Reactive Magnetospinning of Nano- and Microfibers

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Abstract

Reactive spinning of nano- and microfibers that involves very fast diffusion-limited chemical reaction and ion exchange is very challenging for the major nanofiber formation methods. The two-droplet reactive magnetospinning method¹ introduced here offers a new technique for spinning fibers when the polymer formation or post-polymerization modification is limited by diffusion. This method can be realized for two miscible or two immiscible liquids, each with their own merits. The technique is based on the magnetic field-directed collision of the ferrofluid droplets with the liquid droplets that contain complimentary reactants.² The collision, beginning of the chemical reaction, and fiber drawing are self-synchronized. The reactive magnetospinning method is used to synthesize, cross-link, and chemically modify the fiber-forming polymers in the stage of fiber formation. It also provides new opportunities for the fabrication of magnetic and non-magnetic polymer fibers that can be used as scaffolds for tissue engineering and other biomedical applications.

References

A versatile and inexpensive method for controlling the surface relief structure of polymer films over large areas through a two-step imprinting process is demonstrated. First, nanoscale patterns were formed by nanoimprinting elastomer (PDMS) films with a pattern on a DVD disk. Micron-scale patterns were then superimposed on the nanoimprinted PDMS films by exposing them to ultraviolet radiation in oxygen (UVO) through a TEM grid mask having variable micro-scale patterning. UVO exposure leads to a conversion and densification of PDMS to SiO$_x$, leading to micron height relief features that follow a linear scaling relation with pattern dimension. Further, the pattern scopes are shown to collapse into a master curve by normalized feature values. Interestingly, these relief structures preserve the nanoscale features. In this work, the influence of the self-limiting PDMS densification, walls stress at the boundary of micro depression and UVO exposure energy are studied in control of the micro depression scale. This simple two-step imprinting process involving both nanoimprinting and UV radiation, allows for facile fabrication of the dimension adjustable micro-nano hierarchically structures not only on elastomer films but also by imprinting onto thermoplastic polymer films. To explore the universality of the introduced micro-nano hierarchical structure, this well-controlled surface structure is transferred to shape memory materials aiming at the potential applications in electronics, smart adhesives, and deployable structures.
Predicting glass transition of linear polymers using integral equation theory

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The understanding and prediction of glass transition is a major problem of the physics of condensed liquids that has gained the attention of scientific community for more than 50 years. Several different theories are proposed to correlate glass transition with the structure of a material. For example, the Adam – Gibbs theory relates polymers segmental relaxation with its configurational entropy. However, there exists no simple method for computing configuration entropy of a polymer system. In order to make a first approach towards the solution of this problem, the aim of the work presented here is to find a theoretical method capable of computing the configurational entropy. In this work, we employ integral equation theory to calculate configuration entropy of a simple model polymer. This enables to directly test the Adam–Gibbs predictions of glass transition properties viz., glass transition temperature and fragility. Further, we compare the Adam Gibbs theory with several other existing glass transition theories which are based on dynamical quantities. The present work aims to enhance the theoretical understanding of glass transition in polymeric liquids.
Chain dynamics and entanglements in model polymer nanocomposite melts

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It is well known that adding even a small volume percent of nanoparticle (NP) fillers can significantly alter the mechanical strength and viscoelastic properties of polymer melts. The type of ordering of nanoparticles, interparticle spacing, and resulting material properties depend on many parameters that can be experimentally controlled; important parameters include nanoparticle size, surface chemistry, packing fraction, and polymer length. This large parameter space available for polymer nanocomposite (PNC) systems means that trial-and-error design is unlikely to lead to materials with optimal properties, therefore there has been significant research interest in developing a deep understanding of the underlying physics that drives PNC behavior. To this end, we use coarse-grained molecular dynamics simulations to investigate the chain dynamics and entanglement network for simple model PNC materials. Specifically, we use a Kremer-Grest type of bead-spring model to simulate a polymer melt with spherical particles. We place particles randomly in the periodic box and compare the dynamics and entanglement network results (from a primitive path analysis) to those of a bulk polymer melt and to a system with particles placed in a cubic arrangement. We also adjust the strength of the interaction potential between the polymer and nanoparticle to qualitatively consider the effect of changing polymer type or particle surface chemistry. We notice that when all potentials are purely repulsive (polymer does not adsorb on the nanoparticle surface), chain dynamics are hardly affected as nanoparticles are added, even near the surface. From the primitive path analysis, we observe a small reduction in the number of entanglements due to the addition of the NPs. Meanwhile, when the polymers are attracted to the NP surface, the chain dynamics slow near the particle surface. We find the spatial arrangement of nanoparticles has little role in chain dynamics, and only weakly affects the entanglements.
Differential dynamic microscopy of thermoreversible microgel

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Abstract:

Differential dynamic microscopy (DDM) has been used to study the dynamics of thermoreversible, rodlike polymer microgel dispersion in 97% sulfuric acid. The rods are poly(p-phenylenebenzobisthiazole) (PBZT). Differential dynamic microscopy has been developed and used to quantify particle dynamics with a standard light microscope and a camera. A series of images of samples is analyzed using a digital Fourier transform and the relevant dynamics are obtained. Different microscopy approaches have been developed, ranging from bright field to fluorescence-based, polarized and dark-field to study the dynamics of latex, bacteria motility, anisotropic Janus particles and gold particles. But DDM has not been applied to solutions containing typical synthetic macromolecules. Here we use dark-field DDM to measure the dynamics of rigid rods in the form of microgels in sulfuric acid, which is challenging to be measured by traditional techniques such as dynamic light scattering (DLS). We evaluate the time, temperature and concentration dependence on the PBZT microgel dynamics.
Fabrication and Characterization of Semiconducting Metal Oxide Nanofibers from Gas Jet Fiber Spinning Process for Enhanced Photocatalytic Performance

Author: Monoj Ghosh

Semiconducting metal oxides (SMO) are widely used in photocatalysis application. In this study, we demonstrate a novel Gas Jet Fiber (GJF) spinning technique in conjunction with conventional precursor sol–gel chemistry for fabrication of SMO nanofibers with multiple morphologies and controlled dimension. Specifically, mesoporous titanium dioxide (TiO2) and hierarchical bi-component titanium dioxide-vanadium pentoxide (TiO2-V2O5) nanofibers with tailored morphology and dimension are fabricated via the GJF spinning technique. TiO2 nanofibers with controlled dimension, crystal size, and crystal anatase vs rutile phase structures are produced via calcination at 500-700 °C of precursor nanofibers of polyvinylpyrrolidone (PVP) and titanium isopropoxide (TTIP) obtained from the GJF spinning process. On the other hand, a mixture of vanadium isopropoxide (VOIP) and TTIP as precursors along with PVP as a template are used for fabrication of hierarchical nanorods on nanofiber morphological form of TiO2-V2O5 via calcination at 400-600 °C of precursor nanofibers of PVP-TTIP-VOIP. All of these resultant GJF-spun SMO nanofibers are characterized using SEM, TEM, EDX, XPS, FTIR, N2-BET surface analyzer, and XRD for their morphological and crystallographic studies. Further, the SMO nanofibers are used in photocatalytic oxidation of gas phase ethanol at room temperature on exposure to UV-irradiation. The nanofibers show up to an order of magnitude higher photocatalytic activity than commercial grade P25 TiO2 nanoparticles due to slower electron-hole recombination phenomena in the former. The experimental trends are analyzed using electron-hole (e-h) charge recombination inferred from high intensity photoluminescence emission spectra, specific surface area, crystallinity, morphology, and the phase structures.
Pyrene-modified Polyelectrolytes/MWNT LbL Assemblies Extinguish Flames on Polyurethane Foam

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Flame retarding nanocomposite thin films were deposited on polyurethane foam using water-based solutions of cationic and anionic-stabilized multi-walled carbon nanotubes (MWCNT). Layer-by-layer (LbL) assembly was used to coat the open-celled foam to produce uniform protective layers up to 600 nm thick, comprised of cationic polyethylenimine modified with pyrene (PEI-Py), anionic poly(acrylic acid) (PAA), and MWCNT. Coatings of only 6 [PEI-Py/PAA+MWCNT] bilayers (BL) showed tremendous reductions in peak heat release rate (up to 67%) and total smoke release (up to 80%) for the polyurethane foam. This same coating significantly improved the performance of the polyurethane when exposed to horizontal and vertical flame tests. With 9 BL, the foam successfully withstood a vertical burn test, self-extinguishing immediately after removal of the test flame. These dramatic reductions in foam flammability are unprecedented and are attributed to the protective nature of the carbon based char formed from the coating that acts as a protective barrier.
Endgroup Functionalization of Engineering Polyesters with Ureidopyrimidinone

Katelyn R. Houston, Anne-Martine S. Jackson, Ross W. Yost, Howard S. Carman, Valerie Sheares Ashby

The structure-property relationships of end-functionalized glycol-modified poly(ethylene terephthalate) (PETG) of various molecular weights was investigated using the quadruple hydrogen bonding ureidopyrimidinone (UPy) group. The UPy group has been extensively used to end-functionalize low molecular weight polymers with low glass transition temperatures to create supramolecular telechelic materials with improved tensile properties and thermoreversibility. While the effect of the UPy endgroup has been investigated on many aliphatic materials, the effect of these groups has not been broadly investigated for high performance, aromatic polymers. While high molecular weight engineering plastics have excellent mechanical properties, they can be difficult to process. By end-functionalizing low molecular weight engineering polymers with the UPy moiety, issues involving processability could be overcome while maintaining the overall robust properties of the high molecular weight polymer. The terminal functionalization of various low molecular weight PETG derivatives with the UPy moiety was performed via isocyanate-hydroxyl reactions employing different diisocyanate linkers. The subsequent structure-property relationships were studied, and select mechanical properties, such as strain at break, were enhanced after end-functionalization. Ultimately, this study shows that endgroup functionalization with supramolecular moieties provides a promising route to improving the properties of low molecular weight engineering plastics.
Aramid Nanofibers/Graphene Layer-by-Layer Electrodes for Structural Energy and Power

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The development of electrode materials that exhibit both exceptional electrochemical and mechanical properties is increasing in importance. Such a material would enable the development of electrodes for energy and power that can dissipate energy, bear a load, or withstand an impact. In this presentation, we report on a composite electrode containing aramid nanofibers and graphene fabricated via layer-by-layer (LbL) assembly. LbL assembly has been widely studied since the technique is extremely simple and versatile for a design of nanostructured composite materials with controllable properties. Graphene has good electrical properties and mechanical strength due to its unique two-dimensional structure. In addition, recently developed aramid nanofibers, nanoscale Kevlar fibers, are of interest for its high mechanical strength and the enhanced processability for creating composites. Through a combination of these materials, mechanically strong hybrid electrode were fabricated, where aramid nanofibers act as polymer matrix and interfacially interact with graphene sheets. Film growth, structure, and morphology were characterized using scanning electron microscopy, UV-vis spectroscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy. Mechanical properties were explored using atomic force microscopy. Electrochemical performance was also evaluated.
Phase Diagrams of Molecular Gels Formed by 12-Hydroxystearic Acid/n-Alkane Solutions

Tzu-Yu Lai, Kevin A. Cavicchi

It is known that many small molecules can act as organogelators (i.e. low molecular mass organogelator (LMOG)) for organic solvents, where the crystallization of the LMOG into anisotropic crystals forms a three dimensional, load-bearing network, gelling the surrounding solvent. As the gelation is dependent on the underlying phase behavior, measurements of the LMOG-solvent phase diagrams is one route to help answer the question, what makes a good LMOG? In this presentation the phase behavior of a model LMOG, $R$-12-hydroxystearic acid (12-HSA) in different $n$-alkanes is presented. Measurements of the phase behavior using sample inversion, differential scanning calorimetry and cloud point measurements will be discussed. In this system the enthalpic interactions are mostly invariant (i.e. the solubility parameter of the alkane has a small variation with the number of backbone carbons in the alkane). Therefore, the effects of molecular size and entropic effects on the solubility of 12-HSA in organic solvent can be isolated. In addition, in these non-polar solvents association of the 12-HSA in the liquid state strongly influences the phase behavior, where it acts like a supramolecular polymer greatly reducing the entropy of mixing stabilizing the solid phase at low concentration and even driving liquid-liquid phase separation in longer $n$-alkanes. It will be shown that this liquid state aggregation is crucial to the gelation ability of 12-HSA and is a design parameter in the development of tailored LMOGs for specific fluids and applications.
Toward Room-Temperature Additive Manufacturing with High-Performance Polymers

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Abstract: We have investigated methods for generating 3D objects from high-performance engineering polymers at room-temperature. A series of modified PEEK polymers were synthesized to enable enhanced solubility and functionality such that combinations of material jetting, molding, and photo-curing could be explored. We found that soluble variants of PEEK polymer could be applied as solution-based binders to insoluble PEEK powders. These mixtures were successfully used for formation of free-standing 3D objects. We also investigated the optimization of infiltration techniques, thermal curing, and binder composition.
Title: Solution Behavior of Pd₆L₄ Coordination Macroions — the Effect of ligands

Authors: Hui Li, Tianbo Liu, Department of Polymer Science, University of Akron

Abstract: In the presence of small simple counterions, macroions with modest charge density could self-assemble into one-layer hollow spherical structures. The driving force to form this vesicle-like structure is considered as counter-ion mediated attractions. On the other hand, overall hydrophilic transition metal-organic macrocations, consisting of hydrophobic ligands (pyridine-based) and hydrophilic palladium (Pd) metal ions, can be regarded as nano-sized macrocations. One class of the positively charged coordination macroions, Pd₆L₄ (Pd = Pd (II)), is famous for its controllable and precise assembly structure and possible host-guest interaction. By functionalizing the ligands with different organic parts, the macroions could alter the size and charge density. Detecting their self-assembled structures will tell the difference of their solution behavior as well as the discrepancy of macroion clusters. In summary, the small organic ligands have been observed to change the surface charge density, and furthermore, have significant effect on their solution behavior.
Exploring Block-Copolymer Micelle Dynamics for Tunable Cargo Delivery and Reactivity

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Block-copolymer micelles (BCPMs) self-assemble from amphiphilic polymers that can be tailored to form nm-scale vessels. BCPMs are suited for targeted anticancer drug delivery due to their biocompatibility, prolonged circulation time, and in vivo degradability.1 These micelles also find use as tunable “nanoreactors” in large scale synthesis of hydrophobic molecules without need for volatile organic solvents.2

Our group is using NMR spectroscopy and diffusometry3 to study chemical structures and molecular dynamics of BCPMs in order to enhance current understanding of these systems. Here we study a diblock poly (ethylene oxide)-poly (ε-caprolactone) (PEO₅k-b-PCL₈k) that forms spherical micelles at 1 % (w/v) in mixed solvent (D₂O/THF-d₈) solutions.

From 20 – 40 °C, NMR diffusometry shows one diffusion coefficient, meaning no unimers exist in solution. From 40 – 60 °C, we extract two distinct diffusion coefficients (see Figure), supporting the insertion-expulsion unimer exchange mechanism.4 In this coexistence region, we compare relative fractions of unimers and micelles and observe changes in unimer populations (10 – 50%) as a function of block lengths, solvent composition, and temperature.

Increasing temperature (just above body temperature) accelerates micelle unimer dynamics and therefore enables cargo release. We are exploring such external stimuli to trigger drug release in BCPMs and our study sheds light on quantitatively understanding effects of micellar dynamics on drug release or nanoreactor exchange.

References:
Self-Recognition of Two Rod-Shaped Macroions with Different Functional Groups Controlled by Cation-π Interaction

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Two rod-shaped macroions, $[\text{Bu}_4\text{N}]_7[\text{ArNM}_6\text{O}_{17}\text{NC(OCH}_2)_3\text{MnMo}_6\text{O}_{18}(\text{OCH}_2)\text{CNMo}_6\text{O}_{17}\text{NAr}]$ (Ar=naphthyl and 1-methylnaphthyl), with identical charge densities and morphologies except for slight difference of their functional groups were observed to self-assemble into vesicle-like structures in dilute solutions. Interestingly, instead of forming mixture spheres, the two highly similar macroions kept self-sorted and consequently self-assembled into individual supramolecular spheres with size of 30 nm and 55 nm, as confirmed by Laser Light Scattering (LLS) techniques. Control experiments reveal that the dominant driving force during their self-assembly processes is cation-π interaction rather than electrostatic interaction. This may be explained by the substantial enhancement of cation-π interaction, which contributes from the cooperativity of π-π environment on the surface of the self-assembled spheres. Although cation-π interaction is considered as a weaker force compared to electrostatic interaction, this work suggests that the delicate cation-π interaction might be significant in supramolecular assemblies, which leads to self-recognition phenomenon between two highly similar macroions.

National Science Foundation (CHE1305756)
Hollow microcapsules by stitching together of graphene oxide nanosheets with a difunctional small molecule

Author: Qinmo Luo & Peiran Wei

Micron-sized hollow capsules composed of graphene oxide (GO) and small molecule cross-linker are prepared and isolated. These capsules are characterized by XPS, FTIR, and Raman spectroscopies. The cross-linked and non-cross-linked microcapsules show distinct release profiles from each other. Moreover, the microcapsules can be loaded with gold nanoparticles, suggesting these structures are useful in encapsulation technologies.
Polyurea-peptide hybrids: molecular design for mechanical tunability

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Natural materials have been shown to exhibit superior mechanical properties, such as in the case of dragline silk from an Araneus diadematus spider which has a toughness ~40x greater than Kevlar. One strategy by which biological materials tune mechanical properties is via hierarchical design and microstructural development through peptide hydrogen bonding and self-assembly (e.g., β-sheet, α-helix). Inspired by natural materials, a series of peptide polyurethane/ureas were synthesized combining molecular self-assembly via hierarchical arrangement and tunable morphologies through the use of soft segment selection and chemical vs. physical crosslinking. Our focus is to observe solid-state thermal and mechanical properties of fully-synthetic peptidic-hybrid copolymers to elucidate the impact of networks derived from chemical crosslinking within the hard phase, physical crosslinks utilizing different amino acids, and variations in crystalline and amorphous soft segment block choice. Incorporation of peptides units, such as aspartic acid and lysine, at the interface of the hard and soft segment yielded “pseudo” hard segments and tailored tensile modulus based on the hydrogen bonding (controlled with varying peptide repeat length) and peptide content of the material. This work resulted in a better understanding of structure-property relationships to modulate the young’s modulus and achieve variations in morphology (fibrillar vs. globular). Furthermore, processing of these materials into films vs. nanofibers has also been developed to broaden the application of these systems. Ongoing research into stimuli responsiveness of these materials with the goal of manufacturing specialty application products and smart soft-materials is currently underway.

Molecular Dynamics Simulation of Solvent Swollen Block Copolymer Films

Authors: Arvind Modi, Alamgir Karim and Mesfin Tsige

Block Copolymers (BCPs) offer a wide range of solutions to product development varying from electronics to medical industries. Particularly, for electronic industry, BCP templates are extremely fast and cheap route for nanostructure synthesis in addition to offering a fine control over feature size. Current state of solvent processing of thin BCP films for templating applications involves exposure to solvent vapors or immersion into solvent mixtures. Former is being used for decades and the latter has been developed recently. However, both of these strategies are poorly understood and a general strategy for application of these techniques to a given BCP system is evidently lacking. Hence, we perform coarse-grained molecular dynamics simulation of solvent swollen BCP films to understand the kinetics of phase separation and factors affecting final morphology. We systematically study the effect of asymmetry of solvent-block interaction in diblock system on swollen-morphology, inter-layer distance, domain-spacing and interfacial width (or effective \( \chi \)-parameter). We also study the effect of substrate-solvent interaction on polymer- and solvent-surface segregation. In general, we develop a strategy to predict solvent (or solvent combination) for a given BCP system providing an effective and a robust tool for experimentalists.
Investigating the material properties of the *Caulobacter crescentus* adhesive holdfast

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The ability to adhere materials underwater is greatly impeded by the presence of a boundary layer of water between the two adherends, with synthetic adhesives failing due to poor interfacial adhesion. Nature possesses various solutions to this problem, as seen in studied mussels, sandcastle worm and barnacles; however, less complex unicellular organisms such as bacteria are also faced with this problem. One of the primary colonizers of submerged surfaces is the bacteria *Caulobacter crescentus*, which adheres underwater by means of a secreted adhesive holdfast that possesses the highest measured adhesive strength for any microorganism. Little is known about the material properties of this adhesive. We use a combination of spectroscopic and microscopic techniques to elucidate the chemical components of the holdfast, its structural features as well as its interaction with different surface characteristics. An understanding of these properties will provide design ideas for the fabrication of bio-inspired underwater adhesives with potential applications in areas such as engineering, medicine and biomimetics.
Peptide Hydrogels with Controlled H$_2$S release

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H$_2$S is a gasotransmitter that can regulate many physiological pathways. It has been explored to heal wounds and treat diseases such as diabetes and myocardial ischemia-reperfusion. However, the efficient delivery and controlled release of H$_2$S are issues that have hindered its potential applications. Hydrogels formed by self-assembling peptides are supramolecular polymers that can serve as drug delivery matrices. These materials are biodegradable and possess the possibility to mimic the natural extracellular matrix. In this study, a series of peptide hydrogels with the sequence IAVE$_4$ attached to an H$_2$S donor S-arylothiooxime (SATO) were successfully prepared. The peptide sequence IAVE$_4$ was chosen to provide hydrophilicity and form β-sheets in the self-assembled structures. A library of SATO derivatives with substituents ranging from MeO, Me, H, F, and Cl at the para position were synthesized and studied. All peptides with SATO structure (SATO-peptides) demonstrated their ability to release H$_2$S with the trigger of cysteine in PBS. At a concentration of 0.1 mg/mL, which was below the CMC in all cases, the H$_2$S release kinetics were controlled by the substituents in SATO structure, with half-lives ranging from 14.9 min to 35.1 min. As the concentration increased above the CMC, H$_2$S release half-lives increased dramatically. The slow release was likely the result of reduced diffusion of cysteine into the self-assembled nanofibers, which were observed by TEM. Fluorescence and circular dichroism, which showed π-π stacking and β-sheet structures, were used to rationalize the different release rates.
Polythioether Particles Armored with Modifiable Graphene Oxide Nanosheets
Authors: Bradley Rodier, Emily Pentzer

Facile and scalable fabrication methods are attractive to prepare modifiable materials for diverse applications. Herein, we present a method to prepare cross-linked polymeric nanoparticles with graphene oxide (GO) nanosheets covalently attached to the surface using photo-initiated mini-emulsion polymerization and alkene-functionalized GO. The modified GO serves as a surfactant, and the alkene functionalities of GO exposed to the oil-phase are incorporated into the polymer particle through thiol-ene reactions, leaving the unreacted alkene functional groups of the other face of GO available for further functionalization. We then modify the surface of the GO-armored polymer particles with a small molecule fluorophore or carboxylic acid functional groups that bind to Fe$_2$O$_3$ and TiO$_2$ nanoparticles. This methodology provides a facile route to preparing complex hybrid composite materials.
Directed Self-Assembly of Block Copolymers for High Breakdown Strength Polymer Film Capacitors

Emerging needs for fast charge/discharge yet high-power, lightweight and flexible electronics requires the use of polymer film based solid-state capacitors with high energy densities. Fast charge/discharge rates of film capacitors on the order of microseconds are not achievable with slower charging conventional batteries, super-capacitors and related hybrid technologies. However, the current energy densities of polymer film capacitors fall short of rising demand, and could be significantly enhanced by increasing the breakdown strength ($E_{\text{BD}}$) and/or dielectric permittivity ($\varepsilon_r$) of the polymer films. Co-extruded two-homopolymer component multilayered films have demonstrated much promise in this regard showing higher $E_{\text{BD}}$ over that of component polymers. Multilayered films can also help incorporate functional features besides energy storage, such as enhanced optical, mechanical, thermal and barrier properties. In this work, we report accomplishing multilayer, multicomponent block copolymer dielectric films (BCDF) with soft-shear driven highly oriented self-assembled lamellar diblock copolymers (BCP) as a novel application of this important class of self-assembling materials. Results of a model PS-$b$-PMMA system show ~50% enhancement in $E_{\text{BD}}$ of self-assembled multilayer lamellar BCP films compared to unordered as-cast films, indicating that the breakdown is highly sensitive to the nanostructure of the BCP. The enhancement in $E_{\text{BD}}$ is attributed to the ‘barrier effect’ where the multiple interfaces between the lamellae block components act as barriers to the dielectric breakdown through the film. The increase in $E_{\text{BD}}$ corresponds to more than doubling the energy storage capacity using a straightforward directed self-assembly strategy. This approach opens a new nanomaterial paradigm for designing high energy density dielectric materials.
Molecular Dynamics Simulations of Penetrant Diffusions in Lamellar Phase of Tapered Block Copolymers

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Tapered AB block copolymers have a mid-block “tapered” region with a gradient in composition that goes from pure A to pure B (or from pure B to pure A for an inverse taper) between two pure blocks of A and B monomers. This polymer architecture provides a simple, effective way to tune polymeric properties including the polymers’ segmental motion, order-to-disorder transition temperature, and domain spacing or microphase separated state. By performing molecular dynamics simulations with a simple bead-spring model, we show how such properties change as a function of taper length and compare with the existing theoretical and experimental results. For the current study, we are motivated to understand dynamics of small molecules in tapered copolymers because of the potential use of tapers in transport applications such as for battery electrolytes or fuel cell membranes. For this, monomer-sized penetrants with favorable interactions with one of the polymer microphases are added to various lamellar phase systems. Specifically, AB normal and inverse tapered architectures with taper lengths from 0% (diblock) to 100% (full gradient) are considered. The results for normal tapers show that both polymers and penetrants diffuse faster along the lamellae (parallel to the diblock interface) as taper length increases. However, inverse tapered systems show a strong non-monotonic behavior in diffusion as a function of taper length. This is due to the different polymer conformations (such as criss-crossing of chains across the interface) present for inverse tapers, because of their $AB'A'B$ tetra-block-like architecture. The relationships between the different types of chain conformations and dynamics are quantified and analyzed. Recently, we have also considered salt-doped systems (with full long-ranged Coulomb interactions) to explore how ion transport is different than that of uncharged small molecules.
**Molecular Dynamics Simulations of the Gyroid Phase in Block Copolymer Systems**

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Block copolymers are well known to microphase separate into various ordered structures such as lamellae, hexagonally packed cylinders, or the double gyroid phase. The phases retain some of the properties of the pure blocks; for battery electrolyte applications, for instance, this means one block with higher dielectric constant and good mobility could act as an ion carrier while the other could have a high modulus and make the electrolyte mechanically strong. For such transport applications, network phases such as the double gyroid are of particular interest since they are continuously connected in all three dimensions and thus could potentially provide both a high shear modulus and good transport properties through a well-defined 3D network of pathways. In our previous work, coarse-grained molecular dynamics (MD) simulations were performed to study various structures of block copolymer systems. When such systems are initialized from a random state, the system is not only slow to microphase separate, but it is difficult to ensure equilibration to the true lowest free energy structure with right spacing, especially for cubic phases like the gyroid. In this study, we focus our MD simulations on systems that were predicted to form the gyroid phase in prior theoretical work. We initialize the systems in gyroid phase by growing polymers in a constrained random walk such that the A and B blocks are placed on opposite sides of the gyroid interface. This ensures the simulation proceeds with the system in gyroid phase rather than other metastable phases, and equilibration (given that the system is in the gyroid phase with the provided number of polymers per unit cell) occurs relatively quickly. We will discuss our recent data comparing systems of different domain spacings (different simulation box sizes). Overall, this strategy increases our ability to study such gyroid morphologies in detail.
High Oxygen and Moisture Barrier of Oriented Polypropylene Film with Multilayer Thin Film Nanocoatings

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Oriented polypropylene (OPP) film is widely used in packaging. Various techniques such as vapor deposited SiOx and AlxOy and polymer-clay nanocomposites coatings have been applied to improve the gas barrier of OPP film, but these approaches lead to loss of flexibility and transparency. Layer-by-layer (LbL) assembly provides a cost-effective alternative. In this study, commercial OPP film was coated with polymer-clay LbL gas barrier nanocoatings, which improved oxygen and water vapor transmission rate (WVTR). A 30 bilayer polyethylenimine (PEI)/vermiculite (VMT) LbL coating improved the OTR by more than 160X, rivaling most inorganic coatings. WVTR was simultaneously reduced by 42.5% relative to uncoated OPP. This water-based technology is both effective and scalable.
Abstract: Cationic Gemini Surfactants for Enhanced Oil Recovery

Surfactants used for enhanced oil recovery (EOR) has been applied commercially for many years dating back to the 1970s and 1980s\(^1\). Surfactants or surface-active agents are compounds that reduce surface tension between two liquids or a liquid and a solid. In the field of EOR, surfactants are used to reduce the surface tension between rock and oil by water flooding. This process releases trapped oil in presumed depleted oil reservoirs. New gemini (double head) surfactants possess the capability to reduce the surface tension to lower values than previously reported single head surfactants\(^2\). This factor garners attention to gemini surfactants as prime candidates for EOR. We aim to synthesize quaternary ammonium salts, a class of gemini surfactants, previously used as fabric softeners\(^3\). Bis(2-hydroxy-3-(dodecyldimethylammonio)propyl)methylamine dichloride (2a) contains two tails while current industry standards (sodium dodecyl sulfate, cetyltrimethylammonium bromide, and alfoterra 4S G90) all contain one tail. See figure 1 below. These surface-active agents will then undergo physical test, by a tensiometer, to measure critical micelle concentration (cmc). A rock absorption test onto kaolinite clay will be conducted to mimic the worst-case scenario in rock reservoirs. The presentation will describe the synthesis, characterization, and the physical test results of the gemini and single head surfactants. We hypothesize that gemini surfactants will display a superior ability to lower the surface tension of water than current industry leading standards. Lastly, we aim to apply these results to the field of enhanced oil recovery by introducing gemini surfactants to improve tertiary oil recovery methods.

References:


Figures 1: Synthesis of Gemini Surfactant

Synthesis of 2A

\[
\text{NH}_2 + \overset{O}{\underset{Cl}{\text{Cl}}} \overset{\text{epichlorohydrin}}{\underset{\text{stir 12h}}{\text{Cl}}} \overset{\text{OH}}{\underset{\text{ethanol}}{\text{Cl}}} \overset{\text{OH}}{\underset{\text{bis(2-hydroxy-3-chloropropyl)methylamine}}{\text{1A}}} \\
\text{Cl} \overset{\text{OH}}{\underset{\text{H}_2\text{N} \overset{\text{Cl}}{\underset{\text{OH}}{\underset{\text{Cl}}{\text{N}}}}} \overset{\text{stir 12h}}{\text{dodecyldimethylamine (n=12)}} \overset{\text{OH}}{\underset{\text{ethanol}}{\text{bis(2-hydroxy-3-(dodecyldimethylammonio)propyl)methylamine dichloride}} \text{2A}}
\]
Abstract of the Poster for the 12th National Graduate Research Polymer Conference-- Star-like copolymer stabilized noble-metal nanoparticle powders

Pengfei Cao, Yunhui Yan, Joey Mangadlao, Lihan Rong and Rigoberto Advincula

The amphiphilic star-like copolymer polyethylenimine-block-poly(ε-caprolactone) (PEI-b-PCL) was utilized to transfer the pre-synthesized citrate-capped noble metal nanoparticles (NMNPs) from an aqueous layer to an organic layer without any additional reagents. Dynamic light scattering (DLS) and transmission electron microscopy (TEM) were utilized to study the assembly of the polymers coated on the surface of the citrate-capped NMNPs. After removing the organic solvent, the polymer-coated NMNPs in powder form (PCP-NMNPs) were obtained. The excellent solubility of the PEI-b-PCL allows the PCP-NMNPs to be easily dispersed in most of the organic solvents without any significant aggregation. Moreover, the good thermal stability and long-term stability make PCP-NMNPs an excellent NMNP-containing hybrid system for different specific applications, such as surface coating, catalysis and thermoplastic processing of nanocomposite materials.
OBSERVATION OF THE GROWTH OF POLYMER NANOPARTICLES IN SOLVENT SHIFTING PROCESS BY DYNAMIC LIGHT SCATTERING AND ITS APPLICATION

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Abstract

Adding poor solvent into the polymer solution will lead to a shift in solubility and eventually phase separation, which refers to the solvent-shifting process. During this process it has been observed that different sizes of polymer particles are formed. The formation of these polymer nanoparticles have been assumed to follow a well-known “Ouzo Effect” that was previously used to explain the formation of nanoparticles of small-molecular organic molecules by solvent-shifting process, which is also known as homogeneous nucleation and growth. This approach has been used to prepare particles using classic polymers without amphiphilic properties such as poly (lactic acid), polystyrene, and poly (methyl methacrylate). However, the assumed homogeneous nucleation mechanism for the solvent-shifting process has not been proved with obvious evidences, and the desired size and the size distribution of produced polymer nanoparticles were not well controlled.

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In this research we have studied PMMA solution with very low concentration in the system to capture the early stages of concentration fluctuation and the formation of nucleation by adding water utilizing Dynamic Light Scattering technique. Steps of the growth of the polymer particles in the solvent-shifting process were observed and based on the results further production of monodispersed polymer nanoparticles was obtained by our specially designed Porous RC Membrane Solvent-Exchange System.
Differential dynamic microscopy of thermoreversible microgel

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Abstract:

Differential dynamic microscopy (DDM) has been used to study the dynamics of thermoreversible, rodlike polymer microgel dispersion in 97\% sulfuric acid. The rods are poly(p-phenylenebenzobisthiazole) (PBZT). Differential dynamic microscopy has been developed and used to quantify particle dynamics with a standard light microscope and a camera. A series of images of samples is analyzed using a digital Fourier transform and the relevant dynamics are obtained. Different microscopy approaches have been developed, ranging from bright field to fluorescence-based, polarized and dark-field to study the dynamics of latex, bacteria motility, anisotropic Janus particles and gold particles. But DDM has not been applied to solutions containing typical synthetic macromolecules. Here we use dark-field DDM to measure the dynamics of rigid rods in the form of microgels in sulfuric acid, which is challenging to be measured by traditional techniques such as dynamic light scattering (DLS). We evaluate the time, temperature and concentration dependence on the PBZT microgel dynamics.