

New Infrared Transmitting Material via Inverse Vulcanization of Elemental Sulfur to Prepare High Refractive Index Polymers

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The development of polymeric materials for infrared (IR) optical applications has not been achieved due to challenges in designing systems with sufficiently high refractive index (n) and transparency in the IR spectral regime. IR optical technology has numerous potential applications in civil, medical, and military areas, where inorganic semiconductors (e.g., Ge and Si) and chalcogenide glasses have been widely used as materials for device components due to their high refractive index ($n \sim 2.0$ – 4.0) and low losses from 1 – $10 \mu\text{m}$. While such materials are well suited for these applications, they are inherently more expensive, toxic, and difficult to process in comparison to organic polymeric materials.^[1–3]

The preparation of high refractive index polymers (HRIP, where $n \geq 1.7$) have been explored for various optoelectronic device applications, such as, organic light emitting diodes (OLEDs), and microlens components in both charge coupled devices (CCDs) and high performance complementary image sensors (CISs).^[4] In general, the vast majority of organic polymers exhibit relatively low n -values ($n \sim 1.5$ – 1.6) and exhibit high optical losses due to IR absorptions of vibrational modes

from carbon-hydrogen, or heteroatom-hydrogen bonds (e.g., C-H, O-H, and N-H bonds which absorb at 1 – $5 \mu\text{m}$). For use in OLEDs and other devices, the design and synthesis of colorless, transparent HRIPs with $n = 1.6$ – 1.8 in the visible spectrum have been pursued, incorporating either highly polarizable heteroatoms (e.g., P and S) or rigid aromatic moieties.^[5–13] However, further increasing the refractive index of these materials above $n \sim 1.8$ without optical losses in the IR spectrum remains a difficult synthetic chemistry challenge. Hence, there remains an opportunity to design polymeric materials for IR optics that possess significantly higher refractive indices ($n > 1.8$), low loss and are amenable to melt, or solution processing.

Herein, we report on the synthesis and characterization of a high refractive index ($n \sim 1.8$) thermoplastic copolymer for IR optics containing a very high content of S-S bonds (50–80 wt% sulfur). These copolymer materials were prepared by a process termed, *inverse vulcanization*,^[14] where molten sulfur, acting as a solvent,^[15,16] was copolymerized with 1,3-diisopropenylbenzene (DIB) to prepare a chemically stable and processable sulfur plastic (**Figure 1**). This process is a bulk free radical copolymerization conducted in molten sulfur. These materials are intriguing for IR optics, since the S-S bonds in the copolymer are largely IR inactive in the near and mid-infrared regime and impart high n to the macromolecule. To demonstrate the viability of these materials for IR applications we report on the following: optical characterization of the refractive index of poly(sulfur-random-1,3-diisopropenylbenzene) (poly(S-*r*-DIB)) copolymers in the spectral regime of 600–1600 nm, interrogation of the optical transparency of these materials using UV-visible IR absorption spectroscopy from 500–3000 nm, and evaluation of IR imaging capabilities of free-standing poly(S-*r*-DIB) copolymer lenses in the near (1550 nm) and mid-IR (3–5 μm) wavelengths. To our knowledge, this is the first example of high quality near and mid-IR imaging using a high refractive index polymeric material.

The inverse vulcanization process enabled the synthesis of high sulfur-content poly(S-*r*-DIB) copolymers with tunable copolymer composition, along with improved processability over elemental sulfur. Copolymers with varying composition from 50–80 wt% sulfur were prepared by controlling feed ratios of S_8 and DIB in the inverse vulcanization process to afford amorphous, glassy materials. Copolymerization of S_8 with DIB also served to suppress the crystallinity of the sulfurous phase

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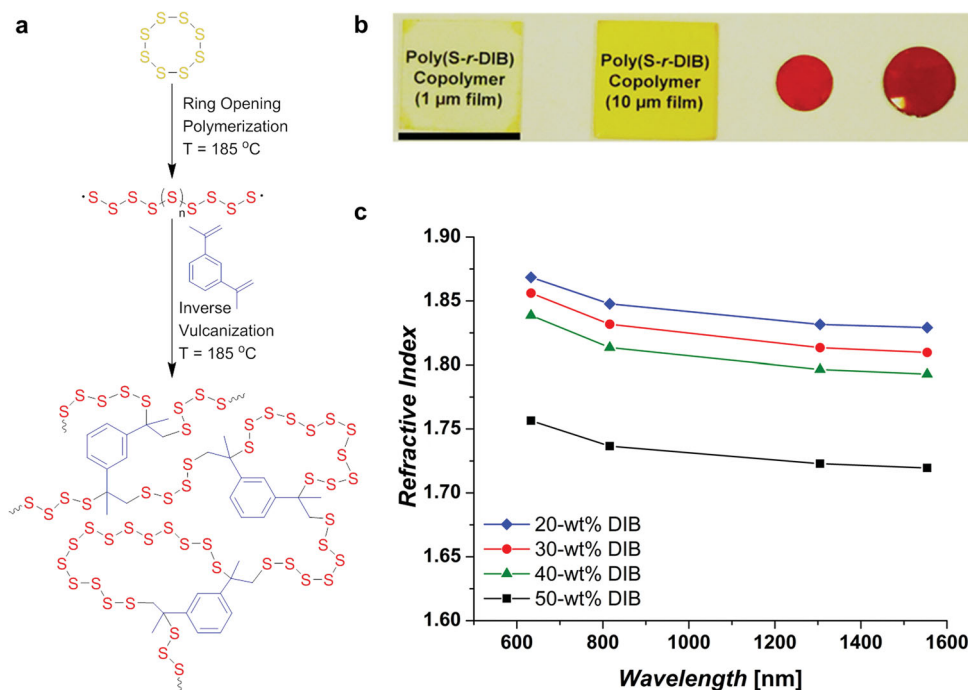


Figure 1. a) Synthetic scheme for the copolymerization of S₈ with 1,3-diisopropenylbenzene (DIB) to form poly(sulfur-random-1,3-diisopropenylbenzene) copolymer. b) Digital image of different thickness poly(S-r-DIB) (80-wt% S₈) copolymer samples (left to right; 1 μm film on glass, 10 μm film on glass, 200 μm free-standing film, and 2 mm free-standing lens) (scale bar = 2.5 cm). c) Refractive indices versus wavelength as a function of poly(S-r-DIB) copolymer composition for 200 μm films; results are the average of values for light polarized parallel and perpendicular to the film surface.

in the copolymer, enabling both melt and solution processing of these materials into optically transparent films, or free standing lenses for IR optical characterization (Figure 1b). The enhanced solubility of the copolymers (relative to elemental sulfur) in organic solvents enabled spin coating of films, which to our knowledge is the first example of thin film processing of a copolymer with such high loadings of sulfur. We previously observed that poly(S-r-DIB) copolymers of high sulfur content (10–4060–90 wt% sulfur) exhibited limited solubility in conventional organic solvents.^[14] However, these sulfur copolymers were observed to readily dissolve into warm 1,2-dichlorobenzene (DCB; above $T = 125$ °C). Using this processing method, stable thin films of controllable thickness (1 to 60 μm) were achieved for copolymers with compositions of 50–80 wt% S₈ (20–50 wt% DIB) by simple variation of the copolymer concentration in DCB (see Supporting Information).

A direct correlation between copolymer composition and refractive indices of these materials was observed using prism coupling optical measurements of free standing 200 μm copolymer films (prepared by thermomechanically forming copolymer powders, see Supporting Information). The highest refractive index was observed for materials with the highest sulfur content (80 wt% sulfur) ranging from $n = 1.865$ to 1.845 from 633 to 1554 nm across the visible and near IR spectra. Moreover, even sulfur copolymers with the lowest content of sulfur (50 wt% sulfur) still retained high refractive indices of $n = 1.765$ to 1.745 in the same spectral window. Tunability in the refractive indices of these sulfur copolymers was achieved by control of the copolymer composition as noted by the intermediate refractive index values of

poly(S-r-DIB) materials with 30 and 40 wt% DIB (Figure 1c). The trend of increasing refractive index with higher sulfur content was attributed to the large polarizability of the sulfur electrons, which shifted the refractive index to higher values in comparison to conventional hydrocarbon polymers (see Supporting Information, Figure S1). The high refractive index of these materials was accompanied by both low optical losses and birefringence from 633 to 1554 nm (Figure 1a and Supporting Information, Table S1). It is important to note the coloration in these poly(S-r-DIB) materials, which is present despite variation in copolymer composition. Similar observations of color from yellow to red have long been known in the homo-ring opening polymerization (ROP) of S₈ to polymeric sulfur and remains largely unexplained, although the formation of radical anion species during the ROP of S₈ have been proposed to be causal.^[17] While this coloration would be problematic for use in the visible spectrum, these absorbances are not an issue for use in the IR applications.

The optical transparency of poly(S-r-DIB) films containing 80 wt% sulfur was interrogated using UV-vis-near-IR transmission spectroscopy over a broad optical window (500–3000 nm) to determine the effect of sample thickness on optical transparency (Figure 2). The fabrication of thin, or free standing films (film thickness from 1 μm to 2 mm) was achieved using either the solution or melt processing methods, (see Supporting Information) which afforded samples exhibiting faint yellow to deep red coloration (Figure 1b). High optical transparency (above 85% transmission) was observed for thin (1 and 10 μm) poly(S-r-DIB) films deposited onto either glass, or NaCl supporting substrates (Figure 2b). A sharp decrease in

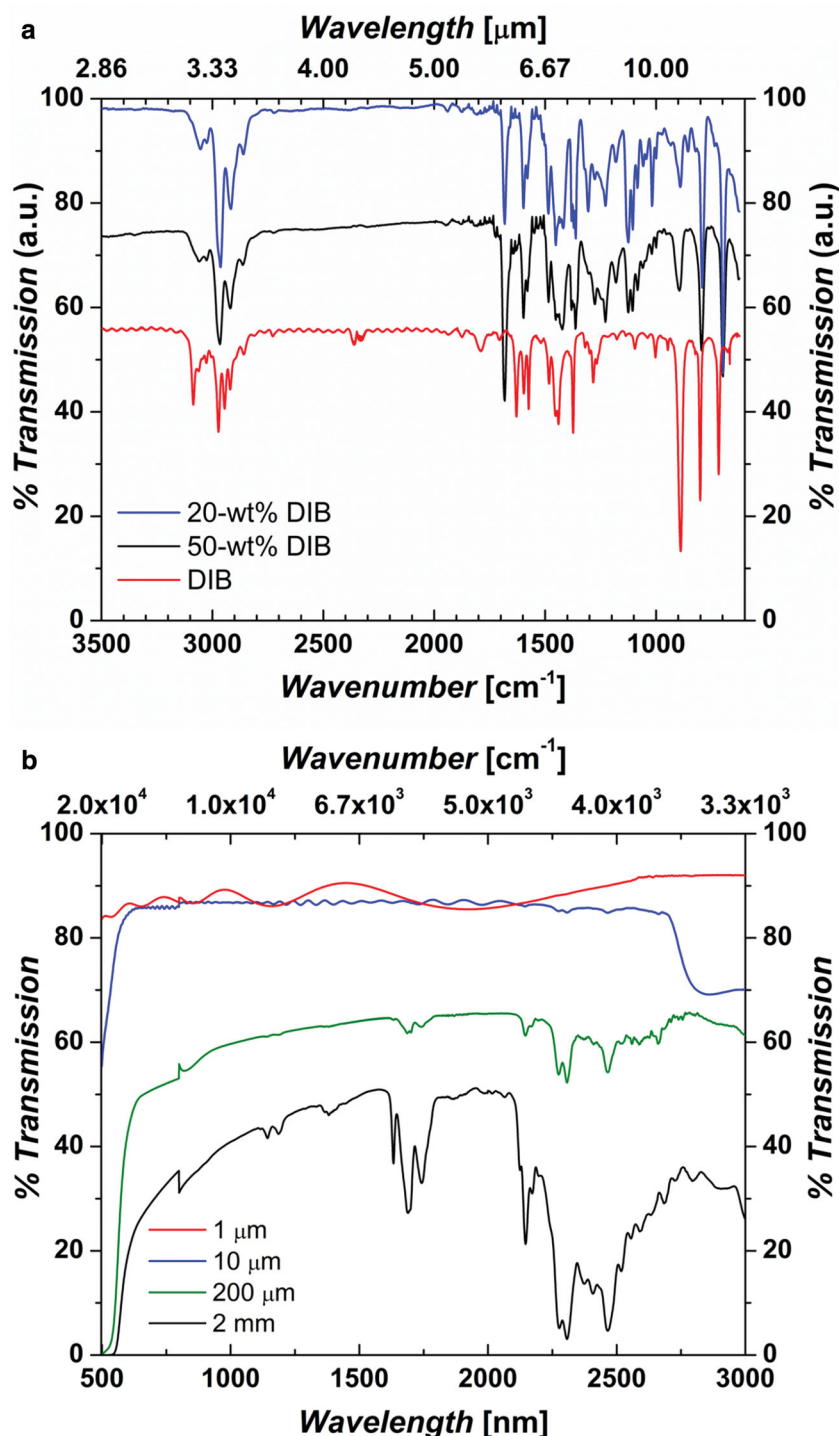


Figure 2. a) Stacked transmission FTIR spectrum (arbitrary transmission units) comparing poly(S-r-DIB) copolymers (20 wt% DIB (top spectrum); 50 wt% DIB (middle spectrum)) to pure 1,3-diisopropenylbenzene co-monomer (bottom spectrum). b) UV-visible-near-IR transmission spectra for 80-wt% Sulfur/20-wt% DIB copolymers with varying thicknesses (1 μm (red); 10 μm (blue); 200 μm (green); 2 mm (black)).

transmission was observed for 10 μm copolymer films on glass above 2500 nm, which was attributed to absorption from the glass substrate itself, as confirmed by minimal absorbance at these wavelengths for 1 μm films cast onto NaCl plates (Figure

2b). The optical transparency for thicker, free standing copolymer films (200 μm & 2 mm) diminished, as expected in comparison to thin films, due to near-IR absorbances from 1500–3000 nm which were attributed to overtones of the C–H vibrations in DIB comonomer units (see Supporting Information, Figure S2).^[18] Nevertheless, the optical transparency of these films could also be tuned by controlling the sulfur content in the poly(S-r-DIB) copolymers (see Supporting Information, Figure S3). These films exhibited low transparency below 600 nm in the visible spectrum, as readily evidenced by the red color of the bulk copolymer material. However, the retention of high transparency in the visible (above 600 nm) and near-IR spectrum was comparable to that of other high refractive index polymers but with the added benefit of retaining a significantly higher refractive index and low optical scattering.^[19–21] Furthermore, the optical transparency of poly(S-r-DIB) copolymers containing 80 wt% sulfur, in comparison to a widely used polymer, such as, poly(methyl methacrylate) (PMMA) was observed to be significantly higher, particularly at wavelengths above 2000 nm (see Supporting Information, Figure S4). Ultimately, the low optical scattering, even for very thick films, provided for high transparency and high refractive index at many wavelengths of technological interest (e.g. 600–1600 nm and 3–5 μm).

A key processing advantage of this process was the ability to mold poly(S-r-DIB) copolymers into arbitrary objects using low viscosity pre-polymer resins (held to low monomer conversion) directly from the reaction mixture. Free standing, high quality poly(S-r-DIB) copolymer lenses were prepared for IR imaging experiments by replicating commercially available glass lenses using PDMS negative molds (N-BK7-Glass, diameter = 15 and 25.4 mm, Figure 3 and Supporting Information, Figure S7). Due to the significantly higher refractive index of the poly(S-r-DIB) copolymers, lenses made from these materials were found to possess reduced focal lengths compared to glass or PMMA (which both have lower refractive indices), particularly in the near and mid-IR regime (see Supporting Information, Table S2). The significant decrease in focal length for these sulfur plastic materials points to the potential for more compact optical systems.

While the optical transparency of poly(S-r-DIB) lenses in the visible region were apparent, the performance of the polymeric lenses in the near and mid-IR wavelengths required further investigation. To interrogate the optical transparency and

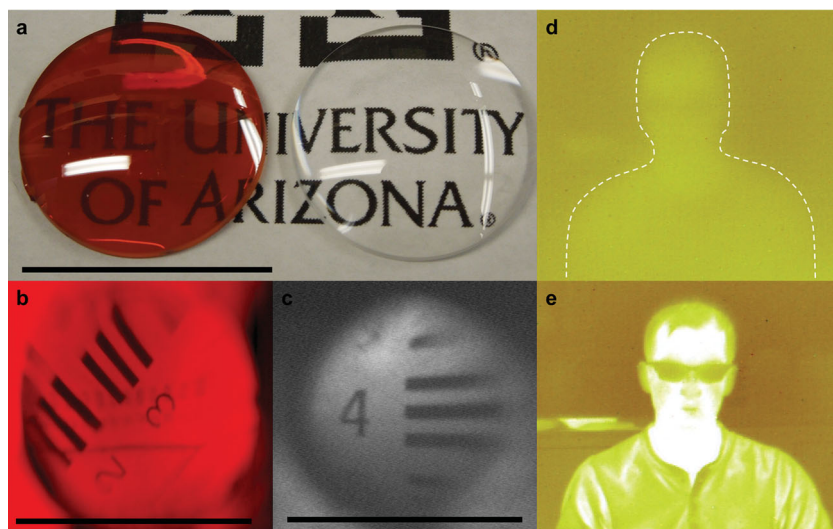


Figure 3. a) Digital image of lenses (left) poly(S-r-DIB) copolymer (80 wt% S_8) and (right) glass (b) digital image of a USAF target through copolymer lens in visible wavelengths and (c) image captured with a near-IR camera of the USAF target illuminated with a 1550 nm laser. (scale bars = 25.4 mm) (d) Thermal imaging of human subject through PMMA film (~1 mm) in the mid-IR (3–5 μm) regime (dotted white line highlights the area where the subject is sitting). (e) Thermal imaging of human subject through 80 wt% S_8 poly(S-r-DIB) copolymer film (~1 mm) in the mid-IR (3–5 μm) regime. (Images are false colored Sepia tone: white corresponds to ~37 °C and brown corresponds to ~24 °C)

determine the image quality when focusing through an 80 wt% S_8 poly(S-r-DIB) lens in the near-IR, a chromium target was illuminated with a 1550 nm laser and the image captured through the lens with a digital near-IR camera (see Supporting Information, Figure S9). Comparison between the images captured in the visible (Figure 3b) and near-IR wavelengths confirmed that at 1550 nm the sulfur copolymer lens maintained high optical transparency and enabled the capture of detailed images (Figure 3c). Further probing into longer wavelengths (3–5 μm) required the use of a mid-IR camera to capture detailed thermograms. An ambient temperature thermal image captured through a sulfur copolymer film (80 wt% S_8) showed low attenuation and detailed resolution of a human subject (Figure 3e). In comparison, a PMMA film of similar thickness showed large attenuation of mid-IR light (Figure 3d). To the best of our knowledge this is the first example of a mid-IR imaging experiment conducted with a high refractive, free-standing polymeric film and verified the high transparency of these novel copolymers at wavelengths where glass and other polymeric materials were opaque (see Supporting Information, Figure S13 and S14).

In conclusion, we demonstrate the preparation and processing of a thermoplastic copolymer via the inverse vulcanization of sulfur to afford high refractive index polymers. Copolymers with compositions ranging from 50–80 wt% sulfur were found to possess high refractive indices ($n > 1.7$) out to 1550 nm. Furthermore, these materials were readily processed via solution, or melt techniques into films, or free standing objects. High quality imaging in the near (1.5 μm) and mid-IR (3–5 μm) regions using a high refractive index polymeric lens was demonstrated for this first time with these materials. These findings are anticipated to open new avenues of research for polymeric materials in IR optical applications.

Experimental Section

Preparation of poly(sulfur-random-1,3-diisopropenylbenzene) (poly(S-r-DIB) copolymers: To a 24 mL glass vial equipped with a magnetic stir bar was added S_8 (4.0 g, 15.6 mmol based on S_8) and heated to $T = 185$ °C in a thermostated oil bath until molten. 1,3-Diisopropenylbenzene (DIB, 1.00 g, 1.08 mL, 6.32 mmol) was then added to the molten sulfur. The resulting mixture was stirred until vitrification of the reaction, at which point the sample was cooled to room temperature affording a red, glassy solid (yield = 4.98 g).

Fabrication of poly(sulfur-random-1,3-diisopropenylbenzene) (poly(S-r-DIB) Copolymer Lenses: To a 24 mL glass vial equipped with a magnetic stir bar was added sulfur (S_8 , 4.0 g, 15.6 mmol based on S_8) and heated to $T = 185$ °C in a thermostated oil bath until molten. 1,3-Diisopropenylbenzene (DIB, 1.00 g, 1.08 mL, 6.32 mmol) was then added to the molten sulfur. The resulting mixture was stirred at $T = 185$ °C until a deep cherry red solution resulted. The solution was poured into the prepared PDMS mold and covered before placing into a heated oven held at $T = 185$ °C and cured until completely vitrified. Once cured the sample was cooled until glassy and removed from the mold.

Spin Coating poly(sulfur-random-1,3-diisopropenylbenzene) (poly(S-r-DIB)) Copolymer Solutions: To an 11 mL glass vial equipped with a magnetic stir bar was added poly(S-r-DIB)

copolymer powder (2.0 g) followed by the addition of 1,2-dichlorobenzene (2.0 mL) before heating to $T = 125$ °C in a thermostated oil bath until a deep red colored solution resulted. Substrates were then spin-coated with the copolymer solutions: 1) 2000 rpm with an acceleration rate of 266 rpm/second for 15 seconds; 2) 8500 rpm with an acceleration rate of 665 rpm/second for 15 seconds. The films are cured in a vacuum oven held at $T = 185$ °C under reduced pressure (~28 in. Hg) for 10 minutes and then for an additional 10 minutes at $T = 185$ °C under ambient pressure. After curing the samples were cooled to room temperature.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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