CHALCOGENIDE HYBRID
INORGANIC/ORGANIC POLYMERS (CHIPs):
PLASTICS FOR INFRARED IMAGING AND
PHOTONICS

by

Tristan S. Kleine

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LIST OF ABBREVIATIONS

1D PhC – one dimensional photonic crystal
AIBN – 2,2’-azobis(2-methylpropionitrile)
ATR – attenuated total reflectance
ATRP – atom transfer radical polymerization
BCP – block copolymer
ChG – chalcogenide glass
CHIPS – chalcogenide hybrid inorganic/organic polymers
CNC – computer numeric control
CP-MAS – cross polarized magic angle spinning
CTA – chain transfer agent
DBR – Distributed Bragg Reflector
DCB – ortho-dichlorobenzene
DCM – dichloromethane
DFT – density functional theory
DIB – 1,3-di-isoproepnylbenzene
DMA – dynamic mechanical analysis
DP – degree of polymerization
FIB – focused ion beam
GPC – gel permeation chromatography
GRIN – graded refractive index
HRIP – high refractive index polymers
Li-S Battery – lithium sulfur battery
LIDAR – light detection and ranging
LWIR – long wave infrared
MCT – mercury cadmium telluride alloy
(m)DSC – (modulated) differential scanning calorimetry
MEMS – micro-electro-mechanical system
MLA – maskless aligner
MMWG – multi-mode waveguide
MWIR – mid wave infrared
NBD – 2,5-norbornadiene
NBD2 – exo-trans-exo-pentacyclo[8.2.1.1.0.0]tetradecadiene (2,5-norbornadiene dimer)
Ni(COD)2 – bis(1,5-cyclooctadiene)nickel(0)
NIR – near infrared
NMP – nitroxide mediated polymerization
NMR – nuclear magnetic resonance
ORMOCHALCS – organically modified chalcogenide polymers
PAG – photoacid generator
PBG – photonic band gap
PDMS – poly(dimethylsiloxane)
PEB – post exposure bake
PGMEA – propylene glycol methyl ether acetate
PMMA – poly(methyl methacrylate)
PVA – poly(vinyl alcohol)
RAFT polymerization – reversible addition fragmentation transfer polymerization
RIC polymers – refractive index contrast polymers
ROP – ring opening polymerization
SEC – size exclusion chromatography
SEM – scanning electron microscopy
SMWG – single mode waveguide
SBOC – para-(tert-butyl) S-(4-vinylphenyl) carbonothioate
SWIR – short wave infrared
Tg – glass transition temperature
TGA – thermogravimetric analysis
THF – tetrahydrofuran
TIB – 1,3,5-tri-isopropenylbenzene
TOPAS – trade name for a class of cyclic olefin copolymers
XRD – X-ray diffraction
ZAP – trade name for spin-on adhesion promoter for ZPU12-480
ZPU12-480 – trade name for a cross-linkable fluorinated acrylate resin
ABSTRACT

This dissertation contains five chapters describing recent advances in the use of a new class of polymeric materials (Chalcogenide Hybrid Inorganic/Organic Polymers (CHIPs)) for infrared imaging and photonics. Plastics are generally not used for these applications given their typically high optical losses at these wavelengths and low refractive indices. CHIPs are a revolutionary class of materials that are composed of a high loading of chalcogen moieties that are copolymerized with organic monomers into the backbone of the polymer. The large chalcogen content in CHIPs enables IR transparency and high refractive indices ($n$), whereas the organic comonomers afford solution and melt processability making these materials highly attractive for use in the aforementioned applications. The last chapter focuses on the development of a novel photopolymer for use in photonic interconnects operating at telecommunication wavelengths. This chapter lays the groundwork for using this photopolymer in “smart print” technologies for optical communications.

The first chapter is a review on the fundamentals and applications of infrared imaging, the current materials used as optical elements in those systems, and examples of polymeric materials that have been developed for the same purpose. IR imaging has numerous applications ranging from medical diagnostics to autonomous vehicle technologies, and is used frequently in the military for night vision. There is a growing consumer market for IR cameras as well, now that the cost of certain components has been reduced. However, expensive semiconductor materials are still used as the optical components. Consequently, there is a desire to replace semiconductors with cheaper, easier to work with plastics. CHIPs address this need as they are more IR transparent than conventional plastics and are
amenable to conventional thermoplastic reforming techniques. These unique features of CHIPS are a result of the chemistry termed “inverse vulcanization” used to prepare them. The inverse vulcanization process uses elemental sulfur as a comonomer and reaction medium. At high temperatures, elemental sulfur is homolytically ring opened, resulting in a high concentration of sulfur radicals which then react with other chalcogens/organic vinylic comonomers. The resulting polymeric material contains a high content of IR transparent polysulfur bonds which is the basis for IR transparency in CHIPS.

The second chapter describes the synthesis of a new organic comonomer for inverse vulcanization designed to improve the thermomechanical properties of CHIPS. Early CHIPS materials prepared using 1,3-di-isopropenylbenzene (DIB) suffered from low glass transition temperatures resulting in a narrow use range. To address this issue 1,3,5-tri-isopropenyl benzene (TIB) was synthesized and used in inverse vulcanization reactions. The higher $f_{avg}$ (number of crosslinkable moieties per monomer unit) associated with TIB afforded a more densely crosslinked material according to dynamic rheological experiments. As expected, this increased crosslink density resulted in CHIPS with dramatically improved glass transition temperatures (approximately twice that of their DIB based analogues) exceeding $T_g > 100$ °C. Despite being highly crosslinked, this new material still exhibited the self-healing properties previously demonstrated for DIB based CHIPS. Most importantly, this new CHIPS material was similarly transparent in the mid wave IR to DIB based CHIPS. This work demonstrated that the thermomechanical properties of CHIPS could be adjusted to fit the demands of practical applications without sacrificing desirable optical properties.
The third chapter explores the method used to further increase the refractive index of CHIPs materials. Refractive index is a volume averaged bulk property, thus higher loadings of sulfur result in higher refractive indices for CHIPs. However, the maximum refractive index possible is limited by the amount (~85 wt%) of sulfur that can be efficiently incorporated into CHIPs. Therefore, a higher refractive index chalcogen must be used to realize higher \( n \). Tellurium is mildly toxic and exceedingly expensive, so selenium was chosen instead. The enabling discovery was that elemental selenium reacts with ring opened sulfur species, generating a reactive mixed chalcogen \textit{in situ}, that copolymerizes with organic crosslinkers. This enabled preparation of CHIPs materials with \( n \leq 2.1 \) demonstrating a marked increase over previously synthesized CHIPs materials. The expected mid wave IR transparency was observed and evaluated by IR imaging experiments as well. Most significantly, certain compositions were found to be solution processable. Access to soluble CHIPs with high refractive indices is critical for the solution-based fabrication of various photonic devices. Only one such device will be discussed in this dissertation, but other examples are currently under development.

The preparation and characterization of 1D photonic crystals (1D PhCs) utilizing selenium containing CHIPs is the topic of the fourth chapter. 1D PhCs are dielectric devices assembled with alternating layers of high and low refractive index material. Layer thickness determines the \( \lambda_{\text{max}} \) of the photonic bandgap while the difference in refractive index (\( \Delta n \)) between layers affects the magnitude of reflection. In this design, larger \( \Delta n \) values facilitate highly reflective mirrors assembled with only a few layers. Consequently, various combinations of metal oxides are often used to achieve large \( \Delta n \). However, entirely inorganic 1D PhCs are brittle, limiting their use in certain applications, and why wholly
polymeric 1D PhCs are of great interest as an alternative design. Fabrication of such devices is complicated by the need to generate a large number of layers to offset the typically small Δn values observed in polymeric 1D PhCs. This issue is addressed by employing ultra-high refractive index CHIPs as one of the layers. 1D PhCs were prepared by spin coating alternating layers of selenium containing CHIPs (high refractive index layer) and cellulose acetate (low refractive index layer). Devices fabricated in this manner were shown to possess >90% reflection with just 11 bilayers, and whose band gap was tuned across the near-infrared (1000-2000 nm).

The fifth chapter is devoted to the preparation of long wave IR (LWIR) transparent CHIPs. Imaging in the LWIR is significantly cheaper than in the mid wave IR, and thus attractive for a variety of consumer applications. CHIPs are transparent in the mid wave IR as a result of low C-H bond content, but this does not necessarily translate to LWIR transparency. This is because the LWIR overlaps with the fingerprint region of the infrared spectrum which encompasses a broader range of vibrational absorption modes. Consequently, even the small amount of organic comonomer present in CHIPs results in opaque materials at longer wavelengths. Interestingly, some organic polymers, like polyethylene, are remarkably transparent over much of the LWIR. Polyethylene itself is not suited towards use as a broadband IR optic due to its polycrystallinity, but indicated polymeric materials could in principle be designed with adequate transparency in this region. To this end, simulated FTIR spectra of various model compounds representative of the corresponding polymeric repeat unit were used to guide the design of LWIR transparent CHIPs. Ultimately, a dimer based on the [2+2] cycloaddition of 2,5-norbornadiene (resulting in the monomer termed NBD2) emerged as a monomer amenable to inverse
vulcanization chemistry and expected to possess improved LWIR transparency. Melt cast windows of CHIPS containing NBD2 or DIB as the organic crosslinker were then prepared with the same thickness and compared in LWIR imaging experiments. The DIB based CHIPS material was opaque at these wavelengths, while the new NBD2 based CHIPS material afforded significantly improved transparency. In the future, this methodology will be expanded to develop more CHIP materials that are suitable for LWIR imaging applications.

The sixth chapter represents a departure from an emphasis on mid-IR transparent materials. Instead, the focus is development of materials for photonics applications at wavelengths relevant to the telecommunications industry (1310 and 1550 nm). In this work, a novel photopolymer (poly(SBOC)) was prepared and demonstrated as a material for fabrication of photonic interconnects. These devices require a high refractive index medium through which light propagates to be surrounded by lower refractive index material. Such patterning is typically achieved through photolithography and a number of solvent development/etching steps. Poly(SBOC) simplifies this process since permanent refractive index changes with high resolution are generated by direct laser writing in dry polymer films. Optical power attenuation through the device (propagation loss) is an important metric of photonic interconnects. To assess this for poly(SBOC), waveguides were fabricated and characterized by the cut back method. The propagation losses observed were ~2 dB/cm and commensurate to values typically observed for hydrocarbon based waveguides. The promising results from this project have resulted in a collaboration with the AIM Photonics program in the College of Optical Sciences at The University of Arizona to develop “smart write” photonic interconnects.
CHAPTER 1 - POLYMERIC MATERIALS FOR THE INFRARED

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1.1 Introduction

Conventionally, the most widespread use of infrared (IR) light is in spectroscopy for the identification of molecular compounds. However, the design of imaging systems for this regime has become an important technological advance as well. Imaging in the infrared (1-14 µm) is used in a variety of areas including defense, where it is essential, along with medicine and autonomous vehicle technology, as camera systems operating at these longer wavelengths enables stand-off detection and non-invasive interrogation of people and objects when no visible light is present. Critical defense applications are enabled by virtue of the long distance that infrared light can travel through the atmosphere. IR imaging systems are generally more expensive than those operating at visible wavelengths which has ultimately limited the widespread use of IR cameras in the aforementioned applications. Part of the high cost is attributed to the necessary use of optical elements (i.e. lenses) made from expensive, difficult to work with semiconductor materials. Semiconductors must be used since metals are opaque across a wide range of frequencies, and oxide glasses/organic plastics exhibit both fundamental vibrations and overtones at the wavelengths of interest, making these materials largely opaque as well. Despite the apparent issues with using organic (i.e. polymeric) materials for infrared imaging, the potential for cheap, easily processable IR optics has spurred attempts to develop plastics specifically designed for this application. Significant advances have been
made in designing plastics that are suitably transparent up to 5 µm, however there is a need to extend this window of transparency to ~14 µm. This has proved considerably more challenging as evidenced by the first examples of such materials only being reported this year. This review has been designed to briefly survey the materials currently used in IR imaging and a perspective on the use of organic plastics at these wavelengths.

1.2 Background

The different regions of the infrared spectrum have been defined based on terrestrial atmospheric absorptions from water, ozone and carbon dioxide. The windows between major absorptions delineate different regions of the IR. The first region is referred to as the short wave IR (SWIR, 1-3 µm) and is largely reflected light\(^1\). Longer wavelengths of infrared light, sometimes called the mid-IR or “thermal IR\(^2\)” refers to photons emitted from black body radiators. The wavelength and intensity of this light can be correlated to the temperature of the black body through Planck’s law, and is the basis for certain applications of IR imaging (namely IR thermography). Information about chemical identity is also contained in the thermal IR. Together, these features make imaging in the thermal IR highly versatile and consequently the main focus of this review. The thermal IR is further segregated into the mid-wave infrared (MWIR, 3-5 µm) and long-wave infrared (LWIR, 7-14 µm) given the strong absorptions of water molecules from ~5-7.5 µm and absorptions from CO\(_2\) dominating beyond 14 µm (Figure 1.1). This nomenclature system is useful when discussing IR imaging systems since application and choice of optical elements/detectors vary depending on the regime.
SWIR imaging can be used in some low light conditions and relies on photomultiplier detectors or near IR (NIR) illumination\textsuperscript{3} to increase contrast under semi-dark or hazy conditions. Moving to longer IR wavelengths offers some distinct advantages over the SWIR with respect to identifying and analyzing targets as previously mentioned. For instance, IR thermography can be used to determine the temperature of an object remotely and has been demonstrated in a variety of applications to rapidly assess otherwise difficult to probe environments. Such examples range from monitoring biological disease states\textsuperscript{4} to failure analysis of building infrastructure\textsuperscript{5} and is heavily used in the microelectronics industry to find faults\textsuperscript{6}. Depending on the temperature of the black body being interrogated, different regimes of the infrared are more or less appropriate for IR thermography as is illustrated in Figure 1.2. The Planck curves shown in this figure demonstrates the relationship between temperature of a black body to the corresponding wavelength range and total spectral irradiance emitted. The hotter an object is, the broader

\begin{figure}
\centering
\includegraphics[width=\textwidth]{atmospheric_windows.png}
\caption{The atmospheric windows in visible and infrared regions. Reprinted with permission from ref. [2], Copyright 2017, Springer Berlin Heidelberg}
\end{figure}
its emission spectrum in addition to an overall higher peak intensity. For example, the 300 K Planck curve (approximately the temperature of a human) illustrates that some of the emitted light will be visible in the MWIR, but peak intensity is centered at ~10 µm. This

![Planck Curves](image_url)

**Figure 1.2:** Planck curves of a black body (after Flir, 2000) at different temperatures (in degrees Kelvin). Ordinate, spectral radiance [W cm⁻² µm⁻¹ sr⁻¹]; abscissa, wavelength in micrometers. Reprinted with permission from ref. [3], Copyright 2003, Springer Nature.

would indicate that imaging of biological subjects in the MWIR is perhaps not the most appropriate regime. In general, lower sensitivity is required when attempting to measure objects at wavelengths closer to their peak intensity\(^7\); thus, for relatively lower temperature objects (**Figure 1.2**), imaging in the LWIR is more appropriate, but detection technology choices must also be considered. In addition to the varied uses of IR thermography, IR imaging can be applied to hyperspectral imaging - a technique that maps a defined portion of the electromagnetic spectrum to each pixel in a detector\(^8\) - which allows for stand-off detection of various analytes and is often used to detect hazardous compounds\(^9,10\) as well
as geological mapping from space\textsuperscript{11}. These unique applications of IR imaging are the driving force for the development of this field but have not realized widespread use given the high cost of such systems, motivating the need to reduce the cost of each component as much as possible.

Imaging in the MWIR is particularly costly due to the detectors used at these wavelengths. These are primarily quantum detectors (i.e. photodiodes) and work essentially like a photovoltaic, whereby absorption of IR photons and separation of charges leads to the generation of current that is interpreted as an electronic signal/response\textsuperscript{12}. The alloy mercury/cadmium/telluride (MCT) is commonly used for this application, as its band gap can be tuned over both the mid and long wave IR by adjusting alloy composition, thus making it a versatile detector material\textsuperscript{13}. However, this technology requires a cooling system to be integrated into the detector (Peltier Thermoelectric Cooling or use of cryogenic liquids) in order to reduce background noise (dark current) which ultimately drives the high cost of this system\textsuperscript{14}. By the same token, these detectors are highly sensitive and contrast is greater in the MWIR than in LWIR imaging\textsuperscript{3,15} which warrants the incurred cost under certain circumstances, namely in defense applications where MIWR cameras are used heavily\textsuperscript{16}.

LWIR imaging has recently become significantly cheaper with the advent of new detector systems designed for this region called microbolometers\textsuperscript{17} which do not require cooling in order to function with high sensitivity. As opposed to the quantum detectors described earlier, microbolometers function by a response to IR heating. Electronic signal generation is based on changes in resistance across a LWIR absorbing material (vanadium oxide or amorphous silicon\textsuperscript{18}) as a consequence of IR heating. Furthermore, temperature
change, and hence resistance, are proportional to the number of impinging IR photons\textsuperscript{10}. Each microbolometer is an individual micro-electro-mechanical system (MEMS) (shown below in Figure 1.3), or pixel; when each pixel is thermally insulated from one another\textsuperscript{20}, they can be joined into a focal plane array that constitutes the detector for a LWIR camera\textsuperscript{12}. While this new design has brought the cost of such detectors down to ~10,000 USD, other technologies are currently being developed and commercialized to further decrease the cost of LWIR cameras\textsuperscript{21}. Access to cheap and compact LWIR cameras has been particularly enabling for imaging and diagnostics of humans\textsuperscript{22} and is of great interest for aiding in self driving vehicles\textsuperscript{23} since LWIR imaging is particularly relevant for these applications.

1.3 Conventional IR Transparent Materials

The next consideration for reducing overall cost of IR imaging systems pertains to the materials used to fabricate the optical elements in IR cameras. The primary

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure13.png}
\caption{a) The structure of the designed microbolometer. $\lambda/4$ cavity structure is adopted to improve infrared absorption; b) SEM image of the processed bolometer pixel. Pixel size: 65 µm x 60 µm; cavity gap: 2.0 µm. Adapted with permission from ref. [18] Copyright 2013, Elsevier}
\end{figure}
Figure 1.4: Transparency windows for various optical materials throughout the visible and infrared regions of the electromagnetic spectrum (Edmund Optics).

consideration here is that the material used needs to be transparent at the wavelengths of interest. The dearth of materials, until relatively recently (early 1950’s\textsuperscript{24,25}), satisfying this condition has made IR optics a relatively new field compared to visible light optics. Figure 1.4 illustrates the current field of materials available for use in IR optics. It also demonstrates why silica (glass), one of the most commonly used materials for optics in the visible, can only be used for applications in the visible-SWIR. Given the IR opacity of oxide glasses in general, group IV semiconductors and chalcogenide glasses are the most widely used classes of materials for IR imaging\textsuperscript{26}. Again, the application and wavelength regime of interest will dictate which specific material is used. While these materials possess the requisite optical properties for IR imaging, they are expensive and generally difficult to process. We posit advancement of this field can be served by development of new materials for these wavelengths; specifically, inherently cheaper and more easily processable, IR transparent plastics.
Figure 1.5: Examples of materials used for LWIR imaging a) germanium (Hyperion Optics) b) chalcogenide glasses (Edmunds Optics Inc.) c) unit cell of 2D sheets of crystalline As$_2$S$_3$ along the b$_0$ axis of the monoclinic crystal. Adapted with permission from ref. [164], copyright (1974). Springer US; structures of As$_2$S$_3$ and As$_2$Se$_3$ are closely related to this structure

The crystalline semiconductors typically used for IR imaging, i.e. silicon, germanium and zinc selenide, necessarily must be grown as pure, single crystals when used as a bulk optic$^{27,28}$. Furthermore, any fabrication of optical elements must be performed by single-point diamond turning which is neither cost efficient nor scalable$^{29}$. With the goal of producing consumer IR cameras, the cost of each component, including the optics (representative examples shown in Figure 1.5), should be reduced as much as possible. Chalcogenide glasses are a possible solution to this issue given their similar transparency to germanium at certain compositions$^{26}$, and can be solution and melt processed unlike crystalline semiconductors. Chalcogenide glasses are amorphous glasses with covalent bonds between chalcogens (Group 6 atoms heavier than oxygen) and metals, typically group 4/5 or some late transition metals$^{30,31}$. Various bulk properties of chalcogenide glasses can be tuned by adjusting the relative ratios of metal and chalcogen in the glass, or by using ternary mixtures. The caveat to this tunability requires that compositions must
remain in the glass forming regime to avoid crystallization. In general, the addition of higher molecular weight species (either the chalcogen or metal) increases refractive index (generally \( n > 2.0 \) for ChGs), but lowers the \( T_g \) as well as narrows the glass forming regime\(^{32} \). Higher molecular weight chalcogens also widen the glass’ optical transmission range to longer wavelengths. Compositions containing tellurium afford the broadest windows of IR transparency, but tellurium is a poor glass former\(^{31} \). Consequently, many efforts focus on selenide glasses which are transparent out to 20 µm and sufficient for LWIR imaging\(^{33} \).

![Figure 1.6: a) Schematic of the molding part in GMP-54-5s; b) The finished lens and lens assembly. Adapted with permission from ref. [29], Copyright 2012, The Optical Society](image-url)
The rheological properties of ChGs make them amenable to melt processing and was first demonstrated for the fabrication of molded optics in 2003 (process used shown in Figure 1.6a). Since ChGs are amorphous materials with glass transition temperatures widely ranging from below 0 to as high as ~400 °C (depending on composition) they can be thermomechanically reformed in much the same way plastics are. This allows for large scale fabrication of drawn optical fibers as well as bulk and microoptic devices for the infrared. A downside to the use of ChGs in IR optics is the scarcity and high cost of raw materials used to manufacture them. Two of the metals commonly alloyed with chalcogens for IR optics (i.e. arsenic and germanium) are either not produced in the United States at all or are heavily imported with expectations that demand for germanium in military and consumer applications will only increase according to the United States Geological Survey Mineral Commodities Summary (2019). Additionally, synthesis of ChGs requires highly refined starting materials free of contaminants and employs a number of high temperature processes to synthesize and purify the glass. Given these considerations, a polymeric based material would potentially offer the same benefits in terms of ease of processability without the stringent synthetic considerations. Chalcogenide glasses may also be solution processed in aqueous base solutions or short chain alkyl amines (propyl/butyl amine), with mixtures of amines and thiols being required to dissolve the selenide containing ChGs. While the term “dissolved” is used extensively in the literature, the process for ChG ink formation is not strictly molecular dissolution, but rather follows a solvent degradation pathway that results in solvent stabilized clusters of ionic species. While solutions of ChGs have successfully been used to ink jet print microoptics, it should be
noted that handling of ChG solutions must be performed under inert atmosphere and in the absence of water, requiring the use of glove boxes\[41\].

1.4 IR Transparent Plastics

Crystalline and non-crystalline (ChG) semiconductors have become the standard materials of choice for IR optics because of desirable optical properties arising from the nature of their constituent atoms. Specifically, the large mass of the atoms found in these materials shifts their absorption to outside the mid and long wave infrared bands. Refractive indices are also typically high for these materials, again due to the presence of large, highly polarizable atoms. The use of polymeric materials for IR optics would then seem to be precluded by the presence of, typically, a large volume of C-C and C-H bonds. This is illustrated in Figure 1.7 which depicts an FTIR spectra of poly(styrene) with the mid and long wave infrared bands highlighted in yellow. Absorptions in the

![FTIR spectrum of polystyrene](image)

**Figure 1.7:** FTIR spectrum of polystyrene denoting the MWIR and LWIR bands and the nature of the vibrations responsible for opacity in these regions
MWIR are dominated by C-H stretching vibrations at \(~3300\) cm\(^{-1}\). The guiding principle in design of MWIR transparent plastics has consequently been to remove as many C-H moieties from the material as possible without sacrificing other desirable material properties. While there is a straightforward approach to engineering MWIR transparency in polymers (removing C-H content), designing around the varied and complicated combinations of rotational/vibrational absorptions in the fingerprint region/LWIR has proved to require a more rigorous approach. Despite apparent challenges associated with development of IR transparent polymers, the attractive processing conditions intrinsically afforded by polymeric materials make the attempt to do so an intriguing prospect. To this end, the Pyun group has developed a new class of materials termed Chalcogenide Hybrid Inorganic/Organic Polymers (CHIPs) which are copolymers of chalcogens and organic monomers. These materials feature a high chalcogen content, and thus desirable bulk properties such as high refractive index and IR transparency, while maintaining the melt and solution processability that would be expected in conventional thermoplastic polymers. Application of CHIPs to IR imaging is a relatively new development, but represents an important first step in replacing semiconductor materials for this application.

Inverse vulcanization (Figure 1.8a-b) facilitates a high sulfur loading (<90 wt%) in CHIPs materials which is why they were first investigated in 2013\(^{46}\) for use as cathodes in lithium-sulfur batteries. The high sulfur content also imbues CHIPs with high refractive indices and makes this class of plastics viable for IR imaging. Homopolymerization of sulfur (i.e. 100 wt% sulfur polymers) has previously been well established, but exhibits a high polymerization floor temperature (159 °C) which prevents formation of stable
The inverse vulcanization process was developed to suppress this depolymerization mechanism by incorporating a small (>10 wt%) amount of a multi-functional organic comonomer that could react via thiol-ene chemistry with sulfur radicals generated by thermolysis of S₈ rings. Inverse vulcanization proceeds in the sulfur melt, in the absence of any co-solvents making it distinct from other polymerizations employing sulfur as a monomer. Using sulfur as the reaction medium is the reason high sulfur loadings were achieved. Due to the high reaction temperatures...
Figure 1.9: 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-infrared 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; f) 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; g) 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-di-isopropenylbenzene co-monomer (bottom spectrum). Adapted with permission from ref. [47], Copyright 2014, John Wiley & Sons.

necessary, and the inherently poor miscibility of sulfur with organic molecules, judicious selection of organic comonomers was required. 1,3-di-isopropenylbenzene (DIB) was
ultimately used as the organic crosslinker in early demonstrations which afforded solution and melt processable, amorphous polymers.

IR imaging through CHiPs was demonstrated in 2014 along with further exploration of the optical properties of CHiPs\textsuperscript{47}. The refractive indices of CHiPs are significantly higher than conventional organic polymers (Figure 1.9f), or even high refractive index polymers (HRiPs, $n > 1.7$)\textsuperscript{48}. Refractive indices of organic plastics can be increased by incorporation of highly polarizable atoms/moieties but such methods rarely attain $n > 1.8$\textsuperscript{49}. The inverse vulcanization process affords an unusually large volume of highly polarizable sulfur and is the basis for the inherently high refractive indices observed in CHiPs materials. Furthermore, refractive indices of CHiPs materials were found to track with chalcogen content as expected, and were found to be as high as $n = 1.865$ when 80 wt\% sulfur was used in the copolymerization. Compositions containing <20 wt\% organic crosslinker are generally not investigated for optical applications since a low organic content typically results in poor thermomechanical properties and reduced solubility. The high sulfur content of CHiPs also implies a large fraction of the chemical bonds in the polymer are comprised of polysulfide bonds which is the basis for the improved MWIR transparency of CHiPs materials. To illustrate this fact, PMMA, and alternately CHiPs, windows of similar thickness were placed in front of a MWIR camera (operating at 3-5 µm) and a human subject was imaged through both windows (Figure 1.9 d,e). The subject was practically invisible when viewed through the PMMA window but could clearly be seen when the CHiPs window was used. Various optical elements demonstrated in this report (windows and lenses) were fabricated from simple PDMS replicas and illustrates the relaxed processing conditions of CHiPs compared to semiconductors typically used for IR
imaging. This report was the first step in demonstrating the possibility of using low cost, easily processable organic polymers for IR imaging and paved the way for future development of this new field.

As was previously mentioned, the glass transition temperatures of CHIPs can be problematically low when a high sulfur content is employed. This is at odds with the desire for higher refractive index and increased IR transparency, which also trends with increasing sulfur content. It is well known that increasing the crosslink density of polymer networks increases glass transition temperature and this feature was leveraged to dramatically raise the $T_g$ of CHIPs (Figure 1.10). At the time, the scope of commercially available monomers that could be polymerized by inverse vulcanization was rather narrow, so a tri-
Figure 1.11: Dark-field optical microscopy images of a) pristine poly(S-r-DIB) and b) poly(S-r-TIB) 1 mm flat panel discs; c) a 405 nm laser diode was set up to irradiate both sulfur copolymers with an optical output power of 7 mW for 5 s; d) digital image of poly(S-r-DIB) after irradiation; e) dark-field optical microscopy image of poly(S-r-DIB) panel after irradiation (35 mJ) revealing the damaged region (white circle) commensurate with spot size of laser; f) dark-field microscopy image and digital image g) of poly(S-r-TIB) panel showing no damage after irradiation; h) digital image of USAF target; images captured with a mid-IR camera, operating at 3–5 μm, of a USAF target, transparent at 3–4 μm: i) IR thermal image of USAF target imaged through a lens mount without sulfur copolymer panel; j) IR thermal image through the poly(S-r-TIB) panel (1 mm thick, 25 mm wide), and k) IR thermal image through the poly(S-r-TIB) panel (1 mm thick, 25 mm wide). Reprinted with permission from ref. [50]. Copyright 2016, American Chemical Society
functional variation of DIB (1,3,5-tri-isopropenylbenzene (TIB)) was synthesized by efficient Suzuki cross-coupling of 1,3,5-tribromobenzene and isopropenylboronic acid pinacol ester. Subsequent inverse vulcanization with sulfur furnished poly(sulfur-random-1,3,5-tri-isopropenylbenzene) (poly(S-r-TIB))$^{50}$. A significant increase in Tg was observed with compositions containing 50 wt% TIB facilitating Tg’s as high as ~130 °C (Figure 1.10d). The trend of decreasing Tg with decreasing organic crosslinker was maintained, with 30 wt% loading of TIB affording materials possessing Tg’s ~70 °C. While this is a fairly moderate Tg, it is still higher than any previously prepared DIB based CHIPs material thus allowing high refractive index and IR transparency to be maintained without sacrificing thermomechanical properties. The utility of the increased thermomechanical properties of poly(S-r-TIB) was demonstrated by a laser damage study. In this experiment, a laser source operating at a wavelength CHIPS materials absorb, was focused on windows of poly(S-r-TIB) and poly(S-r-DIB). It was found the DIB sample succumbed to thermal deformation more quickly than the TIB sample did (Figure 1.11). Heat induced deformation of optical elements handling high power laser sources is problematic$^{51}$, but, as illustrated in this study, can be somewhat addressed by improving the Tg of the optic. Another interesting property with regards to CHIPS materials is that the polysulfide network allows the material to self-heal through activation of the dynamic S-S bonds$^{52}$ (Figure 1.12). Optical elements fabricated from CHIPS are easily repaired by annealing at low temperatures (Figure 1.12 a-i) which cannot be said of conventional IR materials where mild damage to the optic renders the device inoperable and requires extensive rework and polishing. This feature had previously been demonstrated with
Figure 1.12: (a–c) Digital visible wavelength images captured through poly(S-r-DIB$_{30}$) 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-DIB$_{30}$) 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-DIB$_{30}$) 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. Reprinted with permission from ref [82]. Copyright 2015, American Chemical Society. j) In situ rheological characterization of dynamic behavior in poly(S$_{80}$-r-DIB$_{20}$) copolymers at T = 130 °C and 100 rad/s. Regions in the plots represent: (1) initial modulus; (2) 100% strain, 1st damaging cycle; (3) 8% strain, 1st recovery cycle; (4) 100% strain, 2nd damaging cycle; (5) 8% strain, 2nd recovery cycle. Adapted with permission from ref. [52]. Copyright 2014, American Chemical Society
poly(S-r-DIB), but was found to hold true for poly(S-r-TIB) as well, despite poly(S-r-TIB) being more densely crosslinked.

While the refractive indices of these first generation CHIPs materials were notably higher than most organic polymers, they are still lower than the materials typically used for IR imaging which can be as high as $n = \sim 4.0^{53}$. Simply increasing the sulfur content was not feasible as there is a practical limit to how much sulfur the organic comonomers can effectively react with. Not all elemental sulfur is consumed at very high sulfur loadings and can bloom to the surface of CHIPs materials, causing scattering which is detrimental to imaging applications. Furthermore, the refractive index of sulfur itself limits the maximum refractive index values CHIPs can reach if it is the only chalcogen employed. Tellurium is the highest refractive index chalcogen, but is exceedingly expensive and mildly toxic, which are criticisms of the ChG’s used in IR optics. Selenium was therefore

**Figure 1.13:** Flow diagram of poly(S–Se-r-DIB) polymer fabrication. (a) melt and stir S–Se crystalline compound; (b) add DIB and continue stirring; (c) pour molten material into a mold (e.g. a Petri dish), heat to 200 °C (1 h) and then cool to vitrify; (d) retrieve freestanding transparent polymer from mold: scale bar for the poly(S–Se-r-DIB) polymer shown is 1 cm. Reproduced from ref. [55] with permission from The Royal Society of Chemistry, Copyright 2017
selected for incorporation into CHIPs with the hope that cyclic Se\textsubscript{8} would participate in inverse vulcanization reactions in a manner similar to S\textsubscript{8}. Unfortunately, the Se\textsubscript{8} allotropes are highly reactive towards conversion to polymeric selenium under mild conditions making copolymerization between molten Se\textsubscript{8} and organic comonomers impossible\textsuperscript{54}. Two solutions concurrently arose that enabled the incorporation of selenium into CHIPs. The first demonstration was by Boyd et. al.\textsuperscript{55} who utilized a mixed chalcogen (S\textsubscript{90}Se\textsubscript{10}) as the

![Diagram](https://via.placeholder.com/150)

**Figure 1.14:** a) scheme for the synthesis of poly(S-\textit{r}-Se-\textit{r}-DIB); b) refractive indices of poly(S-\textit{r}-Se-\textit{r}-DIB) terpolymers of varying composition vs wavelength; c) digital image of a USAF target (purchased from Edmund Optics); images captured with a mid-IR camera, operating at 3–5 μm, through a poly(S\textsubscript{50}-\textit{r}-Se\textsubscript{20}-\textit{r}-DIB\textsubscript{30}) panel (1 mm thick, 25 mm wide) of d) a USAF target, transparent at 3–4 μm, e) IR thermal image of human arm, and f) higher resolution image of human forearm. Adapted with permission from ref. [56]. Copyright 2017, American Chemical Society.
selenium source (Figure 1.13). This mixed chalcogen was first prepared by reacting
elemental sulfur and selenium at high temperatures in a process analogous to ChG
formation. The mixed chalcogen was then copolymerized under typical inverse
vulcanization conditions with DIB to afford a selenium containing terpolymer, however
refractive indices were not reported. The other approach was to use the sulfur radicals
generated by inverse vulcanization conditions to react with grey selenium, thus affording
a mixed chalcogen in situ that was then crosslinked by addition of DIB (Figure 1.14). This
approach was in fact developed by two different groups contemporaneously, the Pyun
group56 and the Mecerreyes’ group57. The Mecerreyes’ group utilized this material as a
cathode material in Li-Sulfur batteries and found the inclusion of selenium improved
battery performance under high cycle rates. The Pyun group investigated the improved
refractive index of this polymer and its viability as an IR transparent material. The method
developed by the Pyun group afforded high selenium loadings which corresponded to a
significant increase in observed refractive index (n ≤ 2.1) over CHIPS comprised of only
sulfur and DIB. High transmission in the MWIR was maintained through these poly(sulfur-
random-selenium-random-1,3-di-isopropenylbenzene) (poly(S-r-Se-r-DIB)) materials
which was assessed by previously described IR imaging experiments. While very high
loadings of selenium (and hence lower loadings of DIB) afforded poorly soluble CHIPS,
compositions with more moderate loadings of selenium were soluble enough to use in spin
coating applications such as fabrication of highly reflective, wholly polymeric 1D photonic
crystals (1D PhCs). 1D PhCs are alternating layers of low and high refractive index
material and are used in a variety of applications including sensors58 and lasing cavities59.
The photonic band gap (PBG) of 1D PhCs can be tuned by adjusting the thickness of each
layer, while the magnitude of the resulting reflection is proportional to the difference in refractive index between the layers. Given these considerations, metal oxides, chalcogens and semiconductors are often used in conjunction to fabricate 1D PhCs. Using these materials, large refractive index contrast between layers is easily achieved and precise control over layer thickness is accomplished using vapor deposition methods. However, 1D PhCs prepared from these materials are expensive to produce and are inherently brittle. As a result, wholly polymeric 1D PhCs have been investigated which are amenable to large scale solution and melt processing and generally more flexible. The low refractive indices of organic polymers does present an issue if facile fabrication and high reflectivity are desired. Consequently, numerous elegant solutions have been applied to overcome this obstacle. Refractive index contrast can be increased by doping in high $n$ additives\textsuperscript{60–63}, or a large numbers of layers can easily be attained by use of self assembled lamellae\textsuperscript{64,65}, or by relying on automated processes to achieve the same goal\textsuperscript{66–68}. Some attention has been payed to using polymers with intrinsically higher refractive index\textsuperscript{69}, but development of ultra high refractive index, solution processable CHIPS makes this a more viable approach. To this end, poly(S-$r$-Se-$r$-DIB) and cellulose acetate were used to generate a large difference in refractive index ($\Delta n = 0.5$) in a wholly polymeric 1D PhC assembled by spin coating with relatively few layers\textsuperscript{70}. This afforded 1D PhCs with high reflectivity (>90\%) and a tunable bandgap across the SWIR (Figure 1.15). A consideration in the design of 1D PhCs is that all materials employed must be transparent at the wavelengths of interest. This is reasonably attainable in the SWIR with most organic materials, but would be more challenging at longer wavelengths for the reasons previously discussed. The unique IR
transparency of CHPIPs might then also be useful in fabricating 1D PhCs for applications requiring photonic band gaps at longer wavelengths.

Figure 1.15: a) General scheme for the fabrication of highly reflective all polymer Bragg reflectors from CHPIPs materials that possess tunable reflectance across the NIR and SWIR (1.0–2.0 μm); b) schematic representation of the Δn values that can be generated using various classes of materials; transmission spectra recorded in various spots on ~2 cm² Bragg reflectors with 22 layers each: c) 92.6% calculated reflectance at 2113 nm; d) 93.8% calculated reflectance at 1450 nm; e) 93.2% calculated reflectance at 998 nm. Reprinted with permission from ref. [70]. Copyright 2018, American Chemical Society.
Much attention so far has been paid to the use of polymeric materials for imaging in the MWIR. However, given the inherently lower cost of LWIR imaging systems, development of cheap plastic optics for the long wave is of great interest to satisfy the demands of military and consumer applications, as well as point of care diagnostics and self-driving cars\textsuperscript{22,23,71,72}. As previously mentioned, the LWIR overlaps with the fingerprint region which has greatly hindered development of transparent polymeric materials for this region. A notable demonstration of a LWIR transparent polymer at thicknesses necessary for the fabrication

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure16.png}
\caption{a) synthesis of poly(S-r-TVSn); MWIR (3–5 μm) images of human fingers viewed b) through 1.50 mm thick PMMA; (c) through 1.63 mm thick poly(S-r-DIB) ORMOCHALC, and d) through 1.65 mm thick poly(S-r-TVSn); LWIR (7.5–14 μm) images of a hot soldering iron viewed e) in open air, f) through 1.63 mm thick poly(S-r-DIB) ORMOCHALC, and g) through 1.65 mm thick poly(S-r-TVSn) ORMOCHALC. Reprinted from ref. [73] Copyright 2019, American Chemical Society.}
\end{figure}
of bulk optics was provided by Boyd et. al. where a CHIPS material was synthesized using tetravinyl tin as the organic crosslinker\textsuperscript{73} (Figure 1.16). This material exhibited the expected MWIR transparency and high refractive index endemic to high sulfur content CHIPS as well. There have also been a few scattered reports on the synthesis of new

![Figure 1.17: a) Synthesis of poly(phenylene polysulfide). IR transmitting performance of PSN76 film; b) An IR thermal image of PSN76 and Kapton polyimide films on a hand subject. Thermal images of a male subject captured with a long-IR (7.5–13 μm) camera through c) pristine and d) 200% stretched PSN76 films. IR thermal images of a female subject captured through e) scratched, f) healed (by thermal treatment), and g) reprocessed PSN76 films. Insets show photographs and surface OM images of the corresponding films. Scale bars for the photographs and OM images are 3 cm and 300 μm, respectively. Reprinted from ref. [74]. Copyright 2019, American Chemical Society](image-url)
materials (not necessarily sulfur based) that demonstrate LWIR transparency through thin (~200 µm) films (Figure 1.17) or that allude to improved LWIR transparency but do not report any LWIR imaging results\textsuperscript{74-76}. These reports are interesting and important to the field of IR polymer optics, but offer little in the way of explanation regarding the reason for this improved transparency. MWIR plastics were demonstrably more transparent when sulfur replaced much of the hydrocarbon volume in an organic polymer, but such a clear cut thesis for LWIR transparency is missing in the field of IR polymer optics. Given the infancy of this field, a more streamlined, directed approach towards engineering LWIR transparency is critical to the advancement of this area of study. Such a solution was very recently provided by Pyun et. al. with the development of a LWIR transparent CHIPs material determined \textit{a priori} to be transparent at these wavelengths by predictive FTIR simulations\textsuperscript{77}. An obvious starting point for such simulations would be to target symmetrical zero-dipole moment organic comonomers which would have few, if any, absorptions at the wavelengths of interest for LWIR imaging. However, copolymerization with sulfur would likely break this symmetry and polymerization would induce new bond formation between monomers. Computational simulation of all the resulting microstructural environments would not be feasible. Hence a more viable approach was to computationally screen model compounds (MC) exhibiting LWIR spectra with reduced absorption profiles in the 7-14 micron window. To allow for easy quantitative ranking between calculated systems, the sum of integrated molar absorptivity values of the peaks in the region of interest is taken as a figure of merit. The summation of integrated molar absorptivity values in the LWIR region was then designated as \( \varepsilon_{\text{int}} \). A lower \( \varepsilon_{\text{int}} \) value for
the region means a more LWIR transparent sample. This provides an easy quantification method to compare various calculated model

**Figure 1.18:** Comparison of DFT calculated FTIR spectra for equal concentrations of a) norbornane, b) 2,5-norbornadiene, and c) MC 2 (black lines). Red line indicates experimental gas-phase spectra of a) norbornane, b) 2,5-norbornadiene and c) experimental FTIR spectra of poly(S70-r-NBD230). d) Synthetic scheme for synthesis of NBD2 via the nickel catalyzed [2+2] cycloaddition of 2,5-norbornadiene and the inverse vulcanization of NBD2 with elemental sulfur; image shown consists of two 2.3 mm thick diamond polished windows of poly(S50-r-NBD250) where both originated from an originally 3.4 mm thick cast sample. Adapted from ref. [77] Copyright (2019), Wiley-VCH
polymers/compounds quickly. Within this work, computational efforts were primarily intended to screen candidates for LWIR imaging to conserve experimental efforts. As these calculations are done in the gas-phase and combination bands and overtones are not included, $\varepsilon_{\text{int}}$ is not an exact indicator of performance. However, since the fundamental vibrations are more intense than combination bands and overtones, a candidate with a

![Figure 1.19](imageurl)

**Figure 1.19:** a) digital image of LWIR imaging set up and LWIR images taken with a FLIR LWIR camera operating in the 7.5-13 $\mu$m regime in “black hot” mode with inset of patterned PMMA sheet (12 x 12 cm) used as mask for LWIR imaging; b) no window in front of the camera; c) through a 1.3 ± 0.15 mm thick poly(S$_{70}$-r-DIB$_{30}$) window, and d) through a 1.3 ± 0.12 mm thick poly(S$_{70}$-r-NBD$_{230}$) window. Reprinted from ref. [77] Copyright (2019), Wiley-VCH.
significantly high $\epsilon_{\text{int}}$ value almost certainly won’t perform well experimentally. This method was validated by comparing computationally predicted spectra to some known compounds first (Figure 1.18a-b). The model compound (MC2) shown in Figure 1.18c was found to have a favorable $\epsilon_{\text{int}}$ value and justified the synthetic effort to produce the material shown in Figure 1.18d. Thick, free standing, large diameter windows were molded from this new CHIPS material (poly(S-$r$-NBD2)) and used in LWIR imaging experiments that exhibited significantly improved transmission compared to poly(S-$r$-DIB) windows of the same thickness (Figure 1.19). Furthermore, these materials demonstrated remarkably high glass transition temperatures and improved thermal stability relative to poly(S-$r$-DIB). Demonstration of this simulation based approach towards the design of LWIR polymers offers the promise of expanding the scope of materials for this application and the prospect for developing an understanding of the nature of LWIR transparency in certain plastics.

1.5 Conclusion

The role of IR imaging technology in military, consumer and industrial applications, while already significant, will only continue to increase in the future. Consequently, there exists an opportunity, and demand, for development of new IR transparent materials. Specifically, these materials should be low cost and easier to work with than conventionally used IR materials (inorganic semiconductors) which has historically inflated the price of IR imaging packages. These new materials should also exhibit high refractive indices to accommodate imaging systems with small footprints. Organic plastics can certainly be produced on a large scale at low cost and are more amenable to solution and low temperature melt processing conditions, but typically exhibit low refractive indices and
poor IR transparency. In an effort to reconcile this discrepancy, one emerging solution has been the development of certain inorganic/organic hybrid materials that are processable, but also exhibit the desirable optical properties previously mentioned. These new hybrid plastics (CHIPs) are the result of new chemistries developed to accommodate high loadings of inorganic comonomers into this class of materials. The initial reports on these materials have made it clear that the organic comonomer employed plays a critical role in modulating not only important thermomechanical properties, but also IR transparency. Given the infancy of the field of IR transparent polymers, there exists tremendous opportunity for further development of new IR materials based on the development of new organic monomers and expanding the scope of inorganic comonomers. Consequently, advances in this field can most efficiently be driven by close collaboration among the various scientific communities concerned, namely the optical and chemical sciences, and specifically the organic, materials and computational disciplines.
CHAPTER 2 - HIGH REFRACTIVE INDEX COPOLYMERS WITH IMPROVED THERMOMECHANICAL PROPERTIES VIA THE INVERSE VULCANIZATION OF SULFUR AND 1,3,5-TRI-ISOPROPENYLBENZENE

With contributions from Ngoc A. Nguyen (thermomechanical and rheological characterization), Laura E. Anderson (synthetic support), Soha Namnabat (optical characterization), Edward A. LaVilla (optical characterization and imaging experiments), Sasaan A. Showghi (laser damage studies), Philip T. Dirlam (synthetic support), Clay B. Arrington (synthetic support), Michael S. Manchester (synthetic support), Jim Schwiegerling (support of Edward A. LaVilla), Richard S. Glass (synthetic design), Robert A. Norwood (support of Soha Namnabat and data interpretation), Michael E. Mackay (support of Ngoc A. Nguyen and data interpretation), and Jeffrey Pyun (co-author and PI)

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2.1 Introduction

The development of wholly polymeric IR transmitting materials has historically been a tremendous technical challenge, since most polymers intrinsically possess low refractive indices and strongly absorb in the IR spectral window due to the presence of carbon-hydrogen, or heteroatom-hydrogen covalent bonds. While inorganic IR transmitting materials have been demonstrated to exhibit very high refractive indices (n = 2-5)\textsuperscript{79} and high transparency, these materials are relatively expensive and require high processing temperatures for device component fabrication. Hence, the development of polymeric IR transmitting materials is highly desirable from a melt, or solution processing standpoint to enable the fabrication of complex, or unique device architectures for IR and other photonic applications. However, it has been a longstanding challenge to increase the refractive index of organic polymeric materials, which typically exhibit low values (n ~ 1.5-1.6)\textsuperscript{79}. While the preparation of high n-polymers, or polymer composites has been conducted, these
materials typically exhibit high $n$-values with concomitant optical absorption, or exhibit high optical losses$^{80-82}$. Hence, there remains a strong need for new polymeric materials that exhibit very high refractive indices ($n > 1.75$), low optical losses and possess high IR transparency.

We have previously developed a new class of ultra-high refractive index, IR transmitting materials that possessed a high sulfur content (50-90 wt% sulfur) through a process termed *inverse vulcanization* of elemental sulfur ($S_8$) with 1,3-di-isopropenylbenzene (DIB)$^{47,83,84}$; this polymerization and other related processes has also been used by others to prepare a broad range of high sulfur content polymers$^{85-88}$. Poly(sulfur-random-(1,3-di-isopropenyl-benzene))(poly(S-$r$-DIB)) materials exhibited one of the highest refractive indices reported for a polymeric material ($n = 1.75$ to 1.85 from 600-1500 nm) and was sufficiently IR transparent to enable use in IR thermal imaging.

While the incorporation of a high content of S-S bonds was the key to imparting the desirable optical properties into poly(S-$r$-DIB) for IR applications, these polysulfide units also intrinsically lower the glass transition temperature of these copolymer materials ($T_g$ of poly(S-$r$-DIB) range from $T = 43.5$-$49.2 ^\circ C$)$^{83}$.

Herein, we report on the synthesis of a novel IR optical polymer via the inverse vulcanization of sulfur with a trifunctional isopropenyl comonomer, based on 1,3,5-trisopropenylbenzene (TIB). This approached afforded a high sulfur content copolymer possessing high refractive index and high IR transparency with improved thermomechanical properties. Rheological characterization of poly(sulfur-random-(1,3,5-trisopropenylbenzene) (poly(S-$r$-TIB) confirmed the formation of highly crosslinked polymer networks, along with a dramatic increase of the copolymer glass transition
temperature ($T_g$ from 67.1-130 °C) over a broad window of TIB composition (30-50 wt%). The properties of this new sulfur copolymer thermoset are a significant improvement over those from our earlier (poly(S-$r$-DIB) copolymer which possesses relatively lower $T_g$’s ($T = 43.5-49.2$ °C). A useful feature of these sulfur crosslinked thermosets is the presence of S-S units in the copolymer, which allowed for self-healing, or thermal reprocessing of these materials making them a unique addition to the expanding field of dynamic covalent polymers\textsuperscript{89–94}. Furthermore, the incorporation of a high content of S-S bonds in poly(S-$r$-TIB) enable both retention of high refractive indices ($1.721 \leq n \leq 1.836$ from 633-1554 nm) and retention of IR transparency in the 3-5 micron spectral regime required for IR thermal imaging. A key milestone in this research would be to prepare sulfur copolymers possessing comparable thermomechanical properties to those of known optical polymers, such as, poly(methyl methacrylate).

2.2 Results and Discussion

The key step in the synthesis of the poly(S-$r$-TIB) copolymers was driven by the need to discover new comonomers for the inverse vulcanization of S\textsubscript{8} that possessed an average functionality of at least three vinylic groups ($f \geq 3$) and was miscible with molten sulfur. Hence, a logical progression from our initial success with the inverse vulcanization of S\textsubscript{8} with DIB was the use of TIB, which was designed to possess an additional vinylic group relative to DIB to afford more highly crosslinked materials and would be miscible in liquid sulfur to enable high monomer conversions. Since, TIB was not commercially available, the target comonomer was prepared in multi-gram quantities per batch via a Suzuki cross
coupling strategy using a 1,3,5-tribromobenzene core with isopropenyl boronic acid pinacol ester (Figure 2.1a), which proceeded in reasonable yields, (80%).

With TIB in hand, inverse vulcanizations at $T = 180 \, ^\circ C$ in liquid sulfur were initially conducted in glass vials in a thermostated oil bath. TIB comonomer feed ratios of 30-wt% and 50-wt% were investigated and copolymerizations with liquid sulfur were observed to rapidly vitrify within ten minutes and afforded red, transparent glassy materials when allowed to cool to room temperature (Figure 2.1b). We observed that poly(S-$r$-TIB) with both 30-wt% and 50-wt% organic comonomer (herein referred to as poly(S-$r$-TIB$_{30}$) and poly(S-$r$-TIB$_{50}$) were completely insoluble in organic solvents, such as tetrahydrofuran (THF) and toluene. This is in stark contrast to poly(S-$r$-DIB) copolymers that were partially soluble in these solvents (for the 30wt% sulfur content copolymer) and found to be completely soluble at higher DIB compositions (50-wt% DIB) when prepared under similar conditions. Hence, from these vast solubility differences, it was inferred that the poly(S-$r$-TIB) copolymers were heavily crosslinked in comparison to their poly(S-$r$-DIB) analogues as a direct consequence of the higher functionality of the TIB comonomer. In order to quantitatively confirm this, dynamic rheological frequency sweeps (see Appendix A) were conducted on the poly(S-$r$-TIB) copolymers that prove they are in fact more heavily crosslinked than poly(S-$r$-DIB) copolymers. It was also observed that reaction mixtures from the inverse vulcanization of $S_8$ and TIB could directly be used (as was the case of $S_8$ & DIB) as prepolymer resins for melt processing into PDMS replicas to prepare molded discs and windows of poly(S-$r$-TIB) (Figure 2.1c). The refractive indices of the resulting free standing films of poly(S-$r$-TIB) were obtained by prism coupled ellipsometry and were observed to retain the very high refractive
**Figure 2.1:** 

(a) Synthesis of 1,3,5-Trisopropenylbenzene (TIB)

(b) Inverse Vulcanization of di and tri Functional Comonomers

(c) Melt Processing of Poly(S-r-TIB) Copolymer Resins

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**Figure 2.1:** a) Synthesis of TIB; b) inverse vulcanization of DIB, or TIB with S\(_8\) to afford poly(S-r-DIB) or poly(S-r-TIB) copolymers; c) melt processing of poly(S-r-TIB) copolymer resins with PDMS replicas to form molded poly(S-r-TIB).

Index \(n = 1.836\) to 1.792 from 633nm to 1554 nm (see Appendix A) as observed for poly(S-r-DIB) \(n = 1.856\) to 1.810 at similar compositions\(^47\). Furthermore, the poly(S-r-TIB) copolymers remained transmissive in the near IR regime (see Appendix A) indicating that these materials are in fact a viable replacement for DIB based sulfur copolymers as high refractive index, IR transparent materials.
Figure 2.2 **(a)** Plot of storage modulus (G’) as a function of temperature performed with a 3 °C min⁻¹ ramp rate and oscillation frequency of 6.28 rad/s for copolymers poly(S-r-DIB) and poly(S-r-TIB) of varying compositions; **(b)** plot of tan δ as a function of temperature for the same copolymers, obtained under the same conditions as the storage modulus plots.

Differences in the thermomechanical properties of poly(S-r-TIB) and poly(S-r-DIB) copolymers, as a result of the increased crosslink density, were interrogated by isochronal oscillatory shear measurements conducted at T = 30 °C to 180 °C and 1 Hz (**Figure 2.2a**).
We observed a progressive increase in the glass transition of poly(S-\textit{r}-DIB$_{30}$) and poly(S-\textit{r}-DIB$_{50}$) at $T \leq 30$ °C and 55.4 °C, respectively, which were reasonably consistent with our earlier DMA analyses of poly(S-\textit{r}-DIB) copolymers$^8$. However, for poly(S-\textit{r}-TIB$_{30}$) and poly(S-\textit{r}-TIB$_{50}$), we observed a considerably wider range of accessible $T_g$ values ranging from $T = 67.1$ °C to 130 °C over the same copolymer compositions, which is markedly apparent in tan δ peaks of these measurements (Figure 2.2b). DSC measurements (Table 2.1) were similarly conducted and corroborated the dynamic rheological (temperature ramp) measurements. Fox and Loshaek$^9$ demonstrated for an infinite molecular weight polymer (Equation 2.1)

\begin{equation}
T_g = T_g^\infty + K_i \rho_x
\end{equation}

where $T_g^\infty$ is the glass transition temperature for an infinite molecular weight polymer, $\rho_x$, is the degree of crosslinking and $K_i$ is a constant specific to a given system (we will use $K_{DIB}$ for the DIB system and $K_{TIB}$ for the TIB). Firstly, it is clear the TIB system promoted a larger $T_g$ at a given concentration indicative of more crosslinks. Secondly, we calculated $K_i$ for these two systems ($K_{DIB} = 1.3$ and $K_{TIB} = 3.2$) using the DSC data; and it is clearly seen that the TIB system was a much more effective crosslinker. The fact that the values of $T_g$ did not agree between the two measurement techniques was merely reflective of the different temperature ramp rates and was of little concern since we found $K_{TIB} = 3.1$ derived the rheological data (Figure 2.2b) was in good agreement with the DSC value. The temperature ramps could not be operated below room temperature limiting its effectiveness for the 30 wt% DIB system. Nevertheless, the remarkable difference in the $T_g$ of the poly(S-\textit{r}-TIB) due to the higher crosslinking density of this material, afforded for the first
time, a high sulfur content, high refractive index material (with n > 1.75) with a $T_g$ > 100 °C.

To confirm the presence of dynamic S-S units in poly(S-r-TIB) copolymers (see Appendix A) in-situ rheological monitoring of shear induced S-S bond scission at varying strain rates was conducted above $T_g$ (see Appendix A for comparative rheology of poly(S-r-TIB vs poly(S-r-DIB)). Mechanical tensile testing of poly(S-r-DIB) and poly(S-r-TIB) copolymers were also conducted but were found to afford largely similar mechanical strength and toughness (see Appendix A).

Table 2.1 Glass transition temperatures determined by differential scanning calorimetry ($T_g$(DSC)) and dynamic rheological characterization (oscillatory sShear) ($T_g$(OS)) as a function of comonomer concentration

<table>
<thead>
<tr>
<th>Comonomer Content</th>
<th>$T_g$ (DSC) (°C)</th>
<th>$T_g$ (OS) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIB 30 wt%</td>
<td>9.9</td>
<td>-</td>
</tr>
<tr>
<td>DIB 50 wt%</td>
<td>36.5</td>
<td>53</td>
</tr>
<tr>
<td>TIB 30 wt%</td>
<td>51.2</td>
<td>68</td>
</tr>
<tr>
<td>TIB 50 wt%</td>
<td>116</td>
<td>130</td>
</tr>
</tbody>
</table>

To further demonstrate the benefits of poly(S-r-TIB) copolymers for optical applications, flat panel discs were fabricated via melt processing and subjected to irradiation with a laser to assess the dimensional stability of these materials. A comparative analysis of poly(S-r-DIB$_{30}$) and poly(S-r-TIB$_{50}$) was conducted by direct laser diode irradiation at 405nm (a wavelength of high absorption in both poly(S-r-TIB) (see Appendix A) and poly(S-r-DIB)$. Flat panel discs of both sulfur copolymers (25 mm x 1 mm
Figure 2.3: Dark field optical microscopy images of pristine a) poly(S-r-DIB$_{30}$) and b) poly(S-r-TIB$_{50}$) 1 mm flat panel discs; c) a 405 nm laser diode was set up to irradiate both sulfur copolymers with an optical output power of 7 mW for 5 seconds; d) digital image of poly(S-r-DIB) after irradiation, e) dark field optical microscopy image of poly(S-r-DIB$_{30}$) panel after irradiation (35 mJ) revealing damaged region (white circle) commensurate with spot size of laser, f) dark field microscopy image and digital image g) of poly(S-r-TIB$_{50}$) panel showing no damage after irradiation; h) digital image of USAF target; images captured with a mid-IR camera, operating at 3-5 μm, of a USAF target, transparent at 3-4 μm: i) IR thermal image of USAF target imaged thru lens mount without sulfur copolymer panel, j) IR thermal image through poly(S-r-TIB$_{30}$) panel (1 mm thick, 25 mm wide), and k) IR thermal image through poly(S-r-TIB$_{50}$) panel (1 mm thick, 25 mm wide)
samples of poly(S-r-DIB) and poly(S-r-TIB)) were fabricated and subjected to irradiation with a focused laser beam at 405 nm (on each a ~100 μm diameter spot was exposed to 35 mJ with a focused laser beam, **Figure 2.3c**). After irradiation for 5 seconds, significant laser induced heating and damage was observed using dark field optical microscopy of the poly(S-r-DIB) sample, which was attributed to the lower T_g of the material (**Figure 2.3 d,e**). Conversely, under identical conditions, the poly(S-r-TIB) disc remained undamaged due to the enhanced thermomechanical stability of the material (**Figure 2.3 f, g**).

Finally, to confirm that poly(S-r-TIB) copolymers were sufficiently transparent for IR applications, mid-IR (3-5 μm) imaging experiments of a USAF target (**Figure 2.3 h**) were conducted thru poly(S-r-TIB_{30}) and poly(S-r-TIB_{50}) flat panel discs (1 mm thick, 25 mm diameter). In these experiments, a lens mount bearing the sulfur copolymer panel was placed in front of the IR camera to conduct these imaging experiments. Control imaging of the USAF target without a sulfur copolymer panel thru the lens mount (as seen as the yellow circular feature) was performed as a reference (**Figure 2.3 i**). For both poly(S-r-TIB_{30}) (**Figure 2.3 j**) and poly(S-r-TIB_{50}) (**Figure 2.3 k**) panels, high quality imaging was achieved, which confirmed that these materials retained the desirable IR optical properties required for imaging, while possessing improved thermomechanical stability.

### 2.3 Conclusion

In conclusion, we have demonstrated the preparation of high refractive index sulfur copolymers via the inverse vulcanization of sulfur with a new comonomer, 1,3,5-tri-isopropenylbenzene (TIB) to afford high crosslinked polymer networks. The thermal
properties of these new poly(S-r-TIB) copolymers were dramatically improved and were
tuned to exhibit $T_g$’s above 100°C, which is now comparable to those of widely used optical
polymers, such as, poly(methyl methacrylate) (PMMA). Furthermore, we demonstrate the
ability to use these sulfur copolymers as novel transmitting materials for IR thermal
imaging.
CHAPTER 3 - CHALCOGENIDE HYBRID INORGANIC-ORGANIC POLYMERS: ULTRAHIGH REFRACTIVE INDEX POLYMERS FOR INFRARED IMAGING

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3.1 Introduction

The development of synthetic polymers as transmissive materials for use in lenses, windows and integrated optics for IR imaging technologies is an emerging area for a number of defense, consumer, light imaging and ranging (LIDAR) applications. To date, inorganic materials, such as germanium semiconductors, or amorphous chalcogenide glasses (ChG’s) have been utilized as the transmissive material for IR imaging devices. ChG’s possess outstanding properties for mid-IR imaging (i.e., very high refractive index \(n \geq 2.0\), and high IR transparency)\(^{26,96,97}\); however, these materials are expensive, toxic and require very high temperatures for synthesis and fabrication (\(T \geq 300-1000 ^\circ C\)).

ChG’s are formally a class of amorphous semiconductors composed of Group 6 chalcogens (e.g., S, Se, Te) that are covalently bound to a Group 3,4, or 5 atom (e.g., Ga, Sb, As, Ge, P) to form crosslinked polymer network solids. In the synthesis of ChG’s...
elemental sulfur (S8) and/or selenium are mixed with other metal salts in a vacuum sealed glass reactor and heated to highly elevated temperatures (T ~ 1000 °C). We have recently developed a new class of ultra-high refractive index polymers derived directly from elemental chalcogenide chemical feedstocks that are intriguing transmissive material candidates for IR thermal imaging. The introduction of elemental forms of sulfur and selenium are highly desirable as a route to prepare high refractive index materials (n_sulfur ~ 2.0; n_selenium ~ 2.74). We previously developed a new synthetic methodology, termed, inverse vulcanization that enabled the direct use of molten elemental sulfur as the reaction medium and comonomer in a bulk, free radical copolymerization with vinylic and other comonomers to form high sulfur content materials.

Polymers derived from the inverse vulcanization process are macromolecular analogs to ChG’s, where the Group 3,4, or 5 atomic unit in these network solids were replaced with an organic comonomer moiety. These high sulfur content materials are the first examples of chalcogenide hybrid organic/inorganic polymers (CHIPs), which we have demonstrated to exhibit among the highest refractive indices of any synthetic polymeric material (n ~1.75-1.85), excellent optical transparency and suitability for midwave-IR thermal imaging. The replacement of inorganic Group 3,4, or 5 atomic units with organic comonomer units, such as DIB, has been shown to lower the glass transition of these materials (T_g ~ 35-120 °C), but consequently is more readily amenable to conventional polymer processing methods via solution, or melt processing relative to ChG’s. While the inclusion of elemental sulfur to CHIPs has been demonstrated, the incorporation of selenium atoms as main chain units into a (co)polymer backbone is profoundly more challenging. An elegant example of the incorporation of Se units into the back bone of a
polymer was demonstrated by Zhu et al. via self-condensing vinyl polymerization of styrenic selenide inimers that afforded high refractive index \((n = 1.713 \text{ at } 486 \text{ nm})\) low loss materials\(^{104,105}\).

Herein, we report on the preparation of ultra-high refractive index CHIPs via the inverse vulcanization process, where we demonstrate for the first time controllable incorporation of Se-units using grey selenium precursors by simple “cracking” and solubilization with liquid sulfur radicals at dramatically reduced temperatures \((T = 160 ^\circ \text{C})\). The one-pot synthesis of soluble poly(sulfur-random-selenium-random-(1,3-di-isopropenylbenzene)) \((\text{poly(S-r-Se-r-DIB})\) terpolymers was accomplished without the need for synthesis nor purification of any precursor materials. Independent of our efforts, Boyd et al. recently reported on the synthesis of this terpolymer, which the authors refer to as \textit{ORMOCHALCs}\(^{55}\). We describe a streamlined synthesis that reports for the first time methods to increase the mass loading of selenium into CHIPs that enable a profound increase in refractive index \((n)\) of above \(n = 2.0\) from 633 to 1554 nm, which is the highest RI of any synthetic polymer that has been reported. These materials were found to also retain high transmission in the SWIR and MWIR \((1-2.5 \text{ and } 3-5 \mu \text{m respectively})\) allowing for high quality IR imaging of human subjects.

3.2 Results and Discussion

The key challenge in this copolymerization was the cracking and solubilization of grey selenium to enable copolymerization with organic vinylic comonomers. Unlike \(S_8\) which exists in its monomeric form until the floor temperature \((T_f \sim 159 ^\circ \text{C})\), monomeric elemental selenium \((\text{Se}_8, \text{“Red selenium”})\) readily forms polymeric selenium (“Grey
selenium”) in the solid state\textsuperscript{54,106,107}. Grey selenium is stable under most conditions and melts at elevated temperatures, but consists of a mixture of cyclic and polymeric allotropes and is highly immiscible with the vast majority of organic solvents and vinylic comonomers.

**Figure 3.1:** a) Selenium grey exists as a linear polymer when monomeric Se\textsubscript{8} (red selenium) undergoes ROP in the solid state at a wide range of temperatures beneath its T\textsubscript{m} b) ROP schematic and images of liquid sulfur below and above T\textsubscript{f} c) dilution studies of mixtures of sulfur and grey selenium above and below the T\textsubscript{f} of S\textsubscript{8} d) synthesis of poly(S-r-Se-r-DIB) terpolymer CHIPS via inverse vulcanization

(in our hands). The incorporation of selenium into ChG’s has been reported by mixing the neat reagents and heating to highly elevated temperatures (T ~ 900 °C)\textsuperscript{108,109}. 

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Conversely, the copolymerization of elemental sulfur and selenium was reported to occur over a period of hours at $T = 250$ to $300 \, ^\circ C^{110}$, or within minutes under vacuum at $T = 1000 \, ^\circ C^{111}$.

The surprising result from this investigation was that reactive liquid sulfur media was able to react with grey selenium to enable inverse vulcanization with DIB at reduced temperatures ($T = 160 \, ^\circ C$). In this process, liquid sulfur radical species were proposed to create $S$-$Se$ bonds and copolymerize with DIB. We observed that these \textit{in situ} generated mixed chalcogens (Figure 3.1 c,d) were in fact soluble in hot 1,2-dichlorobenzene (DCB), or DIB to form colored solutions, in comparison to grey selenium which remained insoluble when mixed directly with hot DCB or mixed with liquid sulfur at $T = 120 \, ^\circ C$ (which is well below the $T_f$ of sulfur; Figure 3.1 c)). Using this approach, mixtures with up to 42-wt% of grey selenium feed ratios were achieved to form darkly colored, homogeneous solutions at $T = 160 \, ^\circ C$. While the highly colored nature of the medium required special visual inspection to determine the appropriate time to inject DIB (see Appendix B), this inverse vulcanization approach enabled the preparation of the CHIPs terpolymers in a single step using commercial reagents without the need for rigorous purification.

A notable attractive feature of the poly(S-$r$-Se-$r$-DIB) terpolymer CHIPs was the improved solubility of these materials, over previously prepared CHIPs materials, at much lower organic content (DIB 30-wt%) in conventional organic solvents (e.g., THF, toluene, haloarenes). This improved solubility of the terpolymer prepared using comonomer feeds of 50-wt% $S$, 20-wt% $Se$, 30-wt% DIB (poly(S$_{50}$-$r$-Se$_{20}$-$r$-DIB$_{30}$) enabled conventional
purification techniques, such as silica gel chromatography, to be used in order to elucidate the nature and quantity of trace, unreacted starting material/side products of the reaction (see Appendix B). The presence of a volatile species was noted by thermogravimetric analysis and could be removed either after silica gel column chromatography or directly from the crude material by sublimation at 160 °C for 2 hours with a dry ice/acetone trap (see Appendix B). Elemental analysis confirmed that the Se (17.2 %), S (33.5%), C (43.6%) and H (5.6%) content of (poly(S_{50-r-Se_{20-r-DIB}_{30}}) materials purified by column chromatography, or via sublimation (see Appendix B) matched fairly closely with the target comonomer feed ratios, which confirmed that efficient Se incorporation into the terpolymer was achieved, along with a negligible loss of volatile selenium sulfide sublimates. Size exclusion chromatography was also performed on the terpolymers and revealed the presence of a similar mixture of oligomeric species (M_n SEC = 1,100 g/mol, M_w/M_n = 1.8) to that of SECs of corresponding sulfur-DIB copolymers.

Structural analysis via solution NMR spectroscopy (^{1}H, ^{13}C, ^{77}Se) and thermal analysis (differential scanning calorimetry, (DSC) and dynamic mechanical analysis (DMA)), confirmed the formation of statistical terpolymers (see Appendix B). Most notably, ^{77}Se NMR spectroscopy of poly(S_{50-r-Se_{20-r-DIB}_{30}}) revealed the presence of three resonances at 695, 645, 625 ppm (see Appendix B for further discussion), which were indicative of Se-S bonds and the notable absence of Se-C bonds that would be significantly shifted upfield (^{77}Se NMR diphenyl diselenide (CDCl_{3}) δ: 461 ppm). Thermomechanical characterization of poly(S_{50-r-Se_{20-r-DIB}_{30}}) confirmed the formation of a thermoplastic statistical terpolymer as noted by a single glass transition temperature (T_g = 27 °C) from modulated DSC. Dynamic mechanical analysis (DMA) of this terpolymer indicated a
higher glass transition temperature (Tg = 51 °C) (Figure 3.2 a) which was consistent with our earlier findings with poly(S-r-DIB), where DSC determined Tg’s were under-estimated\textsuperscript{47}.

**Figure 3.2:** a) Tan δ plot of poly(S\textsubscript{50}-r-Se\textsubscript{20}-r-DIB\textsubscript{30}) after sublimation (obtained at an applied frequency of 1 Hz and 3 °C min\textsuperscript{−1} ramp rate) and modulated DSC thermogram of the same polymer at a ramp rate of 2 °C min\textsuperscript{−1} b) refractive indices of poly(S-r-Se-r-DIB) terpolymers of varying composition vs wavelength.
The enhanced solubility of the CHIPs materials allowed for solution processing (spin coating) of films less than 10 μm thick on glass substrates for thin film optical characterization, while thicker samples were prepared by pouring prepolymer resins into PDMS replicas and cured in an oven to facilitate further conversion. Free standing films of the CHIPs material were analyzed by prism coupling measurements (Metricon™ prism coupler) in order to determine refractive indices and were found to range from $n = 1.91$ to $1.96$ in the spectral window of 1554 to 633 nm for the most soluble composition, poly(S$_{50}$-r-Se$_{20}$-r-DIB$_{30}$); this is a considerable increase in refractive index from the corresponding poly(S$_{70}$-r-DIB$_{30}$) copolymer that had a refractive index between $n = 1.79$ to $1.83$ over the same spectral range. However, the most striking result was evidenced in the poly(S$_{42}$-r-Se$_{42}$-r-DIB$_{16}$) composition that attained a refractive index from $n = 2.035$ to $2.140$, again over the same wavelength range (Figure 3.2b). Optical absorbance spectroscopy of poly(S$_{50}$-r-Se$_{20}$-r-DIB$_{30}$) was also performed from 350 to 2500 nm and were shown to retain the same high transparency relative to that of corresponding sulfur-DIB compositions at similar thicknesses. This was also true for the FTIR spectra of the CHIPs materials in the SWIR and MWIR regimes, and while the CHIPs material retained the same characteristic vibrational mode at 3.3 μm as is found in sulfur-DIB, it was also similarly transparent over much of the rest of the 3-5 μm range.

To further validate the optical transparency of poly(S$_{50}$-r-Se$_{20}$-r-DIB$_{30}$) materials, free standing windows (1 mm thick) were fabricated via melt processing and applied for imaging with a mid-IR camera. High quality imaging was achieved of a USAF target in the mid IR (3-5 μm) thru a poly(S$_{50}$-r-Se$_{20}$-r-DIB$_{30}$) window under ambient conditions. The high transparency observed from poly(S$_{50}$-r-Se$_{20}$-r-DIB$_{30}$) windows prepared
directly via melt processing indicated that the residual unreacted chalcogenides in the terpolymer film did not impede mid-IR imaging. Furthermore, successful imaging of the

![Image](image_url)

**Figure 3.3:** a) digital image of a USAF target (purchased from Edmund Optics); images captured with a mid-IR camera, operating at 3-5 μm, through a poly(S$_{50}$-r-Se$_{20}$-r-DIB$_{30}$) panel (1 mm thick, 25 mm wide) of b) a USAF target, transparent at 3-4 μm, c) IR thermal image of human arm and d) higher resolution image of human forearm.

right (fore)arm of a human subject was achieved with detailed resolution of the appendage at lower magnification with low attenuation. At higher magnification, excellent resolution of forearm vasculature under these imaging conditions was achieved with distinctive visualization of subcutaneous cephalic and basilica veins as indicated by the higher contrast of the blood vessel network (Figure 3.3 d). The high clarity of these blood vessels from this technique was unexpected and points to the possibility of future uses of these methods
to complement ultrasound imaging techniques which is currently the preferred method employed for diagnostic interrogation of human vasculature.

3.3 Conclusion

In conclusion, we demonstrate the ability to prepare ultra-high refractive index CHIPS via the inverse vulcanization process which can be used as transmissive materials for mid-IR thermal imaging. This material exhibited the highest refractive index of any synthetic polymer where the terpolymer composition directly enables structure-property control in these materials.
4.1 Introduction

The ability to control the propagation of light with a high degree of precision is integral for the fabrication of various optical devices that function in both the visible and infrared (IR) spectrum, such as sensors and light imaging and ranging (LIDAR) systems. One of the most basic optical constructs that allows for such control are Distributed Bragg Reflectors (DBRs) or, more broadly, 1D photonic crystals (1-D PC’s). These reflective films are composed of alternating layers of disparate dielectric materials whose periodicities and differences in refractive index determines, respectively, the wavelength and magnitude of light reflected. The tunability and selectivity of these systems make them uniquely suited towards applications where low power loss light confinement is ideal, such as in microcavities and solar cells. DBR fabrication has been widely conducted via vapor deposition of metals or metal oxides due to the high uniformity of thin films and the high refractive index that allows for high reflectivity to be achieved for a low number of
layers. Hence, fabrication of Bragg mirrors has been conducted using high refractive index

\( n \) metal oxides \((\text{TiO}_2 \ (n = 2.48))^{114}\), various semiconductors\(^{115}\) and chalcogens (tellurium

\( n = 4.80)^{116}\) in conjunction with low \( n \) materials like \( \text{SiO}_2 \ (n = 1.44)^{117} \) to generate high
refractive index contrast \((\Delta n = 0.5 – 3.0)\) and enable high reflectivity for only a few layer
pairs. However, the fabrication of all-polymeric, highly reflective 1D-PCs via solution
processing remains an important challenge, particularly in the IR spectrum.

An important technological challenge that remains for the fabrication of highly
reflective, thin, wholly polymeric DBRs is the creation of high refractive index contrast
\((\Delta n)\) between the polymer layers. The vast majority of engineering plastics typically
exhibit refractive indices in the range of \( n = 1.45 \) to 1.65 which ultimately limits the
refractive index contrast that can be generated for polymeric DBRs. The limitations of low
\( \Delta n \) with conventional synthetic polymers has led to the development of polymer chemistry
and engineering solutions that enable a large number of layers to be rapidly processed to
create high reflectivity films. The engineering challenges associated with fabrication of all
polymeric DBRs with low \( \Delta n \) was demonstrated in the seminal work of Miyamoto et. al.\(^6\)
requiring a custom built, automated spin coater to fabricate 170 alternating layers of
polystyrene \((n = 1.582)\) and polyvinyl alcohol \((n = 1.527)\) \((\Delta n = 0.055)\) in order to achieve
nearly 100% reflectivity at \(~600\) nm. When such a large number of layers is necessary, spin
coating processes for DBRs becomes more challenging as control over thin films (greater
than \(500\) nm) becomes difficult to achieve with high fidelity\(^{118}\) and has been shown to lead
to changes in the peak reflectance of the DBR\(^{119}\). Melt extrusion of multilayer polymer
films for optical applications has been extensively developed (both industrially and
academically) to enable fabrication of highly reflective all polymer DBRs using

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commercial thermoplastic materials. Self-assembly of block copolymers (BCPs) into microphase separated thin films with lamellae morphologies were fabricated by Thomas et al. in order to process DBRs as a route to preparing DBRs, as hundreds of layers can be assembled all at once. This concept of BCP self-assembly was revisited by Grubbs and Atwater by the use of bottle brush block copolymers to create microphase separated films exhibiting periodicities of the lamellar domains that allowed for reflection further into the near-IR (NIR). The selective inclusion of high $n$ metal oxide, semiconductor, and even noble metal nanoparticles as additives in self assembled DBRs has also been explored in attempts to increase the dielectric contrast of each layer. However, the concept of using solution processable polymers possessing very high $n$ has not been widely explored.

Inorganic porous metal oxide 1-D PCs have been fabricated via templated solution processing multi-layers, along with spin coating of discrete nanoparticles to achieve high refractive index contrast and high reflectivity using only a few layers of alternating dielectric materials. However, technical challenges persist to process mechanically robust DBRs with these inorganic materials, particularly for larger scale production using solution processing methods.

Conversely, wholly polymeric DBR systems are inherently more amenable to large scale roll-to-roll solution processing methods but remains limited by access to inexpensive, high refractive index polymers to achieve high refractive index contrast. Early reports on such systems used commercially available organic polymers based on cellulose acetate and poly(N-vinylcarbazole) to fabricate polymer DBRs with $\Delta n = 0.2$. In order to further
**Figure 4.1:** General scheme for the fabrication of highly reflective all polymer Bragg reflectors from CHIPS materials that possess tunable reflectance across the NIR and SWIR (1.0-2.0 μm)

Increase the refractive index contrast in polymeric DBRs, Comoretto and Voit et al. prepared a novel hyperbranched polyvinylsulfide \((n = 1.7)\) that allowed for a higher \(\Delta n = 0.3^{69}\). Inclusion of inorganic nanoparticles into spun coat layers of polymer composites have also been demonstrated by both Comoretto\(^{60,126}\) and Watkins\(^{127,128}\), where \(\Delta n = 0.34\) in DBRs with sufficiently high nanoparticle loadings \((70\%)^{127}\). These seminal reports point to the potential to fabricate reflective, thin polymeric DBRs using solution processing methods, however, the ability to create high refractive index contrasts comparable to the more reflective and thinner inorganic systems, remains an important challenge.
Herein we report on the fabrication of wholly polymeric 1D photonic crystals via spin coating that achieve greater than 90% reflectance at just 22 layers. Furthermore, the peak reflectance was shown to be tunable across the NIR and SWIR spectrum. The key to preparing these devices was synthetic access to Chalcogenide Hybrid Inorganic/Organic Hybrid Polymers (CHIPs)\textsuperscript{47,129–131} containing a high content of selenium and sulfur units which imparted ultra-high refractive index to the polymer material ($n \leq 2.1$) that was also readily solution processable (Figure 4.1). Using CHIPs as the high index layer in an all polymer Bragg reflector, a high refractive index contrast ($\Delta n = 0.5$) was achieved when cellulose acetate was used as the low $n$ layer. This represents the highest index contrast generated for a wholly polymeric Bragg reflector and enabled the remarkable reflectivity observed in these solution processed thin films.

4.2 Results and Discussion

We have previously demonstrated the ability to synthesize high refractive index ($n = 1.75$-$1.85$) polymers by copolymerization of organic monomers with elemental sulfur via a process termed \textit{inverse vulcanization}.\textsuperscript{46,47} Most recently, we have expanded the scope of this polymerization technique to allow for incorporation of selenium atoms to prepare poly(sulfur-\textit{random}-selenium-\textit{random}-(1,3-di-isopropenyl-benzene) (poly(S-r-Se-r-DIB) terpolymers which has allowed access to solution and melt processable synthetic polymers with refractive indices up to $n = 2.1$.\textsuperscript{131} The \textit{inverse vulcanization} process utilizes the homolytic ring opening polymerization of sulfur above its floor temperature of 159 °C to generate sulfuryl radicals that readily copolymerize with both elemental selenium (i.e., grey polymeric Se) and organic, vinylic comonomers (See Appendix B for more detailed
information on poly(S-r-Se-r-DIB) molar mass and $T_g$.) An attractive feature of the inverse vulcanization process is the ability to modulate the refractive index and solubility of CHIPs materials by controlling the organic comonomer feed ratios. This unique feature of CHIPs materials is useful in the fabrication of Bragg reflectors as the ability to select the desired $n$, and hence refractive index contrast, allowing for control over the optical bandgap of the assembled Bragg reflector.

To demonstrate the advantage of fabricating polymer DBRs possessing high refractive index contrast ($\Delta n = 0.5$) computational simulations of the reflectivity (with Essential Macleod thin film software) were conducted on two different Bragg reflector systems: cellulose acetate ($n = 1.47$) with polycarbonate ($n = 1.57$) (a commonly used high refractive index polymer) and cellulose acetate paired with a CHIPs material ($n = 1.96$) (Figure 4.2a). These simulations revealed that only 10 bilayers are needed to achieve greater than 95% reflectance for DBRs possessing a $\Delta n = 0.5$ with CHIPs as the high index layer, while DBRs fabricated with the polycarbonate as the higher $n$ material only achieved less than ~50% reflectance at the same number of bilayers, illustrating the unique benefit CHIPs offer for the efficient fabrication of all polymer Bragg reflectors by spin coating. While DBRs with even higher refractive index contrasts can be generated by using inorganic materials, as has been previously discussed, the use of CHIPs enabled entry for the first time to inexpensive, polymeric, highly reflective films amenable to spin coating or solution processing (Figure 4.2b).

For the fabrication of CHIPs based Bragg reflectors, a modified method from Commerto and Voit et al. was employed, which demonstrated the use of aromatic solvents to dissolve the higher $n$ polymer paired with cellulose acetate solutions in
diacetone alcohol to deposit films with orthogonal solubilities. CHIPs materials were found to be soluble in aromatic solvents, particularly chlorobenzene and toluene. To this end, cellulose acetate was dissolved in diacetone alcohol and the CHIPs (poly(S_{50-r-Se_{20}-r-DIB_{30}}) terpolymer (where the subscripts denote feed ratios and whose composition was

Figure 4.2: a) Simulated reflectance of all polymer Bragg reflectors fabricated from CHIPs/cellulose acetate pairs (black line) and polycarbonate/cellulose acetate pairs (red line) and b) Schematic representation of the $\Delta n$ values that can be generated using various classes of materials.
selected for a balance between solubility and high refractive index) was dissolved in chlorobenzene and diluted with toluene as needed for the processing of thinner layers. Peak reflection ($\lambda$) in a Bragg reflector was tuned for a given system by varying the thicknesses of the two layers in the reflector according to Equation (4.1),

$$t_H = \frac{\lambda}{4n_H}, \quad t_L = \frac{\lambda}{4n_L}$$

where $t$ represents thickness in nm, $n$ is refractive index and $H$ and $L$ denote “high” and “low” index components, respectively. Using this equation, spin curves were assembled in order to target 1.0, 1.5, and 2.0 μm peak reflectivity (see Appendix C for details on fabrication of DBRs at each wavelength).

CHIPs based Bragg reflectors designed for reflection at 1.0, 1.5 and 2.0 microns were characterized via optical transmission and polarized incident angle resolved reflectance measurements to confirm the fabrication of uniformly coated films of high reflectivity at the targeted wavelengths. Reflectance (R) values for these CHIPs DBRs were initially determined via measurement of the optical transmission (T) from 350 to 3000 nm ($R = 100 - T$) which confirmed good agreement of the measured peak reflection wavelength (Figure 4.3) with targeted values from simulations (Figure 4.2a). More strikingly, reflectance values of greater than 90% were observed for these solution processed CHIPs DBRs at 22 layers (Figure 4.3) regardless of measurements in different spots of the film. Furthermore, reflectance values up to 97.5% were also demonstrated by the addition of 3 more bilayers (see Appendix C). Direct reflectance measurements of these CHIPs DBRs also confirmed similar levels of reflectivity (see Appendix C). To confirm the solution deposition of uniform films, transmission measurements of all three
**Figure 4.3:** Transmission spectra recorded in various spots on ~2 cm$^2$ Bragg reflectors with 22 layers each: a) 92.6% calculated reflectance at 2113 nm b) 93.8% calculated reflectance at 1450 nm c) 93.2% calculated reflectance at 998 nm

CHIPs DBRs were conducted in four different locations across the entire ~2 cm$^2$ film where neither the magnitude nor $\lambda_{\text{max}}$ of these reflections were discernibly different for any given region of the sample, indicating good control over device fabrication. To further interrogate the quality of the Bragg reflectors produced, each sample was analyzed by polarization and angular dependent reflectivity (see Appendix C). For all DBRs, a shift in peak reflectance to shorter wavelengths was observed for both s and p polarizations when the angle of
Figure 4.4: a) SEM image of a representative multi-layered film (15 layers) from CHIPs and cellulose acetate fabricated via spin coating and delaminated for imaging from a glass substrate with a PVA release layer designed for reflection at 2.0 μm. b) SEM image of a representative multi-layered film (25 layers) from CHIPs and cellulose acetate fabricated via spin coating and delaminated for imaging from a glass substrate designed for reflection at 2.0 μm; both Bragg reflectors had targeted thickness of 260 nm and 340 nm for the CHIPs and Cellulose Acetate layers respectively.
incidence was increased; whereas the photonic band gap (PBG) narrowed with increasing angle of incidence for \( p \) polarized light the PBG was largely unchanged with respect to the angle of incidence for \( s \) polarized light as expected for classic DBRs\(^{69}\). Additionally, when the angle of incidence was increased, peak reflectance was measured to decrease with \( p \) polarized light, while \( s \) polarized light resulted in marginally higher peak reflectance values and a concomitant decrease in background transmission, again, as would be expected by theory\(^{69}\).

The layered film morphology of the assembled Bragg reflectors was confirmed by cross-sectional SEM imaging of both freeze-fractured and focused ion beam (FIB) milled interfaces. Initial SEM imaging was conducted of freeze-fractured multi-layered (Appendix C for sample preparation and imaging conditions) which revealed the presence of well-defined, layered morphology of CHIPs and cellulose acetate films indicating the sequential spin coating protocol employed does not disrupt film integrity between layers. Furthermore, the domains were determined to have periodicities commensurate to the nominal thicknesses targeted, which indicated good control over device fabrication (Figure 4.4a). However, due to the potential for mechanical damage along these interfaces due to the freeze-fracture, FIB milling (with a gallium ion source) was also conducted of free standing Bragg reflectors to more accurately interrogate the homogeneity of thin film morphology at each interface from the spin coating process. Cross-sectional analysis of these FIB milled samples revealed the fabrication of highly uniform alternating layers of poly(S-\( r \)-Se-\( r \)-DIB) (CHIPs\( _{\text{average thickness}} = 273 \text{ nm} \pm 17 \text{ nm} \)) and cellulose acetate (Ave. Thickness = 309 nm \( \pm 21 \text{ nm} \)) further confirming film homogeneity from the spin coating process.
4.3 Conclusion

In conclusion, we have demonstrated for the first time, fabrication of highly reflective all polymer Bragg reflectors from the highest refractive index contrast attained in such a system ($\Delta n = 0.5$). This allowed for greater than 90% reflectance at just 22 layers of alternating CHIPS and cellulose acetate easily assembled via spin coating and tunability over the NIR and SWIR. This seminal demonstration highlights the advantages of using these high refractive index polymers for IR optical applications and opens new possibilities for the fabrication of ultra-thin IR reflective coatings.
CHAPTER 5 - INFRARED FINGERPRINT ENGINEERING: A MOLECULAR DESIGN APPROACH TO LONG WAVE INFRARED TRANSPARENCY WITH POLYMERIC MATERIALS

With support from Taeheon Lee (synthetic support and materials characterization), Kyle J. Carothers (synthetic support and materials characterization), Meghan Hamilton (computational FTIR spectra), Keith Coasey (thermomechanical characterization of materials), Wallace O. Parker Jr. (solid state NMR analysis) Laura E. Anderson (materials characterization), Liliana Ruiz Diaz (optical characterization), Ludovico Borhi (optical characterization), Michael E. Mackay (support of Keith Coasey), Kookheon Char (contributor of intellectual property), Richard S. Glass (synthetic design), Dennis L. Lichtenberger (computational FTIR spectra and data interpretation), Robert A. Norwood (support of Liliana Ruiz Diaz, contributor of intellectual property, data interpretation), Jeffrey Pyun (co-author and PI)

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5.1 Introduction

Infrared (IR) spectroscopy of organic molecules and polymers has long been used to characterize the presence of functional groups via the observation of vibronic excitations of bonds within the molecule. Vibronic excitations in the spectral range of 1500-500 cm\(^{-1}\) (~7-20 µm) of molecules has classically been referred to as the “fingerprint region”, since the collection of fundamental and non-fundamental vibrations were deemed to be unique (Figure 5.1a)\(^{132}\). The vast number of these coupled vibronic states that are often observed in the solid state have limited the use of synthetic polymers as transmissive materials for long wave (LWIR) Imaging. LWIR thermal imaging is a widely used “nite-vision" method that has importance for transportation, defense and emerging consumer markets for imaging at 7-14 µm (see Figure 5.1b, c for representative images), which overlaps with
the “IR Fingerprint Region”\textsuperscript{133}. Hence, the ability to molecularly design LWIR transparency into organic and hybrid polymers would have tremendous technological significance.

Figure 5.1: a) Stacked FTIR spectra of \(\sim 50\) µm thick free standing films of polyethylene, TOPAS (a cyclic olefin polymer), and poly(S\textsubscript{70}-DIB\textsubscript{30}) (subscripts denote feed ratios of each respective comonomer) with the LWIR regime highlighted b) optical image taken of a human and canine subject at night illuminated by car headlights c) same subjects in b taken with a consumer grade LWIR camera from KIA Telluride SUV
The current state of the art transmissive materials for IR applications are Ge and chalcogenide glasses, which exhibit outstanding refractive index \( n \sim 2.2-4 \) and IR transparency \( (T > 40\% \text{ 3-12 } \mu m) \)\textsuperscript{133}. However, these materials require greater processing requirements for the melt fabrication of lenses, windows and other optical elements. The use of polymeric IR transmissive optical elements would be attractive from a cost and processing standpoint, but have numerous complications that arise from the low IR transparency and much lower refractive index in the IR spectrum. Surprisingly, wholly aliphatic organic polymers, such as, polyethylene, or norbornene-olefinic copolymers (i.e., Topas\textsuperscript{®}) exhibit simplified fingerprint region spectra due to the presence of only (cyclic) aliphatic C-C, sp\(^3\) bonding and hence have been used as thin LWIR barrier coatings Figure 5.1a).\textsuperscript{134}

A major advance in this area was the creation of high sulfur and chalcogenide content polymers, termed, Chalcogenide Hybrid Inorganic/Organic Polymers (CHIPs), that possess high refractive indices \( n = 1.75 \text{ to } 2.1 \) and exhibit high mid wave-IR (MWIR, 3-5 \( \mu m \)) transpariencies due to the drastic reduction of C-H bonds in the material\textsuperscript{47,50,70,83,131}. This first generation CHIPs for MWIR imaging was poly(sulfur-random-(1,3-di-isopropenylbenzene)) (poly(S-r-DIB))\textsuperscript{8,15}. However, due to the presence of organic aromatic moieties, which contain C=C bonds, LWIR transparency and use for LWIR imaging applications remain elusive. A recent advance in the use of chalcogenide hybrid polymers for LWIR was recently demonstrated using aliphatic organotin comonomers units to fabricate bulk films with promising LWIR transparency\textsuperscript{135}. However, the concept
of precise molecular design of IR transparency in the IR fingerprint region remains a tremendous technical challenge, since nearly all organic molecules and materials absorb IR photons in this spectral window.

Herein, we report on a new methodology for the creation of polymeric materials with enhanced LWIR transparency exploiting density functional theory calculations as a predictive screening tool to simulate the IR spectra of candidate materials. Using this approach, high refractive index CHIPs with enhanced thermomechanical properties, improved processing characteristics and LWIR transparency were synthesized, which points to the viability of molecular design approaches for “IR Fingerprint Engineering”.

5.2 Results and Discussion

A major challenge in the design of LWIR transparent organic materials is identifying new structural motifs in organic molecules to mitigate IR absorption from 7-14 μm. To accelerate the discovery of new materials, density functional theory computations were used to simulate the IR spectra of candidate comonomers/polymers and quantitatively rank them according to their sum of integrated molar absorptivity values in the region of interest ($\varepsilon_{\text{int}}$). Smaller $\varepsilon_{\text{int}}$ values indicate higher transmission in this region. Fundamental frequencies and absorption intensities were calculated rapidly and accurately using the EDF2 functional which has been specifically designed for this purpose$^{136}$. Validation of this method for the systems in this study was accomplished by comparing the calculated spectra of the organic monomers to that of their respective gas-phase spectra (See Appendix D)$^{78}$; excellent agreement was found between calculated and experimental spectra of the organic monomers. Additionally, organic monomers were linked by trimeric
sulfur chains to serve as simple molecular models (MC) of new CHIPs (Figure 5.2). The calculated spectrum of MC 2 closely matched the experimental IR spectrum of poly(S$_{70}$-r-NBD$_{230}$) (See Appendix D). Analysis of simulated spectra showed that C=C bonds cause large intensity peaks within the LWIR region (See Appendix D) and that vibrations from the S–S chains do not contribute in this region. This prompted experimental design to focus on eliminating unsaturated and aromatics groups, while maintaining a rigid organic core with low dipole moment.

**Figure 5.2:** DFT calculated FTIR spectra of various sulfated dimers model compounds (MC) (MC 1, 2 and 3). % Transmission is shown for equal concentrations
Simulated IR spectra found that a polymer based on norbornadiene (NBD), MC 3, was an attractive candidate due to its large windows of high transmittance and low ε<sub>int</sub> value (Figure 5.2c). Furthermore, NBD reactivity toward thiyl radicals for thiol-ene chemistry was well-known. However, due to the volatility of NBD (BP ~ 89°C), these compounds could not be used with liquid sulfur in the inverse vulcanization process (T > 130°C). For this reason, a dimer of NBD, hereafter termed “NBD2”, was adopted as it eliminated the volatility issues associated with NBD while maintaining a favorable LWIR profile when modeled as MC 2 (Figure 5.2b). While vinyl<sup>137</sup> and ethylidene<sup>138</sup> functional norbornenes have been elegantly reported for us in inverse vulcanization; NBD and other larger bicyclic olefins have not been explored. Similarly, computational modeling of our first generation CHIPS, poly(S-r-DIB) was achieved by IR simulations of MC 1 based on α-methylstyrene, which confirmed the contributions of C=C bonds in this spectral window (Figure 5.2a).

The synthesis of the NBD2 monomer was prepared according to literature precedence<sup>139</sup> and was then subjected to inverse vulcanization<sup>46,85,102,140</sup> with liquid sulfur (T = 130-160 °C) to afford poly(sulfur-random-NBD2) (Poly(S-r-NBD2) at two different feed ratios (70-wt% S/30-wt% NBD2 & 50-wt% S/50-wt% NBD2). Copolymerization of these comonomers were observed to afford amorphous, yellow glassy, crosslinked networks. Structural characterization of these thermosets was most conclusively obtained using <sup>13</sup>C CP-MAS solid state NMR spectroscopy (Figure 5.3b), which confirmed the norbornyl skeletal framework remained intact after polymerization, as noted by the upfield resonances at 44 and 48 ppm from methylene and methine protons from NBD2. Downfield peaks at 69 ppm confirmed the formation of C-S bonds from the thiol-new addition of sulfur radicals to the cyclic olefinic groups from NBD2.
The preparation of statistical copolymer networks was confirmed by DMA analysis of poly(S-r-NBD2), where a $T_g$ around 100-105 °C (See Appendix D) was observed for both 70/30 and 50/50 compositions of poly(S-r-NBD2), along with an elevated decomposition temperature \( \sim T = 300 \) °C (See 6.3 Appendix D). This enhancement of $T_g$'s and thermal

**Figure 5.3:** a) Synthetic scheme for synthesis of NBD2 *via* the nickel catalyzed [2+2] cycloaddition of 2,5-norbornadiene and the inverse vulcanization of NBD2 with elemental sulfur; image shown consists of two 2.3 mm thick diamond polished windows of poly(S$_{50}$-r-NBD$_{250}$) where both originated from an originally 3.4 mm thick cast sample b) annotated C$^{13}$ CPMAS spectrum of poly(S$_{50}$-r-NBD$_{50}$)
stability is significant, since these thermal properties now approximate those for poly(methyl methacrylate) (PMMA), which is one of the optical industry standards for polymeric optical elements and far superior to poly(S-r-DIB) CHIPs. Inverse vulcanizations with dicyclopentadiene have also recently been reported as route to CHIPs with improved thermomechanical properties \(^{14}\). The thermomechanical features of the NBD2 thermoset offered significant melt processing advantages for the fabrication of optical elements, such as windows, lenses and prisms on the order of 1-3 mm, which for the first time were amenable to diamond polishing to create optical quality elements (See Figure 5.3a).

The refractive index of poly(S-r-NBD2) copolymers we found to range from \(n = 1.80-1.83\) from 600-1500 nm at 70/30 compositions and \(n = 1.74-1.77\) from 600-1500 nm at 50/50 compositions (See Appendix D). To determine the MWIR and LWIR transparency of poly(S-r-NBD2) extensive IR spectroscopic studies were conducted of thin films cast on NaCl plates. These IR spectra and assignments were largely in agreement with classical assignment of major vibrations with predicted functionality (See Appendix D).

Furthermore, to assess the potential for LWIR imaging, comparative IR spectra of poly(S-r-NBD2) films of varying thickness (5-30 \(\mu\)m, 50 \(\mu\)m, 1mm) were obtained (Figure 5.4a). In assessment of IR spectra collected for very thick 1mm films, it is important to note the significant differences in the spectral profile vs thin films, where spectral regions of transparency are now observed as “positive peaks” which reveal windows for LWIR transmission. One of the major analytical challenges in comparing LWIR transparency quantitatively for CHIPs samples is the difficulty in measuring films of exact
Figure 5.4: a) Stacked FTIR spectra of poly(S70-NBD230) at varying thicknesses from ~5-30 µm on a NaCl plate, 60 µm and 1 mm free standing films b) expanded region of the mid-long wave IR spectrum of 1 mm thick films of poly(S70-NBD230) and poly(S70-DIB30) with the 7-14 µm regime shaded
thickness. Small variations in film thickness can significantly affect the LWIR transmittance, hence, we determined that the fabrication of thicker melt processed 1mm films of CHIPs materials of identical composition (ie, 70/30) afforded the most accurate measurements. For 1mm poly(S-r-DIB) films, from 5-14 um, nearly 0%-transmittance (%T) was observed, with the exception of a small shoulder at the tail end of the MWIR and a small window of <5%-T at 10.3 µm in the LWIR. Conversely, a 1mm poly(S-r-NBD2) film exhibited numerous windows of transparency of 40-%T from 5–6.3 um and several other major windows at 7-7.5, 9.1-9.4, 10.2-10.5 and 13.4-14.6 microns, all of which pointed to profound enhancements in LWIR transparency throughout the rationale design described herein (Figure 5.4b).

Figure 5.5: a) digital image of LWIR imaging set up and LWIR images taken with a FLIR LWIR camera operating in the 7.5-13 µm regime in “black hot” mode of with inset of patterned PMMA sheet (12 x 12 cm) used as mask for LWIR imaging b) no window in front of the camera c) through a 1.3 ± 0.15 mm thick poly(S70-r-DIB30) window and d) through a 1.3 ± 0.12 mm thick poly(S70-r-NBD230) window
Finally, LWIR imaging experiments were conducted to determine the transparency of these new poly(S-r-NBD2) films. Films with a minimum thickness of 1 mm were required to conduct meaningful LWIR measurements, as even conventional vinyl and aromatic based polymers exhibit some LWIR transparency. Current IR lenses and windows range from 1-10 mm in thickness, hence thin films in the sub-mm range should not be used for assessing use for LWIR applications, with the exception of thin coatings. Furthermore, there remains a clear need to develop a modular and accurate IR imaging platform to test quantitatively the effects of temperature on LWIR image quality. To alleviate these issues a straightforward system consisting of a LWIR camera and a temperature controlled hot plate, serving as a black body radiator as the IR source for imaging, was assembled (Figure 5.5a). To enable imaging assessments, patterns were cut through a PMMA sheet (4mm) using a CO₂ laser to the desired feature (Figure 5.5a), followed by placing an at least 1mm CHIPs window in front of the LWIR camera. Control experiments of the patterned PMMA sheet without a CHIPs window revealed high resolution imaging at T = 100 °C of the hot plate (Figure 5.5b). Conversely, LWIR imaging thru poly(S-r-DIB) windows were completely opaque (Figure 5.5c). However, when ~1 mm windows from poly(S-r-NBD2) were used, LWIR imaging was restored as noted by clear resolution of the patterned PMMA sheet (Figure 5.5d).

5.3 Conclusion

In conclusion, we report on a molecular design approach toward IR fingerprint engineering utilizing computations and IR simulations to accelerate materials discovery. This enabled the synthesis of new polymeric materials with improved LWIR optical and
thermomechanical properties as demonstrated by IR spectroscopy and IR thermal imaging. In particular, the ability to prepare robust CHIPs thermosets, that are amenable to diamond polishing, points to the direct fabrication of arbitrary optical elements, such as, custom IR lenses, or domes using computer numeric control (CNC) tooling for rapid prototyping and manufacturing.
CHAPTER 6 - REFRACTIVE INDEX CONTRAST POLYMERS: PHOTONIC MATERIALS FOR SPATIAL MODULATION OF REFRACTIVE INDEX

With contributions from Julie I. Frish (equal contributor, device fabrication and evaluation and computational modeling), Nicholas G. Pavlopoulos (electron microscopy characterization), Sasaan A. Showghi (device fabrication), Roland Himmelhuber (device fabrication), Robert A. Norwood (device characterization and support of Julie I. Frish), and Jeffrey Pyun (co-author and PI).

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6.1 Introduction

The ability to control refractive index \( n \), or RI) in polymeric thin films is a central capability required for the fabrication of optical components and devices. While extensive efforts in polymer science have focused on methods to prepare optically transparent polymers, the creation of photoresponsive polymers, where the refractive index can be spatially defined in planar thin films with nanoscopic resolution to create refractive index contrast \( \Delta n \) = difference in RI between domains) is a distinctive technical challenge requiring a new class of RI-tunable materials. Optical devices such as waveguides often employ photolithography on polymer thin films to spatially define regions with suitable refractive index contrast \( \Delta n \sim 10^{-3} \) to enable device fabrication. However, the preparation of polymeric materials that are photo-responsive and chemically designed to create large refractive index contrast upon irradiation has received limited attention. This new chemical approach offers tremendous technological opportunity to create a new class of optical polymers that can streamline the fabrication of polymeric waveguide devices for advanced photonic applications, such as interconnecting silicon photonics optical processing fibers.
Classically, polymer waveguides are optical devices that require a high $n$ polymer region (i.e., “core”) be surrounded by low $n$ polymer films (i.e., “the cladding”), where the high $n$ core film is nano-or micropatterned via photolithography. In most cases, the low $n$ polymer claddings are solution deposited via spin coating methods while the high $n$ core is assembled by multi-step photolithography methods requiring a number of solvent development or dry etching steps. The heavy reliance on etching and development steps is highly undesirable from an industrial standpoint, and as a result, there is a great need for polymer waveguide fabrication methods that use a “dry film” photopatterning processes, where photolithographic writing of RI contrast into a polymer thin film is achieved in a single step, followed by solution deposition of the remaining low $n$ cladding layer. For example, rapid spatial RI modulation of polymer films was developed for polymer based rewritable volume holography\textsuperscript{142,143} but requires that the photorefractive film be electrically poled during irradiation, adding a layer of unnecessary complexity to fabrication. Methods using two photon absorbing processes to spatially induce sufficient $\Delta n$ have also been explored as a route for “dry film” waveguide fabrication\textsuperscript{144–151,152}. However, this process requires the use of femtosecond lasers in direct write configuration which ultimately limits wide-scale deployment of these approaches for device fabrication. Various iterations of the principle that localized increases in densities of polymer films, through crosslinking or as a result of gradient diffusion of dopant molecules after exposure to UV-light and single photon processes\textsuperscript{153–155}, result in increases in RI have also been explored, but face issues with regards to small $\Delta n$ and in some cases reproducibility.
Herein, we describe for the first time the development of a new class of photonic polymers, termed, “Refractive Index Contrast (RIC) Polymers,” that are designed to enable precise spatial RI modulation in solution cast thin films using device amenable techniques,
such as photolithography, by well understood and controlled photochemical processes. The key innovation in this report is the synthesis of novel photoresponsive monomers/polymers (Figure 6.1c) inspired by the pioneering 254 nm IBM polymer photoresists (i.e., t-BOC protected poly(4-hydroxystyrene))\textsuperscript{156}. This concept was harnessed to create the first example of an RIC polymer, by the synthesis of a t-BOC protected poly(vinylthiophenol) (poly(SBOC), Figure 6.1a)) that generates a positive $\Delta n$ ($\sim 10^{-2}$) in thin films after photopatterning which facilitates streamlined waveguide fabrication. Using this approach, we demonstrate a new “dry film” fabrication process for the creation of polymer waveguides where photo-exposed regions exhibit both increased refractive index and formation of crosslinked domains (Figure 6.1b). To our knowledge this is the first example of this class of polymeric materials and is fully elaborated upon from molecule, to material and to final device enablement.

6.2 Results and Discussion

As alluded to previously, the inspiration for the design of photoresponsive, RIC polymers was drawn from the original system of Fréchet, Ito & Wilson et al. referred to as chemically amplified photoresists for 254 nm photolithography. The critical discovery of this system was the use of t-BOC protected poly(4-hydroxystyrene) in conjunction with photoacid generators (PAGs) to enable a photocatalytic, spatially defined deprotection of t-BOC side chain groups to enhance the solubility of photoexposed regions of solution cast thin films (i.e., a “positive tone” polymer photoresists). Hence, in the design of RI-tunable polymeric materials, the polymer backbone of these 254 nm photoresists was modified from poly(4-hydroxystyrene) to poly(4-vinylthiophenol), where the hydroxyl (-OH) group
was replaced with a thiol (-SH) to enhance the refractive index of this material (Figure 6.1a). Furthermore, thiophenol groups are also readily protected with t-BOC moieties, allowing for exact implementation of known UV photolithographic processes to create photopatterns and optical devices. Due to the relatively large weight fraction of the t-BOC protecting group relative to the poly(4-vinylthiophenol) backbone, the t-BOC protected form of the polymer (e.g., poly(SBOC)) exhibited a refractive index (n = 1.54 at 1554 nm) comparable to poly(styrene). After the quantitative deprotection of t-BOC groups, a large increase in refractive index (n = 1.62 at 1554 nm) was observed due to the incorporation of thiol groups to the polymer backbone, with decomposition of the t-BOC group into gaseous byproducts (carbon dioxide, isobutylene, Figure 6.1b). The free thiophenol group also oxidatively dimerized in air, resulting in disulfide formation and crosslinking of the photoexposed regions (Figure 6.1a). Furthermore, synthesis of the t-BOC protected styrenic sulfide monomer (S-BOC) was conducted in a single pot reaction and was polymerized by Reversible Addition Fragmentation Chain Transfer (RAFT) polymerization (Figure 6.1c).

In order to demonstrate the photopatterning capability of poly(SBOC), a maskless lithography system was first used (Heidelberg MLA 150) with a 375 nm diode laser source. Because of this, 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine was used as a PAG as it exhibited peak absorption at 379 nm; the results of this patterning method can be seen in Figure 6.2. Despite the utility of maskless lithographic systems, waveguide devices were ultimately fabricated by exposure through a dark-field mask on a mask aligner with an I-line filter so that re-formulation, with regards to the PAG, could be avoided. Regardless, the exact relationship between fluence and refractive index still needed to be
determined in order to model the appropriate waveguide structures. In order to accomplish this, thin films of poly(SBOC) at the desired PAG loading (5 wt% relative to polymer loading) were spun onto silicon wafers and flood exposed in a Karl-Suss mask aligner with an I-line filter at a range of fluences (100-3000 mJ/cm²) and treated to a 150 °C post exposure bake for 10 minutes. The refractive indices of these films were then determined using the prism.

![Figure 6.2](image)

**Figure 6.2:** Scanning electron micrographs of poly(SBOC) films photopatterned on an MLA with a 5 wt% loading of triazine PAG exposed at a power density of 350 mJ/cm² at 375 nm and thermally developed at 150 °C for 10 minutes.

Coupling method (**Figure 6.3**). A linear relationship between refractive index and fluence was observed between 0 and 1000 mJ/cm²; the refractive index increase tapered off after this point with 3000 mJ/cm² ultimately resulting in a $\Delta n = 3.3 \times 10^{-2}$. For waveguide fabrication, a fluence of 2000 mJ/cm² was ultimately chosen and afforded a $\Delta n = 2.7 \times 10^{-2}$ between the exposed and unexposed regions of the poly(SBOC) film. Modeling waveguides using these RI values, it was determined that single mode waveguiding could
be achieved with waveguide feature sizes attainable by conventional photolithographic techniques.

**Figure 6.3:** Refractive index of poly(SBOC) with a 5 wt% loading of triazine PAG exposed at a range of power densities from 0 to 3000 mJ/cm$^2$ at 365 nm and thermally developed at 150 °C for 10 minutes.

With successful demonstration of the photopatternability of poly(SBOC) and the refractive indices of patterned and non-patterned material in hand, a commercially available photocrosslinkable fluorinated acrylate ZPU12-480 ($n = 1.48$) was chosen as the low $n$ cladding material. The process for waveguide fabrication is depicted in **Figure 6.4a** and detailed in Appendix E, where ZPU12-480 was first deposited and photocured onto a silicon substrate, followed by spin coating of the poly(S-BOC) layer containing 5 wt% PAG. The waveguide features were then printed into a 2 µm thick film of poly(SBOC) with a fluence of 2000 mJ/cm$^2$ at 365 nm and thermally developed at 150°C for 10 minutes. The ZPU12-480 top cladding was then deposited and photocured to afford the final device.
The FIMMwave 3D mode solving software package was also used to model the modes supported by various waveguide geometries made from the poly(S-BOC) and ZPU12-480 components. From these simulations, it was determined single mode waveguides would be supported at up to 3 µm wide. Taking this into account, propagation losses were measured for waveguides printed through the 2 and 16 µm wide spaces in the mask.

Figure 6.4: a) Schematic representation of fabrication process for waveguides with poly(SBOC) as the core and ZPU12-480 as the top and bottom cladding layers; (i): spin coating of ZPU12-480 followed by photocuring (ii): spin coating of poly(SBOC) (iii): photodefinition of waveguide structures through a dark field mask on a mask aligner (iv): spin coating and photocuring of ZPU12-480 top cladding b) Waveguide loss values obtained by the cut back method for waveguides patterned through the 2 µm (black line) and 16 µm (blue line) wide spaces in the mask.
Waveguides produced from this process were characterized by the cut back method to determine propagation loss (dB/cm) at 1550 nm due to this wavelengths’ relevance in the telecommunication industry. The cutback method entails measuring the optical power transmitted by the waveguide at varying propagation lengths, achieved by sequentially cleaving off lengths of the waveguide and measuring the transmitted power at each length. The slope of this data set was then calculated and taken to be the propagation loss; the data generated in Figure 6.4b was obtained by measuring at least six waveguides at a minimum of three different lengths and averaging the optical loss at each length. Because of the C-H bond vibrational overtones present near 1550 nm, propagation loss for hydrocarbon based polymers will always be on the order of 1 dB/cm at 1550nm. The measured losses were ~2 dB/cm for both waveguide dimensions characterized, indicating slight contributions from phenomenon other than C-H absorption processes contributing to the overall loss.

6.3 Conclusion

In conclusion, we have demonstrated the synthesis of a new class of photoresponsive soft matter, referred to as Refractive Index Contrast (RIC) polymers that were designed to allow precise spatial modulation of refractive index through classical photolithography. This unique feature was leveraged to make polymer waveguides using a streamlined fabrication process via photolithographic writing into this polymeric media. Furthermore, waveguides made from this material demonstrated reasonably low propagation loss at the telecom relevant wavelengths 1550 nm. Future work with this system will explore the demonstration of graded refractive index (GRIN) waveguides, as poly(SBOC) has an easily
tunable, dosage dependent refractive index profile, as well as the development of lower propagation loss materials.
APPENDIX A SUPPLEMENTARY INFORMATION FOR CHAPTER 2

This Appendix is included to provide experimental details and supporting information for Chapter 2: High Refractive Index Copolymers with Improved Thermomechanical Properties via the Inverse Vulcanization of Sulfur and 1,3,5-Tri-isopropenylbenzene

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A.1 Materials

1,3-Di-isopropenylbenzene (DIB, 97%, TCI America), Tetrakis(triphenylphosphine) palladium (0) (99%, Sigma-Aldrich), 2-Isopropenyl boronic acid pinacol ester (98%, Frontier Scientific), Cesium carbonate (CsCO₃, 99%, Chem-Impex International, Inc.), 1,3,5-Tribromobenzene (95%, Matrix Scientific), Hexanes (ACS grade, EMD), Toluene (ACS Grade, EMD) and Ethanol (200 proof, Decon Laboratories, Inc.) were used as received without any further purification. Sulfur (S₈, precipitated powder, 99.5-100.5%, Sigma-Aldrich) was used as received for fabrication of materials that were subjected to thermomechanical analysis; samples analyzed by optical and spectroscopic techniques were prepared using sulfur that had been recrystallized three times from toluene. Silica gel (40-63 μm particle size, SilicaFlash F60, Silicycle) was used for all flash column chromatography. Xiameter RTV-4251-S2 Silicone Rubber (Ellsworth Adhesives) and Sylgard 184 Silicone Encapsulant (Dow Corning) were used to prepare the polydimethylsiloxane (PDMS) replicas.

A.2 Instrumentation and Methods

¹H (400 MHz) and ¹³C NMR (100 MHz) nuclear magnetic resonance (NMR) spectra were obtained using a BrukerAvance III 400 MHz spectrometer. Chemical shifts are referenced
to Me₄Si (δ 0.00 ppm) for ¹H NMR and residual CHCl₃ (δ 77.0 ppm) in CDCl₃ for ¹³C NMR. Mass spectrometry was performed with a Bruker 9.4 T Apex-Qh hybrid Fourier transfer ion-cyclotron resonance mass spectrometer. Differential scanning calorimetry (DSC) characterization was carried out using a 2920 Modulated DSC (TA Instruments) running Thermal Solution 1.4E (TA Instruments) or a Discovery DSC (TA Instruments). The measurements were made in the temperature range of -80 °C to 150 °C under a nitrogen atmosphere with a heating and cooling rate of 10 °C/min for three cycles; the second heating cycles were reported. Thermogravimetric analysis (TGA) was performed using Q500 TGA (TA Instruments); the measurements were made in a temperature range of 30 to 800 °C under a nitrogen atmosphere. Tensile testing of thin films (L = ~30 mm, W = ~3 mm, T = ~0.2 mm) was carried out on a RSA III Dynamic mechanical analyzer (TA Instruments) at room temperature with a Hencky strain rate of 0.01 s⁻¹. Frequency sweeps from 0.01 rad/s to 10 rad/s were carried out at 90 °C in the linear regions with a strain amplitude ranging from 0.9% (30 wt% TIB) to 8% (30 and 50 wt% DIB). Rheological characterization was done using an ARES-G2 Rheometer (TA Instruments). Fourier Transform Infrared (FTIR) spectroscopy was performed with a Thermo Nicolet 4700 spectrometer. UV-vis-NIR spectroscopy was performed using a Cary 5000 spectrometer. Refractive index measurements were performed on a Metricon 2010 prism coupler. The samples for rheological, mechanical and DSC characterization were prepared by hot pressing at 145 °C, except for 50 wt% TIB which was done at 160 °C, for 3-4 minutes under a pressure of 0.2 to 1.5 metric tons using a Carver press. Powder X-Ray diffraction (XRD) measurements of ball-milled samples were performed on a Philips X’Pert MPD Pro diffractometer equipped with a copper radiation source (Kα wavelength
of 1.5418 Å). Laser damage experiments were performed using a 405 nm laser diode (Sony, SLD3234VF) set to 7 mW optical output power. Dark field imaging of laser induced damage was performed using a Leica reflective optical microscope. Imaging of USAF targets (Edmund Optics) was performed using a midwave IR camera (Amber Radiance 1 with a germanium lens operating at 3-5 μm).

A.3 Experimental Procedures

A.3.1 Synthesis of 1,3,5-Tri-isopropenylbenzene

To a 500 mL three necked round bottomed flask equipped with a magnetic stir bar was added 1,3,5-tribromobenzene (11.74 g, 37.8 mmol), cesium carbonate (98.85 g, 0.303 mol) and tetrakis(triphenylphosphine) palladium (0) (0.6425 g, 0.556 mmol) then equipped with a condenser and sealed with rubber septa. The reaction flask was placed under an inert atmosphere by flushing with Ar(g) while, separately, a solution of 1,2-dimethoxyethane/H2O/water (37.8 mL / 47.3 mL / 37.8 mL) was purged with Ar(g) for 30 minutes; this solution was then cannulated into the reaction flask under an inert atmosphere. Once the solids in the reaction flask had been dispersed by the solvent mixture, 2-isopropenyl boronic acid pinacol ester (25 g, 0.151 mol) was added to the reaction flask via purged syringe. The reaction mixture was placed in an oil bath and heated at reflux with stirring overnight; once total consumption of the starting material was observed by TLC the reaction solution was removed from the oil bath and cooled to room temperature. The reaction solution was transferred to a separatory funnel and diluted with 400 mL of water and ca. 50 mL of methylene chloride. The layers were separated and the organic layer again washed with water (400 mL); the aqueous layers were combined and back-extracted with methylene chloride (200 mL). The organic layers were combined and washed with a
saturated NaCl\textsubscript{(aq)} Solution (400 mL), dried over anhydrous MgSO\textsubscript{4}, filtered and concentrated under vacuum. The resulting black residue was purified by silica gel flash column chromatography with hexanes as eluent to afford a slightly viscous clear oil (6.2 g, 82.73 \% isolated yield). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.45 (s, 3.0H), 5.38 (m, 3.24H), 5.12 (m, 3.21H), 2.20 (m, 9.61H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 143.8, 141.5, 122.2, 112.9, 22.2. HRMS (ESI)\textsuperscript{+} m/z calculated for C\textsubscript{15}H\textsubscript{18} [M+H] = 199.14813; found: 199.14810.

A.3.2 Preparation of polydimethylsiloxane (PDMS) replicas for fabrication of poly(sulfur-\textit{r}-1,3-di-isopropenylbenzene) (poly(S-\textit{r}-DIB)) and poly(sulfur-\textit{r}-1,3,5-tri-isopropenylbenzene) (poly(S-\textit{r}-TIB)) copolymer windows and discs

To a 150 mL disposable plastic beaker were added Xiameter RTV-4251-S2 Silicone Rubber Base and Xiameter RTV-4251-S2 silicone rubber curing agent or Sylgard 184 silicone encapsulant and curing agent in a 10:1 (wt/wt) ratio. The two components were manually mixed for 3-5 minutes then degassed in a vacuum oven; once the resulting foam had collapsed the resin was poured into a plastic Petri Dish containing the desired master (55 mm x 2 mm Teflon disk for discs or a 25 mm x 4 mm glass window) The sample was again placed in a vacuum oven and degassed for an additional 5 minutes; the pressure was then equilibrated with the atmosphere and the resin was allowed to cure overnight at room temperature (Xiameter replicas) or at 100 °C for 35 minutes (Sylgard replicas). After curing, the glass or Teflon masters were removed from the PDMS.
A.3.3 General Procedure for the preparation of poly(sulfur-\(r\)-1,3-di-isopropenylbenzene) and poly(sulfur-\(r\)-1,3,5-tri-isopropenylbenzene) (poly(S-\(r\)-TIB)) copolymer discs (D = 55 mm, T = 2 mm)

To a 20 mL glass scintillation vial equipped with a magnetic stir bar was added sulfur (S\(_8\), specific masses noted below) and heated to 180 °C in a thermostatted oil bath until a clear, orange molten phase was obtained. At this point, the organic comonomer (DIB or TIB) (specific masses noted below) was injected into the sulfur and the resulting mixture was stirred at 180 °C until the solution became homogenous. The reaction mixture was allowed to stir at this temperature until a color change from yellow to red-orange was noted and before a sudden increase in viscosity was observed (specific times outlined below); this pre-polymer resin was quickly poured into a Xiameter PDMS replica, with a 55 mm x 2 mm reservoir, that had been placed in a 180 °C oven at least 45 minutes prior to pouring.

The sample was covered with a glass Petri dish and was allowed to cure at this temperature for 45 minutes while rotating the PDMS replica containing the mold every ~5 minutes to ensure uniform heating at which point the copolymer was noted to have become dark red. The replicas were then removed from the oven and allowed to cool to room temperature before being removed from the PDMS.

A.3.3.1 Preparation of poly(S-\(r\)-DIB30) copolymer disc with 30 wt% DIB (7 g scale)

The copolymerization was carried out following the general procedure found above with S\(_8\) (4.9 g, 19.1 mmol based on S\(_8\)) and DIB (2.1 g, 13.3 mmol) and poured into the PDMS replica 1.25 minutes after the solution became homogenous.
A.3.3.2 Preparation of poly(S-r-DIB) copolymer disc with 50 wt% DIB (7 g scale)

The copolymerization was carried out following the general procedure found above with S8 (3.5 g, 13.7 mmol based on S8) and DIB (3.5 g, 22.2 mmol) and poured into the PDMS replica 3.5 minutes after the solution became homogenous.

A.3.3.3 Preparation of poly(S-r-TIB) copolymer disc with 30 wt% TIB (7 g scale)

The copolymerization was carried out following the general procedure found above with S8 (4.9 g, 19.1 mmol based on S8) and TIB (2.1 g, 10.6 mmol) and poured into the PDMS replica 10 seconds after the solution became homogenous.

A.3.3.4 Preparation of poly(S-r-TIB) copolymer disc with 50 wt% TIB (7 g scale)

The copolymerization was carried out following the general procedure found above with S8 (3.5 g, 19.1 mmol based on S8) and TIB (3.5 g, 17.7 mmol) and poured into the PDMS replica 2.25 minutes after the solution became homogenous.

A.3.4 General Procedure for the preparation of poly(sulfur-r-1,3,5-tri-isopropenylbenzene) (poly(S-r-TIB)) and poly(sulfur-r-1,3-di-isopropenylbenzene) (poly(S-r-DIB)) copolymer windows (D = 25 mm, T = 1 mm)

To a 1.5 dram glass scintillation vial equipped with a magnetic stir bar was added sulfur (S8, specific masses noted below) and heated to 180 °C in a thermostatted oil bath until a clear, orange molten phase was obtained. At this point, the organic comonomer (specific masses noted below) was injected into the sulfur and the resulting mixture was stirred at 180 °C until the solution became homogenous. The reaction mixture was allowed to stir at this temperature until a color change from yellow to red-orange was noted and before a sudden increase in viscosity was observed (specific times outlined below); this pre polymer
resin was quickly poured into a Sylgard 184 PDMS replica, with a 25 mm x 4 mm reservoir, that had been placed in a 180 °C oven at least 45 minutes prior to pouring. The sample was covered with a glass Petri dish and was allowed to cure at this temperature for 45 minutes while rotating the PDMS replica containing the mold every ~5 minutes to ensure uniform heating at which point the copolymer was noted to have become dark red. The replicas were then removed from the oven and allowed to cool to room temperature before being removed from the PDMS.

A.3.4.1 Preparation of poly(S-r-TIB₃₀) copolymer window with 30 wt% TIB (0.925 g scale)

The copolymerization was carried out following the general procedure found above with recrystallized S₈ (0.6475 g, 2.5 mmol based on S₈) and TIB (0.2775 g, 1.4 mmol) and poured into the PDMS replica 10 seconds after the solution became homogenous.

A.3.4.2 Preparation of poly(S-r-TIB₅₀) copolymer window with 50 wt% TIB (0.925 g scale)

The copolymerization was carried out following the general procedure found above with recrystallized S₈ (0.4625 g, 1.8 mmol based on S₈) and TIB (0.4625 g, 2.3 mmol) and poured into the PDMS replica 2.25 minutes after the solution became homogeneous.

A.3.4.3 Preparation of poly(S-r-DIB₃₀) copolymer window with 30 wt% DIB (0.925 g scale)

The copolymerization was carried out following the general procedure found above with recrystallized S₈ (0.6475 g, 2.5 mmol based on S₈) and DIB (0.2775 g, 1.8 mmol) and poured into the PDMS replica 1.25 minutes after the solution became homogeneous.
A.3.5 Thermomechanical forming of poly(sulfur-\(r\)-1,3-di-isopropenylbenzene) (poly(S-\(r\)-DIB)) and poly(sulfur-\(r\)-1,3,5-tri-isopropenylbenzene) (poly(S-\(r\)-TIB)) copolymer discs for thermomechanical and rheological analyses

Poly(S-\(r\)-TIB) and poly(S-\(r\)-DIB) copolymer samples prepared as described above (55 mm x 2 mm discs) were hot pressed between two Kapton polyimide sheets (McMaster Carr) with a Carver pellet press held at \(T = 145 \, ^\circ\text{C}\) (165 \, ^\circ\text{C} for 50 wt\%TIB) under a pressure of 0.2-1.5 metric tons for 3-4 minutes. The film thickness was controlled by using steel shim-stock (TA Instruments) inserted between the polyimide sheets. The pressure was released from the films and the samples cooled to room temperature via a circulated cooling system.

A.3.6 Dynamic rheological frequency analysis of poly(sulfur-\(r\)-1,3-di-isopropenylbenzene) (poly(S-\(r\)-DIB)) and poly(sulfur-\(r\)-1,3,5-tri-isopropenylbenzene) (poly(S-\(r\)-TIB)) copolymers

Poly(S-\(r\)-TIB\(_{30}\)), poly(S-\(r\)-TIB\(_{50}\)), poly(S-\(r\)-DIB\(_{30}\)), and poly(S-\(r\)-DIB\(_{50}\)) samples with dimensions 9.5 mm diameter and \(\sim 0.4\) mm thickness, prepared \textit{via} the method described in A.3.5, were subjected to dynamic mechanical analysis with oscillatory frequency sweeps ranging from 0.01 to 10 rad/s under 0.9 - 8\% strain amplitude at 90 \, ^\circ\text{C}.

A.3.7 Dynamic mechanical analysis of poly(sulfur-\(r\)-1,3-di-isopropenylbenzene) (poly(S-\(r\)-DIB)) and poly(sulfur-\(r\)-1,3,5-tri-isopropenylbenzene) (poly(S-\(r\)-TIB)) copolymers

Poly(S-\(r\)-TIB\(_{30}\)), poly(S-\(r\)-TIB\(_{50}\)), poly(S-\(r\)-DIB\(_{30}\)), and poly(S-\(r\)-DIB\(_{50}\)) samples with dimensions 9.5 mm diameter and \(\sim 0.4\) mm thickness, prepared \textit{via} the method described in A.3.5, were subjected to a 3 \, ^\circ\text{C} min\(^{-1}\) ramp rate at an oscillation frequency of 6.28 rad/s over a temperature range from 20 to 180 \, ^\circ\text{C}.
A.3.8 Time resolved rheological analysis of self-healing properties of poly(sulfur-\(r\)-1,3-di-isopropenylbenzene) (poly(S-\(r\)-DIB)) and poly(sulfur-\(r\)-1,3,5-tri-isopropenylbenzene) (poly(S-\(r\)-TIB))

Poly(S-\(r\)-TIB\(_{30}\)), poly(S-\(r\)-TIB\(_{50}\)) poly(S-\(r\)-DIB\(_{30}\)), and poly(S-\(r\)-DIB\(_{50}\)) samples with dimensions 9.5 mm diameter and ~0.4 mm thickness were prepared via the method described in A.3.5; the modulus was then measured at some initial condition depending on the copolymer composition. Bond scission was achieved by increasing the strain amplitude for 5 minutes, followed by an annealing step. The modulus was once again recorded under the initial conditions until the initial modulus was regained and subjected to this cycle two more times (excepting the poly(S-\(r\)-TIB\(_{50}\)) sample). See tables below for conditions specific to each sample.

**Table A.1**: Conditions to measure the initial modulus of Poly(S-\(r\)-TIB\(_{30}\)), poly(S-\(r\)-TIB\(_{50}\)) poly(S-\(r\)-DIB\(_{30}\)), and poly(S-\(r\)-DIB\(_{50}\)) copolymers for time resolved rheological analysis of self-healing properties

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Frequency(rad/s)</th>
<th>Strain(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 wt% DIB</td>
<td>130</td>
<td>100</td>
<td>8</td>
</tr>
<tr>
<td>50 wt% TIB</td>
<td>130</td>
<td>100</td>
<td>8</td>
</tr>
<tr>
<td>30 wt% TIB</td>
<td>130</td>
<td>100</td>
<td>1</td>
</tr>
<tr>
<td>50 wt% TIB</td>
<td>160</td>
<td>10</td>
<td>2</td>
</tr>
</tbody>
</table>
Table A.2: Conditions to induce bond scission of Poly(S-r-TIB$_{30}$), poly(S-r-TIB$_{50}$), poly(S-r-DIB$_{30}$), and poly(S-r-DIB$_{50}$) copolymers for time resolved rheological analysis of self-healing properties

<table>
<thead>
<tr>
<th>Bond Scission conditions</th>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Frequency(rad/s)</th>
<th>Strain(%)</th>
<th>Time(min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30 wt% DIB</td>
<td>130</td>
<td>100</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>50 wt% TIB</td>
<td>130</td>
<td>100</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>30 wt% TIB</td>
<td>130</td>
<td>100</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>50 wt% TIB</td>
<td>160</td>
<td>10</td>
<td>50</td>
<td>5</td>
</tr>
</tbody>
</table>

Table A.3: Conditions anneal Poly(S-r-TIB$_{30}$), poly(S-r-TIB$_{50}$), poly(S-r-DIB$_{30}$), and poly(S-r-DIB$_{50}$) copolymers for time resolved rheological analysis of self-healing properties

<table>
<thead>
<tr>
<th>Annealing conditions</th>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Frequency(rad/s)</th>
<th>Strain(%)</th>
<th>Time(min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30 wt% DIB</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>50 wt% TIB</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>30 wt% TIB</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>50 wt% TIB</td>
<td>160</td>
<td>0</td>
<td>0</td>
<td>5</td>
</tr>
</tbody>
</table>
Table A.4: Conditions to measure the recovery modulus of Poly(S-r-TIB$_{30}$), poly(S-r-TIB$_{50}$), poly(S-r-DIB$_{30}$), and poly(S-r-DIB$_{50}$) copolymers for time resolved rheological analysis of self-healing properties

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Frequency(rad/s)</th>
<th>Strain(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 wt% DIB</td>
<td>130</td>
<td>100</td>
<td>8</td>
</tr>
<tr>
<td>50 wt% TIB</td>
<td>130</td>
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<td>8</td>
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<tr>
<td>30 wt% TIB</td>
<td>130</td>
<td>100</td>
<td>1</td>
</tr>
<tr>
<td>50 wt% TIB</td>
<td>160</td>
<td>10</td>
<td>2</td>
</tr>
</tbody>
</table>

A.4 Results and Discussion

A.4.1 Mechanical analysis of poly(sulfur-r-1,3-di-isopropenylbenzene) (poly(S-r-DIB)) and poly(sulfur-r-1,3,5-tri-isopropenylbenzene) (poly(S-r-TIB)) copolymers

Pristine films of poly(S-r-TIB$_{30}$), poly(S-r-TIB$_{50}$), poly(S-r-DIB$_{30}$), and poly(S-r-DIB$_{50}$) with dimensions L ~ 30 mm, W ~3mm, and T ~0.2 mm, were prepared by the method described in A.3.5 and were tested under uniaxial tension on a DMA with a Hencky strain rate of 0.01 s$^{-1}$. Each composition was tested three times.
Figure A.1: Stress-strain curves of poly(S-\textit{r}-DIB) and poly(S-\textit{r}-TIB) Thin films a) poly(S-\textit{r}-TIB$_{30}$), b) poly(S-\textit{r}-TIB$_{50}$), c) poly(S-\textit{r}-DIB$_{30}$), and d) poly(S-\textit{r}-DIB$_{50}$)

Table A5: Comparison of mechanical properties of various compositions of poly(S-\textit{r}-DIB) and poly(S-\textit{r}-TIB) sulfur copolymers as thin films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Young's Modulus (GPa)</th>
<th>Tensile Energy to Break ($\times 10^3$ J/m$^3$)</th>
<th>Strain at break (%)</th>
<th>Tensile Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 wt% TIB</td>
<td>1.74±0.15</td>
<td>2.77±1.34</td>
<td>1.63±0.51</td>
<td>19.5±3.9</td>
</tr>
<tr>
<td>50 wt% TIB</td>
<td>1.1±0.08</td>
<td>1.87±0.86</td>
<td>2.33±0.55</td>
<td>9.43±3.06</td>
</tr>
<tr>
<td>30 wt% DIB</td>
<td>0.43±0.08</td>
<td>36.13±1.35</td>
<td>228.33±25.11</td>
<td>2.33±0.15</td>
</tr>
<tr>
<td>50 wt% DIB</td>
<td>1.21±0.28</td>
<td>1.06±0.48</td>
<td>1.27±0.31</td>
<td>10.1±2.11</td>
</tr>
</tbody>
</table>
A.4.2 Plot of refractive Index as a function of wavelength for poly(sulfur-\(r\)-1,3,5-tri-isopropenylbenzene) (poly(S-\(r\)-TIB)) copolymers

![Refractive Index Plot](image)

**Figure A.2**: Transverse electric (TE) refractive index as a function of wavelength for poly(S-\(r\)-TIB\(_{30}\)) and poly(S-\(r\)-TIB\(_{50}\))

A.4.3 FTIR and UV-Vis transmission plots of poly(sulfur-\(r\)-1,3,5-tri-isopropenylbenzene) (poly(S-\(r\)-TIB)) copolymers

![Transmission Plots](image)

**Figure A.3**: UV-vis-near IR transmission plots of 30 and 50 wt% poly(S-\(r\)-TIB) copolymers of free standing 1 mm thick films and powdered copolymer hot-pressed between NaCl salt plates for 30 minutes at 200 °C
Figure A.4: FTIR transmission plots of 30 and 50 wt% poly(S-r-TIB) copolymers a) of free standing 1 mm thick films and powdered copolymer hot-pressed between NaCl salt plates for 30 minutes at 200 °C; b) of free standing 1 mm thick films and powdered copolymer ground with KBr and pressed into a pellet
A.4.4 Differential Scanning Calorimetry (DSC) analysis of poly(sulfur-\textit{r}-1,3-di-isopropenylbenzene) (poly(S-\textit{r}-DIB)) and poly(sulfur-\textit{r}-1,3,5-tri-isopropenylbenzene) (poly(S-\textit{r}-TIB)) copolymers

**Figure A.5**: Differential scanning calorimetry thermograms of poly(S-\textit{r}-DIB) and poly(S-\textit{r}-TIB) copolymers take from the 2\textsuperscript{nd} cycle with a temperature ramp rate of 10 °C/min; comparison based on percent loading and nature of organic crosslinker
A.4.5 Thermogravimetric analysis (TGA) of poly(sulfur-r-1,3,5-tri-isopropenylbenzene) (poly(S-r-TIB)) and poly(sulfur-r-1,3-di-isopropenylbenzene) (poly(S-r-DIB)) copolymers

![Weight Loss vs Temperature graph](image)

**Figure A.6:** TGA of poly(S-r-DIB) and poly(S-r-TIB) copolymers at various compositions

A.4.6 Dynamic rheological frequency analysis of poly(sulfur-r-1,3-di-isopropenylbenzene) (poly(S-r-DIB)) and poly(sulfur-r-1,3,5-tri-isopropenylbenzene) (poly(S-r-TIB)) copolymers to determine degree of crosslinked network microstructures

![Dynamic Rheology Graph](image)

**Figure A.7:** a) Dynamic rheological frequency sweeps performed at 90 °C in the linear regions for both poly(S-r-DIB) and poly(S-r-TIB) at varying compositions; b) solubility comparison of 50 wt% DIB (left) and TIB (right) in THF

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In order to determine the relative degree of crosslinking between sulfur copolymers utilizing DIB or TIB as the organic crosslinker, dynamic rheological frequency sweeps were performed on sulfur copolymers of varying composition prepared by curing the samples in PDMS replicas. If a material is crosslinked then the system cannot relax at low frequencies and the storage modulus achieves a frequency independent value, sometimes written as $G_e$, reflective of the degree of crosslinking. In fact, the more crosslinked a polymeric material is, the higher is $G_e$. It appears as if the DIB systems can relax at low frequencies as $G'$ is found to curve downward with decreasing frequency. This is particularly noticeable for the 30 wt% DIB material although it is clear the 50 wt% DIB system shows that it will relax if lower frequencies were available (Figure A.7). The 30 wt% TIB (Figure A.7) sample shows no signs of relaxation at low frequency demonstrating it is more fully crosslinked. Dynamic rheological frequency sweeps were not performed for poly(S-\(\tau\)-TIB\(_{50}\)) because the experiment must be conducted above $T_g$ of the material, and as the $T_g$ of this composition was found to be 130 °C, it was determined that performing the frequency sweep experiment at the required temperature could potentially decompose the material itself. However, it was noted that poly(S-\(\tau\)-TIB\(_{50}\)) was completely insoluble in tetrahydrofuran whereas the corresponding poly(S-\(\tau\)-DIB\(_{50}\)) is the most soluble composition for the DIB series (Figure A.7), further indicating that TIB based sulfur copolymers are more heavily crosslinked.
A.4.7 Time resolved rheological analysis of self-healing properties of poly(sulfur-r-1,3-di-isopropenylbenzene) (poly(S-r-DIB))

![Graph showing dynamic behavior in poly(S-r-DIB) copolymers](image)

**Figure A.8:** In situ, time resolved rheological characterization of dynamic behavior in poly(S-r-DIB) copolymers: a) 30 wt% DIB; b) 50 wt% DIB. Regions in the plot represent: 1) initial modulus; 2) 1\textsuperscript{st} damaging cycle; 3) 1\textsuperscript{st} recovery cycle; 4) 2\textsuperscript{nd} damaging cycle; and 5) 2\textsuperscript{nd} recovery cycle. Specific conditions for each copolymer in each step are given in Table A.1-Table A.4.
Dynamic rheological behavior experiments of poly(S-\(r\)-DIB\(_{30}\)) were initially conducted by determination of the storage modulus for pristine poly(S-\(r\)-DIB) samples at \(T = 130\ \degree C\) by application of a low strain rate (8\%) at a constant frequency (100 rad/s) within the linear deformation regime (Figure A.8a-b, region 1). These samples were then subjected to a high strain amplitude (100\%) for five minutes to promote S-S bond scission as evidenced by a substantial drop in the storage modulus (\(G'\), Figure A.8a-b, region 2). After five minutes at the annealing conditions (\(T = 100\ \degree C\) in the absence of oscillation or strain) the strain rate and temperature were increased to 130 \degree C and 8\%, respectively, and a time dependence of \(G'\) was measured to ascertain the time required for recovery of the initial storage modulus due to S-S bond formation (Figure A.8a-b, region 3). Once the original modulus was recovered, the strain amplitude was again increased (100\%) to test for cyclability of shear induced S-S bond scission and recovery (Figure A.8a-b, regions 4 and 5). As can be seen in Figure A.8a-b, region 5 and cycles thereafter, the damage/recovery cycling was repeatable for high sulfur content poly(S-\(r\)-DIB) copolymers. The exact shear modulus and healing dynamics of these poly(S-\(r\)-DIB) copolymers were slightly different than our previous reports of rheological self-healing experiments, however, we attribute this to different curing conditions for the poly(S-\(r\)-DIB) copolymers used in this study, since the exact conditions required for poly(S-\(r\)-TIB) were used to enable direct comparison of the thermomechanical properties of these copolymers.

The self-healing rheological experiments conducted for poly(S-\(r\)-TIB) copolymers required different conditions relative to poly(S-\(r\)-DIB) due to the enhanced thermomechanical properties of these materials. Hence, for poly(S-\(r\)-TIB\(_{30}\)) copolymers, dynamic rheology experiments were conducted by determination of the pristine storage
modulus at a constant frequency (100 rad/s) and $T = 130 \, ^{\circ}\text{C}$ but with a reduced strain rate (1%). Polysulfide bond scission was induced by increasing the strain amplitude to 100% for 5 minutes, followed by an annealing step at $T = 100 \, ^{\circ}\text{C}$ in the absence of oscillation or strain. The initial measurement conditions for poly(S-$r$-TIB$_{30}$) were again applied to observe the recovery of the cleaved S-S units in the sulfur copolymer backbone. Under these conditions, a dramatic reduction in the storage modulus of this materials was observed (Figure A.9b, region 2) followed by rapid recovery (429 sec) of the initial modulus (Figure A.9b, region 3). Further cycling of these applied strains confirmed the presence of dynamic covalent S-S bonds. Similar measurements to confirm the presence of S-S bonds in poly(S-$r$-TIB$_{50}$) were also conducted using dynamic rheology characterization, but required initial measurement conditions of higher temperature ($T = 160 \, ^{\circ}\text{C}$), low strain (2%) and low frequency (10 rad/s) (Figure A.9c, region 1). To induce the scission of S-S bonds an applied strain of 50% for five minutes was required to produce plastic deformation (Figure A.9c, region 2) that more slowly recovered the initial modulus when the strain was reduced back to 2% (Figure A.9c, region 3) after an annealing step at $T = 160 \, ^{\circ}\text{C}$ in the absence of oscillation or shear for five minutes. In comparison to poly(S-$r$-DIB$_{50}$) (Figure A.8b), longer relaxation times were observed for the poly(S-$r$-TIB) sample from 836 sec to 2853 sec, respectively. The more sluggish recovery of the initial modulus in poly(S-$r$-TIB) system was directly due to the lower content of S-S bonds, as has been noted in our previous work$^{52}$. Nevertheless, these collective studies definitively prove the retention of a high content of dynamic covalent S-S bonds in these poly(S-$r$-TIB) that point to the ability for these materials to be healable and melt-reprocessable (despite the high crosslinking density).
Figure A.9: a) Illustration of dynamic covalent bonds in high content sulfur copolymers where R is a di-isopropenyl moiety for poly(S-r-DIB) and a tri-isopropenyl moiety for poly(S-r-TIB) copolymers. In situ, time resolved rheological characterization of dynamic behavior in poly(S-r-TIB) copolymers: b) 30 wt% TIB; c) 50 wt% TIB. Regions in the plot represent: 1) initial modulus; 2) 1st damaging cycle; 3) 1st recovery cycle; 4) 2nd damaging cycle; and 5) 2nd recovery cycle. Specific conditions for each copolymer in each step are given in Table A.1-Table A.4
A.4.8 Powder X-Ray Diffraction (XRD) of poly(sulfur-r-TIB) copolymers

To confirm homogeneity of the polymer in the cured samples, powder diffraction XRD measurements were conducted on poly(S-r-TIB\textsubscript{30}) and poly(S-r-TIB\textsubscript{50}) and compared to elemental sulfur (Figure A.10). For both poly(S-r-TIB) samples, uniform, amorphous peaks were observed without any discernable peaks for crystalline S\textsubscript{8}, which confirmed that full conversion of monomeric sulfur was observed and that cured samples were homogeneous sulfur copolymer glasses.

Figure A.10: Powder X-Ray Diffraction (XRD) pattern for Elemental sulfur, poly(S-r-TIB\textsubscript{30}) and poly(S-r-TIB\textsubscript{50})
APPENDIX B SUPPLEMENTARY INFORMATION FOR CHAPTER 3

This Appendix is included to provide experimental details and supporting information for Chapter 3: Chalcogenide Hybrid Inorganic/Organic Polymers: Ultrahigh Refractive Index Polymers for Infrared Imaging

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B.1 Materials

Selenium (Se, powder, 100 mesh, reagent grade, Aldrich). 1,3-Di-isopropenylbenzene (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.

B.2 Instrumentation and Methods

USAF 1951 Resolution Targets purchased from Edmund Optics chromium patterns were prepared by vapor deposition onto glass. Spin-coating was performed on a Larueell 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). Modulated differential scanning calorimetry (DSC) characterization was carried out using a Discovery DSC (TA Instruments) from -80 – 80 °C with an overall heating rate of 2 °C/min and a 60 second periodic modulation of ±1 °C. Thermogravimetric analysis (TGA) was performed
using Q500 TGA (TA Instruments); the measurements were made in a temperature range of 30 to 700 °C under a nitrogen atmosphere with a ramp rate of 10 °C/min. Dynamic mechanical analyses were done using an RSA III Dynamic mechanical analyzer (TA Instruments). Elemental analyses were carried out using a Perkin Elmer PE2400-Series II, CHNS/O analyzer or an ICP-OES Optima 5300. NMR spectra were collected using a 500 MHz Bruker Avance DRX NMR with a broad band probe. 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.

B.3 Experimental Procedures

B.3.1 Synthesis of poly(S-r-Se-r-DIB) with the following composition (42-wt% S₈, 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-di-isopropenylbenzene (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 \( T = 150 \, ^{\circ}{\text{C}} \) 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.

B.3.2 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 (S\(_8\) 1.5 g, 46.78 mmol) and heated to \( T = 160 \, ^{\circ}{\text{C}} \) 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 (\( T = 150 \, ^{\circ}{\text{C}} \)) where selenium (Se, 0.6 g, 7.59 mmol) was then directly added to the molten sulfur medium. 1,3-Di-isopropenylbenzene (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 \( T = 150 \, ^{\circ}{\text{C}} \) 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 (1.0113g) was then suspended in 450 mL of tetrahydrofuran and stirred at 50°C in an oil bath for 17 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: 0.5408 g (54% recovery)) (see Figure B.3-Figure B.6 for NMR discussion)

B.3.3 General procedure for the preparation of poly(sulfur-random-selenium-random-1,3-di-isopropenylbenzene) (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-Di-isopropenylbenzene (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.

**B.3.4 General procedure for preparation of thin films on glass substrates from 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 terpolymer 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 µm 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.

**B.3.5 General procedure for preparation of spun coated 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 terpolymer 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 µm 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.
B.4 Results and Discussion

B.4.1 Synthesis of poly(S-r-Se-r-DIB) Terpolymers

B.4.1.1 Reaction conditions for inverse vulcanization

As described in the manuscript, the inverse vulcanization approach for these materials was conducted initially in liquid sulfur at $T = 160 \, ^\circ C$, followed by addition of grey selenium to form reactive in-situ mixed chalcogen species that were miscible and able to copolymerize with DIB (Figure B.1). 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 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 (Figure B.2). 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. $^1$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 ($\delta$ 5.37 and 5.10 ppm).
Figure B.1: Synthesis and purification scheme for poly(S-\textit{r}-Se-\textit{r}-DIB) terpolymers

Figure B.2: Representative reaction apparatus with external light source to facilitate visual inspection of terpolymerization reaction mixtures of liquid sulfur, grey selenium and DIB.
B.4.1.2 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-di-isopropenylbenzene copolymers) in typical organic solvents enabled isolation of the target terpolymer and determination of unincorporated sulfur, or selenium. As alluded to in the manuscript, solvent extraction of the crude terpolymer (1, Figure B.1) was conducted to remove insoluble mixed selenium sulfides and any residual S\textsubscript{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\textsubscript{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, Figure B.1). Also, 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 °C. 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, Figure B.1). 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.
**B.4.1.3 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 (*Figure B.1*). Elemental analysis of isolated (crude) terpolymer after sublimation (C% = 20.55; H% = 1.88; S% = 41.46; Se% = 21.68).

**B.4.2 Nuclear Magnetic Resonance Spectroscopy (NMR) of poly(sulfur-random-selenium-random-1,3-di-isopropenylbenzene) (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 (*Figure B.1*) 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. Furthermore, 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 $^1\text{H}$ NMR spectrum of poly(S$_{50}$-r-Se$_{20}$-r-DIB$_{30}$) confirmed the presence of aromatic peaks at $\delta = 6.8$-$7.8$ ppm and methyl protons at $\delta = 1.0$-$2.2$ ppm (Figure B.3). The complexity of the spectra from methyl protons at $\delta = 1.0$-$2.2$ ppm was consistent with the formation of statistical copolymers generated from terpolymerization due to the formation of different microstructures and compositional heterogeneity. Resonances at $\delta = 2.9$-$3.4$ 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 B.3: $^1\text{H}$ NMR spectrum of poly(S$_{50}$-r-Se$_{20}$-r-DIB$_{30}$) terpolymer in CDCl$_3$.](image)
Figure B.4: $^1$H NMR spectrum of 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 presence of C-S bonds and aromatic moieties in the poly(S$_{50}$-r-Se$_{20}$-r-DIB$_{30}$) terpolymer (Figure B.5). The spectral region from $\delta = 18$-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 $\delta = 125$-152 ppm.
Solution $^{77}$Se NMR experiments conducted in THF/CDC1$_3$ further confirmed the presence of Se-S bonds in the poly(S$_{50}$-r-Se$_{20}$-r-DIB$_{30}$) terpolymer (Figure B.6). 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/CDC1$_3$, 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 ($\delta = 695, 645$ 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$^{158}$ 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.

![77Se NMR spectrum of poly(S50-r-Se20-r-DIB30) terpolymer in THF/CDC13.](image)

**Figure B.6:** 77Se NMR spectrum of poly(S50-r-Se20-r-DIB30) terpolymer in THF/CDC13.

B.4.3 Gel Permeation Chromatography (GPC) of poly(sulfur-random-selenium-random-1,3-di-isopropenylbenzene) (poly(S-r-Se-r-DIB)) terpolymer powder

Size exclusion chromatography was performed on poly(S50-r-Se20-r-DIB30) that had been purified by THF extraction and subsequent SiO2 gel column chromatography. While the SEC showed the presence of a broad distribution of low molecular weight oligomers (MnSEC = 1,100 g/mol, PDI = 1.8; Fig. S6), this is consistent with the chromatograms of previously prepared high sulfur content copolymers.
Figure B.7: Size exclusion chromatography of poly(S\textsubscript{50}-r-Se\textsubscript{20}-r-DIB\textsubscript{30}) terpolymer

(M\textsubscript{SEC} = 1,100 g/mol, PDI = 1.8)

B.4.4 Thermal Gravimetric Analysis (TGA) of poly(sulfur-random-selenium-random-1,3-di-isopropenylbenzene) (poly(S-r-Se-r-DIB)) terpolymer powder

Figure B.8: TGA of poly(S\textsubscript{50}-r-Se\textsubscript{20}-r-DIB\textsubscript{30}) terpolymer after sublimation
Thermal gravimetric analysis of the 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.

B.4.5 Thermomechanical characterization of poly(S\textsubscript{50}-r-Se\textsubscript{20}-r-DIB\textsubscript{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\textsubscript{50}-r-Se\textsubscript{20}-r-DIB\textsubscript{30}) terpolymers by confirmation of a single glass transition (T\textsubscript{g}) temperature. Modulated DSC conducted in the temperature window of T = -80 °C to 80 °C confirmed the presence of a single T\textsubscript{g} at 27.33 °C. The observation of both a single T\textsubscript{g} for the terpolymer in conjunction with the \textsuperscript{77}Se NMR spectroscopic evidence (Figure B.6) supports true terpolymer formation. Additionally, since T\textsubscript{g}'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\textsubscript{g} at 51.1 °C.
B.4.6 Analysis of refractive indices as a function of poly(sulfur-random-selenium-random-1,3-di-isopropenylbenzene) (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 3.2b and Table B.1).
**Table B.1**: TE Refractive index measurements of the poly(sulfur-random-selenium-random-1,3-di-isopropenylbenzene) (poly(S-r-Se-r-DIB)) terpolymers as compared to poly(sulfur-random-1,3-di-isopropenylbenzene) (poly(S-r-DIB)).

<table>
<thead>
<tr>
<th>Wavelength (nm):</th>
<th>1554 (nm)</th>
<th>1305 (nm)</th>
<th>816 (nm)</th>
<th>633 (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Material Composition (wt.%):</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-DIB (70:30)</td>
<td>1.787</td>
<td>1.791</td>
<td>1.809</td>
<td>1.834</td>
</tr>
<tr>
<td>S-Se-DIB (50:20:30)</td>
<td>1.912</td>
<td>1.916</td>
<td>1.945</td>
<td>1.963</td>
</tr>
<tr>
<td>S-Se-DIB (42:42:16)</td>
<td>2.035</td>
<td>2.087</td>
<td>2.099</td>
<td>2.140</td>
</tr>
</tbody>
</table>

B.4.7 UV-visible/near-infrared analysis of poly(sulfur-random-selenium-random-1,3-di-isopropenylbenzene) (poly(S-r-Se-r-DIB)) terpolymer films

![UV-Vis spectra of poly(S\textsubscript{50}-r-Se\textsubscript{20}-r-DIB\textsubscript{30}) terpolymer films at varying thicknesses](image)

**Figure B.10**: UV-Vis spectra of poly(S\textsubscript{50}-r-Se\textsubscript{20}-r-DIB\textsubscript{30}) terpolymer films at varying thicknesses

The transmittance spectra of 3 flat samples with different thickness (2, 28 and 490 µm) are shown in **Figure B.10**. 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 measurements show a small spike at 800 nm due to the detector change inside of the spectrophotometer.

B.4.8 Fourier transform infrared (FTIR) spectroscopy of poly(sulfur-random-selenium-random-1,3-di-isopropenylbenzene) (poly(S-r-Se-r-DIB)) terpolymer films

![FTIR spectra](image)

**Figure B.11:** Stacked FTIR spectra of poly(S\textsubscript{70}-r-DIB\textsubscript{30}) and poly(S\textsubscript{50}-r-Se\textsubscript{20}-r-DIB\textsubscript{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 Figure B.11. 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.

B.4.9 Infrared Imaging of poly(sulfur-random-selenium-random-1,3-di-isopropenylbenzene) (poly(S-r-Se-r-DIB)) terpolymer windows

An imaging setup was constructed to demonstrate the optical transparency of the S-Se-DIB 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.
APPENDIX C SUPPLEMENTARY INFORMATION FOR CHAPTER 4

This Appendix is included to provide experimental details and supporting information for Chapter 4: One Dimensional Photonic Crystals Using Ultra-High Refractive Index Chalcogenide Hybrid Inorganic/Organic Polymers

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C.1 Materials

Sulfur (S8, sublimed powder, reagent grade, Sigma Aldrich), selenium (Se, powder, 100 mesh, reagent grade, Sigma Aldrich), 1,3-di-isopropenylbenzene (DIB, 97 %, Sigma Aldrich), chlorobenzene (CB, 99%, Sigma Aldrich), tetrahydrofuran (HPLC grade, MilliporeSigma), cellulose acetate (Mn~50,000, Sigma Aldrich) 4-hydroxy-4-methyl-2-pentanone (diacetone alcohol, 99+%, Acros), Activated Neutral Alumina (~60 mesh, Alfa Aesar), Poly(vinyl alcohol) (99+% hydrolyzed, Sigma Aldrich) Uncoated glass slides (25.0mm x 75.0mm, 1.0 mm thick, VWR) were commercially available and used as received without refinement.

C.2 Instrumentation and Methods

Spin-coating was performed on a Laurell Technologies Corporation Spin Coater (Model: WS-400BZ-6NPP/LITE). Film refractive index measurements were performed on a Metricon 2010 prism coupler while film thickness measurements were done with Veeco Dektak 150 profilometer. Transmittance analysis was carried out on a UV-Vis-NIR Cary 5000 spectrophotometer in the 350-3000 nm spectral range while reflectance measurements were made on a UV-Vis-NIR Cary 7000 spectrophotometer with the Cary
Universal Measurement Accessory (UMA). The beam size of the spectrometer in transmittance measurements is 3.5 mm and is increased by a factor of two during reflectance measurements due to the configuration of the measurement. Field-emission scanning electron microscopy (FE-SEM) was performed using a Hitachi S-4800 Type II/ThermoNoran NSS EDS Field Emission Scanning Electron Microscope. Carbon coating of mutli layered films for electron microscopy was accomplished using a Leica EM ACE200 Vacuum Coater. An FEI Helios 660 NanoLab Dual Beam SEM/FIB was used to mill and image the Bragg Reflectors.

C.3 Experimental Procedures

C.3.1 Preparation of cellulose acetate solutions for spin coating

To a 250 mL round bottom flask equipped with a magnetic stir bar was added cellulose acetate (4.00 g) and diacetone alcohol (100 mL). The mixture was heated to 130°C until all cellulose acetate was completely dissolved. The solution was cooled and then filtered through a 1.5 μm nylon filter.

C.3.2 Preparation of poly(sulfur-random-selenium-random-1,3-di-isopropenylbenzene) (poly(S-r-Se-r-DIB)) terpolymer solutions for spin coating

Poly(S_{50}-r-Se_{20}-r-DIB_{30}) (1.15 g) was taken up in chlorobenzene (8 mL) where it was then heated in a 120 °C thermostated oil bath for 15 minutes to saturate the solution. The solution was allowed to cool to room temperature and settle out overnight where it was then centrifuged at 5000 rpm for 10 minutes. After centrifugation, the solution was decanted from the centrifuge tube. The terpolymer in chlorobenzene solution was then
passed through a 5 micron Nylon filter, a 1.5 μm nylon filter, a 0.45 μm PTFE filter, and a 0.2 μm PTFE filter to remove any remaining particulates.

C.3.3 General Procedure for CHIPs Distributed Bragg Reflector Fabrication

A glass microscope slide was cut to a 1in x 1in square. The substrate was then cleaned via sequential methanol, isopropanol, and acetone rinsing. Approximately 1 mL of cellulose acetate solution was drawn onto a syringe then dispensed until the entire glass slide was covered, then spun for 60 seconds. The glass slide was then placed on a 100°C hot plate for 2 minutes to evaporate any residual solvent in the film. The substrate was then removed from the hot plate and allowed to cool to room temperature before being placed back on the spin coater. The CHIPs solution was then filtered through a 0.2 μm PTFE filter directly onto the Bragg reflector stack and again spun for 60 seconds. The stack was again dried on 100°C hot plate for 2 minutes. This process was repeated until the desired number of layers had been reached. Profilometry was used to determine the spin speeds that would yield the desired film thicknesses.

C.3.3.1 Fabrication of 1000 nm Bragg Reflector

In order to achieve peak reflection at 1000 nm, thickness of 171 nm and 127 nm were targeted for the cellulose acetate and CHIPs layers, respectively. In order to achieve these thicknesses, a 0.03 g/mL solution of cellulose acetate in diacetone alcohol was used and the first layer (on glass) was spun at 2000 RPM for 60 seconds; the spin speed was slowed to 1500 RPM when the cellulose acetate solution was being spun on top of a CHIPs layer (i.e all subsequent layers). The saturated CHIPs solution in chlorobenzene was diluted 1:1
with toluene and spun at 1500 RPM for 60 seconds in order to achieve the desired film thickness.

*C.3.3.2 Fabrication of 1500 nm Bragg Reflector*

In order to achieve peak reflection at 1500 nm, thickness of 256 nm and 190 nm were targeted for the cellulose acetate and CHIPs layers, respectively. In order to achieve these thicknesses, a 0.04 g/mL solution of cellulose acetate in diacetone alcohol was used and the first layer (on glass) was spun at 5500 RPM for 60 seconds; the spin speed was slowed to 5300 RPM when the cellulose acetate solution was being spun on top of a CHIPs layer (i.e all subsequent layers). The saturated CHIPs solution in chlorobenzene was spun at 4400 RPM for 60 seconds in order to achieve the desired film thickness.

*C.3.3.3 Fabrication of 2000 nm Bragg Reflector*

In order to achieve peak reflection at 2000 nm, thickness of 340 nm and 260 nm were targeted for the cellulose acetate and CHIPs layers, respectively. In order to achieve these thicknesses, a 0.04 g/mL solution of cellulose acetate in diacetone alcohol was used and the first layer (on glass) was spun at 2000 RPM for 60 seconds; the spin speed was slowed to 1600 RPM when the cellulose acetate solution was being spun on top of a CHIPs layer (i.e all subsequent layers). The saturated CHIPs solution in chlorobenzene was spun at 1200 RPM for 60 seconds in order to achieve the desired film thickness.

*C.3.4 Distributed Bragg Reflector Fabrication with PVA release layer for delamination and electron microscopy*

It was difficult to reliably and cleanly freeze fracture free standing Bragg Reflector films given how thin the samples were. To address this, a relatively thick layer of PVA (~7.3
μm) was first deposited on the glass substrate. The PVA was deposited from a 20wt% solution of PVA in water and was spun onto a glass slide at 500 rpm for 30 seconds. The PVA film was dried at 120 °C for 3 min. The rest of the Bragg Reflector was assembled on top of the PVA layer as outlined in the preceding section. Once the desired number of layers had been reached, the back of the glass substrate was scored with a diamond tipped pen, and cleaved. The cleaving process causes delamination of the PVA film (along with the supported Bragg Reflector) which was then removed and the multilayered structure was interrogated by SEM.

C.4 Results and Discussion

C.4.1 UV-Vis spectroscopy of DBR materials

In order to ensure maximal reflectance was obtained, both the high and low refractive index materials (poly(S-Se-DIB) and cellulose acetate) must have negligible absorbances at the targeted reflective wavelength. To this end, UV-Vis spectroscopy was performed on both materials to confirm neither material had absorbances at the target peak reflections (Figure C.1)
Figure C.1: **a)** Optical transmission of relatively thick films of cellulose acetate (red line) and poly(S-r-Se-r-DIB) (black line) **b)** UV-Vis spectra of poly(S_{50}-r-Se_{20}-r-DIB_{30}) terpolymer films at varying thicknesses

C.4.2 Transmission and reflectance measurements of DBRs

With successfully fabricated Bragg mirrors in hand, transmission measurements were made using an Agilent Cary 5000 UV-vis-NIR spectrophotometer from 350 to 3000 nm. A direct transmittance setup allows normal incidence measurements and losses due to surface scattering are more accurately represented as the beam only travels once in the sample. It also allows measurements at the center of the sample. Since neither the cellulose acetate nor the terpolymer have absorption near the peak reflections of instance, then the transmittance $T$ can be used to determine the reflectance with the relationship $R = 100 - T$. 
Figure C.2: a) transmission spectra of a 28 layer CHiPs DBR with targeted peak reflection at 1500 nm; experimental peak reflection is 1421 nm with a calculated reflectance of 97.5% and b) reflectance spectra of the same CHiPs DBR as in a and obtained at a 5.5 degree incident angle of reflection; experimental peak reflection is 1412 nm and 95% reflectance
Figure C.3: Reflectance spectra recorded in various spots on ~2 cm² Bragg reflectors with 22 layers each at 5.5 degree incident angle of reflection a) 91.5% reflectance at 2107 nm b) 92.6% reflectance at 1437 nm c) 91.59% reflectance at 994 nm

Each Bragg reflector was also analyzed by polarized angle dependent reflectance measurements to interrogate the quality of the devices and are shown in Figure C.4-Figure C.6. A Carey 7000 UV-Vis-NIR spectrophotometer with the Carey Universal Measurement Accessory (UMA) was used to collect reflection spectra. The UMA allows the user to control the orientation of the sample relative to the input beam, and the position of the detector in relation to the sample. In order to generate reflection spectra, the position of the detector was modified to collect the specular reflection from the Bragg reflector. This
meant that if the incident light was oriented at an angle $\theta$ from the normal of the Bragg reflector, the detector would be located at an angle of $2\theta$ away from the incident light. Additionally, the UMA has the functionality to set the polarization of the incident light to be $s$ polarized, $p$ polarized, or unpolarized. Before each measurement, a baseline using air was taken using the Spectrometer. This ensured that an accurate reflection or transmission spectrum of the Bragg reflector would be measured. Then, a measurement schedule could be generated, in which one could prescribe a combination of detector positions and sample orientations. This, along with a selected polarization and wavelength range, generated the experimental data of the designed Bragg reflectors. The polarized, angled dependent spectra shown in Figure C.4 c-d, Figure C.5 c-d, and Figure C.6 c-d were collected in this manner to interrogate the quality of the Bragg reflectors produced, and compared to the theoretical spectra generated in Macleod thin film software (Figure C.4 a-b, Figure C.5a-b, and Figure C.6 a-b). To better observe the trends in shift of photonic band gap width, peak wavelength of reflection and magnitude of reflection, heat maps based on data collected from the reflectance spectra were also compiled (Figure C.4e-f, Figure C.5e-f, and Figure C.6e-f). Between the raw reflectance data and these heat maps, the expected trends in each Bragg reflector can be seen.
Figure C.4: a) simulated reflectance spectra for 2000 nm Bragg reflector with s-polarized light b) simulated reflectance spectra for 2000 nm Bragg reflector with p-polarized light c) stacked angular dependent reflection spectra of a 2000 nm Bragg reflector under s-polarized light d) stacked angular dependent reflection spectra of a 2000 nm Bragg reflector under p-polarized light e) heat map of the angular dependent reflection spectra of a 2000 nm Bragg reflector under s-polarized light f) heat map of angular dependent reflection spectra of a 2000 nm Bragg reflector under p-polarized light
Figure C.5: a) simulated reflectance spectra for 1500 nm Bragg reflector with s-polarized light b) simulated reflectance spectra for 1500 nm Bragg reflector with p-polarized light c) stacked angular dependent reflection spectra of a 1500 nm Bragg reflector under s-polarized light d) stacked angular dependent reflection spectra of a 1500 nm Bragg reflector under p-polarized light e) heat map of angular dependent reflection spectra of a 1500 nm Bragg reflector under s-polarized light f) heat map of the angular dependent reflection spectra of a 1500 nm Bragg reflector under p-polarized light.
Figure C.6: a) simulated reflectance spectra for 1000 nm Bragg reflector with s-polarized light b) simulated reflectance spectra for 1000 nm Bragg reflector with p-polarized light c) stacked angular dependent reflection spectra of a 1000 nm Bragg reflector under s-polarized light d) stacked angular dependent reflection spectra of a 1000 nm Bragg reflector under p-polarized light e) heat map of angular dependent reflection spectra of a 1000 nm Bragg reflector under s-polarized light f) heat map of the angular dependent reflection spectra of a 1000 nm Bragg reflector under p-polarized light
C.4.3 Refractive index measurements of crude poly(S$_{50}$-r-Se$_{20}$-r-DIB$_{30}$) and cellulose acetate

Refractive index measurements for crude (poly(S$_{50}$-r-Se$_{20}$-r-DIB$_{30}$) were obtained by fabrication of free standing films described in previous publications$^{131}$. The refractive index values for cellulose acetate, however, were obtained by spin coating sufficiently thick films of cellulose acetate from diacetone alcohol.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>1554</th>
<th>1305</th>
<th>816</th>
<th>633</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer Composition</td>
<td>(poly(S$<em>{50}$-r-Se$</em>{20}$-r-DIB$_{30}$)</td>
<td>1.912</td>
<td>1.916</td>
<td>1.945</td>
</tr>
<tr>
<td></td>
<td>Cellulose acetate</td>
<td>1.455</td>
<td>1.455</td>
<td>1.63</td>
</tr>
</tbody>
</table>

### C.4.4 Scanning Electron Microscopy of multi-layer DBRs

Electron microscopy was initially performed on Bragg Reflectors prepared with a PVA release layer, as previously described (see SI Section II). Beginning with a multi-layer Bragg reflector film on glass, the following protocol was developed to allow for imaging of the low contrast films with minimal charging/deformation and without need for metallic nanoparticle sputtering or ultramicrotome techniques. The PVA/Bragg reflector film (~ 2 mm x 5 mm) was removed from the glass substrate by scoring followed by careful delamination with a razor blade. The middle of the sample was then notched with a razor blade, submerged in liquid nitrogen for 60 seconds, removed from the liquid nitrogen, and quickly fractured (within 5 seconds) along the notched edge to yield a cleaved cross section of the film. The sample was then mounted on a 90° sample stage between two pieces of conductive carbon tape, resulting in a free standing section of the film (~ 1 mm) between...
the two pieces of carbon tape. To both prevent charging and improve image quality, the Leica ME ACE200 Vacuum Coater was used to deposit 20 nm of amorphous carbon onto the freeze-fractured edge of the film. This method could both be applied to thin (6 layer) and thick (up to 16 layer) Bragg reflectors without any significant procedural modifications.

Edge-on imaging of the sample was subsequently performed on a Hitachi S-4800 SEM equipped with a Field Emission tip at a sample working distance of 8 mm, an accelerating voltage of 5.0 kV, and an emission current of 11.3 μA. Whereas films that were not carbon-coated exhibited significant charging and deformation, edge-on carbon coating was found to greatly increase sample stability without affecting contrast of alternating terpolymer/cellulose acetate layers (Figure C.7). The thickness of each layer was determined by making at least 40 linear measurements across the width of the layer (using ImageJ software\textsuperscript{159}), interspaced as evenly as possible then taking the average of these measurements.

![Original SEM image of a representative multi-layer Bragg reflector used to confirm the morphology of the device.](image)

**Figure C.7**: Original SEM image of a representative multi-layer Bragg reflector used to confirm the morphology of the device.
Through the process of optimizing electron microscopy imaging conditions for these multi layer polymer Bragg reflectors, a number of samples of varying number of bilayers were imaged. Below (Figure C.8) shows another representative cross section (also prepared by freeze fracture methods) of a Bragg reflector with a fewer number of layers; Bragg reflectors with fewer number of layers are inherently easier to fabricate and facilitated high throughput of samples for optimizing imaging conditions. The image in Figure C.8 demonstrates the reproducibility of well-defined boundaries between the cellulose acetate and CHIPS layers.

**Figure C.8:** Electron micrograph of a Bragg reflector with a fewer number of layers obtained with a scanning electron microscope (FE-SEM, JSM- 6701F, JEOL) operated at an acceleration voltage of 5.0 and 10.0 kV

For samples with a larger number of layers (i.e. 25) it was found that these films could be directly delaminated from the glass substrate, however they proved difficult to freeze fracture in such a way as to yield a pristine edge. Instead, An FEI Helios 660 NanoLab Dual Beam SEM/FIB was used to mill and image the Bragg Reflectors. The ion source was
a Tomahawk Ga\(^+\) ion beam with an accelerating voltage of 30.0 kV and beam current of 0.79 nA at a working distance of 13.0 mm; electron micrographs of the milled regions were collected at 1000x magnification with an accelerating voltage of 5.00 kV, a beam current of 0.4 nA using a TLD detector (through the lens detector) in DHV mode (down hole visibility). Due to the geometry constraints of the ion beam and electron beam, and sample the milled sections could not be imaged normal to the electron beam; the thickness values measured were then corrected based on the 38° angle relative to the electron beam. Additionally, the electron micrograph was stretched by a factor of 1.452 in y-axis (Figure C.9b) to again account for the tilt of the face of the milled sample relative to the electron beam.

**Figure C.9:** a) electron micrograph of a 25 layer Bragg reflector designed for reflection at 2 μm that was milled with a Ga\(^+\) ion beam and imaged on an FEI Helios 660 NanoLab Dual Beam SEM/FIB b) electron micrograph of the same image as in Figure but stretched by a factor of 1.452 in y-axis to account for the offset in angle between the face of the milled sample and the electron beam; both scale bars represent 1 μm
This Appendix is included to provide experimental details and supporting information for Chapter 5: Infrared Fingerprint Engineering: A molecular Design Approach to Long Wave Infrared Transparency with Polymeric Materials

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D.1 Materials

Elemental sulfur (S\textsubscript{8}, precipitated powder, 99.5-100.5\%, Sigma Aldrich), 2,5-norbornadiene (97\%, Alfa Aesar), 1,4-dioxane (ACS reagent grade, Sigma Aldrich), polyethylene (Mn = 5,500 g/mol, PDI = 2.73, Aldrich), TOPAS (Advanced Polymers) Sylgard 184 Silicone Encapsulant (Dow Corning), and Xiameter RTV-4251-S2 Silicone Rubber (Ellsworth Adhesives) (both elastomers used to prepared PDMS replicas for molding various, free standing, sulfur copolymer objects) were used as received. Bis(1,5-cylooctadiene)nickel(0) [Ni(COD)\textsubscript{2}] (98\%, Strem Chemicals Inc.) was used as received and stored under nitrogen below room temperature.

D.2 Instrumentation and Methods

Solution \textsuperscript{1}H and \textsuperscript{13}C NMR Nuclear Magnetic Resonance (NMR) spectra were obtained using a BrukerAvance III 400 MHz spectrometer; chemical shifts were referenced to Me\textsubscript{4}Si (δ 0.00 ppm) for \textsuperscript{1}H NMR spectra and the CHCl\textsubscript{3} solvent residual signal (δ 77.0 ppm) for \textsuperscript{13}C NMR spectra. Solid state NMR spectra were collected with a Varian 500 spectrometer at 125 MHz (\textsuperscript{13}C) for powdered samples (ca. 40 mg) spinning 7 kHz at the magic angle (in 4 mm zirconia rotors) with high power “spinal” \textsuperscript{1}H decoupling. \textsuperscript{1}H-\textsuperscript{13}C cross-polarization (“tancpx” program) was made under the Hartmann-Hahn condition with 90° pulses of 2.5
µs (1H) and 4 µs (13C). Parameters for the TOSS sequence at 7 kHz were optimized using a glycine standard. Chemical shifts were referenced to tetramethylsilane (0 ppm) using secondary standards of adamantane (13C at 38.5 and 29.4 ppm). Equilibrium geometry and IR frequency calculations were performed with Spartan’18v1.4.0160. Density functional theory with the EDF2 model was used with either the 6-31+G* or 6-31G* basis sets136,160 dependent on molecule size. Both basis sets were used with norbornane and norbornadiene to confirm that the difference is negligible for these types of systems. Calculated IR frequencies (cm⁻¹) and intensities (integrated absorption strengths, km mol⁻¹) were taken from Spartan and used to create the simulated IR spectra in the figures by program Spectrum, a program developed by the authors. The Spectrum program adds the vibrational peak absorptions into the spectrum according to their peak positions and a Lorentzian line shape with a user-selected Lorentzian line width. A width of 20.0 cm⁻¹ was chosen for all peaks to model the average peak widths observed in the experimental data. Data is plotted in %Transmission for equal concentrations of all calculated structures. A Specac mini hot press was used to press polyethylene and TOPAS films. Elemental Analysis was performed using a Perkin Elmer PE2400-Series II, CHNS/O analyzer. High resolution mass spectrometry was performed on a Bruker SoariX XR instrument and samples were introduced via direct probe APCI. Thermogravimetric Analysis (TGA) was performed on a TA Instruments TGA Q500 under an atmosphere of nitrogen from 30 to 800 °C with a ramp rate of 10 °C min⁻¹. Modulated Dynamic Scanning Calorimetry (mDSC) was performed using a Discovery DSC (TA Instruments) with an overall heating rate of 3 °C min⁻¹ with a ± 0.239 °C temperature modulation every 30 seconds. Dynamic Mechanical Analysis was carried out using an RSA III Dynamic Mechanical Analyzer (TA...
Instruments) from 23 to 175 °C with a ramp rate of 3 °C min⁻¹, 1Hz frequency, and strain amplitude of 0.05% (10 mm gap). Refractive indices were measured using a Metricon 2010 prism coupler. Fourier Transform Infrared (FTIR) spectroscopy was performed with a Thermo Nicolet 4700 spectrometer as well as a home-made solution ATR cell with a CaF₂ window. Long Wave Infrared (LWIR) imaging experiments were performed using a FLIR E40 Compact Infrared Camera operating in the wavelength range of 7.5-13 µm. Diamond polishing was performed Tucson Optical Research Corp (Tucson, AZ).

D.3 Experimental Procedures

D.3.1 Synthesis of NBD2

![Figure D.1: Scheme for the synthesis of NBD2](image)

Compound (1) illustrated in the scheme above was prepared by adapting literature procedure¹³⁹. A flame dried 25 mL schlenk flask was equipped with a magnetic stir bar and cooled under a flow of Ar(g). Norbornadiene (5.0 mL, 49.6 mmol) and 1,4-dioxane (5.4 mL) were added to the flask and Ar(g) was bubbled through the resulting solution for 15 minutes. Under a strong flow of Ar(g), Ni(COD)₂ (69.5 mg, 0.25 mmol) was quickly added to the stirred solution; the reaction vessel was then sealed under the argon atmosphere. As the nickel catalyst dissolved, the solution turned yellow initially, followed by a transition to a deep red/magenta that was initially homogeneous but began to develop a white/tan precipitate over the course of the first 24 hours of the reaction while being stirred at room
temperature. After this initial 24 hours, a second equivalent of norbornadiene (5.0 mL, 49.6 mmol) was added to the reaction mixture and the vessel was placed into a 55 °C oil bath and allowed to react at this temperature for another 48 hours. During this time more precipitate formed and the supernatant lost its red color, becoming more orange. The reaction mixture was then cooled to room temperature and diluted with tetrahydrofuran (5-10 mL) then precipitated with methanol (~20 mL) while stirring. The resulting heterogeneous mixture was then dried to a tan solid via rotary evaporation. This solid was transferred to a sublimation apparatus and sublimed at 100 °C at 0.15 Tor for 4 hrs with a dry ice/acetone mixture cooling the cold finger onto which a white crystalline solid was deposited and determined to be the desired product (3.4240 g, 37.8% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.01 (t, $J = 1.8$ Hz, 4H), 2.63 (m, $J = 1.7$ Hz, 4H), 1.70 (d, $J = 8.8$ Hz, 2H), 1.35 (s, 4H), 1.24 (d, $J = 8.9$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 136.16, 44.21, 42.22, 39.80. Solution cell ATR FTIR (heptane): 3060.2, 3128.9 (C-H), 1563.5 (C=C) cm$^{-1}$. Elemental (expected): C: 91.25%, H: 8.75%; (found): C: 91.38%, H: 8.72%. HRMS (APCI): [M+H]$^+$ Calculated: 185.1252, Found: 185.13271.

D.3.2 Inverse vulcanization of NBD2 with elemental sulfur (>1 g scale) for TGA, DSC and solid state NMR spectroscopy

In order to facilitate the various characterization techniques employed on poly(S-r-NBD2) copolymers, large scale (>1 g) copolymerizations were carried out with two different feed ratios (50 and 70 wt% sulfur feed ratio). Oligomerization and oven curing (in PDMS molds) of poly(S-r-NBD2) copolymers was typically performed at 160 °C (discussed later); however, we have found that vial curing S-NBD2 copolymers at scales larger than
1 g require lower temperatures and longer reactions times to avoid an observed
discoloration of the final network. While inverse vulcanization reactions canonically are
performed above the ring opening temperature of orthorhombic sulfur (159 °C),
temperatures as low as 135 °C have been demonstrated to provide enough energy to initiate
the copolymerization by ring opening of more highly strained rings present in the sulfur
mixture in small concentrations.

D.3.2.1 Synthesis of poly(S$_{50}$-r-NBD$_{250}$)
A 20 mL vial equipped with a magnetic stir bar was charged with elemental sulfur (1.0 g,
50 wt%) and NBD2 (1.0 g, 50 wt%); this mixture was crudely mixed in the vial then placed
in a 135 °C oil bath and heated with stirring at this temperature until vitrifcation was
observed (100 min) plus an additional 20 min at the same temperature. The reaction was
then allowed to equilibrate at room temperature whereupon the contents were extracted
from the vial (1.8834 g recovered). CHS Elemental Analysis: Expected; C: 45.63%, H:
4.38%, S: 50.00 %. Found; C: 46.00%, H: 4.45%, S: 49.52 %.

D.3.2.2 Synthesis of poly(S$_{70}$-r-NBD$_{230}$)
A 20 mL vial equipped with a magnetic stir bar was charged with elemental sulfur (1.4 g,
70 wt%) and NBD2 (0.6 g, 30 wt%); this mixture was crudely mixed in the vial then placed
in a 135 °C oil bath and heated with stirring at this temperature until vitrification was
observed (55 min) plus an additional 9 min at the same temperature. The reaction was then
allowed to equilibrate at room temperature whereupon the contents were extracted from
the vial (1.8653 g recovered). CHS Elemental Analysis: Expected; C: 27.38%, H: 2.63%,
S: 70.00 %. Found; C: 26.88%, H: 2.42%, S: 70.08 %.
D.3.3 Synthesis of poly(S-r-NBD2) samples for refractive index measurements

D.3.3.1 General procedure for free standing films of poly(S_{50}-r-NBD2_{50})

PDMS replicas of 1 cm x 1 cm x 1 mm glass slides in Sylgard 184 were first prepared in order to fabricate free standing films of Poly(S_{50}-r-NBD2_{50}) for refractive index measurements. These replicas were then placed in a 160 °C oven and allowed to reach thermal equilibrium over the course of ~30 minutes. A 20 mL vial equipped with a magnetic stir bar was charged with elemental sulfur (0.75 g, 50 wt%) and NBD2 (0.75 g, 50 wt%) then shaken to mix the two monomers. The reaction vessel was then placed in a 160 °C oil bath and the comonomers oligomerized for 7 minutes then poured into the PDMS replicas. The samples were then cured in the oven at 160 °C for 45 minutes; samples were then removed and cooled under a weight evenly distributed by a glass slide with a Kapton film as a release layer pressure to obtain flat samples sufficient for prism coupled ellipsometry measurements.

D.3.3.2 General procedure for glass substrate supported films of Poly(S_{70}-r-NBD2_{30})

A 1.5 dram vial equipped with a magnetic stir bar was charged with elemental sulfur (0.35 g, 70 wt%) and NBD2 (0.15 g, 30 wt%) and roughly mixed in the vial. The reaction vessel was then placed in a 160 °C oil bath and the comonomers oligomerized for 7.5 minutes. At this point a portion of the slightly viscous, yellow, homogenous solution was poured onto a glass microscope cover slip at thermal equilibrium on a 160 °C hot plate. A second similarly pre-heated glass microscope cover slip was then placed on top of the viscous resin and surface tension between the resin and glass cover slips spread the oligomerized resin across both pieces of glass. The film was cured for 15 minutes at 160 °C on the hot plate;
the top cover slip was removed gently from the still hot film, the hot plate was turned off, and the sample allowed to reach room temperature slowly.

D.3.4 General procedure for synthesis of poly(S-\textit{r}-NBD2) molds for DMA

PDMS replicas of 10 mm x 30 cm x 1 mm laser cut polycarbonate masters in Xiameter RTV-4251-S2 were first prepared in order to fabricate free standing films for DMA. These replicas were placed in a 160 °C oven to preheat before oligomerized resins of poly(S-\textit{r}-NBD2) were poured into them and cured.

\textit{D.3.4.1 Poly(S}_{50}\textit{r}-NBD2}_{50} DMA samples

A 1.5 dram vial equipped with a magnetic stir bar was loaded with elemental sulfur (0.50 g, 50 wt\%) and NBD2 (0.50 g, 50 wt\%) and mixed in the vial. The vial was then placed in a 160 °C oil bath for 7 minutes. During this time the two monomers became miscible and afforded a yellow, viscous solution which was then poured into pre-heated PDMS molds. The mold was then cured for 45 minutes, removed from the oven and cooled under a weight evenly distributed by a glass slide with a Kapton film as a release layer before being removed from the PDMS replica. Three samples of this composition were ultimately used to determine the Tg of poly(S\textit{50-r}-NBD2\textit{50}) by DMA.

\textit{D.3.4.2 Poly(S}_{70}\textit{r}-NBD2}_{30} DMA samples

A 1.5 dram vial loaded with a magnetic stir bar along with elemental sulfur (0.70 g, 70 wt\%) and NBD2 (0.30 g, 30 wt\%) was shaken to mix the two reagents then placed in a 160 °C oil bath. The comonomers were oligomerized in the oil bath for 5 minutes, affording a yellow, homogenous, viscous resin, that was then poured into a preheated PDMS mold in a 160 °C oven. The mold was cured in the oven for an additional 45 minutes, after which
it was removed from the oven and cooled under a weight evenly distributed by a glass slide with a Kapton film as a release layer before being removed from the PDMS. Four samples of this composition were used to determine the Tg of poly(S$_{70}$-r-NBD$_{230}$) by DMA.

D.3.5 Processing of polyethylene and TOPAS into free-standing thin films for FTIR

For both the polyethylene and TOPAS films, 2-3 pellets of the material was placed inside the Specac 50 µm shim with Kapton films as release layers on the top and bottom platens. Samples were then heated to the desired temperature, thermally equilibrated, and pressed at the desired pressure and for the desired time. The free standing films were then placed into the IR cards provided by Specac and sealed; the thickness of the sample was then measured in a number of spots using a micrometer and averaged.

D.3.5.1
A polyethylene film was prepared by pressing pellets at 125 °C under 1 Ton of pressure for 1 minute. Thickness: 72.5 ± 5.2 µm

D.3.5.2
A TOPAS film was pressed at 180 °C for 5 minutes under 1.5 Tons of pressure. Thickness: 51.3 ± 0.5 µm

D.3.6 Synthesis of varying thickness poly(S$_{70}$-r-NBD$_{230}$) films for FTIR

D.3.6.1 15-30 µm thick film on NaCl plate

A 1.5 dram vial equipped with a magnetic stir bar was charged with elemental sulfur (0.35 g, 70 wt%) and NBD2 (0.15 g, 30 wt%) and then shaken to mix the contents. The vial was then placed in a 160 °C oil bath to oligomerize the two comonomers. After 6.5 minutes in the oil bath, 1 drop of the yellow resin was dropped onto a NaCl plate that had been brought to thermal equilibrium with a 160 °C oil bath. A piece of Kapton film was placed on-top
of the drop of poly (S<sub>70</sub>-r-NBD<sub>230</sub>) oligomer; surface tension spread the resin across the surface of the salt plate. The film was cured for 15 minutes, the Katpon removed, and the cured film on the NaCl plate was slowly cooled to room temperature. The thickness of the film ranged from ~5 µm at the thinnest point to ~30 µm at the thickest.

**D.3.6.2 60 µm thick free standing film**

0.5 of poly(S<sub>70</sub>-r-NBD<sub>230</sub>) was oligomerized in the same manner as described directly above. Instead of being pouring onto a salt plate, a portion of the resin was dropped into the interior of a doughnut shaped Kapton shim that had been placed on another square of Kapton film, both of which had been previously pre heated on a hot plate set at 160 °C. A second square of Kapton film was placed over the resin and the film cured at 160 °C for 15 minutes then allowed to cool slowly to room temperature. The FTIR spectra was recorded then thickness measured due to the fragility of the thin free standing film; the film was measured with a micrometer at the center and was found to be 60 µm thick, further measurements were not possible as the brittle film was destroyed during this process.

**D.3.6.3 1 mm thick free standing film**

The same procedure used to make the DMA samples in B.3.4 was followed in order to prepare the 1 mm thick samples for FTIR analysis. The notable difference being that a glass microscope slide (also preheated in the oven) was placed over one half of the mold with a weight placed on top of it to ensure a higher degree of precision over the resulting thickness (1.05 ± 0.02 mm).

**D.3.7 Synthesis of a 1 mm thick poly(S<sub>70</sub>-r-DIB<sub>30</sub>) film for FTIR**

To a 3.70 mL (1 dram) glass scintillation vial equipped with a magnetic stir bar was added elemental sulfur (S<sub>8</sub>, 700 mg, 21.8 mmol) and transfer in to pre-heated to 185 °C oil bath
until a clear orange colored molten phase was formed. Then, 1,3-di-isopropenylbenzene (DIB, 0.35 mL, 300 mg, 1.85 mmol) was added into the liquid sulfur and the resulting mixture was stirred at 185 °C for additional 5 minutes after forming clear homogeneous solution. The pre-polymerized viscous solution was transferred into a pre-heated mold whose dimension is 30 mm (height) x 10 mm (wide) x 1 mm (depth) in an oven held 185 °C. The sample was covered with a glass Petri dish and cured for 45 minutes. After being cooled sample and mold at room temperature, the PMDS mold was carefully peeled to get the p(S7-r-DIB3) sample. The samples thickness was measured for 5 point and average value is 1.009 (± 0.001) mm.

D.3.8 Synthesis of a poly(S70-r-NBD230) window for imaging experiments

A 65 mm diameter x 3.175 mm thick acrylic laser cut disc was replicated in Xiameter RTV-4251-S2 which, after curing, was placed in a 160 °C oven to pre-heat. Once accomplished, NBD2 (2.7 g, 30 wt%) and sulfur (6.3 g, 70 wt%) were combined in a 20 mL vial equipped with a magnetic stir bar and mixed thoroughly before being placed in a 160 °C oil bath. After 14 minutes, a homogenous burnt orange, viscous solution was obtained which was poured into the PDMS replica in the oven and cured for 45 minutes. The mold was then removed from the oven and allowed to cool to room temperature before being removed from the PDMS and being used for LWIR imaging experiments. The thickness was measured across the sample and was found to be 1.36 ± 0.15.

D.3.9 Synthesis of a poly(S70-r-DIB30) window for imaging experiments

To a 20 mL glass scintillation vial equipped with a magnetic stir bar was added elemental sulfur (S8, 4.55 g, 142 mmol) and transferred into a pre-heated to 185 °C oil bath
until a clear orange colored molten phase was formed. Then, 1,3-di-isopropenylbenzene (DIB, 2.18 mL, 1.95 g, 12.3 mmol) was added into the liquid sulfur and the resulting mixture was stirred at 185 °C for additional 5 minutes after forming a clear homogeneous solution. The pre-polymerized viscous solution was transferred into a pre-heated mold whose dimension is 55 mm (diameter) x 1 mm (depth) in an oven held at 185 °C. The sample was covered with a glass Petri dish and cured for 45 minutes. After being cooled sample and mold at room temperature, the PMDS mold was carefully peeled to get the p(S7-r-DIB3) window. The thickness was measured across the sample and was found to be 1.33 ± 0.12.

D.4 Results and Discussion

D.4.1 Discussion of materials currently used for the LWIR, simulated FTIR spectra, and analysis of experimental FTIR spectra

D.4.1.1 Conventional transmissive materials for the LWIR

Current materials for imaging in the LWIR typically use semiconductors (i.e. germanium) and chalcogenide glasses; these are transparent in the LWIR because the constituent atoms are much larger than those present in organic materials (i.e. C, H, O, X) and absorb at longer wavelengths outside the region of interest. While the design of a symmetrical zero-dipole moment molecule would be feasible in principle, applying this to polymers would typically break this symmetry and polymerization induce new bond formation between monomers. Hence a more viable approach in the design of new organic comonomer motifs was the use of compounds with LWIR spectra with either simple absorption files, or with absorbances outside the 7-14 micron window where possible.
**D.4.1.2 Quantitative ranking of new candidates for LWIR transparent CHIPs:**

To allow for easy quantitative ranking between calculated systems, the sum of integrated molar absorptivity values of the peaks in the region of interest is taken as a figure of merit. The integrated molar absorptivity values (with standard absorption units of km mol$^{-1}$) are taken directly from the Spartan ’18 output file, where they are labelled as “Intensities”. We designate the summation of integrated molar absorptivity values in the LWIR region as $\varepsilon_{\text{int}}$. A lower $\varepsilon_{\text{int}}$ value for the region means a more LWIR transparent sample. This provides an easy quantification method to compare various calculated model polymers quickly. Within this work, computational efforts are primarily intended to screen candidates for LWIR imaging to conserve experimental efforts. As these calculations are done in the gas-phase and combination bands and overtones are not included, $\varepsilon_{\text{int}}$ is not an exact indicator of performance. However, since the fundamental vibrations are more intense than combination bands and overtones, a candidate with a significantly high $\varepsilon_{\text{int}}$ value almost certainly won’t perform well experimentally. Based on this treatment, we found the $\varepsilon_{\text{int}}$ of MC 2 is approximately twice that of MC 3 due to the approximate doubling of vibrational modes in this region (MC 2, 106 modes, $\varepsilon_{\text{int}} = 241$; MC 3, 55 modes, $\varepsilon_{\text{int}} = 131$). The translation of this comparison to the actual polymers also assumes that each polymer has the same number of organic monomers. The MC 1 model yielded a slightly larger $\varepsilon$ integrated molar absorptivity value from fewer vibrational modes (46 modes, $\varepsilon_{\text{int}} = 254$) from the computational screening process, but suffered from some individually intense absorptions in the middle of the region. The computed spectrum is included in Figure 2 for comparison.
**D.4.1.3 Analysis of experimental FTIR spectra:**

To determine the MWIR and LWIR transparency of poly(S-r-NBD2) extensive IR spectroscopic studies were conducted. IR spectra of films (5-30 μm) deposited onto NaCl plates were conducted for analytical assessment of vibrational absorbances of major functional groups (Figure 5.4a), which were in agreement in with the $^{13}$C CP-MAS NMR spectroscopy. Vibrational peaks at 3000 cm$^{-1}$ (3.3 microns) were assigned to C-H aliphatic moieties from sp$^3$ hybridized carbons formed after inverse vulcanization. Weak absorptions at 3100 cm$^{-1}$ from C-H olefinic groups were attributed to trace dangling bonds of norbornene end groups. Vibrational absorptions from 1400-600 cm$^{-1}$ (7-14 um) were also observed in the fingerprint region as has long been known for organic compounds. However, the most fundamental vibrational modes could be tentatively assigned from the DFT calculations, which simulated weak C-C bond and C-H bending vibrations in the region of 1200 cm$^{-1}$, 900 and 700 cm$^{-1}$ while weak C-S vibrational peaks are calculated at ~600-650 cm$^{-1}$ and S-S bond vibrations are below 500 cm$^{-1}$. The simulated IR spectra of poly(S-r-NBD2) of thin films were in good agreement with experimental spectra. These comparisons confirmed that the norbornane dimeric framework exhibited considerably better transparency than aromatic containing polymers, which confirmed that C=C bonds should be avoided to minimize LWIR opacity.
Figure D.2: Comparison of DFT calculated FTIR spectra for equal concentrations of a) norbornane b) 2,5-norbornadiene and c) MC 2 (black lines). Red line indicates experimental gas-phase spectra of a) norbornane\textsuperscript{78} b) 2,5-norbornadiene\textsuperscript{78} and c) experimental FTIR spectra of poly(S\textsubscript{70-r}-NBD\textsubscript{230})
D.4.2 NMR Spectroscopy of NBD2

The NMR spectra for NBD2 prepared using the procedure described furnishes the exo-trans-exo isomer as the major product with a small amount of exo-trans-endo isomer; the isomers were assigned based on literature precedent\textsuperscript{161}.

Figure D.3: (a) $^1$H and (b) $^{13}$C NMR spectra of NBD2
D.4.3 Solution FTIR ATIR spectroscopy of NBD2

![Solution ATR FTIR spectra of NBD2](image)

**Figure D.4:** Solution ATR FTIR spectra of NBD2

A 100 mM solution of NBD2 in heptane was prepared by dissolving 0.1842 g of NBD2 in heptane in a 10 mL volumetric flask. The CaF$_2$ window used in the solution cell limits the transmission window to ~1100 cm$^{-1}$.

D.4.4 Refractive index measurements of poly(S-$r$-NBD2)

Depending on the composition of Poly(S-$r$-NBD2), the sample preparation slightly varied; for poly(S$_{70}$-$r$-NBD$_{230}$), thin films on glass substrates were prepared, while poly(S$_{50}$-$r$-NBD$_{250}$) samples were prepared as thicker, free standing films. This was because thin films of poly(S$_{50}$-$r$-NBD$_{250}$) on glass were found to develop spider webbing cracks across the entire film upon cooling; this phenomenon was not observed for poly(S$_{70}$-$r$-NBD$_{230}$) thin films on glass. Three samples of each composition were prepared and analyzed by prism coupled ellipsometry with the standard deviation for any given data point being <0.002; the compiled results can be seen in **Figure D.5**.
Figure D.5: Refractive index measurements over the 633-1554 nm wavelength range of Poly(S-$r$-NBD2) with 70 and 50 wt% feed ratios of elemental sulfur obtained by prism coupled ellipsometry

D.4.5 TGA of poly(S-$r$-NBD2)

Figure D.6: TGA thermograms of Poly(S-$r$-NBD2) with 70 and 50 wt% feed ratios of elemental sulfur performed under a nitrogen atmosphere from 30 to 800 °C with a ramp rate of 10 °C min⁻¹
As can be seen in Figure D.6, sulfur copolymers prepared by inverse vulcanization with NBD2 possess a suprisingly higher thermal stability than those prepared with styrenic monomers (including 1,3-di-isopropenyl benzene) which typically have an onset of degradation ~200 °C. Poly(S_{50-r-NBD250}) exhibits less than 5 wt% mass loss before the onset of degradation (285.03 °C) while poly(S_{70-r-NBD230}) was found to be slightly more stable with less than 5 wt% mass loss before onset of degradation at 299.35 °C.

D.4.6 mDSC of poly(S-r-NBD2)

Figure D.7: Second scans of modulated Differential Scanning Calorimetry (mDSC) thermograms of a) 50 wt% feed ratio and b) 70 wt% feed ratio of sulfur; scans were performed from -80 - 280 °C with an overall heating rate of 3 °C min\(^{-1}\) with a ± 0.239 °C temperature modulation every 30 seconds.

mDSC experiments were performed on poly(S-r-NBD2) copolymers initially to attempt to discern the glass transition temperatures of these materials. However, the reversing heat flows for both compositions (grey lines in Figure D.7) were found to be largely featureless across the temperature range scanned. This is a known phenomenon for
crosslinked materials and was why DMA was ultimately used to determine the Tg’s of these sulfur copolymers.

D.4.7 DMA of poly(S-r-NBD2)

![DMA curves for poly(S-r-NBD2) with a) 50 wt% feed ratio and b) 70 wt% feed ratio of sulfur; scans were performed from 23 to 175 °C with a ramp rate of 3 °C min⁻¹, 1Hz frequency, and strain amplitude of 0.05% (10 mm gap).]

The glass transition temperatures from the \( \tan \delta \) curves (shown in Figure D.8) were determined by smoothing the first derivative of the \( \tan \delta \) curves and overlaying that with the original data; the point at which the first derivative had a value of 0.0 on the y axis and intersected the peak of the \( \tan \delta \) curve was located and the corresponding value on the x (temperature) axis was taken to be the Tg. At least three samples of each composition where analyzed in this way and poly(S₅₀-r-NBD₂₅₀) was determined to have a Tg of 104.5 ± 8.2 °C while poly(S₇₀-r-NBD₂₃₀) was determined to have a Tg of 100.9 ± 3.3 °C.

The preparation of statistical random copolymers was confirmed by DMA analysis of poly(S-r-NBD2), where a Tg around 100-105 °C was observed for both 70/30 and 50/50
compositions of poly(S-\(-\text{NBD2}\)). DMA was required for these determinations, since DSC thermograms were featureless, as is commonly observed for thermoset materials. A progressive increase in $T_g$ with high NBD2 was initially anticipated as common for copolymer thermoplastics, however, since this material was a thermoset, a progressive plateau of $T_g$ with crosslinked feed ratios in commonly observed$^{162}$. This is one of the highest $T_g$’s observed for CHIPs at high sulfur content ($>_70$-wt%), as noted by the much lower $T’_g$s of our earlier materials based on DIB (Poly(S-\(-\text{DIB}\) $T_g < 40\text{C}$ at 70/30 composition) and TIB (Poly(S-\(-\text{TIB}\) $T_g \sim 66\text{C}$)$^{50}$. A notable enhancement of the thermal stability of poly(S-\(-\text{NBD2}\)) copolymers vs poly(S-\(-\text{DIB}\)) was observed by TGA of these materials, where the onset of decomposition was enhanced by $\sim100$ C. While TIB copolymers were previously demonstrated to enhance $T_g$ of CHIPs with higher comonomer content, enhancements at this level were not attainable at these high sulfur content compositions, which are required to retain the desired optical properties.

The thermosetting features of the NBD2 inverse vulcanization offered significant melt processing advantages for the fabrication of optical elements, such as windows, lenses and prisms. Using this approach windows and other elements in the order of 1-3 mm could be prepared by casting into PDMS molds followed by diamond polishing to the desired thickness and geometry. Prisms of cm thickness and dimensions were also prepared via casting into molds and diamond polishing, where the prisms were rigorous assessment of RI and optical transmittance. To our knowledge, this is the first CHIPs thermoset exhibiting this level of thermomechanical stability to enable this type of curing and polishing, which are classically employed processing methods for optical element fabrication.
D.4.8 Solid state CP MAS NMR spectroscopy of poly(S-r-NBD2)

Figure D.9: Solid state CP MAS NMR spectra of poly(S-r-NBD2) copolymers with a) 50 wt% feed ratio and b) 70 wt% feed ratio of sulfur. Solid state $^{13}$C CP-MAS NMR spectrum of poly-(S-NBD2) prepared with a) 50 wt% feed ratio of sulfur collected with 3 ms contact, 1 s delay and TOSS to eliminate the spinning sidebands and b) 70 wt% feed ratio of sulfur collected with 50 µs contact and 10 s delay.
The two samples (50 and 70 wt% sulfur feed ratio) exhibited very different NMR behavior. The poly(S$_{50}$-r-NBD$_{250}$) sample gave a fairly well resolved $^{13}$C NMR spectrum (Figure D.9a). The dominant sharp signal at 44 ppm, with a longitudinal relaxation time ($T_1$) of approximately 11 s, arises from the flexible aliphatic carbons of NBD2. Carbons bonded directly to sulfur are denoted by signals at 59, 68 and 73 ppm (Figure D.10). The CP-TOSS spectra (Figure D.9a) show that 4% of the carbons remain olefinic after polymerization. That is, the 4 olefinic carbons of the NBD2 monomer (29% C=) were not completely consumed for poly(S$_{50}$-r-NBD$_{250}$). The poly(S$_{70}$-r-NBD$_{230}$) sample exhibited $^{13}$C broad lines, no olefins and considerable signal area near 60 ppm from C-S carbons (Figure D.9b). Unlike poly(S$_{50}$-r-NBD$_{250}$), no $^{13}$C signals were detected using direct polarization pulses (e.g. onepulse, Dpth, Hahn echo). Divergent probe tuning and weakly effective $^1$H pulses (see Figure D.11) suggested paramagnetic character for this sample. However, $T_1$ relaxation was slow, since the signal intensity decreased on decreasing the relaxation delay. This crushed powder exhibited deliquescence during hand-milling in air to load the rotor.
Figure D.10: a) $^{13}$C NMR shifts (ppm), with error margin, for a representative molecule predicted using ACD (version 2018); b) De-convolution (Lorentzian lines) of the solid state $^{13}$C CP-MAS TOSS NMR spectrum of poly(S$_{50}$-r-NBD$_{250}$) with comparison of observed and simulated spectra.
Figure D.11: One-pulse solid state $^1$H MAS NMR spectra of poly(S$_{50}$-r-NBD$_{250}$), (left) and poly(S$_{70}$-r-NBD$_{230}$) (right), as a function excitation pulse length. Signal inversion (near 8 µs) was observed poly(S$_{50}$-r-NBD$_{250}$), but could not be realized for poly(S$_{70}$-r-NBD$_{230}$).
D.4.9 Diamond polishing and evaluation

Samples for diamond polishing were fabricated by first preparing Sylgard 184 PDMS replicas of 25 mm diameter glass masters. A mixture of sulfur (1.75 g, 50 wt%) and NBD2 (1.75 g, 50 wt%) were oligomerized in a 20 mL vial with stirring in a 160 °C oil bath for 17.5 minutes; at this point the mixture was a dark orange, viscous solution that was then poured into the previously prepared PDMS replica that had been brought to thermal equilibrium in a 160 °C oven. The mold was cured for 45 minutes, removed from the oven and cooled to room temperature under an evenly distributed weight; the mold was subsequently extracted from the PDMS replica and submitted for grinding/polishing to afford a smooth, flat finish on both sides of the window; three samples were subjected to this treatment. The initial thickness of the as-cast molds was 3.4 mm, two samples were ground and polished down to 2.3 mm and the final sample was ground and polished down to 0.8 mm.

The process for grinding the poly(S-r-NBD2) material included large bevels, grinding with general shop practice and polishing of the surface was accomplished with a low NAP Pellon PAD and OPELIEN Polishing Compound (20% OPELIEN and water mixture) and care was taken to keep the sample cool throughout the process.
This Appendix is included to provide experimental details and supporting information for Chapter 6: Photoresponsive Polymers with Spatial Modulation of Refractive Index: A photolithographic Medium for Polymer Waveguides

E.1 Materials

4-bromostyrene (98%, Alfa Aesar), nBuLi in hexanes (2.5M, Acros Organics), hexanes (ACS grade, Macron Fine Chemcials), dry tetrahydrofuran (THF) (DriSolv, EMD Millipore Corp.), di-tert-butyl dicarbonate (BOC anhydride) (99.5% Chem. Impex Int’l Inc.), magnesium sulfate (anhydrous, EMD Millipore Corp.), sulfur (99.5%, precipitated, Sigma Aldrich), diethyl ether (ACS grade, J.T. Baker), silica gel (SiliaFlash F60, 230-400 mesh, Silicycle), ethyl acetate (ACS grade, Macron Fine Chemcials), toluene (ACS grade, Fisher Scientific), dichloromethane (DCM) (ACS grade, Fisher Scientific), propylene glycol methyl ether acetate (PGMEA) (99%, Alfa Aesar), ZAP-1020 and ZPU-12-480 (ChemOptics, Inc.), 3-(trichlorosilyl)propyl methacrylate (95%, Gelest), 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine (98% Sigma Aldrich), and silicon wafers (University Wafer) were used as received. 2,2’-Azobis(2-methylpropionitrile) (ABIN) (98%, Sigma Aldrich) was recrystallized from warm methanol three times. RAFT CTA (4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid) was prepared according to literature procedure\textsuperscript{163}. 

\textsuperscript{163}
E.2 Instrumentation and Methods

Size exclusion chromatography (SEC) was performed in a tetrahydrofuran (THF) mobile phase with a Waters 1515 isocratic pump running three 5-μm PLgel columns (Polymer Labs, pore size $10^4$, $10^3$, and $10^2$ Å) at a flow rate of 1 mL/min with a Waters 2414 differential refractometer and a Waters 2487 dual-wavelength UV-vis spectrometer. Molar masses were calculated using the Empower software (Waters), calibrated against low polydispersity linear polystyrene standards. $^1$H and $^{13}$C NMR nuclear magnetic resonance (NMR) spectra were obtained using a BrukerAvance III 400 MHz spectrometer. Chemical shifts are referenced to Me$_4$Si ($\delta$ 0.00 ppm) for $^1$H NMR and residual CHCl$_3$ ($\delta$ 77.0 ppm) in CDCl$_3$ for $^{13}$C NMR. Elemental analysis was performed on a Perkin Elmer PE2400-Series II, CHNS/O analyzer at NuMega Resonance Labs. Carbon coating of photopatterned films for electron microscopy was accomplished using a Leica EM ACE200 Vacuum Coater. An FEI Helios 660 NanoLab Dual Beam SEM/FIB was used to record the SEM micrographs. Differential scanning calorimetry (DSC) characterization was performed on a Thermal Analysis Instruments TA 2920 Modulated DSC. Thermogravimetric analysis (TGA) was performed using a Thermal Analysis Instruments TA High-Res TGA 2950 Thermogravimetric Analyzer. FTIR spectra were recorded on a Thermo Nicolet Avatar 360 FT-IR ESP with the Thunderdome ATR accessory (germanium crystal). Spin coating was performed on a Laurell Technology Corporation WS-650SZ-6NPP/LITE. O$_2$ plasma cleaning was performed on Plasma-Preen II-862. UV curing of ZPU was performed using an ELC 4001 Light Curing Unit from ElectroLite Corporation with a power density of 30.5 mW/cm$^2$ at 365 nm. Poly(SBOC) films were arbitrarily patterned $via$ direct laser patterning on a Heidelberg MLA 150 with a 375 nm diode laser.
source and waveguides used in cutback measurements to assess propagation loss were printed on a Karl-Suss MA6 Mask Aligner. Thickness measurements were done with Veeco Dektak 150 profilometer. Power loss through the poly(SBOC) waveguides was determined using a Keysight Technologies 86038B Photonic Dispersion and Loss Analyzer tunable laser source set at 1550 nm and 1.0 mW. Alignment of the single mode fiber to the waveguides was completed using the Melles Griot Nanomax-HS 17MAX604 stage positioner. Images of the modes were found using the MTI LSC-70 infrared camera. Power was measured using the Newport Multi-Function Optical Meter model 2835-C and Newport Universal Fiber Optic Detector model 818-IS-1.

E.3 Experimental Procedures

E.3.1 Synthesis of SBOC

![Scheme for synthesis of SBOC](image)

**Figure E.1**: Scheme for synthesis of SBOC

A Flame dried, three necked round bottomed flask was equipped with a magnetic stir bar, sealed with rubber septa and placed under an argon atmosphere. The flask was subsequently charged with hexanes (100 mL), dry tetrahydrofuran (100 mL) and 4-bromostyrene (8.08 g, 44.0 mmol); this mixture was cooled to -78 °C in a dry ice-acetone bath. Once cooled, a solution of nBuLi (2.5 M in hexanes) (17.6 mL, 44.0 mmol) was added dropwise via purged syringe to the reaction mixture to afford a white/yellow suspension that was stirred at -78 °C for 1.5 hours. At this point, elemental sulfur (1.408 g,
44.0 mmol on an S atom basis) was added at -78 °C, then warmed to -20 °C in a dry ice-ethanol/ethylene glycol bath (1:9 ethanol:ethylene glycol) and stirred for 30 minutes, followed by di-tert-butyl dicarbonate (19.2 g, 88.0 mmol) and stirred at this temperature for 2 hours. The reaction mixture was then poured into water (150 mL) and separated in a separatory funnel with diethyl ether (300 mL). The aqueous phase was extracted with diethyl ether (150 mL) and the organic phases were combined and washed with a saturated sodium chloride solution (300 mL). The organic phase was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure to afford a yellow oil. This oil was sublimed at 60 °C for 1.5 hours to remove the excess di-tert-butyl dicarbonate; the sublimed residue was then purified by silica-gel column chromatography, first in ethyl acetate/hexanes (7.5% ethyl acetate, 92.5% hexanes) then in ethyl acetate/hexanes (2% ethyl acetate, 98% hexanes) to afford a colorless, viscous oil (4.1607 g, 40.0 %yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.49 ppm (m, 2h), 7.42 ppm (m, 2h), 6.72 ppm (dd, $J$ = 17.6, 10.9 Hz, 1H), 5.79 ppm (dt, $J$ = 17.6, 0.7 Hz, 1.1H), 5.31 ppm (dt, $J$ = 10.9, 0.7 Hz, 1.2H), 1.53 ppm (s, 9.5H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 167.89, 138.72, 136.13, 135.06, 127.86, 126.91, 115.43, 85.71, 85.30 ppm. Elemental analysis; expected: C: 66.07, H: 6.82, S: 13.57, O: 13.54 %; found: C: 65.68, H: 7.20, S: 13.87 %.

E.3.2 RAFT polymerization of poly(SBOC)

**Figure E.2**: Scheme for RAFT polymerization of SBOC
To a 25 mL schlenk flask equipped with a magnetic stir bar was added SBOC (4.54 g, 21 mmol), RAFT CTA (42.4 g, 0.105 mmol), AIBN (8.61 mg, 0.053 mmol) and toluene (2.27 mL). This mixture was homogenized with stirring and the schlenk flask sealed and then purged by bubbling Ar\textsubscript{(g)} through the solution for 20 minutes. The reaction vessel was then placed in a thermostated 70 °C oil bath and stirred at this temperature for 16 hours. The polymerization was quenched by exposure to air and diluted in DCM and isolated by precipitation into ice cold hexanes to afford a slightly yellow powder. This powder was re-dissolved in DCM and precipitated into ice cold hexanes; this process was repeated until no monomer remained as evidenced by \textsuperscript{1}H NMR (2.97 g, 79.3% recovery based on conversion). 82.5% Conversion, \( M_{\text{SEC}} = 39,765 \text{ g/mol} \), PDI = 2.18. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \): 7.47-6.96 ppm (broad, 2H), 6.85-6.22 ppm (broad, 2H), 2.17-1.15 ppm (broad, 12H).

E.3.3 RAFT polymerization of poly(SBOC) kinetics with DP ≈ 200

In order to study the kinetics of the polymerization, a stock solution of SBOC (1.0 g, 4.62 mmol), RAFT CTA (9.34 mg, 0.024 mmol), AIBN (1.9 mg, 0.012 mmol) and toluene (0.50 mL) was prepared and an equal volume (0.15 mL) was dispensed into 8 ampoules containing magnetic stir bars. Each ampoule was degassed by 5 sequential freeze-pump-thaw cycles in liquid nitrogen and flame sealed under vacuum. All ampoules were then placed in a thermostated 70 °C oil bath with stirring then removed at various time points and quenched by plunging into liquid nitrogen to arrest polymerization. The ampoules were then broken and the contents dissolved in deuterated chloroform for \textsuperscript{1}H NMR analysis, then concentrated under reduced pressure then re-dissolved in THF for SEC analysis.
E.3.4 RAFT polymerization of poly(SBOC) kinetics with DP ≈ 50

RAFT polymerization kinetics at lower target DPs were carried out in much the same manner described above, with the exception that the stock solution of reagents was made using SBOC (0.50 g, 2.31 mmol), RAFT CTA (18.6 mg, 0.046 mmol), AIBN (3.8 mg, 0.023 mmol) and toluene (0.25 mL) and an equal volume of solution (0.15 mL) was dispensed into 4 ampules.

E.3.5 Waveguide fabrication

Silicon wafers were cleaved to approximately (2 x 6 cm) with the long dimension cleaved perpendicular to the major flat of the wafer to ensure efficient cleaving along the minor flat during cut back measurements. The cleaved wafers were cleaned by sequential rinsing with acetone and isopropyl alcohol then treated to O2 plasma for 1 minute. ZAP-1020, the ZPU12-480 adhesion promotor was then spun onto the silicon substrate using a two step protocol (500 RPM for 5 seconds, followed by 2500 RPM for 30 seconds), dried at 115 °C for 1 minute, and then allowed to cool to room temperature before ZPU12-480 was filtered through a 0.45 μm filter and spun on the wafer also using a two step protocol (500 RPM for 5 seconds, followed by 2500 RPM for 30 seconds). The ZPU was photocured using a broadband UV source with a power density of 30.5 mW/cm2 at 365 nm for 5 minutes under an atmosphere of N2(g). In order to ensure good adhesion between the hydrocarbon poly(SBOC) and highly fluorinated ZPU, the ZPU coated wafer was then subjected to O2 plasma for 1 minute followed by vapor deposition of 3-(trichlorosilyl)propyl methacrylate. This was accomplished by heating the 3-(trichlorosilyl)propyl methacrylate in a sealed glass petri dish containing the silicon wafer at 90 °C for 5 minutes. The wafer was then coated with a solution of poly(SBOC) in PGMEA, filtered through a 0.45 μm filter,
containing 5wt% (relative to mass of polymer) 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine as photoacid generator. A 2 µm uniform film of poly(SBOC) on top of the ZPU was obtained by spin coating at 750 RPM from a solution of poly(SBOC) in PGMEA (30 wt/v%) with 5 wt/wt% (relative to polymer loading) of the triazine PAG, and then drying at 90 °C for 2 minutes on a hot plate. Waveguides were then printed into the poly(SBOC) on the mask aligner at a calculated fluence of 2000 mJ/cm² at 365 nm based on the measured power when the I-line filter was present. The waveguide structures were then fully developed on a hot plate at 150 °C for 10 minutes. Again, the wafer was subjected to O₂ plasma for 1 minute followed by deposition of ZAP applied and dried in the same manner as described earlier. The ZPU top cladding was then deposited and cured, again, in the same manner as described above.

E.3.6 Film preparation for determination of refractive indices of deprotected poly(SBOC)

Films of poly(SBOC) 30 wt/v% in PGMEA with 5wt% (relative to mass of polymer) 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine as photoacid generator were spun at 500 RPM for 1 minute on silicon wafers followed by drying at 90 °C for 2 minutes. These coated silicon wafers were then flood exposed at various fluences of 365 nm light from the mask aligner (100, 250, 500, 1000, 2000 and 3000 mJ/cm²) using a square pattern and then developed on a hot plate at 150 °C for 10 minutes. Un-exposed films were similarly subjected to the same post exposure bake treatment; as spun films were also prepared. All measurements were repeated in triplicate from separately prepared films. Select films from this series were also used to obtain ATR-FTIR spectra.
E.3.7 Scanning electron microscopy of photopatterned poly(SBOC)

Films of poly(SBOC) 30 wt/v% in PGMEA with 5wt% (relative to mass of polymer) 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine as photoacid generator were spun at 500 RPM for 1 minute on silicon wafers followed by drying at 90 °C for 2 minutes. These films were then photopatterned with the pre-programmed dose array with a fluence of 350 mJ/cm$^2$ at 375 nm and subjected to a 150 °C, 10 minute post exposure bake.

![SEM micrographs of poly(SBOC) films containing 5 wt% triazine PAG pattered with a fluence of 350 mJ/cm$^2$ at 375 nm of a) a portion of the MLA dose array, b) a higher magnification of the same region imaged in a), c) a different region of the MLA dose array and d) a higher magnification of the region imaged in c. All micrographs were obtained at an accelerating voltage of 1.0 kV and a current of 6.4 nA.](image)

**Figure E.3:** SEM micrographs of poly(SBOC) films containing 5 wt% triazine PAG pattered with a fluence of 350 mJ/cm$^2$ at 375 nm of a) a portion of the MLA dose array, b) a higher magnification of the same region imaged in a), c) a different region of the MLA dose array and d) a higher magnification of the region imaged in c. All micrographs were obtained at an accelerating voltage of 1.0 kV and a current of 6.4 nA.
E.4 Results and Discussion

E.4.1 Radical polymerization of poly(SBOC)

While the BOC group serves as a handle to tune the refractive index of poly(SBOC) films, it was also crucial in actually facilitating free radical polymerization of the monomer (Figure 6.1). Thiols have appreciable chain transfer constants (~20 for styrenics) which, if present in monomer concentrations, would preclude the formation of high molecular weight polymer. The BOC group obviates this problem, but this does not necessarily mean that SBOC was compatible with all conventional forms of radical polymerization. ATRP was attempted with SBOC but no conversion was ever observed and was likely the result of coordination of the thioester to the copper catalysts; thioethers and thioesters are known to be difficult to polymerize under ATRP conditions. NMP was also attempted, and while high conversion was achieved, only low molecular weight products were observed in SEC analysis. $^1$H NMR studies of the isolated material actually showed the formation of thiolene AB step growth oligomers indicating substantial deprotection of the BOC group at 120 °C despite TGA analysis suggesting this group was thermally stable until 180 °C. This anomaly also offered insights into the AIBN catalyzed free radical polymerization experiments which yielded gels; here, while polymerization through the vinyl bonds dominated, thermal deprotection of the BOC group unmasked thiols that could dimerize to give disulfide crosslinks in the material. Differential scanning calorimetry (DSC) analysis of successfully synthesized poly(SBOC) showed an increase in $T_g$ during repeated thermal cycling despite the fact the experiment did not exceed 150 °C. This was attributed to thermal deprotection of the BOC group and the resulting crosslinking event that occurs. In
order to confirm that trace thermal deprotection of S-BOC groups lead to the “arm first like” star coupling observed in the RAFT polymerization of SBOC with target DP = 200, the polymerization was performed with a lower target DP (DP = 50) as well. Lower target DPs resulted in the polymerization attaining high conversions (>90%) without significant coupling reactions as observed by SEC analysis.

E.4.2 RAFT polymerization of poly(SBOC) kinetics with DP = 50

As can be seen in Figure E.4, multi-modal molecular weight distributions were observed at high conversion and were accompanied by a sharp increase in PDI above ~70% conversion when high target DPs were employed. Conversely, much better control over PDI was observed for lower target degrees of polymerization Figure E.5. Additionally, only two molecular weight populations are observed at very high conversions compared to the four distinct populations observed at high conversion with DP = 200. Comparison of the two sets of kinetic experiments would suggest that the reaction leading to arm first star coupling is the result of a slow background reaction (i.e. thermal decomposition and dimerization of side chains) that is out competed at shorter reaction times by propagation.
Figure E.4: a) semi-log kinetic plots b) molecular weight and polydispersity as a function of conversion and c) SEC chromatograms of the RAFT solution polymerization of SBOC [3.08] M in toluene: SBOC/CTA/AIBN = 200/1/0.5.
Figure E.5: a) semi-log kinetic plots b) molecular weight and polydispersity as a function of conversion and c) SEC chromatograms of the RAFT solution polymerization of SBOC [3.08 M] in toluene: SBOC/CTA/AIBN = 50/1/0.5.
E.4.3 NMR spectroscopy of SBOC monomer

Figure E.6: a) $^1$H NMR and b) $^{13}$C NMR spectrum of SBOC in d-chloroform

E.4.4 NMR spectroscopy of poly(SBOC)

$^1$H NMR spectroscopy of poly(SBOC), shown in Figure E.7, demonstrates that while the arm first star coupling-like reaction that takes place to give multimodal distributions in the SEC chromatograms of the material, the actual percent decomposition must be very small as the integration remains what would be expected for a polymerization of SBOC proceeding without any thermal decomposition.
**Figure E.7:** $^1$H NMR spectrum of poly(SBOC) synthesized via RAFT polymerization in d$_2$-methylene chloride

E.4.5 FTIR spectroscopy of poly(SBOC)

Shown below are ATR-FTIR absorption spectra for poly(SBOC) before and at various stages of deprotection. The film thermally, and quantitatively, deprotected exhibited complete attenuation of the carbonyl stretching frequency at 1722.6 cm$^{-1}$ attributed to the carbonyl group of the SBOC monomer. Additionally, a new peak in the spectrum of the thermally deprotected film appeared at 2562 cm$^{-1}$ which was attributed to the resultant thiophenol moiety that is un-masked after deprotection and this stretching frequency was absent in the as-spun film of poly(SBOC). Both the carbonyl and thiophenol vibrational
frequencies were found in the photochemically deprotected films illustrating that while photochemical deprotection is not quantitative, as in the thermal deprotection, it does in fact proceed to some degree.

**Figure E.8:** Stacked ATR-FTIR absorption spectra of poly(SBOC) on silicon wafers: in the absence of irradiation, after being flood exposed at 2000 mJ/cm² with 365 nm light and a 10 minutes 150 °C post exposure bake (PEB), and after thermal deprotection (200 °C for 30 minutes); background absorptions from water removed

E.4.6 Refractive index measurements of poly(SBOC) films

Following the thermal deprotection of poly(SBOC) with FTIR showed that after 30 minutes at 200 °C the carbonyl stretching frequency had completely attenuated. Based on this, poly(SBOC) 30 wt/v% in PGMEA containing 5 wt% triazine PAG were spun onto a silicon substrate and dried at 90 °C for 2 minutes. The substrate was then heated at 200 °C for 30 minutes; then the wavelength dependent refractive index data shown in **Figure E.9**
was then obtained via the prism coupling method. It should also be noted that the refractive index of as-spun films was slightly lower (1.54 ± 0.0087 @1554 nm) than films treated to the standard PEB treatment and is probably the result of a background deprotection reaction initiated by thermally decomposed PAG.

![Graph showing refractive index values for poly(SBOC) with 5 wt% triazine PAG after quantitative thermal deprotection at wavelengths from 633 to 1550 nm.](image)

**Figure E.9:** Refractive index values for poly(SBOC) with 5 wt% triazine PAG after quantitative thermal deprotection at wavelengths from 633 to 1550 nm

E.4.7 Investigating dimensional changes during deprotection and subsequent crosslinking of thin, substrate supported films of poly(SBOC)

A film of poly(SBOC) 30 wt/v% in PGMEA containing 5 wt% triazine PAG was spun onto a silicon substrate and dried at 90 °C for 2 minutes. This substrate was cleaved into approximately three equal pieces. The first third was untouched and used as a reference for the initial film thickness measurement. The second third was flood exposed at 2000 mJ/cm² with 365 nm light on the mask aligner and subjected to a 10 minute 150 °C post exposure bake (PEB). The last third was first photochemically crosslinked by uniform irradiation on the mask aligner at 2000 mJ/cm² with 365 nm light then thermally developed at 150 °C for
10 minutes followed by thermal deprotection at 200 °C for 30 minutes. The initial photochemical crosslinking in the third sample was done to minimize any reflow of the film that could potentially occur at temperatures well above the T_g of poly(SBOC), required for quantitative thermal deprotection. Each film thickness was then measured by surface profilometry, and the results are shown in Figure E.10. It should be note that the volume loss (and hence thickness change) arise from the mass loss reaction associated with the deprotection of the BOC group and evolution of the resultant gases leaving the film; the percent thickness change in the thermally (i.e. quantitatively) deprotected film was commensurate to the percent change in mass (by TGA) at 200 °C as shown in Figure E.11.

![Figure E.10: Surface profilometry of poly(SBOC) films after various thermal and photochemical treatments](image)

**Figure E.10:** Surface profilometry of poly(SBOC) films after various thermal and photochemical treatments
E.4.8 Thermal analysis of poly(SBOC)

Thermal gravimetric analysis (Figure E.11) was performed on poly(SBOC) with a heating rate of 10 °C / minute from 0 to 700 °C in an inert atmosphere of nitrogen gas. The first mass loss event (-44.7 wt%) corresponds directly to the concurrent loss of carbon dioxide (44.01 g/mol, 18.6 wt%) and isobutylene (56.1 g/mol, 23.7 wt%) from the polymer as a result of the thermal decomposition of the BOC protecting group present in each repeat unit (236 g/mol). This thermal decomposition event was useful in terms of providing a processing window for poly(SBOC) that was not to be exceeded as well as providing a useful route to quantitatively deprotect the material in order to determine the maximum refractive index difference that could be generated assuming 100% BOC deprotection.

Figure E.11: Thermal gravimetric analysis of poly(SBOC) with a heating rate of 10 °C / minute in a nitrogen atmosphere from 0 to 700 °C
DSC analysis of poly(SBOC) was first performed in a DSC cell continually flushed with nitrogen gas at a heating rate of 10 °C from 0 to 180 °C (Figure E.12a). As a result of scanning through the midpoint of the thermal deprotection of the BOC group, each successive scan results in more unmasked thiols, increasing the degree of crosslinking and increasing the T\textsubscript{g}. Because of this crosslinking event the T\textsubscript{g} was observed to increase from 110.4 to 123.2 °C between the 2\textsuperscript{nd} and 3\textsuperscript{rd} heating cycles and an accurate T\textsubscript{g} could not be obtained from the first scan before deprotection and crosslinking. In order to try and alleviate this, Modulated DSC (mDSC) was performed with the cell temperature never exceeding 150 °C, which is below the onset of decomposition as noted by TGA. However, again, an increase in observed T\textsubscript{g} between the second and third scan was observed, albeit with a smaller difference than when the temperature was swept through the point of onset of thermolysis of the BOC group as well as overall lower observed T\textsubscript{g}’s for the second and third scans. It would appear thermal deprotection leading to crosslinking and hence an increase in T\textsubscript{g} can occur before the nominal onset of BOC thermolysis and could help explain the mechanism by which arm first star coupling reactions are observed in the SEC analysis of this material under RAFT polymerization conditions.
Figure E.12: a) Differential Scanning Calorimetry (DSC) analysis of poly(SBOC) with a heating rate of 10 °C / minute in a nitrogen atmosphere from 0 to 180 °C. b) Modulated Differential Scanning Calorimetry (MDSC) analysis of poly(SBOC) with an overall heating rate of 3 °C/ minute with a modulation of ±2 °C/ 60 seconds from 25 – 150 °C.
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