Supporting Information

Chalcogenide Hybrid Inorganic/Organic Polymers (CHIPs): Ultra-high Refractive Index Polymers for Infrared Imaging

Laura E. Anderson,[†,#]Tristan S. Kleine,[†,#] Yueyan Zhang,[†] David D. Phan,[ξ] Soha Namnabat,[◊] Edward A. LaVilla,[◊] Lilliana Ruiz Diaz,[◊] Soha Katrina M. Konopka,[†] Michael, S. Manchester,[†] Jim Schwiegerling, [◊] Richard, S. Glass, [†] Michael, E. Mackay[§,€], Kookheon Char,[*‡] Robert A. Norwood[*◊], 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, [◊]College of Optical Sciences, University of Arizona, Tucson, Arizona 85721, United states, [ξ]Department of Chemical and Biomolecular Engineering, University of Delaware, 150 Academy Street, Newark, Delaware 19716, United States, [‡]School of Chemical and Biological Engineering, Program of Chemical Convergence of Energy and Environment, The National Creative Research Initiative Center for Intelligent Hybrids, Seoul National University, Seoul 151-744, Korea

*corresponding authors

Email: jpyun@email.arizona.edu; rnorwood@email.arizona.edu; khchar@snu.ac.kr

Table of Contents

IV) References

I) Materials and Instrumentation.

Selenium (Se, powder, 100 mesh, reagent grade, Aldrich). 1,3-Diisopropenylbenzene (DIB, 97 %, Aldrich), Chlorobenzene (CB, 99%, Aldrich), Triton X-100 (Laboratory grade, Aldrich), Sylgard 184 Silicone Encapsulant (Dow Corning), Kapton® Polyimide film (0.001″ thickness, McMaster-Carr), uncoated glass master lenses (15.0mm Dia. x 75.0mm FL, Edmund S3 Optics) were commercially available and used as received without refinement. Sulfur (S8, sublimed powder, reagent grade, Aldrich) was recrystallized from Toluene three times. USAF 1951 Resolution Targets were purchased from Edmund Optics chromium patterns were prepared by vapor deposition onto glass. Spin-coating was performed on a Laruell Technologies Corporation Spin Coater (Model: WS-400BZ-6NPP/LITE). Thermomechanical forming was done with a 25 kN hydraulic lamination hot press equipped with dual temperature controlled platens (MTI Corporation). Sources used were a Thorlabs 1550 nm laser model S1FC1550 (maximum power ~ 2.5 mW) and a Thorlabs 1310 nm DFB laser S3FC1310 (maximum power ~ 1.8 mW). A conventional erbium doped fiber amplifier was used from Hangzhou Eric Communication Co (Model 1517) with 17 dBm or 40 mW output power. An IR camera from Electrophysics Micronviewer (Model 7290a) was used to record digital images when working with infrared sources. A Raytheon Amber Radiance 1 infrared video camera (filtered to 3-5 µm with a Germanium window) was utilized to capture ambient temperature mid-IR thermograms. Film refractive index measurements were performed on a Metricon 2010 prism coupler while film thickness measurements were done with Veeco Dektak 150 profilometer. The transmittance analysis was carried out with a Cary 5000 UV-Vis-NIR spectrophotometer in the 350-3000 nm spectral range. The data was normalized to exclude the transmission of the glass substrate (~92% in the visible range). Fourier Transform Infrared (FTIR) spectroscopy was done with a Thermo Nicolet 6700 spectrometer in the Mid-Infrared range (MIR), 4000-500 cm^{-1} wavenumber (2.5-20µm wavelength, respectively).

II) Experimental Procedures

Synthesis of poly(S-*r*-Se-*r*-DIB) with the following composition (42-wt% S_8, 42-wt% Se, 16-wt% DIB):

To a 11 mL glass vial equipped with a magnetic stir bar was added sulfur (S8 1.26 g, 39.30 mmol) and heated to T = 160 °C in a thermostated oil bath until a clear orange colored molten phase was formed. The vial was then transferred to an adjacent thermostatted oil bath (T = 150 °C) in a thermostated oil bath where selenium (Se, 1.26 g, 15.955 mmol) was then directly added to the molten sulfur medium. 1,3-diisopropenylbenzene (DIB, 0.41 g (0.52 mL), 3.03 mmol) was then directly added to the molten sulfur-selenium medium via syringe. The resulting mixture was stirred at T = 150 °C for 1 to 1 ½ hours, which resulted in vitrification of the reaction media. The product was then taken directly from the vial using a metal spatula and removal of the magnetic stir bar for determination of yields after allowing the reaction mixture to cool to room temperature which afforded a dark red glass (yield: 2.98 g). This material was only sparing soluble in organic solvents and hence was not subjected to purification by column chromatography. For the fabrication of films, or windows for optical characterization, melt processing methods were used from bulk reaction mixtures.

Synthesis of poly(S-*r*-Se-*r*-DIB) with the following composition (50-wt% S_8, 20-wt% Se, 30-wt% DIB):

To a 11 mL glass vial equipped with a magnetic stir bar was added sulfur (S8 1.5 g, 46.78 mmol) and heated to T = 160 °C in a thermostated oil bath until a clear orange colored molten phase was formed. The vial was then transferred to an adjacent thermostatted oil bath (T = 150 °C) where selenium (Se, 0.6 g, 7.59 mmol) was then directly added to the molten sulfur medium. 1,3-Diisopropenylbenzene (DIB, 0.9 g (0.97 mL), 5.69 mmol) was then directly added to the molten sulfur-selenium medium via syringe. The resulting mixture was stirred at T = 150 °C for 1 to 1 ½ hours, which resulted in vitrification of the reaction media. The crude solid was then submerged in a dry ice-acetone bath for 5 min to embrittle the material to facilitate removal from the glass vial. This brown-orange solid was then ground into a fine powder with a mortar and pestle. The powder was then suspended in 1200 mL of tetrahydrofuran and stirred at 50°C in an oil bath for 10 hours, leaving behind a grey/orange intractable impurity that was removed by vacuum filtration. The filtrate was concentrated down onto silica and then loaded onto a silica gel plug, followed by elution with hexanes to first remove any unreacted sulfur and soluble selenium sulfides. The elution profile was then switched to pure THF to elute the terpolymer which was recovered by concentrating the THF fractions under reduced pressure to afford an orange solid. (Yield: 0.54 g (54%)) (see Fig. S2-S5for NMR discussion)

1. General procedure for preparation of poly(sulfur-*random*-selenium-*random*-1,3-diisopropenylbenzene) (poly(S-*r*-Se-*r*-DIB)) terpolymer windows

To a 11 mL glass vial equipped with a magnetic stir bar was added sulfur (S8 1.5 g, 46.78 mmol) and heated to T = 160 °C in a thermostated oil bath until a clear orange colored molten phase was formed. The vial was then transferred to an adjacent thermostatted oil bath (T = 150 °C) where selenium (Se, 0.6 g, 7.59 mmol) was then directly added to the molten sulfur medium. 1,3-Diisopropenylbenzene (DIB, 0.9 g (0.97 mL), 5.69 mmol) was then directly added to the molten sulfur-selenium medium via syringe. The resulting mixture was stirred at T = 150 °C, then after 48 minutes the vial was removed from the thermostated oil bath, poured into a PDMS replica (preparation of replica described hereafter), and transferred to a 165 °C oven to cure for 26 minutes. The mold containing the polymer was then removed from the oven and allowed to cool to room temperature. Once cool the polymer and the mold could be separated to yield a freestanding window. The PDMS replica was prepared as follows: In 50 mL disposable plastic beaker were combined the silicone elastomer base and silicone elastomer curing agent in a 10:1 (v/v) ratio. The solution was thoroughly mixed and then poured over the glass master lenses to be replicated. The samples were placed in a vacuum oven and pressure was reduced in order to fully remove any bubbles. Once devoid of bubbles the samples were moved to a heat oven held at T = 80 °C and cured for 2 hours. After completely curing the sample was released from the form and the replicas carefully removed from the master lenses.

2. General procedure for preparation of thin films onto glass substrates from poly(sulfur-*random*-selenium-*random*-1,3-diisopropenylbenzene) (poly(S-*r*-Se-*r*-DIB)) terpolymer solutions

250 mg of the purified terpolymer was taken up in 1 mL of chlorobenzene where it was then heated on a 120 °C hot plate for 15 minutes or until the tepolymer powder is completely dissolved in the hot chlorobenzene. The solution was allowed to cool to room temperature where it was

then filtered twice with a 0.2 um filter. Once filtered, 0.5 mL of the solution was deposited on a glass slide and spun at 2000 RPM's for 30 seconds. The terpolymer coated glass was then placed on a 120 °C hot plate for two minutes in order to dry the film/remove any residual solvents from the film.

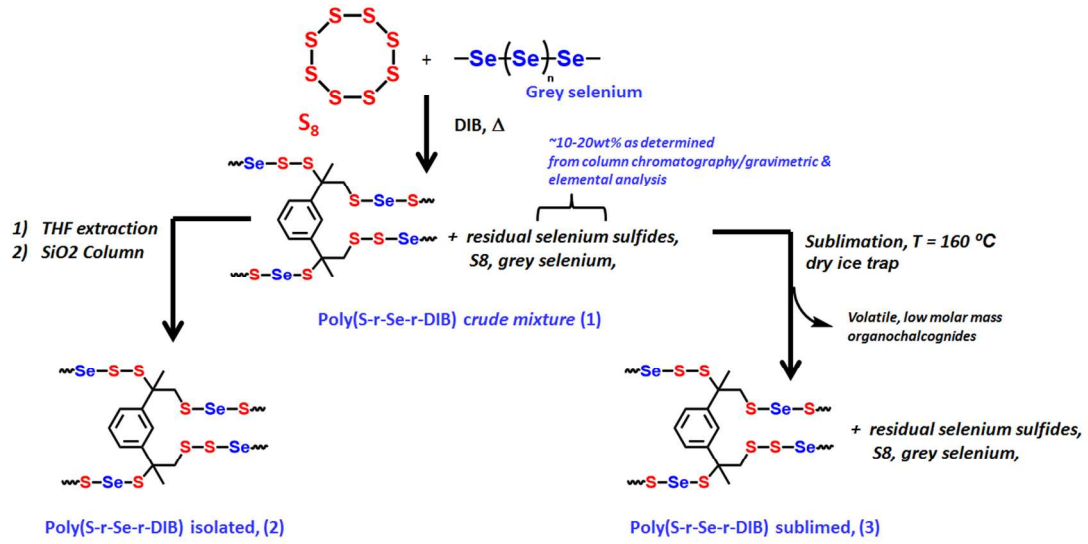
3. General procedure for preparation of spin coated poly(sulfur-*random*-selenium-*random*-1,3-diisopropenylbenzene) (poly(S-*r*-Se-*r*-DIB)) terpolymer films on NaCl plates for FTIR analysis

250 mg of the purified terpolymer was taken up in 1 mL of chlorobenzene where it was then heated on a 120 °C hot plate for 15 minutes or until the tepolymer powder is completely dissolved in the hot chlorobenzene. The solution was allowed to cool to room temperature where it was then filtered twice with a 0.2 um filter. Once filtered, 0.5 mL of the solution was deposited on a NaCl salt plate and spun at 2000 RPM's for 30 seconds. The terpolymer coated salt plate was then placed on a 120 °C hot plate for two minutes in order to dry the film/remove any residual solvents from the film.

III) Results and Discussion Section

Synthesis of poly(S-*r*-Se-*r*-DIB) Terpolymers

Reaction conditions for inverse vulcanization. As described in the manuscript, the inverse vulcanization approach for these materials was conducted initially in liquid sulfur at T = 160 ºC, followed by a portion-wise addition of grey selenium to form reactive in-situ mixed chalcogen species that were miscible and able to copolymerize with DIB (Scheme S1). The mixture of elemental sulfur and selenium at these elevated temperatures was strongly colored and difficult to see thru under ambient conditions, which complicated visual inspection of the reaction medium. This further complicated visual determination of homogeneity of these *in-situ* mixed chalcogens for the next injection of DIB to complete the inverse vulcanization process (i.e., terpolymerization). Pre-mature injection of DIB into a heterogeneous reaction medium resulted in incomplete comonomer incorporation due to poor mixing. To alleviate this issue, reaction vessels immersed in transparent silicone oil baths were illuminated with a proximally placed external light source (Fig. S1). Furthermore, the reactive *in-situ* generated mixed chalcogens were readily diluted in hot DCB, which also enabled unambiguous determination of reaction time vs. homogeneity of the reaction medium for appropriate injection of DIB. For terpolymerizations conducted at T = 160 ºC, homogeneous mixed chalcogen liquid phases were observed to form with 15 minutes and were amenable to grey selenium loadings of up 50-wt% relative to liquid sulfur (i.e., 1:1 wt ratio). Upon rapid injection of DIB to this reactive medium, complete vitrification of the reaction medium was observed within a 30 minutes to form a red, glassy solid, which was soluble in THF and $CHCl_3$ for the poly(S_{50}-*r*-Se_{20}-*r*-DIB_{30}) terpolymer. ^{1}H NMR spectroscopy of the crude terpolymer reaction mixture in $CDCl_3$ confirmed complete consumption of DIB as noted by the disappearance of sharp vinyl protons resonances (δ 5.37 and 5.10 ppm).



Scheme S1: Synthesis and purification scheme for poly(S-*r*-Se-*r*-DIB) terpolymers

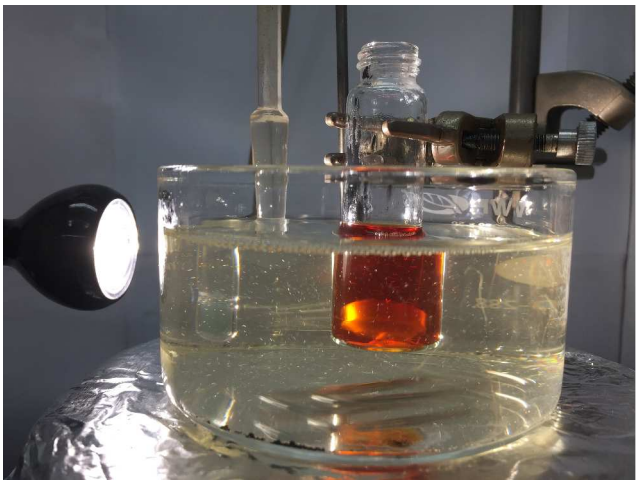


Figure S1: Representative reaction apparatus with external light source to facilitate visual inspection of terpolymerization reaction mixtures of liquid sulfur, grey selenium and DIB.

Purification of poly(S_{50}-r-Se_{20}-r-DIB_{30}) terpolymers via column chromatography. The improved solubility of poly(S-*r*-Se-*r*-DIB) terpolymers (in particular, relative to our poly(sulfur-*random*-(1,3-diisopropenylbenzene copolymers) in typical organic solvents enabled isolation of the target terpolymer and determination of unincorporated sulfur, or selenium. As alluded to the manuscript, solvent extraction of the crude terpolymer (**1**, Scheme S1) was conducted to remove insoluble mixed selenium sulfides and any residual S_8, or selenium grey. The vast majority of the crude terpolymer reaction mixture was found to be comprised of poly(S-*r*-Se-*r*-DIB) (~80-85 wt%), as determined by the recovery of the unreacted elemental chalcogens. We observed a trace amount of selenium sulfides/S_8 accompanied the terpolymer during the solvent extraction process, which could be easily removed via silica gel column chromatography via initial elution with hexanes, followed by gradient elution with THF to recover the isolated terpolymer

(**2**, Scheme S1). This purification process allowed for structural characterization of the terpolymer via elemental analysis, thermal analysis and NMR spectroscopy (in particular, ^{77}Se). We observed that melt processed forms of crude poly(S-*r*-Se-*r*-DIB) possessed comparable optical properties (refractive index, transparency) to purified terpolymers, which enabled their direct use for IR imaging as shown in the manuscript (Fig. 3). However, we did observe in the crude terpolymer the presence of a small amount of a volatile species (~ 10-wt%) which could be readily removed by sublimation of the material for 2 hrs at T = 160 ºC. For most melt processed molded materials, this trace volatile species was removed during the curing/molding process under vacuum, but is recommended to be removed before further processing (**3,** Scheme S1). As alluded in the manuscript, it was highly desirable to invoke bulk melt processing of neat reaction mixtures to form larger molded objects for IR imaging, but to also have access to soluble processable samples for structural characterization purposes.

Elemental analysis of poly(S_{50}-r-Se_{20}-r-DIB_{30}) terpolymers: Elemental analysis of isolated terpolymer after column chromatography (C% = 43.6; H% = 5.6; S% = 33.5; Se% = 17.2) indicated the successful incorporation of all the comonomers (feed ratios = 50-wt% sulfur, 20-wt% selenium, 30-wt% DIB). This analysis confirmed that a high content of Se units were introduced into the copolymer at nearly identical terpolymer composition to the comonomer feed, while sulfur incorporation into the terpolymer was slightly incomplete (~70% sulfur conversion into terpolymer), presumably due to the formation of trace insoluble selenium sulfides generated *in-situ* (Scheme S1). Elemental analysis of isolated (crude) terpolymer after sublimation (C% = 20.55; H% = 1.88; S% = 41.46; Se% = 21.68).

Nuclear Magnetic Resonance Spectroscopy (NMR) of poly(sulfur-*random*-selenium-*random*-1,3-diisopropenylbenzene) (poly(S_{50}-*r*-Se_{20}-*r*-DIB_{30})) terpolymers

Solution ^{1}H, ^{13}C, ^{77}Se NMR spectroscopy were conducted of the purified and soluble poly(S_{50}-*r*-Se_{20}-*r*-DIB_{30}) terpolymer (**2**, Scheme S1) to confirm the incorporation of aromatic and aliphatic DIB units into the copolymer and to confirm the formation of C-S bonds from S_8-DIB copolymerization. Due to the complexity of the spectra, full assignment of copolymer microstructure and tacticity was not conducted, but NMR spectroscopy did provide structural evidence for aromatic and aliphatic functional groups moieties from DIB units, as well as C-S bonds generated from copolymerization. Furthemore, the presence of Se units in the terpolymer allowed, for the first time, interrogation of the terpolymer backbone microstructure using solution ^{77}Se NMR spectroscopy which unambiguously confirmed the formation of true terpolymers.

A general survey of the ^{1}H NMR spectrum of poly(S_{50}-*r*-Se_{20}-*r*-DIB_{30}) confirmed the presence of aromatic peaks at δ = 6.8-7.8 ppm and methyl protons at δ = 1.0-2.2 ppm (Figure S2). The complexity of the spectra from methyl protons at δ = 1.0-2.2 ppm was consistent with the formation of statistical copolymers generated from terpolymerization due to the formation of different microstructures and compositional heterogeneity. Resonances at δ = 2.9-3.4 ppm were observed and correspond to methylene peaks in the terpolymer backbone which were bonded to sulfur comonomer units. The methylene

protons in poly(S-*r*-DIB) copolymers were significantly shifted downfield as a consequence of C-S bond formation.

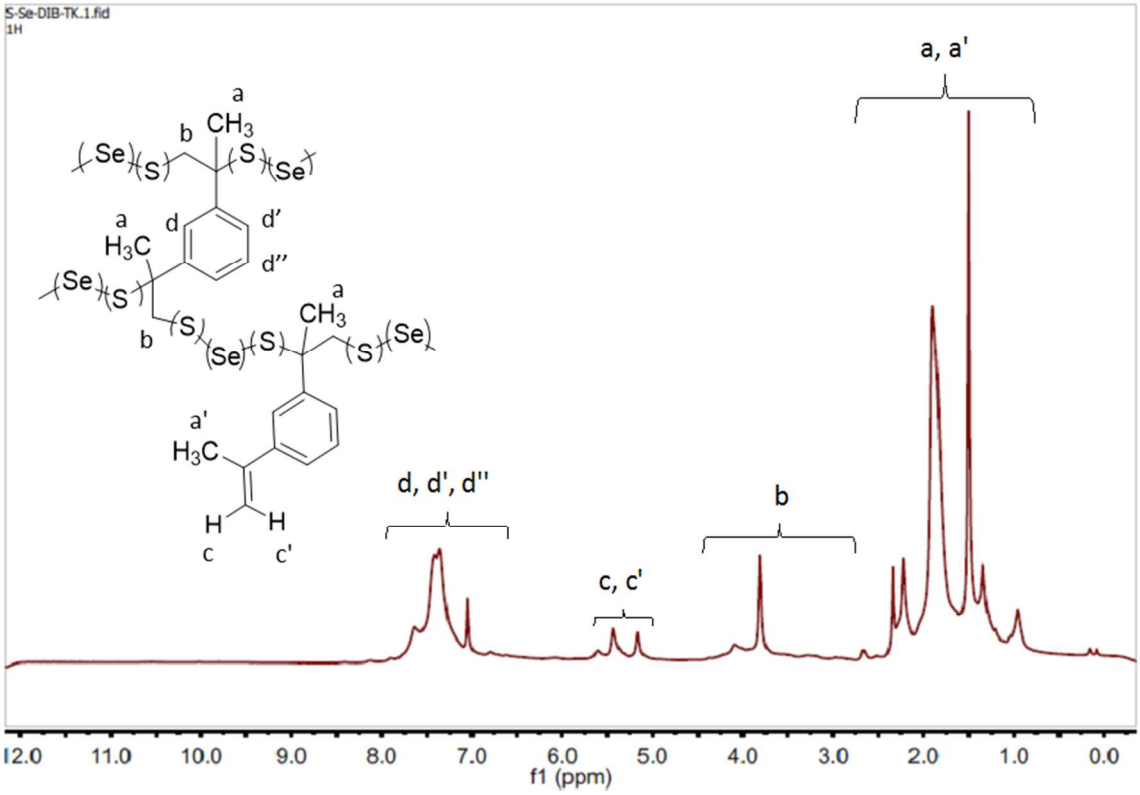


Figure S2 : ^{1}H NMR spectrum of poly(S_{50}-*r*-Se_{20}-*r*-DIB_{30}) terpolymer in $CDCl_3$.

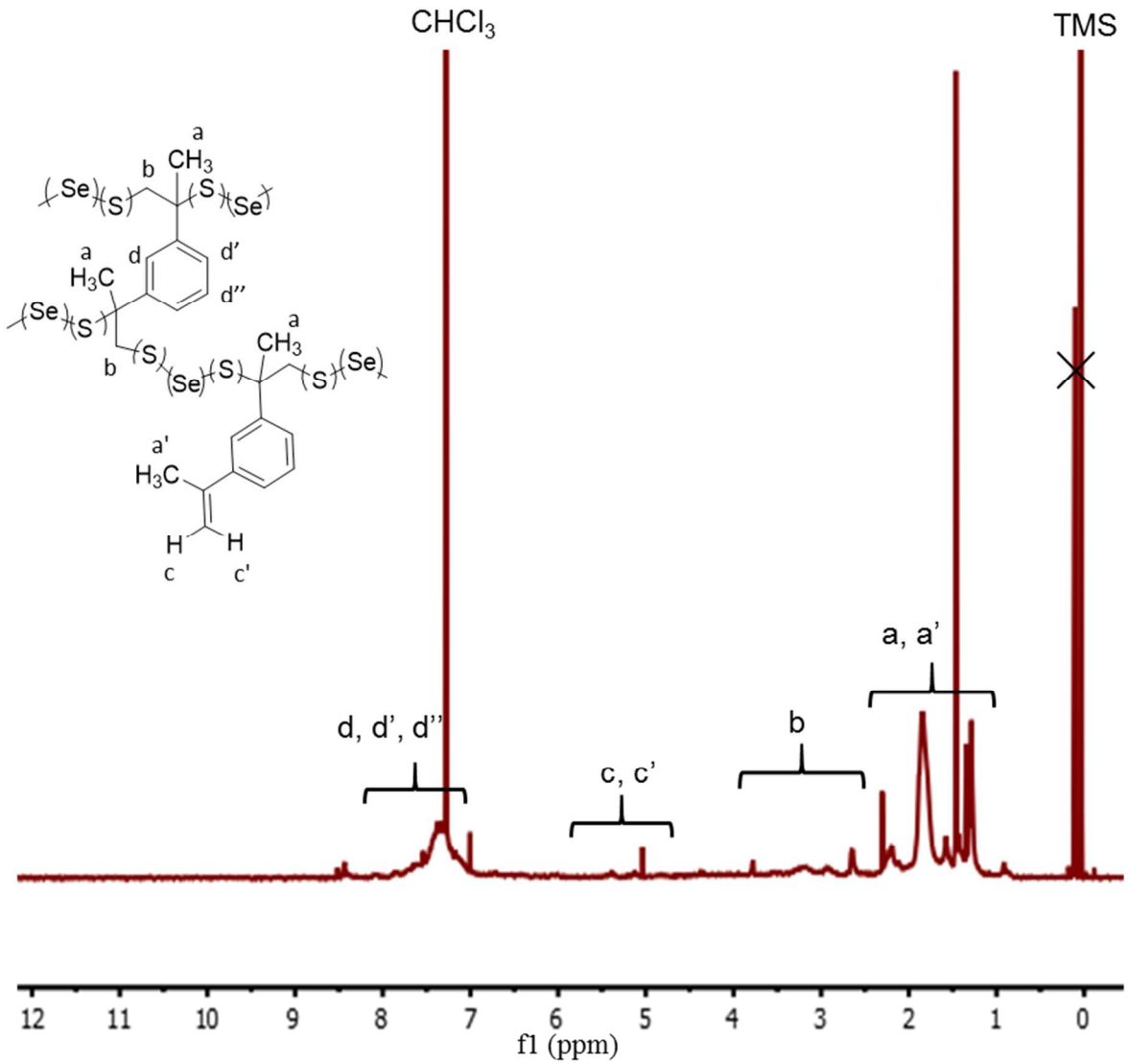


Figure S3 : ^{1}H NMR spectrum of crude poly(S_{50}-*r*-Se_{20}-*r*-DIB_{30}) terpolymer in $CDCl_3$ after purification by sublimation at 160 °C for two hours with a dry ice/acetone trap.

Solution ^{13}C NMR experiments further confirmed the the presence of C-S bonds and aromatic moieties in the poly(S_{50}-*r*-Se_{20}-*r*-DIB_{30}) terpolymer (Figure S4). The spectral region from δ = 18-35 ppm in which the methyl peaks from DIB units appear was complex, as observed in the ^{1}H NMR spectra, due to the formation of different microstructures and compositional heterogeneity, which was also evidence for terpolymerization. As expected, aromatic carbons from DIB units were observed at δ = 125-152 ppm.

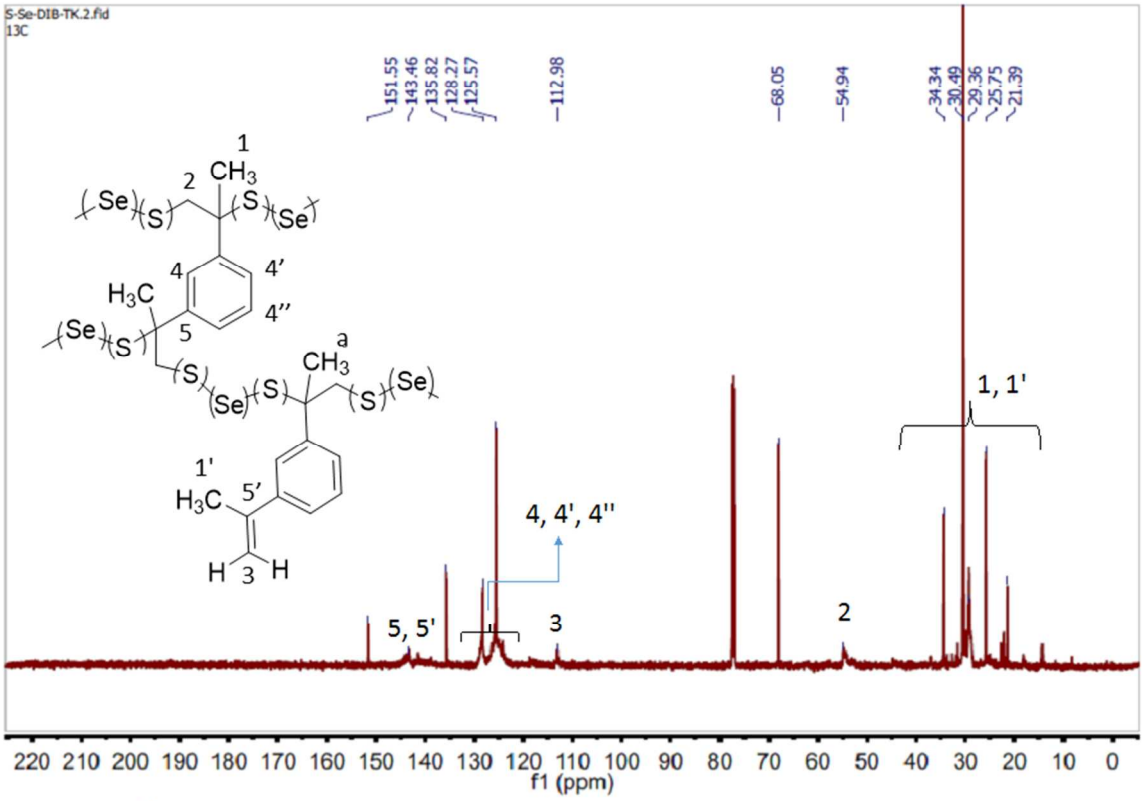


Figure S4: ^{13}C NMR spectrum of poly(S_{50}-*r*-Se_{20}-*r*-DIB_{30}) terpolymer in $CDCl_3$.

Solution ^{77}Se NMR experiments conducted in THF/$CDCl_3$ further confirmed the the presence of Se-S bonds in the poly(S_{50}-*r*-Se_{20}-*r*-DIB_{30}) terpolymer (Figure S5). The use of ^{33}S NMR spectroscopy to study previous sulfur copolymers made by inverse vulcanization was unsuccessful due to the low sensitivity of this nuclei and technique. Conversely, ^{77}Se nuclei had sufficient abundance and sensitivity to enable direct confirmation of Se-S bonds in the terpolymer backbone. Furthermore, since grey selenium, or selenium sulfides were sparingly soluble in THF, or THF/$CDCl_3$, all resonances observed in ^{77}Se NMR spectra could directly be assigned to Se- units in the terpolymer. Three resonances for the poly(S_{50}-*r*-Se_{20}-*r*-DIB_{30}) terpolymer were observed (δ = 695, 645 and 625) and were assigned to different microstructures of Se-S units in the terpolymer backbone, pointing to a statistical composition of these comonomer units. Furthermore, these assignments were in agreement with earlier ^{77}Se NMR spectroscopic assignments by Laitinen et al[5]. for selenium sulfides, which clearly confirmed that presence of Se-S bonds. The presence of Se-C bonds (which would be expected to be farther upfield) were not observed, but could not be ruled out due to SNR limitations.

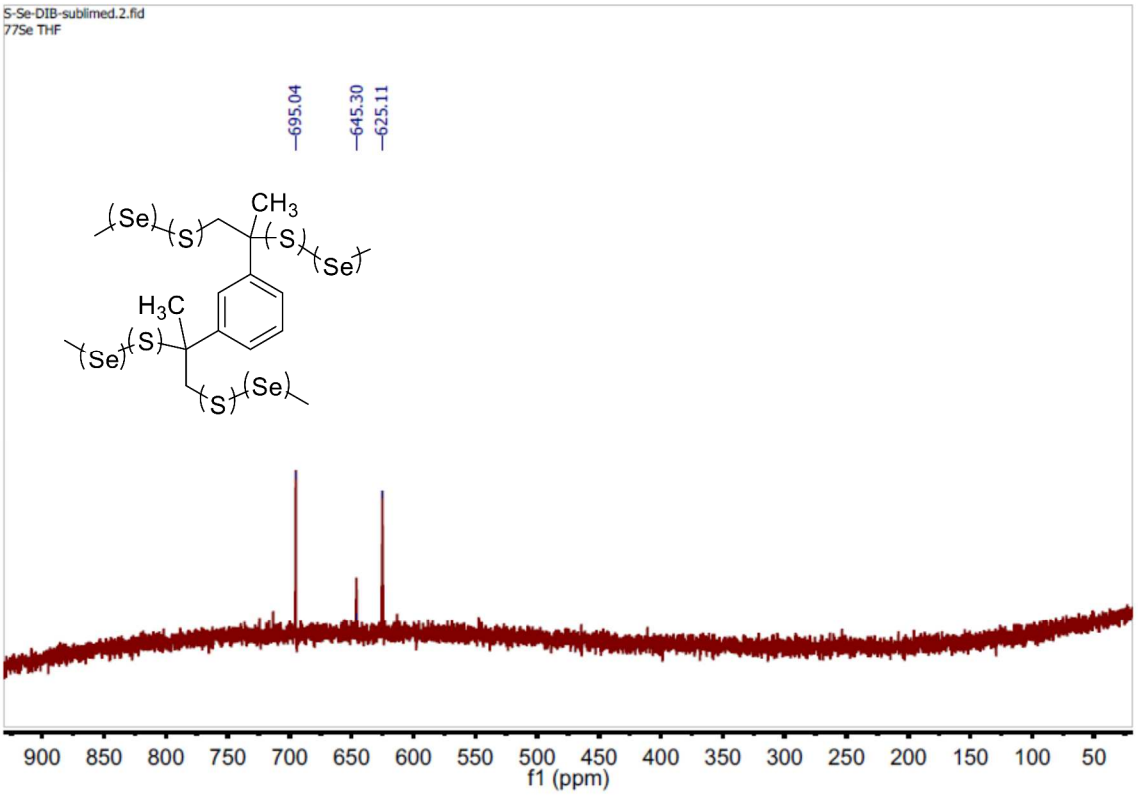


Figure S5: ^{77}Se NMR spectrum of poly(S_{50}-*r*-Se_{20}-*r*-DIB_{30}) terpolymer in THF/$CDCl_3$.

Gel Permeation Chromatography (GPC) of poly(sulfur-*random*-selenium-*random*-1,3-diisopropenylbenzene) (poly(S-*r*-Se-*r*-DIB)) terpolymer powder

Size exclusion chromatography was performed on poly(S_{50}-*r*-Se_{20}-*r*-DIB_{30}) that had been purified by THF extraction and subsequent SiO_2 gel column chromatography. While the SEC showed the presence of a broad distribution of low molecular weight oligomers (Mn_{SEC} = 1,100 g/mol, PDI = 1.8; Fig. S6), this is consistent with the chromatograms of previously prepared high sulfur content copolymers.

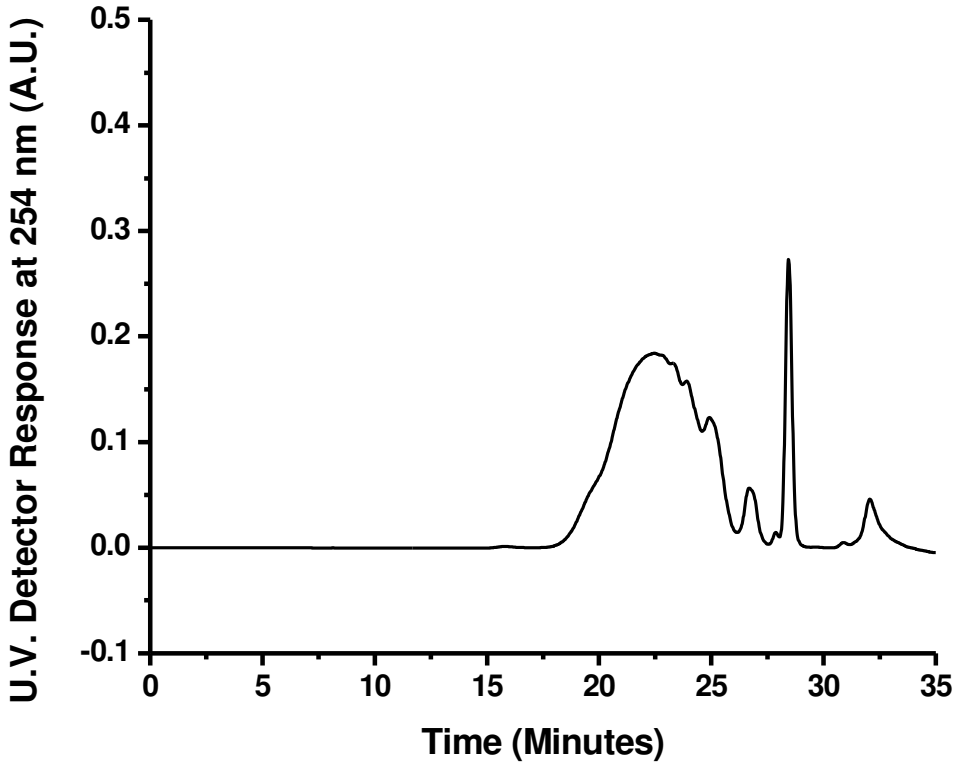


Figure S6 – Size exclusion chromatography of poly(S_{50}-*r*-Se_{20}-*r*-DIB_{30}) terpolymer (Mn_{SEC} = 1,100 g/mol, PDI = 1.8)

Thermal Gravimetric Analysis (TGA) of poly(sulfur-*random*-selenium-r*andom*-1,3-diisopropenylbenzene) (poly(S-*r*-Se-*r*-DIB)) terpolymer powder

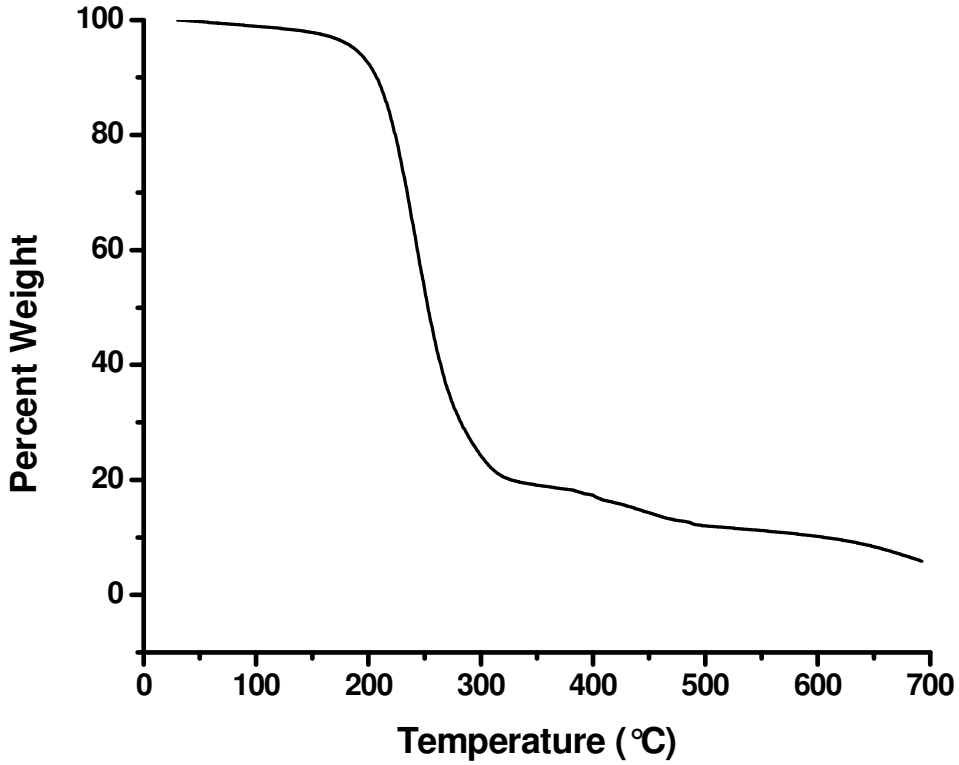


Figure S7 – TGA of poly(S_{50}-*r*-Se_{20}-*r*-DIB_{30}) terpolymer powder

Thermal gravimetric analysis of the crude terpolymer shows an onset of decomposition around 200 °C that is consistent with previously reported high sulfur content copolymers. The terpolymer exhibited less than 1% degradation at 150 °C and less than 5% up to 200 °C.

Thermomechanical characterization of poly(S_{50}-*r*-Se_{20}-*r*-DIB_{30}) terpolymers via modulated differential scanning calorimetry and dynamic mechanical analysis.

Modulated differential scanning calorimetry experiments were conducted to ensure formation of true poly(S_{50}-*r*-Se_{20}-*r*-DIB_{30}) terpolymers by confirmation of a single glass transition (Tg) temperature. Modulated DSC conducted in the temperature window of T = -50 ºC to 80 ºC confirmed the presence of a single T_g at 27.33 ºC. The observation of both a single T_g for the terpolymer in conjunction with the ^{77}Se NMR spectroscopic evidence (Fig. S5) supports true terpolymer formation. Additionally, since Tg's determined from DSC were previously found to be under-estimated for sulfur copolymers prepared *via* inverse vulcanization, DMA was conducted of these terpolymers, which revealed a higher T_g at 51.1 ºC.

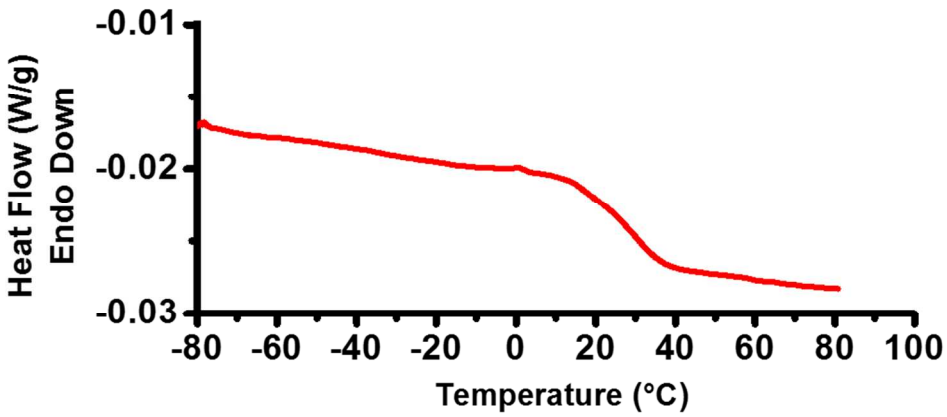


Figure S8: Modulated DSC thermogram of poly(S_{50}-*r*-Se_{20}-*r*-DIB_{30}) at a ramp rate of 10 °C min^{-1}

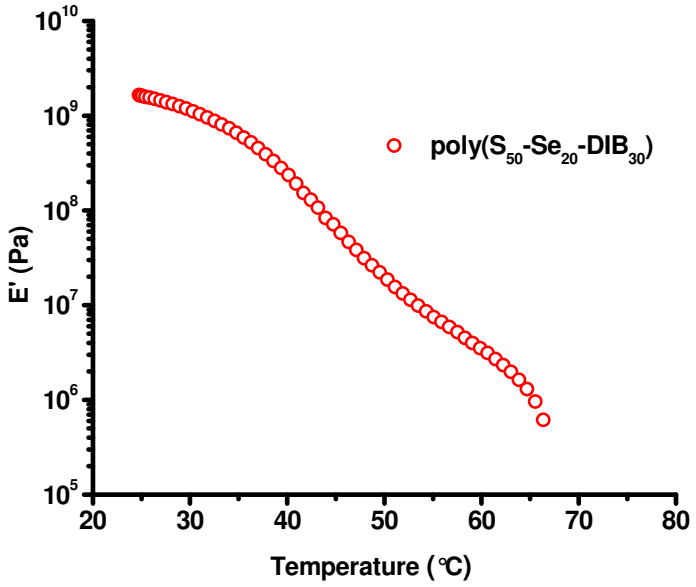


Figure S9: Plot of storage modulus (E') as a function of temperature performed with a 3 °C min^{-1} ramp rate at an applied frequency of 1 Hz of poly(S_{50}-*r*-Se_{20}-*r*-DIB_{30})

Analysis of refractive indices as a function of poly(sulfur-*random*-selenium-*random*-1,3-diisopropenylbenzene) (poly(S-*r*-Se-*r*-DIB)) terpolymer composition

The refractive indices of the freestanding films were measured using a Metricon 2010 Prism coupler system. Measurements were performed for numerous points on each sample and averaged in the bulk medium measurement mode. Light polarized perpendicular to the plane of incidence ("TE") and in the plane of incidence ("TM") had very similar refractive indices, which indicated that material has very low birefringence (Figure 2b and Table S1).

Wavelength (nm):		1554 (nm)	1305 (nm)	816 (nm)	633 (nm)
Material Composition (wt.%):	S-DIB (70:30)	1.787	1.791	1.809	1.834
	S-Se-DIB (50:20:30)	1.912	1.916	1.945	1.963
	S-Se-DIB (42:42:16)	2.035	2.087	2.099	2.140

Table S1 – Refractive index measurements of the poly(sulfur-r*andom*-selenium-r*andom*-1,3-diisopropenylbenzene) (poly(S-*r*-Se-*r*-DIB)) terpolymers as compared to poly(sulfur-r*andom*-1,3-diisopropenylbenzene) (poly(S-*r*-DIB)).

UV-visible/near-infrared analysis of poly(sulfur-*random*-selenium-*random*-1,3-diisopropenylbenzene) (poly(S-*r*-Se-*r*-DIB)) terpolymer films

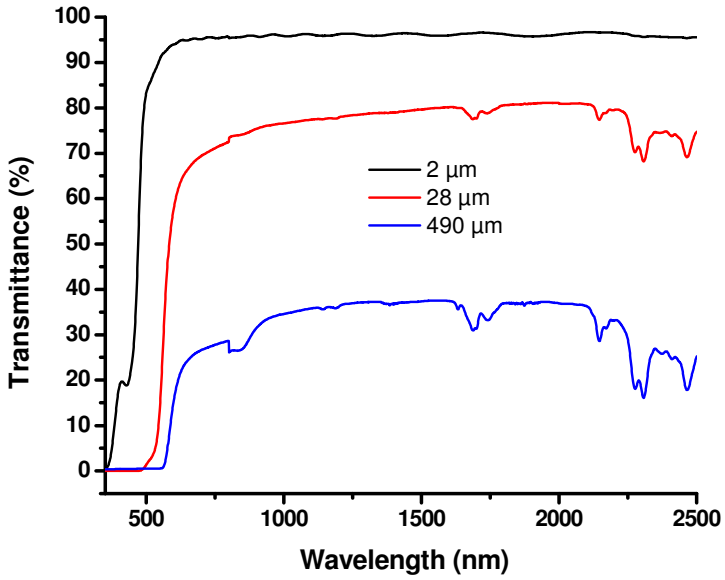


Figure S10 – UV-Vis spectra of poly(S_{50}-*r*-Se_{20}-*r*-DIB_{30}) terpolymer films at varying thicknesses

The transmittance spectra of 3 flat samples with different thickness (2, 28 and 490 µm) are shown in Fig S10. Samples with relative small thickness (~1-5µm) present high optical transparency from 550 to 2500 nm. As the thickness increases, the transmission decreases according to Beer–Lambert law, which severely affects the UV spectra, while allowing the transmission of visible and NIR irradiance. Small narrow absorption peaks are observed in thicker samples near 1700, 2150, 2300, and 2470 nm wavelengths. The overall transmittance decreases about 10% for wavelengths larger than 2100 nm due to large particle interaction between incident light and the

material. The measurements show a small spike at 800nm due to the detector change inside of the spectrophotometer.

Fourier transform infrared (FTIR) spectroscopy of poly(sulfur-*random*-selenium-*random*-1,3-diisopropenylbenzene) (poly(S-*r*-Se-*r*-DIB)) terpolymer films

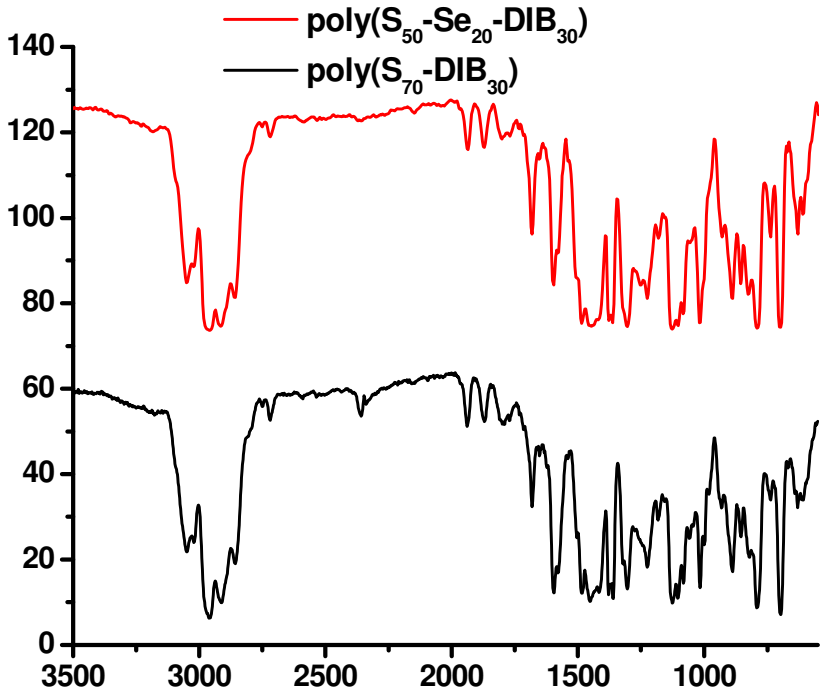


Figure S11 – Stacked FTIR spectra of poly(S_{70}-*r*-DIB_{30}) and poly(S_{50}-*r*-Se_{20}-*r*-DIB_{30}), both approximately 200 μm coated on NaCl substrates, show similar transparency in the regions of interest for IR thermal imaging.

The IR transmittance spectrum of a poly(S_{50}-*r*-Se_{20}-*r*-DIB_{30}) sample (200 μm) is shown in Fig S11. The material presents a broad absorption peak near 3000 cm^{-1} (3.33μm wavelength) and reduced optical transmission from 1750 to 500 cm^{-1} (5.47 to 2.5μm wavelength); this is largely consistent with the poly(S_{70}-*r*-DIB_{30}) sample with similar thickness.

Infrared Imaging of poly(sulfur-*random*-selenium-*random*-1,3-diisopropenylbenzene) (poly(S-*r*-Se-*r*-DIB)) terpolymer windows

An imaging setup was constructed to demonstrate the optical transparency of the Se-SDIB terpolymer. Using a Raytheon Amber Radiance 1 Mid-IR camera, a background image is taken first to provide a baseline for image comparison. A 1mm thick window was prepared and mounted on board in an intermediate plane between the camera objective lens and the subject. The camera lens was then adjusted to find the best focus of the subject behind the sample. Camera settings need to be adjusted for contrast and

brightness due to background noise in the scene and saturation of detector pixels. A series of images are then taken without changing any camera settings or focus of the camera. Areas of blur or reduction of contrast in images taken through the sample are due to the non-flat nature of the window faces, which introduce different levels of aberration including defocus or blurring. These issues can easily be corrected with more careful window preparation. Overall the poly(S-*r*-Se-*r*-DIB) shows outstanding optical transmission characteristics and is well suited for imaging in the mid-IR region.

IV) References

[S1] Perot, A.; Fabry, C. Theorie et Applications d'une Nouvelle Methode de Spectroscopie Interferentielle. *Ann. Chim. Phys*. **1899**, *16* (7) 289-338.

[S2] Kasarova, S. N.; Sultanova, N. G.; Ivanov, C. D.; Nikolov, I. D. Analysis of the Dispersion of Optical Plastic Materials. *Opt. Mater*. **2007**, *29* (11) 1481-1490.

[S3] Chung, W. J.; Griebel, J. J.; Kim, E. T.; Yoon, H.; Simmonds, A. G.; Ji, H. J.; Dirlam, P. T.; Glass, R. S.; Wie, J. J.; Nguyen, N. A.; Guralnick, B. W.; Park, J.; Somogyi, A.; Theato, P.; Mackay, M. E.; Sung, Y.-E.; Char, K.; Pyun, J. The use of elemental sulfur as an alternative feedstock for polymeric materials. *Nat. Chem.* **2013**, *5* (6) 518-524.

[S4] Griebel, J. J.; Namnabat, S.; Kim, E. T.; Himmelhuber, R.; Moronta, D. H.; Chung, W. J.; Simmonds, A. G.; Kim, K.-J.; van der Laan, J.; Nguyen, N. A.; Dereniak, E. L.; Mackay, M. E.; Char, K.; Glass, R. S.; Norwood, R. A.; Pyun, J. New Infrared Transmitting Material via Inverse Vulcanization of Elemental Sulfur to Prepare High Refractive Index Polymers. *Adv. Mater.* **2014**, *26* (19) 3014-3018.

[S5] Laitinen, R.S.; Pakkanen, T.A. ^{77}Se n.m.r Study of the Sulphur-Selenium Binary System. *J. Chem. Soc., Chem. Commun.* **1986**, *17* 1381-1382

[S6] Griebel, J. J.; Nguyen, N. A.; Namnabat, S.; Anderson, L. E.; Glass, R. S.; Norwood, R. A.; Mackay, M. E.; Char, K.; Pyun, J. Dynamic Covalent Polymers via Inverse Vulcanization of Elemental Sulfur for Healable Infrared Optical Materials. *ACS Macro Lett.* **2015**, *4* (9) 862-866.