

1st Scientific Meeting

9 AM – 8 PM

November 22, 2013

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Hattiesburg, MS**

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USM Polymer Science

Macromolecular Studies Graduate Student Association
(LSU)

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APTEC Meeting
November 22, 2013
University of Southern
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Scientific Program

Coordinators: Macromolecular Student Graduate Student
Association (LSU), Graduate Studies Student Association
(Tulane), and USM Polymer Science

Time	Speaker	Title
9:15	Professor Mays	Macromolecular Architectures and Polymer Characterization <i>University of Tennessee-Knoxville</i>
10:00	Exley, Sarah	Antimicrobial efficacy and selectivity of polymeric antimicrobial peptide mimics that contain primary amine and guanidinium moieties prepared via aqueous RAFT polymerization <i>University of Southern Mississippi</i>
10:15	Abel, Brooks	Versatile Brush Architectures for siRNA Delivery via Controlled Polymerization/Click Chemistry <i>University of Southern Mississippi</i>
10:30	Zheng, Rubo	Hydrophobically modified biopolymer creates coatings on liposomes for drug delivery and on carbon microspheres for in situ groundwater remediation <i>Tulane University</i>
10:45	Rosu, Cornelia	Characterization and Applications of Polypeptide Composite Particles Prepared by Click Chemistry <i>Louisiana State University</i>
11:00	Huberty, Wayne	Synthesis and characterization of a water soluble, non-ionic, α -helical, rod-like polymer <i>Louisiana State University</i>
Break		
11:30	Parsons, Keith	Polymer Micelles as Molecular Templates for Size Control in Gold Nanoparticle Synthesis <i>University of Southern Mississippi</i>
11:45	Zhu, Zifu	Light Scattering Maxima near CMC and Enhanced Surfactant Supramicellar Assembly by Hydrophobic Dopant <i>Tulane University</i>
12:00	Zhang, Boyu	Exploring the Effect of Amphiphile Architecture: Synthesis, Characterization and Self-assembly of Both Cyclic and Linear Poly(ethylene glycol)-b-Polycaprolactone <i>Tulane University</i>

12:15	Myers, Brittany	Synthesis and Characterization of Star-Dendritic-Linear Polymers for use as Unimolecular Micelles <i>Tulane University</i>
12:30	Lunch	
1:45	Arora, Jaspreet	A Novel Method of Spatially Controlled Vesicle Capture Using Hydrophobically Modified Chitosan in Breath Figures <i>Tulane University</i>
2:00	Li, Ang	Cleavable Core-Crosslinked Micelles based on Amphiphilic Block Copolypeptides <i>Louisiana State University</i>
2:15	Goetz, Jim	UV-Cured Perfluorinated Side Chain Crystalline Stimuli-Responsive Networks: Free Volume Behavior and Transport of Light Gases <i>University of Southern Mississippi</i>
2:30	Hoff, Emily	Hydrazone-Based Dynamic Covalent Chemistry for Reversible Brush Surface Modification <i>University of Southern Mississippi</i>
2:45	Olatinwo, Mutairu	X-Ray Grating Interferometry for Dynamic Tomography of Brominated Flame Retardant and Antimony Oxide Additives in High Impact Polystyrene, HIPS <i>Louisiana State University</i>
3:00	Mota- Morales, Josue	Frontal polymerization in polymerizable “deep-eutectic solvents” <i>Louisiana State University</i>
3:15	Krzeminski, David	Linear impact exposure and thermal annealing treatment on the mechanical properties of an American football helmet outer shell material <i>University of Southern Mississippi</i>
3:30	McFaul, Colin	During synthesis observation of Lower Critical Solution Temperature behavior via Second-Generation ACOMP. <i>Tulane University</i>

Break		
4:00	Cong, Rongjuan	Challenges and recent advances in polyolefin characterization <i>The Dow Chemical Company</i>
4:20	Zhe, Zhou	Challenges and recent advances in polyolefin characterization The Dow Chemical Company
4:30	Industrial Panel	
5:00	APTEC Board Member	APTEC Vision
5:10	Dinner	
6:30-8	Poster session	

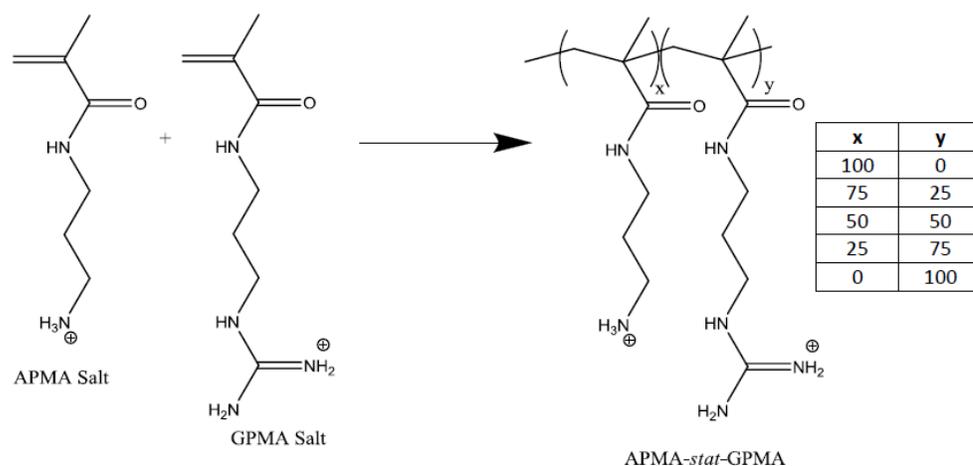
Presentation Abstracts

Antimicrobial efficacy and selectivity of polymeric antimicrobial peptide mimics that contain primary amine and guanidinium moieties prepared via aqueous RAFT polymerization

Sarah E. Exley, Lea C. Paslay, Sabine Heinhorst, Sarah E. Morgan

Naturally occurring antimicrobial peptides (AMPs) are amphipathic molecules that have been shown to eliminate a wide range of bacteria. The hydrophilic regions of AMPs have an abundance of lysine and arginine amino acid residues, which are protonated and positively charged under physiological conditions. Due to electrostatic attraction, the positively charged AMPs bind with the negatively charged bacterial cell membrane and promote cell death. Literature on AMPs mimics has shown, however, that depending upon the prevalence of either lysine or arginine, the mechanism of cell death varies from membrane disrupting to cell penetrating, respectively. The goal of this research, therefore, is to determine the bacterial toxicity and selectivity of AMP mimics that are comprised of varying ratios of aminopropyl methacrylamide (APMA), a lysine mimic, and guanadinopropyl methacrylamide (GPMA), an arginine mimic, and analyze how compositional changes affect the mechanism of cell death in gram-positive (*B. subtilis*) and gram-negative (*E. coli*) bacteria. This is accomplished through the synthesis, via RAFT polymerization, of various statistical copolymers that demonstrate well-defined compositional ratios of APMA and GPMA, antimicrobial, biocompatibility and membrane disruption testing.

Versatile Brush Architectures for siRNA Delivery via Controlled Polymerization/Click Chemistry



Brooks A. Abel and Charles L. McCormick

We report the preparation of macromonomers via post-polymerization modification of polymers produced by reversible addition-fragmentation chain transfer (RAFT) polymerization with thiol-reactive oxanorbornenes. Subsequent polymerization of oxanorbornene-functional macromonomers by ring opening metathesis polymerization (ROMP) affords the corresponding molecular brushes in a controlled fashion. This versatile route facilitates use of “off-the-shelf” styrenic, acrylamido, and acrylate-based RAFT polymers prepared under conditions specific to the monomer-type (e.g. polymerization in aqueous or organic media) for convenient synthesis of a variety of molecular brush polymers. Furthermore, end group transformation of RAFT polymers using methanethiosulfonate-functional oxanorbornenes results in molecular brush polymers possessing side chains linked to the brush backbone via disulfide linkages, the latter serving as *in-situ* trigger sites for drug delivery. Future work focuses on molecular brushes specifically prepared for the targeted delivery of siRNA to cancer cells.

Hydrophobically modified biopolymer creates coatings on liposomes for drug delivery and on carbon microspheres for in situ groundwater remediation

Rubo Zheng,¹ Jingjing Zhan,¹ Matthew B. Dowling,² Srinivasa R. Raghavan,² Joy St. Dennis,¹ Jibao He¹ and Vijay T. John^{1,*}

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²Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742

We present results of work showing that hydrophobically modified chitosan that with long alkyl groups has a protective influence on liposomes, allowing enhanced stabilities in serum for drug delivery. The alkyl groups partition into the lipid bilayers allowing the chitosan to form a coating that stabilizes the liposome. Details of liposome structure and morphology are characterized through cryo-electron microscopy. As the concentration of hydrophobically modified chitosan is increased, the system transitions from a liquid to a gel where the liposomes act as nodes in a network structure. We further show that hydrophobically modified chitosan can also stabilize carbon microsphere in water through hydrophobic interactions. Detailed NMR characterizations indicate attachment of the alkyl groups onto the microspheres. Carbon microspheres as a carrier for nano-scale zero-valent iron particles are of much potential in the remediation of chlorinated compounds. Effective in situ groundwater remediation requires the successful delivery of these reactive systems through soil without aggregation. The coating of the environmentally benign biopolymer therefore leads to suspension stability of these microspheres through electrostatic and steric repulsion. Moreover, our results indicate that with hydrophobically modified chitosan, this system has optimal transport characteristics in groundwater saturated sediments with carbon microspheres attachment efficiency of 0.04 calculated from breakthrough data of transport experiments.

Characterization and Applications of Polypeptide Composite Particles Prepared by Click Chemistry

Cornelia Rosu,¹ Rafael Cueto,¹ Lu Zou², Chanjoong Kim² and Paul S. Russo¹

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Louisiana State University, Baton Rouge, LA, 70803*

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Polypeptide composite particles, PCPs, with a magnetic core and an α -helical homopolypeptide shell have been produced by combining ring-opening polymerization and Huisgen's 1,3-dipolar cycloaddition also known as click chemistry. The shell consisting either of alkyne-end terminated poly(γ -stearyl-L-glutamate), alkyne-PSLG or alkyne-end terminated poly(N^{ϵ} -carbobenzyloxy-L-lysine), alkyne-PCBL, was prepared by ring-opening polymerization of the corresponding N-carboxyanhydrides using propargylamine as an initiator. Covalent attachment of the azide functional group onto the core surface was achieved by nucleophilic substitution with sodium azide of bromine furnished fluorescent silica coated magnetite particles. The click hybrid was obtained by coupling azide-functionalized magnetic particles with alkyne-end terminated homopolypeptide in tetrahydrofuran, THF, or dimethylformamide, DMF, in the presence of copper bromide (I) and pentamethyldiethylene triamine, PMDETA. The desired sparse coverage with polypeptide was confirmed by TGA analysis. Shell molecular weights were measured by GPC and MALDI-TOF and their conformation was investigated by FTIR. A blend of techniques such as XRD, TEM, XPS, FTIR, DLS and SQUID were used to investigate the nature of the composite particles. PSLG-click hybrid was found to be a good support for lipase from *Candida Rugosa* immobilization. These particles also dispersed in a surfactant aqueous solution. Suspension of the PSLG-click hybrid particles in a liquid crystal, LC, rodlike PSLG matrix enabled a good control of the clustery behavior under applied magnetic field. PSLG-click PCPs also self-assembled in different morphologies. PCPs behavior in a LC matrix may help to understand the dynamics of the complex fluids. Under stress, PCBL-click particles showed shear thinning tendency and behaved as a non-Newtonian stiff material.

This work has been supported by Grants DMR-1005707 from the National Science Foundation.

Synthesis and characterization of a water soluble, non-ionic, α -helical, rod-like polymer

Wayne Huberty, Paul Russo

*Department of Chemistry and Macromolecular Studies Group,
Louisiana State University, Baton Rouge, LA 70803*

The industrial use of stiff polymers in high-performance situations where strength and weight are important has increased so dramatically that they have gained accepted use in common vernacular, e.g. carbon fiber. From another perspective, very stiff polymers are scientifically interesting because they provide the most rudimentary structure available. This makes rod-like polymers the ideal candidate for comparison to theory. Although there are several highly stiff polymers available, they are challenging to use due to poor solubility, high temperatures, polydispersity, or harsh solvents. Despite these drawbacks rod-like polymers have many benefits. Therefore, a non-ionic, water soluble, α -helical rod-like polymer has been synthesized and its characterization will be discussed.

Polymer Micelles as Molecular Templates for Size Control in Gold Nanoparticle Synthesis

Keith H. Parsons, Charles L. McCormick

Polymeric molecular templates offer a new route to synthesis of uniform gold nanoparticles (AuNPs) with on-demand size control. Stimuli-responsive block copolymers have been synthesized with pH-responsive blocks that serve the dual purpose of inducing self-assembly and gold salt reduction. These polymer micelles, in the presence of NaAuCl₄, act as molecular templates for AuNP synthesis by controlling the size and shape of the nanoparticle through the length of the gold-reducing block. Polymers with varying block lengths have been synthesized to establish a relation between block length and AuNP size. Once “on-demand” AuNP size control has been established, other polymer morphologies will be explored to demonstrate control over AuNP geometry.

Light Scattering Maxima near CMC and Enhanced Surfactant Supramicellar Assembly by Hydrophobic Dopant

Zifu Zhu and Wayne F. Reed
Tulane University, New Orleans, LA, 70118

A sharp maximum in light scattering occurs in many surfactant solutions when they are diluted through their critical micelle concentration (CMC). This effect has historically been linked to impurities in the micellar solutions. Monitoring of the scattering and intrinsic viscosity behavior of sodium dodecyl sulfate (SDS) micelles under a gradient dilution when they are deliberately loaded with an impurity (dodecanol) allows unusual features of the scattering maximum to be explored and linked back to micelle behavior. The concentration at which the onset of the maximum occurs, its width, and the scattering amplitude are directly related to the ratio of impurity to surfactant and further correlated with the loading capacity of the micelles. The data suggest that the micelles do not simply release their hydrophobic payload at the CMC; rather, the dopant causes a morphological change from normal micelles into supramicellar assembly. A three-component model is proposed that self-consistently yields maximum micellar dopant loading, supramicellar assemblies, and dopant solubility in solution.

Exploring the Effect of Amphiphile Architecture: Synthesis, Characterization and Self-assembly of Both Cyclic and Linear Poly(ethylene glycol)-b-Polycaprolactone

Boyuan Zhang, Hong Zhang, Yeji Li, Jessica N. Hoskins, Ravinder Elupula, Scott M. Grayson

Tulane University, Department of Chemistry, New Orleans, LA, 70118

Amphiphilic polymers are of interest for a range of applications because of their inherent ability to self-assemble into discrete objects. Controlling the size and stability of such aggregates is particularly important for drug delivery applications, as the size is one of the most critical features in determining its biodistribution, and the stability can be utilized to enable a controlled release of a therapeutic payload. A substantial body of work has already been carried out by numerous investigators in order to define and control the parameters of simple linear block copolymers, (those containing a series of polar repeat units followed by a second series of non-polar repeat units.) However, only a limited amount of work has focused on cyclic polymers, owing to the difficulty in preparing such macromolecules in high purity. Recently, our research group has reported an efficient technique for preparing cyclic polymers using the highly efficient copper-catalyzed azide-alkyne cycloaddition reaction (CuAAC) in order to link the end groups of a linear polymer. The relative ease of this technique has already enabled the preparation of cyclic block copolymers. However, in order to investigate the biological applications of these macromolecules, a biocompatible and biodegradable cyclic polymer has been investigated, based on blocks of poly(ethylene glycol) and poly(caprolactone).

Synthesis and Characterization of Star-Dendritic-Linear Polymers for use as Unimolecular Micelles

Brittany K. Myers and Scott M. Grayson

Department of Chemistry, Tulane University, New Orleans, LA 70118

The ability to encapsulate guest molecules has garnered a lot of attention for conventional micelles. Yet, small molecule amphiphiles are known to yield micelles with limited stability and even amphiphilic linear polymers are susceptible to disaggregation at low concentrations. For this reason, branched, covalently-bound amphiphilic units are attractive because the resulting “unimolecular micelles” are robust when conventional micelles would disaggregate and exhibit no critical micelle concentration. One way to construct modular unimolecular micelles is to incorporate linear polymers between dendritic branching units. For example, unimolecular micelles can be prepared from a star core, such as polyethylene glycol (PEG) with dendrons, and an exterior linear chain such as polycaprolactone (PCL). These molecules are attractive both fundamentally and practically because they can be used to probe the structural parameters which define aggregation behavior and encapsulation. Furthermore, these molecules have potential to be used as drug delivery vehicles, sequestering agents, and surfactants.

A Novel Method of Spatially Controlled Vesicle Capture Using Hydrophobically Modified Chitosan in Breath Figures

Jaspreet S. Arora, Thiruselvam Ponnusamy, Vijay T. John

Dept of Chemical & Biomolecular Engineering,

Tulane University, New Orleans

Breath Figures are a morphological class of porous polymers with highly ordered structures. They can be fabricated by simply casting a polymer solution in an organic solvent under humid conditions. The cooling effect produced by the solvent evaporation leads to condensation of water droplets on the surface. These ordered arrays of droplets stay apart and once they sink inside the polymer solution, more water droplets condense on the surface around which a polymer film forms. Upon complete evaporation of the solvent and water, pore formation takes place. We hypothesized that if we used an aerosol mist carrying a nanoparticle solution instead of humid air, we could place the nanoparticles specifically in the ordered pores of the breath figures.

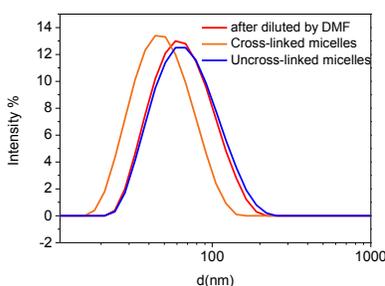
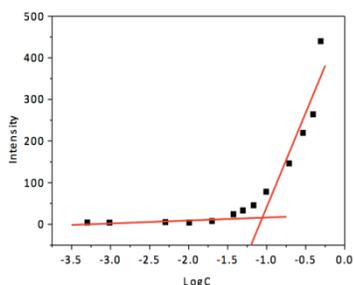
We synthesized breath figures by spin coating polystyrene polymer films (pore size 1 micron) while passing a humid aerosol mist of a solution of hydrophobically modified chitosan (HMC). HMC stays in the condensed water droplets and as the droplets evaporate, they deposit only inside the pores of the breath figures. The mechanism of the formation of these HMC microarrays will be discussed. Once the HMC was deposited selectively in the pores, it was used to capture liposomes selectively in the pores. This spatially control vesicle capture is facilitated by the fact that the hydrophobes attached to the chitosan backbone in HMC have a tendency to insert themselves in the bilayer hydrophobic region of the liposomes. This leads to tethering of liposomes only inside the pores which is shown by epifluorescent microscopy, confocal microscopy and electron microscopy. Furthermore, cryo scanning electron microscopy analysis shows that these captured vesicles are intact. The versatility of this technique allows placement of biomolecules precisely in the pores of the ordered polymer films in a single step.

Cleavable Core-Crosslinked Micelles based on Amphiphilic Block Copolypeptoids

Ang Li and Donghui Zhang

Department of Chemistry and Macromolecular Studies Group, Louisiana State University, Baton Rouge, LA 70803

Cleavable core-crosslinked micelles composed of linear poly(*N*-ethyl glycine)-*b*-poly(*N*-decyl glycine)-*r*-poly(*N*-propargyl glycine)s [PNEG-*b*-P(NDG-*r*-NPgG)s] were prepared by sequential ring-opening polymerization of *N*-alkyl *N*-carboxyanhydride monomers and subsequent cross-linking of the hydrophobic P(NDG-*r*-NPgG) core with a disulfide containing cross-linker through alkyne-azide cycloaddition in aqueous solution. The morphology has been characterized by transmission electron microscopy (TEM) and dynamic light scattering (DLS), revealing that both cross-linked and uncross-linked micelles are spherical in shape ($R_h = 75$ and 52 nm) and have narrow size distribution ($PDI = 0.19$ and 0.19). The cross-linked micelles show stability and swellability in DMF, a non-selective solvent for the copolypeptoids. The cross-linked micelles can be used to encapsulate hydrophobic moieties such as 1-anilinonaphthalene-8-sulfonic acid (1,8-ANS), a fluorescence probe. The encapsulated moieties can be slowly released in the presence of dithiothreitol (DTT), as evidenced by gradual decrease of fluorescence intensity over a period of 12 hours. The cross-linked micelles showed minimal cytotoxicity when incubated with 3T3 cells.



Uv-Cured Perfluorinated Side Chain Crystalline Stimuli-Responsive Networks: Free Volume Behavior and Transport of Light Gases

Jim Goetz

Comb shaped, side-chain crystallizable polymers are an interesting platform for developing temperature responsive membranes for medical and packaging applications. Previous work has shown a drastic change in permeability through the melting of aliphatic side chain crystalline order but sample preparation proved to limit their applicability.¹⁻⁴ Therefore, it is interesting to produce these films in industrial viable ways and to find chemical structures that result in smaller changes in permeability through a thermal transition. UV photopolymerization allows for the rapid production of large areas of materials and benefits from low energy consumption and rapid cure times. The focus of this study was to utilize UV photopolymerization to fabricate perfluorinated side chain polymer films with liquid crystalline order and to investigate the film's free volume behavior and transport properties.

Several perfluorinated side chain acrylates of different lengths, combined with small amounts of crosslinker and photoinitiator, were UV cured resulting in amorphous and thermotropic liquid crystalline thin films. Thermal and morphological characterization indicates the disruption of the liquid crystalline phase through the isotropic transition in LC films; giving rise to an increase in permeability and free volume while the amorphous film showed no dramatic change in transport or free volume. Furthermore, light gas transport was used as a probe of the side chain crystalline morphology confirming channeling of light gases in the crystalline domains. Permeability selectivities of small gasses were also analyzed and the results show promise for new applications for UV photopolymerized networks.

Hydrazone-Based Dynamic Covalent Chemistry for Reversible Brush Surface Modification

Emily A. Hoff, Chase A. Tretbar, Will K. Adkins, Derek L. Patton

The development of surface modification techniques for “on-demand” control of surface properties is essential in order to engineer modular surface platforms with a high degree of control over complexity, functionality, and responsiveness to external stimuli. Most examples of surface modification are irreversible; however, “on-demand” reversible functionalization of surfaces would enable strategies such as “catch-and-release” and “reusable” surfaces important for advances in biosensors, self-healable materials, antifouling coatings, etc. Dynamic covalent chemistry (DCC) can be used to establish reversible covalent bonds that are responsive to external stimuli such as pH, UV light, and temperature. Dynamic covalent hydrazone linkages, which are formed through an imine reaction of a hydrazide moiety and an aldehyde or ketone, are responsive to changes in pH while still exhibiting reasonable product stability thus making this chemistry an ideal handle for controlling surfaces properties.

In order to facilitate “on-demand” control of surface properties, pH-responsive, reversible hydrazide linkages were incorporated as substituents on polymer brush surfaces via surface-initiated atom transfer radical polymerization (SI-ATRP) and subsequent post-polymerization modification (PPM). Dynamic covalent surfaces were then achieved through the formation of hydrazone linkages with various aldehydes. This research investigated changes in surface wettability via an *in situ* exchange reaction between surface bound aldehydes and aldehydes in solution enabling changes in functionalization without separate hydrazone formation and reversal steps. Furthermore, the exchange reaction was examined over multiple cycles with x-ray photoelectron spectroscopy, grazing-angle ATR-FTIR spectroscopy, and UV-Vis spectroscopy.

Frontal polymerization in polymerizable “deep-eutectic solvents”

Josué David Mota-Morales

Department of Chemistry, Louisiana State University, USA

Deep eutectic solvents (DES) formed between a variety of acrylates and ammonium salts exhibit certain properties of ionic liquids that make them suitable for free radical polymerization.^[1] The use of DES not only as a monomer but also as the solvent prevents the use of additional solvents (i.e. typically of organic nature) and offers a green tool for the synthesis of functional polymers and composites, i.e. an all-in-one synthetic method. We have recently explored this approach for the preparation of poly(acrylic acid) loaded with lidocaine hydrochloride^[2] and composites of poly(acrylic acid)/carbon nanotubes^[3].

The versatility offered by this sort of polymerizable compounds allowing their tailor-made design for application as polymeric materials in fields ranging from scaffolds for biomaterials, molecular imprinted polymers and drug delivery systems to porous materials for separation, catalysis, etc. Together with their versatility, the most outstanding feature of the DES here described is that its polymerization occurs in an all-in-one fashion covering many of the principles of Green Chemistry. Thus, besides of all the possible applications, the added benefit of sustainability makes of this a very interesting route of synthesis.

Linear impact exposure and thermal annealing treatment on the mechanical properties of an American football helmet outer shell material

David E. Krzeminski^{1,2}, Dilhan Fernando¹, Nadine M. Lippa^{1,2}, Trenton E. Gould PhD ATC², Scott G. Piland PhD ATC², James W. Rawlins PhD¹

¹ School of Polymers and High Performance Materials

² School of Human Performance and Recreation

The University of Southern Mississippi, Hattiesburg, MS, USA

The purpose of this study was to investigate the effects of impact exposure and thermal annealing on the impact performance, as well as the tensile and surface mechanical properties, of an American football helmet outer shell material. Helmet-grade plaques ($T_g \approx 150^\circ\text{C}$) of 1/8" thickness were randomly assigned into four groups: non-impacted, non-impacted/annealed, impacted, and impacted/annealed. Impact tests were performed using an instrumented drop tower upon a helmet surrogate system comprised of a plaque stacked atop 1.0" VN600 foam. Randomly selected plaques underwent a 175°C annealing treatment for 5 minutes and then air cooled. Color change was quantified per CIELAB scale. Tensile mechanical properties were measured using modified ASTM-D638 Type I specimens harvested directly from plaques. Surface mechanical properties were quantified using load-controlled quasi-static nanoindentation at five pre-selected loads. The impact treatment of 12 repetitive trials was validated ($p < 0.05$) to cause a change in plaque impact performance. The annealing treatment was verified ($p < 0.05$) to colorimetrically erase impact-induced whitening; however, annealing did not alter the impact performance of a plaque with a 12 trial history. For tensile tests, impact and thermal annealing treatments altered ($p < 0.05$) bulk mechanical properties. Annealing just above T_g aesthetically recovered the helmet-grade plaque, and potentially rejuvenated the thermo-mechanical history of the engineered material. For nanoindentation, only annealing altered ($p < 0.05$) surface properties up to a depth of $\sim 1.0 \mu\text{m}$. Our findings warrant exploring the effects of annealing helmet outer shells as a method to provide greater helmet life-span consistency and potentially mitigate the risk of sports-related head injury.

During synthesis observation of Lower Critical Solution Temperature behavior via Second-Generation ACOMP

Colin McFall

We observe the onset of lower critical solution temperature (LCST) behavior in an N-isopropyl acrylamide (NIPAM)/Acrylamide (Am) copolymer system. We do this by combining several temperature-controlled single-angle light scattering flow cells with our established Automatic Continuous Monitoring of Polymerization (ACOMP) system.¹ For batch copolymer reactions, this demonstrates that the LCST is visible almost immediately in the reaction, and is consistent with previous reports.² We use our Simultaneous Multiple Static Light Scattering (SMSLS)³ instrument for high-throughput measurements of the LCST and salting-out of the resulting polymers. These results confirm and extend past results.⁴

Finally, we apply a novel semi-batch copolymerization method to this system.⁵ Using this, we are able to drive the instantaneous composition from Am homopolymer to NIPAM homopolymer. All intervening compositions are seen during the reaction. We are then able to use SMSLS for high-throughput studies of samples taken from this semi-batch reaction. These samples show an onset LCST equal to that expected for the highest NIPAM-content polymers in the system at the time. They also show a very broad transition due to the composition dispersity in the population.

Poster Abstracts

Iodine-Catalyzed Cycloalkenylation of 1,2-dihydro-2,2,4-trimethylquinoline derivatives.

Suraj K. Ayer, Binit Sharma Poudel and Jean Fotie

As part of our continue effort to determine the full scope of the iodine-catalyzed regioselective cycloalkenylation on arylamines through a reaction with cyclic ketones developed in our lab, a series of cycloalkenylated 1,2-dihydro-2,2,4-trimethylquinoline derivatives have been synthesized. Throughout this presentation, we will discuss the preparation and the characterization of these compounds.

Catalysts for the Double-Bond Isomerization of Long Chain Olefins

James Bruno and Kerry Dooley*

This project examines the double-bond (positional) isomerization of long-chain (C16-C18) olefins. The goal is to make highly internal olefins from 1-olefin feeds. Internal, long chain olefins are used in the manufacture of paper sizing agents and as deep-sea drilling fluids.

Solid acid, base, and organometallic catalysts were evaluated in the positional isomerization of 1-hexadecene. Branched products and oligomers were also generated in varying amounts. The catalysts included commercial sulfonated poly(styrene-co-divinylbenzene) (PS/DVB), perfluorinated ion exchange resins (Nafion) supported on silica and alumina, acidic zeolites, tungstated zirconias, supported sodium, and iron pentacarbonyl.

Catalysts were tested in packed bed reactors to determine selectivity to internal olefins. Activity depended on strength of acid sites, acid site density, and degree of crosslinking. The more promising catalysts (PS/DVBs, Nafion, and zeolites) were evaluated under continuous flow until at or near deactivation. Deactivated catalysts were analyzed to determine mode of deactivation and regenerability. Macroreticular ion exchange resins with low acid site densities had the highest selectivity to internal olefins.

Synthesis and Characterization of Polypeptide-GRGDS Conjugates as Multivalent Probe for Integrin Activation and Cell Adhesion

Jinbao Cao, Donghui Zhang

A series of water-soluble non-ionic co-polypeptides consisting of poly(α -propargyl-L-glutamate) and poly{N ϵ -2-[2-(2-Methoxyethoxy)ethoxy]acetyl-L-lysine} were synthesized by ring opening copolymerization (ROP) of the corresponding N-carboxyanhydrides in different ratios using benzyl amine as initiator. Cell adhesion peptide GRGDS (Gly Arg Gly Asp Ser) bearing azide functionality at the G terminus was prepared by solid phase peptide synthesis (SPPS). Copolypeptides with various densities of pedant GRGDS (2-8% mol%) were further prepared by copper catalyzed alkyne-azide cycloaddition chemistry. Successful synthesis of GRGDS-polypeptide conjugate was verified by ¹H-NMR spectroscopy. Circular dichroism (CD) analysis reveals that conjugates adopt helical conformations in aqueous solution. Preliminary cell adhesion study indicates that the conjugates are able to induce cell adhesion and spreading. The conjugate will be further utilized to investigate biological processes such as integrin activation and signaling in future.

Synthesis and Analysis of Copper β -Diketonate Molecular Complexes

Jonathan Casey, Andy Maverick, and Paul Russo

The area of research this project is associated with is inorganic and macromolecular chemistry. The research is the synthesis and analysis of the Molecular Organic Material of copper (II) complexes. On the inorganic side, it is synthesizing silicon based ligands, with the copper (II) metal. This chemistry aims at creating material for hydrogen storage, methane storage, or as a containment material for various chemical compounds.

In the workup of the Copper (II) complexes, these materials are not able to be analyzed by traditional forms of analysis. Copper (II) is paramagnetic and cannot be analyzed by NMR. The copper complex material does not form crystals, so X-Ray Crystallography cannot analyze its structure. Other techniques such as ESI-TOF Mass Spectrometry and Atomic Force Microscopy have given different information, but each technique suffers from its own unique limitations.

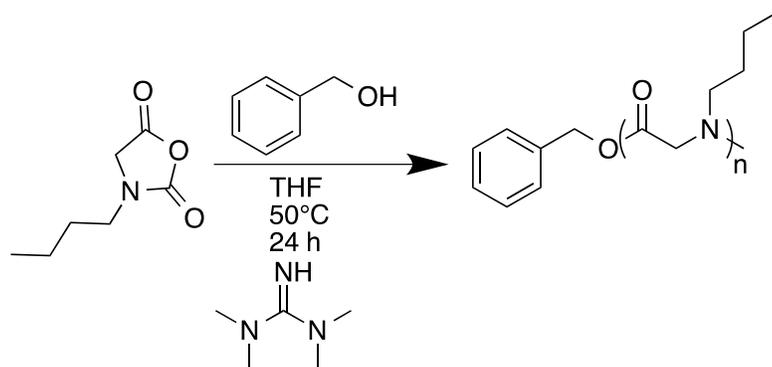
In ESI-TOF Mass Spectrometry, the material may be polymeric and may fragment similar to the Metal Organic Material being analyzed. This may distort the characterization of the molecule being examined. In Atomic Force Microscopy, the size of the particles is analyzed. The significant limitation of AFM is that it does not give the chemical composition of the material. It is limited by describing only the physical size and properties of the material.

Analytical Ultracentrifugation (“AUC”) can be used to determine the molecular weights of unknown molecules. AUC determines the molecular weight of the molecules by the diffusion of molecules in solution versus the concentration gradient created by the centrifugal field. AUC measurements of our soluble product could help us determine whether it contains different copper complexes.

1,1,3,3-Tetramethylguanidine-Promoted Ring-Opening Polymerization of N-Butyl N-carboxyanhydride using an Alcohol Initiator

Brandon A. Chan, Sunting Xuan, and Donghui Zhang

N-butyl N-carboxyanhydride (Bu-NCA) was polymerized in THF to produce poly(N-butyl glycine) using benzyl alcohol initiator and 1,1,3,3-tetramethylguanidine organocatalyst. Poly(N-butyl glycine) (PNBG) with controlled polymer molecular weight ($M_n = 2.9\text{-}20.5$ kg/mol) and narrow size distribution (PDI=1.04-1.11) can be obtained by controlling the initial monomer to initiator ratio and conversion. The reaction exhibits characteristics of a living polymerization, as evidenced by the linear increase of M_n with conversion and the successful chain extension experiments. Kinetic studies revealed that the reaction is first-order dependent on the monomer concentration with a slow initiation ($k_i = 0.019$ s⁻¹) relative to the propagation ($k_p = 10^4$ s⁻¹). MALDI-TOF MS and ¹H NMR analysis confirmed that the polymer chains were terminated with benzyl alcohol end groups. Polymerization in other solvents such as toluene, DMF and CH₂Cl₂ or using other alcohol initiators such as EtOH and iPrOH yielded PNBGs whose molecular weights deviated to varying extents from the theoretical values based on single-site initiation. Alcohols with lower pKa appear to initiate the polymerization more efficiently than those with higher pKa, resulting in more controlled M_n in the former than the latter. The polymerization has been successfully extended towards the synthesis of block copolymers based on poly(ethylene glycol) and PNBG by using a PEG-OH initiator and TMG promoter.



Malleable and Self-Healing Polymer Networks based on Dynamic Imine bond Exchange

Albert Chao and Donghui Zhang

A dynamic network based on reversible imine bond exchange has been prepared by reacting poly(ethylene glycol) bis(3-aminopropyl) with benzene-1,3,5-tricarboxaldehyde in 3:2 ratio in DMF. the organogel is malleable at room temperature with self-healing capability. Dynamic mechanical analysis (DMA) of the organogel revealed that the gel undergoes irreversible deformation under constant stress and stress relaxation under constant strain due to dynamic bond exchange within the network. NMR studies on the model compound revealed rapid imine bond exchange reaction in solution. When the stoichiometry of the tiraldehyde and di-amine monomers are changed or benzene-1,3,5-tricarboxaldehyde is replaced with terephthalaldehyde, gelation was not observed in DMF.

Magnetic nanoparticles functionalized with surface-immobilized fluorescent conjugated polymers

Sourav Chatterjee, Cornelia Rosu, Evgueni E. Nesterov and Paul S. Russo

Development of novel fluorescent chemo- and biodetection methods has received an increased interest because of their many current and potential applications. Core-shell hybrid nanostructures can be used as stimuli-responsive materials for such applications. They combine the properties of the core and shell which neither can display alone. A hybrid particle can be easily tuned to expand the range of responses and also to achieve enhanced sensitivity. This work proposes a novel model to study magneto-optical phenomena at the nanoscale. The model uses composite particles carrying a magnetic inclusion of magnetite, Fe_3O_4 and a fluorescent shell of conjugated polymers (such as poly(thiophene)s and poly(p-phenylene)s or block copolymers of both). The magnetic core was prepared by the sol-gel process. The size of the magnetic core was engineered to lie in the superparamagnetic domain. Protection against oxidation of ferrofluid with silica as primer was achieved by a modified Stöber procedure. The shell was covalently attached via surface-initiated chain-growth polycondensation. A variety of techniques such as TGA, TEM, and DLS were used to confirm the product at each step. The effect of the particle size and shell thickness on the magneto-optical properties was investigated.

Oil dispersion using hydrophobins

Yuwu Chen, Paul Russo and Francisco R. Hung

Molecular simulation studies were performed to explore the feasibility of using hydrophobins, a class of proteins, in the dispersion of oil. Hydrophobins are a class of proteins produced by filamentous fungi in soil. Preliminary experimental results from the Russo group with the hydrophobin Cerato ulmin (CU) suggests that these proteins can efficiently encapsulate oil and air in cylindrical structures, which implies a striking surface activity. These properties, when combined with the abundance of these proteins, have motivated applications such as removal of diesel fuel from contaminated fresh water. Because of their ease of (biosynthetic) manufacture, it is possible to imagine stockpiling hydrophobins for potential use as ‘natural’ oil spill dispersants. However, a fundamental understanding of the interfacial properties of hydrophobins when they encapsulate oil (to form ‘blobs’) or gases (to form bubbles), is crucial to determine whether CU can be an efficient oil/gas dispersant. Here we investigated the properties of hydrophobins on air/water and oil/water interfaces using potential of mean force (PMF) calculations and classical molecular dynamics (MD) simulations, using both all-atom and coarse-grained representations. Relevant interfacial properties, such as free energies, density profiles, structure and stability of small blobs and bubbles are investigated and discussed in this study.

Effects of TRIS and pH modification on sodium deoxycholate hydrogel formation and application

Kelsey McNeel and Isiah Warner

This research aims to determine the effects of modifications, including the addition of tris(hydroxymethyl)amino-methane (TRIS) and variation of pH, on the formation of sodium deoxycholate hydrogels. Furthermore, the modified properties of these gels can be exploited in various applications, including the formation of organic nanoparticles and drug release. Physical properties of the hydrogels were found to be tunable through the use of TRIS addition and pH variation. The hydrogels were characterized using several techniques, namely visual observation, TEM, POM, DSC, rheometry, and XRD. Mechanical strength, crystallinity, and sol-gel temperature were found to increase with TRIS concentration within a given pH value. These properties may enable the use of hydrogels in bioengineering and optical devices. However, present investigations include nanofabrication and injectable drug release applications. A series of **nanoparticles** composed of a **Group of Uniform Materials Based on Organic Salts (nanoGUMBOS)** were formed within the hydrogel structure, and the resulting size of the nanoGUMBOS was found to be tunable with TRIS concentration and variations in pH. The rheological investigation of the hydrogels revealed a unique two phase behavior upon shearing that yields unprecedented potential for use as an injectable drug delivery vehicle. Due to the varied mechanical properties of the hydrogels, it was also expected that release profiles from the gels would be tunable. Modifications of TRIS concentration and pH have been shown to tune the release of model drugs from sheared (pseudo-injected) hydrogels.

Physical properties of surface-active hydrophobins

Xujun Zhang, Brad Bralock, Wayne Huberty, Lawrence Aiken and Paul S. Russo

Hydrophobins are a group of surface-active fungal proteins. They are amphiphilic in nature and have the ability to self-assemble. As a result, hydrophobins have gained popular attention for different applications, such as coating, emulsion stabilization, surfactant, etc. Here, two hydrophobins, cerato ulmin and a commercial preparation, were studied. The basic physico-chemical properties of the encapsulated hydrophobins were examined by changing the pH, concentrations, gases and oils. Also, using static and dynamic light scattering, the effect of concentration on the aggregation behavior of the hydrophobins was determined. Furthermore, circular dichroism spectroscopy exhibited the secondary structures of proteins as a function of time and temperature.

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Characterization of Poly (2-oxazolines) with MALDI-TOF Mass Spectrometry

Esteban Duran Lara, Karolina A. Koskowska and Scott M. Grayson

Poly(2-oxazolines) represent a diverse category of functional macromolecules, as their side chain can be tuned to easily provide hydrophobic, water soluble and/or thermal-responsive materials. However, these compounds are notoriously difficult to synthesize as their cationic polymerization is sensitive to trace impurities that can lead to chain transfer byproducts. As a result, high molecular weight poly(oxazolines) (>60,000) are exceedingly difficult to prepare. Because end group fidelity is of critical importance in providing synthetic access to more complex architectures, (e.g. block copolymers, star polymer, graft polymers, cyclic polymers, etc.) methods for qualitatively and quantitatively determining end group functionalization are invaluable. Traditional characterization techniques employed by small-molecule chemists such as NMR spectroscopy, GPC, MS and IR do not afford sufficiently precise measure of end group functionalization, because the signal from the repeat units overwhelms those of the end groups. However, MALDI-TOF MS provides an exceptionally powerful tool for determining end group functionality and confirming end group transformations. In this study, the purity of poly(oxazoline) end groups was determined by detailed MS end group analysis. End group modifications to incorporate “click” functionalities were also explored, and their subsequent conjugation reactions confirmed by both MALDI-TOF MS and GPC.

Surface-Initiated Atom Transfer Radical Polymerization from Boron Nitride Nanotubes

Muhammad Ejaz, Satish C. Rai, Kai Wang, Weilie Zhou and Scott M. Grayson

Initiator for surface-initiated atom transfer radical polymerization (SI-ATRP) was immobilized onto the surface of boron nitride nanotubes (BNNTs) via a radical trapping process from decomposition of bis-(4-bromomethylbenzoyl) peroxide. Styrene and glycidyl methacrylate were polymerized onto initiator-immobilized BNNTs by SI-ATRP. It was confirmed that all the BNNTs were coated with a uniform layer of grafted polymer.

Synthesis of Multi-arm cages via “Click” Coupling

Ravinder Elupula, Boyd A. Laurent and Scott M. Grayson

A variety of polymer architectures have been synthesized and investigated because of their strong correlation between nanoscale architecture to physical properties. So far, many researchers have developed a variety of synthetic tools to access a wide range of polymeric architectures and tailor the properties of macromolecules for their diverse application. Some of the few examples include hyperbranched perfluorinated/hydrophilic block copolymers for antifouling coatings, branched and dendritic structures for targeted drug delivery, globular polymers for the microelectronics industry, dendrimers for light harvesting applications, and polymer grafted scaffolds for catalysis. Synthetic routes for the preparation of various polymer architectures have long been a goal for polymer chemists, owing to their unique topology and physical properties.

Recently Laurent and Grayson reported an efficient method for synthesizing cyclic macromolecules using “click” chemistry which has proven to be a versatile way for making macrocycles. Also Tezuka reported the synthesis of multicyclic polymers by cyclization via ionic pre-assembly followed by a covalent fixation. Further, the use of multicyclic “cryptands” demonstrated selective and strong interaction with potential guests. Inspired by these concepts, the synthesis of multicyclic “cage” polymers was explored. Controlled radical polymerization techniques, such as atom transfer radical polymerization (ATRP), nitroxide mediated polymerization (NMP), and reversible addition fragmentation transfer polymerizations (RAFT) are powerful tools for preparing well defined polymeric architectures. ATRP is a particularly attractive approach for making star precursors because of the ability to modify the terminal end group in very high yields. The synthesis of polymer “cages” can be achieved by further clicking these end functionalized star polymers with a small molecule alkynylated caps consisting a complementary number of arms with respect to the polymer.

Improved Dendritic Calibrants for Highly Accurate Mass Determination for a Variety of Analytes

Joseph A. Giesen; Brittany K. Myers; Scott M. Grayson

Current calibration techniques for mass spectrometry instruments utilize macromolecules, dendrimers, and well-defined peptides. Synthetic polyester-based dendritic calibrants offer a highly versatile alternative to peptides and protein calibrants. Synthetic dendritic calibrants are characterized by ease of synthesis, wide mass range, high purity, long shelf-lives, and exceptional solvent and matrix compatibility. The core of these calibrants also offers a highly useful and diverse platform for a variety of applications through simple modification. Internal calibrants are superior to external calibrants and provide the highest accuracy and precision in the mass determination of an unknown sample, as the determined mass is dependent on acquisition parameters. However, in many cases internal calibrants can only be employed if sufficient mass difference exists between the calibrant and analyte. Beginning with a tris-Iodo core produces a calibrant with a negative mass defect which allows for their use internally by eliminating the likelihood of confusion of the calibrant and analyte signals. Comparatively, beginning with an amine core allows for ionization with a proton. This is preferred when working with peptides and other biological samples. Core variation allows for greater utility of these calibrants.

Polyester Dendrons from Multi-functional Cores and their Physical Properties

Joanna E. Lapucha, Brittany K. Myers, Joseph A. Giesen, Scott M. Grayson

Dendrimers are core-functionalized polymers with a globular shape due to their regularly branched repeat units. Various core molecules can be used, including molecules with two, three, four or more alcohol functionalities, in addition to polymers with alcohols as their end groups or along their backbone. Via repetitive monomer coupling and deprotection steps, the molecule increases in dendritic size with each iteration, based on the number of branch points on each monomer. A property of interest is the amphiphilic character of these macromolecules, where ester linkages predominate in the core and hydroxyl-terminated branches define the periphery. Other qualities that give dendrimers significant potential for applications are the hyperfunctionality of the periphery that results from successive iterations as well as the physical conformations adopted to accommodate the steric crowding of atoms. Globular dendrimers are a useful substrate for simulation and experimental characterization of physical properties, because unlike other synthetic polymers, they can be prepared as monodisperse macromolecules. Conversely, dendronized polymers and linear-dendritic hybrids are polydisperse dendrimers that combine the properties of linear polymers with effective dendritic “wedges” along the backbone or as the end groups. These molecules are of interest due to the fact that they can be further modified using the dendritic functionalities. Therefore, a library of dendritic polymers are being prepared, including those with a tetrafunctional pentaerythritol core, a bis-functional poly(ethylene glycol) core, a monofunctional poly(ethylene glycol) core, and an tris-hydroxyl-terminated acrylamide core. The properties of each compound will be studied with emphasis on hydrogen bonding’s physical effects as well as the physical conformations adopted when subject to increasing dendritic growth.

Simultaneous Multiple Static Light Scattering: applications for Lower Critical Solution Temperature, protein aggregation, and long-term stability studies

Colin McFaul, Michael Drenski, Wayne Reed

We describe the current instantiation of our Simultaneous Multiple Static Light Scattering instrument (SMSLS).¹ The instrument consists of eight sample cell holders and eight lasers. These are made of anodized aluminum, and dyed black. Each sample holder can be heated individually. Currently two samples can also be cooled. Each laser independently shines into a different sample cell holder, and a single-angle (90°) light scattering signal is recorded for each sample. All of the optics and the samples are fixed in a light-tight box. A photograph of the instrument is shown in Figure 1.

We have used SMSLS for high-throughput measurements of lower critical solution temperature (LCST) behavior in polymer samples, protein aggregation,² and dissolution and solubility of polymers. This allows for rapid characterization of temperature-dependent properties of polymers and proteins.



Figure 1. A photograph of the open SMSLS. Shown are the eight lasers, and the eight sample cells. 3 mL sample cells are placed in the cell holders. One cell shows the peltier/fan attachment that allows for cooling.

Enhanced dispersed oil droplet stability using modified natural biopolymer

Venkataraman P, Tang J, Frenkel E, Olasehinde Owoseni, McPherson GL, He J, Raghavan SR, Kolesnichenko V, Bose A, John VT

Dispersants such as COREXIT 9500A are used in oil spill remediation with the objective of reducing the oil-water interfacial tension and breaking the slick into small oil droplets that are entrained in the water column for microbial degradation. However, the dispersants do not provide an effective barrier against coalescence of the droplets. The objective of this research is to enhance the stability of the dispersed oil droplet through the application of environmentally benign biopolymers. We specifically focus on hydrophobically modified polysaccharides where alkyl groups are attached to the polymer backbone. We hypothesize that the hydrophobic side chains preferentially anchor themselves in the oil phase resulting in the formation of a protective polymer layer around the droplet. The enhanced stability of the emulsion can be attributed to increased electrostatic repulsions as well as presence of polymer layer as a barrier to coalescence. Our results show that the addition of hydrophobically modified chitosan following the application of chemical dispersant to an oil spill can potentially reduce the use of chemical dispersants. Increasing the molecular weight of the biopolymer changes the rheological properties of the oil-in-water emulsion to that of a weak gel. The ability of the biopolymer to tether the oil droplets in a gel-like matrix has potential applications in the immobilization of surface oil spills for enhanced removal.

PEI Supported on Nanostructured Particles as Solid Absorbent for CO₂ Capture

Yueheng Zhang, Yingqing Wang, Yang Su, Olasehinde Owoseni

It is widely believed that emission of greenhouse gases such as CO₂ contributes significantly to global warming. The CO₂ emitted from large point resources, which accounts for most of the global CO₂ emission, can be captured to reduce the emission of CO₂. Amine scrubbing is currently used to capture CO₂ from flue gas on industrial scale. However, this technique suffers several disadvantages such as the highly energy intensive nature of the process and corrosive effects of the amine solution. Developing solid absorbent is promising to address these issues. Polyethyleneimine (PEI), a liquid polymer, is known to have the ability to react with CO₂. In this study, we developed several types of novel silica-supported PEI as solid absorbents for CO₂ capture application. By systematically changing the morphology of the silica particles, the capacity of capturing CO₂ was improved. The support particles were synthesized from inexpensive precursors and through a semi-continuous method which allows for large scale synthesis of the materials. The morphology of these particles was characterized by electron microscopy. The surface area and pore size distribution were acquired from Brunauer–Emmett–Teller equation. The capacity of CO₂ capture was measured by thermo gravimetric analysis.

Facile Synthesis of Multiwalled Carbon Nanotube/Zinc Phosphate Heterostructure as a Dual Purpose Corrosion Control Pigment

Greg Curtzwiler

The cost of corrosion in the United States was estimated to be 1 trillion dollars in 2012 due to assets deterioration and corrosion prevention and control processes. As a result, much attention has been devoted to enhancing corrosion control coatings through the addition of corrosion inhibiting pigments and increasing barrier properties to electrolytes and oxidative species which initiate corrosion. The high aspect ratio and surface area of carbon nanotubes (CNTs) makes them an attractive choice for use as a modifying barrier material specific to water and oxygen within surface coatings. Combining the barrier properties of CNTS with traditional corrosion inhibiting compounds, such as zinc phosphate, could result in combinations of polymers and inhibitors that provide improved corrosion control characteristics. The research presented herein was performed with the objective to demonstrate the synthesis potential for zinc phosphate modified multiwalled carbon nanotube and combinations with tethered epoxy prepolymers for characterization and study of barrier focused coatings.

“STICKY” THIOL-ENE POLYMER NETWORKS

Brian R. Donovan, Ethan F.T. Hoff, Jared S. Cobb, Arthur LeBlanc,
Bradley J. Sparks, Derek L. Patton

The adhesive capabilities of intertidal marine species, such as mussels, have recently provided a wealth of inspiration toward the design and development of new materials. Mussels show a unique ability to affix themselves to wet, heterogeneous surfaces such as rocks, and maintain adhesion under the high-energy, turbulent environment of the intertidal zones. While the natural adhesives employed by these organisms are a complex mixture of proteins, 3,4-dihydroxyphenylalanine (DOPA) has been identified as a common constituent that plays a central role in the curing and interfacial interactions of the adhesive plaques. DOPA is thought to play two primary roles in such bioadhesives: first, to facilitate cross-linking via the formation of di-DOPA linkages leading to solidification of precursor proteins, where cross-linking may occur via oxidative, enzymatic, or redox induced radical chemistry and, second, to facilitate adhesion to heterogeneous substrates via DOPA's ability to undergo hydrogen bonding, π - π aromatic interactions, and metal-ligand complexation with a variety of surface functionalities. Inspired by the salient features of natural bioadhesives, interest in designing synthetic polymeric systems that incorporate DOPA and analogous catecholic moieties as active adhesive constituents has proliferated in recent years. In this presentation, we report the synthesis of new multifunctional monomers containing pendent catechols. These catechol monomers show improved miscibility with multifunctional thiols and enes commonly used in thiol-ene polymerizations enabling solvent-free resin systems. This presentation will describe our efforts to evaluate the effect of the pendent catechol moiety, in the nonoxidized form, on photopolymerization kinetics, thermal, thermomechanical, and adhesive properties of the catechol modified thiol-ene networks.

Dispersion and Stabilization of MWCNTs in an Epoxy Thermoset Prepolymers using Continuous Reactors

Brian M. Greenhoe and Jeffrey S. Wiggins

The realization of theoretical properties for nanocomposites is dependent on optimal distribution of reinforcements at the nano-scale. With carbon nanocomposites becoming relevant in high performance materials, a fundamental understanding of multiwalled carbon nanotube (MWCNT) dispersion states in glassy polymer matrices has become an important area of research. In this study, dispersion states were varied through the continuous reaction of epoxy prepolymers with MWCNTs using a 16mm PRISM co-rotating twin screw extruder ($L/D = 25$). CNT dispersion was optimized through controlling shear states in the reactor which proved capable of debundling CNT agglomerates through the extent of prepolymer conversion and rheology through reactor temperature control. The MWCNTs were stabilized with a reduction in reagglomeration by increasing the prepolymer viscosity in the continuous polymerization reactor. Dispersion states were quantified via Transmission Electron Microscopy (TEM).

Thermomechanical Properties and Conversion Kinetics of Thermal and Photo Initiated Thick-Set Thiol-Ene Networks

Andrew P. Janisse, Kristen M. Van de Voorde, Scott G. Piland, Daniel A. Savin

The goal of this study is to compare physical properties of thickset thiol-ene networks produced through two different initiation techniques. Typically, thermally initiated radical reactions progress slower and have lower conversions than analogous photocured networks. Photocuring of thick-set networks is limited, however, by the ability of activating light to penetrate into the uncured resin due to part thickness and/or optical clarity. If the speed of the thiol-ene click reaction allows a thermally initiated system to reach similarly high conversions compared with photocured networks, then the favorable properties of thiol-ene networks will be able to be applied to previously unattainable applications.

Four different thiol and two alkene-functional (ene) monomers of varying functionalities, backbone chemistry and rigidity were used to form eight networks with T_g s ranging from -35°C to 55°C . The wide range of T_g s was used to evaluate relationship between final network T_g and the temperature at cure for both photo and thermally initiated networks. Real-time Fourier Transform Infrared spectroscopy (RT-FTIR) was used both to determine conversion of thiol-ene networks in real time and to monitor conversion profiles at different depths of photo or thermally cured thick-set samples with ATR-FTIR. Thermomechanical properties were determined with DMA, and thermal transitions were monitored with DSC. The network properties of thermally initiated systems were found to be comparable to those photocured. In addition, thermally cured samples were able to achieve a more consistent conversion throughout the full depth of a thick thiol-ene sample.

Surface and Interfacial Behavior: Chain-End Segregation in Polyethersulfone Solution Cast Films

Katrina M. Knauer and Sarah E. Morgan

The study of a class of materials almost always begins with the development of an understanding of properties in the bulk state. However, pure bulk phases are idealizations rather than widely encountered realities. It is actually the study of surface critical phenomena that has led to a number of new important insights into polymer behavior. Much of what exists in molecular modeling and experimental literature explains the behavior of flexible or modified chains. There is still a lack of accepted models that adequately explain structural organization and dynamics of semi-rigid and rigid rod polymers at surfaces and interfaces, which limits their effective use in important applications such as coatings, membranes, and medical and dental devices. This work presents a fundamental study of chain-end segregation at the polymer-air interface for a series of polyethersulfone (PESU) films cast from solution. Commercial PESU was fractionated into systems of varying molecular weight and characterized via gel permeation chromatography (GPC) and light scattering. Grazing angle attenuated total reflectance spectroscopy (GATR-FTIR), contact angle, and atomic force microscopy (AFM) was applied to characterize the surfaces of the films. Chain-end interaction energies were modeled via molecular dynamics. Through combined experimental and simulation analysis of these systems, refined models of PESU (and by extension semi-rigid/rigid rod polymers) behavior at the polymer-air interface will be developed that will enable further advancement of PESU applications.

Cyclization and Reactivity of Controlled Polyacrylonitrile Based Precursors via RAFT

Jeremy Moskowitz, Christopher Childers, Amit Sharma, Jeffrey Wiggins

In order to advance polyacrylonitrile-based carbon fibers it is important to understand the fundamentals of the polymer architecture and the mechanisms which convert the polymer into carbon fiber. With the advent of living polymerization techniques, including reversible addition fragmentation chain transfer (RAFT) polymerization, it is now possible to synthesize controlled precursor architectures with well-defined backbones, molecular weights, and polydispersities. This study aims to determine the reactivity ratios of acrylonitrile (AN) with two comonomers, acrylic acid (AA) and N-isopropylacrylamide (NIPAM), in the presence of a reversible chain transfer agent (CTA). Knowledge of the reactivity ratios will aid in targeting specific copolymer compositions. It was shown that NIPAM units are more uniformly distributed along the polymer backbone compared to AA units. This inherent property leads to more efficient cyclization of the nitrile moieties in the polymer which could be precedent for more profound effects in the carbon fiber properties.

HYBRID DUAL CROSS-LINKIED POLYMER NETWORKS VIA RING OPENING METATHESIS POLYMERIZATION OF NORBORNENE AND THERMAL RING-OPENING POLYMERIZATION OF BENZOXAZINE

Jananee Narayanan, Derek L. Patton*

A novel class of dual cross-linked hybrid network has been developed incorporating both norbornyl and benzoxazine based polymer networks targeting a wide range of tunable thermal and mechanical properties within the same system. Benzoxazine containing bisfunctional norbornene cross-linker (Nor-BZO) was synthesized and blended separately with two different reactive comonomers – 5-ethylidene-2-norbornene (ENB) and dicyclopentadiene (DCPD). The dual-crosslinked hybrid networks were synthesized by sequential ring opening metathesis polymerization (ROMP) of norbornene monomers using Grubbs catalyst, followed by thermal ring opening polymerization of benzoxazines. The curing processes for the formation of hybrid networks were systematically monitored by FT-IR analysis and differential scanning calorimetry (DSC). DSC analysis showed a ring opening exotherm at high temperature due to increasing rigidity with the network formation and cross-linking. TGA showed an increase in the initial weight loss (5% and 10%) with the addition of dicyclopentadiene monomer indicating enhanced thermal stability. Glass transition temperature by TMA showed a decrease in glass transition temperature with increasing concentrations of dicyclopentadiene monomer resulting from reduction in the extent of cross-linking. Similar studies were conducted using Nor-BZO /ENB crosslinking systems. Thus, by mixing different concentrations of norbornene based monomer/cross-linker systems - a broad range of tailorable thermal and mechanical network properties were attained in the final hybrid network.

“Polysoaps” to Serve as Uni-Molecular Micelles for Oil Spill Remediation and Drug Delivery Applications

Phillip Pickett

Conventional surfactants exhibit disadvantages upon sequestration of material in dilute concentrations and are typically environmentally harmful due to their toxicity. In this work a series of micelle-forming, amphiphilic copolymers or “polysoaps” with potential as dispersants for oil spill remediation in the marine environment has been synthesized via statistical RAFT copolymerization of specific molar ratios of 2-acrylamido-2-methylpropane sulfonic acid (AMPS) and n-dodecyl acrylamide (DDAM). Control over composition, degree of polymerization, polydispersity, and reaction kinetics were attained by conducting the copolymerizations at 60 degrees Celsius in dimethylformamide with AIBN and CEP as the initiator and chain-transfer agent, respectively. Molecular weight, hydrodynamic dimensions, composition- and concentration-dependent associative properties, and hydrophobic domain characteristics in water for copolymers with 10, 20, 30, 40, 50, and 60 mol % feed of DDAM have been studied utilizing NMR, SEC/MALLS, DLS, SLS, surface tensiometry, and fluorescence spectroscopy. It was found that the lower hydrophobic content (10%, 20%, and 30% DDAM) polysoaps form multimeric associations as indicated by increasing hydrodynamic dimensions as concentration is increased. On the other hand, the higher hydrophobic content (40%, 50%, and 60% DDAM) polysoaps form uni-molecular micelles with consistent sizes and with distinct hydrophobic cores over the entire concentration range probed. While using pyrene as a probe, UV-Vis absorbance experiments provided additional insight into the sequestration properties of the polysoaps. The higher hydrophobic content polysoaps show increased capabilities for dissolution of pyrene as compared to SDS above its CMC. Finally, the cytotoxicity of these polysoaps was determined utilizing KB cell lines in which the polysoaps exhibited up to 60x less cytotoxicity than SDS as measured by IC50 values. The results of this study point to the potential of uni-molecular micelles for oil spill remediation, allowing sequestration and subsequent hydrocarbon break-down by endogenous bacteria in the marine environment.

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