “XL13” and “DB30” amphiphiles, the unmodified control (0 $\mu\text{mol/g}$) and 5 $\mu\text{mol/g}$ samples showed substantial amounts of adhesion. In contrast, samples at 10 $\mu\text{mol/g}$ or higher had significantly reduced HF and platelet adhesion. Overall, these modified silicones show enhanced thromboresistance and potential for use in blood-contacting devices.

Erythrocyte membrane-camouflaged nanocarriers with tunable paclitaxel release kinetics via macromolecular stereostructure

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Nanocarriers have considerable potential for treatments of various diseases. In particular, biomimetic cell membrane-camouflaged polymeric nanocarriers (CMNs) possess advantages related to the functional diversity of cell membranes and the physicochemical tailorability of synthetic polymers. Recently, we have developed a facile approach for the fabrication of erythrocyte (red blood cell, RBC) membrane-camouflaged polymeric nanocarriers (RBC-CMN) that exhibit tunable paclitaxel (PTX) release kinetics by altering macromolecular stereostructure. For this approach, polylactide (PLA) was employed as a biocompatible synthetic polymer having known stereocomplex interactions, which provide for control over the thermomechanical properties *via* polymer tacticity. Isotactic and atactic PLAs of similar molar masses ($M_n = 8500\text{--}8700$ Da) and dispersities (< 1.1) were synthesized *via* organocatalyzed ring-opening polymerizations. Uncoated PLA nanocarriers, varying in degrees of stereocomplexation, had comparable hydrodynamic diameters (*ca.* 90 nm) according to dynamic light scattering (DLS) measurements. Differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) analyses of lyophilized nanoconstructs suggested retention of PLA stereocomplexation upon loading the hydrophobic anti-cancer drug PTX. RBC membrane coating improved the colloidal stability, relative to uncoated PLA nanocarriers in PBS solution (1x, pH = 7.4). Stereocomplexed PLA RBC-CMN exhibited the slowest PTX release rate, compared to amorphous (6-fold), isotactic (4-fold), and 50% stereocomplexed (2-fold) PLA counterparts, during the first 12 h in PBS (1x, pH = 7.4) at 37 °C. RBC-CMN were observed to be non-cytotoxic, and displayed lower immunogenic responses compared to RBC membrane vesicles.

Stable polyanhydrides based on ricinoleic acid

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Polyanhydrides have been investigated as carriers for controlled delivery of several drugs. Polyanhydrides are desirable as controlled release carriers because of their surface eroding properties. Polyanhydrides have inherent high reactivity toward water, which prompts rapid hydrolytic degradation. Due to the high rate of hydrolysis, polyanhydrides endure surface erosion rather than bulk degradation.

Gliadel wafer, an approved polyanhydride copolymer of carboxyphenoxy propane and sebacic acid is a bioresorbable medicinal implant that is used to deliver carmustine, an anticancer agent to cerebral tumor sites. Nevertheless, the number of polyanhydride products existing in the market is fewer compared to polyester. Even though polyanhydrides are easy and inexpensive to synthesize and scale up, they exhibit a short shelf-life. Polyanhydrides are prone to hydrolytic degradation and depolymerisation via anhydride interchange during storage. Hence, polyanhydrides need to be kept at freezing storage conditions that restricting their usage in drug delivery products.

Nowadays, alternating polyanhydride copolymers show extended shelf-life. Notably, we synthesized polyanhydride with improved stability and shelf-life. This polyanhydride is synthesized from ricinoleic and sebacic acid with alternating ester-anhydrides, which is stable at 25 °C for more than 18 months. The alternating architecture provides improved stabilization through the hydrophobic side chains by hindering hydrolytic cleavage and anhydride interchange.

Fabrication and characterization of electrospun shape memory polymers

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Many medical procedures today require biomaterials which are adaptive in order to treat complex conditions. The aim of this project is to combine the versatility of shape memory polymers (SMPs) with the biocompatibility of the electrospinning fabrication technique. SMPs are often beneficial for medical applications as they allow for significant shape change in difficult to access areas. For example, SMP foams have recently received FDA approval as minimally invasive occlusive devices. Electrospinning is an advantageous fabrication technique for tissue contacting devices due to high porosity, flexibility, and ECM like microstructure. Presented in this study is the fabrication and characterization of a crosslinkable, electrospun SMP with good mechanical and shape memory properties. Various electrospinning parameters such as viscosity, voltage, and feed rate were tested to determine their influence on fiber morphology. Tensile testing demonstrated the influence of UV exposure time, crosslinker concentration, and photoinitiator concentration on mechanical properties. Finally, DMA testing was performed to establish percent recovery strains and recovery stresses. An understanding of these properties will be important in directing biomedical applications of this material.

Controlled release of camptothecin from functional polyphosphoramidate nanoparticles exhibiting acid-triggered degradation

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Camptothecin (CPT) is a promising anticancer drug that has shown remarkable anticancer activity in preliminary clinical trials, though the therapeutic potential of this agent has been limited due to its poor solubility and the facile conversion of the original lactone form into a less active hydrolyzed form at neutral pH. Fundamental synthetic methodology was advanced to allow for the preparation of a functional polyphosphoramidate-based (PPA-based) block copolymer which underwent aqueous assembly into functional nanoparticles that inhibited premature CPT hydrolysis at pH 7.4 and accelerated CPT release under pH 5 (ca. 4x faster compared to pH 7.4). Two degradable oxazaphospholidine monomers, with one carrying alkyne functionality, were designed and synthesized to access well-defined block PPAs ($\bar{D} < 1.1$) via sequential organocatalytic ring opening polymerizations (ROPs). The resulting amphiphilic block copolymers (PEOMP-*b*-PBYOMP) were then assembled into nanostructures with different sizes and morphologies determined by the molecular composition. As shown in the scheme, well-dispersed nanoparticles physically loaded with 10 wt% CPT were prepared, which allowed the aqueous suspension of CPT at concentrations up to 5.2 mg/mL, significantly exceeding the aqueous solubility of the drug alone (<2.0 µg/mL). Drug release studies indicated that release of CPT was remarkably accelerated at pH 5 compared to that at pH 7.4, and that the premature hydrolysis of CPT was effectively inhibited at pH 7.4. Cytotoxicity studies are being actively pursued to further demonstrate the effectiveness of the system, while the alkyne functionality of the polymer will allow for easy post-modifications, such as dye-conjugation for imaging.

Degradable polyphosphoester-based nanoparticles carrying silver-based antimicrobials for the treatment of bacterial infections

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Cystic fibrosis (CF) is an inherited disease of the secretory glands. The primary cause of death of patients with CF is respiratory failure from lung infections caused by bacteria, especially *Pseudomonas aeruginosa*. In this study, we constructed novel biocompatible and degradable polyphosphoester (PPE)-based polymeric nanoparticles that are capable of carrying silver cations through different mechanisms: formation of silver acetylides, silver-yne interactions, electrostatic interactions, or complexation between silver and sulfur. These PPE-based block copolymers were synthesized by efficient sequential ring-opening polymerizations of phospholane monomers, followed by post-polymerization chemical modifications to afford different amphiphilic block copolymers, which self-assembled into nanomaterials capable of loading large amounts of silver. In particular, PPEs with residual alkynes were extremely effective toward silver loading, consuming most of the pendant alkyne groups along the polymer backbone, with a silver loading content of ~15% (w/w). Raman spectroscopy revealed that silver was loaded into the nanoparticles *via* formation of silver acetylides and silver-yne complexation. The silver-loaded nanoparticles released silver in a sustained manner, and displayed enhanced *in vitro* antibacterial activities against cystic fibrosis-associated pathogens over silver acetate. To address the bacterial infections more effectively, anionic shell-crosslinked knedel-like (aSCK) nanoparticles were developed, where antibiotic minocycline was loaded in the core-shell interfaces of the aSCK nanoparticles *via* hydrophobic and electrostatic interactions, in conjunction with the silver cations loaded into the shell through electrostatic interaction with carboxylate groups and coordination with two sulfur atoms. The combination allowed a reduced dosage of both therapeutics to achieve the same antimicrobial effect, demonstrating their potential as a next-generation antibiotic to combat the threats presented by multi-drug resistant pathogens.

Poly(D-glucose carbonate)-based crosslinked networks designed for renewable and degradable coatings in challenging situations

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Polymer coatings, with tunable chemical compositions, hydrophobicities/hydrophilicities, topographies, mechanical properties, *etc.*, have been actively explored during the last few decades. Employing coatings on surfaces is typically intended to provide specific protection, control friction or adhesion, introduce biocompatibility, or prevent corrosion. In this work, a series of renewable and degradable poly(D-glucose carbonates) (PGCs) was developed for various coating applications, including anti-icing and anti-biofouling. Novel sugar-based coating materials with diverse functionalities can be achieved through controlled organocatalyzed ring-opening polymerization of five- or six-membered cyclic carbonates derived from glucose, followed by post-polymerization modification. These complex PGC coatings were fabricated on vinyltrimethoxysilane-functionalized glass substrates. The PGCs were characterized using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA), while the coating layers were investigated using atomic force microscopy (AFM) and contact-angle measurements. Understanding the surface features and physicochemical properties of PGC coatings is expected to guide the design of materials optimized toward different applications, including challenging conditions of biofouling or ice formation.

Synthesis & Sustainability

Designing for degradation: Utilizing topology, architecture and stoichiometry to control polymer degradation *in vivo*

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Complex biological tissues are highly elastic in nature, and efforts to repair or replace cartilage, tendon, muscle, and vasculature have been ongoing for decades. The primary challenge has been the lack of materials that possess the mechanical, chemical and resorption characteristics necessary for the design process. These properties have been difficult to collectively mimic in synthetic resorbable biomaterials. In this work, we report a series of copolymer systems that utilize topology, architecture and stoichiometry to control polymer degradation *in vitro and in vivo*. These materials are highly tunable and in some cases elastic with concomitant control over the mechanical and resorption properties. Herein, we will demonstrate both the programmable degradation and tunable mechanical properties of these elastomers highlighting their potential for use in soft tissue regeneration.

Stereochemically-directed elastomer properties

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A wide range of polymer materials can be constructed from a vast array of chemical resources. In a biomaterials context, careful design can elicit desired properties to interface with biological systems or even direct their behaviour. Our work is focussed on the development and application of degradable biomaterials and sustainable polymers. These areas naturally compliment one-another. The richness of resource in terms of functional group provides ample opportunity to design new degradable materials with novel, targeted properties while simultaneously potentially providing a lower resistance to their eventual application from regulators.

Our work is fundamentally based around the discovery of new materials and methodologies by which to make them. We are particularly focussed on the development of new (organo) catalytic and efficient 'click' chemistry methods for the sustainable synthesis and functionalisation of degradable polymeric materials as well as developing new materials from sustainable feedstocks. We also have a strong focus on how this chemistry can control the properties of the materials that we make through both structure and stereochemistry to control properties at the macroscopic level (i.e. degradability and mechanical properties), microscale (control over structure via 3D printing and emulsion methodologies) and nanoscale (self-assembly and ordering) to realise new biomaterials for application in delivery and tissue engineering applications.

This presentation will focus on the design of degradable polymer materials with controllable functionality, stereochemistry and degradation rates, specifically focusing on materials that display elastomeric behavior^{1,2} that may be suitable for biomedical applications.

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Investigating new sources for and applications of cellulose nanocrystals

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Cellulose nanocrystals (CNCs) have attracted attention in recent years as potential green nanomaterials. CNCs are highly crystalline nanofibers that can be isolated from a variety of renewable biosources, including cotton, sisal, wood, and sea tunicates. The diameters range from 5 to 30 nm and the lengths range from 100 nm to several micrometers depending on the biosource and method of isolation. CNCs have several advantages as a nanomaterial, including biosustainability, biorenewability, relatively low production cost, and low cytotoxicity. They generally have high surface area, low density, low coefficient of thermal expansion as well as high elastic moduli of about 80-150 GPa, depending on the biosource. We have been investigating the use of CNCs to access mechanically-dynamic composites, reinforcing agents for aerogels and to access nano-emulsions and latexes. We have also been investigating new possible sources for CNCs and have targeted the large, perennial grass hybrid *Miscanthus Giganteus*, which is a commercial crop currently used for energy production, as a new potential commercially viable source of cellulose nanomaterials.

Polyisobutylene and BASF's commitment to sustainability

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Polyisobutylene (PIB), under the tradename OPPANOL[®], is a core business for BASF, spanning over 80 years of experience in manufacturing and understanding of properties and applications. OPPANOL[®] is a unique thermoplastic that exhibits excellent barrier properties, tack and non-polar characteristics leading to its chemical inertness and resistance to oxidative attack. This presentation will introduce OPPANOL[®] and how the product provides a key sustainability advantage in specific applications. The discussion will transition toward a high-level overview of how BASF continues their commitment to sustainability using bio-gas and bio-naphtha in the Verbund manufacturing processes, allowing customers the opportunity to contribute to the reduction of greenhouse gas emissions and a reduction in a fossil feedstock.

Accelerated hydrolytic degradation of ester-containing biobased epoxy resins

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The accelerated hydrolytic degradation of biobased epoxy resins containing ester linkages was investigated. Epoxidized biobased molecules were utilized as sustainable replacements for the diglycidyl ether of bisphenol A (DGEBA) as an epoxy monomer, including epoxidized vanillic acid (EVA, derived from lignin), epoxidized plant-based phenolic acids (epoxidized salicylic acid, ESA, and 4-hydroxybenzoic acid, E4HBA), and epoxidized soybean oil (ESO). All biobased epoxy monomers contain esters (3 per molecule for ESO and 1 per molecule for EVA, ESA and E4HBA), in contrast to DGEBA (containing no esters). The epoxidized molecules were cured through reaction with an anhydride curing agent. Epoxy resins derived from EVA, ESA, and E4HBA exhibited comparable glass transition temperatures to that of the DGEBA-based epoxy resin. All biobased epoxy resins underwent rapid degradation in a basic solution as compared to the conventional DGEBA-based epoxy resin. ESO- and ESA-based epoxy resins exhibited the fastest degradation rates, whereas E4HBA- and EVA-based epoxy resins exhibited more moderate degradation rates. Variations in degradation rate are attributed to differences in epoxide content, monomer structure, degree of hydrophilicity, crosslink density, and proximity to glass transition temperature. The degradation profiles, mass loss as a function of exposure time in the basic solution, showed good agreement with predictions from a solid-state kinetic model. Mass spectrometry and scanning electron microscopy analyses confirmed the epoxy resins underwent hydrolytic degradation, through a surface erosion mechanism.

Novel applications and developments utilizing photopolymerizations

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Photopolymerization reactions have been explored and utilized since the time of the ancient Egyptians; however, development of new photopolymerization methodologies and applications continues at an ever more rapid pace. Traditionally, photopolymerization of multifunctional monomers results in highly crosslinked materials suitable for applications as optical lenses, optical fiber coatings, and dental materials. These reactions are ubiquitous not only because of the nature of the final polymer product, but also for the characteristics of the reaction itself. Photopolymerizations are far more energy efficient than their thermal counterparts, are typically performed in a solventless manner that is more environmentally compatible, the reactions occur rapidly at ambient conditions, and the polymerization can be controlled in both time and space.

Here, we will focus on two distinct vignettes related to our photopolymerizations work including the development of novel click-reaction based photopolymerization reactions and materials and development of polymer networks with dynamic covalent links that exhibit unique responses to exposure to light that alleviate stress and lead to shape and compositional changes. First, we will discuss the potential and application of photopolymerization reactions based on click reactions. These unique polymerizations enable fabrication of low stress, highly functional, homogeneous materials with the facile ability to induce a multistage polymerization reaction suitable for the formation of holographic and other optical materials. We will next present work on covalent adaptable networks (CANs) that incorporate dynamic covalent bonds as crosslinks within the network that respond to light to (de)activate the dynamic bond character. These materials are able to change shape and stress-state when exposed to light, facilitating application as novel optical and actuating materials.

Precision polymer nanoparticles**Rachel K. O'Reilly**

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Polymerization-induced self-assembly (PISA) is a versatile method to prepare nanoparticles of various morphology. Traditionally, nanoparticles are prepared via self-assembly of pre-formed polymers in H₂O. Rigorous optimization is often required in these systems, involving iterative cycles of polymer synthesis, self-assembly, and evaluation of the self-assembled morphologies. PISA offers an elegant solution to the tedious procedures of conventional self-assembly by forming the particles in situ as the polymerization progresses. PISA involves chain-extension of a hydrophilic macroinitiator (or macro-chain-transfer agent) with monomers that are miscible with water, but form a hydrophobic, immiscible polymer, driving self-assembly. PISA can be conducted at high solids contents under a wide variety of reaction conditions (i.e., low or high temperature, variable solvent mixtures, or in the presence of drugs or biomacromolecules). However, monomers which can be utilized in PISA are often difficult to identify from their chemical structures alone, and experiments are often necessary to determine their usefulness in PISA. We have been developing synthetic methods and developing predictive tools to expand the scope of PISA and also show its application in the design of functional materials.

Metal-organic light initiated radical (MILRad) polymerization**Eva Harth**

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The lecture will discuss the discovered metal-organic light initiated radical (MILRad) polymerization in its ability to prepare block copolymers in a one-pot and a sequential process from olefins and vinyl polar monomers. Metal-organic catalysts known for their insertion polymerization of olefins can be activated by blue light to be switched to a radical pathway. The scope of the radical polymerization as well as the insertion polymerization will be discussed and is supported by computational data. The details and background of the challenges combining an insertion route with a radical mechanism is explained and the benefits of this newly discovered method is laid out towards a new route to prepare novel materials with a higher degree of variation and function.

Studies at the interface of organic synthesis and polymer chemistry: Role of macromolecular isomers**Craig Hawker**

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The orthogonal functionalization of polymeric materials is a critical design strategy for the “bottom-up” fabrication of nanostructured systems. In synthesizing these nanostructures, functional group interconversion and efficient organic transformations are key to obtaining materials with exceptional properties. The design of multi-functional building blocks for common polymeric materials and their extension to commercial products will be demonstrated. In addition, a novel methodology for printing 3D objects with spatially resolved mechanical and chemical properties is reported. Photochromic molecules are used to control the lateral resolution of orthogonal photopolymerization processes through coherent bleaching fronts, providing large depths of cure and rapid build rates without the need for moving parts. The use of resin mixtures containing independent photocrosslinking systems coupled with a simple LED projector allows for simultaneous and selective curing, providing access to 3D-objects with chemically and mechanically distinct domains. The power of this approach is showcased through the one-step fabrication of bioinspired soft joints and mechanically reinforced “brick-and-mortar” structures using tailored photochromic dyes.

Polystyrene/polyglycidol homo and copolymers and their self-assembly into functional nano- and microparticles

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Amphiphilic copolymers containing large number of functional groups as well as nano- and microparticles formed by copolymer self-assembly play an important role as carriers of catalysts and biomolecules, in particular proteins and nucleic acids. In this paper we describe synthesis and self-assembly of copolymers with various architecture containing linear polystyrene and linear and/or brush polyglycidol blocks using two strategies. The first one consists in synthesis of polyglycidol-derived macromonomers with vinyl end-groups and their subsequent copolymerization with styrene in the water-based media. This method yields composite microparticles with polystyrene inner parts and outer layer containing polystyrene-*g*-polyglycidol copolymer granules with about 30 nm size. The diameters of the (nano/micro)particles could be controlled in a range from 60 to 830 nm and they have narrow diameter distribution (D_w/D_n from 1.011 to 1.088, where D_w and D_n denote the weight and number average diameters, respectively). Interactions of fibrinogen with these microparticles revealed that they have the hydrophilic-hydrophobic patchy structure. Modification of the microspheres by converting them into microspheroids will be presented. The second strategy consists in sequential polymerization of styrene and polyglycidol with blocked hydroxyl groups and their subsequent deblocking after copolymerization. The synthesis yielded polystyrene-*b*-polyglycidol copolymers. Using these copolymers as precursors of macroinitiators the copolymers with polystyrene-*b*-(polyglycidol-*g*-polyglycidol) structure were synthesized. Behavior of the copolymers in water as function of their architecture was investigated indicating formation of polymer micelles and micellar aggregates.

Acknowledgment: This work was financially supported by the National Science Centre (Poland) Grants UMO-2018/29/B/ST4/02178 and UMO-2018/29/B/ST8/01721.

Removal of heavy metals from water using pressure-stable, imprinted polymers

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It is difficult to remove heavy metal ions from water because heavy metal ions bind only weakly to common ion exchange resins, getting outcompeted by the “hard” ions in water. In this research ion exchange resins are imprinted with the heavy metal ions, increasing the binding strength of the heavy metal ions and thus allowing them to compete for the resin binding sites. The capacity of these resins was increased by increasing the surface area of these resins. The capacity of the resins for different heavy metal ions will be presented. Competitive ion binding was used to identify the different binding sites in the resin. Additionally, a method will be presented that increases the pressure-stability of the imprinted resins.

Intertwining polymers with control**Zachariah A. Page**

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The synergistic unification of two disparate polymer networks to effectively harness the beneficial properties of each has led to impressive soft, yet tough, materials. Preeminent examples include double network hydrogels and, more recently, interpenetrating polymer network elastomers. Although both structure and morphology of these networks have an unequivocal effect on their properties, synthetic challenges have limited the depth of our understanding. This presentation will describe preliminary results on orthogonal chemical transformations for systematically interrogating these fascinating networks.

The best of both worlds: High-throughput multidetector UPLC

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Gel permeation / size exclusion chromatography (GPC/SEC) is the most well-known method for polymer and macromolecular analysis. As the technique has become more pervasive, there has been a push toward greater efficiency, by way of reduced run times, minimal solvent, and sample consumption. The development of ultra-performance liquid chromatography (UPLC) has accommodated these issues, by employing low volume, high resolution columns and pumps with the ability to handle higher pressure generated by these columns. These features allow for more efficient polymer analyses, but unfortunately, the technique still relies on the need for column calibration to provide relative molecular weight values.

While UPLC represents the evolution of GPC/SEC to a quicker, more efficient method, the development of advanced detectors provided an orthogonal means of improvement. Increasingly sophisticated detectors, including light scattering and viscometer detectors, have been successfully incorporated in GPC/SEC systems to offer complete characterization of a sample. Recently, Malvern Panalytical has introduced a version of tetra detection that is compatible with UPLC conditions and, through a collaboration with Waters Corp. and their ACQUITY Advanced Polymer Chromatography (APC™) system, has brought advanced detection to UPLC analysis. This combination allows complete polymer characterization including absolute molecular weight, hydrodynamic size, compositional analysis, and branching analysis accomplished in less than 15 minutes.

Rational design and synthesis of electrochemically stable and processable PANI- like polymers

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The discovery of new materials are based on an advanced understanding of the chemistry and properties of previously known materials. Polyaniline (PANI) stands out among the many different conducting polymers (CPs) such as polyacetylene (PA), polythiophene (PTh), poly(3,4-ethylenedioxythiophene) (PEDOT), and polypyrrole (PPy), due to its outstanding air and moisture stability in the conductive state. It is also simple to prepare, can be made highly conductive, redox reversible and cost effective. PANI is one of the very few CPs that have gained some large scale commercial applications, mostly in printed circuit board manufacturing (final finishes, used in millions of m² every year), antistatic and electrostatic dispersive (ESD) coatings, and corrosion protection. Even so, PANI has great potential for applications in many other fields such as supercapacitors and batteries, electronic devices as hole-injection layers, solar cells, biosensors, and toxic metal recovery. Unfortunately, practical applications of PANI in these fields are plagued by the material's electrochemical instability, and the lack of standard/optimized deposition methods. Currently, all efforts to improve the electrochemical stability and processability of PANI films have not been able to sufficiently overcome these deficiencies for commercial applications.

We have designed and prepare a "PANI-like" polymer by introducing phenoxazine in the backbone of a polymer with solubilizing group on nitrogen and conjugated with phenylenediamine. The polymer maintains the PANI backbone, but also contains the fused oxazine moiety to introduce rigidity to the polymer, and branch chain alkyl group for processability. Interestingly, the polymer had good solubility in chloroform and most importantly, the acid doped state was electrochemically stable. We will discuss the design strategy, synthesis and electrochemical results in this presentation.

Fluorogenic controlled polymerization amplification strategies for detection of biological analytes

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The development of strategies for signal amplification in aqueous media could enable new diagnostic platforms for the detection of water-soluble analytes such as biomolecules. We have developed a fluorogenic polymerization approach to amplify initiator signal by the detection of visible fluorescence upon polymerization in real-time. Controlled polymerization approaches such as atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain-transfer (RAFT) allow for fluorescence to correlate with initiator or RAFT agent concentration. This fluorogenic polymerization approach is compatible with biomolecules in solution and can be performed directly from an initiator-modified protein surface. Fluorogenic polymerization therefore represents a new approach toward signal amplification and biomolecular detection.

**Synthesis of well-defined polymeric adhesives:
Chemical functionalities and crosslinking effect on properties**

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Adhesives are nonmetallic polymer materials which possess the ability to join together two independent surfaces by chemical and physical bonding. Despite the importance of adhesives on various applications under complex environment, most of the existing adhesives are single purpose, single material-based, and singular in function. The talk discusses multi-functional adhesives that exceed conventional role of adhesive: 1) electronically conducting adhesives, 2) adhesives for biomedical applications, and 3) stimulus responsive adhesives. Those listed special functionalities of new adhesives were due to chemical functional groups on the synthesized linear polymers. For instance, the photodegradable adhesives contains nitrobenzyloxycarbonyl crosslinker which can be cleaved under light exposure. The photocleavage of nitrobenzyl crosslinker yielded significant reduction of adhesion strength. Likewise, introduction of specialized functional group provides customized and extraordinary properties to the adhesive. In addition to the special functional group, crosslinking controls adhesion property by influencing polymer chain mobility, viscous flow, and creep behavior. The well-controlled crosslinking enhances adhesion property. However, too high and low crosslinking lead the polymer stiff and liquid, respectively. The type of chemistry in crosslinking also have a strong effect on adhesive applications. For example, crosslinking method for biomedical adhesives should not involve in any toxic catalysts and/or byproducts. The talk will demonstrate a series of new adhesives synthesis that precisely controls polymer's chemical functionalities and crosslinking, which govern adhesion and additional extraordinary properties.

Modulating particle-polymer interaction via particle morphology

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Particle-polymer interaction determines the interfacial compatibility between filler and matrix in polymer composites, which usually needs to be manipulated in order to obtain high performance composites. Surface modification of filler particle (or modification of polymer) is the most widely used and effective approach to modulate the polymer-particle interactions. However, this inherently brings about extra chemical moieties into the system, which may not be always welcome. For example, in biomedical materials, the addition of any extra chemicals will result in tedious evaluation procedures, which are time-and-money consuming. On the other hand, varying morphology of filler particle only can keep the chemistry unchanged, thus avoid the above concerns. Modulating particle-polymer interaction via particle morphology may provide a complimentary yet effective approach to enhance the interfacial compatibility. Through a few examples, we demonstrated that the surface curvature can affect the particle-polymer interactions, thus composite materials with enhanced performances can be achieved.

Modern organic reactions as tools to access unique polymer architectures

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To foster the discovery of new technologies across most fields, the development of polymers with constantly increasing complexity is required. Since the specific function of these polymers is dictated by their molecular structure (monomer composition, molecular weight distributions, self-assembly at the nanoscale, etc.), the invention of unique methods of polymerization and of selective reactions for the functionalization of macromolecules remains essential. This presentation will focus on the design of new approaches to complex polymers with an emphasis on controlling the monomer sequence and 3D architecture. These new materials are currently constructed in the Michaudel lab with an eye toward applications in the fields of energy, medicine, and sustainability.

Intelligence, both living and non-living, in shape-morphing polymersLaura K. Rivera, Cedric P. Ambulo, Taylor H. Ware*Bioengineering
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Stimuli-responsive polymers often seek to mimic the intelligence of living organisms, where multiple inputs lead to a predictable series of outputs. Here, two orthogonal strategies, one non-living and one living, to create materials that respond in a complex manner to specific environmental conditions will be discussed. First, we will discuss direct ink write printing to control molecular orientation, and therefore the stimulus-response, in liquid crystal elastomers. This processing approach enables 3D structures where stimulus-response, geometry, and activation temperature can be programmed. Using a dual thiol-ene reaction scheme, we control the phase transition temperatures of 3D-printable LCEs from 12 °C to 54 °C. We also 3D print multiple LC inks into single structures to allow for the production of untethered, thermo-responsive structures that sequentially and reversibly undergo multiple shape changes. Towards this end, we demonstrate a sensing gripper that grasps an object at one elevated temperature but bends away from that object at higher temperatures. Notably, the stimulus-response of these structures is derived wholly from physical properties, while the stimulus-response of living organisms is derived in-part from genetic information. To bridge this gap, we will discuss a new strategy to fabricate living cell – synthetic hydrogel composites capable of undergoing programmed shape change. These living composites are acrylic hydrogels embedded with *Saccharomyces cerevisiae*, Brewer's yeast. As the cells are higher modulus (~100×) than the gel, cell proliferation results in a macroscopic shape change of the composite. Importantly, genetic engineering provides a platform to tune both the perception and responses of the living composite. We have shown that living composites can be synthesized using engineered yeast strains with light-responsive optogenetic *Arabidopsis thaliana*-derived sensors. As a result, the shape change (up to 300% volume change) of these composites can be patterned spatially and temporally by using low-power blue light. It is expected that these strategies to synthesize 'intelligent' shape-morphing polymers may enable new approaches to engineering challenges from soft robots to smart medical devices.

Surface-initiated PET-RAFT polymerization under metal-free and ambient conditions using enzyme degassing

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We report an open-to-air method for the efficient synthesis of surface-tethered polymer brushes based on photoinduced reversible addition-fragmentation chain transfer (PET-RAFT) polymerization. Key to this approach is an enzyme-assisted strategy using glucose oxidase to facilitate the in situ removal of oxygen during the polymerization process. Control experiments in the absence of glucose oxidase confirm the importance of enzymatic deoxygenation for successful polymerization of a variety of acrylamide, methacrylate, and acrylate monomers. In accordance with controlled polymerization kinetics, a linear increase in brush height as a function of irradiation time for a range of light intensities in the absence of sacrificial RAFT agents is demonstrated. Importantly, the use of light to mediate growth and the inherent monomer versatility of PET-RAFT allow for the facile fabrication of well-defined polymer brushes under aqueous conditions.

Polymeric clickase accelerate the copper click reaction of small molecules, proteins, and cells

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The CuAAC reaction has emerged as one of the most powerful tools for bioconjugation. Unfortunately, many CuAAC couplings remain limited by low substrate concentration and the need for mild conditions in competitive biological environments. By harnessing the supramolecular substrate binding provided by amphiphilic polymers, we report a group of SCNPs capable of exhibiting enzyme-like CuAAC catalysis. The nanoparticles are developed by intramolecularly covalent crosslinking through a “folding and crosslinking” strategy to prevent aggregation. It is shown that the polymeric structure significantly increases the catalytic efficiency for most of substrates, and the CuI-SCNP exhibit to be the fastest catalyst for the click reaction. With small molecules, the CuI-SCNPs operate in an “uptake mode”, bringing substrates inside the polymeric scaffold and in proximity to the copper catalytic sites. Unexpectedly the same CuI-SCNP performs a more efficient click reaction on protein surfaces and cell surface glycans than small molecule catalysts, although the catalysis between macromolecules is usually unfavorable due to the steric effect. Experimental and simulation studies suggest that these SCNPs feature an additional “attach mode” for protein substrate and interact their catalytic sites to protein surface. This work provides a highly efficient tool for CuAAC at low substrate concentration and more broadly point to a wider capability for catalytic SCNPs and for polymers in general, especially as it relates to bio-applications.

Overview of Tosoh: GPC/SEC Experts

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Tosoh Bioscience LLC provides liquid chromatography products to laboratories and manufacturing plants in the Americas. Our all-in-one dedicated GPC system, the EcoSEC GPC System, is predominantly used in the chemical and polymer industries while our EcoSEC High Temperature GPC System is ideal for the polyolefin and oil industries. The LenS3 MALS detector allows direct measurement of molecular weight and provides best-in-class sensitivity. The determination of radius of gyration of smaller macromolecules below 10 nm in gyration size, R_g , is now possible for the first time in history! In addition, TSKgel GPC columns for ambient and high temperature applications are available.

The company is a subsidiary of Tosoh Corporation in Japan, the parent of the Tosoh Group, which comprises over 100 companies worldwide and a multiethnic workforce of over 12,000 people and generated sales of ¥822.9 billion (US \$7.4 billion at the average rate of ¥100.85 to the US dollar) in fiscal 2018, ended March 31, 2018.

Ring-opening metathesis polymerization of a macrocyclic stilbene-based monomer

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We have investigated the synthesis and ring-opening metathesis polymerization (ROMP) of a unique macrocyclic stilbene-based monomer. The kinetic profile of the polymerization was studied, including the propensities for the complete initiation and secondary metathesis (chain transfer). Ultimately, we found that high initiation efficiency was achieved, and that the rate of chain transfer was competitive with propagation during polymerization. We discuss the modular synthesis of the monomer, ROMP kinetics, attempts to limit the rate of chain transfer, and potential applications of this new system.

Dock n' Block: Supramolecular end-group guides for the synthesis of sequence-controlled covalent multiblock copolymers

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Using well known supramolecular chemistry, we are developing a new method for the sequence-controlled supramolecular assembly of oligomer or polymer blocks and subsequent covalent tethering to yield multiblock copolymers that are synthetically inaccessible using known methods. Small molecules designed to bring compatible click groups close together through highly specific H-bonding interactions have been shown to preferentially bind two units in the presence of other equally reactive functional groups. This specific non-covalent direction of covalent linkages can be applied at oligomer/polymer end groups to give several potential benefits to the synthesis of multiblock copolymers. By creating a library of end-group caps with three functionalities, a binding unit, a click unit, and a functional group that can be tethered to a polymer, we plan to make macromonomers capable of forming covalent multiblock copolymers with unprecedented selectivity, increased molecular weights, higher block numbers and more diverse block types than previously reported. This novel synthetic method combines supramolecular chemistry, sequence-controlled synthesis and multiblock copolymer systems to allow the preparation of new materials.

Effect of small molecules on self-assembly of hydrogen-bonded layer-by-layer films

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We have explored the capability of dimethyl sulfoxide (DMSO) to control the mode of film growth and layer intermixing of hydrogen-bonded poly(methacrylic) acid (PMAA)/polyvinylpyrrolidone (PVP) layer-by-layer (LbL) films. As a strong hydrogen-bond acceptor, DMSO breaks water structure and strongly interacts with PMAA, thus affecting chain hydration and its capability to hydrogen bond with a polymer partner. Isothermal titration calorimetry (ITC) studies revealed the endothermic nature of PVP/PMAA hydrogen bonding in aqueous solutions and at low DMSO content, indicating the importance of release of water from the polymer solvation shells. However, as content of DMSO increased above ~25 vol %, the enthalpy switched its sign to negative, indicating the enhanced contribution of the heat released due to interpolymer hydrogen bonding to the free energy of complex formation. In good agreement with experiments in solution, thickness of PVP/PMAA films increased with DMSO concentration, showing a maximum at 60 vol % DMSO content, as indicated by ellipsometry. Fourier transform infrared spectroscopy (FTIR) showed that while DMSO was present within the films after deposition from the mixed solvents, it was easily washed out in aqueous solutions. Most importantly, DMSO content significantly affected the internal structure of deposited films as revealed by neutron reflectometry (NR) studies. NR showed that interpenetration of deuterated PMAA chains within a hydrogenated LbL matrix strongly enhanced at increasing concentration of DMSO. The dependence of film intermixing on DMSO content was strongly history dependent, and the effect of DMSO on film intermixing was strongest when DMSO was present in the film deposition solutions.

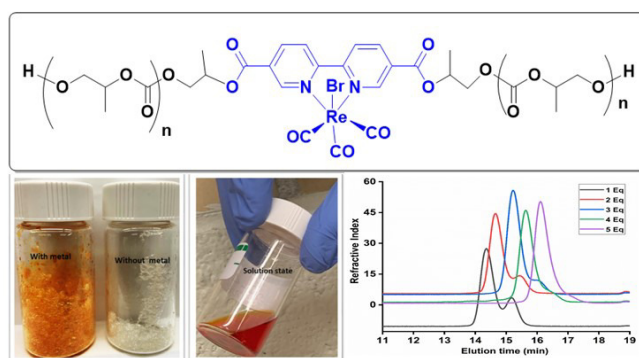
Incorporation of functionalized rhenium(I) bipyridine catalysts into polycarbonates *via* chain transfer chemistry

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In an attempt to expand the library of chain transfer agents during immortal copolymerization of epoxides/ CO_2 for making high value added materials, we hereby report on the utilization of tris-carbonyl-bromo(5,5'-dicarboxyl-2,2'-bipyridine)rhenium(I) as a chain transferring agent during such chemistry. These reactions were catalyzed by the binary (salen)CoO₂CCF₃/onium salt system in DCM/Toulene (1:1 v/v) solvent mixture under ambient temperature and high pressure. The resultant metal incorporated polycarbonates were characterized by ¹H NMR, FT-IR and MALDI-TOF-MS spectroscopies. The molecular weights of these polymers were determined by using GPC, which clearly shows that with increase in CTA loading in the polymerization reactions the molecular weights of the resultant polymers decrease which is also supported by the Mn determination by using ¹H NMR spectroscopy. These polymers show narrow polydispersity indices (PDI) in GPC, which lie in the range of 1-1.5. These novel polymers could have potential applications in electrocatalytic CO₂ reduction reactions.



- (1) Huang, Z.; Wang, Y.; Zhang, N.; Zhang, L.; Darensbourg, D. J., *Macromolecules* **2018**, *51*, 9122-9130.
- (2) Yang, G.-W.; Zhang, Y.-Y.; Wang, Y.; Wu, G.-P.; Xu, Z.-K.; Darensbourg, D. J., *Macromolecules* **2018**, *51*, 1308-1313.

An engineering approach to find the possible path to polypeptides in the prebiotic world

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The synthesis of polypeptides has been a long-standing problem in the field of prebiotic chemistry and pharmaceutical industries. Although it is generally accepted that amino acids were present on the prebiotic Earth, the plausible mechanism to form long chain polypeptides is still unclear. Because of the high activation energies and the formation of side products, direct peptide bond formation will not occur unless high temperature or activating agents are used. Here, we found a simple system composed of hydroxy acids and amino acids that is capable of forming peptide bonds under mild conditions. Hydroxy acids form metastable oligoesters in the oscillating (hot dry/cool wet) system and transform into mixed copolymers via the ester-amide exchange reaction. To further understand the kinetic behavior of this copolymerization, we first tracked the growth of initial species from a valine/ lactic acid mixture in a closed system reactor. A mathematical model was developed to simulate the reactions and evaluate the rate constants at different temperatures. These reactions can be described by an empirical Arrhenius equation even when the reaction occurred in the solid (dry) state. Further calculations for activation parameters showed that the ester-mediated pathway facilitates amide bond formation by lowering activation entropies. Finally, deep eutectic solvents were used as a green medium for the copolymerization of valine and lactic acid. We found deep eutectic solvents further reduced the complexity of the copolymers. These results not only demonstrate a simple system exhibiting key features for the emergence of peptides at mild conditions, but also provide a sustainable way to synthesize polypeptides.

Pseudo-living polymerization of dienes and polar vinyl monomers catalyzed by neodymium phosphate complexes

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Ziegler-Natta type catalysts have been extensively used for the polymerization of olefins and dienes. However, these catalysts can be disadvantageous due to their poor solubility in organic solvents, easy deactivation by polar monomers and high polydispersity index (PDI) of the synthesized polymers. Thus, a neodymium-based catalyst with chloride and triisobutylphosphate ligands ($\text{NdCl}_3 \cdot 3\text{TIBP}$) is developed for the polymerization of dienes and polar vinyl monomers. Single crystals of $\text{NdCl}_3 \cdot 3\text{TIBP}$ were isolated and its structure was determined using X-ray diffraction showing a discrete complex. The catalytic activity of $\text{NdCl}_3 \cdot 3\text{TIBP}$ combined with triisobutylaluminum (TIBA) as a co-catalyst was performed for the polymerization of isoprene and bio-based myrcene (96% 1,4-cis and ~1.6 PDI). The catalytic system is also active for the homopolymerization of polar vinyl monomers (butyl acrylate and methyl methacrylate - ~64% syndiotacticity) and generates block copolymers by sequential monomer addition. A pseudo-living polymerization of the neodymium catalytic system was observed based on the kinetic studies. $\text{NdCl}_3 \cdot 3\text{TIBP}$ /TIBA system demonstrates good catalytic activity for the polymerization of dienes while keeping stereospecific control of the reaction.

Organic radical polymer-electrolyte interactions from Flory-Huggins theory

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For many years, alternatives to lithium ion batteries have been researched, including the use of conductive polymers for completely organic batteries. Redox-active polymers, such as conjugated polyaniline and organic radical poly(2,2,6,6-tetramethylpiperidinyloxy-4-ylmethacrylate) (PTMA), have been studied as electrode materials for organic batteries. One major consideration for the design of organic batteries is the interaction between the polymer and electrolyte. For example, linear PTMA may dissolve in the electrolyte solution and thus degrade battery capacity, therefore crosslinked PTMA is gaining interest as a cathode material. To predict these polymer-solvent interactions, the Flory-Huggins interaction parameter, which is proportional to the difference between the polymer and solvent Hildebrand solubility parameters, is calculated. To complete this calculation, the solubility parameter of PTMA must be known and is determined by a solubility spectrum, where the behavior of PTMA in a wide variety of solvents is qualitatively observed. Additionally, titrations and viscosity measurements are conducted to provide more precise estimates of the PTMA solubility parameter. In conjunction with experimental determination, group contribution methods are also utilized to estimate the PTMA solubility parameter. Using the measured and calculated solubility parameter, the Flory-Huggins interaction parameter is calculated for PTMA with current electrolyte systems. Membrane osmometry will be used to confirm the accuracy of the PTMA Flory-Huggins interaction equation. Once confirmed, the PTMA Flory-Huggins interaction equation will be used to discover new electrolyte solvents to improve battery performance.

Emergent properties of sequence-defined conjugated oligomers

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Our understanding of how primary monomer sequence affects functional properties in synthetic oligomers and polymers is relatively underdeveloped when compared with our knowledge in biological polymers such as proteins and DNA. Few studies have investigated sequence-based structure/property correlations and consequently the practical implications for materials applications are poorly understood. This knowledge gap is in part due to synthetic availability. Here, we report the synthesis as well as electron-transport properties of a series of discrete, sequence-defined conjugated oligomers. Using an iterative synthetic approach, we successfully prepared a systematic series of oligomers with a diversity of length and sequence characteristics. Characterization included UV-vis absorption spectroscopy and single-molecule conductance measurements and the data was analyzed with insight from Density Function Theory (DFT) calculations. Our findings demonstrate that sequence definition has a significant impact on the molecular properties. In particular, we found the intramolecular electron transport at single-molecule level varies by more than 10-fold depending on the sequence. From a broad perspective, we anticipate that these findings will inform the molecular design of next-generation polymer-based nanoelectronics.

Hydrogen-bonded films of synthetic polyphenol polymers with prolonged antioxidant activity

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Linear polyphenols, poly(N-(3,4-dihydroxybenzyl) methacrylamide) (P2HMA) and poly(N-(3,4,5-trihydroxybenzyl) methacrylamide) (P3HMA), were synthesized and used with poly(ethylene oxide) (PEO) for assembly of layer-by-layer films. The thickness and composition of the films were monitored by spectroscopic ellipsometry and Fourier transform infrared spectroscopy, respectively. Self-association of gallol groups of P3HMA resulted in exponential growth and strong chain intermixing in the P3HMA/PEO system, while P2HMA/PEO films deposited linearly. P3HMA/PEO coatings could be easily deposited on a variety of substrates, including polymer felts, rendering them antioxidant. Assembly of antioxidant polymers preserved their functionality, while dramatically extending the time scale for radical scavenging by the films. Importantly, both the time and the magnitude of the antioxidant activity could be controlled at the step of film assembly by number of polymer layers within P3HMA/PEO films.

Naturally-sourced, degradable polycarbonates for the reduction of plastic waste accumulation in the natural environment

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Society's love of single use plastic products, for the enormous benefits and convenience they bring to our everyday lives, is truly causing a global crisis. Even with growing awareness, 8 million tons of plastic are entering our oceans each year, and at the current pace, it is predicted that plastic will actually outweigh fish in the world's oceans by the year 2050. Due to the urgency of this global issue, our research focuses on the development of degradable engineering bioplastics. By utilizing waste biomass feedstocks, employing a "plug-and-play" platform system allowing versatility of the polymer's thermal, mechanical, and degradation properties, and exploiting the ability of the materials to degrade in any environment containing sufficient moisture to regenerate natural product-based building blocks, we aim to be part of the solution to the global plastic crisis.

Controlling phase change salogel mechanics *via* polymer-crosslinker bond dynamics

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Strength and reversibility of bonding between physical crosslinkers and polymer chains can strongly determine the ultimate gel mechanics. In this study, we report on controlling the strength of phase-change salogels *via* crosslinker geometry, functionality, and the density of functional groups in the polymer chain. Phase-change salogels consisted of polyvinyl alcohol (PVA) dissolved in an inorganic phase change material (PCM) – lithium nitrate trihydrate (LNH), crosslinked within temperature-responsive networks by hydrogen-bonding amine-terminated molecules. These systems demonstrated reversible temperature-controlled gelation in the temperature range from 15 to 50 °C. The effect of crosslinker geometry (linear vs. branched) and concentration on the gelation temperature was explored. Diethylenetriamine and a second-generation amino-terminated dendrimer, G2, respectively, were used as linear and branched amines. Our results indicate that fewer total number crosslinker moles is required to induce gelation in the case of the branched crosslinker due to the higher average binding energy than in the case of linear crosslinker. The activation energy for crosslinker-polymer bond dissociation will be measured for the linear and branched crosslinker using dynamic light scattering (DLS) and rheological studies. Finally, our findings revealed that density of -OH groups in polymer chain, regulated by the degree of PVA hydrolysis, is another important factor which controls the gelation temperature and gel mechanical properties.

Water-based nanocoatings for flame retardant wood

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Home structure fires are responsible for a majority of fire deaths and injuries in the United States. Wood is a key component of home construction due to its excellent mechanical properties and renewability, but it is inherently flammable. Layer-by-layer (LbL) assemblies, which have been shown to effectively flame retard various substrates, require too much time to assemble on wood due to the slow adsorption kinetics at wood's heterogeneous surface. To circumvent this, two different strategies have been employed. First, a waterborne polyelectrolyte complex (PEC), comprised of environmentally benign polyethyleneimine and sodium hexametaphosphate, was applied in two steps and was shown to significantly increase wood's time to ignition (TTI), while decreasing peak heat release rate (pkHRR) and total heat release (THR). The second strategy employs alterations of the wood's surface chemistry to dramatically improve the deposition and performance of a nanobrick wall LbL coating, comprised of buffered chitosan and vermiculite clay. This approach renders wood flame resistant, preventing ignition during direct flame exposure, with only two bilayers. These unique water-based coatings provide an environmentally benign means to potentially render wood construction much safer.

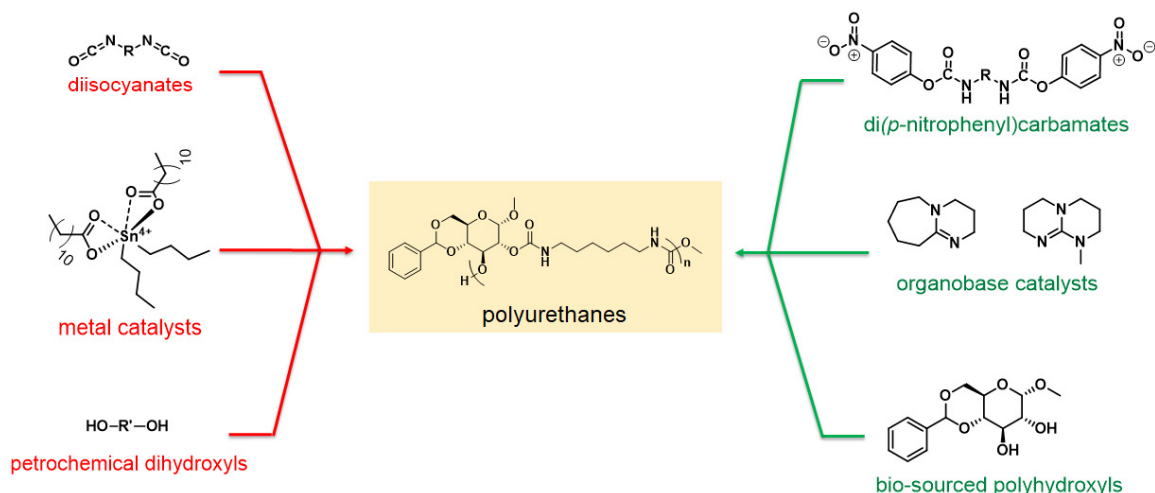
An efficient and mild synthesis for polyurethanes using a glucose-derived biorenewable co-monomer

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Polyurethanes (PUs) are an important class of polymers that are used for a multitude of industrial applications. However, the toxicity and non-renewability of the monomer diols, catalysts, and in particular, the diisocyanate reagents have led to the investigation of less hazardous and more renewable alternatives. Polymerizations involving the reaction of diamines with cyclic carbonates and the use of diols with methyl or phenyl dicarbamates have been studied extensively. Nonetheless, there has been limited research using the more labile di(*p*-nitrophenyl)carbamates with diols to form PUs. Inspired by the potential for di(*p*-nitrophenyl)carbamates to exhibit increased reactivity over methyl or phenyl dicarbamates, the work that will be presented has involved screening of conditions for PU synthesis using di(*p*-nitrophenyl)carbamates, organobase catalysts, and bio-sourced diols, such as methyl 4,6-O-benzylidene- α -(D)-glucopyranoside. Unlike the linear dimethyl and diphenyl carbamates, this system achieves higher polymer molecular weight, without vacuum, after 1 h and 40 °C than a conventionally-produced PU after 8 h at the same temperature. Additionally, these polymers exhibit similar properties and tunability that are found in industrial PUs but more difficult to replicate in some other diisocyanate-free methods. Screening of other bio-sourced diols will probe the compatibility of these di(*p*-nitrophenyl)carbamates with primary, secondary, and even tertiary alcohols. This work, therefore, is also expected to add to the existing library of bio-sourced and renewable monomers that may be capable of replacing petrochemical feedstocks in PU synthesis. The fundamental study of this class of diisocyanate analogues is expected to have far-reaching implications for improving the sustainability of PU synthesis, with this alternative, synthetic route being of broad interest.



Extreme heat shielding by clay/chitosan nanobrick wall on flexible foam

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Flexible polyurethane foam (PUF) is widely used in bedding, transportation, and furniture, despite being highly flammable. In an effort to decrease flammability, an environmentally benign flame retardant nanocoating was deposited on polyurethane foam using layer-by-layer assembly. Foam treated with eight bilayers of chitosan and vermiculite clay was subjected to three different fire scenarios: 10 s torch test, cone calorimetry, and a 900 s burn-through test. In each fire scenario, the nanocoating acts as a thermal shield from the flames by successfully protecting the backside of the PUF, whereas the side directly exposed to the flame results in a hollowed nanocoating that maintains the complex three-dimensional porous structure of the foam. Cone calorimetry reveals that the coating reduces the peak heat release rate and total smoke release by 53 and 63%, respectively, whereas a temperature gradient greater than 200 °C is observed across a 2.5 cm thick coated foam sample during the rigorous burn-through fire test. The thermal shielding behavior of this polymer/clay nanocoating makes this system very attractive in improving the fire safety of polyurethane foam used for various insulating and cushioning applications.

Enhanced ordering in lamellar PS-b-PMMA polymer using ionic Liquid

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Block Co Polymers such as PS-b-PMMA phase separates when casted into a thin films above T_g . Symmetric PS-b-PMMA forms lamellar morphology that can be useful in energy storage such as capacitors, lithium ion batteries, fuel cells and can also function as barrier materials, artificial colors, ion transport channels etc. Since PMMA is Silicon surface selective and PS is free surface selective ideal lamellar morphology is parallel. However due to low χ , block mobility and low surface tension differential parallel lamellae orientation in thin films is only limited to low MW and thickness typically below 70 k MW and 6 Lo . Here we demonstrate the use of an additive such as Ionic Liquid ([EMIM][TFSI]) to induce parallel lamellae orientation in PS-b-PMMA films to have extended to larger thickness and MW limit. Our findings include the induction of parallel lamellar orientation over a thickness of up to 20 domain length and MW of up to 160 k. Our findings has been thoroughly verified using advanced characterization techniques such AFM, GISAXS and Neutron Reflectivity, to study the films through the surface and bulk of the films. These findings may extend the applications of the films in the myriad of energy storage and ion conductive applications.

A halide-free Zeigler-Natta-type catalyst for stereospecific diene polymerization

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Zeigler-Natta catalysts have long been used to polymerize dienes with *cis* selectivity for use in synthetic rubber applications, and improvements to these catalysts has been an active area of research for decades. These catalysts generally contain a halide or, alternatively, include a separate halide donor in addition to the co-catalyst (referred to as “binary” or “ternary” systems, respectively). In this work, we present a counterexample – a halide-free neodymium phosphate catalyst which polymerizes dienes with high *cis* selectivity in conjunction with triisobutylaluminum with no halogen or psuedohalogen present. The polymerization proceeds with desirable pseudo-*living* kinetics and produces 96% *cis*-1,4 content.

Organic dye sequestration from water with a urea functionalized porous organic polymer

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Selective binding of anions using synthetic receptors is a challenging problem in supramolecular chemistry. Additionally, the performance of these receptors in aqueous solvents, where anion desolvation penalties are high is a further complication. Previous efforts have used macrocycles and cage type structures, which often require lengthy and complex syntheses. In this work, we are using a three dimensionally crosslinked porous organic polymer (POP) containing urea sidechain functional groups. Urea is a widely known, neutral anion receptor capable of both accepting and donating hydrogen bonds. However, most urea motifs incorporated in small molecules and polymers do not bind to anions in water due to the competition from solvent hydrogen bonding. To overcome this issue, we propose to encapsulate the urea receptor into a hydrophobic, POP with a cage-like pore structure. We hypothesize that the pore structure of the hydrophobic framework will help desolvate the anionic guests allowing the target to be sequestered and bind to the urea receptor in the pores. As a proof of concept, we present the synthesis and characterization of a urea functionalized porous organic polymer for the sequestration of organic dyes from water.

Synthetic concepts and strategies for a ribosomal approach to sequence-defined polymers

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Despite access to a near limitless diversity of building blocks and a vast array of polymerization techniques, synthetic polymers are largely confined to a narrow range of high-order structures when compared to natural biopolymers. The lower levels of structural sophistication and complexity observed in synthetic polymers is due in part to an inability to induce perfect sequence control in a tractable and scalable manner. Inspired by nature's ability to control sequence we have leveraged chemical synthesis, Flexizyme, and cell-free protein synthesis technologies to utilize new substrates, form new bonds, and in-turn synthesize novel sequence-defined polymers via ribosome-mediated polymerization.

Sustainable and degradable epoxy resins containing multifunctional biobased components

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Lignin was investigated as a sustainable source to produce epoxy resins with desirable physical behavior. Epoxy resins are thermoset polymers widely used in composites, coatings and adhesives, with applications spanning automotive and aerospace industries, structural components, and wind turbine blades, among others. Vanillic acid, a product of lignin depolymerization, was investigated as a replacement for the diglycidyl ether of bisphenol A (DGEBA) in anhydride-cured epoxy resins. Vanillic acid was functionalized with epoxide groups and subsequently cured with an anhydride curing agent. The resulting vanillic acid-based epoxy resins exhibited high glass transition temperatures and similar elongation at break and tensile toughness as compared to conventional DGEBA-based epoxy resins. The presence of ester groups in the cured network was also exploited as a route to enhance the end-of-life options for the epoxy resins. The accelerated hydrolytic degradation behavior of the ester-containing epoxy resins was explored, through monitoring of the polymer mass loss after exposure to a basic solution at moderate temperatures. The vanillic acid-based epoxy resins exhibited rapid degradation in a basic solution, in contrast to the slow degradation rate of the traditional DGEBA-based epoxy resin. The mass loss behavior showed good agreement with predictions from a solid-state kinetic model and mass spectrometry confirmed the mechanism was surface erosion through ester hydrolysis.

Rapid ordering of block copolymer films by utilizing the effect of as cast nucleation

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The self-assembly of Block Copolymers (BCPs) provides a facile and cheaper alternative to produce nanostructures for next generation nanomanufacturing via directed self-assembly. The rapid and continuous processing of BCPs is a necessity to realize their full potential for use in industrial applications. Additionally, the underlying molecular mechanisms involved in BCP self-assembly are not completely understood. We are trying to understand the molecular mechanism governing self-assembly of BCPs and use the acquired knowledge to devise innovative processes for rapid and template-free self-assembly of BCPs. In this work, we demonstrate a way for rapid ordering (~10 sec) of BCPs using pre-nucleated grains in as-cast films imparted by judicious choice of casting solvent and film casting method. The rapid solvent evaporation results in formation of short range ordered BCP nanostructures which act as nuclei for subsequent ordering of BCP to larger grains during thermal annealing. The solvent evaporation quenches the BCP morphology in a weakly segregated state. These weakly segregated domains undergo a transition to equilibrium segregation in melt state. The time dependence of increase of domain spacing in weakly segregated as cast morphology to the equilibrium state shows a non-linear trend. Controlling the as cast morphology followed by Cold Zone Annealing allows the rapid fabrication of perpendicularly oriented poly(styrene)-block-poly(methyl methacrylate) lamellar structures in 20-500 nm thick films. This rapid self-assembly approach may pave the way for use of BCP self-assembly in industrial applications. Additionally, we study the effect of different solvent and film casting methods to understand the phase separation and nucleation in as cast films.

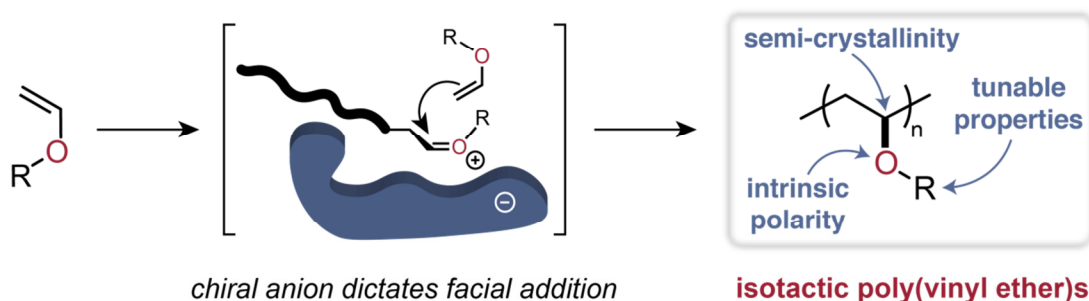
Catalyst-controlled stereoselective polymerization to form polar, vinyl ether-based thermoplastics

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The physical properties exhibited by synthetic materials are directly linked to their microstructures. Introducing even limited degrees of stereoregularity to otherwise atactic materials can have pronounced effects on their thermal, mechanical, and optical properties. In comparison to coordination polymerizations (e.g., polyethylene, polypropylene, etc.), cationic polymerization methods typically result in materials with undesirable mechanical properties due to low degrees of stereoregulation. To address this challenge, we have designed chiral counterions that systematically bias the reactivity and chain-end stereochemical environment during cationic polymerization. This approach overrides conventional chain-end stereochemical bias to achieve catalyst-controlled stereoselective polymerization. The method is general to vinyl ether substrates and provides access to a range of homopolymers and copolymers with high degrees of isotacticity. The obtained materials represent a new class of semi-crystalline thermoplastics with a unique combination of mechanical and surface properties. This presentation will discuss the application of this methodology to a variety of vinyl monomers, as well as the impact of isotacticity and monomer design on the properties of the obtained materials.



Sustainable hydrogel-base materials for capture and storage of excessive liquid water through ring-opening copolymerization with bio-based materials and carbon dioxide

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Water is essential to life on Earth, however accessing, capturing, and releasing good quality water is difficult in many parts of the world. Currently, common methods of solidifying water use superabsorbent polymers (SAPs), a class of materials that absorbs large quantities of water without dissolving due to their ionic nature and interconnected structure. For instance, sodium salts of cross-linked poly(acrylic acid) and starch are widely used as SAPs commercially. Although these materials can effectively capture water at >100-fold their mass, they are petrochemically-derived, non-degradable materials that only solidify water. To address these concerns, we present herein, our approach to incorporate natural products and carbon dioxide (CO₂) in the production of degradable SAPs. Implementation of degradable bio-based polymeric materials not only benefit the environment but utilize the renewability of natural products. In addition, the use of CO₂ as an inexpensive C1 feedstock is highly attractive since it is cost-effective, nontoxic, and abundant. Through the metal salen catalyst-promoted ring-opening copolymerization of epoxides with CO₂, the synthesis of sustainable polycarbonates will be discussed. An initial focus includes the advancement of epoxide-CO₂ copolymerization using naturally-derived monomers. Following chemical modification to incorporate hydrophilic side chain moieties, the polycarbonates produced are expected to serve as naturally-derived and hydrolytically degradable analogues of the well-established poly(acrylic acid). Furthermore, these materials are designed to act as simple sustainable fertilizer-releasing water containment systems.

An automated platform for controlled polymer synthesis

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The precise control over macromolecular chemical composition and architecture is the hallmark of biological polymers giving rise to a wide variety of material properties and functionalities. Polymer chemists have work to emulate nature's synthetic aptitude through the development of controlled polymerizations, enabling the production of polymers of uniform and predefined molecular weight, controlled topology, and precise functionalities. However, recent efforts to produce complex materials from controlled polymerizations have suffered from tedious multistep synthesis or limited control, imposing practical limits on versatility and tunability.

Here we develop an automated synthesis platform to design and produce polymers with any molecular weight distribution profile. We present the fundamental fluid mechanical framework for the design of laboratory scale polymerization flow reactors, and demonstrate the platform's universality by implementing a wide range of controlled polymerizations. Additionally, the automated platform has been implemented for the topology control of bottlebrush polymers. This work demonstrates the ability to shift the manual labor of chemical synthesis to a digital realm where a higher level of precision can be achieved. Our technological development will lead to a significantly accelerated and simplified synthesis procedure, enabling the rapid testing of ideas.

Real-time insight into the doping mechanism of redox-active organic radical polymers

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In recent years, organic radical polymers have received great attention as active materials for fast-charging battery electrodes. Organic radical polymers are electrochemically active owing to the reversible reduction-oxidation (redox) reaction of pendant radical groups and offer a vast synthetic landscape for customization. Interest in these polymers as battery electrodes has grown due to its high theoretical capacities, fast electron transfer kinetics, and long cyclability. One commonly studied stable nitroxide radical polymer is poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA). Upon oxidation or charging, the neutral nitroxide radical transfers an electron to the current collector, resulting in an oxoammonium cation. Simultaneously, anions dope the polymer cathode to maintain charge neutrality. Upon reduction or discharging, the polymer is de-doped and the neutral nitroxide radical is retrieved. Electronic charge transfer within the organic radical polymer occurs by an electron hopping mechanism with Brownian motion of the redox centers.

Although there is much more understood about electron transfer in organic radical polymers, there is significantly less understood regarding mass transfer and the doping mechanism, which is equally important for understanding the overall redox mechanism. Here, we specifically examine ion transport in PTMA cathodes for nonaqueous batteries. Using *in situ* electrochemical quartz crystal microbalance with dissipation monitoring (EQCM-D), we quantitatively observe the ion transport (or doping) process in organic radical polymers during the redox reaction for the first time. Our results show that two counterion transfer modes dominate: doping by lithium-ion expulsion and doping by anion uptake. The dominance of one mode over the other is controlled by anion type, electrolyte concentration, and timescale. These results impact any scenario in which electrolyte is in contact with a non-conjugated redox active polymer and present a means to quantify doping effects. This work is reported in Wang, S., Li, F., Easley, A.D., & Lutkenhaus, J.L., *Nature Materials* 18 (1), 69-75 (2019).

Solvent induced switchable phase separation of polymer-grafted nanoparticle blends

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Polymer-grafted nanoparticles (PGNPs) have attracted great attention in the past few years for the application of nanoelectronics, medical diagnosis, and enhanced mechanical properties. However, these applications require the particles to form well-controlled structures. We developed a method to switch the phase-separated structures of poly(methyl methacrylate) silica (PMMA-SiO₂) and poly(styrene) silica (PS-SiO₂) blends by using direct immersion annealing (DIA). Our results show that by varying the solvents in the DIA solution, two different and switchable morphologies are formed in the PMMA-SiO₂/PS-SiO₂ blends. By repeating the process for over 10 times, it reveals that the switchable process is stable. Kinetic study also shows that the process is efficient, which stabilizes within 30 seconds.

Unusually fast and large actuation from multilayer polyelectrolyte thin films

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Polymers responsive to external stimuli (e.g., electric field, chemical vapor, light) are of great interest for smart materials such as sensors and soft robotics. A vapor-driven multilayer polymer actuator, capable of fast and large-scale actuation, is described here. This Janus-like actuator is prepared with two polyelectrolyte multilayer systems (polyethylenimine (PEI)/poly(acrylic acid) (PAA) and polyurethane (PU)/poly(acrylic acid) (PAA)) using layer-by-layer assembly (LbL). The differing hydrophilicity of these two nanocoatings results in different swelling behavior in water and organic solvents, which leads to vapor-responsive mechanical motion. The bending/curling degree of this polymeric actuator can be precisely controlled by changing the thickness ratio of the two layers. A vapor sensor was constructed to demonstrate the environmental detection ability of this unique actuator.

Self-assembly of block copolymers with ionic liquid crystals in thin films

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Block copolymers (BCPs) self-assemble into ordered nanostructures leads to plenty of promising applications in the area of electronics and energy storage. Thus, improving the ordering of BCP is crucial to optimize its performance in different applications. Addition of Ionic Liquids (ILs) to BCPs has been reported a facile method to realize fast ordering because of its plasticization effect and wetting characteristics tunability. With similar chemical structure to IL, Ionic Liquid Crystals (ILCs) are liquid-crystalline salts also consisting of cations and anions. Differently, liquid-crystalline nature and thermotropic transition will provide ILC with more fascinating features than IL when it is added to BCP. However, BCP/ILC system has not been well studied as BCP/IL system does. In this study, the effect of the addition of ILC on the self-assembly of BCP under different annealing condition has been investigated by using Atomic Force Microscopy (AFM) and Grazing-Incidence Small-Angle X-ray Scattering (GISAXS). It can be highlighted that the addition of ILC can promote the ordering of BCP without enlarging the domain size due to its thermotropic transition.

Functionalization of graphene oxide with multi-hydroxy-containing phosphoramidate: Preparation and flame-retardation on epoxy resin

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Graphene and its derivatives have shown promising flame retardant effects for polymers due to strong barrier properties, high thermal stabilities and surface adsorption capability etc. To enhance the flame-retardant efficiency of graphene-based fillers, many approaches have introduced P/N flame retardants onto graphene by chemical grafting reactions which consume lots of solvent and take complicated processes. In this work, a novel functionalized graphene oxide (f-GO) decorated with phosphorus/nitrogen (P/N)-containing molecules was fabricated using a facile water-based procedure. The chemical structure and micro-morphology were well characterized by a combination of experimental and theoretical methods. Reactive force fields based molecular dynamics simulations revealed at the atomic level that the GO sheets are successfully functionalized with P-N flame retardant molecules by means of hydrogen bonds. Subsequently, f-GO with extremely low loading was introduced into epoxy resin (EP) for reducing its flammability. Thermogravimetric analysis suggests that f-GO significantly reduces the maximum mass loss rate of EP and enhanced the char-yield during heating. Combined with the results of a microscale combustion calorimeter and limiting oxygen index, EP/f-GO2 showed better flame retardancy than the other nanocomposites. Furthermore, the presence of 2 wt% f-GO substantially reduced the fire hazard of EP, resulting in 29.3% decline in the peak heat release rate, as well as 73% and 65% reduction in total smoke production and rate of smoke release, respectively, according to cone calorimetric tests. Based on the analyses of the char layers, f-GO was determined to promote the formation of a more protective phosphorus-containing char barrier for EP during combustion, indicating an effective condensed phase flame retardant mechanism.

Improving mechanical properties of fatty acid-derived thermoplastic elastomers by incorporating a transient network

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Thermoplastic elastomers (TPEs) are widely used in electronics, clothing, adhesives and automotive components due to their high processability and flexibility. ABA triblock copolymers, in which A represents glassy end-blocks and B a rubbery midblock, are commercially available TPEs. The most commonly used triblock copolymer TPEs contain glassy polystyrene end-blocks and rubbery polydiene mid-blocks. However, commercial TPEs are derived from petroleum whose manufacturing and disposal have undesired environmental impacts, motivating the development of TPEs from sustainable sources. Vegetable oils and their fatty acid derivatives are attractive alternatives to petroleum due to their abundance and low cost. Our group has previously reported replacing polydienes in commercial TPEs with sustainable polyacrylates derived from fatty acids. However, polymers with bulky constituents, such as the long alkyl side-chains of fatty acid-derived polymers, typically exhibit poor mechanical performance due to lack of entanglements in the rubbery matrix. To improve the mechanical properties, transient networks were incorporated into the fatty-acid derived midblock through either hydrogen bonding or ionic interactions. In the first approach, triblock copolymers were synthesized containing polystyrene end-blocks and poly(lauryl acrylate) (PLAc) as the midblock. Hydrogen bonding was incorporated by including acrylamide as a comonomer in the PLAc midblock. The presence of hydrogen bonding in the TPE matrix significantly enhanced the modulus, strain at break, and tensile strength. In the second approach, triblock copolymers were synthesized with poly(methyl methacrylate) end-blocks and a PLAc midblock, and ionic interactions were introduced into the midblock by neutralizing the comonomer methacrylic acid. The enhancement of tensile strength increased linearly with the logarithm of the midblock relaxation time, up to as much as 16-fold improvement, without losing significant extensibility.

Assembling poly(styrene)-b-poly(dimethylsiloxane) functionalized with triazole groups through DIP-coating and its copper complexes

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Films of poly(styrene)-b-poly(dimethylsiloxane) functionalized at the end of the polymer chain with triazole group were assembled through dip-coating technique using different solvents, nanostructures were produced and analyzed through the atomic force microscopy. The well-defined diblock copolymer was synthesized through anionic and ATRP techniques followed by functionalization of an azido group at the end of the polymer chain, the triazole molecule was introduced by the use of click chemistry. Copolymer films were prepared by immersing N-Type (100) silicon wafers in the different polymers' solutions using the Dip-Coating technique. The velocity of the immersion and withdraw was 2 mm by minute. The hydrophobic PDMS-PS-T complexed with copper was dissolved in polar solvents which indicate it became more hydrophilic due probably to a complex formation between triazole group and copper metal. Depending on the polarity of the solvent, different nanostructures were obtained as nanoplates, nanotriangle, and nanofibers which is due to the self-assembly behavior of the diblock copolymer. Also, it was observed that copper nanoparticles were located at the nanostructure perimeter. Self-assembly of PDMS-PS-T is a solvent-depend process and the triazole group at the end of the polymer chain is able to complex the copper salts forming materials with an important potential in catalysis application, in a green process.

APO-BMI and the two-tone billet: A material investigation into polymorphism

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APO-BMI glass syntactic foams have suffered from intermittent “two-tone” coloration issues for over a decade. Historically, this issue has been approached through a series of very methodical processing parameter manipulations with target billet density changes having the largest effect in two-tone manifestation. The darker regions display greater density than the lighter regions and are always found on the upper part of the billet (Figure 1). However, little is known regarding the root cause of this discoloration. APO-BMI, the monomeric species used to produce this billet, is a known polymorph: a material capable of different molecular packing orders.

Polymorphic species can be the result of different structural conformations or solvate/hydrate species and may have different properties such as melting point, color, and density, among others. This polymorphic behavior is hypothesized to be the cause of the two-tone discoloration. Analysis of the different APO-BMI polymorphs through differential scanning calorimetry (DSC), Fourier-transform infrared (FTIR) spectroscopy, and thermogravimetric analysis (TGA) was performed. Three polymorphic species have been identified, including a previously unidentified hydrate. Through characterization and better understanding of these polymorphic phenomena, we have successfully achieved a single-tone billet under conditions in which only two-tone samples have been previously observed.

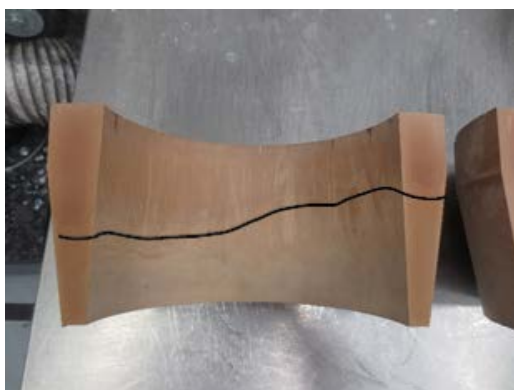


Figure 1. Cross-section of billet displaying two-tone behavior (two-tone delineation marked just below natural material border)



Figure 2. Single-tone billet achieved under conditions known to drive two-tone phenomenon

Energy and Electronics

Synthesis and applications of semiconducting polymers

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This lecture will focus on new synthetic methods for the formation of conjugated polymers and emerging applications. New synthetic methods include living chain-growth and step-growth metal free polymerizations to create conducting polymers. These methods open new possibilities for the formation of functional assemblies in addition to eliminating the use of catalytic systems that can give rise to trace impurities. Polymer optical properties are also of interest and in addition to the use of their emissive properties, we have been exploring magneto-optical effects. In particular conjugated materials give rise to large rotations of the plane of polarization of light propagating along the axis of an applied magnetic field. This is known as the Faraday effect and the ability to measure small changes in the plane of polarization can be used to make sensors capable of detecting miniscule magnetic fields. Traditionally materials that display this behavior are inorganic solids containing unpaired electrons. However, organic semiconducting polymers have recently been shown to display large Faraday rotations that exceed those of inorganic materials. The ability to move to processable tailorable organic optical structures is very attractive for the construction of new generations of sensors. Design principles to create materials with large Faraday rotations using helical semiconductor polymer structures and integrated open shell electronic structures will be presented.

Pyrrole-based organic semiconducting materials for organic electronics applications

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Pyrrole is an excellent building block for the synthesis of organic semiconductors. However, the synthesis of pyrrole organic semiconductors is challenging because pyrroles are prone to oxidation. The smallest *S*, *N*-heteroacene, thieno[3,2-*b*]pyrrole is a good building block for organic semiconductors due to its electron density, asymmetry, and easily modifiable NH group. Recently we shown that organic semiconductors from thieno[3,2-*b*]pyrrole display “nearly-ideal” OFET characteristics without compromising charge carrier mobilities or threshold voltages. [1] We have varied the structure and topology to investigate the relatively under-explored banana shape thieno[3,2-*b*]pyrrole organic semiconductors and the influence of the heteroatom.[1-3] Banana shaped donor-acceptor molecules with benzothiadiazole, fluorinated benzothiadiazole acceptors and thieno[3,2-*b*]pyrrole donor (TP-BT2T-BT and TP-FBT2T-TP) have been reported by our group (Figure 1), and the OFET parameters were evaluated in a bottom-gate/bottom-contact (BGBC) OFET architecture. Hole mobility of $0.08 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was measured for the molecule (TP-BT2T-BT) with benzothiadiazole as the acceptor.[1] The molecule containing fluorinated benzothiadiazole (TP-FBT2T-BT) showed hole mobility of $1.57 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. [2] Lengthening conjugation by synthesizing conjugated polymers was employed to facilitate the hole transport and to obtain comparatively stable semiconductors. Our group reported the donor-acceptor polymer containing thienopyrrole donor and diketopyrrolopyrrole acceptor, P(DPP-TP) (Figure 1), and the OFET parameters were evaluated with bottom-gate/top-contact (BGTC) OFET architecture. An increase in hole mobility to $0.12 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was observed for the polymer (P(DPP-TP)) as compared to the conjugated small molecules.[4] We will discuss also discuss the synthesis and characterization of three organic semiconductors containing terminal thieno[3,2-*b*]pyrrole moieties and central aryl-vinylene-aryl units {phenyl-vinylene-phenyl (PVP), furan-vinylene-furan (FVF) and thiophene-vinylene-thiophene (TVT)}. By changing the aromatic group in the central unit, optical and electrochemical properties were systematically varied.

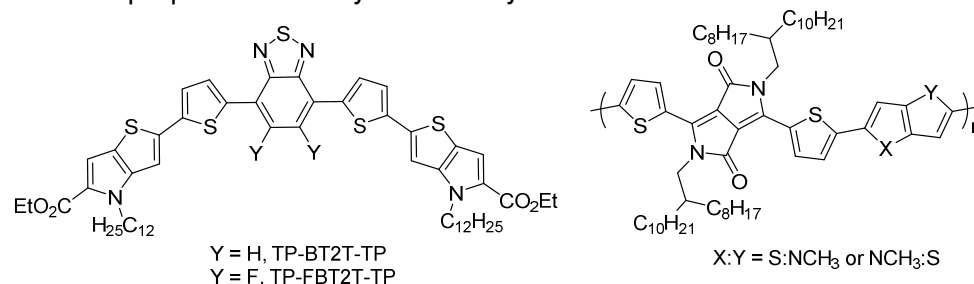


Figure 1. Pyrrole based donor-acceptor small molecules and polymers for OFETs

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Materials for transient electronics**John A. Rogers**

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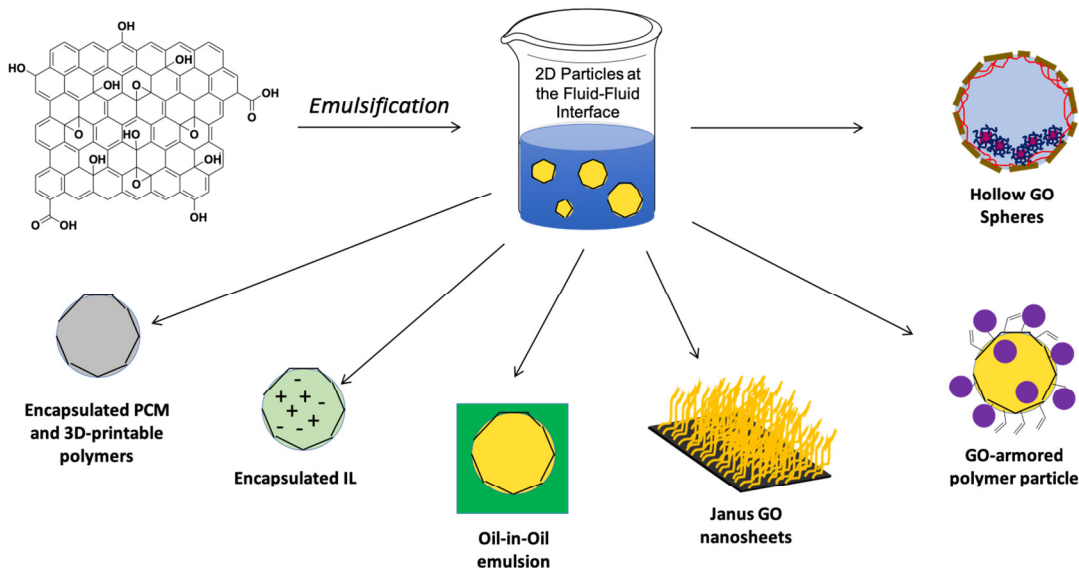
A remarkable feature of modern integrated circuit technology is its ability to operate in a stable fashion, with almost perfect reliability, without physical or chemical change. Recently developed classes of electronic materials create an opportunity to engineer the opposite outcome, in the form of 'transient' devices that dissolve, disintegrate or otherwise disappear at triggered times or with controlled rates. Water-soluble transient electronics serve as the basis for potentially far-reaching applications in zero-impact environmental monitors, 'green' consumer electronics and bio-resorbable biomedical implants. This presentation describes the foundational concepts in chemistry, materials science and assembly processes for bioresorbable electronics in 1D, 2D and 3D architectures, the latter enabled by approaches that draw inspiration from the ancient arts of kirigami and origami. Wireless sensors of intracranial temperature, pressure and electrophysiology designed for use in treatment of traumatic brain injury and nerve stimulators configured for accelerated neuroregeneration provide application examples.

Pickering emulsions stabilized by 2D particle surfactants and their applications

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The interface between two fluids is not only important for defining reactivity of dislike materials, but it is also useful in the preparation of stable higher order structures. The Pentzer lab has developed 2D carbon-based nanosheets that assemble at different fluid-fluid interfaces including oil-water, oil-oil, ionic liquid-water, and ionic liquid-oil and demonstrated the use of these Pickering emulsions to template higher order composite structures. Graphene oxide (GO) and its functionalized analogues are used as the 2D particle surfactants, and are especially attractive given they have properties distinct and complimentary to the more commonly studied spherical and rod-like counterparts, and because these nanosheets are multifunctional (e.g., antimicrobial, good gas barriers, precursor to electrically conductive nanosheets, etc.). Recent advances from the Pentzer lab will be reported, including preparation of Janus nanosheets, oil-in-oil emulsions, encapsulated ionic liquids, compartmentalization of phase change materials, and GO coatings for 3D printable polymers to prepare conductive structures. This work makes use of fundamental organic chemistry reactions and thus gives access to unique structures and assemblies of interest for a broad range of applications in a scalable fashion.



Ultra-thin conformal coating for spin-on doping applications

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As devices become ever smaller and more sophisticated, there is also a general need for creating high quality defect-free thin coatings of polymers on three-dimensional wafer topography. To address this challenge, we developed a spin-on polymer brush material, which comprises of a dopant moiety with a universal adhesive dopamine end group. We demonstrate that the polymer coating is highly conformal and free of pinhole defects, even when only a few nm thick, or when coated over high aspect ratio over 200 nm deep trench topography. Our investigations demonstrate that the dopamine end group enables stable sub-10 nm thick conformal coatings on three-dimensional surfaces.

Furthermore, on acute three-dimensional semiconductor topography, the creation of highly doped abrupt, ultra-shallow junctions with lateral control are essential for successful source-drain contacts. In consideration of this need, we extended the above polymer brush concept further by incorporating a suitable implant dopant atom, such as boron, into the monomer structure. After conformal coating and a subsequent rapid thermal annealing process, the dopant atom is driven into the semiconductor substrate underneath the polymer film. This is potentially very useful for uniform all-around doping of 3-dimensional topography such as FinFETs or Nanowire-FETs. A high dopant dosage on silicon substrate with appropriate shallow implant characteristics was demonstrated for the end-functionalized dopant polymer brush, highlighting one of the promising applications of such conformal coatings.

Dendrimeric Pi-conjugated polymer hybrids and electrochemically molecularly imprinted polymer (E-MIP)s sensors

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Pi-Conjugated or electrochemically conducting polymers have inspired the development of new materials properties in polymers. Often these polymers are linear or oligomeric in nature to have some interesting charge transfer or electron transport properties. Dendrimeric polymers inspire the synthesis of functional hyperbranched systems with different properties related to end-group functionality, dendrimer-box concepts, and high-molecular weight (MW) viscoelastic properties. In the span of our work on dendrimeric materials, we have focused to incorporate aspects of energy transfer and charge transfer properties combined with hybrid nanoparticle systems. Dendrimers have enabled controlled aggregation and self-assembly in 2-Dimensional planar substrates. Using mostly convergent routes, we have demonstrated these key properties in polythiophenes and polycarbazoles. In the second part of this talk, the focus is mostly on the development of dendrimer inspired electrochemical-molecular imprinted polymers (E-MIPS) to develop highly selective and sensitive sensors. Different transducer devices were utilized to enable sensing of various analytes such as drugs, nerve agent analogs, explosives, etc. These directions have shown the possibilities for rational dendrimeric polymer design development from innovative synthetic routes to functional devices.

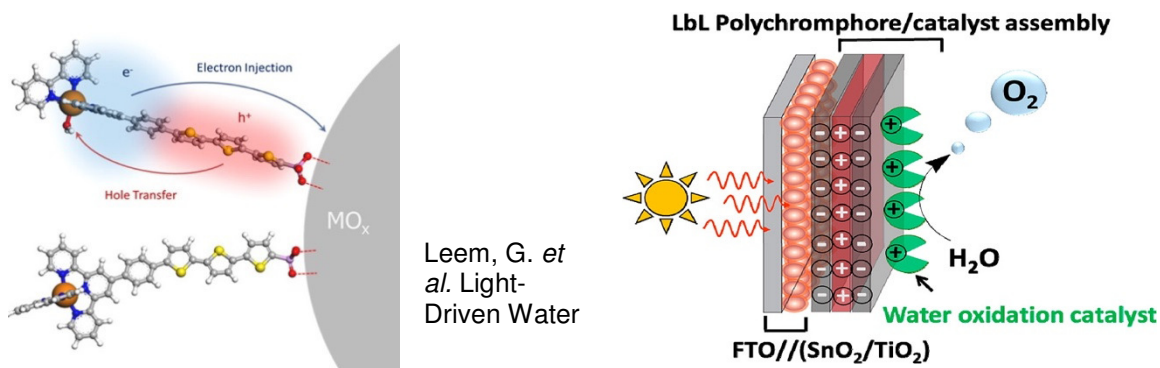
Chromophore-catalyst assemblies for solar fuels

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The dye-sensitized photoelectrochemical cell (DSPEC) represents a novel approach to combining molecular chromophores and catalysts with semiconductors to effect light driven production of solar fuels. A multidisciplinary approach has been used to develop and study molecular and polymer assemblies for light driven water oxidation at a DSPEC photoanode and proton reduction at a photocathode. The work aims to understand mechanisms and dynamics for the photoprocesses occurring at the molecular/semiconductor interfaces. The talk will present an overview of work done during the past several years, involving the design, construction and study of molecular and polymer-based assemblies of light absorbing chromophores and catalysts, primarily aimed at water oxidation at the DSPEC anode.



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Three-dimensional morphological analysis of polymer blends through combined ToF-SIMS/AFM

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In this talk I present three dimensional analysis of complex organic and polymeric blends using time-of-flight secondary ion mass spectroscopy (ToF-SIMS). ToF-SIMS enables three-dimensional compositional analysis using a focused ion beam along with an argon cluster beam for depth profiling. Combined with atomic force microscopy (AFM), topographical and compositional information can be acquired simultaneously. ToF-SIMS is a powerful technique for elucidating the structure and chemistry of complex polymeric and organic blends where optical, electron, and surface probe microscopy may be unable to resolve chemical differences. We demonstrate the 3-D analysis of blends of bottlebrush polymers and linear polymers, asphaltene deposits, and polymeric multilayers. We demonstrate the use of ToF-SIMS to quantify compositions in blend samples and understand the phase behavior of blends and mixtures. ToF-SIMS/AFM is a powerful technique that enables analysis of unlabeled polymer blends, composites, and self-assembling systems. The authors thank the National Science Foundation (CBET-1626418) for support and access to the TOF-SIMS/AFM through the MRI program.

Influence of distortions and defects in soft matter crystals for metamaterials and energy storage

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Materials based on the double gyroid multicontinuous tubular structure can exhibit exotic properties due to the unique 3D network structure. The nature, frequency and potential influence of topological defects present in the interpenetrating gyroid networks on various metamaterial properties is an open question. We examined a polystyrene – polydimethylsiloxane diblock copolymer possessing the double gyroid morphology in order to identify and classify the types of topological defects present. The large volume reconstructions were made by sequentially ion beam milling and low voltage electron beam imaging. Different types of local point-like and surface defects were examined. Point like topological defects include node functionality defects, network breaks and network-network joints (bridges). Grain boundaries constitute surface defects arising during impingement of growing grains. Defects will influence properties ranging from charge and mass transport, to wave propagation and band gaps, and battery performance in materials with the gyroid structure.

The Crawford group: At the interface of sensors and soft materials**Kaitlyn E. Crawford**

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Established in 2017 at the University of Central Florida in Orlando, the Crawford Group, known also as the Soft Functional Materials and Sensors Lab, seeks to cultivate the synergy found in working across disciplines such as materials science, bioengineering, nanotechnology, chemistry and medicine, to address overarching human-health and environmental challenges relevant to our 21st Century society. Specifically, the Crawford group develops soft functional materials that are designed for dynamic use at the biological interface. Research interests related to these efforts include: block copolymers, nanomaterials, interfacial interactions, soft matter synthesis and characterization, self-assembly, wearable sensors, and bionic materials. At the Polymers for Advanced Technologies Workshop, Dr. Crawford will introduce critical foundries from which she is building her independent research and share details of emerging projects in her group related to the interests of the polymer chemistry and bioelectronics community, to receive feedback from senior peers, and to actively engage in the symposium through discussion and participation throughout.

Bridging the gaps with nitrogen, silicone and sulfur atoms for efficient BHJ solar cells

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Integration of heteroatoms, such as nitrogen, silicon and sulfur, into molecular structures are in particularly interesting because these atoms are capable of imparting desirable material properties and provide a means for affording high performance bulk heterojunction (BHJ) solar cells. In this contribution, heptacyclic dithienocyclopentacarbazole (DTC)-based non-fullerene acceptors (NFAs) and other new derivatives featuring additional nitrogen and silicon atoms are reported. In addition, a new type of sulfur-based substituents is introduced to improve molecular planarity. These newly synthesized NFAs are combined with suitable p-type polymer and the corresponding photovoltaic properties are characterized.

Heating, curing, and welding of 3D printed carbon nanotube-polymer systems by locally induced RF heating

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A key obstacle facing 3D-printed plastic parts in engineering applications is the weak weld between successive filament traces, which often leads to delamination and mechanical failure. This is the chief obstacle to the use of thermoplastic additive manufacturing. We have recently demonstrated a novel concept for welding 3D-printed thermoplastic interfaces using intense localized heating of carbon nanotubes (CNTs) by electromagnetic irradiation. We apply CNT-loaded coatings to 3D printer filament; after printing and microwave exposure, this is shown to improve the weld fracture strength. These remarkable results open up entirely new design spaces for additive manufacturing and also yield new insight into the coupling between dielectric properties and electromagnetic field responses for nano-filled materials. Further study has shown that low-frequency RF fields can couple with CNT networks, allowing for a variety of rapid scanning techniques without any need for shielding. We have demonstrated that such techniques can be used to induce rapid localized heating in a range of technologies, including thermoset 3D printing and automotive thermoset curing.

Turning the tables: from polymer insulator to heat conductor

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Interdisciplinary research in functional polymers and advanced manufacturing holds the key to solving the existential challenges of energy, healthcare and the environment facing humanity. Many of the technological advances that we take for granted today, such as solar cells, came from fundamental advances in materials research and manufacturing techniques. Development of heat conducting polymers would open up a diverse array of thermal applications ranging from energy harvesting to electronics cooling. In this talk, I will present our research on molecular engineered polymers with desired thermal properties and provide fundamental understanding how multiscale structure controls these properties [1-3]. I will also address how the science and engineering of these materials are transformed by advanced manufacturing. First, stretched polyethylene films transfer heat four times faster than stainless steel [1,3]. Second, we have designed and developed amorphous polymers with a 10-fold increase in thermal conductivity by chemical vapor deposition technique [2]. Third, by leveraging advanced manufacturing technologies, I will discuss thermally conductive polymer-based materials by 3D printing. I will conclude with a brief discussion of future research that will further develop functional polymers and integrated systems by advanced manufacturing.

Keywords: heat conducting polymers; thermal energy; electronics cooling, advanced manufacturing (3D printing).

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Ambient temperature waterborne polymer/reduced graphene oxide nanocomposite films:
Effect of reduced graphene oxide distribution on electrical conductivity

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Graphene has enormous potential as an ideal filler in nanocomposite polymeric materials for a wide range of applications such as coatings, electronic devices, and electromagnetic shielding. We have prepared ambient temperature film-forming and electrically conductive polymer/reduced graphene oxide (rGO) nanocomposite films based on styrene and n-butyl acrylate by environmentally friendly aqueous latex based routes, namely miniemulsion polymerization using graphene oxide (GO) as surfactant and “physical mixing” approaches (i.e. mixing of aqueous polymer latex with aqueous GO), followed by heat treatment of the films to convert GO to rGO. The distribution of GO sheets and the electrical conductivity depend strongly on the preparation method, with electrical conductivities in the range 9×10^{-4} – 3.4×10^2 S/m. Physical mixing approaches resulted in higher electrical conductivity than miniemulsion approaches, which is attributed to the former providing a higher level of self-alignment of rGO into larger linear domains. These results present substantial insight into how the distribution of GO sheets within hybrid nanocomposites can be controlled by preparation method, thus enabling nano-engineering design for specific potential applications.

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Nature-inspired structural supercapacitor electrodes based on dopamine functionalized graphene oxide

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Structural energy storage devices address both energy storage and structural functionalities in a single unit leading to significant mass and volume savings in aircraft, vehicles, and satellites. Here, we utilize the ‘brick and mortar’ structure of nacre to fabricate mechanically strong supercapacitor electrodes using vacuum filtration. We report on electrodes consisting of branched aramid nanofibers (BANFs) and reduced dopamine functionalized graphene oxide (rGO-DOPA). Recently developed branched aramid nanofibers, nanoscale Kevlar® fibers, are of great interest due to their exceptional mechanical properties, such as ultimate strength and stiffness. rGO has remarkable properties such as high electrical conductivity, high surface area, and excellent mechanical properties. BANFs interact with rGO through hydrogen bonding and π - π stacking interactions. The interfacial interactions were enhanced by functionalizing GO with dopamine – a highly adhesive molecule mimicking the mussel proteins. Moreover, calcium ions were added to chelate with the rGO-DOPA flakes. We studied the effect of the interface modifications and BANF composition on the mechanical and electrochemical performance. This study provides an efficient strategy for generating stronger structural electrodes.

A tale of redox-active organic radical polypeptides as electrode materials: From full organic batteries to electron transfer kinetics

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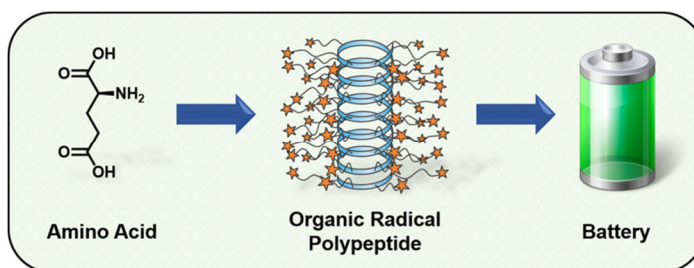
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This work seeks to develop polymer nanocomposites containing organic redox-active moieties as electrode components to circumvent the drawbacks of conventional lithium ion batteries, *e.g.*, use of scarce resources, safety concerns, high carbon emissions, and high-cost recycling. L-Glutamic acid-based polypeptides with pendant 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) and viologen moieties were designed for utilization as viable materials for next-generation battery cathodes and anodes, respectively, due to their stabilities and redox processes. The helical structure adopted by these polypeptides provides opportunities to control the placement of the redox-active moieties in three-dimensional space by tuning their distribution along the polymer backbones. This presentation will highlight the synthetic processes to prepare redox-active polypeptides and the fabrication of peptide-based full organic batteries, followed by the investigation of physical, structural and electrochemical properties and electron transfer kinetics studies of the materials, by utilizing a variety of thermal, spectroscopic, imaging and electrochemical techniques. It is anticipated that the synthetic development of polypeptide-based electrodes will provide insights into the mechanism of electron transfer in redox-active materials and, ultimately, address the need for high-performance and sustainable alternative energy sources (*e.g.*, supercapacitors, biosensors) towards a greener and more sustainable world, which is facing a never-ending demand for energy technologies.



Thermoelectric performance improvement of polymer nanocomposites by selective thermal degradation

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Our current energy production results in a tremendous amount of waste heat. In an effort to more efficiently utilize dissipated heat, multilayer thin films, comprised of poly(diallyldimethylammonium chloride) (PDDA), graphene, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and double-walled carbon nanotubes (DWNT), were prepared using layer-by-layer assembly followed by heating in an inert atmosphere to degrade film constituents to varying degrees. PEDOT:PSS was used to stabilize graphene and DWNT. A 20 QL thin film, that is 21 nm thick, heated to 425 °C for 60 minutes exhibits a simultaneous increase in electrical conductivity and Seebeck coefficient as compared to an unheated film. This behavior is not commonly observed in bulk thermoelectric materials. The power factor of this film is $153 \text{ uW m}^{-1} \text{ K}^{-2}$, which is an order of magnitude larger than the unheated control. This marked improvement in thermoelectric performance is the result of degrading the insulating PDDA:PSS complex from the film, while maintaining the highly ordered conductive network formed during layer-by-layer deposition. This strategy of thermally degrading non-conductive material required for film fabrication can be used to prepare numerous high performing thermoelectric materials.

Topological design of a hole transporting molecular bottlebrush system for highly anisotropic alignment in solution-processed thin films

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In modern organic electronics and optoelectronics, anisotropic packing/alignment of charge transport functionalities has been recognized as a crucial factor for construction of high-performance devices. Depending upon the inherent charge transport direction within a device, molecular-scale “edge-on” orientation of charge-transporting hosts is favorable for organic field-effect transistors (OFETs), while the “face-on” orientational counterpart is preferential for organic light-emitting diodes (OLEDs) and organic photovoltaics (OPVs).

Solution-cast polymer thin films for hole transport layer (HTL) devices in OLED display applications have been proposed in recent years. In this regime, a key requirement for the HTL device is high hole mobility and transport to the emission layer. We developed a novel solution-cast polymeric material that can achieve unprecedented high degrees of anisotropy, which we attribute to successful alignment of the charge carrying moieties. The structure-property relationship between obtained anisotropic data with polymer topology, monomer selection, and charge carrier group will be described in detail, as well as the effect of film processing. These results will be then correlated with measurement of charge transport using hole-only device and compared to control devices using the compositionally analogous polymer films but with little or no anisotropic molecular packing. While the films of this study were too thin to fully interpret the results in terms of measured hole mobility, the preliminary data indicate facile charge transport is commensurate with a high degree of anisotropic alignment. From these results, we propose the topological design strategy for anisotropic alignment of polymer, which is of potential usefulness for solution-processable HTL films with high charge mobilities.

Tannic acid: A potential small molecule binder for silicon electrodes in lithium-ion batteries

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Increasing demand for portable electronic devices, electric vehicles, and grid scale energy storage has spurred interest in developing high capacity rechargeable lithium ion batteries (LIBs). For this, researchers have been extensively studying materials with high lithium ion storage capability, especially silicon, to replace the graphite anode in LIBs. Silicon is a non-toxic, abundantly available material and has a theoretical gravimetric capacity of 3579 mAh/g with a low operating potential of 0-1 V vs. Li/Li⁺. However, silicon has not yet been commercialized as an anode material due to large volume variation (>300 %) during lithiation and delithiation which pulverizes silicon particles ultimately leading to battery failure. These problems can be overcome by using a binder that can hydrogen bond with the hydroxyl groups on silicon nanoparticles. Here, we demonstrate using tannic acid (TA), a natural polyphenol derived from wood, as a binder for silicon anode in lithium ion batteries. The resultant silicon electrodes demonstrated decent cycling stability with a capacity of 1000 mAh/g for 200 cycles which can be attributed to the presence of abundant hydroxyl (OH) groups (14.8 millimoles of OH/g of polymer). Also, water processability makes the electrode synthesis process environmentally friendly. This work demonstrates that a molecule with high hydrogen bonding capability can be used as a binder and that modifications in TA can further improve its performance as a binder in silicon anode.

Extreme deformation and extraordinary energy absorption of MWCNT mats under ballistic impact

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We investigate the energy absorption characteristics and associated deformation behavior of free standing thin films of multiwall carbon nanotubes (MWCNTs) using a micro-projectile impact test. Films from 50-250nm thickness are impacted with SiO₂ microprojectiles at velocities from 300-900 m/s. The interconnected network of multiwall carbon nanotubes (MWCNT) sample while having quite modest quasi-static mechanical properties shows strong energy absorption at the extreme strain rates resulting from ballistic impact. As the spherical projectile engages the film, the bundles of MWCNT tubes straighten and translate into the impact region, dissipating the kinetic energy of the projectile via frictional interactions between tubes and stretching of the network, ultimately leading to fracture of principal tubes. The specific energy absorption depends on velocity and film thickness and can range up to 10 MJ/kg. This is about an order of magnitude higher specific energy absorption than for Kevlar and other ballistic materials.

Core-shell inverse amphiphilic molecular polymer bottlebrush additives to increase lubricity in lubricants

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Studies conducted by industrial countries have shown that friction alone can consume 20% of global energy consumption (roughly 119 Exajoule).¹ Nanoparticles additives in lubricants has been demonstrated as a successful method to improve the tribological properties of base oils, however, issues with lubricant degradation at higher temperatures and stresses decreases the nanoparticles efficiency long-term.^{2,3} As a consequence the materials presented here have been specifically designed to improve the lubricity of lubricants. The goal of this project is to design polymeric materials capable of acting as lubricant additives to reduction friction in machineries and save energy by enhancing tribological practices. Grafting-through synthesis of inverse amphipolar core-shell block copolymer macromolecular polymer brushes (BCP-MPBs), or bottlebrushes is presented. Norbornenyl-([poly(acrylic acid)]-*block*-[polyolefin]) (NB-(PAA-*b*-PO)) macromonomers were prepared through RAFT polymerization and the desired bottlebrush polymers, with heirarchical structures, were obtained *via* ROMP of the norbornenyl moiety. The combination of these well-established techniques provided well-defined polymer bottlebrushes with narrow dispersities, 1.5. Preliminary tribological studies utilizing a Poly(norbornenyl-([poly(acrylic acid)]-*block*-[poly(hexyl acrylate)])) bottlebrush in a 0.2 wt% solution an anti-wear additive when decanes was utilized as a base oil resulted in a 5 mN decrease in frictional force. Future work will focus on altering bottlebrush dimension and directly comparing the bottlebrush polymer with and without varying metal centers incorporated.

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