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TITLE:

Synthesis of Terpolymers at Mild Temperatures Using Dynamic Sulfur Bonds in Poly(S-Divinylbenzene)

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SUMMARY:

The goal of this protocol is to initiate polymerization using dynamic sulfur bonds in poly(S-divinylbenzene) at mild temperatures (90 °C) without using solvents. Terpolymers are characterized by GPC, DSC and ^{1}H NMR, and tested for changes in solubility.

ABSTRACT:

Elemental sulfur (S_8) is a byproduct of the petroleum industry with millions of tons produced annually. Such abundant production and limited applications lead to sulfur as a cost-efficient reagent for polymer synthesis. Inverse vulcanization combines elemental sulfur with a variety of monomers to form functional polysulfides without the need for solvents. Short reaction times and straight forward synthetic methods have led to rapid expansion of inverse vulcanization. However, high reaction temperatures (>160 °C) limit the types of monomers that can be used. Here, the dynamic sulfur bonds in poly(S-divinylbenzene) are used to initiate polymerization at much lower temperatures. The S-S bonds in the prepolymer are less stable than S-S bonds in S_8, allowing radical formation at 90 °C rather than 159 °C. A variety of allyl and vinyl ethers have been incorporated to form terpolymers. The resulting materials were characterized by ^{1}H NMR, gel permeation chromatography, and differential scanning calorimetry, as well as examining changes in solubility. This method expands on the solvent-free, thiyl radical chemistry utilized by inverse vulcanization to create polysulfides at mild temperatures. This development broadens the range of monomers that can be incorporated thus expanding the accessible material properties and possible applications.

INTRODUCTION:

Conversion of organosulfur compounds to S_8 during petroleum refinement has led to the amassing of large stockpiles of sulfur[1]. Elemental sulfur is primarily used for the production of sulfuric acid and phosphates for fertilizers[2]. The relative abundance provides a readily available and inexpensive reagent making elemental sulfur an ideal feedstock for materials development.

Inverse vulcanization is a relatively new polymerization technique that repurposes sulfur into functional materials[3]. The S_8 ring converts to a diradical, linear chain upon heating above 159 °C. The thiyl radicals then initiate polymerization with monomers to form polysulfides[3]. In addition to traditional radical polymerizations, inverse vulcanization has been utilized to initiate polymerization with benzoxazines[4]. The resulting polymers have been used for a wide range of applications including cathodes in Li-S batteries[1,5-7], self-healing optical lenses[8-9], mercury and oil sorbents[5,10-15], thermal insulators[15], to aid in the slow release of fertilizer[16] as well as demonstrating some antimicrobial activity[17]. One group has provided a thorough systematic analysis of these polysulfides providing more information about the insulating character and mechanical properties with varied S content[18]. The specific details may aid in further applications development. The dynamic bonds present in these materials have also been utilized to recycle the polysulfides[19,20]. However, the high temperatures required by inverse vulcanization, typically 185 °C, and lack of miscibility with S_8, limit the monomers that can be used[3].

Early efforts focused on the polymerization of aromatic hydrocarbons, extended hydrocarbons, and natural monomers with high boiling points[5]. These methods have been expanded by using poly(S-styrene) as a prepolymer improving miscibility between S_8 and more polar monomers including acrylic, allylic, and functionalized styrenic monomers[21]. Another method utilizes nucleophilic amine activators to enhance reaction rates and lower reaction temperatures[22]. However, many monomers have boiling points well below 159 °C and thus require an alternate method for polysulfide formation.

In the stable crown form, S-S bonds are the strongest, thus requiring high temperatures for cleavage[23]. In polysulfides, sulfur is present as linear chains or loops, allowing S-S bonds to be cleaved at much lower temperatures[1,24]. By using poly(S-DVB) (DVB, divinylbenzene)as a prepolymer, a second monomer with a lower boiling point such as 1,4-cyclohexanedimethanol divinylether (CDE, boiling point of 126 °C), can be introduced[24]. This work demonstrates further improvement by lowering the reaction temperature to 90 °C with a family of allyl and vinyl ether monomers. Reactions incorporating a second monomer remain solvent-free.

PROTOCOL:

1. Synthesis of poly(S-divinylbenzene)

1.1 To prepare poly(S-divinylbenzene), combine elemental sulfur (S_8) and divinylbenzene (DVB) at various weight ratios (30:70, 40:60, 50:50, 60:40, 70:30, 80:20, and 90:10 of S_8:DVB). Prepare the reaction according to prior methods described below[3,25].

NOTE: All reactions here were conducted on a 1.00 g scale. A typical reaction contains 500 mg of S_8 and 500 mg of DVB.

1.1.1 Place the reagents in a 1-dram vial equipped with a magnetic stir bar. Insert the vials in an oil bath at 185 °C for 30 min.

1.1.2 Remove the samples from the oil bath and immediately quench the reaction by placing the vials in liquid nitrogen. Break open the vials to remove the polymer. Liquid nitrogen not only quenches the reaction but also aids in complete removal of the polymer.

CAUTION: All samples are extremely hot upon removing from bath. Use caution when handling the samples. Use proper PPE when dealing with broken glass.

2. **Preparation of terpolymers**

2.1. Synthesize terpolymers by combining poly(S-DVB) and an additional monomer in a 1-dram vial equipped with a magnetic stir bar.

NOTE: All samples were prepared on a 600 mg scale. Monomers examined include 1,4-cyclohexanedimethanol divinyl ether (CDE), cyclohexyl vinyl ether (CVE), and allyl ether (AE).

2.1.1. Crush poly($S_{30\text{-}90\%}$-$DVB_{10\text{-}70\%}$) with a mortar and pestle for higher surface area interaction with CDE. Alter the composition by varying the ratio of poly(S-DVB):CDE from 1:1 to 1:100 by weight. Additional monomers are only tested at a 1:1 ratio of poly($S_{50\%}$-$DVB_{50\%}$):monomer.

2.1.2. Place the samples in an oil bath at 90 °C for 24 h and then cool to room temperature. Longer reaction times are required for some monomers.

2.1.3. Some reactions will not result in complete monomer incorporation. For those reactions, dissolve the soluble polymer portions in dichloromethane (DCM) and precipitate in cold methanol. For samples with limited solubility, wash the solid polymer samples with cold methanol to remove any unreacted monomer.

2.2. Prepare terpolymers using maleimide

NOTE: Maleimide does not have a low boiling point. However, it does have just one reactive site towards thiyl radical modification.

2.2.1. Synthesize poly(S-DVB) prepolymer using slightly altered methods. Combine sulfur and DVB at a 30:70 S_8:DVB ratio. Combine the reagents in a glass vial equipped with a magnetic stir bar on a 5.00 g scale.

2.2.2. Place the vials in an oil bath at 185 °C for 1 h. Immediately place the samples in liquid nitrogen upon removal from the oil bath.

2.2.3. Combine the prepolymer with maleimide in a 1-dram glass vial with a 3:1 poly(S-

DVB):maleimide ratio (w/w). Prepare all samples on a 200 mg scale and dissolve in 10 mg/µL of dimethylformamide (DMF). Place the vials in an oil bath at 100 °C for 24 h.

CAUTION: Inverse vulcanization reactions produce a small amount of gas. For reactions above a 1.00 g scale, use larger vials or drill a hole in the vial cap to prevent the build-up of pressure.

NOTE: Prepolymers that are more malleable cannot be crushed into a powder. However, these polymers soften very easily when heated providing miscibility with most monomers.

2.3. Monitor percent conversion for the addition of a variety of monomers (CDE, CVE, AE, and maleimide).

2.3.1. Prepare all samples using poly(S-DVB) as described in section 2.2.1-2.2.2. Synthesize poly(S-DVB-CDE), poly(S-DVB-CVE), and poly(S-DVB-AE) in a 1-dram glass vial with a 3:1 poly(S-DVB):monomer ratio by weight. A typical sample should have 150 mg of prepolymer and 50 mg monomer. No solvent is needed for most of these polymerizations. However, in order for maleimide and poly(S-DVB) to interact fully, 20 µL of DMF must be added.

2.3.2. Remove the samples at various time points (t= 0, 15, 30, 60, 180, 360, 720, and 1440 min). Dissolve the polymer in 600 µL of chloroform-*d* and analyze them by ^{1}H NMR.

3. Control polymerizations

3.1. Synthesize poly($S_{50\%}$-$DVB_{50\%}$) as described in section 1.1. The sample can then be used in three control reactions. Combine the finely crushed polymer with additional DVB. Place only poly(S-DVB) in a separate vial. Heat all samples at 90 °C for 24 h, then cool them to room temperature.

3.2. Test elemental sulfur under a variety of conditions in order to confirm that sulfur from the polymer rather than S_8 is required for polymerization. Conduct individual reactions by combining S_8 with CDE, DVB, and AE, as well as using S_8 alone. Combine S_8, CDE, and poly($S_{50\%}$-$DVB_{50\%}$) in another vial. Heat all samples at 90 °C for 24 h, then cool to room temperature.

4. Polymer characterization

4.1. Use thin layer chromatography (TLC) for initial detection of S_8 in polymers. Spot polymer samples onto silica TLC plates with hexanes eluent. In hexanes, S_8 has a R_f value of 0.7, and polymers do not move from the baseline, $R_f \approx 0$.

4.2. Analyze all polymers by ^{1}H NMR in chloroform-*d*. Integrate the resulting ^{1}H-NMR spectra to determine the extent of the reaction. Prepare all samples by dissolving the polymer of interest in chloroform-*d*. Perform simple filtration to remove undissolved particulates.

4.3. Analyze the samples by gel permeation chromatography (GPC) using DCM eluent. Use a

GPC with two mesopore columns in sequence and a refractive index detector for analysis.

4.3.1. Due to the relatively low solubility of most terpolymers and broad polydispersity, dissolve each polymer at a seemingly high concentration, 75 mg/mL in DCM. Remove particulates from the soluble portion using a 0.45 µm hydrophobic filter.

4.3.2. Determine the number average and weight average molecular weights (M_n and M_w respectively) based on a calibration curve of polystyrene standards. Use these values to obtain the polydispersity index (PDI).

4.4. Study the thermal properties of the polymer samples. Fill the aluminum pans with 30-50 mg of polymer providing enough sample to adequately discern the glass transition temperature (T_g) from the resulting thermograms. Scan the samples from -50 °C to 150 °C at a rate of 10 °C/min, cool back to -50 °C at 20 °C/min and heat them again to 150 °C at 10 °C/min. Obtain all T_g values from the second scan.

5. **Solubility studies**

NOTE: Terpolymers demonstrated highest solubility in DCM. Solubility of the polymers can be altered by varying the composition.

5.1. Measure approximately 150 mg of each polymer into a pre-weighed vial and dissolve in DCM to reach 75 mg/mL. Dissolve the samples for 8 h before removing the soluble portion. Wash the insoluble portion with DCM two times and dry the remaining insoluble sample in an oven for 10 min to remove remaining solvent.

5.2. Reweigh the vial after letting the vial cool to room temperature. Calculate the percent solubility by determining the difference in starting and final weights.

REPRESENTATIVE RESULTS:

Poly(S-DVB) was synthesized according to published protocols using high temperatures (185 °C) to initiate S_8 ring cleavage forming radicals[3]. These radicals then initiate polymerization with DVB. The molten sulfur and liquid DVB eliminate the need for solvents. Within 30 min, sulfur and DVB react completely for form poly(S-DVB). Upon removal from the vial, the polymer is a hard, brittle material at lower sulfur content (30-40%). Mid-range sulfur content (50-60%) produces a tacky material that is very malleable, and higher sulfur content (70-90%) forms a tough and flexible solid. Furthermore, the polymers become more opaque with increasing sulfur content. This material then serves as a prepolymer for further modification. Dynamic sulfur bonds within poly(S-DVB) can be utilized to initiate polymerization with additional monomers (**Figure 1**).

A family of vinyl and allyl ethers were combined with poly(S-DVB) and heated at 90 °C to form terpolymers. Both monofunctional and difunctional monomers were tested. These monomers were chosen due to their relatively low boiling points (95 – 147 °C) to examine the effectiveness of reduced reaction temperatures. All monomers tested were successfully polymerized, confirmed by NMR (**Figure 2**). Maleimide which has a higher boiling point and a higher melting point, ~90 °C, was also tested to determine if this method would still be successful. A small amount of solvent was required to obtain interaction with the prepolymer. The monomer content for all polymerizations were monitored over the course of 48 h (**Figure 3**). Control reactions were performed to determine the role of poly(S-DVB) versus S_8 in the polymerization (**Figure 4**). The products were examined by ^{1}H NMR and TLC to examine changes to the polymer structure, monomer incorporation, and to determine if S_8 was fully incorporated.

A variety of polymerizations were conducted to examine the polymer structure of poly(S-DVB-CDE). The sulfur, DVB, and CDE content were altered and characterized by GPC and differential scanning calorimetry (DSC) (**Figure 5**). Both increased sulfur content and the addition of CDE led to an overall decrease in the T_g. After an initial decrease in the molecular weight, the addition of CDE led to an overall increase in chain length.

The inclusion of CDE into poly(S-DVB) changed the characteristics of the prepolymer. With a 1:1 poly($S_{50\%}$-$DVB_{50\%}$):CDE ratio, the polymer exhibited a mocha brown color compared to the reddish black prepolymer color. The material was also able to resist any physical force applied by hand to break apart the polymer. Even light scratching of the polymer showed minimal surface deformation. This is in stark contrast to the poly($S_{50\%}$-$DVB_{50\%}$) prepolymer's tacky and malleable properties.

The terpolymer solubility in DCM was also examined by varying S_8:DVB ratio and the CDE content (**Figure 6**). Maximum solubility was achieved for poly(S-DVB) synthesized with 40-50% sulfur. The addition of CDE led to decreased polymer solubility in these samples. However, the opposite occurred for high sulfur content poly(S-DVB). Initially, very low solubility in DCM was observed, but incorporating CDE into the polymers substantially improved solubility in DCM.

FIGURE AND TABLE LEGENDS:

Figure 1: **Formation of poly(S-DVB) prepolymer via inverse vulcanization followed by mild temperature modification to form poly(S-DVB-CDE).** The additional monomers used to modify the poly(S-DVB) are depicted in blue.

Figure 2: ^{1}H NMR spectra of poly(S-DVB) in red, poly(S-DVB-CDE) in purple, and 1,4-cyclohexane dimethanol divinyl ether monomer in blue. The spectrum of poly(S-DVB-CDE) shows the presence of aromatic protons from the prepolymer, alkyl protons from the cyclohexane ring, and the formation of new HC-S bonds. This figure has been reproduced from *Macromolecules* **51**, 7233-7238 (2018)[24]. Reprinted with permission from *Macromolecules* Copyright 2018 American Chemical Society.

Figure 3. Percent conversion of 1,4-cyclohexanedimethanol divinyl ether (CDE), cyclohexyl vinyl ether (CVE), allyl ether (AE), and maleimide by poly(S-DVB). Compounds with vinyl groups, CVE and CDE, reacted the most rapidly. The internal double bond of maleimide reacted notably slower than the other monomers tested.

Figure 4. Characterization of control polymerizations. (**A**) ^{1}H NMR spectrum of control polymerizations: reheated poly(S-DVB), poly(S-DVB) in chloroform-*d.* (**B**) Thermograms of S_8 and CDE without (red) and with (blue) poly(S-DVB). (**C**) Detection of elemental sulfur by TLC including elemental sulfur (S_8), poly($S_{50\%}$-$DVB_{50\%}$) [1], S_8 + poly($S_{50\%}$-$DVB_{50\%}$) + CDE [2], S_8 + CDE [3] and poly(S-DVB-CDE) [4].

Figure 5: **Polymer molecular weight and glass transition temperature at varied sulfur content.** (**A**) Characterization data of poly(S-DVB-CDE) by GPC and DSC. (**B**) GPC traces and (**C**) DSC traces of poly(S-DVB) prepolymer made with 30% S (red), and poly(S-DVB-CDE) produced by concurrent addition of poly(S-DVB) and CDE (black) and produced by heating prepolymer for 5 min before CDE addition (blue). This figure has been modified to include multiple figures from *Macromolecules* **51**, 7233-7238 (2018)[24]. Reprinted with permission from *Macromolecules* Copyright 2018 American Chemical Society.

Figure 6. **Solubility of poly(S-DVB) and poly(S-CDE).** (**A**) Image and (**B**) percent solubility of poly(S-DVB) at varied S_8:DVB ratios. (**C**) Image of poly(S-DVB-CDE) made with 50% S at varied prepolymer:CDE ratios. (**D**) Percent solubility of poly(S-DVB-CDE) with 30-90% S at varied prepolymer:CDE ratios. This figure has been reproduced from *Macromolecules* **51**, 7233-7238 (2018)[24].

DISCUSSION:

The primary benefit of this method is the ability to form polysulfides at mild temperatures, 90 °C versus >159 °C for traditional inverse vulcanization. The extended sulfur chains and sulfur loops in poly(S-DVB) are less stable than S-S bonds in S_8[23,26]. Lower temperatures can then be used to cause homolytic scission and thiyl radical formation[24]. For monomers with melting points well below the reaction temperature, this can still be accomplished without the need for solvents. Stable polymers were obtained with 1,4-cyclohexanedimethanol CDE, CVE, and AE (**Figure 1**). This is especially noteworthy for CVE, a monofunctional compound. There has been successful polymerization of styrenic compounds by inverse vulcanization[21,27]. However, without cross-linking from the monomer, most other monofunctional compounds do not form stable polysulfides leading to depolymerization and precipitation of S_8. Poly(S-DVB-CVE) showed no signs of depolymerization, even after 6 months[24].

A slightly different protocol is needed for monomers with high melting points. Maleimide was also incorporated to determine how monomers with melting points near the reaction temperature would affect the reaction. Initially, no interaction between the prepolymer and maleimide was observed. For this monomer, a higher reaction scale was utilized for the prepolymer synthesis. Larger reaction scales tend to decrease the T_g of poly(S-DVB) allowing better interaction with the monomer. Although this improved the interaction some, there was still distinct separation between poly(S-DVB) and the maleimide. A small amount of DMF had to be added at 10 mg reactants/µL DMF for a successful reaction. However, poly(S-DVB) still provides the benefit of stabilization for this monofunctional compound.

Fabrication of all terpolymers was monitored by ^{1}H NMR to determine the percent monomer incorporation. Monomers with vinyl groups, CDE and CVE, reacted the most rapidly (**Figure 2**). Difunctional CDE demonstrated > 90% conversion and solidification within 1 h. Allyl ether took slightly longer to react likely due to the depressed reaction rates of allyl groups[28]. Maleimide took the longest to react and only reached ~70% incorporation after 48 h. The slow initial reactivity may be due in part to the limited interaction between the poly(S-DVB) and maleimide. However, maleimide also contains an internal alkene that does not readily undergo radical propagation. This is likely a major contribution to the limited maleimide incorporation overall.

Control polymerizations were conducted by heating poly(S-DVB) in the presence of additional DVB and reheating poly(S-DVB) with no additional monomer. Polymer structures were examined by ^{1}H NMR to compare the formation of HC-S bonds (2-5 ppm) versus HC-C bonds (1-2 ppm) formed by radical propagation (**Figure 3A**). Heating poly(S-DVB) in the absence of monomers showed no notable changes to the polymer structure. Combining poly(S-DVB) with additional DVB resulted in comparable HC-C:HC-S bond formation relative to the prepolymer. Unlike CDE, alkene peaks were observed by ^{1}H NMR even when poly(S-DVB-DVB) was precipitated into methanol. The presence of partially incorporated monomers with unreacted double bonds have been observed in other polymer systems[29].

Additional controls were conducted by combining S_8 with different monomers in the absence of poly(S-DVB) prepolymer to determine if the prepolymer alone initiates polymerization. Although S_8 must be heated above 120 °C to melt on its own, an incomplete reaction occurred when S_8 was combined with CDE at 90 °C for 72 h. However, when examined by TLC and DSC, there was still unreacted elemental sulfur remaining (**Figure 3B,C**). When the same control was repeated with DVB and AE, no reaction occurred after 72 h. To determine if additional sulfur rather than just additional monomers could be incorporated, a reaction combining a 1:1:1 weight ratio of S_8:CDE:poly(S-DVB) was conducted. A substantial portion of the added sulfur was polymerized; however, the reaction was incomplete leaving some unreacted S_8 in the sample (**Figure 3B**).

Prepolymer and terpolymer solubility was investigated in DCM at 75 mg/mL (**Figure 5**). Poly(S-DVB) with high sulfur content demonstrated limited solubility, which has been observed previously[3]. However, the incorporation of some CDE improved solubility substantially. Beyond 1:50 poly(S-DVB):CDE ratio, extensive cross-linking led to a less soluble, more gel-like network. Although terpolymer samples appear homogenous (**Figure 5A**), solubility tests demonstrated samples contain fully soluble and fully insoluble portions. Polymer insolubility may be caused by regions of high sulfur content, extensive cross-linking and/or high molecular weight. Only the soluble fraction was used for characterization by NMR and GPC (**Figure 4**). Since there are likely competing effects between high sulfur content and cross-linking, it is difficult to discern how the NMR spectra are affected by insolubility. For GPC, the soluble fraction likely underestimates the overall molecular weight and PDI of the terpolymers. Despite these challenges, poly(S-DVB-CDE) demonstrated improved solubility relative to many of the prepolymer samples providing more complete information.

The field of inverse vulcanization has grown rapidly since it was first introduced. Short reaction times, solvent-free synthesis, and the development of functional materials make this method very attractive. However, high reaction temperatures preclude the use of many monomers. Utilizing dynamic sulfur bonds of polysulfides to initiate polymerization has decreased the reaction temperature substantially to 90 °C. Additionally, monofunctional monomers can be combined into stable polymers. This development allows more monomers to be utilized creating a diverse set of materials. Developing polymers with a wider range of physical properties will likely expand the use of recycled waste to create functional polymers.

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DISCLOSURES:

The authors have nothing to disclose.

REFERENCES:

1. Griebel, J.J., Glass, R.S., Char, K., Pyun, J. Polymerizations with Elemental Sulfur: A Novel Route to High Sulfur Content Polymers for Sustainability, Energy and Defense. *Progress in Polymer Science.* **58**, 90-125 (2016).

2. Chung, W.J. et al. Elemental Sulfur as a Reactive Medium for Gold Nanoparticles and Nanocomposite Materials. *Angewandte Chemie International Edition.* **50**, 11409-11412 (2011).

3. Chung, W.J. et al. The Use of Elemental Sulfur as an Alternative Feedstock for Polymeric Materials. *Nature Chemistry.* **5**, 518-524 (2013).

4. Shukla, S.; Ghosh, A.; Roy, P. K.; Mitra, S.; Lochab, B., Cardanol Benzoxazines - A Sustainable Linker for Elemental Sulphur Based Copolymers via Inverse Vulcanisation. *Polymer.* **99**, 349-357 (2016).

5. Worthington, M. J.H., Kucera, R.L., Chalker, J.M. Green Chemistry and Polymers Made from Sulfur. *Green Chemistry.* **19**, 2748-2761 (2017).

6. Boyd, D.A. Sulfur and Its Role In Modern Materials Science. *Angewandte Chemie International Edition.* **55**, 15486-15502 (2016).

7. Shukla, S., Ghosh, A., Sen, U.K., Roy, P.K., Mitra, S., Lochab, B. Cardanol Benzoxazine-Sulfur Copolymers for Li-S Batteries: Symbiosis of Sustainability and Performance. *Chemistry Select.* **1**, 594-600 (2016).

8. Griebel, J.J., et al. Dynamic Covalent Polymers via Inverse Vulcanization of Elemental Sulfur for Healable Infrared Optical Materials. *ACS Macro Letters.* **4**, 862-866 (2015).

9. Griebel, J.J., et al. New Infrared Transmitting Material via Inverse Vulcanization of Elemental Sulfur to Prepare High Refractive Index Polymers. *Advandced Materials.* **26**, 3014-3018 (2014).

10. Crockett, M.P. et al. Sulfur-Limonene Polysulfide: A Material Synthesized Entirely from Industrial By-Products and Its Use in Removing Toxic Metals from Water and Soil. *Angewandte Chemie International Edition.* **55**, 1714-1718 (2016).

11. Hasell, T., Parker, D.J., Jones, H.A.; McAllister, T., Howdle, S.M., Porous Inverse Vulcanized Polymers for Mercury Capture. *Chemical Communications.* **52**, 5383-5386 (2016).

12. Thielke, M.W., Bultema, L.A., Brauer, D.D., Richter, B., Fischer, M., Theato, P. Rapid Mercury(II) Removal by Electrospun Sulfur Copolymers. *Polymers.* **8**, 266 (2016).

13. Worthington, M. J. H. et al. Laying Waste to Mercury: Inexpensive Sorbents Made from Sulfur and Recycled Cooking Oils. *Chemistry A European Journal*. **23**, 16219-16230 (2017).

14. Worthington, M. J. H. et al. Sustainable Polysulfides for Oil Spill Remediation: Repurposing Industrial Waste for Environmental Benefit. *Advanced Sustainable Systems*. **2**, 1800024 (2018).

15. Abraham, A. M., Kumar, S. V.,Alhassan, S. M. Porous Sulphur Copolymer for Gas-phase Mercury Removal and Thermal Insulation. *Chemical Engineering Journal.* **332**, 1-7 (2018).

16. Mann, M. et al. Sulfur Polymer Composites as Controlled-release Fertilisers. *Organic and Biomolecular Chemistry*. (2018) DOI: 10.1039/C8OB02130A.

17. Deng, D., Hoefling, A., Théato, P., Lienkamp, K. Surface Properties and Antimicrobial Activity of Poly(sulfur-co-1,3-diisopropenylbenzene) Copolymers. *Macromolecular Chemistry and Physics*. **219**, 1700497 (2018).

18. Diez, S., Hoefling, A., Theato, P. Pauer, W. Mechanical and Electrical Properties of Sulfur-Containing Polymeric Materials Prepared via Inverse Vulcanization. *Polymers*. **9**, 59 (2017)

19. Parker, D. J., Chong, S. T., Hasell, T. Sustainable Inverse-vulcanised Sulfur Polymers. *RSC Advances*. **8**, 27892–27899 (2018).

20. Arslan, M., Kiskan, B., Yagci Y. Recycling and Self-Healing of Polybenzoxazines with Dynamic Sulfide Linkages. *Scientific Reports*. **7**, 5207 (2017)

21. Zhang, Y.Y., Konopka, K.M., Glass, R.S., Char, K., Pyun, J. Chalcogenide Hybrid Inorganic/Organic Polymers (CHIPs) via Inverse Vulcanization and Dynamic Covalent Polymerizations. *Polym Chemistry.* **8**, 5167-5173 (2017).

22. Zhang, Y. et al. Nucleophilic Activation of Elemental Sulfur for Inverse Vulcanization and Dynamic Covalent Polymerizations. *Journal of Polymer Science Part A: Polymer Chemistry*. **57**, 7-12 (2019).

23. Tobolsky, A. V. Polymeric Sulfur and Related Polymers. *Journal of Polymer Science: Polymer Symposia.* **12**, 71-78 (1966).

24. Westerman, C.R., Jenkins, C.L. Polysulfides Initiate Dynamic Monomer Incorporation Forming Cross-linked Terpolymers. *Macromolecules*. **51**, 7233-7238 (2018).

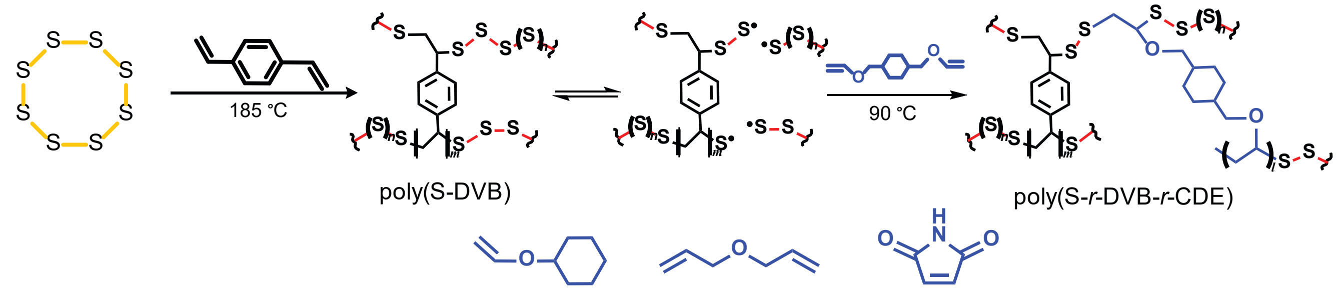
25. Arslan, M., Kiskan, B., Cengiz, E. C., Demir-Cakan, R., Yagci, Y. Inverse Vulcanization of Bismaleimide and Divinylbenzene by Elemental Sulfur for Lithium Sulfur Batteries. *European Polymer Journal.* **80**, 70-77 (2016).

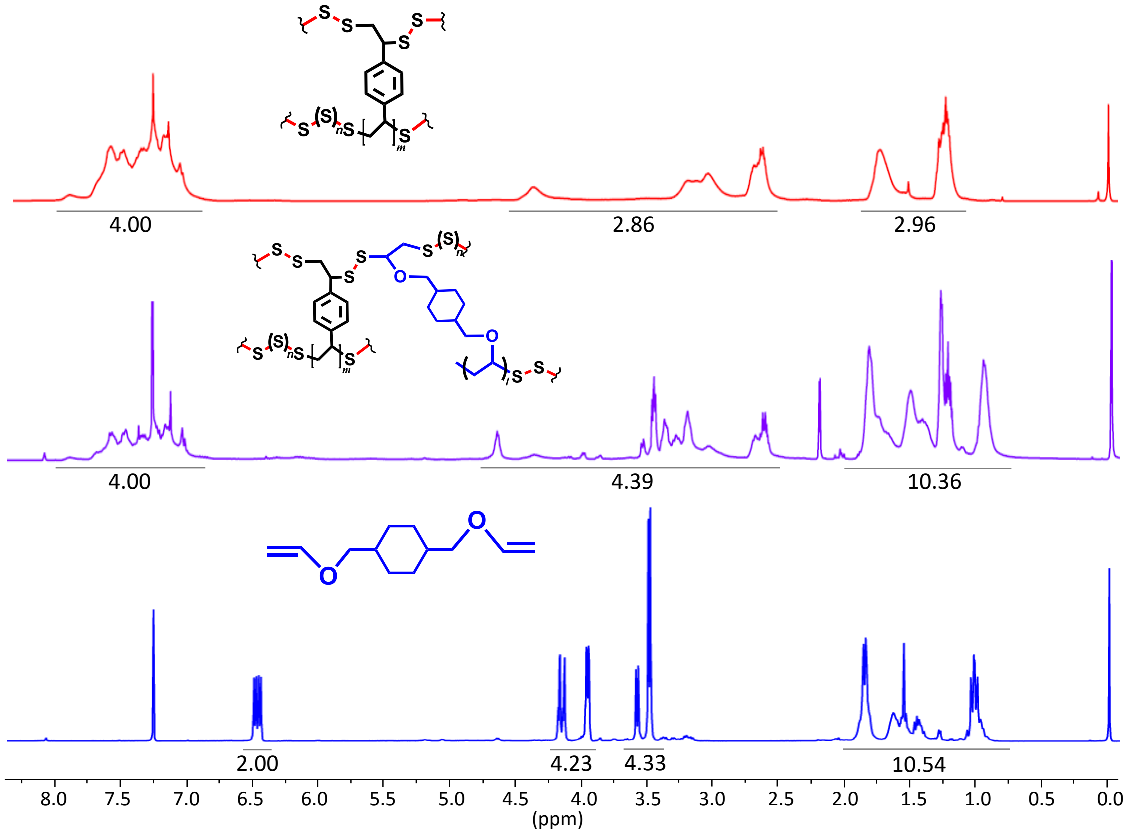
26. Pickering, T.L., Saunders, K.J., Tobolsky, A.V. Disproportionation of Organic Polysulfides. *Journal of the American Chemical Society.* **89**, 2364-2367 (1967).

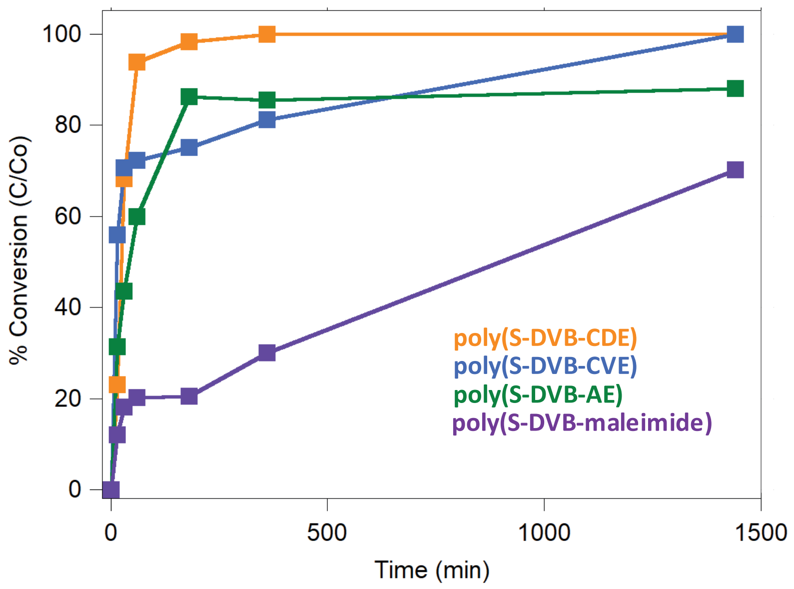
27. Zhang, Y.Y. et al. Inverse Vulcanization of Elemental Sulfur and Styrene for Polymeric Cathodes in Li-S Batteries. *Journal of Polymer Science Part A: Polymer Chemistry.* **55**, 107-116 (2017).

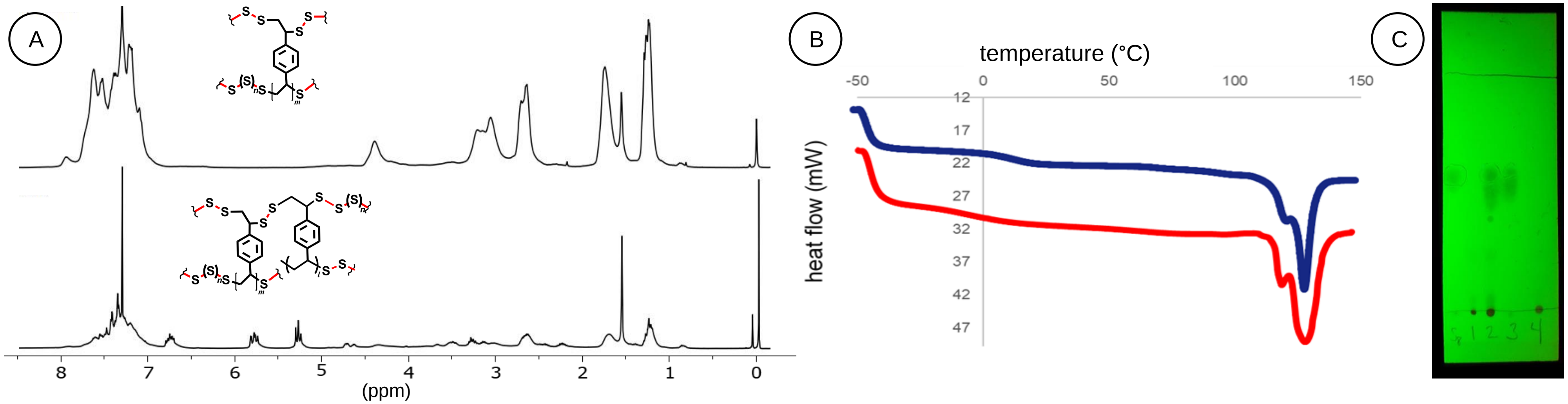
28. Zubov, V.P., Kumar, M.V., Masterova, M.N., Kabanov, V.A., Reactivity of Allyl Monomers in Radical Polymerization. *Journal of Macromolecular Science: Part A.* **13**, 111-131 (1979).

29. Wei, Y.Y. et al. Solution Processible Hyperbranched Inverse-Vulcanized Polymers as New Cathode Materials in Li-S Batteries. *Polymer Chemistry.* **6**, 973-982 (2015).


185 °C
poly(S-DVB)
90 °C
poly(S-r-DVB-r-CDE)

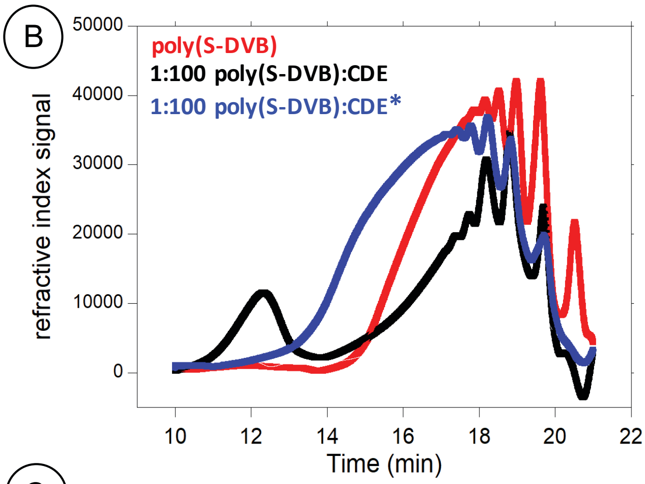

S
(S)
n
m
l
O
4.00
2.86
2.96
4.00
4.39
10.36
2.00
4.23
4.33
10.54
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

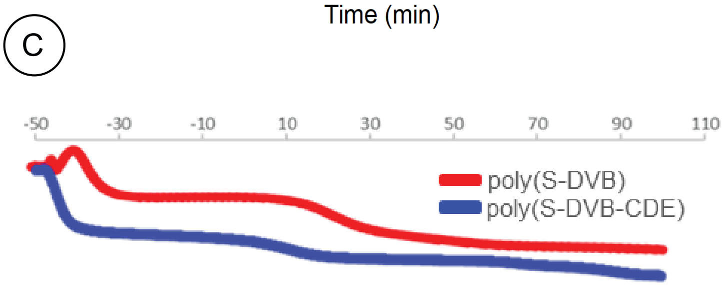

100
80
60
40
20
0
% Conversion (C/Co)
0
500
1000
1500
Time (min)
poly(S-DVB-CDE)
poly(S-DVB-CVE)
poly(S-DVB-AE)
poly(S-DVB-maleimide)

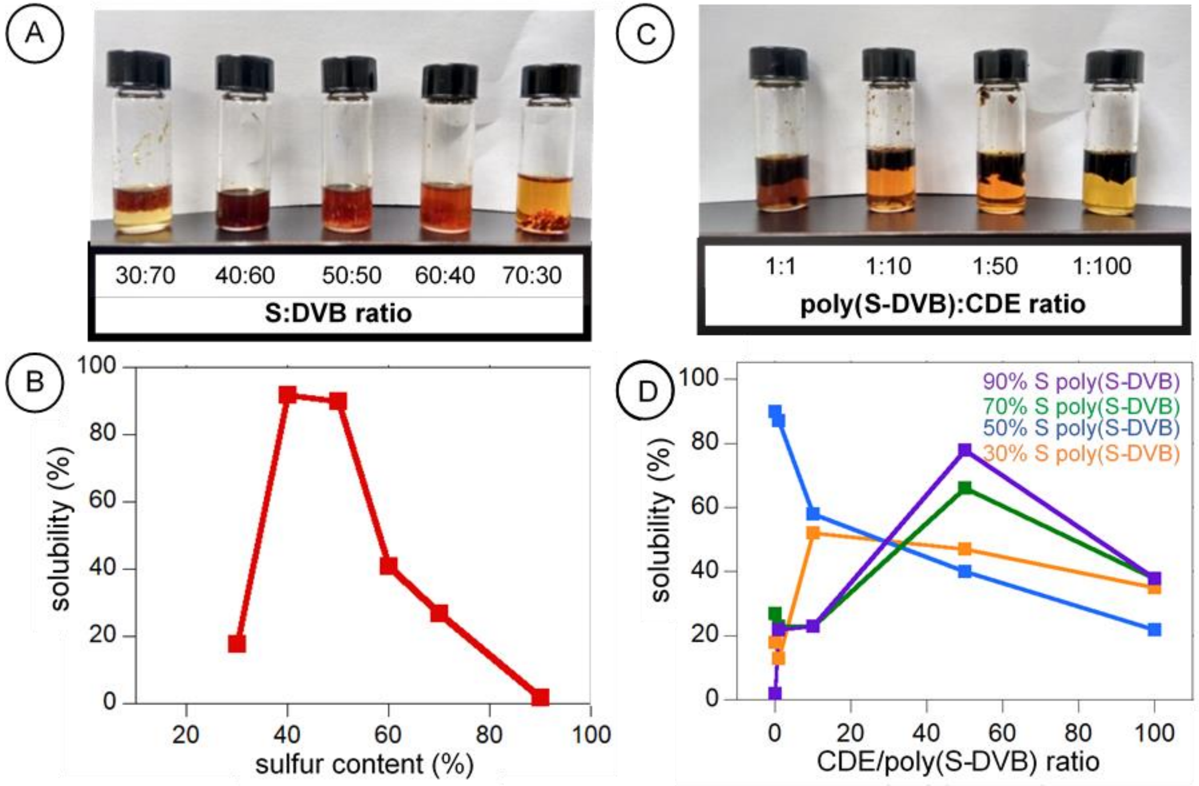

A
(S)
n
m
8
7
6
5
4
3
2
1
0
(ppm)
B
temperature (°C)
-50
0
50
100
150
heat flow (mW)
12
17
22
27
32
37
42
47
C
S 1 2 3 4

A

S:DVB ratio	poly(S-DVB): CDE ratio	M_w (g/mol)	PDI	T_g (°C)
30:70	1:0	2700	2.5	73
	1:1	1600	2.0	45
	1:10	2400	2.4	1
	1:50	3200	2.9	-6
	1:100	6100^{a}	4.0	-^{b}
50:50	1:0	3700	2.7	52
	1:1	1200	1.8	14
	1:10	1100	1.7	31
	1:50	1900	2.0	10
	1:100	2800	2.1	9
70:30	1:0	--^{c}	--	28
	1:1	700	1.4	20
	1:10	1700	2.4	11
	1:50	2100	2.3	2
	1:100	3400	2.4	8






A
30:70
40:60
50:50
60:40
70:30
S:DVB ratio
C
1:1
1:10
1:50
1:100
poly(S-DVB):CDE ratio
B
solubility (%)
0
20
40
60
80
100
20
40
60
80
100
sulfur content (%)
D
90% S poly(S-DVB)
70% S poly(S-DVB)
50% S poly(S-DVB)
30% S poly(S-DVB)
solubility (%)
0
20
40
60
80
100
0
20
40
60
80
100
CDE/poly(S-DVB) ratio

Click here to access/download;Table of Materials;JoVE_Materials.xlsx

Name of Material/ Equipment	Company	Catalog Number
Sulfur, 99.5%, sublimed, ACROS Organics	Fisher Scientific	AC201250250SDS
divinylbenzene	Fisher Scientific	AA4280422
1,4-Cyclohexanedimethanol divinyl ether, mixture of isomers	Sigma Aldrich	406171
Cyclohexyl vinyl ether	Fisher Scientific	AC395420500
Allyl ether	Sigma Aldrich	259470
maleimide	Sigma Aldrich	129585
dichlormethane	Fisher Scientific	D37
N,N-dimethylformamide	Fisher Scientific	D119
Auto sampler Aluminum Sample Pans, 50µL, 0.1mm, Sealed	Perkin Elmer	B0143017
Auto sampler Aluminum Sample Covers	Perkin Elmer	B0143003
EMD Millipore 13mm Nonsterile Millex Syringe Filters - Hydrophobic PTFE Membrane, 0.45 um	Fisher Scientific	SLFHX13NL

Comments/Description

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CORRESPONDING AUTHOR

Name: Courtney Jenkins

Department: Chemistry

Institution: Ball State University

Title: Assistant Professor

Signature: Cori

Date: 12/21/2018

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Response to Reviewer Comments

Editorial Comments

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3. For in-text referencing, please put the reference number before a period or comma.
4. Please ensure that all text in the protocol section is written in the imperative tense as if telling someone how to do the technique (e.g., "Do this," "Ensure that," etc.). Any text that cannot be written in the imperative tense may be added as a "Note."
5. Please add a one-line space between each of your protocol steps.
6. Please make all schemes as figures. Please renumber all figures in the order of their appearance and ensure that all figures are numbered correctly.
7. For each figure, please provide a title and a short description in figure legend.
8. Please do not abbreviate journal titles for all references.
9. Please remove trademark (™) and registered (®) symbols from the Table of Equipment and Materials.

Response:

All editorial comments have been addressed as detailed below.

1-2. The manuscript has been carefully proof read and copyright permissions have been obtained and provided.

3. All reference numbers have been placed before punctuation.

4-5. The protocol section has been changed to the imperative tense and the spacing has been fixed.

6. Scheme 1 was changed to Figure 1 and the numbering on all other figures have been adjusted.

7. Descriptions have been added to Figures 1-3 and titles have been added to Figures 4-6 so that all figures now have clear titles and captions in the legends.

8. All journal titles are now written out fully.

9. The trademark symbol has been removed from the Table of Equipment and Materials

Reviewer: 1

Comment:

I think it would also be good to add some high resolution images of the polymers produced so that it is clear how their colour or mechanical properties change between each terpolymer. The video that will be forthcoming should be an excellent opportunity to do this: please include not just the synthesis, but also some video demonstrations of the properties of each polymer (Are they flexible? Hard? Tacky? Brittle? Friable? Etc).

Response:

Discussion about the properties of each polymer is a good suggestion. The video should offer a great opportunity to clearly show changes to the polymer color and demonstrate the mechanical properties of the polymer. The following text has been added to the Representative Results section of the manuscript regarding poly(S-DVB) on p. 5 and poly(S-DVB-CDE) on p. 6.

“Upon removal from the vial, the polymer is a hard, brittle material at lower sulfur content (30-40%). Mid-range sulfur content (50-60%) produces a tacky material that is very malleable, and higher sulfur content (70-90%) forms a tough and flexible solid. Furthermore, the polymers become more opaque with increasing sulfur content.”

“The inclusion of CDE into poly(S-DVB) changed the characteristics of the prepolymer. With a 1:1 poly(S50%-DVB50%):CDE ratio, the polymer exhibited a mocha brown color compared to the reddish black prepolymer color. The material was also able to resist any physical force applied by hand to break apart the polymer. Even light scratching of the polymer showed minimal surface deformation. This is in stark contrast to the poly(S50%-DVB50%) prepolymer’s tacky and malleable properties.”

Comment:

In addition to the suggestions above, the authors should include a few citations of other properties and applications of these sulfur materials in the introduction. I believe this is important because it illustrates how Jenkins' monomer insertion method is likely to have far reach in material synthesis and the many applications that follow. For instance:

1. Sustainable inverse-vulcanised sulfur polymers. Parker, Chong, Hasell.

RSC Adv 2018, 27892. This paper shows, among other things, that polysulfides prepared by inverse vulcanisation can be recycled into different shapes. This is a bit different concept than the 'self-healing' or repairable applications first demonstrated by Pyun (though the chemistry is similar). This is an important concept in recycling and repurposing these materials.

2. Worthington et al. Chem. Eur. J. 2017, 23, 16219-16230. This is a paper from the Chalker lab that is a comprehensive study on using sulfur polymers in mercury capture. It should be cited because it is the only study of mercury sorption that includes mercury metal, organic, inorganic and mercury gas. For mercury metal, it is actually oxidised to cinnabar. In this way, the sulfur polymers are not merely physical *sorbents, they are reactive sorbents. This is consistent with the dynamic S-S bonds that Jenkins and Pyun use in their insertion methods.*

3. Chalker has also used these sulfur polymers as oil sorbents. This application in oil sorption is mentioned in the introduction, but I don't think this paper was cited. Please cite: Worthington et al. Adv. Sustainable Syst. 2018, 1800024.

4. Alhassan has shown that sulfur polymers are excellent for thermal insulation. This is a unique application and should be cited: Chemical Engineering Journal 332 (2018) 1-7. They also test mercury vapour sorption.

5. Theato and Lienkamp have studied a very interesting and distinct application of sulfur polymers as antimicrobial surfaces. The data is preliminary and hard to interpret, but it is the first paper in this space and an opportunity for development. With a broader range of monomers now available perhaps this can be advanced. Please cite Macromol. Chem. Phys. 2018, 219, 1700497

6. Hasell and Chalker also published a recent paper in using sulfur polymers in fertiliser applications. Like the antibacterial application, this is a completely distinct use of polymers made by inverse vulcanisation. Please cite: Mann et al. Sulfur polymer composites as controlled-release fertilisers. Org. Biomol. Chem. 2018, in press. DOI: 10.1039/c8ob02130a

7. Theato and Pauer have prepared terpolymers previously and have shown that using sulfur and two organic monomers gives interesting mechanical and electrical properties. These reactions are all done at high temperature, unlike in the submitted manuscript, but it is a good paper to cite as an example of how sulfur terpolymers have interesting and even tunable properties. Please cite: Polymers 2017, 9, 59, doi: doi:10.3390/polym9020059

8. An alternative method to make sulfur polymers at lower temperature is to use nucleophilic activators. This strategy, reported by Glass, Char and Puyn, is mechanistically distinct from Jenkins' method, but it should still be cited: J. Polym. Sci., Part A: Polym. Chem. 2019, 57, 7-12

Response:

Thank you for pointing out the benefit of including more polymer applications in the manuscript. All of the requested citations have now been included (sources 13-20 and 22). Additional text has been added to the introduction section on p. 1 and is included below.

"The resulting polymers have been used for a wide range of applications including as cathodes in Li-S batteries[1,5-7], self-healing optical lenses[8-9], mercury and oil sorbents[5,10-15], thermal insulators[15], to aid in the slow release of fertilizer[16] as well as demonstrating some antimicrobial activity[17]. One group has provided a thorough systematic analysis of these polysulfides providing more information about the insulating character and mechanical properties with varied S content[18]. The specific details may aid in further applications development. The dynamic bonds present in these materials have also been utilized to recycle the polysulfides[19,20]."

"Another method utilizes nucleophilic amine activators to enhance reaction rates and lower reaction temperatures[22]."

Reviewer: 2

Comment:

Reaction of elemental S reaction is not limited to traditional chemistry associated with double and triple bonds. There are benzoxazine linkages which are susceptible too (Polymer 2016, 99, 349-357; Sci. Rep. 2016, 6, 1-13; ChemistrySelect, 2016, 1, 594-600), where so-formed copolymers are explored for battery work. It needs to be mentioned in introduction

Response:

Thank you for pointing out the missing information and citations. The requested citations have been added (sources 4 and 7) along with the text below.

"In addition to traditional radical polymerizations, inverse vulcanization has been utilized to initiate polymerization with benzoxazines[4]."

Comment:

Data w.r.t. CDE is only shown, respective data and change in behavior with the incorporation of other co-monomers should be given. CDE data has already provided by this group in their earlier publication. Author stated "this figure has been reproduced from Macromolecules". What is new in the current work needs to be presented. A comparative analysis helps.

Response:

Full characterization was completed only for CDE due to the rapid reaction times for this monomer compared to other monomers. Performing full characterization including a range of S contents and prepolymer:monomer ratios on all of the monomers would take a substantial amount of time and would be outside the scope of this particular article. Since JoVE is a methods focused journal, the authors decided it was more important to include a very thorough investigation of one monomer rather than trying to include every monomer tested to provide the audience with a general idea of the range of physical properties that could be obtained.

Comment:

A generalised synthetic scheme should be there in the beginning to assist the understanding. Monomers examined include 1,4-cyclohexanedimethanol divinyl ether (CDE), cyclohexyl vinyl ether (CVE), and allyl ether (AE), maleimide that should be illustrated.

Response:

Figure 1 has been updated to include the additional monomers utilized in the polymerization. The figure legend has been altered to include the text below.

"The additional monomers used to modify the poly(S-DVB) are depicted in blue."

Comment:

Please rewrite" Within 30 min, poly… is fabricated." It is not fabrication?

Response:

The text has been rewritten as requested and is included below.

“Within 30 min sulfur and DVB react completely for form poly(S-DVB).”

Reviewer: 3

Comment:

In the abstract, in reference to the potential for comonomers to be used, simply say, "However, high reaction temperatures (> 160 °C) limit...".

Response:

The text has been rewritten as requested and is included below.

“However, high reaction temperatures (>160 °C) limit the types of monomers that can be used.”

Comment:

In Section 2.3.1, is the DMF added solely to dissolve the poly(S-DVB-maleimide) polymer? It would be helpful to include a brief statement explaining its purpose.

Response:

Additional text was added to section 2.3.1. This section now includes the text below.

“No solvent is needed for most of these polymerizations. However, in order for maleimide and poly(S-DVB) to interact fully, 20 µL of DMF must be added.”

Comment:

"Aluminum" is misspelled in Section 4.4.1

Response:

The spelling error has been corrected and the manuscript has been checked thoroughly for additional errors.

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Publication:	Macromolecules
Publisher:	American Chemical Society
Date:	Sep 1, 2018

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