

Preparation of Dynamic Covalent Polymers via Inverse Vulcanization of Elemental Sulfur

Jared J. Griebel,^{†,‡} Ngoc A. Nguyen,^{‡,§} Andrei V. Astashkin,[†] Richard S. Glass,[†] Michael E. Mackay,^{*,§,||} Kookheon Char,^{*,⊥} and Jeffrey Pyun^{*,†,⊥}

[†]Department of Chemistry and Biochemistry, University of Arizona, 1306 East University Boulevard, Tucson, Arizona 85721, United States

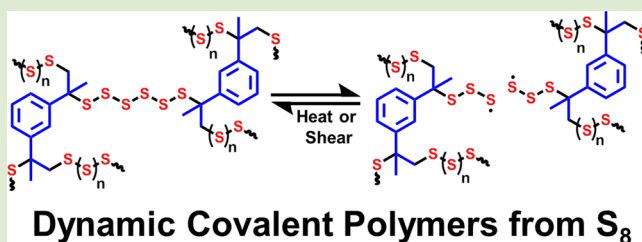
[§]Department of Materials Science and Engineering, University of Delaware, 201 DuPont Hall, Newark, Delaware 19716, United States

^{||}Department of Chemical and Biomolecular Engineering, University of Delaware, 150 Academy Street, Newark, Delaware 19716, United States

[⊥]School of Chemical and Biological Engineering, Program for Chemical Convergence of Energy and Environment, The National Creative Research Initiative Center for Intelligent Hybrids, Seoul National University, Seoul 151-744, Korea

Supporting Information

ABSTRACT: The synthesis of dynamic covalent polymers with controllable amounts of sulfur–sulfur (S–S) bonds in the polymer backbone via inverse vulcanization of elemental sulfur (S₈) and 1,3-diisopropenylbenzene (DIB) is reported. An attractive feature of the inverse vulcanization process is the ability to control the number and dynamic nature of S–S bonds in poly(sulfur-*random*-(1,3-diisopropenylbenzene)) (poly(S-*r*-DIB) copolymers by simple variation of S₈/DIB feed ratios in the copolymerization. S–S bonds in poly(S-*r*-DIB) copolymers of high sulfur content and sulfur rank were found to be more dynamic upon exposure to either heat, or mechanical stimuli. Interrogation of dynamic S–S bonds was conducted in the solid-state utilizing electron paramagnetic resonance spectroscopy and *in situ* rheological measurements. Time-dependent rheological property behavior demonstrated a compositional dependence of the healing behavior in the copolymers, with the highest sulfur (80 wt % sulfur) content affording the most rapid dynamic response and recovery of rheological properties.



The preparation of synthetic macromolecules containing dynamic covalent bonds has been recently investigated as a versatile approach to prepare stimuli-responsive and self-healing polymeric materials.¹ The ability of covalent bonds to dissociate and reform allows one to develop structurally dynamic polymeric systems that can adapt their structure, morphology, or composition, enabling a macroscopic response to an external stimulus.^{2–6} A key requisite for the preparation of these kinds of polymeric materials is the installation of dynamic functional groups using synthetic methods that are orthogonal to the polymerization process.

A number of dynamic covalent chemistries have been incorporated in polymers to create stimuli-responsive materials via disulfide exchange,^{7–9} radical mediated addition–fragmentation chain transfer reactions,^{10–14} alkoxyamine exchange reactions,^{15,16} transesterification reactions,^{17–19} and thermoreversible Diels–Alder reactions.^{20–22} Furthermore, supramolecular polymers with dynamic capabilities have been prepared through the incorporation of hydrogen bonding motifs,²³ π – π stacking functionalities,²⁴ and metal–ion ligand interactions.^{25–27} However, in the vast majority of these cases, the dynamic or exchangeable chemical bonds required to

impart stimuli-responsiveness (e.g., disulfides, hydrogen bonding groups) need to be explicitly installed as disparate, orthogonal functional groups relative to the polymerizable moieties (e.g., vinyl). The recent work of Rowan et al. on the preparation of polymeric disulfide networks via oxidative polymerizations of di- and tetrasulfide comonomers is a notable example where the dynamic covalent bonds were installed in the polymer forming reaction and accessed to create self-healing films and shape memory materials.¹⁴ However, in a general sense, there remain opportunities to directly install dynamic covalent bonds into polymeric materials via polymerization methods with inexpensive monomers.

Recently, we reported on the use of inverse vulcanization to enable the direct conversion of S₈ into chemically stable and processable sulfur copolymers. Using this approach, the sulfur content (and number of S–S bonds) was controlled by variation of comonomer feed ratios used in the copolymerization.²⁸ Synthetic access to polymeric materials with a high

Received: October 24, 2014

Accepted: November 25, 2014

Published: November 26, 2014

content of S–S bonds afforded materials with novel electrochemical and optical properties that were exploited for high capacity lithium–sulfur (Li–S) batteries and high refractive index polymers for IR optics.^{29–31} Both of these examples demonstrate that certain useful bulk properties can emerge in polymeric materials that are comprised of long chain S–S bonds. However, exploitation of the chemical nature of these bonds (in this case, the presence of dynamic bonds) in these sulfur-based polymers has not been explored.

Herein, we report on the preparation of dynamic covalent polymers via inverse vulcanization, where labile S–S bonds were controllably installed by the direct copolymerization of S₈ with DIB (Figure 1). Furthermore, reversible scission of S–S

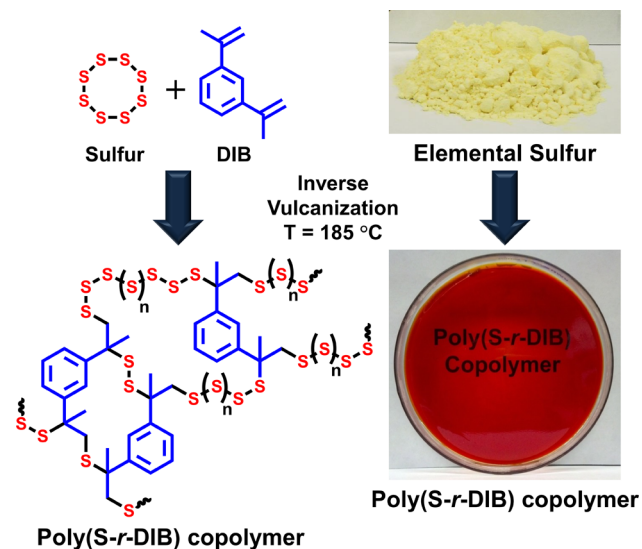


Figure 1. Synthetic scheme for preparation of poly(Sulfur-*random*-1,3-diisopropenylbenzene) copolymers utilizing the bulk inverse vulcanization process.

bonds in these poly(sulfur-*random*-(1,3-diisopropenylbenzene) (poly(S-*r*-DIB)) copolymers was achieved by external thermomechanical stimuli (i.e., both heat and shear), where sulfur-rich copolymer compositions correlated with more facile reversible bond scission as revealed by self-healing rheological characterization. We attribute these findings to lower bond dissociation energies of S–S bonds in longer S–S chains, as observed in copolymer systems with well-defined polysulfide materials (i.e., disulfide, trisulfide, tetrasulfide).³² To our knowledge, this is the first example where the nature of the dynamic chemical bonds in a polymeric material could be directly controlled by a simple variation of copolymer composition.

To interrogate the presence of dynamic S–S bonds in poly(S-*r*-DIB) samples, copolymers with varying content of sulfur (35, 50, 70, and 80 wt %) were prepared and characterized using both electron paramagnetic resonance (EPR) spectroscopy and rheological measurements. Due to the limited solubility of high sulfur content copolymers, the development of characterization methods capable of detecting the thermal or mechanical generation of sulfur radicals from neat solid samples of these materials was required. These specific compositions were chosen because the stoichiometric ratios of S₈ to DIB afforded tunable copolymer microstructures ranging from short polysulfide (35 wt % sulfur, *n* ~1 bridging sulfur, Figure 2) to longer polysulfide (80 wt % sulfur, *n* ~ 10

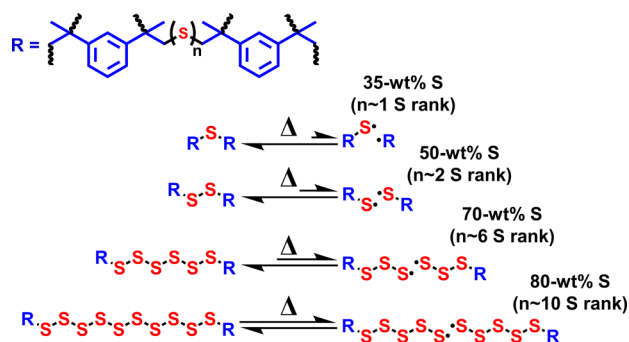


Figure 2. Schematic representation of dynamic behavior under stimulus ($T = 100\text{ }^{\circ}\text{C}$) in poly(S-*r*-DIB) copolymers as a function of dynamic S–S bond content.

bridging sulfurs, Figure 2) spacers between the DIB units. Based on previous investigations of small molecule di-, tri-, and tetrasulfide compounds and polymers, bond dissociation energies of S–S bonds were observed to decrease with increasing sulfur rank (i.e., number of S–S bonds).³³ These general trends in sulfur rank were anticipated to directly affect the dynamic behavior of poly(S-*r*-DIB) copolymers.

To confirm the formation of sulfur radicals upon thermal activation of S–S bonds in poly(S-*r*-DIB) copolymers, EPR spectroscopic spin trapping experiments were conducted with the samples of varying sulfur content (as described above) in the presence of 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), which is able to trap sulfur centered radicals (Figure 3a). The

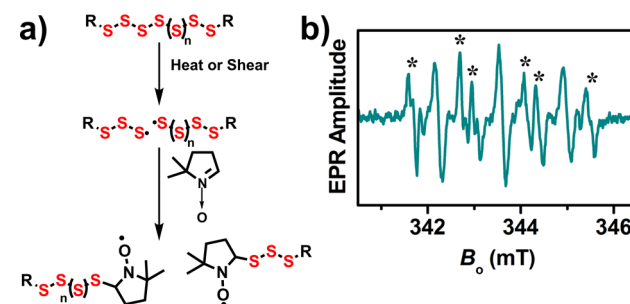


Figure 3. (a) Trapping of sulfur radicals generated under dynamic conditions to enable spectroscopic analysis. (b) Room temperature EPR spectrum of the 50 wt % sulfur copolymer in the presence of DMPO (soluble fraction in toluene, see the Supporting Information for details). The asterisks mark the lines of the sulfur-centered spin adduct.

specific thermal conditions for the sample preparation ($T = 100\text{ }^{\circ}\text{C}$, 1 h) were chosen based on the earlier findings of Tobolsky et al., where the homolytic scission of disulfides in various polysulfide materials was observed at $100\text{ }^{\circ}\text{C}$.³² Solution blending of DMPO into a thermally annealed poly(S-*r*-DIB) copolymer sample yielded EPR active species observed in the $g = 2$ region (Figure 3b). The analysis of the EPR spectra (see Supporting Information) reveals the presence of the DMPO spin adduct with a sulfur-centered radical species (marked by asterisks in Figure 3b), which confirms that the S–S bonds in poly(S-*r*-DIB) are dynamically forming the sulfur radicals at $T = 100\text{ }^{\circ}\text{C}$. Native copolymers treated under identical conditions without DMPO did not show detectable EPR signals.

Further evidence of dynamic S–S bonds in poly(S-*r*-DIB) copolymers and the influence composition has on the dynamic behavior was determined via in situ rheological monitoring of

shear induced S–S bond scission at varying strain rates at $T = 130\text{ }^{\circ}\text{C}$. Self-healing rheology experiments were conducted at $T = 130\text{ }^{\circ}\text{C}$ since the melt viscosities of poly(*S-r*-DIB) copolymers were observed to be too high at $T = 100\text{ }^{\circ}\text{C}$ (as conducted for the EPR spin trapping experiments). Additionally, these experiments were conducted at temperatures well above the glass transition temperature (T_g) of the various copolymers studied ($T_g = 9, 20, \text{ and } 28\text{ }^{\circ}\text{C}$ for poly(*S-r*-DIB) with 80, 70, and 50 wt % sulfur, respectively, see Figure S2) to decouple the effects of dynamic S–S bond content and copolymer T_g with self-healing dynamics. Ultimately, these rheological measurements provided direct evidence of S–S bond scission as a function of sulfur rank in poly(*S-r*-DIB) materials and closely tracked with composition effects.

Dynamic rheological behavior experiments were conducted by initial determination of the storage modulus for pristine copolymer samples by application of a low strain rate (8%) at a constant frequency (100 rad/s) within the linear deformation regime (Figure 4, region 1). These samples were then subjected to a high strain amplitude (100%) for 5 min to promote S–S bond scission as evidenced by a substantial drop in the storage modulus (G' , Figure 4, region 2). After 5 min, the strain rate was once again decreased (8%), and a temporal dependence of

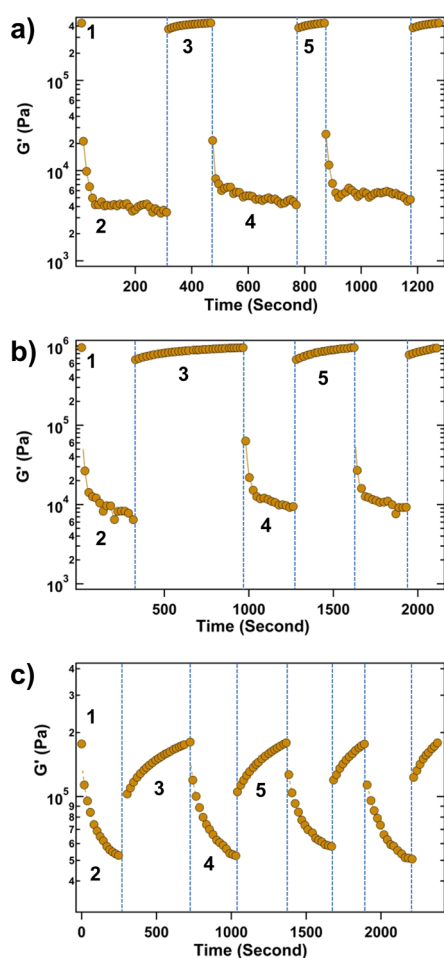


Figure 4. In situ rheological characterization of dynamic behavior in poly(*S-r*-DIB) copolymers at $T = 130\text{ }^{\circ}\text{C}$ and 100 rad/s: (a) 80 wt % sulfur; (b) 70 wt % sulfur; and (c) 50 wt % sulfur. Regions in the plots represent: (1) initial modulus; (2) 100% strain, 1st damaging cycle; (3) 8% strain, 1st recovery cycle; (4) 100% strain, 2nd damaging cycle; (5) 8% strain, 2nd recovery cycle.

G' was measured to ascertain the time required for recovery of the initial storage modulus due to S–S bond formation (Figure 4, region 3). Once the original modulus was recovered, the strain amplitude was again increased (100%) to test for cyclability of shear-induced S–S bond scission and recovery (Figure 4, regions 4 and 5). As can be seen in Figure 4, the damage/recovery cycling was repeatable for high sulfur content poly(*S-r*-DIB) copolymers (Figure 4, region 5 and cycles thereafter). A direct correlation between copolymer composition and dependence on the dynamic recovery time was observed, where sulfur copolymers of high sulfur rank ($n \approx 10, 80\text{ wt } \%$ sulfur) exhibited a dramatically faster recovery of the original storage modulus (149 s, Figure 4a). Poly(*S-r*-DIB) of lower sulfur rank ($n \approx 6, 70\text{ wt } \%$ sulfur) rapidly recovered 95% of the initial storage modulus at lower applied strains (25 s) but required longer recovery times to fully recover to 100% of the initial storage modulus (655 s, Figure 4b). Poly(*S-r*-DIB) ($n \approx 2, 50\text{ wt } \%$ sulfur) was still observed to undergo reversible S–S bond scission as noted by a dramatic reduction of the storage modulus upon increasing applied strain. These copolymers exhibited distinct self-healing profiles as noted by a reduced recovery of the storage modulus at short times (58% of modulus in 30 s, Figure 4c) and longer times for complete healing of the material to the originally observed storage moduli (421 s). Finally, the poly(*S-r*-DIB) copolymers with $n \sim 1$ (35 wt % sulfur) did not exhibit a self-healing behavior (as evidenced by rheological measurements) under identical conditions, presumably due to the large content of monosulfide bonds (i.e., C–S–C bonds, see Figure S3, Supporting Information), and they deformed in a manner consistent with conventional thermoplastic polymers. In this class of materials, the stress becomes large enough to affect the sample integrity and it is impossible for any recovery to occur. It is also interesting to note that after the first damage/recovery cycle in higher sulfur content copolymers (50–80 wt % sulfur) the process of recovery quickens in subsequent cycles. We attribute this phenomenon to the reorganization of the copolymer microstructure into a state that favors recombination of sulfur radicals generated during the chain scission process induced at high strain amplitudes.

In conclusion, we demonstrate the preparation of stimuli-responsive, dynamic covalent copolymers via the inverse vulcanization of elemental sulfur, where the self-healing dynamics of these materials was controlled by simple variation of copolymer composition. These copolymers represent a new class of self-healing materials where the unique properties of S–S bonds can be exploited (i.e., batteries, optics, and coatings).

■ ASSOCIATED CONTENT

📄 Supporting Information

Preparation and characterization of sulfur copolymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: jpyun@email.arizona.edu.

*E-mail: khchar@snu.ac.kr.

*E-mail: mem@udel.edu.

Author Contributions

‡These authors contributed equally to this work (J.J.G. and N.A.N.).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge the NSF (CHE-1305773), the WCU Program through the NRF of Korea funded by the Ministry of Education, Science and Technology (R31-10013) for support of this work. K.C. acknowledges the NRF for the National Creative Research Initiative Center for Intelligent Hybrids (2010-0018290). University of Delaware's funding provided through the Department of Materials Science and Engineering.

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