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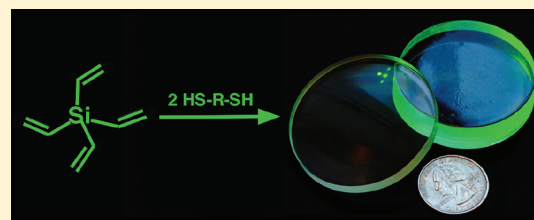
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S Supporting Information

ABSTRACT: The self-initiation of the thiol–ene coupling reaction of tetravinyl monomers containing main group elements and trivinyl heterocycles with alkyl and aryl dithiols resulted in the formation of highly cross-linked prepolymer gels which upon final curing at 120 °C yielded hard, monolithic polymeric materials. Because of the presence of highly polarizable main group elements such as Si, Ge, Sn, and S and the relative absence of highly electronegative elements, the resulting polymers exhibited high refractive indices ranging from 1.590 to 1.703 and Abbe numbers between 24.3 and 45.0. All of the polymers were highly transparent over the UV–vis region of the spectrum. Moreover, due to the high cross-linked density achievable in specific compositions, very hard materials capable of being ground and polished could be produced. The range of compositions produced yields important structure–property relationships, indicating the effect of monomer structure on mechanical and optical properties.



1. INTRODUCTION

Transparent optical-quality plastics are extremely important in many commercial optical applications, including camera and projector lenses, and in optometric applications, including prescription eyewear and contact lenses. These materials afford large advantages over metal oxide glasses in areas such as weight reduction and fracture resistance. A number of optical figures of merit must be achieved for a polymer to be useful for specific optical application. These include the refractive index (n), the Abbe number, and the percent transmission of light over the spectral range of interest. In addition, depending on the application, mechanical properties such as hardness, fracture toughness, and scratch resistance are also significant. Current optical polymer technology revolves principally around well-established polymers such as poly(methyl methacrylate)s, polycarbonates, polythiureas, polyvinylcarbazoles, and polyisocyanates.¹ Of the various optical properties, the refractive index is one of the most significant; as it dictates the shape and size, the lens must be to be utilized in a specific application. As such, much effort has been expended in developing high refractive index polymers. The primary approach to control the refractive index in a polymer is through the incorporation of polarizable atoms and groups, either as part of the backbone or as attached pendant groups. The basis for this approach lies in the concept of molar refractivity of the constituent monomers.² Constituents and monomers with high molar refractivity include aromatic and other unsaturated organic groups and groups containing polarizable main group heteroatoms, particularly sulfur. As such, polythiourethanes, polynaphthalenes, and polvinylcarbazoles exhibit refractive indices in the range of ~ 1.6 – 1.70 , which occupy the high end of the refractive index range for organic polymers.¹

We report here the development of hybrid organic/inorganic thermoset polymers that utilize constituent monomers containing a preponderance of highly polarizable atoms such as Si, Ge, Sn, and S.³ These polymers exhibit refractive indices that, on average, occupy the high end of the range of polymer refractive indices from 1.590 to 1.703. They also have Abbe numbers acceptable for most applications, are highly transparent, and, for many examples, are extremely hard and can be fabricated and polished into optical-quality monoliths. The repeat unit of the polymer is generated through the thiol–ene coupling reaction.^{4–7} As has been noted previously, polymers formed by this reaction are particularly attractive for fabricating high index optical materials due to the fact that highly polarizable sulfur atoms are an intrinsic part of the repeat unit and that polymers can, in principle, be made which contain no highly electronegative, low-polarizability atoms such as N and O.^{8,9} The problem with bulk polymers made through thiol–ene coupling reactions is that monolithic materials with the requisite strength and hardness required for optical applications are difficult to achieve due to the generally poor cross-link densities realized in this type of polymerization.⁸ For this reason, thiol–ene polymers have typically been made and studied as films or in hybrid compositions with other polymers to impart strength.^{8,10} We have overcome these problems by increasing the monomer functionality and through the use of a slow, self-initiation polymerization process.

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2. EXPERIMENTAL SECTION

Materials. Tetravinylsilane, tetraallylsilane, tetraallylgermanium, trimethyltrivinylcyclotrisiloxane, and tetramethyltetravinylcyclotetrasiloxane were obtained from Gelest and used as received. Tetravinyltin, triallyltriazinetriene, 1,3-benzenedithiol (99%), ethanedithiol, pentanedithiol, and azobis(isobutyronitrile) (AIBN) were purchased from Aldrich and used as received. Tetravinylgermane was synthesized using a published procedure.^{11,12} It is important to note that reagent purity is extremely important in achieving hard materials. While most reagents were used as received, the highest purity was always utilized if there was a choice. In the case of tetravinylgermane, two fractional distillations were required to obtain sufficient purity to yield hard materials.

Synthesis. Photoinitiation. Stoichiometric solutions of vinyl and thiol monomers were mixed until homogeneous reaction mixtures were obtained; they were then transferred to quartz cuvettes. N₂ gas was bubbled through the monomer mixtures for about 15 min prior to UV exposure. The monomer solutions were then exposed to UV light using an Hg–Xe arc lamp (OREAL Instruments) to accomplish the polymerization. In order to avoid the excessive heating and thereby the boiling of the reaction mixture, they were exposed to UV light (exposure time of 2 min) in a discrete manner with 5 min intervals between two successive exposures.

Thermal Initiation. To a stoichiometric solution of vinyl and thiol monomers, AIBN (0.1 wt %) was added under constant stirring in a glass vial. Gelation was extremely rapid, occurring at room temperature (~22 °C) in ~10 min.

Self-Initiation. Fifteen different monomer mixtures were prepared by combining the polyvinyl monomers with the thiol monomers in specific mole ratio such that the number of vinyl groups equaled the number of thiol groups (e.g., for TVS–EDTH the mole ratio was 1:2). Addition of one type of monomer into another was performed in a glass vial in a dropwise fashion under constant stirring so as to achieve homogeneous reaction mixtures. The monomer mixtures were then allowed to gel at an ambient condition (temperature ~20 °C) which was accomplished in 2–48 h depending on the constituent monomers. After gelation, the prepolymers were subjected for final curing at 120 °C for 24 h in an oven to yield hard polymer samples. Samples for DMA analysis were made in Teflon molds of the appropriate dimension required for the dynamic mechanical analysis (DMA).

Characterization. The mechanical properties such as storage modulus, Young's modulus, and tan delta plots of the polymers as a function of temperature were studied using a dynamic mechanical analyzer (Q800 analyzer, TA Instruments). The measurements were performed on a thin rectangular polymer slab starting from –55 to 150 °C using a ramp rate of 3 °C/min at a constant frequency (1 Hz) and constant amplitude (15 μm).

Differential scanning calorimetry (DSC) analysis of the polymers was performed on a thermal analyzer (Model Q100, TA Instruments). Samples were scanned in the temperature range from –50 to 150 °C with a heating rate of 10 °C/min under nitrogen flow (50 mL/min). Cooling of the sample was provided RCS cooler (Model No. RCS 90, refrigerated cooling system).

Viscosity was measured on a Brookfield Model DV-II viscometer using an LV #4 spindle in an open container containing the monomer mixtures. The reported viscosities are Brookfield viscosities and not absolute viscosities.

²⁹Si solid-state MAS NMR spectra were obtained on a Varian INOVA 500WB spectrometer at the resonance frequency of 99.393 MHz (magnetic field 11.74 T). The polymer samples were ground to fine powder and were loaded into a 4 mm HXY CP/MAS probe for the analysis. A recycle delay of 5 s was used, and samples were spun at 10 kHz. The chemical shift values were referenced to TMS at 0 ppm.

Optical transmission measurements were performed on polished polymers using a UV–vis spectrophotometer (Lambda 900, Perkin-Elmer). Sample were ground and polished to a path length of 2.5 mm. The refractive indices were obtained at 546 nm using an Abbe refractometer (NAR-4T) at 20 °C.

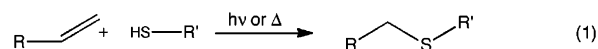
The bulk density of the polymers was obtained by placing dry, preweighed samples in a glass pycnometer and filling rest of the

volume with distilled water at 20 °C. The densities were calculated from the weight difference and the known density of the liquid water at 20 °C. Five observations were taken for each sample, and the average was used for the density calculation.

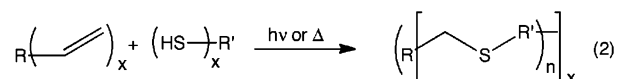
Quantum mechanical estimates of the heat of formation were carried out using semiempirical, PM3 level of theory in the Hyperchem suite of computational software.

3. RESULTS AND DISCUSSION

The thiol–ene coupling reaction (reaction 1), which is typically included in the category of “click” chemistry due to its facile



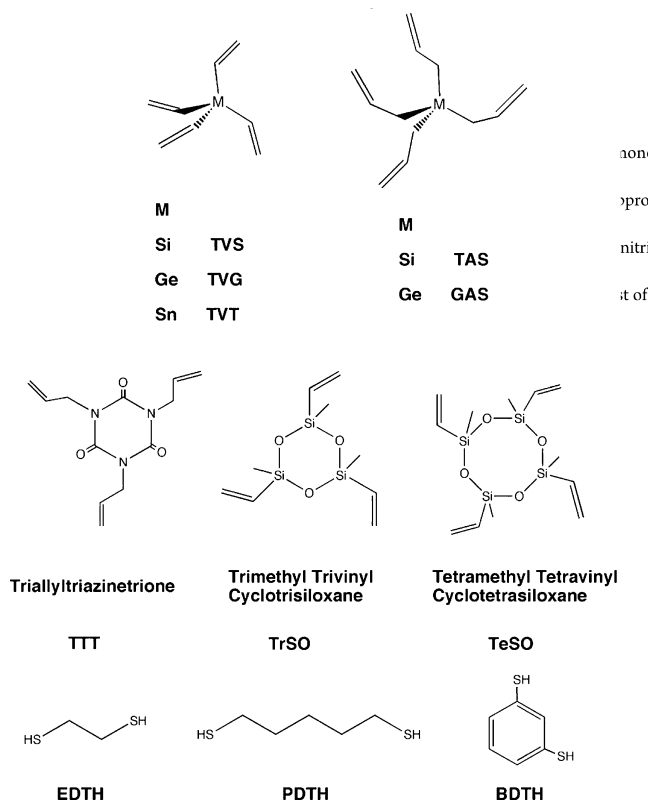
nature, has been used extensively for materials and polymer applications and has been the subject of a number of thorough reviews in recent years.^{4,5,7,8,10} For the generation of a polymeric material where the repeat unit is created solely through thiol–ene coupling, a functionality of 2 or higher must be present in the thiol and ene monomers, with higher functionality ($x > 2$) potentially leading to cross-linked materials (reaction 2).



The reaction goes by a free-radical-based step-growth mechanism and is typically initiated photochemically, either through the use of molecular photoinitiators such as diaryl ketone or directly by exciting the thiol chromophore with ultraviolet light to create radicals.^{5,13,14} It can also be initiated through the use of thermally activated radical initiators such as azobis(isobutyronitrile) (AIBN), as was done in earlier work on thiol–divinylbenzene polymerization.¹⁵ As mentioned, thiol–ene polymerization has the potential to produce high refractive index materials, but the reaction typically does not produce structurally hard materials for use in optical applications due to the low amount of cross-linking often inherent in the step-growth mechanism. One route to overcoming this problem, as suggested by Fairbanks et al., is to use monomers that possess a high degree of functionality to potentially achieve higher cross-link densities.⁸ The choice of vinyl monomers, which are shown in Table 1, includes tetrahedral vinyl-containing group 14 elements Si, Ge, and Sn. Along with their high functionality, it was hypothesized that the main group elements from third and lower rows would impart a higher refractive index to the bulk polymer due to the high polarizability of these elements.³ Precedent for the choice of this group of monomers arises from studies in which tetravinylsilane has been used successfully to create dendrimeric-type structures from thiol–ene coupling chemistry.^{8,16,17} In addition, several cyclic systems containing a high degree (≥ 3) of vinyl functionality were also utilized. The motivation for use of these heterocyclic ring systems lies in the report that triallyltriazinetriene (TTT) forms hard glassy bulk polymers with trimethylolpropane tris(3-mercaptopropionate) (TriThiol1).⁵

Synthesis. Initial attempts were made to synthesize bulk polymers starting from tetravinylsilane (TVS) and the dithiol monomers, ethanedithiol (EDTH) and benzenedithiol (BDTH). Polymerization was initially carried out using two of the established approaches: direct photoinitiation through the use of UV light and initiation using a thermally activated radical initiator, azobis(isobutyronitrile) (AIBN).^{13,15}

Table 1. Vinyl and Thiol Monomers



The choice of direct photoinitiation over the use of secondary initiators such as diaryl ketones was due to the fact that most of the initiators tend to remain unconsumed in the polymer, where they can potentially affect its structural and optical properties.⁵

The secondary choice of AIBN was predicated on the fact that it provided a purely thermal initiation route and that it had been used previously in making bulk thiol–ene polymers.¹⁵ It was found that initiation by both of these methods resulted in the rapid formation of a gel, which was allowed to harden further for a period of several days. After aging and hardening, the polymer samples, while existing as free-standing monoliths, were still soft and quite flexible. In an attempt to further drive the cross-linking process and increase hardness, thermal curing of the samples was carried out by slowly heating at a rate of 0.5 °C/h to a final temperature of 120 °C. This resulted in materials that were much more robust, albeit yellow in color (Figure 1a,b). Above 120 °C, decomposition occurred, while

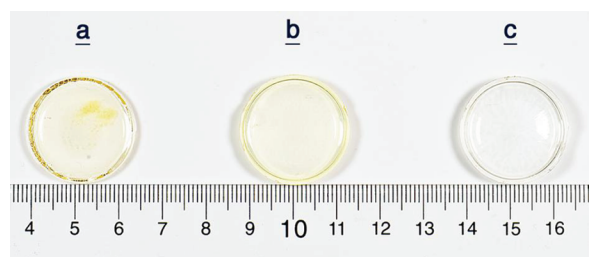


Figure 1. Monolithic TVS–EDTH samples after thermal curing at 120 °C for 24 h polymerized through (a) direct photoinitiation, (b) thermal (AIBN) initiation, and (c) room-temperature polymerization (scale in cm).

curing at lower temperatures yielded materials that were significantly softer. The density, Young's modulus, and glass transition temperature for both samples are listed in Table 2. As

Table 2. Properties of TVS–BDTH and TVS–EDTH Thiol–Ene Polymers Made through Different Initiation Methods

polymer	density (g/cm ³)	Young's modulus (MPa)	T _g (°C)
TVS–BDTH			
photoinitiation	1.40	510	63
thermal-initiation (AIBN)	1.43	530	59
self-initiation	1.43	668	69
TVS–EDTH			
photoinitiation	0.99	21	43
thermal Initiation (AIBN)	1.01	89	39
self-initiation	1.06	108	42

can be seen, the physical properties of the TVS–BDTH samples made through photoinitiation and with AIBN had similar properties, although those made with AIBN tended to be more robust. The difference between the two initiation techniques was more pronounced for the TVS–EDTH polymers, where photoinitiation yielded significantly softer materials. For reasons that will be discussed, the TVS–BDTH materials were significantly harder and had a higher glass transition temperature than did the TVS–EDTH materials.

Prior studies of free radical polymerizations in other cross-linked optical polymers have observed that high initiator concentrations tend to lower glass transition temperature in a polymer due to excess chain termination events that reduce the achievable molecular weight.¹⁸ Since it is known that thiol–ene reactions can self-initiate without the introduction of an initiator in some systems (a property typically discussed in relation to the shelf life of thiol–ene mixtures), we hypothesized that if polymerization in our system of monomers could be carried out in the absence of initiation, polymers with better mechanical properties might be realized.⁵ To test this hypothesis, stoichiometric mixtures of TVS–BDTH and TVS–EDTH were allowed to react at room temperature (~22 °C). The viscosity of the solution was monitored over time (Figure 2); initially,

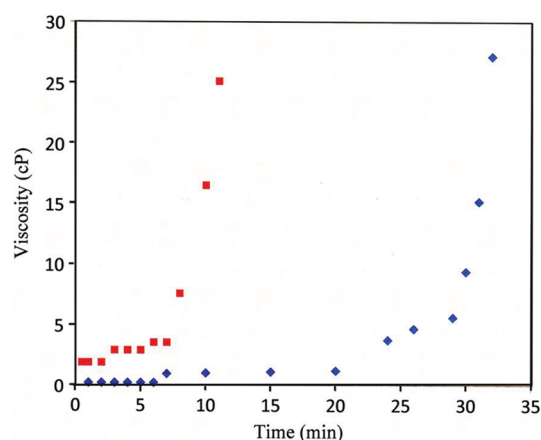


Figure 2. Viscosity changes over time for the reaction between tetra vinylsilane and (■) 1,3-benzenedithiol and (◆) 1,2-ethanedithiol.

there was a slow increase in viscosity followed by an abrupt increase, signifying gel formation. For TVS–BDTH and TVS–EDTH, gelation occurred at approximately 10 and 32 min, respectively. The origin of the self-initiation mechanism is not completely understood, although recent studies have indicated that radicals resulting from an ene–thiol charge transfer complex initiate the polymerization.^{19,20} In our systems, addition of the free radical scavenger hydroquinone to the TVS–EDTH system resulted in strong inhibition of the gelation, indicating that the reaction was still proceeding through a mechanism involving free radicals. Synthesis was also carried out in the dark to verify that the reaction was not simply being initiated by adventitious light. The properties of the polymer made in darkness were unchanged, indicating that adventitious photo-initiation was not occurring. As with the samples made through the direct initiation processes, room-temperature polymerization and hardening yielded somewhat flexible materials. Further hardening of the polymer was achieved through curing at 120 °C for a period of 24 h.

The use of thermal self-initiation to drive the polymerization yielded significant improvements in the mechanical properties of the polymer. As can be seen in Table 2, the Young's modulus for the self-initiated TVS–BDTH polymers was found to be 668 MPa, which was markedly higher than the photo- and AIBN-initiated materials by 24% and 21%, respectively. Data obtained from the DMA analysis for the three methods of initiation of the TVS–BDTH system are shown in Figure 3.

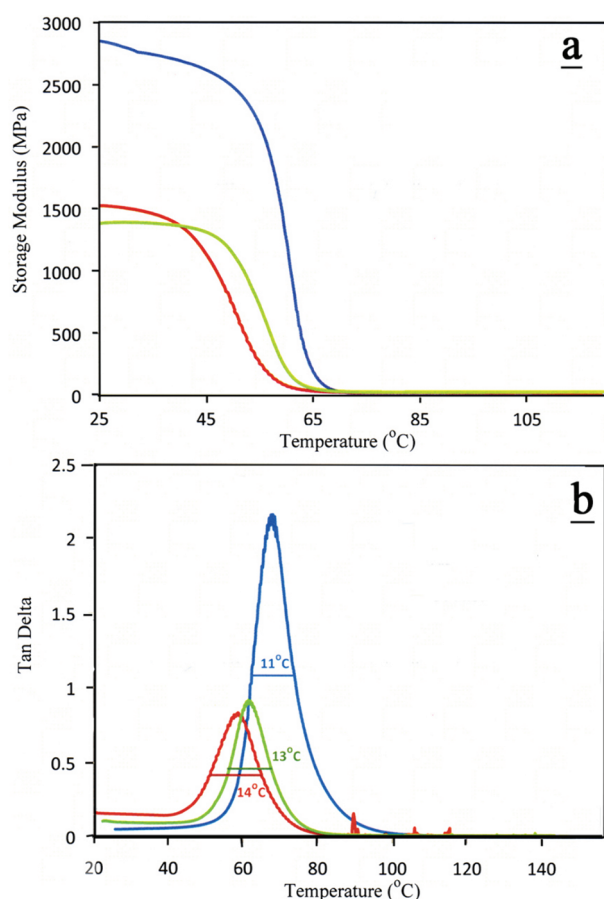


Figure 3. (a) Storage modulus and (b) tan delta plots obtained from dynamic mechanical analysis for tetra vinylsilane-1,3-benzenedithiol polymers made from (red) thermal (AIBN), (green) photochemical, and (blue) self-initiation. Note: error in width ± 0.5 °C.

As can be seen, the storage modulus and the glass transition temperature, as determined from the peak in the loss tangent and from DSC data, are similar for the photo- and AIBN-initiated polymers; however, both of these quantities are significantly higher for the self-initiated system. Also of interest is the effect of the different initiation protocols on the uniformity of the cross-link density, a measure of which is the width of the loss tangent measured at half height.^{8,21} As can be seen (Figure 3), the photo- and AIBN-initiated materials have loss tangent widths which are, within experimental error, the same at 13 ± 0.5 and 14 ± 0.5 °C, respectively, while the width of the self-initiated materials is significantly narrower at 11 ± 0.5 °C, suggesting a more uniformly cross-linked material.

The effect of the three different initiation procedures that were explored and the effect of the thermal curing protocol on the degree of cross-linking can be seen quantitatively using ^{29}Si solid-state NMR spectroscopy. The chemical shift of the ^{29}Si nucleus is quite sensitive to the electron-donating ability of the ligands.^{22,23} As such, systematic changes in the alkyl group, going from stronger to weaker electron donors, will result in an upfield shift of the Si nucleus to lower ppm values. Relative to tetramethylsilane (TMS), which is set to zero, other alkyl groups, where the silicon is bound to four methylene carbons, tend to be slightly downfield from TMS. So, for example, tetraethylsilane has a chemical shift of 7.1 ppm, while tetraallylsilane, which is less electron donating, has a chemical shift of -2.0 ppm. For tetra vinylsilane, the starting monomer for our polymers, the chemical shift is well upfield at -21.5 ppm due to the weak donating ability of the vinyl groups.²⁴ As vinyl groups are replaced with alkyl groups, as happens during polymerizations, the ^{29}Si chemical shifts will appear systematically upfield by approximately incremental values between -21.5 and ~ 7 ppm (the presence of the thioether group will shift it somewhat upfield) so that each species, $\text{Si}(\text{CH}_2\text{CH}_2\text{S}-)_{4-n}(\text{CH}=\text{CH}_2)_n$, as n goes from 0 to 4, will have a specific assignable resonance. Such analysis has been done extensively in studies of sol–gel polymerization of silicon alkoxides.^{22,23} The solid-state ^{29}Si MAS NMR spectra of TVS–BDTH made by the three initiation methods collected after gelation and room temperature aging and after thermal processing to 120 °C are shown in Figure 4. As can be seen, different ^{29}Si resonances

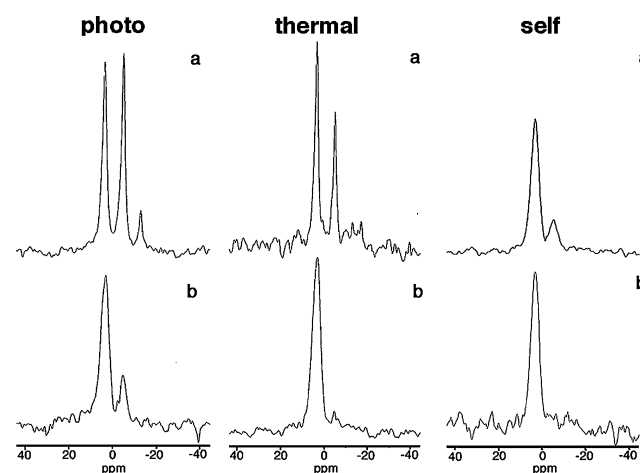


Figure 4. ^{29}Si SS CP/MAS NMR spectra of tetra vinylsilane-1,3-benzenedithiol polymer made through thermal (AIBN), photochemical, and self-initiation (a) after gelation and room temperature aging and (b) after thermal curing at 120 °C.

associated with different degrees of reaction are observed. In all samples, a sharp resonance is observed at 3.8 ppm, which we assign to a Si atom completely surrounded by thioalkyl groups, $\text{Si}(\text{CH}_2\text{CH}_2\text{S}-)_4$, which represents silicon atoms that are completely cross-linked. The ^{29}Si NMR for the UV-initiated materials (Figure 4a), collected after gelation and aging but before thermal curing, show three well-resolved resonances all separated by about 8 ppm. Along with the resonance at 3.8 ppm of the completely alkylated species, the two other resonances are observed downfield at -4.6 and -12.8 ppm and can be assigned to the mono- and divinylsilicon species, $\text{Si}(\text{CH}=\text{CH}_2)(\text{CH}_2\text{CH}_2\text{S}-)_3$ and $\text{Si}(\text{CH}=\text{CH}_2)_2(\text{CH}_2\text{CH}_2\text{S}-)_2$, respectively. This indicates relatively poor cross-linking, with a majority of the Si atoms still having pendant vinyl groups and, therefore, not being cross-linked. The materials made using AIBN initiation are better cross-linked, as they show only the two resonances: the fully alkylated and the monovinyl species (a very small amount of divinyl can be seen in the spectrum). Finally, as indicated by their mechanical properties, the self-initiated materials have the highest degree of cross-linking, with only a small amount of monovinyl species observed. The effect of thermal processing at 120°C on the cross-linking can also be clearly seen in the NMR spectra (Figure 4b). In all cases, the effect of thermal processing is to greatly reduce the amount of vinyl-containing Si, leaving predominantly the fully cross-linked species. In the case of the UV-initiated polymer, unreacted vinyl groups still remain. The AIBN-initiated materials (Figure 4b) are almost fully cross-linked, although some very small amount of monovinyl species can be discerned near the baseline. The self-initiated materials appear to be fully cross-linked, within the sensitivity of the NMR experiment, as only the fully alkylated resonances remain after thermal processing. It is important to note that the NMR results are quite consistent with the DMA studies and support the conclusion that the observed mechanical properties are due to the degree of cross-linking in the polymer. In all cases, significant mechanical improvement was realized through the thermal curing to 120°C , which it directly attributable to greater cross-link density as evidenced by the NMR data. Moreover, the mechanical properties, as measured by the Young's modulus, were highly dependent on the polymerization method, with photoinitiation yielding the least robust materials and self-initiation the most. Consistent with this, the degree of cross-linking observed in the NMR spectrum indicates that self-initiation yields the highest cross-linking density and photoinitiation the least. At this juncture, however, we do want to emphasize that there are numerous methods of initiating thiol-ene polymerization and those compared here are, necessarily, a small subset of all possible methods. As such, other approaches might well prove to be superior for making optical-quality bulk polymers from these monomers.

For the TVS-EDTH composition, the effects of the different polymerization procedures and the benefits of self-initiation appear to be more pronounced. The photoinitiated materials proved to very soft, as evidenced by the low values for the Young's modulus (Table 2). The hardness improved with AIBN initiation, although, ultimately, self-initiation yielded the hardest materials. Overall, however, the mechanical properties of these compositions, regardless of the method of synthesis, were poor relative to the TVS-BDTH materials. The DMA data (Figure S1) show a very broad loss tangent with an fwhm $\geq 27^\circ\text{C}$ for all methods of preparation. Moreover, as T_g is approached, the storage modulus drops rapidly (much more so

than is observed for TVS-BDTH), and just above T_g the sample tends to weaken and fracture. These data indicate that this system has much more inhomogeneous cross-linking. This likely arises from the fact that these flexible groups can undergo intramolecular ring formation, which effectively limits the overall cross-linking density of the polymer (Figure 5a).

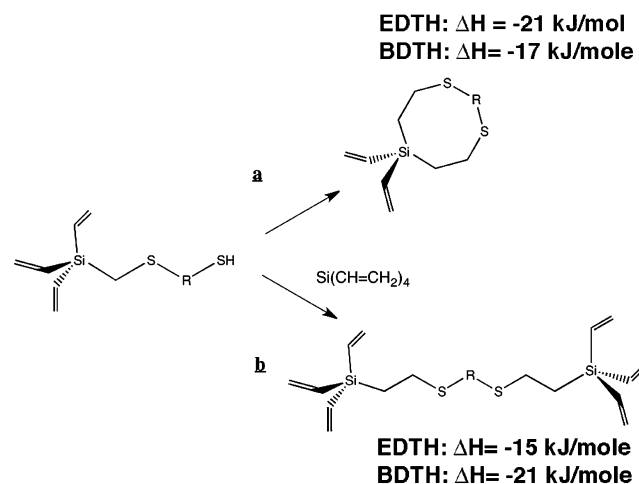


Figure 5. Cyclization (a) and cross-linking (b) pathways and associated enthalpies of thiol-ene polymerization reactions.

This effect has been discussed previously for free radical vinyl polymerizations and is likely to have a pronounced effect on the mechanical properties of the thiol-ene polymers reported here.²⁵ In the case of 1,3-benzenedithiol, the formation of a bond between two vinyl groups on a single silicon and the sulfur atoms on the ortho positions of the aromatic ring would create a strained ring that would be thermodynamically less favorable than intermolecular bond formation. This is supported by semiempirical PM3 calculations, which estimate the enthalpy of cyclization (Figure 5a) of EDTH to be around 4 kJ/mol more favorable than that of the BDTH. Comparing the estimated enthalpies of the cross-linking reaction (Figure 5b), the enthalpy for cross-linking of BDTH is 6 kJ/mol more exothermic than that of EDTH. In fact, the calculations suggest that for EDTH cyclization is the thermodynamically preferred route, while for BDTH, cross-linking is favored.

Finally, irrespective of their relative mechanical properties, the TVS-EDTH and TVS-BDTH polymers obtained through self-initiation were colorless after thermal processing (Figure 1c) and exhibited high transparency, with an average optical transmission across the visible region of the spectrum (400–700 nm) of $\geq 89\%$. The yellowing in samples made by the other initiation processes appears to arise, at least in part, from the oxidation of unreacted vinyl groups during heating. This can be demonstrated through polymerization and thermal processing of samples containing progressively higher TVS to EDTH mole ratios. At mole ratios above stoichiometric, which contain excess unreacted vinyl groups, progressively darker and more highly colored materials are produced (Figure S2).

Mechanical Properties. The same synthetic approach, utilizing self-initiated room temperature polymerization followed by thermal annealing, was used for the other monomer combinations. For all of the compositions, the densities, Young's moduli, and glass transition temperatures were determined (Table 3). All of the materials form free-standing monoliths

Table 3. Properties of Thiol–Ene Polymer Monoliths

polymer	density (g/cm ³)	Young's modulus (MPa)	T _g (°C) DSC/DM
TVS–BDTH	1.43	668	60/69
TVG–BDTH	1.39	627	46/56
TTT–BDTH	1.53	551	59/66
TeSO–BDTH	1.75	520	51/38
TVS–EDTH	1.06	108	21/42
polymer	density (g/cm ³)	Young's modulus (MPa)	T _g (°C) DSC
TrSO–BDTH	1.36	74	26
TVS–PDTH	1.16	26	4
TVT–BDTH	1.24	26	21
TAS–EDTH	1.14	21	2
TeSO–EDTH	1.28	19	19
TAG–EDTH	1.19	18	–19
TAG–PDTH	1.23	18	–26
TrSO–EDTH	1.63	17	–2
TAG–BDTH	1.22	14	20
TAS–PDTH	1.32	13	nd ^a

^and = not determined.

with high transparency and, as will be discussed, most have refractive indices that are regarded as high for polymeric materials. However, we found that the subset of materials that could be successfully ground and polished into an optical component were those with Young's moduli above ~100 MPa. Those materials include the TVS–EDTH and TVS–BDTH polymers discussed above and the BDTH polymers of the tetravinylgermanium (TVG) and the heterocycles, triallyltri-azirine (TTT) and trimethyltrivinylcyclotetrasiloxane (TeSO).^{9,26} As a proof of concept, large monolithic examples of the TVS–EDTH and TVS–BDTH polymers were fabricated and then successfully ground and polished on commercial optical lens grinding equipment (Figure 6).



Figure 6. Monolithic sample of (left) TVS–BDTH and (right) TVS–EDTH ground and polished into optical flats (diameter = 5 cm).

Scrutiny of the data in Table 3 indicates that, in general, the mechanical properties of the polymers depend greatly on the flexibility of the constituent monomers.⁵ For the systems used here, it is clear that the more flexible cross-linking groups yield materials with the lowest T_g and Young's moduli. For example, among the dithiol cross-linking groups, there is a dramatic drop in the Young's modulus and T_g in going from an ethane to a pentane in the dithiol monomer. A similar decrease in T_g and Young's modulus is also seen in going from ethylene to allene groups in the tetravinyl monomers (e.g., TVS vs TAS). This effect may arise in part from the torsional flexibility of the chains; however, the dominant factor is likely from the

intramolecular cyclization processes discussed previously, which reduces the cross-link density of the polymers. One interesting series is the tetravinyl Si, Ge, and Sn monomers. Tetravinyl silane and germanium form extremely hard polymer samples with BDTH, consistent with their tendency to cross-link as opposed to cyclize. Tin, however, forms extremely soft materials with very low Young's moduli. This appears to arise from thermal instability of the polymer, in which degradation, as evidenced by the onset of strong brown coloration, occurs at the 120 °C temperature at which we typically thermally anneal the materials. As such, lower-temperature processing (40 °C) was used for these materials, resulting in a less robust, though colorless material with good transparency. The origin of this may be in the decrease in metal–ligand bond energies observed in going down a group in the p-block elements.²⁷ The significance of the structure–property data in Table 3 is that they suggest that the proper choice of monomers has a large effect on the mechanical properties of the polymer. This arises both due to the influence of their structural characteristics on their ability to cross-link and on their thermal stability as it relates to achieving a high cross-link density.

Optical Properties. The well-established design strategy for the production of polymeric materials with high refractive indices is the introduction of polarizable atoms or groups into the polymer network.² The element commonly used is sulfur, and many design strategies for increasing the refractive index involve synthetic methodologies aimed at increasing the amount of sulfur in the network. The potential for thiol–ene polymer to generate materials with high refractive indices lies in part in the fact that the repeat unit contains sulfur, but also because monomers can be chosen so that no highly electronegative atoms such as oxygen and nitrogen are present. The systems described here further extend this design strategy through the use of monomers containing other polarizable main group elements such as Si, Ge, and Sn that, in conjunction with S, add to the overall polarizability of the bulk polymer. The effect of these polarizable main group elements can be readily seen in the refractive index measurements (Table 4).

Table 4. Optical Properties of Thiol–Ene Polymers

polymer	RI (546 nm)	Abbe number	% transmission (at 633 nm)
TVT–BDTH	1.703	nd ^a	88
TVG–BDTH	1.692	nd	92
TAG–BDTH	1.690	24.3	90
TVS–BDTH	1.687	26.3	92
TrSO–BDTH	1.665	nd	91
TTT–BDTH	1.660	28.7	92
TeSO–BDTH	1.660	nd	90
TVS–EDTH	1.656	34.0	87
TrSO–EDTH	1.655	nd	89
TeSO–EDTH	1.654	nd	92
TAG–EDTH	1.620	39.9	86
TAS–EDTH	1.610	36.3	89
TVS–PDTH	1.599	41.0	90
TAG–PDTH	1.590	45.0	90
TAS–PDTH	1.570	41.5	87

^and = not determined.

In going down the row from Si to Sn, the refractive index shows a steady increase, with TVT–BDTH achieving the highest refractive index we observe at 1.703. Unfortunately, as we noted

previously, these materials tend to be quite soft. The best composition, in terms of both mechanical and optical properties, is TVG–BDTH, which has a Young's modulus of 627 MPa and a refractive index of 1.692. The three heterocycles, TTT, TrSe, and TeSO, have, on average, lower refractive indices than do the tetravinyl group 14 elements, although they are all above 1.6, which places them in the higher refractive index range. The lower refractive index is likely due to the presence of electronegative oxygen and nitrogen in the heterocycle.

From analysis of the data in Table 4, several significant structure–property relationships can be deduced. If we compare the refractive indices for TVS–EDTH and TVS–PDTH, they are observed to drop from 1.656 to 1.599 as the hydrocarbon chain length increases. This suggests that by reducing the relative amount of the more electronegative first-row main group atoms to the more polarizable second-row atoms, an increase in the refractive index is realized. In a similar fashion, as the vinyl monomer goes from ethylene to allene, the refractive indices drop, as can be seen by comparing TVS–EDTH and TAS–EDTH, where the refractive index goes from 1.656 to 1.610.

The Abbe numbers, for the subset of the sample for which it was measured, range from ~24 to 45 and, consistent with prior observations, tend to decrease with increasing refractive index (Figure 7).^{28,29} In these materials, the decrease in Abbe number

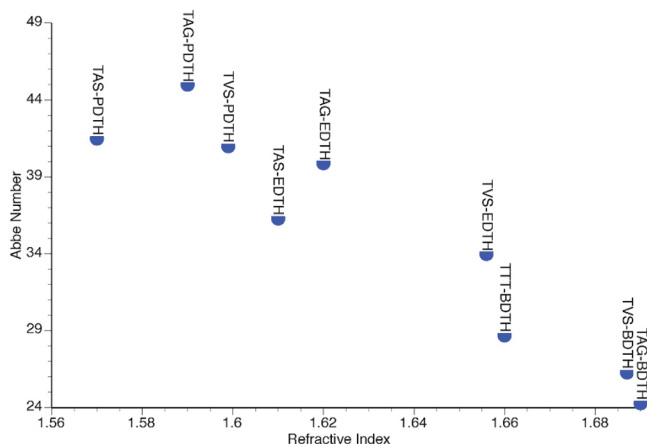


Figure 7. Refractive index dependence of the Abbe number for a selected series of thiol–ene polymers.

with increasing refractive index can be in part attributed to the fact that benzenedithiol, which is the dithiol monomer used in the highest refractive index compositions, is an aromatic species with an optical absorption in the near-UV range. The refractive index measured at 486.1 nm, which is used in the determination of the Abbe number, will be close to the absorption and, hence, will increase, thereby reducing the Abbe number. Scrutiny of the graph in Figure 7 indicates that there are two places where both the refractive index and the Abbe number increase. This occurs in going from TAS to TAG for the PDTH and EDTH dithiol monomer. In both of these cases, the dithiol is constant and the central metal in the vinyl monomer goes from Si to Ge. In going down the column, the polarizability of the metal increases, thereby increasing the refractive index. As the data indicate, however, there is not a concomitant decrease in the Abbe number, suggesting that by using main group elements from the third or lower rows as primary building blocks of

optical polymers and by avoiding groups with absorption in the near-UV range, it may be possible to achieve materials with both high refractive indices and high Abbe numbers.

CONCLUSION

We have successfully synthesized a series of bulk inorganic/organic hybrid polymers utilizing the thiol–ene coupling reaction to generate the repeat unit of the polymer. This was accomplished by using vinyl monomers with a high functionality and by polymerizing the polymers through a slow self-initiation process that reduced the amount of radical species in solution. These materials exhibit, on average, high refractive indices, resulting from the fact that the thiol–ene coupling reaction contributes a highly polarizable sulfur group to the polymer chain and from the incorporation of polarizable main group elements through the use of group 14 tetravinyl-containing monomers. Very good structural properties were achieved for several of the compositions due to a high cross-link density realized through the use of monomers which inhibited intramolecular cyclization processes and facilitate intermolecular cross-linking. Taken together, the specific polymers produced and the design strategies attained from this work potentially represent a useful contribution to the field of optical polymers. Moreover, as many other suitable monomers can potentially be selected with the appropriate properties to generate both high refractive indices and structural integrity, this potentially represents a new class of high refractive index polymer.

ASSOCIATED CONTENT

Supporting Information

DMA analysis of TVS–EDTH (Figure S1) and studies showing the origin of coloration in thiol–ene materials due to excess unreacted vinyl being present (Figure S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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