Investigation of trans-1,4-Polyisoprene as an Organogelator for Organic Solvents

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Organogels are an interesting class of soft materials where an organic fluid is immobilized by the addition of a suitable organogelator. A variety of organogelators, ranging from small molecules to polymers, have been researched and developed for novel applications ranging from drug delivery to consumer products such as deodorant and shampoo. In this study, the ability of trans-1,4-polyisoprene (TPI) to act as an organogelator is examined. TPI is the geometric isomer of cis-1,4-polyisoprene (CPI). While CPI is a viscoelastic liquid at room temperature, TPI is semi-crystalline with a melting temperature of ca. 60 °C. TPI's crystallinity provides high mechanical strength, cut abrasion and electrical insulation, and it is used as a processing additive, such as improving the green strength of synthetic polyisoprene. It was hypothesized that TPI would act as a good organogelator if it was able to crystallize in organic solution and form a three-dimensional percolating network. Gelation of TPI/organic solvent was tested by dissolving TPI (10 wt%) at elevated temperature and then cooling. Gelation was qualitatively confirmed by inversion, where a gelled solution did not flow over long time scales. TPI was observed to gel n-alkanes, anisole and butyl acetate. TPI failed to gel phthalates (insoluble) and aromatic solvents (soluble at RT), THF (soluble at RT) and ethyl acetate (insoluble). The gels were further characterized to determine the minimum gelation concentration, gel transition temperatures as a function of composition, and gel morphology. The gel transition temperature vs. concentration curve was consistent with the melting point depression of a solute in solution expected for gelation driven by the crystallization of TPI. Finally, efforts to dry the TPI gels to generate functional xerogels will be presented.

Functionalized Polyurethanes for Biomedical Applications

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Polyurethanes have many applications in the medical field as well as a wide vareity of other industrial applications, such as coatings and tubings. This work will investigate the result of the addition of functionalized diols into common industrially used polyurethane systems. A library of diol monomers containing a variety of different amino acid pendant groups have been synthesized previously. Polyurethanes were then synthesized with the addition these monomers containing amino acid like pendant groups to mimic some functionality and properties found in nature. These homopolymers were characterized to determine the inherit properties of these materials. Polyurethanes were then synthesized by incorporating monomers from this library into the hard block segments as chain extenders. PTMO was selected as the soft segment. The properties and functionality of these mateirals were then investigated for future applications.

Molecular Dynamics of Structural Phase Transformation in NiTi Shape Memory Alloy

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Nickel-Titanium (NiTi) alloys have been the subjects of practical interest since the 1960s, when it was discovered that the alloys exhibit shape memory and pseudoelasticity. While there have been many experimental studies aimed to understand the structural phase transformations in NiTi alloys, clear understanding at the atomic level have not yet been understood. Herein, we investigate the structural phase transition in NiTi alloy using molecular dynamics (MD) simulations. We considered different system sizes ranging from 12,000 to 100,000 atoms applying mechanical strain of 0 to ~15%. Although the phase transition was found to be dependent on smaller system, it was found to be almost independent of system size for reasonably large systems. The effect of fine or affine deformation was found to exhibit similar behavior among the different system sizes. The phase transition was also characterized by calculating g(r) before and after the application of mechanical strain. Results of the present MD simulations were found to be in agreement with the recent experimental reports.

Synthesis of poly(ethylene oxide)-*block*-poly(ε-caprolactone) copolymers using "Click" Chemistry

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Poly(ethylene oxide)-*b*-poly(ε-caprolactone) (PEO-b-PCL) is a diblock copolymer with a variety of properties with numerous applications. In this diblock, the PEO block is hydrophilic, while the PCL block is hydrophobic, giving the diblock an amphiphilic nature. Both blocks have similar melting points and glass transition temperatures. In this study, the diblock was formed via a copper catalyzed "Click" reaction between an alkyne functional group and an azide functional group.

Two synthetic routes were examined, using premade PEO and PCL and functionalizing the polymers, and using ring opening polymerization to polymerize the PCL while functionalizing the PEO. The second route consisted of an alkyne functionalized initiator that was used to polymerize the PCL and converting the PEO-OH to the azide functionality with a two-step reaction. In both cases, the two polymers were reacted together with the "Click" reaction, to give the diblock product. Once the products of these reactions were purified, H-NMR was used to confirm structures and GPC was used to determine the molecular weight of the polymerized PCL.

Thermoresponsive Star Polymers Undergoing Topology Changes

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Stimuli responsive polymers are one of the most exciting and quickly emerging areas of scientific research because of its ability to be incorporated into commercial products. In this project thermally responsive polymers were synthesized via Atom Transfer Radical Polymerization (ATRP) arm first method by polymerizing n-butyl acrylate at 60ºC for 4 hours at which point the cross-linker, a divinyl compound with Diels-Alder functionality, was injected into the reaction flask to create a star polymer. The cross-linker gives the polymer its thermally responsive characteristics because the Diels-Alder bond is a reversible under thermal stimuli. The polymer undergoes a topology change when thermally treated, as it is no longer able to form star polymers and instead forms a linear polymer. For further investigation there is interest to incorporate this polymer into layer by layer coatings to observe how the topology change of the polymer affects the rehealability of the film.

A Novel Conjugated Polymer for Use in Pseudocapacitors

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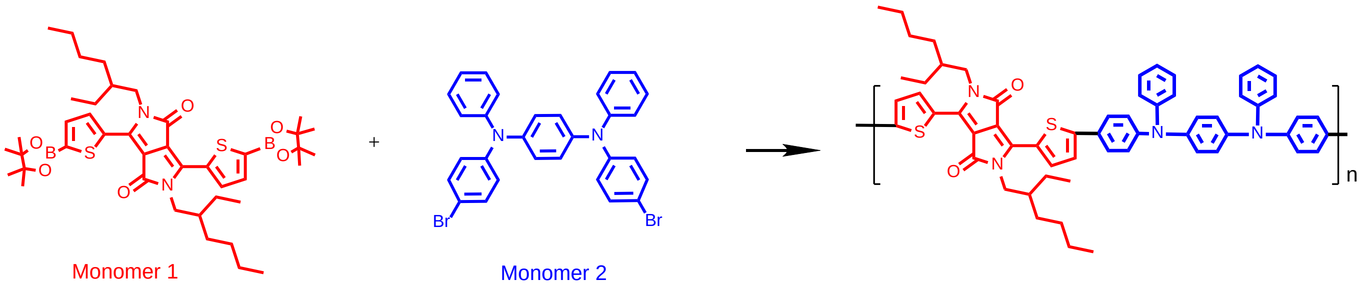
A novel conjugated alternating co-polymer consisting of EH-TDPP (2,5-*bis*(2-ethylhexyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione), monomer 1 in the figure below, and BDBD (*N1*,*N4*-*bis*(4-phenyl)-*N1*,*N4*-diphenylbenzene-1,4-diamine), monomer 2 in the figure below, was synthesized. All intermediate products, as well as the final monomers and polymer, were analyzed by NMR and UV spectroscopy. The molecular weight of the polymer was analyzed by GPC. To analyze the polymer's performance in a psuedocapacitor, cyclic voltammetry was used. Future work involving the synthesized polymer includes testing in an asymmetric pseudocapacitor.



Synthesis and Characterization of Thermoresponsive, Biodegradable Polyesters.

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Polymeric biomaterials offer great promise for their potential impact within the medical field. Specifically, the development of ‘smart’ materials capable of responding to external stimuli such as pH, light, and temperature has become increasingly popular due to their possible applications for controlled release of therapeutics. The most widely used thermoresponsive biomaterials are based on acrylamides that undergo a reversible hydrophilicity change at a specific lower critical solution temperature (LCST). However, the nondegradable backbone of polyacrylamides limits their use in *vivo*. Recently the Joy Lab has developed a library of novel thermoresponsive polyesters inspired by polyacrylamides. The solution behavior of these thermoresponsive polyesters is similar to that of thermoresponsive elastin-like peptides (ELPs) as evidenced by the effect of urea, sodium chloride, polymer molecular weight, and polymer concentration on solution cloud point temperatures. The resulting thermoresponsive biodegradable polyesters exhibit a range of LCSTs dependent on structure and environment conditions as well as inherent hydrolytic degradability.

The Effect of the Freeze/ Thaw Process on the Mechanical Behavior of Double-Network Hydrogels in Finite Tensile Deformation

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Double-network (DN) hydrogels consist of a highly cross-linked polyelectrolyte network with another interpenetrating network of a softer neutral polymer and demonstrate greatly improved strength and toughness compared to single network hydrogels. A notable quality of these DN hydrogels is that they display necking when under tension, due to the transition that occurs when the first network starts to break and the second network takes the load. However, when the water inside the DN hydrogel is frozen and subsequently thawed, the necking behavior is suppressed and strain hardening behavior is observed. It is hypothesized that this change is due to the volume expansion during the freezing of the water, which makes up approximately 90 wt. % of the hydrogel. When the water expands, it is thought to damage the internal structure of the hydrogel network by breaking portions of the first network.

To examine the effect of the freeze/ thaw (F/T) process, DN hydrogels synthesized from 2-acrylamido-2-methylpropane sulfuric acid (AMPS) and acrylamide (AAm) with different cross-linking densities in the first network were studied after applying the F/T process a specified number of times. Tensile tests and water content measurements were conducted on each sample and a consistent trend appeared. As the number of F/T cycles is increased, the energy required for deformation of a sample decreases and the water content of the sample increases. This supports the theory that the F/T process damages the hydrogel, weakening it and allowing more water into the network.

A Study of Surface Energy Effects on Spider Silk Adhesion

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The high tensile strength of spider silk cannot fully be utilized in prey capture if the prey does not initially adhere to the silk upon contact. Viscid capture silk is the sticky spiral in an orb weaving spider's web. This type of silk consists of aqueous droplets found along the silk strands much like beads on a string. The droplets, which contain salts and glycoproteins, act as glue, to trap or slow down insects upon contact so that the spider can locate and immobilize the prey. This project examines how the droplets interact with surfaces of different surface energies.

Using a Photron FastCAM high speed camera mounted on an optical microscope, videos were made of the genus *Larinioides* viscid glue droplets contacting and also being removed from two different glass surfaces. Furthermore, the pull off force required to remove a silk strand from both types of surfaces was tested using a NanoBionix tensile testing machine. The surfaces used were a plain glass coverslip with a water contact angle of ~30° (hydrophilic) and a 1H, 1H, 2H-Perfluoro-1-dodecene plasma coated glass coverslip with a water contact angle of >90° (hydrophobic).

Preliminary analysis of the droplet contacting the glass surfaces showed similar spreading rates and behavior on both the hydrophilic and hydrophobic surfaces. However, at a constant pull off rate, the adhesive contact area for the hydrophilic glass contact decreases faster than the adhesive contact area on the hydrophobic glass coverslip. Analysis of the pull-off forces associated with both hydrophobic and hydrophilic contacts is currently underway.

Conversion kinetics for self-assembled organic-inorganic complexes to ordered nanostructured inorganic materials

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Over the last two decades, block copolymer templating of inorganic materials has enabled precise nanostructure control of mesoporous (2-50 nm) materials. Depending on the framework chemistry, these materials exhibit promising performance for numerous applications, such as catalysis, separations, and battery electrodes. Here, we examine the reactions associated with the cooperative-assembly of an amphiphilic block copolymer with a metal nitrate-citrate complex, which has been shown to enable a diversity of new framework chemistries. These chemistries evolve through a series of reaction pathways on heating where the metal nitrate-citrate complex is initially converted to metal carbonate at modest temperatures, and at elevated temperatures the metal carbonate subsequently converts to metal oxide. In this work, a kinetic study of the transition from the metal nitrate-citrate to metal carbonate has been explored to understand the requirements for producing a highly ordered mesoporous film and the associated mechanisms.

In this work, the changes in chemical composition of cobalt nitrate-citrate: poly(ethylene glycol methacrylate-*b*-butyl acrylate) thin films was quantified *ex-situ* by Fourier transform infrared spectroscopy (FTIR) for temperatures from 160 to 240 ^{0}C. These chemical changes were found to be well correlated with the film thickness as determined by *in-situ* ellipsometry. For all temperatures investigated, all films undergo a rapid conversion to metal carbonate within one minute. Unexpectedly, there is no strong temperature dependence on this solid state reaction with no resolvable differences in the reaction rate despite 80 ^{0}C difference. These data suggest that the conversion is diffusion limited.

Neural Growth Factor Encapsulation in Electrospun Nanofibers

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Neural growth factors are responsible for transmitting signals for development and growth in neural cells. This includes stimulation and inhibition of many cellular functions, and in today's medicinal world, they can be used to repair damaged nerves. The problem, however, is finding an appropriate method to deliver the precise NGF concentrations to the neural cells. In the past, many methods such as intravenous injection, oral delivery, and bolus injection have been employed without clinically relevant efficacy. However, one idea being explored in this study is encapsulating the NGF in SGnPs (sugar-glass nanoparticles), or inverse micelles, and then incorporating them into degradable nanofibers to be placed at the desired site of action. This approach offers three significant advantages. First, proteins are easily denatured when exposed directly to enzymes and other physical and chemical processes occurring at body temperature, as is the case with injections and oral deliveries[1]. Thus, encapsulating NGFs in SGnPs ensures that they are protected. Second, the SGnPs have been shown to preserve NGF function over time, and third, nanofiber dimensions can be tuned precisely to control delivery rates[2].

In this study, the formation of SGnPs is examined to determine the parameters which influence the size of micelles. A constant size is necessary to maintain a consistent release of NGF from the degradable nanofibers and to ensure that the proper amount of NGF will be released. Additionally, electrospun polymer nanofibers with SGnPs are characterized and a protein release study is examined to discern the efficacy of the nanofiber/SGnP combination.

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Electron Transfer Dissociation Pathways of Multiply Charged Polymethacrylates

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Collisionally Activated Dissociation (CAD) and Electron Transfer Dissociation (ETD) tandem mass spectrometry methods were employed to obtain structural information for polymethacrylates. Previous polymer mass spectrometry research has focused on the CAD method of fragmentation which occurs after a collision with inert gas molecules builds up internal energy leading to bond cleavages. In the ETD method, multiply charged ions dissociate via a different fragmentation method that allows complementary structural information to be obtained. In ETD, the precursor cation is activated by an electron transfer from a radical anion causing random dissociation patterns while conserving the labile bonds. It was hypothesized that the random dissociation patterns will provide additional structural information on the polymer. Backbone fragmentations in ETD differ from CAD, revealing specific information about the backbone that particularly can be useful in analysis of alternating copolymers. Based on the research completed, it can be noted that ETD produces a much less complex spectrum than CAD, enabling easier interpretation of data and more specific identification of polymer side chains. The simpler spectrum allows for easier determination of the location of backbone fragmentations. Finally, our results indicate that when comparing two isomers of polymethacrylates, ETD experiments can reveal information regarding intermolecular non-covalent interactions such as hydrogen bonding within a polymer. Tandem mass spectrometry information is important because it provides an additional analytical method to study polymer structures.

Contact Angles, Surface Energy, and Crude Oil Absorption

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This study focuses on various types of aerogels and their surface energy. An aerogel is a high porosity, low density, solid material with a three dimensional network structure. The purpose of studying the surface energy is to determine the aerogel's polarity. Polarity should be one of the factors that indicates the aerogel's performance in the absorption of hydrocarbon liquid. The study is separated into two different parts. The first part is the contact angle tests on compressed aerogels using deionized water and methylene iodide. The deionized water contact angle tests are used to determine the hydrophobicity of the aerogel. The results of the methylene iodide contact angle tests will be used to determine polarity of the material when used in conjunction with the deionized water contact angle results. The second part of the study is the performance of the aerogel in the crude oil absorption tests. This test should give an indication of the relationships between characteristic data and the amount of crude oil absorbed by the aerogel. A variety of aerogels will be tested: silica, syndiotactic polystyrene (sPS), polyimide, polyurea, and polyurethane.

Novel Fabrication of PVC Microparticles in Siloxane Elastomers and Its Effect to: Thermal and Mechanical Properties of Microcomposite

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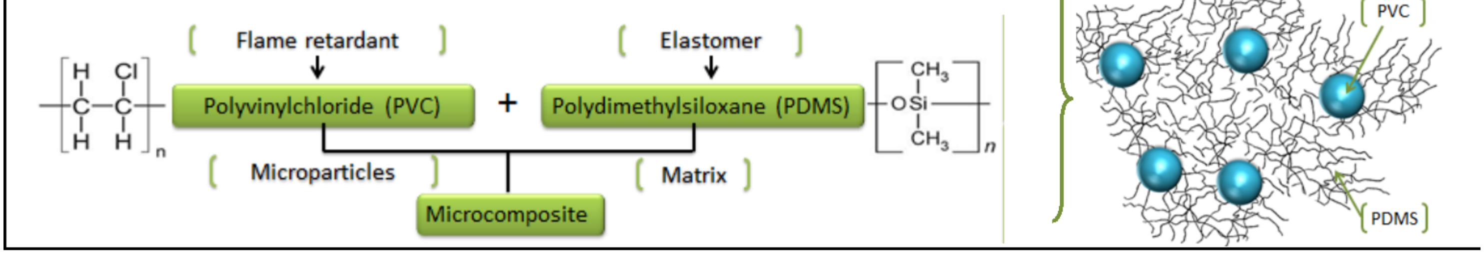
Elastomers are widely used in industrial applications such as seals, tires, belts, membranes, and adhesives. It is common to introduce inorganic fillers to increase the modulus and tensile strength. It is a challenge to prevent aggregation and degradation of the elastomer's mechanical properties. In this research we have developed a novel dialysis method for fabricating polyvinylchloride (PVC) nanoparticles in suspension. However, the addition of these PVC particles in a polydimethylsiloxane (PDMS) solution results in microscopic holes and cracks, morphological defects which could degrade the mechanical properties. To address this limitation, a novel *in situ* method was developed for generating and dispersing micron-size particles of PVC directly into an elastomeric matrix of PDMS. This resulted in a highly uniformed distribution of microparticles in the PDMS matrix. This process takes advantage of the miscibility properties of the materials, allowing dispersion of the microparticles without the need to expend the large amounts of energy required for mixing. These microparticles do not change the mechanical properties of the PDMS, but increase the thermal resistance of the PDMS elastomers.



Gel Properties of Polyisoprene and Stearic Acid Shape Memory Composites

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Shape memory polymer blends consist of a permanent cross-linked network and a temporary network. The former generates large entropic forces upon deformation that drive shape recovery while the latter inhibits the entropy-driven recovery of the system and is designed to be easily modulated [1]. A previous study by Weiss *et. al.* indicated that shape memory behavior is consequential of dipolar interactions between an ionomeric permanent network and crystalline zinc stearate temporary network [2]. However, Brostowitz *et. al.* demonstrated shape memory behavior by swelling natural rubber (NR) with stearic acid (SA), a composite devoid of an ionomeric phase [3]. It is believed that SA crystals inhibit the entropic movement of the cross-linked network back to its unstrained state until the system is brought to its switching temperature (T_s)—the melting point of stearic acid ($T_m = 70^oC$). Above this temperature, shape memory is observed as the system is entropically driven to recovery.

In this study, we aim to test the validity of the above statement by better characterizing the interactions of the permanent (NR) and temporary (SA) networks [4]. Differential scanning calorimetry (DSC) showed one-phase mixing at all SA concentrations. Optical microscopy also demonstrated one-phase mixing at all concentrations and revealed cooling rate dependent crystal formation. Using plate-plate oscillatory shear rheology, the viscoelastic properties of the SA/NR composites were investigated and found to have a SA concentration dependence. Each of these findings suggest tunable shape memory can be achieved with these composite materials.

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Synthesis of Linear and Hyperbranched Glycopolymers

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Polysaccharides play an important role in many biological processes. One role is pathogen recognition due to their interaction with proteins. As a result, synthetic carbohydrate-containing polymers, glycopolymers, could potentially have useful medical applications like aiding in drug delivery. Previous studies have shown that depending on the polymers architecture, linear vs. hyperbranched, the binding affinity to lectins (i.e. ConA) could be increased.[1] The goal of this project is to study the effect of reaction conditions, such as solvent, temperature, catalyst, and time, used during atom transfer radical polymerization (ATRP) on the percent conversion, molecular weight (Mn), and polydispersity index (PDI) of the linear and hyperbranched glycopolymers.

The glycopolymers were synthesized by polymerizing inimers via self-condensing vinyl polymerization (SCVP), that contained chlorine or bromine halogen initiators, in order to study the kinetics of the mechanism. Hyperbranched glycopolymers with M_n 10.7-16.6 kDa were synthesized by varying the initiator/catalyst concentration with the aim of comparing the polymer architecture with the protein biding ability.

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