

Dynamic Covalent Polymers via Inverse Vulcanization of Elemental Sulfur for Healable Infrared Optical Materials

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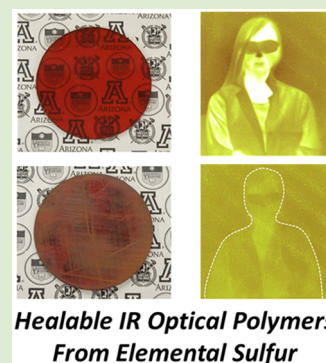
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S Supporting Information

ABSTRACT: We report on dynamic covalent polymers derived from elemental sulfur that can be used as thermally healable optical polymers for mid-IR thermal imaging applications. By accessing dynamic S–S bonds in these sulfur copolymers, surface scratches and defects of free-standing films of poly(sulfur-random-1,3-diisopropenylbenzene) (poly(S-r-DIB)) can be thermally healed, which enables damaged lenses and windows from these materials to be reprocessed to recover their IR imaging performance. Correlation of the mechanical properties of these sulfur copolymers with different curing methods provided insights to reprocess damaged samples of these materials. Mid-IR thermal imaging experiments with windows before and after healing of surface defects demonstrated successful application of these materials to create a new class of “scratch and heal” optical polymers. The use of dynamic covalent polymers as healable materials for IR applications offers a unique advantage over the current state of the art (e.g., germanium or chalcogenide glasses) due to both the dynamic character and useful optical properties of S–S bonds.



The development of stimuli-responsive polymers has been recently investigated as a means to healable materials.¹ While a number of functional groups have been utilized to create dynamic covalent polymers, these typically require that the dynamic functional groups are orthogonal to the polymer forming reaction.^{2–5} However, disulfide and polysulfide bonds are a class of dynamic covalent functional groups that can be installed via the polymer forming reaction by direct (co)-polymerization with elemental sulfur (S₈) or di/polysulfides.^{6–8} The early work by Tobolsky et al. on polyurethane copolymer networks demonstrated the stress-relaxation properties imparted via the inclusion of di- and tetrasulfide bonds.^{9–11} More recently, Rowan et al. reported the preparation of polymeric disulfide networks via oxidative polymerizations of di- and tetrasulfide comonomers to create self-healing films and shape memory materials.¹² We recently reported on the synthesis of dynamic covalent polymers via the inverse vulcanization of S₈ and 1,3-diisopropenylbenzene (DIB), enabling the generation of the first dynamic covalent polymers with composed primarily of dynamic bonds. In this system, the dynamic behavior in high sulfur content copolymers was directly controlled by the comonomer feed ratios and copolymer composition, demon-

strating that such properties were modulated by altering sulfur rank (number of S–S bonds) within these materials.¹³

To date, numerous applications of dynamic covalent polymers have been explored, with an emphasis on the creation of stimuli-responsive macromolecules and self-healing materials.^{5,14,15} In these materials, the primary function of the dynamic covalent bonds served to enable reversible bond scission, or reorganization within the macromolecular framework. However, there remains opportunities to create dynamic covalent polymeric materials that exhibit multiple functions in addition to those related to reversible bonds. In this respect, the use of dynamic S–S bonds is attractive since this functional group is both stimuli-responsive (e.g., to light, heat, mechanical force) and possesses intriguing optical properties. We previously demonstrated the use of sulfur copolymers as a new class of mid-IR transmitting materials for thermal imaging applications.¹⁶ However, the preparation of polymeric materials that possess both useful stimuli-responsive dynamic bonds and

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optical properties has not been explored due to the low weight percentage of S–S bonds in previously reported systems.

Herein, we report on the preparation of dynamic covalent copolymer possessing unique optical polymers for mid-IR imaging via the inverse vulcanization of S_8 and DIB. Mid-IR ($3\text{--}5\ \mu\text{m}$) lenses and windows are currently fabricated from semiconductors such as germanium zinc selenide, or chalcogenide glasses (e.g., $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$) where imaging performance is compromised after minor scratches, or defects are incurred in the material (see Figure 1a for examples).

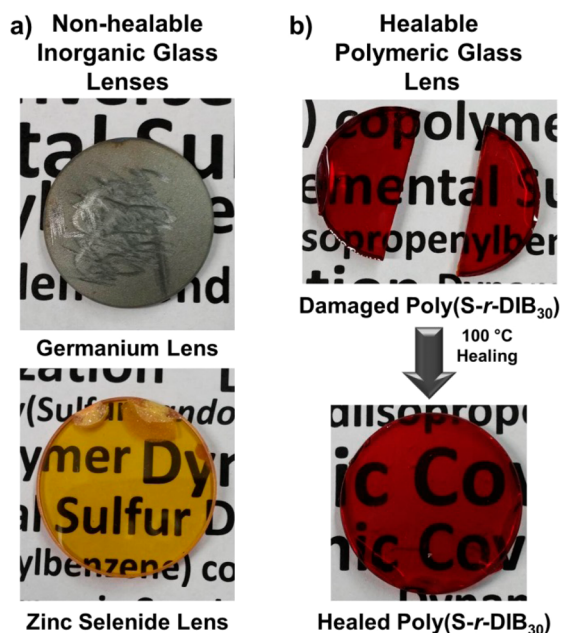


Figure 1. (a) Damaged inorganic lenses (germanium lens (top) and zinc selenide lens (bottom)) that cannot be repaired for IR imaging. (b) Poly(*S-r*-DIB₃₀) copolymer lens which is drastically damaged but repaired and functional by thermal annealing at 100 °C.

Hence, the use of an optical polymer possessing dynamic covalent bonds enables healing of these types of defects and reuse of damaged lenses/windows (windows in this context refers to a flat free-standing panel of the material). To our knowledge, this is the first example of a healable optical polymer and is a new application for dynamic covalent materials.

An in depth investigation into the effects of thermal curing on the inverse vulcanization of S_8 and DIB was conducted to enable the preparation of free-standing films of poly(sulfur-random-1,3-diisopropenylbenzene) (poly(*S-r*-DIB)) copolymers with 30 wt % DIB (poly(*S-r*-DIB₃₀), Figure 1) for fracture-healing studies and IR imaging experiments. We previously reported that the inverse vulcanization methodology was readily applied to bulk polymerization processes in glass reactors and was also amenable to oven curing methods of prepolymer resins poured into PDMS molds.^{16–18} Optimization of processing prepolymer resins in PDMS molds was the primary objective of this study since these methods most readily afforded free-standing lenses or windows for IR thermal imaging.

A major challenge that is encountered in the preparation and characterization of main chain dynamic covalent polymers is dealing with the rearrangement of S–S bonds in the polymer backbone during melt-reprocessing into films or other forms.

These processing issues were encountered when analyzing the inverse vulcanization of S_8 and DIB at 185 °C under different conditions: (a) in a 20 mL glass vial stirred in a thermostated oil bath; (b) vacuum oven cured in glass Petri dishes; and (c) vacuum oven cured in PDMS molds. In these initial studies, the solubility of poly(*S-r*-DIB) copolymers with 50 wt % DIB (poly(*S-r*-DIB₅₀)) varied, depending on the polymerization process that was used. For example, in our earlier reports, poly(*S-r*-DIB₅₀) that were prepared in glass vial reactors were found to afford low molar mass, branched copolymers with macrocycle loops that readily dissolved in nonpolar organic solvents.¹⁸ Conversely, poly(*S-r*-DIB₅₀) samples oven cured in PDMS molds were found to be largely insoluble due to network formation as noted by a significant gel fraction (~ 80 wt %) when swollen with the same nonpolar solvents (see Supporting Information).

Hence, to better understand how the method of production affected copolymers prepared via inverse vulcanization, a survey of the mechanical properties for each of these processing methods (bulk polymerizations in glass reactors vs oven curing in glass and PDMS molds) was conducted on the poly(*S-r*-DIB₃₀) copolymers (Figure 2). For these experiments, sulfur

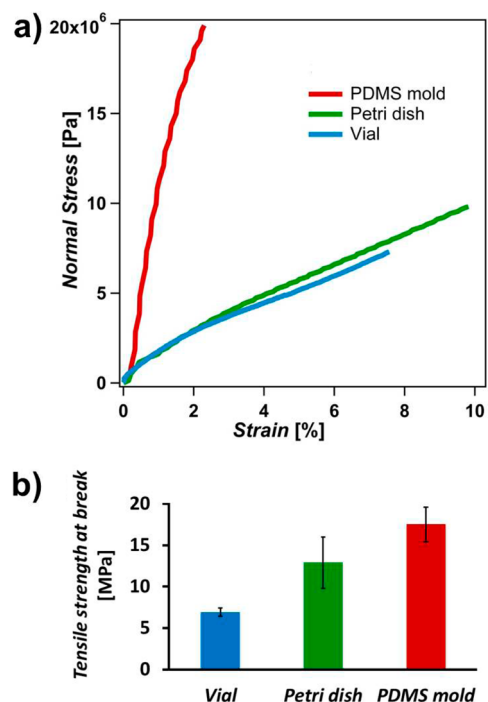


Figure 2. (a) Stress–strain curves for poly(*S-r*-DIB₃₀) copolymers prepared by various methods at 185 °C: vial synthesized (blue curve); cured in a Petri dish (green curve); and cured in a PDMS mold (red curve). (b) Plot of tensile strength at break for polymers depicted in (a).

copolymers prepared from the different curing methods were melt pressed at 150 °C for 3 min into free-standing 200 μm films for mechanical tensile testing. As we and others demonstrated, polymers with S–S bonds exhibit dynamic behavior above ~ 90 °C, thus, the microstructure of the copolymers should become dynamic, allowing for further improvement in properties as the macrocycle loops open and afford a more networked structure (see Supporting Information).^{12,13,19} However, this also meant that the melt-processing step, necessary for mechanical and rheological characterization,

resulted in S–S bond rearrangement in the backbone (depending on conditions) and potentially altered the copolymer molar mass and architecture. Despite this inherent complication, these studies were conducted to enable qualitative assessment of the thermomechanical properties of these materials from different curing methods.

In these experiments, sulfur copolymers prepared in 20 mL glass vials in a thermostated oil bath at 185 °C were found to exhibit the lowest tensile strength at break (6.9 ± 0.5 MPa). Conversely, films derived from sulfur copolymers cured in glass Petri dishes (12.9 ± 3.1 MPa), or PDMS molds (17.5 ± 2.1 MPa) exhibited superior tensile strength relative to films melt-processed from copolymers prepared in glass vials (Figure 2a,b). We attributed these variations in properties to differences in heat transfer which affected the degree of polymerization in the bulk reactions. Due to the lower effective temperatures incurred during oven curing by using the thermally insulating PDMS molds, higher degrees of polymerization were obtained, thus enabling a more networked structure.

Dynamic rheological characterization was then conducted on poly(S-*r*-DIB₃₀) samples cured in PDMS molds to interrogate the copolymer architecture as a more quantitative proof of the network microstructure. The frequency independent response for the storage modulus in the low frequency region at 60 °C for the copolymer sample pointed to the formation of polymer networks (i.e., $E' > E''$; Figure 3a).²⁰ Thermal activation of the dynamic S–S bonds at 100 °C afforded an increase in modulus due to the generation of a higher cross-link density after annealing the copolymer (orange curves, Figure 3a). This particular temperature for annealing and self-healing was found to be sufficiently above the glass transition temperature (T_g , 43.5 °C from $\tan \delta$) of the poly(S-*r*-DIB₃₀) copolymers to allow mobility and generate an adequately low concentration of polymeric sulfur radicals to favor coupling toward higher molar mass products.

To further deconvolute the rearrangement of S–S bonds during melt-processing into copolymer thin films, a series of self-healing experiments with melt-processed films (thickness ≈ 200 μm) were conducted using uniaxial tensile testing on damaged and rehealed films. For these studies films were damaged via razor blade scoring (50% of the initial width, see Supporting Information), followed by thermal healing of the film at 100 °C to allow S–S bond formation. For the films prepared from poly(S-*r*-DIB₃₀) copolymers a tensile strength of 17.5 ± 2.1 MPa and percent elongation at break of $2.8 \pm 1.8\%$ was initially observed. Scoring the films resulted in significantly diminished properties (4.8 ± 1.0 MPa and $0.88 \pm 0.55\%$, respectively; Figure 3b). Thermal rehealing of a scored sample was conducted by annealing at 100 °C inside a heated oven for 5 min to recover the tensile strength 13.4 ± 1.1 MPa and the percent elongation at break to $1.91 \pm 1.48\%$ (Figure 3b) without the need for any other hot-pressing steps. By comparison poly(S-*r*-DIB₆₅) copolymer, which is a thermoplastic composed primarily of monosulfide linkages, did not exhibit this type of thermal healing recovery of the initial modulus after damaging the sample (see Supporting Information, Figure S11). Overall, these findings reveal that while a number of challenges exist in the processing of dynamic covalent polymers, appropriate conditions can be utilized to recover mechanical losses in the material properties incurred during melt-processing.

Finally, to demonstrate a new application for dynamic covalent and self-healing polymers, we applied the thermal

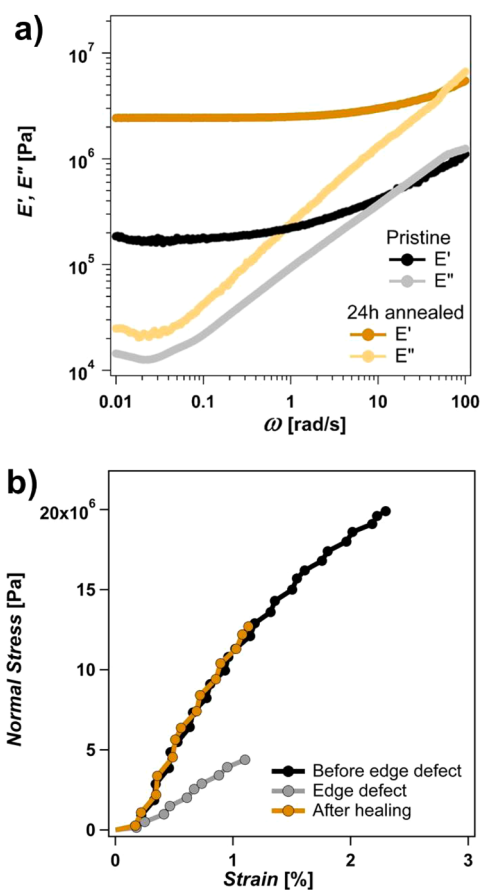


Figure 3. (a) Frequency sweeps performed at 60 °C for as-prepared poly(S-*r*-DIB₃₀) copolymer windows (E' (black circles) and E'' (grey circles)) and windows annealed 24 h at 100 °C (E' (brown circles) and E'' (yellow circles)). (b) Stress–strain curves for poly(S-*r*-DIB₃₀) copolymers: before edge defect (black circles); 50% edge defect (grey circles); after healing at 100 °C for 5 min (tan circles).

rehealing of fabricated poly(S-*r*-DIB₃₀) windows (55 mm × 2 mm) as a “scratch and heal” system for IR transmitting materials.

As alluded to earlier, IR of lenses or windows fabricated from germanium or chalcogenide glasses are rendered unusable from surface scratches or other defects. However, for windows or lenses fabricated from poly(S-*r*-DIB) materials, scratches, indentation, or complete fracture could be thermally healed using the methods previously described. In our original report, 20 wt % DIB copolymers were utilized to fabricate lenses and windows for IR imaging.¹⁶ However, the rigors of thermal annealing experiments necessitated the utilization of the higher DIB content (30 wt % DIB copolymer, poly(S-*r*-DIB₃₀) that possessed a higher T_g and enhanced thermomechanical properties. Furthermore, poly(S-*r*-DIB) copolymers possessing higher DIB compositions (both 30 and 50 wt % DIB) were found to be sufficiently transparent in the mid-infrared spectral regime necessary for thermal imaging (3–5 μm ; see Supporting Information, Figure S12).

A series of mid-IR thermal imaging experiments were performed using windows fabricated from poly(S-*r*-DIB₃₀) copolymers both before and after thermal healing of surface scratches (Figure 4). As prepared, copolymer windows were demonstrated to afford quality images of a human subject in both the visible (Figure 4a) and mid-IR (Figure 4d). Environmental scanning electron microscopy (e-SEM) of

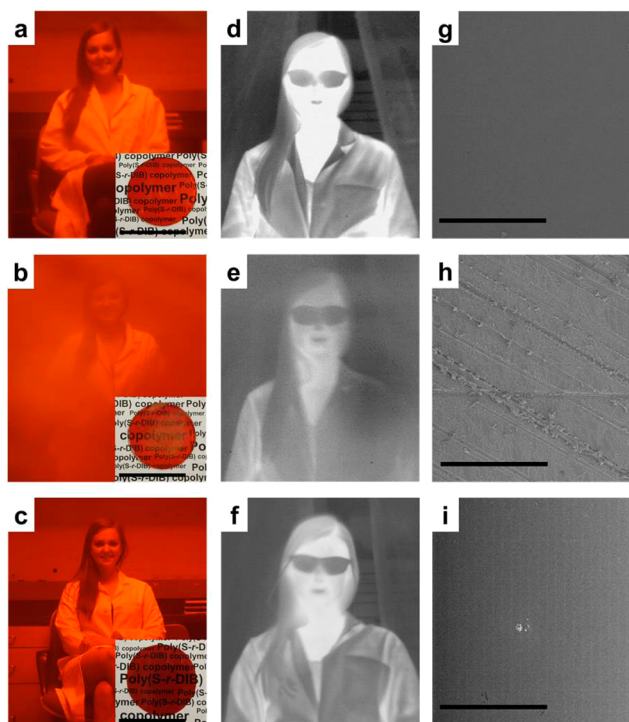


Figure 4. (a–c) Digital visible wavelength images captured through poly(*S-r*-DIB₃₀) copolymer window of a female subject: (a) pristine window; (b) damaged window; (c) self-healed window. Insets: Digital images of windows over printed text. (d–f) Digital, mid-infrared wavelength (3–5 μm) images captured through poly(*S-r*-DIB₃₀) copolymer window of a female subject: (d) pristine window; (e) damaged window; (f) self-healed window. (g–i) Environmental scanning electron microscopy (e-SEM) images of poly(*S-r*-DIB₃₀) copolymer window surface: (g) pristine window; (h) damaged window; (i) self-healed window. Scale bars for insets in (a)–(c) are 5.5 cm and for (g)–(i) are 300 μm .

these pristine windows also confirmed the absence of any surface defects or roughened surface topography on the micron scale (Figure 4g). However, after abrasion of the copolymer window with coarse grain sandpaper, both visible (Figures 4b) and thermal IR images (Figure 4e) were significantly distorted due to the scattering and high aberration arising from the roughened surface topography. Loss in imaging quality of these roughened windows was further confirmed by e-SEM, as noted by oriented micron-sized scratches (Figure 4h). Healing of these surface defects was achieved by thermal annealing of copolymer windows between PDMS disks at 100 °C for 72 h. Recovery of high quality imaging in both the visible (Figure 4c) and thermal IR regimes (Figure 4f) was confirmed after this thermal healing process, along with the regeneration of a smooth, featureless surface topography, as imaged from e-SEM (Figure 4i). While an extended healing time was necessary to recover the original smoothness required for thermal imaging, the dimensional integrity of the window during the healing process was high even without the use of a mold (3.4% increase in window diameter).

In conclusion, we demonstrate the use of a sulfur based copolymer as a healable transmitting material for IR thermal imaging applications. Furthermore, to our knowledge, this is the first example of exploiting both the desirable optical properties and dynamic nature of S–S bonds to make a thermally reprocessable IR optical polymeric material.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details for the preparation and characterization of sulfur copolymers. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00502.

(PDF)

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Notes

The authors declare no competing financial interest.

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