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Realizing High Refractive Index Thiol-X Materials: A General and Scalable Synthetic Approach

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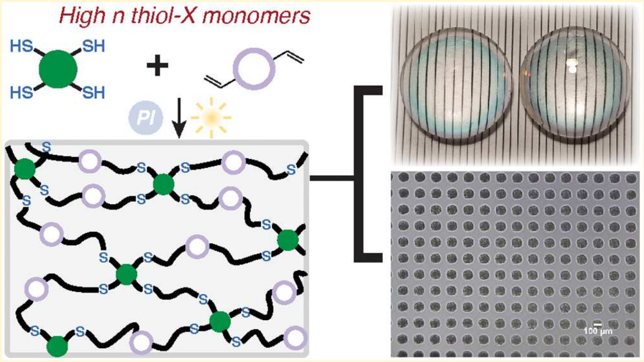
Supporting Information



ABSTRACT: **Photopolymers formed from the family of thiol-X "click" reactions notably form sulfur-containing thioether linkages. While sulfur-containing materials are conventionally expected to result in high refractive index (n_D/20 °C > 1.6) materials, this expectation is rarely realized with thiol-X photopolymers, because of the lack of monomers with sufficiently high refractive indices. Here, an efficient, modular synthetic strategy to obtain high refractive index thiol-X monomers is presented. The efficacy of the overall approach is demonstrated using only commercially available starting compounds to yield low viscosity (<500 cP) liquid multifunctional thiol and diallyl ether monomers with high refractive indices (n_D/20 °C > 1.64). These synthesized monomers underwent rapid thiol-ene photopolymerizations to high conversions, achieving refractive index values (n_D/20 °C) up to 1.669 in uniform crosslinked networks exhibiting typical narrow and well-defined loss tangent (tan δ) peaks. The convenience of the low-viscosity, high optical quality thiol-ene resins was demonstrated in the fabrication of two functional optical components. First, a plano-convex lens was aspherized using an overmolding procedure. Second, a two-dimensional grating was fabricated using a two-stage material and a photomask exposure.**

Polymers represent an integral class of optical materials, because of their advantages in their ease of processing, weight, cost, impact resistance, and versatility in control over material properties.[1] Photopolymers further extend the utility of thermally cured polymers by offering on-demand speed of cure at ambient temperatures and low energy consumption with spatial control over the formation of material properties such as refractive index.[2] The pairing of precision optics with high performance photopolymers has led to a range of niche and emerging applications, including optical adhesives, replication molding of complex optical surfaces,[3] nanoimprint lithography (NIL),[4,5] gradient refractive index (GRIN) optics,[6] holographic optical elements (HOEs),[7−9] and vat photopolymerization additive manufacturing.[10,11]

A key metric required to achieve high performance in many of the aforementioned applications is the ability to obtain high refractive index values (defined herein as n_D > 1.6). While significant progress has been made in the pursuit of high refractive index polymers,[12−14] a majority of these strategies involve a thermally driven polymerization, such as polycondensation or inverse vulcanization, to produce the high refractive index polymer.[15−20] However, since thermal polymerizations do not afford good spatial control, these high refractive index values are typically only realized in the spatially uniform case. Furthermore, additional considerations such as color,[17,20] processability, or synthetic accessibility/scalability[12−14,16,18,21] further preclude these approaches from their use in many photopolymerization-based applications. Significantly, among the body of work for high refractive index

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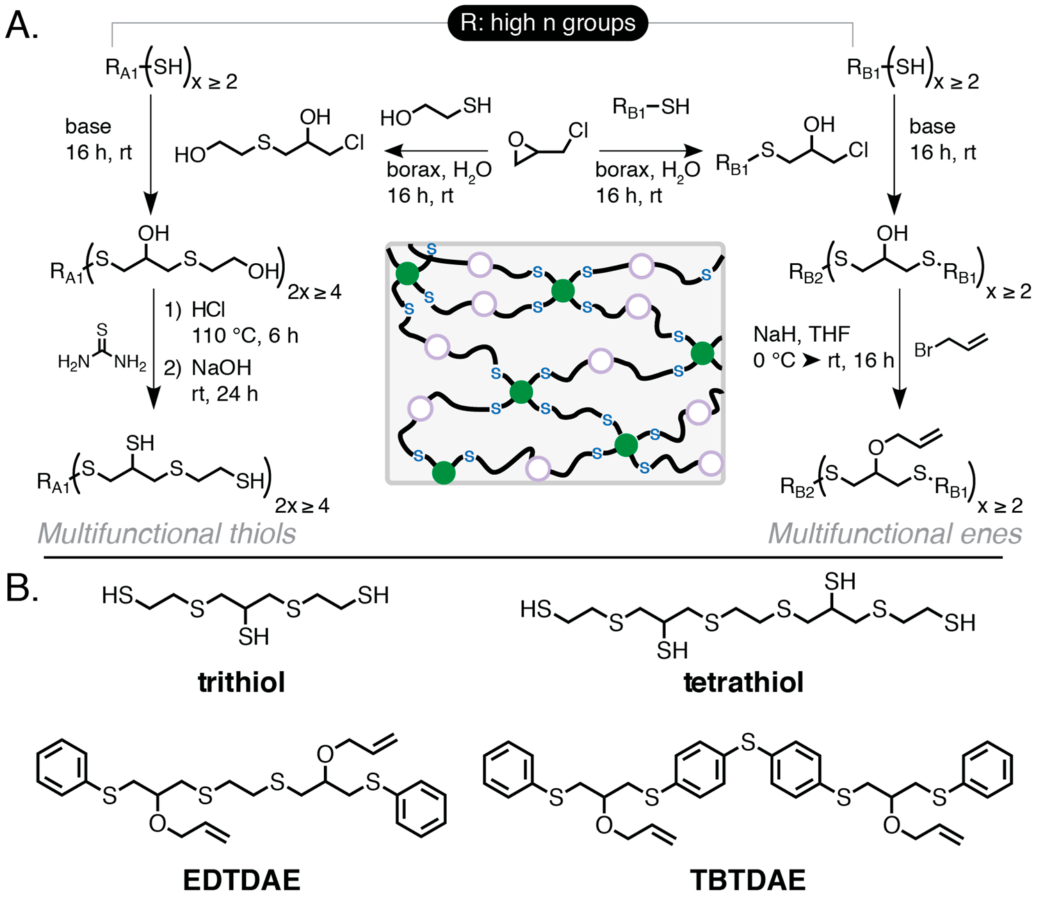
Scheme 1. (A) General Synthetic Framework for Obtaining High Refractive Index Multifunctional Thiol and Ene Monomers. (B) Chemical Structures of Synthesized Thiol and Ene Monomers Used in This Study[a]



[a]Alkyl trithiol and tetrathiol were synthesized with overall yields of 74% and 66%, respectively, while diallyl ether monomers containing either an alkyl-core (1,2-ethane dithiol) or aromatic (4,4′-thiobisbenzenethiol) core were synthesized with overall yields of 66% and 85%, respectively.

polymers, only a small subset are applicable toward photopolymerizations.[21,22] However, emerging high-value applications such as additive manufacturing,[10] GRIN optics, and HOEs each require spatial variations in refractive index, with preference for large refractive index modulations. In this respect, there has been limited work on the rational design of customizable monomers capable of achieving high refractive index photopolymers.[22,23]

The family of thiol-X reactions embody a model set of reactions for the rapid and efficient formation of high refractive index materials, because of their intrinsic incorporation of sulfur at every formed thioether linkage. Because of their step-growth development, polymers with low shrinkage stresses are obtained with minimal oxygen inhibition constraints. However, with a few exceptions,[22−24] there are limited instances of thiol-X photopolymerizations realizing high refractive index materials. This discrepancy is because commercially available thiol-X monomers are either relatively low in refractive index (n_D/20 °C ≤ 1.55, based on relatively low overall sulfur content in the monomer) or prohibitively expensive (more than \$100/g). To justify these points, a widely used tetrathiol such as pentaerythritol tetrakis(3-mercaptopropionate) (PETMP),[25−27] has a quoted literature refractive index value (n_D/20 °C) of only 1.531, because of the presence of the ester groups and other hydrocarbon portions of the molecule.[23,28] On the other hand, the high refractive index 1,3-benzene dithiol (n_D/20 °C = 1.6331), used by Stiegman et al. to achieve monolithic materials with n values up to 1.7, costs more than 400 times that of PETMP, on a dollars per gram basis.[29]

To address the deficiency in photopolymerizable high refractive index monomers, researchers have explored multiple approaches to monomer design, including acrylates functionalized with fluorenyl, thiadiazole and diphenyl thioether moieties,[30] 9,9-diaryl-substituted fluorene-based thiols,[31] and new siloxane-based tetravinyl monomers.[24] While high refractive index values (in the range of 1.6−1.7) were achieved, these monomer designs were restricted in the consideration of other important properties and characteristics. Therefore, the motivation of this work was to devise an accessible synthetic framework to develop a customizable range of photopolymerizable high refractive index monomers. Here, a synthetic strategy for the rational, tailored design of high refractive index thiol-X monomers is presented and validated using inexpensive, widely available starting materials to produce in moderate scale (tens of grams) a set of multifunctional low-viscosity liquid (< 500 cP) thiol and ene monomers. The set of synthesized multithiol and diallyl ether monomers all possessed high refractive index values (n_D/20 °C > 1.6) while exhibiting excellent resin solubility in bulk, and polymerized rapidly and efficiently using mild irradiation conditions (405 nm LED irradiation at 10 mW/cm^2 for 10 s) at ambient conditions. The resulting thiol-ene photopolymer films achieved refractive index (n_D/20 °C) values ranging from 1.63 to 1.67, with Abbe numbers between 25 and 32.

The proposed synthetic strategy, outlined in Scheme 1, principally utilizes efficient thiol-X "click" reactions[25,26] (i.e., thiol-epoxide and thiol-halide) to design multifunctional thiol and ene monomers. The rationale behind this overall approach is guided by the distinct advantages that are offered. First, both sets of monomers (thiol and ene) incorporate flexible thioether linkages throughout the monomer design, which is an effective method for increasing the refractive index without substantially increasing the viscosity or sacrificing the solubility characteristics of a given monomer. Second, since both sets of monomers share the same underlying structure, mutual compatibility is expected to improve their mutual compatibility as neat thiol−ene resins. Resin solubility without the use of solvents is a key desired trait for a majority of photopolymerization uses and is especially valuable for high-volume applications, such as vat photopolymerization three-dimensional (3D) printing. Next, since each reaction step provides a design freedom over the choice in (i) pendant group, (ii) backbone core, and, in the case of the ene, (iii) polymerizable group, a high degree of customizability is afforded to achieve monomers with tunable material specifications.[32] Finally, the thiol-epoxy and thiol-halide reactions are not only efficient, achieving good overall yields, but they also rely upon widely available, inexpensive reactants. To validate this synthetic framework, a representative set of multifunctional monomers was synthesized and then evaluated for use in a classical thiol−ene photopolymerization as a case study. Using only commercially available starting materials, low-viscosity liquid monomers with high refractive indices and high Abbe numbers were targeted.

A key enabler for either route (multifunctional thiol or ene) is the first step which involves the quantitative and selective thiol-epoxide ring-opening reaction of epichlorohydrin to form the corresponding intermediate chlorine linker. While many approaches exist for the selective thiol-epoxide reaction,[33] a previously reported borax-catalyzed procedure[34] was found to be very convenient for a green and efficient large-scale synthesis. For the route to multifunctional ene monomers, a high refractive index monofunctional thiol was used. Here, using thiophenol (literature n_D/20 °C value of 1.588), up to 100 grams of the desired compound, 1-chloro-3-(phenylthio)-2-proponal (CPTP), was readily synthesized as a colorless, low-viscosity liquid. For high refractive index multi-thiols, the desired goal was to obtain a set of sulfur-rich alkyl structures without other heteroatoms or aromatic groups present. The primary intention behind this was to achieve low viscosity liquid monomers that could achieve high refractive index values without being significantly absorptive or dispersive.[12,13,35] Given this preference, we were inspired by patents filed by Mitsui Chemicals disclosing a scalable route to a sulfur-containing alkyl trithiol using epichlorohydrin and 2-mercaptoethanol as the starting materials.[36] The same procedure disclosed in the patent was followed to form the trithiol compound. However, to obtain higher functionality thiols (i.e., >3), the aforementioned approach of using a Cl-linker was utilized. Here, the required Cl-linker was instead a diol synthesized by the selective thiol-epoxide ring-opening of epichlorohydrin with 2-mercaptoethanol using the same borax-catalyzed procedure[34] to produce the colorless liquid, 1-chloro-3-(hydroxyethylthio)-2-propanol (CHETP).

The second step involves the selection of a multi-thiol "core" that reacts with the Cl-linker via a thiol-halide nucleophilic substitution reaction under basic conditions, using an organic base such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). For the ene route, this thiol-halide step produces an intermediate compound containing secondary hydroxyl groups equivalent in functionality to that of the chosen multi-thiol "core". Since this "core" forms the backbone of the monomer and the resultant polymer, it is the most influential component for controlling the final properties and characteristics of the final monomer and polymer. While fewer choices are commercially available for multi-thiols (especially for functionalities of >2), several higher refractive index multifunctional thiols previously reported in the literature are readily employed.[16,37,38] Here, the commercially available dithiols, 1,2-ethane dithiol (EDT) and 4,4′-thiobisbenzenethiol (TBT), were chosen as alkyl and aromatic "cores" for the demonstrative example ene compounds, respectively. Using DBU as a base, the dithiol was coupled with CPTP in toluene to form the corresponding diol (i.e., EDT−OH and TBT−OH). Notably, high refractive index multi-thiols such as TBT are typically insoluble in neat thiol−ene resins; however, here, they were readily incorporated. For the thiol route, a multi-thiol "core" was similarly employed with CHETP under basic conditions to obtain a higher-functionality hydroxyl compound via a thiol−halide substitution. In a similar vein to the multifunctional ene monomers, the multithiol forms the core of the molecule and is chosen to tune material properties as needed. Here, EDT was coupled with CHETP using sodium hydroxide (NaOH) as the base in absolute ethanol to form the tetrafunctional alcohol intermediate (tetra−OH).

In the final step for the ene monomers, the respective diols were then converted using allyl bromide to their respective diallyl ethers, **EDTDAE** and **TBTDAE**, with high overall yields of 66% and 85%, respectively. Both EDTDAE and TBTDAE monomers are liquids with viscosity values of 56 and 582 cP, respectively, in addition to refractive index (n_D/20 °C) values of 1.5927 and 1.6453, respectively. Other than allyl ethers, note that a range of other polymerizable groups can be affixed to the hydroxyl functionalities using established coupling procedures, such as alkynes, (meth)acrylates, norbornenes, vinyl ethers, etc. In the case of the thiol monomers, the final step involves the conversion of the hydroxyls to thiol by reaction with thiourea, followed by acid hydrolysis. The trithiol and tetrathiol example compounds were synthesized with overall yields of 74% and 66%, respectively, with both monomers being colorless liquids with viscosities of 43 and 189 cP, respectively, and accompanying refractive index (n_D/20 °C) values of 1.6355 and 1.6473, respectively. Although the synthetic route involve three steps overall, compared to other synthetic routes to multi-thiols presented in the literature, the reactions were higher yielding and required significantly less-expensive reactants for the same number of steps.[16,39] Overall, through a judicious choice of substrates, the presented synthetic framework permits the balancing of traditionally competing optical property requirements (such as absorption, color, and dispersion) against refractive index, in addition to other non-optical property considerations, such as monomer viscosity, solubility, and thermomechanical properties (T_g and moduli). In this regard, the presented methodology provides a systematic and tailored approach to materials design that extends beyond high refractive index optical applications.

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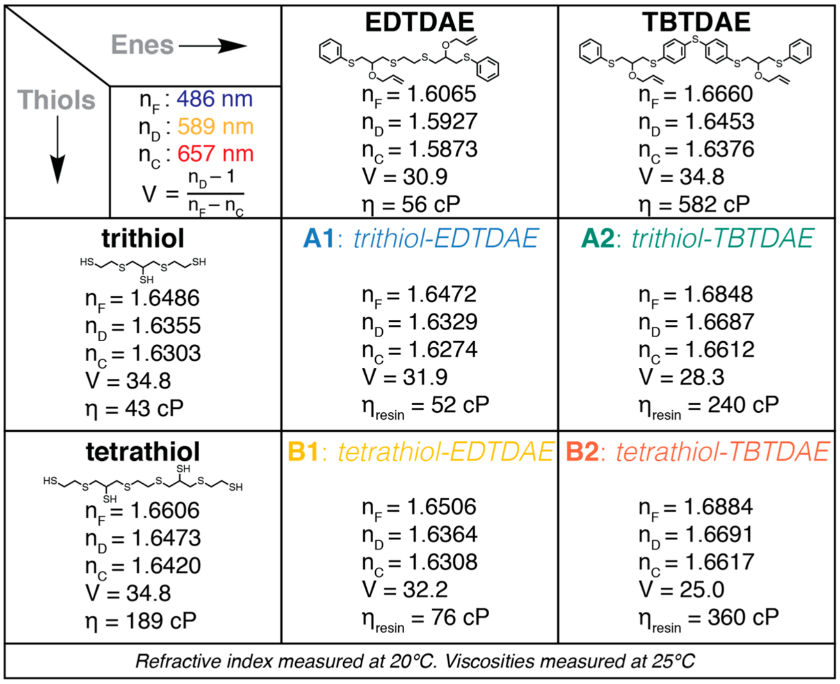

Enes → / Thiols ↓ n_F : 486 nm n_D : 589 nm n_C : 657 nm $V = \frac{n_D - 1}{n_F - n_C}$	**EDTDAE** $n_F = 1.6065$ $n_D = 1.5927$ $n_C = 1.5873$ $V = 30.9$ $\eta = 56$ cP	**TBTDAE** $n_F = 1.6660$ $n_D = 1.6453$ $n_C = 1.6376$ $V = 34.8$ $\eta = 582$ cP
trithiol $n_F = 1.6486$ $n_D = 1.6355$ $n_C = 1.6303$ $V = 34.8$ $\eta = 43$ cP	**A1**: *trithiol-EDTDAE* $n_F = 1.6472$ $n_D = 1.6329$ $n_C = 1.6274$ $V = 31.9$ $\eta_{resin} = 52$ cP	**A2**: *trithiol-TBTDAE* $n_F = 1.6848$ $n_D = 1.6687$ $n_C = 1.6612$ $V = 28.3$ $\eta_{resin} = 240$ cP
tetrathiol $n_F = 1.6606$ $n_D = 1.6473$ $n_C = 1.6420$ $V = 34.8$ $\eta = 189$ cP	**B1**: *tetrathiol-EDTDAE* $n_F = 1.6506$ $n_D = 1.6364$ $n_C = 1.6308$ $V = 32.2$ $\eta_{resin} = 76$ cP	**B2**: *tetrathiol-TBTDAE* $n_F = 1.6884$ $n_D = 1.6691$ $n_C = 1.6617$ $V = 25.0$ $\eta_{resin} = 360$ cP
Refractive index measured at 20°C. Viscosities measured at 25°C		

Figure 1. Table of refractive index, Abbe number, and viscosity values for synthesized multithiol and diallyl ether monomers, as well as the resulting thiol−ene resins/photopolymers. The refractive index was measured at 20 °C at wavelengths of 486, 589, and 657 nm for the liquid monomers and the solid photopolymer film. Viscosity measurements were taken at 25 °C for the liquid monomers and unpolymerized thiol−ene resin. Thiol−ene resins were made from each thiol and ene monomer combination at stoichiometric amounts of thiol to ene groups with ∼0.5 wt % 2,4,6-trimethylbenzoyl diphenylphosphine oxide (TPO) photoinitiator.

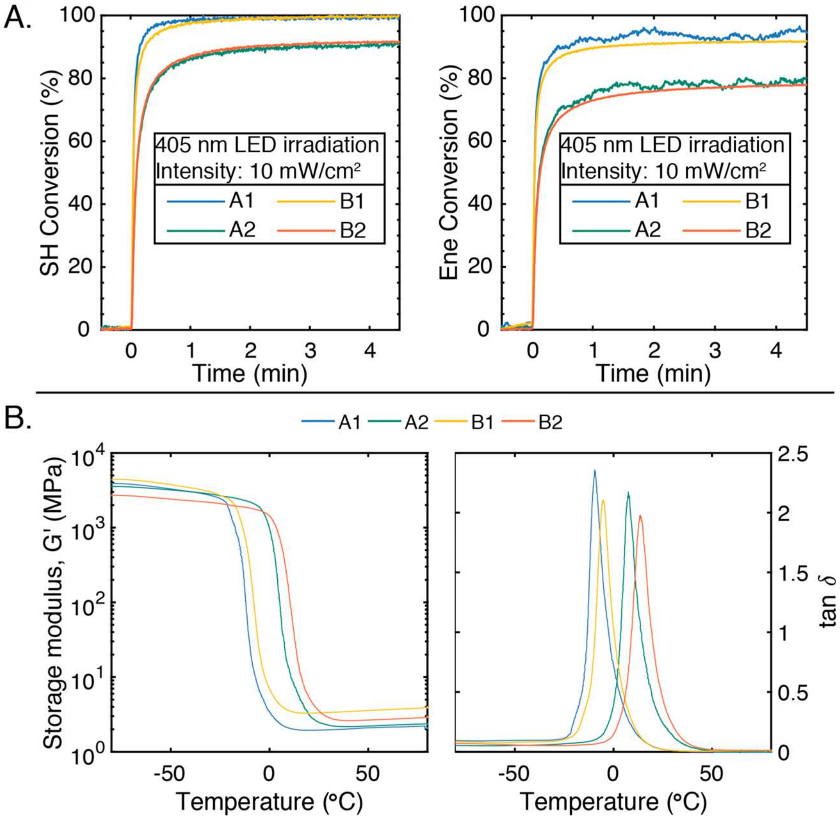

Figure 2. Photopolymerization reaction kinetics and thermomechanical properties of thiol−ene resins. (A) Real-time FTIR measurements of thiol (left) and ene (right) conversion for each resin showing high conversions were rapidly achieved. (B) Storage modulus, G′, (left) and tan δ (right) plots versus temperature for each thiol−ene photopolymer film characteristic of step-growth networks. Narrow loss tangent (tan δ) profiles for all four systems indicate a highly homogeneous crosslinked thiol−ene network.

The synthesized monomers were further evaluated in a classical thiol−ene photopolymerization according to the resin systems outlined in Figure 1. Using stoichiometric formulations (i.e., SH:ene = 1:1) of each synthesized thiol and ene monomer, resins with low viscosities (50−400 cP) formed transparent films with high refractive index values (n_D/20 °C = 1.633−1.6691), and relatively low dispersions (25−32). As expected, the aromatic dithiol core present in TBTDAE efficiently increases the refractive index by ~0.03 over the alkyl counterpart, although this comes at the expense of increased dispersion (i.e., lower Abbe number). Interestingly, the influence of the higher sulfur-containing tetrathiol was fairly marginal over the trithiol.

Examining the photopolymerization reaction kinetics using real-time Fourier transform infrared (FTIR) spectroscopy, both thiol and allyl groups reacted quickly upon 405 nm irradiation at a moderate intensity of 10 mW/cm^2, as observed in Figure 2A. While high conversions exceeding the gel point were achieved for both thiol and allyl (C═C) groups, there were two observable discrepancies in the results. First, the thiol conversion was higher than the allyl conversion for all systems. This observation was reasoned to be due to the secondary nature of the allyl ether double bonds causing the allyl peak used for the integration to be convoluted. The second discrepancy was that the conversions (thiol and allyl) of the trithiol systems (i.e., A1 and A2) were consistently higher than the tetrathiol systems (i.e., B1 and B2). An explanation for this result was the lower purity of the tetrathiol compound, as verified via NMR spectroscopy (see the Supporting Information), from which it was estimated to be ~90%.

Aside from achieving high refractive index values at relatively high Abbe numbers, a broad range of thermomechanical properties was accessed, as shown in Figure 2B, from the four photopolymer systems with glass-transition temperatures (T_g) values between −9 °C to 13 °C and rubbery moduli (at 40 °C) between 2.0 MPa and 3.5 MPa. Such rubbery, low T_g materials are generally expected for thiol−ene polymers.[25,28,40] These soft, high refractive index materials are particularly well-suited for prototyping of replication optics or producing ophthalmic implants such as intraocular lens.[41] For other applications requiring stiffer materials, the outlined approach can be modified accordingly to incorporate rigid structures. Nevertheless, the step-growth nature of the thiol−ene polymerization characteristically produced uniform networks with narrow glass-transition regimes, as evident by the distinct and narrow tan δ curves for each presented thiol−ene system. Curiously, these specific thiol−ene systems also exhibited elevated tan δ values (2.2−2.5), compared to other thiol−ene systems signifying good damping and energy-dissipating qualities.

Photocurable liquid monomers are commercially used as optical adhesives and to fabricate replicated optics, both of which require good optical transmission and clarity across the designed wavelengths, as well as a match in refractive index with the substrate. While several resins exist for the refractive index range of <1.6, higher refractive index glasses (or other media) ideally require a closely matched value (± 0.1 or less). However, the associated advantages of using photocurable optical-grade resins, such as the ease of production and high throughput, are severely limited by prohibitively viscous resins. In this respect, the set of monomers prepared (resin viscosity range of 73−340 cP) are far superior to existing high refractive index commercial resins such as NOA 170, which has a quoted viscosity range of 4400−5500 cP.[42] Using the highest refractive index system, resin B2 (tetrathiol-TBTDAE), this facile overmolding procedure was employed to aspherize a spherical plano-convex lens using a PDMS negative mold.[3] As seen in Figure 3A, the optical clarity and surface finish of the thiol−ene photopolymer overmold (right side) is of sufficiently high quality that the 1-mm-spaced vertical lines look indistinguishably clear with either lens. However, as expected, the high refractive index overmold increased the optical power and numerical aperture (NA) of the lens, resulting in a greater magnification (~1.5×) of the lens.

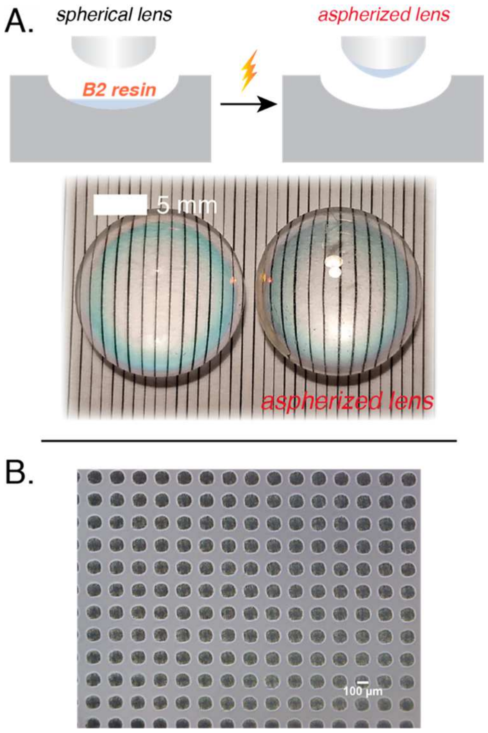

Figure 3. Applications for low-viscosity, high refractive index thiol−ene resins. (A) Thiol−ene resin B2 was employed in a simple overmolding procedure to aspherize a spherical lens using a negative PDMS mold. The side-by-side photograph presents the pristine spherical plano-convex lens (left) and the overmolded aspherized lens (right) over an array of lines spaced 1 mm apart. The higher refractive index overmold increased the optical power and numerical aperture (NA) of the lens, as shown by the larger magnification. (B) Thiol−ene resin A2 was used to record two-dimensional, micrometer-scale refractive index structures via an irradiation through a photomask on a two-stage material (stage 1, poly(urethane−thiourethane); stage 2, thiol−ene).

Another application for high refractive index photocurable monomers is their use in two-stage materials to record high-fidelity refractive index structures. Here, a model two-stage material consists of a first-stage poly(urethane−thiourethane) network with a second-stage thiol−ene, using the A2 resin system. A 250-μm-thick film of this material was irradiated using a 405 nm LED source through a photomask to record a two-dimensional array of refractive index structures (100 μm circles) with good fidelity, as shown by the optical microscope image in Figure 3B.

Herein, a versatile and effective synthetic strategy for achieving high refractive index thiol-X monomers was presented. Based on efficient thiol-X “click” chemistries, a vast range of customizable structures were accessed to produce monomers with a useful set of characteristics and properties. These novel monomers can enable the tailored designs for new materials useful for several existing and emerging photopolymer-based applications. This synthetic strategy was validated using only commercially available substrates, producing a representative set of photopolymerizable thiol and ene monomers. These compounds exhibited low viscosities (<400 cP) and easily achieved refractive index values (n_D/20 °C) of >1.6. Tested together, the synthesized monomers reacted quickly to form clear and transparent crosslinked polymer films with good optical properties (n_D/20 °C = 1.633−1.669 and Abbe number values of 25−32) and thermomechanical properties (sub-zero T_g values and narrow tan δ peaks) typical of thiol−ene polymers. The utility of such low-viscosity, high refractive index photocurable monomers was demonstrated in a rapid overmolding replication example, whereby an optically clear aspherized lens was reliably obtained showing an expected increase in optical power and NA, because of the higher refractive index photopolymer overmold. Finally, the use of thiol−ene photopolymerizations in a two-stage photopolymer material was demonstrated with a photomask exposure to record an array of micrometer-scale high refractive index features within an otherwise homogeneous, transparent film. Overall, the facile and scalable nature of the presented synthetic strategy can be leveraged to design and optimize photopolymer materials for a targeted set of properties and performance.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmaterialslett.9b00331.

> Experimental information ^{1}H and ^{13}C NMR spectra of all synthesized compounds (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

GRIN, gradient refractive index; HOE, holographic optical elements; NIL, nanoimprint lithography

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