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14. ABSTRACT

The Butler Polymer Research Laboratory in the Department of Chemistry at the University of Florida (UF) is the home to over 100 researchers in advanced polymer materials. Within this, the Polymer Chemistry Characterization Laboratory (PCCL) is a user facility that houses an extensive suite of state-of-the-art equipment for the synthesis and characterization of macromolecular and supramolecular materials. In this proposal, funding was used for purchase of instrumentation that is critical for the mechanical and thermomechanical testing of advanced materials. This included a TA Instruments Q800 Dynamic Mechanical Analyzer and a TA Instruments HR-2 Discovery

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ARO-DURIP Final Report: Acquisition of Dynamic Mechanical Analyzer and Stress-Controlled Rheometer for the Mechanical Characterization of Advanced Materials

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1. Executive Summary

The Butler Polymer Research Laboratory in the Department of Chemistry at the University of Florida (UF) is the home to over 100 researchers in advanced polymer materials. Within this, the Polymer Chemistry Characterization Laboratory (PCCL) is a user facility that houses an extensive suite of state-of-the-art equipment for the synthesis and characterization of macromolecular and supramolecular materials. *In this proposal, funding was used for purchase of instrumentation that is critical for the mechanical and thermomechanical testing of advanced materials.* This included a TA Instruments Q800 Dynamic Mechanical Analyzer and a TA Instruments HR-2 Discovery Hybrid Rheometer. The instruments were purchased in May 2016 and delivered in July 2016. After some unforeseen infrastructure improvements, the instruments were installed, and training was performed, in November 2016. As a critical enhancement to our current capabilities, these tools provide the ability to monitor structural properties of novel materials. Presented here is ongoing work in the areas of (1) self-healing hydrogels, (2) cyclic polyolefins, (3) organogel characterization, and (4) functionalized polyolefins with minimal or no structural defects via ADMET polymerization. This equipment has accelerated progress of this research, and it will continue to impact research and student education for years to come.

2. List of Figures

3. Instrument training and management

These instruments were installed in November 2016. Generally, each instrument within the PCCL has three students assigned; the primary is the most senior student, with the secondary and tertiary students providing additional support. As the primary student graduates, the others are promoted, and a new tertiary is named. This approach ensures continuity in the operation, training and maintenance of each instrument in the PCCL. Students specifically request the instruments they manage in the PCCL; in general this will be an instrument they use extensively in their own research. As such, the students have a vested interest in (1) making sure all instruments are running at the highest level, (2) knowing exactly how each instrument operates, and (3) ensuring other students are trained in proper operation and care of the instrument.

Figure 1. Rheometer (left) and DMA (right) equipment set up in the Polymer Chemistry Characterization Laboratory in the Chemistry Department at the University of Florida. Mr. Kyle Bentz (left, expected graduation December 2017) is the primary student who trains other students on the correct loading of samples, operation, and data interpretation of rheological data.

4. Summary of significant results

(a) Dynamic covalent hydrogels (Sumerlin)

In this project, the self-healing behavior of a hydrogel crosslinked with boronate esters was controlled *via* the restriction of polymer chain mobility. This was achieved by copolymerization of a boronic acid monomer, (2-(3-acrylamidopropanamido)phenyl)boronic acid (APAPBA), with the thermoresponsive monomer N,N–isopropylacrylamide (NIPAM). Near the cloud point of the copolymer, polymer chain mobility is reduced due to aggregation of the NIPAM sections of the polymer as well as expulsion of water. This reduced mobility prevents the rearrangement of bonds needed for self-healing. In Figure 2, frequency sweeps were conducted on a hydrogel synthesized from P(APAPBA-*co*-NIPAM) crosslinked with poly(vinyl alcohol). These sweeps were initially conducted at 25 °C, then near the cloud point of P(APAPBA-*co*-NIPAM) at 37 °C, and then at 25 °C again. The frequency sweep at 37 °C shows an earlier G′/G″ crossover than at 25 °C, which represents a longer relaxation time for the hydrogel. This correlates well with self-healing tests conducted at 37 °C where the hydrogel was unable to self-heal upon being cut in half. Upon return to 25 °C, the G′/G″ crossover recovers to its original value.

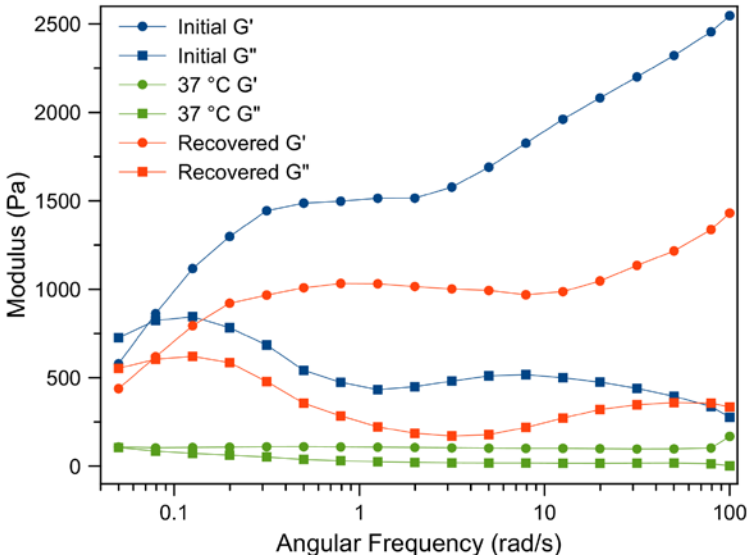

Figure 2. Frequency sweeps of P(APAPBA-*co*-NIPAM) block copolymers showing self-healing capabilities via heating above the LCST of the PNIPAM block.

(b) Rheology of cyclic polypropylene (Savin, Veige, Sumerlin)

Polyolefin manufacturing eclipsed 170 million tons in 2016, but the cyclic versions of these important materials are synthesized in small quantities or simply synthetically inaccessible. Recent work in the Veige group has developed synthetic techniques to produce large quantities of cyclic polypropylene (cPP). From a fundamental standpoint, the rheology of cyclic polymers is not well understood. It has been shown experimentally that even a small impurity of linear polymer increases the viscosity of the cyclic polymers to the linear limit, eliminating any benefit in the processibility. Thus the ability to form cPP ***exclusively*** is of key fundamental and applied interest. Preliminary rheology was performed on a cPP sample with M_n of 37 kDa. This sample

showed beautiful thermorheological simplicity, and the time-temperature superposed master curve is shown in Figure 3. The Williams-Landel-Ferry plot (inset of Figure 3) exhibited an exemplary fit to determine C_1 and C_2 for this polymer. We are in the process of synthesizing and characterizing linear atactic PP for comparison, and expect to publish these results soon. For these results, the upper heated plate accessory purchased for the rheometer was critical to ensure no thermal gradients in these materials at higher temperature.

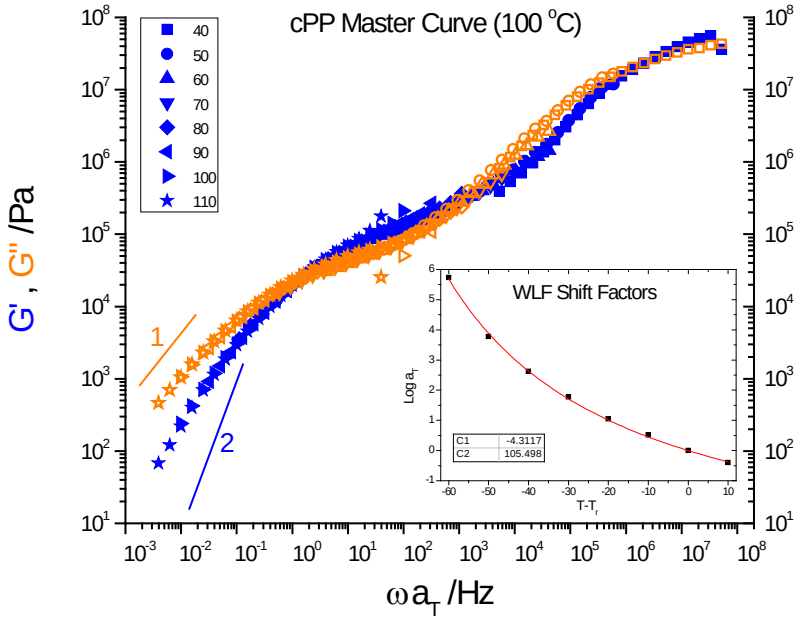

Figure 3. Rheological master curve at 100 °C for cPP. Data were taken at 3 % strain at temperatures between 40 °C and 110 °C, and a time-temperature superposition was performed. Shift factors were fit to the WLF equation (inset.)

(c) Synthesis and characterization of precision aliphatic polysulfones via ADMET polymerization (Wagener)

The Wagener group is producing new materials that present potential for use in high-temperature energy devices and even gas barriers. Of special interest are precision poly(aliphatic sulfones). The basic design exploits ADMET polymerization developed by the Wagener group, which allows for precise placement of acid functionality on polyolefins. These sulfones exhibit excellent thermal properties, melting upwards of 180 °C. High melting temperatures are a result of the precise spacing of sulfone groups allowing for assembly into periodic layers. Current efforts aim to refine synthetic methods to achieve high molecular weight polymer and investigate mechanical properties. Figure 4 shows preliminary DMA for two different poly(sulfones) produced through the ADMET process., before and after hydrogenation. It is observed that hydrogenation increases T_m by over 75 °C, with a corresponding increase in modulus below T_m. We are working to produce more materials for more detailed characterization.

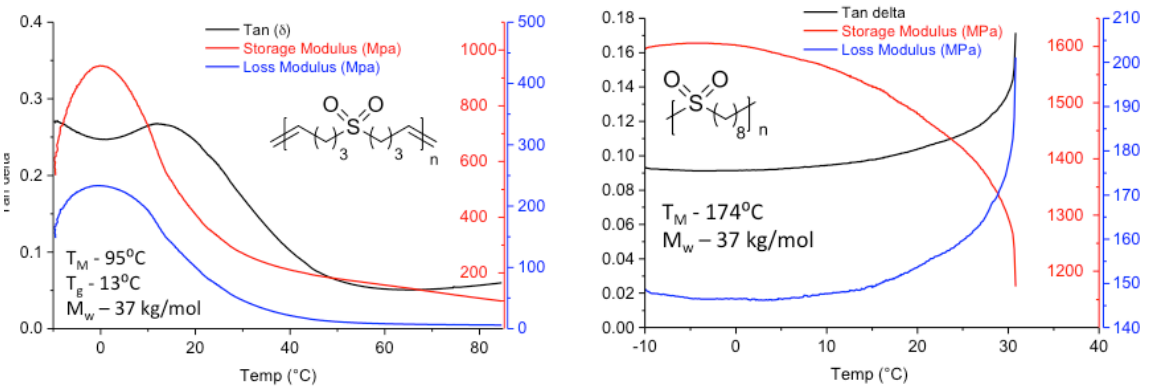

Figure 4. Isochronal DMA temperature sweeps of poly(sulfones) produced from the ADMET process. (Left): As synthesized, prior to hydrogenation. (Right): Post hydrogenation. As seen, the modulus and T_m increase upon hydrogenation. Future DMA will exploit the controlled humidity chamber accessory, which is also being used for DMA characterization of hydrogels above.

(d) Comparison Between Cavitation and Shear Rheology (Savin)

Cavitation rheology (or Maximum Bubble Pressure Rheology) is a recently developed, versatile, inexpensive, *in situ*, and non-destructive characterization technique for soft materials such as organogels and hydrogels. However, it is currently poorly understood how the modulus obtained from the cavitation experiment correlates with that obtained from traditional oscillatory shear rheology. A series of crosslinked polyacrylamide hydrogels were synthesized and shear rheological properties were investigated by performing oscillatory frequency sweeps (Figure 6). All gels, with the exception of the highest polymer content, displayed frequency-independent response over the range studied. The moduli increased from about 0.65 kPa for the 0.5 wt% hydrogel to about 5.03 kPa for the 1 wt% hydrogel. However, when subjected to the cavitation experiment, markedly increased values for moduli were measured, as shown in Figure 1 inset. On average, the cavitation modulus was nearly two orders of magnitude higher than the corresponding shear modulus. Whereas shear rheology at 5% strain requires chain rearrangement and mobility, the cavitation experiment requires covalent bonds to be broken due to the nature of the polyacylamide hydrogels and the size of the cavity formed. Currently ongoing experiments are aimed at determining the relation between the cavitation and shear experiment for dynamic-covalent, as well as physically crosslinked hydro- and organogels.

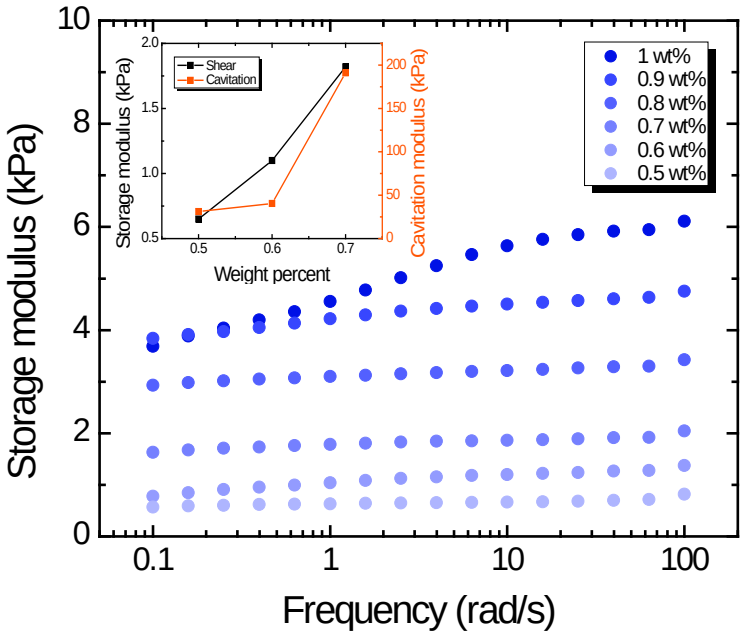

Figure 5. Oscillatory frequency sweeps of poly(acrylamide/*bis*-acrylamide) hydrogels at various wt %. All frequency sweeps were performed at 5% strain at 25 °C. *Inset*: Comparison of storage modulus from oscillatory frequency sweep and cavitation experiment as a function of hydrogel wt %.

(e) Impact on education and training

The addition of DMA and rheometer instruments has helped contribute to the educational goals of UF and in broadening participation of women and underrepresented participants. The BPRL houses nearly 100 researchers actively engaged in macromolecular and supramolecular science within the Chemistry Department at UF. Within the BPRL are many underrepresented minority students. For example, the Savin group has nine graduate students, two of whom are Hispanic, one African-American, and five women. His group also trains five undergraduate students, three of whom are women. The Chemistry Department at UF is consistently one of the top five Ph.D. student-producing institutions in the nation, including 43% of graduates who are female. From an education standpoint, Savin has incorporated an expanded rheology section in his course CHM 5511: Physical Chemistry of Macromolecules (at the graduate level,) and he will be teaching an entire course on polymer rheology and viscoelasticity in Spring 2018. Finally, these instruments will be used in another chemistry course entitled, “Cooking in the Latin Kitchen” to measure the viscoelastic properties of cheese produced through various methods.

(f) Ongoing and future work in the Butler Polymer Laboratories

There are additional projects that will use the DMA and rheometer instruments now available in the PCCL. For example, the Sumerlin group is attempting to characterize stimuli-responsive methacrylate networks of varying glass transition temperature. The networks are prepared by copolymerizing several ratios of butyl methacrylate to methyl methacrylate in the presence of a bismethacryloyl Diels-Alder crosslinker, triethylene glycol dimethacrylate, or no crosslinker, to

afford a series of thermally reversible networks with permanently crosslinked and uncrosslinked controls. The aim of this work is to probe the effect of backbone glass transition temperature on the change in mechanical properties brought about by the retro Diels-Alder reaction. In addition, the Savin group is using DMA to study energy-absorbing networks. The objective of this work is to develop biocompatible, energy-absorbing materials that can be used as personal protective equipment, such as mouthguards or multi-impact helmets, or as replacements for cartilage or intervertebral disks. The central platform for energy-absorbing materials is based on thiol-ene network thermosets, which have demonstrated advantages for impact energy mitigation and tunability in properties through chemical modification.

5. Bibliography – Presentations resulting from work performed from this grant:

1. R. Nicholas Carmean, Hao Sun, Christopher P. Kabb, Megan R. Hill, Yuqiong Dai, Michael B. Sims, Troy E. Becker, Brent S. Sumerlin "Controlled Polymerization for Ultra-High Molecular Weights and Polymers Capable of Topological Transformations" Emergent Macromolecular Systems 2017, CUNY Advanced Science Research Center and Hunter College, New York, New York, June 2017. Invited.
2. Hao Sun, R. Nicholas Carmean, Megan R. Hill, C. Adrian Figg, Jessica Cash, Brent S. Sumerlin "Macromolecular Metamorphosis: An Alternative Approach to Stimuli-Responsive Materials" Advanced Polymers via Macromolecular Engineering (APME 2017), Ghent, Belgium, May 2017. Invited.
3. Brent S. Sumerlin "Synthesis of Next-Generation Responsive, Biological & Dynamic Materials" Max Planck Institute for Polymer Research, Mainz, Germany, seminar, May 2017.
4. Christopher S. O'Bryan, Christopher P. Kabb; Sangwoo Park, Brent S. Sumerlin, Thomas E. Angelini "The role of multivalent ion – polyelectrolyte interactions in microgel rheology" Annual Meeting of The Society of Rheology, Houston, Texas, October 2017.
5. Angela A. Pitenis, Christopher P. Kabb, Juan Manuel Urueña, Sean Niemi, Kylie Van Meter, Brent S. Sumerlin, Thomas E. Angelini, W. Gregory Sawyer "Hydrogel wear" Society of Tribologists and Lubrication Engineers (STLE) Annual Meeting & Exhibition, Atlanta, GA, May 2017. Oral.
6. Eric Fuller, Hao Sun, Brent S. Sumerlin, Carlos Rinaldi "Magnetically Triggered Drug Release from Nanoparticles" Biomedical Engineering Society (BMES) Annual Meeting, Phoenix, AZ, October 2017.
7. Georg M. Scheutz, Brent S. Sumerlin "Dynamic Thiol-Disulfide Exchange of Cyclic Disulfides for Self-Healing Hydrogels" Florida Annual Meeting and Exposition - FAME 2017 (ACS), Palm Harbor, FL, May 2017. Poster.
8. Tomohiro Kubo, Kyle C. Bentz, Kristin C. Powell, C. Adrian Figg, Jeremy L. Swartz, Maxym Tansky, Anuj Chauhan, Daniel A. Savin, Brent S. Sumerlin "Amphiphilic Homopolymers via Successive Chemoselective Post-Polymerization Modification" Florida Annual Meeting and Exposition - FAME 2017 (ACS), Palm Harbor, FL, May 2017. Poster.
9. Christopher P. Kabb, Christopher S. O'Bryan, W. Gregory Sawyer, Brent S. Sumerlin "Reversible-covalent hydrogels linked by photosensitive coumarin dimers"

Florida Annual Meeting and Exposition - FAME 2017 (ACS), Palm Harbor, FL, May 2017. Oral.

10. Christopher P. Kabb, Christopher S. O'Bryan, W. Gregory Sawyer, Thomas E. Angelini, Brent S. Sumerlin "Reversible-covalent hydrogels linked by photosensitive coumarin dimers" Florida Annual Meeting and Exposition - FAME 2017 (ACS), Palm Harbor, FL, May 2017. Poster.
11. Hao Sun, Christopher Kabb, Yuqiong Dai, Megan Hill, Brent Sumerlin "Macromolecular Metamorphosis" Materials Research Society (MRS) National Meeting, Phoenix, AZ, April 2017. Invited.
12. Hao Sun, Christopher Kabb, Yuqiong Dai, Megan Hill, Brent Sumerlin "Topological transformations via dynamic-covalent chemistry" ACS National Meeting, San Francisco, CA, April 2017. Invited.
13. Christopher P. Kabb, Christopher S. O'Bryan, W. Gregory Sawyer, Thomas E. Angelini, Brent S. Sumerlin "Reversible-covalent hydrogels linked by photosensitive coumarin dimers" Biomaterials Day 2017, Gainesville, FL, March 2017, poster.
14. Brent S. Sumerlin, R. Nicholas Carmean, Georg Scheutz, C. Adrian Figg "Exploiting Light to Push the Limits of Controlled Radical Polymerization" Pan-Poly Conference, Sao Paulo, Brazil, March 2017. Keynote.