Inverse Vulcanization of Vinyl-polycyclic Aromatic Hydrocarbon Monomers and Dynamic Covalent Polymerization with Liquid Crystalline Monomers

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ABSTRACT: Recently, sulfur polymers have attracted great attention due to their self-healing ability and shape memory behavior. In this work, we report the effect of pendant ring structures on the thermomechanical and shape memory behavior of liquidcrystalline sulfur terpolymers. Copolymers were prepared via inverse vulcanization from various vinyl-polycyclic aromatic hydrocarbon (PAH) monomers, and the sulfur-PAH copolymers were subsequently reacted with the liquid crystal monomer (RM257) to prepare cross-linked terpolymers. The PAH monomers with various pendant groups reacted similarly to styrene and the glass transition temperature (T_g) increased as the number of fused rings in the pendant group increased. The LC-sulfur terpolymers could be thermally healed and reprocessed above the dynamic temperature due to the dynamic sulfur–sulfur bonding in the polymer. Two types of shape memory behavior are demonstrated: (i) a macroscopic folding and unfolding shape memory process and (ii) a microscopic optical surface grating shape memory process. Permanent shapes were prepared above the dynamic temperature, and temporary shapes were created between the T_g and the dynamic temperature and then fixed by lowering the temperature below the T_g . The stretched terpolymers containing liquid crystal components exhibited good birefringence, with a dichroic ratio of ~1.36.

KEYWORDS: Inverse vulcanization, sulfur, glass transition, thermomechanical properties, shape memory, self-healing

INTRODUCTION

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Inverse vulcanization is an active area of polymer research that has been gaining traction since the foundational work was published in 2013.¹ Inverse vulcanization takes advantage of low-cost, earth abundant sulfur to produce products that can be used in a range of applications including adhesives,^{2,3} batteries,^{1,4} fertilizers,⁵ flame retardant polymers,⁶ heavy metal remediation,⁷⁻¹⁰ infrared optics,¹¹⁻¹⁶ and rubber curing agents.¹⁷ Since there are many potential applications for this polymer class, it is necessary to examine associated fundamental properties and structure-property correlations. Sulfur polymers with different glass transition temperatures $(T_{\rm g})$ ranging from -30 to 170 °C have been reported^{18–21} and can be used for various purposes depending on the glass transition temperature. Therefore, it is very useful to control T_{o} for a more efficient use of sulfur polymers in various device applications. Previous reports have investigated the effect of adding additional reactive sites to increase $T_{\rm g}$ of inverse vulcanization polymers, finding that increasing the number of reactive sites can dramatically increase the T_g of the polymer.²²

Recently, the inverse vulcanization of various size cycloalkene rings were studied and their reported glass transition temperatures increased with increasing ring size and double bond reactive site density (i.e., cross-link density).²⁰ In a more recent paper, sulfur copolymers with high $T_{\rm g}$ (>100 °C) were prepared using norbornadiene dimer cross-linkers, and the relaxation behavior due to S–S bond exchange was studied for the first time through rheological studies.²³ To briefly summarize, the $T_{\rm g}$ of sulfur polymers can be controlled by the sulfur content and the type of cross-linkable comonomer used for inverse vulcanization, especially the number of reactive sites in the comonomer.^{18–23}

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Scheme 1. Synthetic Scheme for the Inverse Vulcanization of Various V-PAHs followed by Subsequent Dynamic Covalent Polymerization with a Liquid Crystal Monomer (RM257)



The self-healing properties of sulfur-containing polymers have attracted attention because the sulfur–sulfur bonds in sulfur copolymers can exhibit dynamic covalent exchange behavior to repair physical damage.^{24–27} Griebel et al. reported that poly(S-r-DIB) copolymers prepared through the inverse vulcanization of elemental sulfur (S₈) and 1,3-diisopropenylbenzene (DIB) exhibit self-healing properties using rheological methods.¹⁸ The authors showed that dynamic sulfur–sulfur bonding can be directly controlled in poly(S-r-DIB) copolymers through the simple control of the copolymer composition. In addition to self-healing properties, others have reported the shape memory behavior of sulfur polymers.^{28–31}

To the best of our knowledge, there are no systematic studies of the size effect of side groups on the T_{g} , shape memory behavior, and self-healing properties of inverse vulcanization polymers containing liquid crystalline components. In this study, we report the effect of side group pendant structure on the thermomechanical properties and shape memory behavior of the liquid crystalline sulfur terpolymers. Liquid crystal polymers can have excellent mechanical properties and unique optical properties. The liquid crystal monomer used in this study can be used as a cross-linker for sulfur-LC polymers, which can increase the T_{g} improve mechanical stability, and exhibit optical properties. This is an approach to further control the thermomechanical properties using liquid crystal monomers in polymers prepared via inverse vulcanization. The $T_{\rm g}$ of these terpolymers increases by 30 $^{\circ}{\rm C}$ compared with the copolymers. Additionally, we observed that these sulfur terpolymers possess shape memory and selfhealing behaviors. These sulfur polymers, having self-healing and shape memory behaviors, can be used in several optical and security applications.

MATERIALS AND METHODS

Elemental sulfur was purchased from Strem Chemicals. 9-vinylanthracene (9VA, > 98%) was purchased from TCI. Styrene (Sty, 99.5%), and 1-vinylnaphthalene (1VN, 95%) were purchased from Thermo Scientific. RM257 (>97%) was purchased from Synthon. 1pyrenecarboxaldehyde (99%), potassium tert-butoxide (>98%), methyltriphenylphosphonium bromide (98%), and THF (>99.9%) were purchased from Aldrich. Hexanes (99.9%) and ethyl acetate (99.9%) were purchased from Fisher Chemical. All chemicals were used as received except 1-vinylnapthalene was purified using a short silica plug washed with hexanes/ethyl acetate to remove polymerized material. Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC2500 from -50 to 150 °C at 10 °C min⁻¹. ¹H NMR was performed on a Bruker Ascend 400 spectrometer in CDCl₃ (7.26 ppm) as used for reference. Fourier transform infrared (FTIR) spectroscopy was performed on salt plates (NaCl) using a Thermo Scientific Nicolet iS50 FTIR under nitrogen atmosphere. Samples for FTIR measurements were prepared between NaCl salt plates. Gel

permeation chromatography (GPC) was performed with a Waters Acquity APC GPC with two Waters APC BEH columns (125,450) using THF as the eluent and refractive index detector. The molecular weights were calibrated against polystyrene standards (Waters, M_p = 0.266K, 0.474K, 3.47K, 9.130K, 17.6K, 66.0K, 34.8K, 66.0K, 277 K, 552 K, 1210K, 1800K). Dynamic Mechanical Analysis (DMA) was performed on a TA Discovery DMA850 with a frequency of 1 Hz and a heating rate of 2.5 °C·min⁻¹ under nitrogen atmosphere using Tensile mode. The sample size for DMA measurements was ~0.5 mm × ~3 mm × ~15 mm ($T \times W \times L$). The hot pressing was performed on a Specac Mini-Film Maker using a 500 μ m shim.

Synthesis of 1-Vinylpyrene (1VP). 1-vinylpyrene (1VP) was not available commercially, so it was synthesized from pyrenecarboxaldehyde using the Wittig reaction.³²

Inverse Vulcanization of Vinyl Monomers. Sulfur (0.250 g, 7.80 mmol) was added to a small vial equipped with a Teflon-coated magnetic stir bar and a chosen monomer (0.250 g), yielding a 50/50 (w/w) polymer formulation. The vial was then lowered into an oil bath set to 165 °C (or 135 °C for styrene) and stirred until complete monomer consumption was observed by ¹H NMR. Upon monomer consumption, the vial was removed from the oil bath and allowed to cool to room temperature (RT). The nomenclature for inverse vulcanization using styrene (Sty), 1VN, 9VA and 1VP is poly(sulfur*random*-styrene) (p(S-*r*-Sty)), p(S-*r*-1VN), p(S-*r*-9VA), and p(S-*r*-1VP), respectively.

Dynamic Copolymerization. The given copolymer (0.250 g) prepared as described above was added to a small vial equipped with a Teflon-coated magnetic stir bar and RM257 (0.250 g, 0.42 mmol). The vial was then lowered into an oil bath set to 165 °C and stirred for 1 h. At this point, the stir bar ceased moving due to increased viscosity. The vial was then removed from the oil bath, allowed to cool to RT, and placed in a Dewar filled with liquid nitrogen for 1 min. The vial was broken with a hammer, and the pieces of polymer were collected for further processing. The nomenclature for the terpolymer using p(S-r-Sty), p(S-r-1VN), p(S-r-9VA), and p(S-r-1VP) is poly(sulfur-random-styrene-random-RM257) (p(S-r-Sty-rRM257)), p(S-r-1VN-r-RM257), p(S-r-1VN-r-RM257), and p(S-r-1VP-r-RM257), respectively.

Hot Pressing of Terpolymers and Preparation of DMA Samples. For thermomechanical measurements and shape memory tests, hot-pressed films were prepared. The resulting terpolymers were added to a hot press with Kapton film release layers placed on the top and bottom of the polymer pieces. The samples were pressed at 140 °C and 0.5 tons of pressure for 10 min. The press was then allowed to cool to RT while under pressure. Once cooled to RT, they were removed along with the Kapton release films. The pressed samples were further processed into strips by heating on a hot plate to between 75 and 85 °C and cutting with a razor blade.

RESULTS AND DISCUSSION

Preparation and Thermal Properties of the Sulfur Copolymers. The preparation of sulfur copolymers by inverse vulcanization and liquid crystalline sulfur terpolymers is schematically described in Scheme 1. The colors of the copolymer products varied from light yellow to dark red and

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Figure 1. DSC profiles of inverse vulcanization polymers produced from (a) styrene, (b) 1-vinylnaphthalene, (c) 9-vinylanthracene, and (d) 1-vinylpyrene measured from -50 to 150 °C at 10 °C·min⁻¹. The second heating run was used.



Figure 2. DSC profiles of terpolymers prepared from sulfur, RM257, and (a) styrene, (b) 1-vinylnaphthalene, (c) 9-vinylanthracene, and (d) 1-vinylpyrene measured from -50 to $150 \,^{\circ}$ C at $10 \,^{\circ}$ C min⁻¹. The second heating run was used. DMA T_g is shown in parentheses. (e) Summary of glass transition temperatures of copolymers and terpolymers obtained by DSC and DMA.

were all soluble in dichloromethane (DCM) and tetrahydrofuran (THF) (Figure S1). For all reactions, complete consumption of the vinyl monomer was observed after 1 h of reaction, except for styrene (5 h), due to the lower reaction temperature. The proton NMR spectra in Figure S2 were similar to the previously reported inverse vulcanization of styrene.³³ Broad peaks in the 3–5 ppm range are associated with S–C–H bond ranges, indicating formation of a sulfur containing polymer. In the aromatic region (\sim 7–8 ppm), broad peaks associated with the respective pendant groups are present in each spectrum. GPC traces of the respective products point to species that are oligomeric with typical molecular weights of only a few hundred g mol⁻¹ when calibrated against polystyrene standards (see Table S1 and Figure S3). It was difficult to determine if there was any correlation of molecular weight to pendant group size, given

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Figure 3. Dynamic mechanical analysis (DMA) of four terpolymers. (a) p(S-r-Sty-r-RM257), (b) p(S-r-1VN-r-RM257), (c) p(S-r-9VA-r-RM257), and (d) p(S-r-1VP-r-RM257).

the limited accuracy of GPC analysis with low molecular weight oligomers. For FTIR, given the structural similarity between the monomers, there were few distinguishing spectral features between the polymers (see Figure S4).

The DSC traces show that no unreacted elemental sulfur was present, however, other allotropes of sulfur not incorporated into the polymer structure may be present as mentioned in recent publications on "dark sulfur".³⁴⁻³⁶ The DSC trace of the p(S-r-Sty) copolymer shows a T_g of ~0 °C, which is similar to that previously reported in literature (Figure 1a).³³ The addition of a fused ring to the aryl system (e.g., 1VN) increases the T_g of p(S-r-1VN) to ~8 °C (Figure 1b). The trend of increasing T_g with an increasing number of fused rings continues for p(S-*r*-9VA) with an observed T_g of ~14 °C, and for p(S-r-1VP) with the highest reported T_g of ~19 °C as shown in Figure 1c-d. The trend of increasing T_g with increasing size of the PAH side chains is expected because larger PAHs increase the potential for $\pi - \pi$ stacking interactions and steric hindrance between polymer chains that can be affected by bulky side group structures. It should be noted that for p(S-r-9VA), a slight H_2S odor was observed and confirmed by black PbS formation on a Pb(OAc)₂ test strip. The color of this copolymer was significantly darker than those of the other copolymers. It is possible that other species may also have formed during the polymerization process, as suggested during the attempted homopolymerization of 9VA.³⁷

Preparation and Thermal Properties of the Liquid Crystalline Sulfur Terpolymers. For the preparation of the liquid crystalline sulfur terpolymers, the copolymers and liquid crystalline monomer (RM257) were mixed at 165 °C for 1 h and allowed to react until the mixture reached a viscosity where the stir bar could no longer move (Scheme 1). The terpolymers were homogeneous upon cooling and had a color ranging from light yellow to deep red. In many reports on inverse vulcanization and dynamic copolymerization, high (>50 wt %) sulfur content is desired and self-healing properties have mainly been reported in higher sulfur content polymers.^{18,28,30,31} Although the sulfur content of the terpolymers prepared in this study is only 25 wt %, reprocessing and thermal self-healing are still observed. To further investigate the trends of T_g associated with the pendant groups of the polymer, the terpolymers were examined by both DSC and DMA for the present trends with an increased T_{σ} with pendant group size. Interestingly, as shown in Figure 2, the terpolymers with the LC component have a glass transition temperature that is about 14-40 °C higher than that of the copolymers. The $T_{\rm g}$ obtained by DMA is higher than that obtained by DSC because a mechanical input was used for the DMA measurement. Unexpectedly, the significantly higher T_g (~84 °C) of p(S-r-9VA-r-RM257) was observed (Figure 2c), which may arise from side reactions, possibly additional crosslink reaction, as mentioned during the copolymer synthesis. The potential side reaction could be a Diels-Alder reaction,^{38,39} which anthracene derivatives readily undergo, which appears to cause a cross-linking reaction observed in this study. As mentioned in the previous section, the p(S-r-9VA)copolymer has a relatively broader polydispersity than other copolymers, possibly due to the side reaction, likely causing the 9VA terpolymer to have a high T_{g} . This side reaction affects the $T_{\rm g}$ of the 9VA terpolymer and will be a focus of a future investigation. All glass transition temperatures of the copolymers and terpolymers obtained by DSC and DMA are summarized in Figure 2(e).

Figure 3 shows the thermomechanical data of four terpolymers measured using DMA. The storage modulus (E') and loss modulus (E') begin to decrease through loss tangent (tan δ) before reaching a plateau in the rubbery region to a level dependent on the cross-link density and the rigidity due to the side group structure.^{40,41} The rubbery plateau indicates the formation of a network structure of the terpolymers. T_g is obtained as the peak value of tan δ . All terpolymer samples have a storage modulus higher than 1 GPa in the glassy state ($T < T_g$) and a relatively broad T_g . Using the thermomechanical data reported in Figure 3, the cross-link

density of these terpolymers was calculated by the following equation: $\nu_{\rm e} = E'_{\rm high}/(3RT_{\rm high})$, where ν_{ε} is the cross-linking density and $E'_{\rm high}$ is E' at $T_{\rm high}$. $T_{\rm high}$ is the temperature 30 °C higher than T_g (e.g., in the rubbery plateau region).^{42–46} Since $T_{\rm high}$ should be lower than the self-healing rearrangement temperature (~90 °C), we choose T_{high} only 30 °C higher than T_{g} . Because the T_{g} of the p(S-r-9VA-r-RM257) terpolymer is close to the rearrangement temperature, the cross-link density cannot be determined. All samples except p(S-r-9VA-r-RM257) have similar cross-link densities of about 0.105-0.147 mol dm⁻³. It has been reported that the mechanical properties of sulfur polymers can be controlled by the sulfur content and the type of cross-linkable comonomer for inverse vulcanization, especially the number of reactive sites in the comonomer. Wie and co-workers reported sulfur polymers with T_{σ} in the range of -30 to 170 °C and glassy state storage modulus in the range of 1 to 4 GPa.¹⁹ Previously, cross-link densities of about 0.3 to 3 mol dm⁻³ for thermally treated sulfur rich polymers (SRP),¹⁹ about 0.68 to 2.5 mol dm^{-3} for liquid crystalline elastomers,⁴⁵ and about 2.1 to 7.3 mol dm^{-3} for glassy liquid crystalline polymers^{44,46} have been reported. Although sulfur terpolymers have a relatively low cross-link density compared to these liquid crystalline polymers, the terpolymers still have a relatively high storage modulus (higher than 1 GPa) in the glassy state. The LC component can influence the mechanical properties of the terpolymer. After DMA measurements, the two terpolymers, p(S-r-Sty-r-RM257) and p(S-r-1VN-r-RM257), were broken and then repaired by hot pressing at 140 °C, which is above the rearrangement temperature, to confirm their self-healing properties. As observed in Figure S5, the repaired films of these terpolymers show almost identical thermomechanical data (E', E''), and tan δ) as the original films, indicating excellent self-healing behavior.

Shape Memory Behaviors of Liquid Crystalline Sulfur **Terpolymers.** All terpolymers except p(S-r-Sty-r-RM257) show shape memory behaviors at room temperature. P(S-r-Styr-RM257) was excluded because its T_g was lower than room temperature, and the temporary shapes could not be fixed at room temperature. Figure 4 shows photographs of each of the polymers during the shape fixing and recovery process. The first column shows the permanent shape programmed into the polymer while hot pressing the polymer pieces into flat discs at 140 °C. Because the hot-pressing temperature is higher than the rearrangement temperature, the flat permanent shape can be prepared. It should be noted that at a temperature higher than the rearrangement temperature, a variety of permanent shapes other than flat shapes can be prepared. The temporary twisted shape is created by mechanically twisting at a temperature above the $T_{\rm g}$ of the terpolymer below the rearrangement temperature (90 °C), and fixed by lowering the temperature to RT (Figure 4, middle column).^{18,23,4} Upon reheating to a temperature above each respective T_{g} , the samples return to their original flat permanent shape (Figure 4, right column). Here, we briefly describe the shape memory mechanism of sulfur-LC terpolymers. First, twisted temporary shapes were prepared by twisting mechanically at temperatures above T_{g} , and the twisting deformation primarily reduces the structural entropy of the constituent network chains. The temporary shape was then fixed by cooling to a temperature below its T_{g} while keeping the external forces constant, i.e., maintaining the external twisting deformation. During cooling,



Figure 4. Photographs of p(S-r-1VN-r-RM257) (first row), p(S-r-9VA-r-RM257), (second row), and p(S-r-1VP-r-RM257) (third row) in their flat permanent shape (left column), temporary twisted shape (middle column), and restored flat permanent shape (right column).

the terpolymer transitions to a more rigid glassy state, where the deformed network chains are kinetically frozen in a low entropy state. The external forces were then released, and the polymer retained its temporary twist conformation. Shape recovery was achieved by heating the terpolymer through T_{o} , allowing the network chains to regain their mobility and relax to the thermodynamically favored maximal-entropy state, thus changing the terpolymer from the temporary to its permanent shape. The terpolymers with temporary folded shapes are shown in Figure S6. Flat permanent shapes were prepared at 140 °C, the highest processing temperature in this study, and the thermal stability of the terpolymers was tested at this temperature. Figure S7 shows the TGA data for the terpolymers measured at 140 °C for 1 h. All terpolymers exhibit a loss of less than 2 wt % under these conditions, which could include moisture loss and mass loss of the polymer. To prepare the permanent shape, the samples were hot pressed at 140 °C for 10 min and a weight loss of less than 0.5 wt % is observed under these conditions. This indicates that the terpolymers are stable at this temperature during the preparation of the permanent shape.

The surface shape memory behavior of the terpolymers was also studied. Scheme 2 outlines the process of generating an optical grating with p(S-r-1VN-r-RM257). A simple optical grating was first prepared on PDMS with micrometer size dimensions of 6 μ m end-wall to end-wall distance (Λ) and 1 μ m in height (h). The PDMS grating was then used as a stamp to replicate the grating pattern into the surface of p(S-r-1VN-r-RM257) at 140 °C, programming the grating as the permanent shape. The grating sample was pressed with a flat glass slide at 75 °C (between T_g and the dynamic temperature) to remove the grating and cooled to RT to fix the temporary flat surface temporary shape. The optical grating was restored by simply heating the sample above its T_g and allowing it to cool to RT. Figure 5a displays a photograph of the diffraction pattern generated from a 632.8 nm HeNe laser passing through the patterned polymer (permanent shape). A continuous wave

Scheme 2. Schematic for the Preparation of an Optical Grating on p(S-r-1VN-r-RM257)



Figure 5. Photographs and optical microscopy images of the surface shape memory behavior demonstrated with an optical grating. The optical grating on the surface of p(S-r-1VN-r-RM257) is demonstrated with a 632.8 nm HeNe laser generating (a) a diffraction pattern and (b) the grating pattern can be seen under an optical microscope. (c) By temporarily removing the optical grating by flattening the surface, the laser no longer produces a diffraction pattern, and (d) the patterns are no longer visible under an optical microscope. (e) Upon reheating the sample, the optical grating returns and the laser diffraction pattern is restored and (f) the grating pattern is restored when viewed under an optical microscope.



Figure 6. Optical microscopy images of (a) the sheared p(S-r-1VN) copolymer and (b) the p(S-r-1VN-r-RM257) terpolymer with 100% strain at various angles under crossed polarizer conditions. A and P represent analyzer and polarizer, and the yellow arrow indicates the direction of rotation of the sample.

HeNe laser with an output power of 0.7 mW and a beam diameter of 3 mm was used. The corresponding optical

microscopy image (Figure 5b) displays the line pattern of the programmed optical grating. The temporary flat surface sample



Figure 7. (a) UV-vis spectra and (b) polar plots of the stretched p(S-r-1VN-r-RM257) terpolymer.

shows no diffraction pattern (Figure 5c) and no grating pattern (Figure 5d). When the p(S-r-1VN-r-RM257) terpolymer was heated to 75 °C, above its T_{gr} the same laser diffraction pattern as the initial one reappeared (Figure 5e) and was observed under an optical microscope (Figure 5f). These terpolymers with bulk and surface shape memory behaviors can be used in reusable brails, actuators, and self-healing anticounterfeiting materials for optical security and encryption.

Birefringence often occurs due to the effects of preferential molecular orientation through stretching or shearing processes. Figure 6 shows POM images of the sheared p(S-r-1VN)copolymer and stretched p(S-r-1VN-r-RM257) terpolymer (100% strain). The p(S-r-1VN) copolymer is very brittle and difficult to stretch due to its low molecular weight. To align the molecules, the copolymer is sheared between two glass slides at room temperature. As shown in Figure 6(a), the sheared p(S-r-1VN) copolymer does not exhibit birefringence under crossed polarizer conditions. This is probably due to its T_{g} being below room temperature, and the copolymer is amorphous. However, the p(S-*r*-1VN-*r*-RM257) terpolymer can be stretched to twice its original length, and as shown in Figure 6(b), the stretched terpolymer exhibits birefringence at various angles under crossed polarizer conditions. Figure 7(a) shows some of the UV/vis spectra of the stretched p(S-r-1VN-r-RM257) terpolymer as a function of the polarization angle. The polarization angle is controlled using a linear polarizer. At various polarization angles, the terpolymer shows birefringence changes and the associated polar plot is shown in Figure 7(b). The dichroic ratio, which is the ratio of the absorbance of light polarized parallel (A_{\parallel}) and perpendicular (A_{\perp}) directions, of the stretched terpolymer (D) is ~1.36 $(A_{\parallel}/A_{\perp})$. The order parameter (S) obtained from the dichroic ratio is ~0.15. This highly stretched terpolymer can be used in self-healing fabrics and self-healing optical components, including polarizers and display components.

CONCLUSIONS

Sulfur containing copolymers and terpolymers were prepared via the inverse vulcanization of vinyl-PAHs with differently sized pendant groups and, for the first time, dynamic covalent polymerization of a difunctional liquid crystal monomer, RM257. Inclusion of an LC component increases the T_g of the terpolymers and allows controlling the T_g of sulfur-based polymers for a variety of applications. The measured T_g

appears to increase with the size of the PAH group. Interestingly, the 9VA terpolymer has a very high T_{g} , of 54 °C (DSC) and 84 °C (DMA), which may be due to a crosslinkable side reaction. Understanding the mechanism of the side reaction will help to further control the T_g values of 9VA copolymers. The self-healing properties of the copolymers and terpolymers were demonstrated using fractured samples that healed above the rearrangement temperature. Two permanent shapes, a macroscopic flat shape and a microscopic surface grating shape, were prepared above the rearrangement temperature, and the temporary shapes were prepared at a temperature between T_g and the rearrangement temperature. This combination of self-healing properties and shape memory behaviors is expected to permit the use of these sulfur polymers in a number of applications, including IR transparent materials and antimicrobial materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsapm.4c01376.

Characterization of sulfur copolymers and terpolymers using GPC, ¹H NMR, FTIR, TGA and DMA measurements (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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