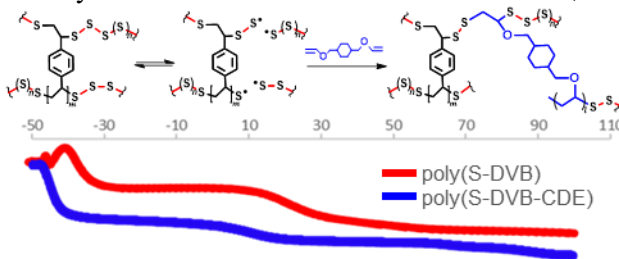


## Repurposing Petroleum Waste into Functional Materials

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### Research Progress

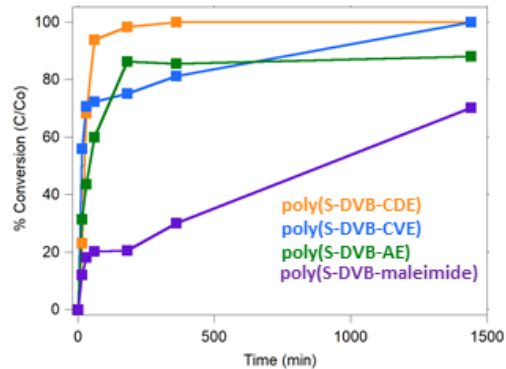
This research seeks to gain fundamental information about polysulfides formed by inverse vulcanization (IV). The petroleum waste product elemental sulfur and a variety of monomers have been combined to synthesize polysulfides without the need for solvents. The low cost and synthetic ease have led to the rapid growth of IV. However, the high temperatures required to initiate polymer formation limit the available monomers. Sulfur's natural structure is a very stable 8-membered crown. In this form, the S-S bonds are the strongest and require temperatures  $>159\text{ }^{\circ}\text{C}$  for cleavage and radical formation. In polysulfides formed by IV, sulfur is present as linear chains or loops, which require less energy and therefore much lower temperatures for homolytic scission. Here, poly(S-divinylbenzene) [poly(S-DVB)] was used as a prepolymer capable of radical formation at temperatures as low as  $90\text{ }^{\circ}\text{C}$ . By using the dynamic sulfur bonds in poly(S-DVB) to initiate polymerization, a second monomer with a lower boiling point such as 1,4-cyclohexanedimethanol divinylether (CDE) was introduced (**Figure 1**).



**Fig. 1:** Formation of poly(S-DVB) via inverse vulcanization followed by modification at  $90\text{ }^{\circ}\text{C}$  to form poly(S-DVB-CDE). DSC curves depicting the change in  $T_g$  from the copolymer to the terpolymer. Image reproduced from *Macromolecules*. **2018**. 51, 7233-7238.

Poly(S-DVB-CDE) was synthesized with varied sulfur, DVB, and CDE content to examine the impact of the polymer composition on the molecular weight, glass transition temperature ( $T_g$ ), and solubility. Incorporating CDE led to an initial decrease in the molecular weight followed by an overall increase as more CDE was added. Using prepolymers with high sulfur content as well as including CDE led to an overall decrease in the  $T_g$ . Prepolymers with high sulfur content typically have low solubility in many solvents. By adding CDE, polysulfide solubility in DCM was substantially improved. For prepolymers that were already soluble in DCM, no substantial changes in solubility occurred when small amounts of CDE were added. Both results are especially beneficial for solvent-based characterization techniques such as NMR. However, if enough CDE is added, extensive cross-linking creates a gel-like network with low solubility. H-NMR analysis allowed the polymer microstructure to be investigated by comparing radical propagation versus thiol-ene bonding within these terpolymers. The addition of small amounts of CDE led to the formation of new HC-S bonds. As more CDE was added, the availability of S radicals decreases, causing an increase in HC-C bonds likely due to radical propagation between monomers.

A family of vinyl and allyl ethers with boiling points as low as  $95\text{ }^{\circ}\text{C}$  were combined with poly(S-DVB) and heated at  $90\text{ }^{\circ}\text{C}$  to form terpolymers. Stable terpolymers were obtained with CDE, cyclohexyl vinyl ether (CVE), and allyl ether (AE). This was quite significant for the monofunctional compound CVE. Without cross-linking from the monomer, most other monofunctional compounds in polysulfides are unstable and undergo depolymerization. Even a challenging monomer such as maleimide which has both a single internal alkene and a high melting point,  $\sim 90\text{ }^{\circ}\text{C}$ , was successfully polymerized. However, a small amount of solvent was required to improve interaction with the prepolymer. Each of these reactions were monitored for 48 h (**Figure 2**). Vinyl groups react the fastest while the internal double bonds of maleimide are substantially slower due to limited propagation.



**Fig. 2:** % conversion of CDE, CVE, AE, and maleimide by poly(S-DVB) into polysulfides. Reproduced from *J. Vis. Exp.* **2019**. 147, e59620.

Even though IV is quite new, many alterations to the technique have been introduced. Fundamental analysis of the polymer structure in response to altered synthetic conditions is well underway. An initial literature search was conducted to determine the range of methods that are being used under the umbrella of inverse vulcanization. Four primary categories of different synthetic methods were found. Poly(S-DVB) samples were then fabricated using each of these methods. Additionally, the reaction time and temperature were altered as well as performing the synthesis when exposed to air versus under inert gas. Copolymers have been characterized by NMR and gel permeation chromatography (GPC) and changes to solubility have been examined. In the coming year, further analysis by differential scanning calorimetry (DSC) and ATR-IR and raman spectroscopy will provide additional insight into the polymer structures.

Methods developed with the help of ACS PRF funding has expanded on the solvent-free, thiyl radical chemistry utilized by inverse vulcanization to create polysulfides at mild temperatures. The dynamic sulfur bond in polysulfides was exploited to substantially reduce the reaction temperature from  $> 159\text{ }^{\circ}\text{C}$  to  $90\text{ }^{\circ}\text{C}$ , comparable to typical radical polymerization without the need for solvent. Incorporation of different monomers along with varying feed ratios of sulfur and CDE enabled the physical properties to be tailored. Additional studies are being carried out to further understand the polymer structure and how it is impacted by a variety of synthetic techniques. Dramatically lower temperatures broaden the types of materials that can be made and expands the creation of functional polymers from repurposed petroleum waste.

### Research Impacts

Support from the ACS PRF has led to the publication of one paper (Westerman, C. R.; Jenkins, C. L. "Dynamic Sulfur Bonds Initiate Polymerization of Vinyl and Allyl Ethers at Mild Temperatures." *Macromolecules*. **2018**. 51, 7233-7238.) with one student co-author and another paper (Westerman, C. R.; Walker, P. M. Jenkins, C. L. "Synthesis of Terpolymers at Mild Temperatures Using Dynamic Sulfur Bonds in Poly(S-Divinylbenzene)." *J. Vis. Exp.* **2019**. 147, e59620.) with two student co-authors who participated in both writing the manuscript and filming their experiments. These accomplishments have helped the PI achieve publication of articles and student training, both of which are essential for progress toward tenure at an undergraduate focused institution. Data collected as part of the fundamental work funded by PRF are being used as preliminary data for applications to obtain future funding.

The PI attended the National ACS Meeting in spring 2019 where she was able to network with a variety of scientists in the field, meet with a collaborator, and attend networking events. Connecting with the Council for Undergraduate Research was especially helpful for meeting other faculty working at primarily undergraduate institutions. PRF funds also allowed undergraduate students to present their work at multiple conferences in the past year. There were three poster presentations at the Indiana STEM Louis Stokes Alliance for Minority Participation Annual Conference. One poster presentation at the Emerging Researchers National Conference in STEM where Princess Walker won third place in the Materials Science Division as well as a travel award. Students also attended the National Meeting of the American Chemical Society where three students funded by PRF presented posters. These students also had the opportunity to attend a variety of networking functions.

With the help of PRF funding, students in the Jenkins group were able to learn polymer synthesis and a variety of instrumentation techniques including NMR, ATR-IR, UV-Vis spectroscopy, GPC, and DSC. Additionally, regular group meetings and semester reports allowed students to practice both written and verbal communication skills as well as use common chemistry software including ChemDraw and MNova.

All of these experiences have prepared students to be successful after graduation. Funding for student wages allowed the PI to expand the group to include two new students to the group, both in their senior year, which helped them gain research experience before graduating. In the past year many of these students graduated. All of them are remaining in STEM. Three students are pursuing their PhD's at Purdue University and Arizona University. One student is now working as a chemist at Cargill in Chicago, IL.

