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Sulfenyl Chlorides: An Alternative Monomer Feedstock from Elemental Sulfur for Polymer Synthesis

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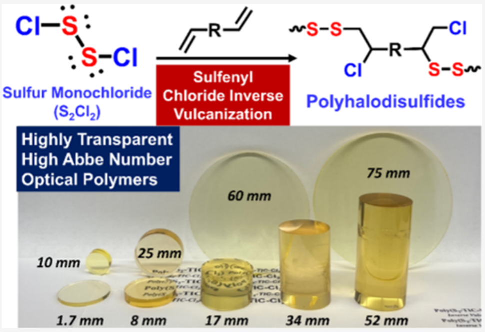
ABSTRACT: A polymerization methodology is reported using sulfur monochloride (S_2Cl_2) as an alternative feedstock for polymeric materials. S_2Cl_2 is an inexpensive petrochemical derived from elemental sulfur (S_8) but has numerous advantages as a reactive monomer for polymerization vs S_8. This new process, termed sulfenyl chloride inverse vulcanization, exploits the high reactivity and miscibility of S_2Cl_2 with a broad range of allylic monomers to prepare soluble, high molar-mass linear polymers, segmented block copolymers, and crosslinked thermosets with greater synthetic precision than achieved using classical inverse vulcanization. This step-growth addition polymerization also allows for preparation of a new class of thiol-free, inexpensive, highly optically transparent thermosets ($\alpha = 0.045$ cm^{-1} at 1310 nm), which exhibit among the best optical transparency and low birefringence relative to commodity optical polymers, while possessing a higher refractive index ($n > 1.6$) in the visible and near-infrared spectra. The fabrication of large-sized optical components is also demonstrated.



■ INTRODUCTION

The electrophilic addition of organosulfenyl chlorides (RS−Cl) to olefinic substrates, such as norbornene, is a highly efficient, catalyst-free reaction that proceeds via ionic episulfonium intermediates, followed by chloride anion addition with anti-stereochemistry to form β-halothioether groups (Figure 1a).[1−3] This reaction is mechanistically distinctive but analogous to the "thiol-X addition reaction" of thiols to unsaturated compounds, which include thiol-ene, thiol-yne, and thiol-isocyanate reactions.[4−9] The use of inorganic sulfenyl chlorides, such as S_2Cl_2, as a feedstock for polymers has significant potential for utilization of elemental sulfur generated from petroleum refining. Polymerization with elemental sulfur (S_8) has recently emerged as an important area of polymer chemistry and sustainability.[10] A major advance in this area was the discovery of inverse vulcanization by Pyun et al. in 2013,[11] which uses molten elemental sulfur as a monomer and a bulk medium for free radical polymerizations with unsaturated organic comonomers to prepare high-sulfur-content polymers possessing useful electrochemical, optical, adhesive, and chemical scavenging properties.[12−15] However, the poor miscibility of numerous organic monomers in liquid sulfur, along with the high temperatures required for this process, limited the scope of polymers that can be prepared.[10,12−15] Furthermore, the ability to control basic features of the polymer structure, namely, molar mass, composition, and architecture, remain challenging using inverse vulcanization.

Hence, there is a compelling opportunity to use inexpensive sulfur base chemicals produced from petroleum refining as monomers for polymerization toward S_8 utilization (Figure 1b). Notable examples of sulfur base chemicals (base chemical is a term from the petrochemical sector) include sulfuric acid (H_2SO_4, made from oxidation and hydrolysis of S_8) and carbon disulfide (CS_2, made from reaction of S_8 with methane).[10] CS_2 has been used as a monomer in chain-growth or coordination polymerization to produce thiocarbonyl-containing polymers.[16−18] Chlorination of S_8 affords sulfenyl chlorides, such as sulfur dichloride (SCl_2) and sulfur monochloride (S_2Cl_2).[2,3,19] S_2Cl_2 is a thermally and chemically stable (when excluded from water, or nucleophiles) yellow liquid that is very miscible with conventional organic comonomers, in stark contrast to liquid elemental sulfur. Direct polymerization of S_2Cl_2 with di- or triolefinic comonomers would afford a new class of linear or network halodisulfide polymers. S_2Cl_2 is an atom-economical A_2 monomer for step-growth polymerization

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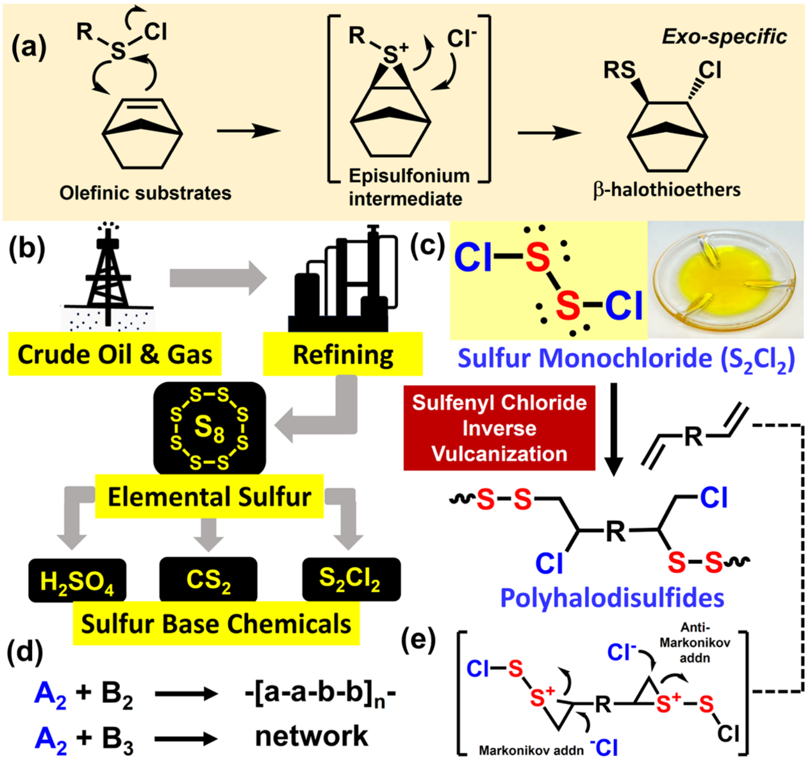


Figure 1. (a) Proposed mechanism for electrophilic addition of sulfenyl chlorides to olefinic substrates, such as norbornene, which proceed via ionic episulfonium intermediates to form C−S and C−Cl bonds. (b) Generalized scheme for the production of elemental sulfur and S_8-derived sulfur base chemicals, such as sulfuric acid (H_2SO_4), carbon disulfide (CS_2), and sulfur monochloride (S_2Cl_2), from refining of crude oil and gas. Processes for the production of hydrocarbons are omitted for simplicity. (c) Structure and liquid form of sulfur monochloride under ambient conditions. (c, d) Concept of using S_2Cl_2 as an A_2 monomer for step-growth polymerization with olefinic monomers termed sulfenyl chloride inverse vulcanization. (e) Proposed scheme for episulfonium intermediates present in SC-IV with S_2Cl_2 and bis-vinyl comonomers.

(Figure 1c, d) that is envisioned to form episulfonium intermediates that upon either Markovnikov or anti-Markovnikov addition of chloride anion nucleophiles produces regioisomeric microstructures of primary and secondary alkyl halides (Figure 1c−e). There have been only a handful of reports on using sulfur monochloride as a comonomer in polymerization, which include copolymerizations with olefinic and aniline-based monomers, but primarily afforded oligomers, insoluble materials, or degradable scaffolds for drug delivery.[20−23] The intramolecular cyclization of RS−Cl groups to electrophilic moieties (e.g., arenes, olefins) has been exploited for the synthesis of heterocyclic small molecules,[19] but it is conversely problematic for step-growth polymerizations, as cyclization side-reactions limit monomer conversion.[24] S_2Cl_2 in particular has a long history of use in crosslinking/vulcanization of natural rubber, styrene-butadiene rubber, and butyl rubber, where sulfenyl chlorides are significantly more reactive than insoluble elemental sulfur-based agents and must be done at room temperature (RT) to form crosslinked rubber, which is referred to as "cold vulcanization." This early polymer chemistry is historically notable for the preparation of elastomeric polymeric materials; however, successful step-growth polymerization of S_2Cl_2 with olefinic comonomers remained unsuccessful for the preparation of high-molar-mass linear and network polymers.[25]

Herein, we report on a new process, termed sulfenyl chloride inverse vulcanization (SC-IV), which is a next-generation advance over the inverse vulcanization of S_8 using an alternative, highly reactive sulfur base chemical from petroleum refining (Figure 1c). This is the first step- growth addition polymerization of S_2Cl_2 with olefinic monomers to afford high molar-mass linear thermoplastics and optically transparent thermoset materials. This approach profoundly expands the scope of accessible monomers relative to those demonstrated for S_8-inverse vulcanization while also allowing for precision polymer synthesis of a diverse array of homopolymers, segmented block copolymers, and crosslinked networks. This methodology is particularly attractive for preparing sulfur-containing polymers without the need for thiol monomers, which are a more expensive feedstock and limited in scope in comparison to other commodity monomers.[26] The use of thiol-free polymer chemistry is particularly attractive for high-volume consumer plastic optics and emerging 3D sensing industries that requires commodity optical polymers with high transparency in the visible to near-infrared spectrum, low chromatic dispersion, and high refractive index coupled with robust thermomechanical properties.[27−33]

■ RESULTS AND DISCUSSION

Monomer Design and SC-IV Polymerization. An initial survey of commercially available olefinic monomers revealed that activated olefins, such as styrenics and norbornenes, reacted violently with bulk S_2Cl_2 even at reduced temperatures, while (meth)acrylates were effectively unreactive (see the Supporting Information, pg. S67−S69). Conversely, allylic monomers, such as 1,3-diallyl isophthalate (DAI), or 1,4-diallyl terephthalate (DAT), were found to be miscible and chemically stable when mixed at both room and elevated temperatures in neat S_2Cl_2, which prompted the focus of this study on allyl monomers. To suppress both intra- and

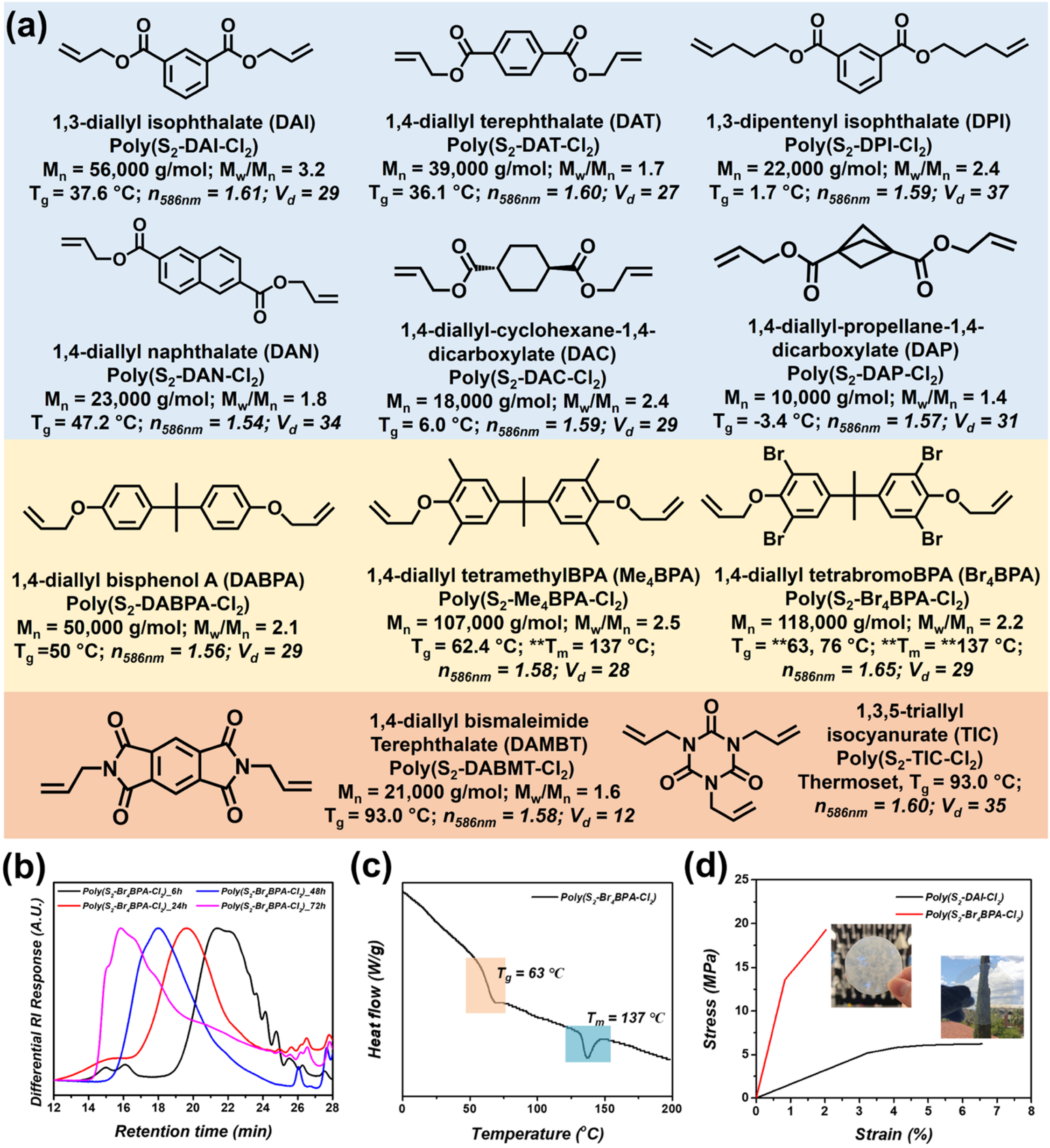
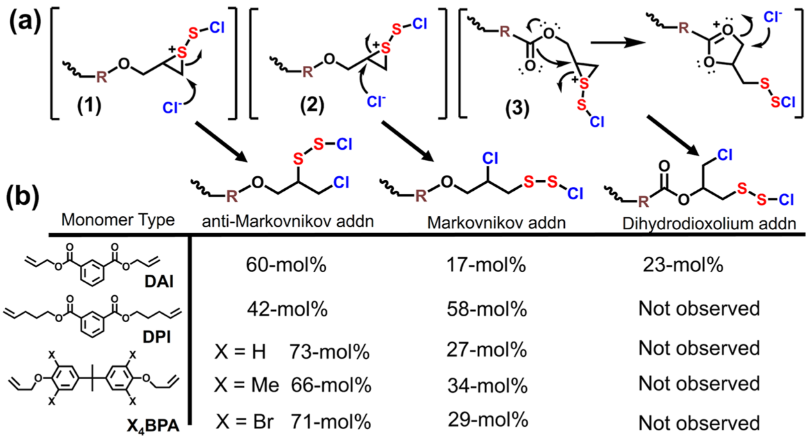


Figure 2. (a) Bis-allylic monomers used for successful SC-IV in using either bulk or solution polymerizations using the design principles from Figure 3a using classical aromatic step-growth monomer cores, along with cyclohexyl and propellane motifs to prepare soluble, linear thermoplastic disulfide materials, including polymer characterization data of molecular mass, polydispersity, glass transition, refractive index value at 586 nm, and Abbe number. (b) SEC chromatograms of SC-IV of S_2Cl_2 and Br_4BPA affording high M_W poly(S_2−Br_4BPA−Cl_2) M_n = 116,500; M_w/M_n = 3.1. (c) DSC thermogram of high molar-mass poly(S_2−Br_4BPA−Cl_2). (d) Tensile testing stress vs strain plots of poly(S_2-DAI-Cl_2) and poly(S_2−Br_4BPA−Cl_2); insets are free-standing films (400 μm thick) of each material.

cyclization reactions of allylic molecules with S_2Cl_2, the use of rigid aromatic (DAI, DAT, DAN) and cycloalkane (DAC) monomers with rigid diester spacers was explored for SC-IV, along with bisphenol A cores (BPA, Me_4BPA, Br_4BPA) (Figure 2a). Notable monomers that required synthesis were the diallyl propellate diester (DAP) containing a compact rigid propellane unit, the dipentenyl isophthalate to introduce flexible spacers, and the diallyl bismaleimide terephthalate (DABMT) to introduce rigid cycloimide units to the final polymers. Polyhalodisulfides prepared from SC-IV were given the general abbreviations of poly(S_2−R−Cl_2) (see Figure 2a, Table S1 in the Supporting Information). Surprisingly, all of these monomers were observed to efficiently undergo SC-IV with S_2Cl_2, reaching a high vinyl group conversion (p > 0.90) affording high-molecular-weight polymers (M_n = 18,000−116,500 g/mol; see Figure 2a), as confirmed by size-exclusion chromatography (SEC). Diallyl Br_4BPA was observed to afford soluble polymers of very high molar mass by SC-IV, with M_w values exceeding 300,000 g/mol (Figure 2b).

Monomer Effects on Structure−Property Relationships. *Thermal and Mechanical Properties.* Structure−property correlations of linear polyhalodisulides from Figure 2a were conducted with respect to bulk thermomechanical properties. Thermal properties of polyhalosulfides from DAI and DAT as determined from differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) indicated glass transitions around room temperature (T_g = 36−37 °C, Figure 2a, Table S1). To modulate the thermal properties, variation of



Monomer Type	anti-Markovnikov addn	Markovnikov addn	Dihydrodioxolium addn
DAI	60-mol%	17-mol%	23-mol%
DPI	42-mol%	58-mol%	Not observed
X_4BPA, X = H	73-mol%	27-mol%	Not observed
X = Me	66-mol%	34-mol%	Not observed
X = Br	71-mol%	29-mol%	Not observed

Figure 3. (a) Proposed mechanism for ring-opening of episulfonium intermediates with chloride anions to form the anti-Markovnikov, Markovnikov, or dihydrodioxolium addition isomeric units in the SC-IV of monomers from (b). (b) Molar ratios of the isomeric microstructures as determined from NMR spectroscopic analysis.

the diallyl diester cores was conducted to introduce larger naphthalate hard segments poly(S_2-DAN-Cl_2, T_g = 47.2 °C; T_m = 142.3 °C) and non-aromatic cycloalkanes based on poly(S_2-DAC-Cl_2) (T_g = 6.3 °C) or poly(S_2-DAP-Cl_2, T_g = 22.4 °C). The introduction of a longer pentenyl spacer vs allyl groups was investigated by polymerization of DPI, which was observed to significantly lower the glass-transition of poly(S_2-DPI-Cl_2, T_g = 1.7 °C). Polyhalodisulfides prepared from diallyl Me_4BPA and Br_4BPA monomers were observed to afford semicrystalline materials at a sufficiently high molar mass (Figure 2a) with melting transitions (T_m) above T = 100 °C and T_g values ~50−60 °C (e.g., poly(S_2−Br_4BPA−Cl_2), T_g = 63.4 °C, T_m = 137.2 °C (Figure 2c)). Finally, the highest glass transition observed for these linear polyhalodisulfides poly(S_2-DABMT-Cl_2, T_g = 93.0 °C) was achieved by the introduction of rigid cycloimide groups. The thermal stabilities of all of these polyhalodisulfides were determined using TGA, which indicated that these materials were thermally stable to temperatures of above 250 °C ($T_{\text{decom TGA}}$ ~ 260 °C), which were comparable to well-established optical polymers, such as poly(methyl methacrylate) (PMMA), or halogenated polymers, such as poly(vinyl chloride) (PVC) (see Figure S75). Polymer processing using solution casting of poly(S_2-DAI-Cl_2) (M_n = 56,000 g/mol) and poly(S_2−Br_4BPA−Cl_2) (M_n = 116,500 g/mol) afforded free-standing films (400 μm thickness), which were used for mechanical tensile testing. These polymers were derived from the most inexpensive commercially available allylic monomers and were amenable to large-scale production required for polymer processing. Solution-casting was conducted (vs hot-pressing) to fabricate larger-area samples for tensile testing to avoid potential degradation of C−Br bonds in poly(S_2−Br_4BPA−Cl_2) during processing. Poly(S_2-DAI-Cl_2) was observed to afford a lower tensile strength (5 MPa) but a slightly higher elongation at break (9%) relative to poly(S_2−Br_4BPA−Cl_2), which exhibited a higher tensile strength (20 MPa) imparted from the BPA core, but with more brittle fracture (2% elongation at break, Figure 2d). In summary, facile modulation of thermomechanical properties in these materials was clearly demonstrated using SC-IV, allowing for modulation of T_g's and T_m's spanning over a range of 100 °C, pointing to the control and versatility afforded from this new process. Conversely, this type of control over thermal properties in S_8-derived polymers from inverse vulcanization required almost a decade of development from groups around the world.[10]

Optical Properties. For new optical polymers, the optical properties of interest include the wavelength-dependent refractive index (RI, or n) and the optical transmittance (% T). For use as plastic lenses in consumer eyeware, or mobile devices, polymers should have high RI (n > 1.65), sufficiently low dispersion, and robust thermomechanical properties while also being amenable to polymer processing.[28−32] Simply reporting on one of these properties (e.g., only high RI) without identification of the optical spectral window of use only partially informs on the viability of new polymers for plastic optics.[27] A measure of dispersion is an application-specific Abbe number (V_D), which quantifies how the RI of a material changes over the spectral range of interest. An example of V_D, appropriate to the visible spectrum, is shown in eq 1, where n_D, n_F, and n_C are the refractive indices of the material at the wavelength of the sodium D (589.2 nm), hydrogen F (486.1 nm), and hydrogen C (656.3 nm) lines, respectively. Current commodity optical polymer technologies revolve principally around well-established thermoplastic or thermoset polymers, such as PMMA, polyallylcarbonates (commercially, CR-39 from PPG), or polycarbonates that possess very high Abbe number polymers (V_D ~ 59) and very low birefringence, but with low RI (n ~ 1.49). Highly aromatic plastics, such as polystyrene, polycarbonates, and polyimides, possess higher refractive indices (n ~ 1.55−1.75) but have significantly lower Abbe numbers and higher birefringence, with values below V_D < 30, which render these unusable for consumer eyeware and may be strongly colored. Higher birefringence in plastic optics results in haziness and prevents fabrication of thicker optical elements that retain high transparency, as will be later discussed.

$$\text{Abbe number } (V_D) = \frac{n_D - 1}{n_F - n_C} \qquad \begin{aligned} n_C &= \text{RI at 656 nm} \\ n_D &= \text{RI at 589 nm} \\ n_F &= \text{RI at 486 nm} \end{aligned} \qquad (1)$$

Optical characterization of polyhalodisulfides (see Figure 2a, Table S1) was conducted using ellipsometry of spin-coated thin films (for RI and V_D) and ultraviolet−visible−infrared (UV−vis−IR) transmission spectroscopy for evaluation of optical transmittance. General trends for the RI of these

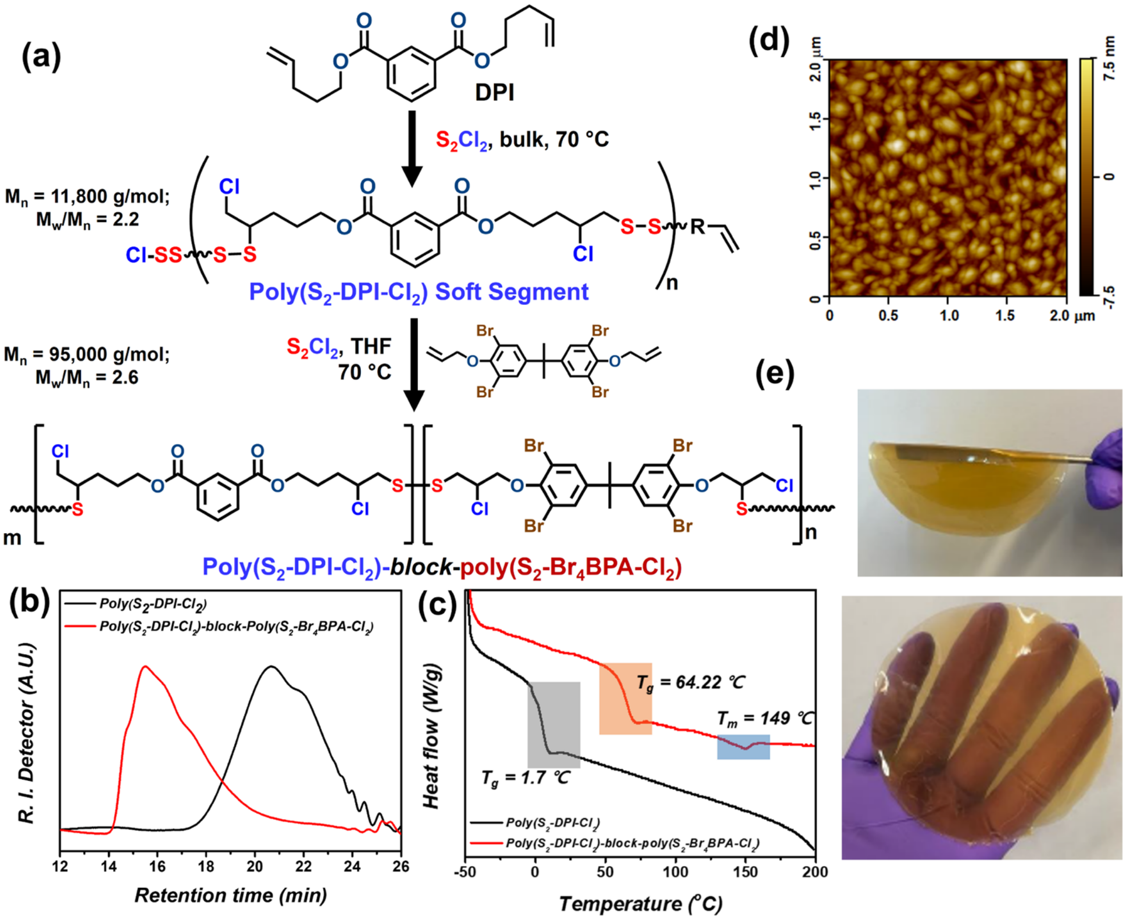


Figure 4. (a) Synthetic scheme for segmented block copolymers via sequential SC-IV using a prepolymer step-growth polymerization approach. (b) SEC-THF chromatograms and DSC (c) of the poly(S_2-DPI-Cl_2) prepolymer (M_n = 11,800 g/mol; M_w/M_n = 2.2) and the poly(S_2-DPI-Cl_2)-*block*-poly(S_2−Br_4BPA−Cl_2) M_n = 95,000 g/mol; M_w/M_n = 2.6. (d) AFM height image of microphase-separated thin films of the poly(S_2-DPI-Cl_2)-*block*-poly(S_2−Br_4BPA−Cl_2). (e) Free-standing flexible thin films from solution-casting of the poly(S_2-DPI-Cl_2)-*block*-poly(S_2−Br_4BPA−Cl_2) copolymer..

polymers closely correlated with the molar ratios of C/H/S/O in the final material composition. Phthalate polymers from DAI, DAT, and DPI exhibited RI values around $n_{586\ \mathrm{nm}}$ = 1.59−1.61 and Abbe numbers in the range of V_D = 29−40, where variations of the monomer to high C/H content monomers, such as DAN, resulted in slightly lower RI (n = 1.54) and higher Abbe numbers (V_D = 34). RI values ($n_{585\ \mathrm{nm}}$ = 1.58−1.59) were slightly reduced from non-aromatic polyhalodisulfides from cyclohexane (DAC) and propellane (DAP) cores since aromatic groups possess higher molar refraction values[24] while still retaining comparable Abbe numbers (V_D = 29−40). The highest RI ($n_{586\ \mathrm{nm}}$ = 1.64) was achieved for the brominated disulfide polymer (poly(S_2−Br_4BPA−Cl_2)), which was not surprising given the high molar refraction of Br atoms,[29] as evidenced by the reduced RI ($n_{586\ \mathrm{nm}}$ = 1.58) for the methylated BPA polymer poly(S_2-Me_4BPA-Cl_2); Abbe number values for BPA-based polymers were in the range of V_D = 27 to 29. The polyimide-based disulfide material from the DABMT monomer exhibited a slightly lower RI value ($n_{585\ \mathrm{nm}}$ = 1.57), along with a low Abbe number (V_D = 17), due to the red coloration of the final material. However, with the exception of poly(S_2-DABMT-Cl_2), spin-coated thin films (100 μm on glass, Figure S74) or free-standing films of polyhalodisulfides (Figure 2d-insets) exhibited low coloration (Figure S76) and high optical transmittance across the visible, near-, and short wave IR spectrum.

Structural Characterization of Polyhalodisulfides. To ascertain the microstructures formed during the SC-IV of allylic monomers, in-depth NMR spectroscopic characterization was conducted using one-dimensional (1D) (^{1}H, ^{13}C, 13C−DEPT) and two-dimensional (2D) measurements (HSQC) of polyhalodisulfides from the diallyl diesters (DAIs), diallyl BPAs, and dipentenyl diesters (DPIs) to quantify the regioisomeric molar ratios as a function of organic comonomer structure (see Figures 3, and S80−S84). As shown in Figure 3, RS−Cl addition to homoallylic monomers proceeded by episulfonium formation, followed by either anti-Markovnikov (Figure S80a(1)) or Markovnikov (Figure S80a(2)) addition of the chloride anion to form either secondary or primary alkyl halides, respectively. Furthermore, other ring-opening pathways of episulfonium intermediates are possible by attack of auxiliary polar groups, such as esters, to form dihydrodioxolium intermediates, which after chloride anion attack (Figure S80a(3)) formed alternative isomeric side products. Polyhalodisulfides prepared from diallyl BPA monomers afforded a similar molar ratio of primary vs secondary alkyl halides (∼70:30 mol %, Figure S80), indicating the higher specificity of the anti-Markonikov addition in these polymerizations. In the case of diallyl diester (DAI), attack of

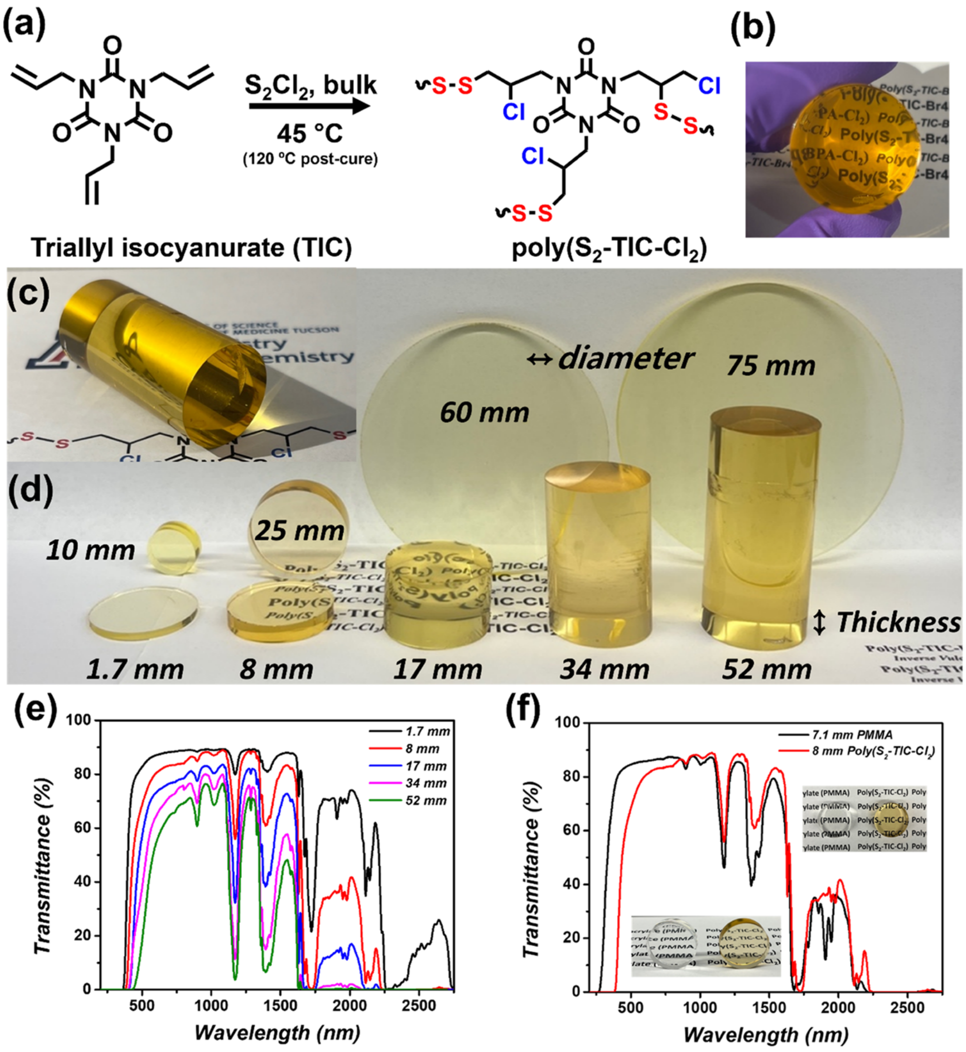


Figure 5. (a) Synthetic scheme for bulk SC-IV with TIC to prepare optically transparent glassy thermosets. (b) Top-down and (c) side-on view of poly(S_2-TIC-Cl_2) windows (thickness = 52 mm). (d) Large-scale thermoset windows of varying thicknesses and diameters prepared via bulk SC-IV. (e) Optical transmission spectra of poly(S_2-TIC-Cl_2) windows from 200 to 2750 nm from thicknesses of 1.7−53.0 mm. (f) Optical transmission spectra of PMMA (7.1 mm thick) vs poly(S_2-TIC-Cl_2) (8.0 mm thick) windows; inset is 25.0 mm-diameter windows of these samples.

episulfonium intermediates by the ester group resulted in the formation of dihydrodioxolium intermediates, which afforded a small fraction of a third isomeric unit containing a microstructure unit with both primary alkyl chlorides and primary disulfides (23 mol %) in addition to microstructures from both anti-Markovnikov (60 mol %) and Markovnikov (17 mol %) additions (Figure 3b). However, suppression of this dihydrodioxolium intermediate was achieved by incorporation of a longer pentenyl spacer on the isophthalate group (i.e., the DPI monomer), which afforded a microstructure composed of only primary and secondary alkyl halides (58:42 molar ratios, respectively, Figure 3b). The retention of sulfide units in polyhalodisulfides prepared by SC-IV was confirmed by close agreement of elemental analysis of the sulfur content vs S_2Cl_2 feed ratios used in these polymerizations (Table S1). Furthermore, both soluble linear and crosslinked polyhalodisulfides were observed to be degradable through reduction of disulfide units by solution treatment with dithiothreitol (DTT, Figures S77−S79).

Segmented Block Copolymers via SC-IV Prepolymer Step-Growth Polymerization. The synthesis of segmented block copolymers possessing microphase-separated hard and soft segments[32] was conducted using a two-stage, one-pot SC-IV process. In the first step, a soft segment prepolymer from poly(S_2-DPI-Cl_2) was prepared (M_n = 11,800 g/mol; M_w/M_n = 2.6; T_g = 1.7 °C) via bulk SC-IV of S_2Cl_2 and DPI, followed by efficient chain extension with the sequential addition of the bis-allyl Br_4BPA monomer and S_2Cl_2 for incorporation of hard segments to form the high-molar-mass segmented block copolymers of poly(S_2-DPI-Cl_2)-*block*-poly(S_2-Br_4BPA-Cl_2) (M_n = 95,000 g/mol; M_w/M_n = 2.2, Figure 4a,b). The overall composition designed for this segmented copolymer possessed around 70 mol % poly(S_2-DPI-Cl_2) units to prepare a soft copolymer reinforced by crystallized phase-separated domains of poly(S_2−Br_4BPA−Cl_2). The validity of this design was conducted by DSC of the poly(S_2-DPI-Cl_2)-*block*-poly(S_2−Br_4BPA−Cl_2) segmented copolymer, which revealed the presence of two thermal transitions corresponding to a glass transition (T_g = 64 °C) and a weak transition at higher temperatures, which was assigned to a melting transition (T_m = 149 °C) for the Br_4BPA hard segments (Figure 4c). To confirm that phase-separated morphologies were obtained, spin-coated thin films of the segmented poly(S_2-DPI-Cl_2)-*block*-poly(S_2−Br_4BPA−Cl_2) copolymer on SiO_2 wafers were prepared and imaged using noncontact-mode atomic force microscopy (AFM, Figure 4d and Figure S70). The AFM height image confirmed the presence of a microphase-separated morphology with corrugated spherical and elongated features with primary domains on the order of 50 nm coincident with larger aggregate domains on the order of 150 nm ubiquitously spaced in a continuous lossy matrix. Solution processing of this segmented block copolymer afforded flexible free-standing films (Figure 4e), which was dramatically different from the brittle glassy or viscous fluid homopolymers discussed previously in Figure 2a. Tensile testing of these free-standing films revealed enhanced elongation at break (tensile strength = 9 MPa, elongation at break = 250%, Figure S71) as a consequence of the segmented copolymer design, where the introduction of the soft poly(S_2-DPI-Cl_2) phase significantly reduced the brittleness of these materials in comparison to the poly(S_2−Br_4BPA−Cl_2) homopolymer (tensile strength = 21 MPa, elongation at break = 2%, Figure 2d). These enhanced mechanical properties point to the modularity and synthetic control of the SC-IV process using the appropriate polymerization of allylic monomers.

Optically Transparent Glassy Thermosets. As a final example to validate the step-growth nature of SC-IV, crosslinked polymer networks were prepared by the A_2 + B_3 polymerization of S_2Cl_2 with 1,3,5-triallyl isocyanurate (TIC), which has the advantage of being a low-cost, commercially available, liquid reagent. SC-IV of S_2Cl_2 and TIC were conducted in bulk at 45 °C for 4 h, followed by a postbake cure (T = 120 °C, 20 h) to form crosslinked, yellow-tinted glassy polymers (Figure 5a,b). These thermoset materials exhibited excellent thermomechanical properties (T_g = 93 °C; tensile strength = 28 MPa, 1.8% elongation at break, Figure S87) and favorable optical properties ($n_{586\text{nm}}$ = 1.61, V_d = 38), where the absence of aromatic moieties in the TIC monomer resulted in an improved Abbe number (Figure 2a). Since these electrophilic addition reactions proceeded without the formation of byproducts, the SC-IV process was amenable to melt-casting of liquid resins to form large optical windows. This discovery was significant from a polymer chemistry standpoint as only a few robust step-growth addition polymerizations are widely used from commercial, inexpensive monomers (e.g., isocyanates, epoxides). The facile nature of this bulk polymerization was demonstrated by the fabrication of large, defect-free plastic optics in the form of flat circular windows (diameter = 25 mm) of varying thicknesses (1.7−52 mm) and diameters (10−75 mm), which, after sandpaper-polishing, afforded yellow-tinted, highly transparent thermoset windows (Figure 5b−d). The high optical quality of the thickest (52 mm) or widest (75 mm) thermoset windows from direct melt-casting of monomers is particularly striking, given how suppression of bubbles or defects is challenging for large optical components without the use of compression molding fabrication. Optical transmittance (%T) measurements from 300 to 2500 nm of these thermoset windows showed excellent optical transparency over the visible spectrum above 500 nm and in important spectral windows in the NIR and SWIR, namely, from 800 to 1100 nm, and at telecom wavelengths (1310 and 1550 nm) with greater than 80−90%T achieved for 1.7 and 8 mm thick samples, while also remarkably retaining 60−70%T for ultrathick 52 mm windows in the NIR spectrum (Figure 5e; note that these transmittance values include Fresnel reflection at the front and back surfaces of the window, which for a refractive index of 1.60 reduces transmission by 5.3% per surface). To contextualize the significance of these results, direct transmittance comparisons were made against arguably the most transparent commodity optical polymer to date, PMMA, using PMMA windows in the range of 1−14 mm thickness. These measurements confirmed that PMMA ($n_{586\text{nm}}$ = 1.49, Figure S85) exhibited better transparency from 400 to 500 nm vs poly(S_2-TIC-Cl_2) windows of comparable thickness (due to the yellow tint). However, above 500 nm, poly(S_2-TIC-Cl_2) windows exhibited comparable or even higher transmittance, particularly at longer wavelengths, such as 1310 nm, where over 90%T was observed (Figure 5f). With these series of poly(S_2-TIC-Cl_2) and PMMA transmittance measurements in hand, transmittance values were corrected for Fresnel reflection and the absorption coefficient (α) was determined at 1310 and 1550 nm for both materials, confirming that the poly(S_2-TIC-Cl_2) thermoset exhibited lower absorption at 1310 nm (α = 0.045 cm^{-1}) and at 1550 nm (α = 0.124 cm^{-1}) vs PMMA (α = 0.075 and 0.180 cm^{-1}, respectively[34]). Furthermore, poly(S_2-TIC-Cl_2) possesses a very low birefringence (Δn = 0.0012 at 633 nm, Table S2), which accounts for the high transparency retained for thick optical elements (Figure 5e), a distinct advantage over polycarbonate (another commodity optical polymer), which possesses a 10-fold higher birefringence (Δn = 0.0148 at 633 nm, Table S2) and cannot be used for thick plastic optics due to birefringence-derived haziness. PMMA is known to exhibit extremely low birefringence (Δn < 0.0005, Table S2). The excellent optical transparency and low chromatic dispersion of these polymers in the NIR spectrum can also be quantified by defining the NIR Abbe number ($V_{\text{D NIR}}$) at 940, 1310, and 1550 nm from ellipsometric data revealing very high NIR Abbe numbers for poly(S_2-TIC-Cl_2) ($V_{\text{D NIR}}$ = 103) and PMMA ($V_{\text{D NIR}}$ = 110) and slightly lower values for polycarbonate ($V_{\text{D NIR}}$ = 96) (see Figures S85 and S86). In summary, poly(S_2-TIC-Cl_2) possesses several distinctive figures of merit over the two most widely known commodity optical polymers, PMMA and polycarbonate, namely, higher RI ($n \sim 1.6$), extremely low absorption coefficients in the NIR and low birefringence, while using inexpensive monomers, which we demonstrate are amenable to fabrication of large-sized plastic optics. While the yellow tinting of poly(S_2-TIC-Cl_2) precludes direct use for certain commodity consumer eyeware, numerous optical applications at longer visible or infrared wavelengths are accessible, which are not complicated by this coloration. Notably, the exceptional performance of poly(S_2-TIC-Cl_2) polymers in the near-IR is well-suited to 3D sensing applications such as facial recognition, augmented reality (AR), and gaming, where the increased refractive index leads to substantially larger (~25%) collection angles and fields of view than possible with conventional optical polymers.[35]

■ CONCLUSIONS

In conclusion, the discovery of a S_2Cl_2 step-growth addition polymerization, termed sulfenyl chloride inverse vulcanization, is reported. This process exploits the use of an inexpensive sulfur base chemical, S_2Cl_2, as a novel monomer for bulk or solution polymerization with allylic comonomers to prepare for the first time soluble high molecular weight linear homopolymers, segmented block copolymers, and highly transparent glassy crosslinked networks. This method affords a new class of optical thermosets that has distinct optical figures of merit over state-of-the-art commodity optical polymers, such as PMMA or polycarbonate, while using inexpensive monomers amenable to fabrication of large-sized optical elements. These polyhalodisulfides are also degradable through reduction of disulfide bonds in the polymer backbone. The findings reported here mark an important fundamental advance impacting the fields of petroleum science, polymer chemistry, and optical materials.

■ EXPERIMENTAL METHODS

General Procedure for the Polymerization of S_2Cl_2 with Diallyl Monomers. To a 10 mL vial equipped with a magnetic stir bar were added sulfur monochloride (S_2Cl_2, 1.688 g, 1 mL, 12.5 mmol) and diallyl isophthalate (3.078 g, 2.72 mL, 12.5 mmol) to T = 70 °C in a thermostated oil bath. The reaction mixture was stirred at 500 rpm for 18 h until vitrification. After the vitrification of the poly(S2-DAI-Cl_2) medium, the reaction mixture was cooled to room temperature and dissolved in tetrahydrofuran (15 mL) and precipitated methanol (30 mL) to isolate the polymeric product. For this purification process, three additional cycles were conducted, followed by drying of the product at 60 °C under a vacuum, affording a white solid (yield = 3.56 g, M_n = 50,700 g/mol, M_w/M_n = 1.96).

General Procedure for the Polymerization of S_2Cl_2 with Triallyl Monomers. To a 20 mL vial equipped with a magnetic stir bar were added sulfur monochloride (S_2Cl_2, 1.688 g, 1 mL, 12.5 mmol, 1.25 equiv) and triallyl isocyanurate (TIC, 2.4927 g, 10 mmol, 1.0 equiv) to an oil bath heated to T = 45 °C under Ar. The reaction mixture was stirred at 1000 rpm until the reaction medium increased in bulk viscosity. The magnetic stir bar was then removed from the reaction vial, and the reaction temperature was then increased to 120 °C for 12 h. A yellow-tinted thermoset window was then collected from the vial.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c10317.

Materials and instrumentation with full experimental and characterization details; results and discussion; and references (PDF)

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare the following competing financial interest(s): R.A.N. is an owner and officer of Norcon Technologies Holding, Inc. with which a financial conflict of interest exists. The other authors declare no competing financial interest.

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