

# Thiol–Isocyanate–Ene Ternary Networks by Sequential and **Simultaneous Thiol Click Reactions**

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Thiol-isocyanate-ene ternary networks with systematic variations (100/100/0, 100/80/20, 100/ 60/40, 100/40/60, 100/20/80, and 100/0/100) were prepared by sequential and simultaneous thiol—ene and thiol-isocyanate click reactions. The thiol-isocyanate coupling reaction was triggered thermally or photolytically to control the sequence with the thiol-ene photopolymerization. Triethyl amine (TEA) and 2,2-dimethoxy-2-phenyl acetophenone (DMPA) were used for the sequential thermally induced thiol-isocyanate coupling and photochemically initiated thiol-ene reaction, respectively. A thermally stable photolatent base catalyst (tributylamine tetraphenylborate salt,  $TBA \cdot HBPh_4$ ) capable of in situ generation of tributylamine by UV light was used with isopropylthioxanthone (ITX) for the simultaneous thiol-isocyanate/thiol-ene curing systems. The kinetics of the hybrid networks investigated using real-time IR indicate that both thiol-isocyanate and thiol-ene reactions were quantitatively rapid and efficient (>90% of conversion in a matter of minutes and seconds, respectively). The  $T_{\rm g}$  of the thiourethane/thiol-ene hybrid networks progressively increases (-5 to 35 °C by DSC) as a function of the thiourethane content due to the higher extent of hydrogen bonding, also resulting in enhanced mechanical properties. Highly uniform and dense network structures exhibiting narrow full width at half-maximum (~10 °C) were obtained for both the sequential and the simultaneous thiol click reactions, resulting in identical thermal properties that are independent of the sequence of the curing processes.

### Introduction

Thiol chemistry continues to attract attention due to its efficiency and versatility with numerous thiol reactions being regarded as click reactions.<sup>1</sup> In particular, thiol-ene free-radical photopolymerizations (Scheme 1) proceed via a highly robust, oxygen resistant reaction that has been widely used in making polymeric materials and in functionalizing small molecules.  $^{\hat{2}-1\hat{0}}$  Additionally, the nucleophilic addition of thiols to isocyanate groups in the presence of a strong

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base catalyst (Scheme 2) is also reported to give 100% yield in a matter of seconds with few, if any, side products.<sup>11</sup> These two thiol-based reactions proceed by free-radical or anionic chain processes,<sup>7-11</sup> respectively. It has been reported that base catalysts have a pronounced effect on the thiol-isocyanate reaction since the base catalyst makes the carbonyl carbon of isocyanate more electron deficient while also producing a very strong nucleophilic thiolate ion<sup>11–15</sup> that results in rapid thiol-isocyanate coupling reactions. We recently reported that highly elastic novel segmented polythiourethane elastomers could be synthesized by reacting a dithiol, an oligomeric dithiol, and a diisocyanate in the presence of triethylamine (TEA).<sup>11</sup> High conversions of greater than 95% were achieved within 10 min at room temperature, and the nanophase separation of the segmented structure was controllable by the thiol-isocyanate reaction.

There have been several multicomponent simultaneous or sequential systems based on thiol Click reactions. Wei et al. demonstrated that thiol-ene free-radical and vinyl

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ether cationic photopolymerization resulted in crosslinked networks that effectively combined the thermal and mechanical properties inherent to each system while also taking advantage of the kinetic nature of each reaction.<sup>16</sup> The combination of thiol-ene and thiol-epoxy reactions to form hybrid networks indicated that highly cross-linked and high  $T_{\rm g}$  polymer materials could be formed with significantly reduced shrinkage and stress when the polymerization kinetics of each reaction were manipulated appropriately.<sup>17</sup> Recently, incorporation of urethane functional groups into thiol-ene networks to introduce strong hydrogen bonding for enhancing physical and mechanical properties has been reported.<sup>1,18,19</sup> However, these urethane-modified thiolene networks were essentially based on the simple photopolymerization of thiols and urethane-modified ene oligomers that had been prepared separately by an isocyanate coupling reaction with hydroxyl-terminated enes. This approach leads to significant difficulties since the tetra-functional ene monomers are highly viscous with extensive hydrogen bonding occurring prior to the photopolymerization process. To overcome this problem and generate polymer networks with significant hydrogen bonding while still beginning with low viscosity monomers, sequential or simultaneous thiol-isocyanate and thiol-ene reactions were performed on a single formulation that contained all necessary components.

Herein, we report thiol—isocyanate—ene reaction systems that polymerize by two thiol Click reactions that are performed either sequentially or simultaneously, that is, a thiol—isocyanate coupling reaction and a thiol—ene reaction. The sequence of the two reactions is controlled by the applied reaction triggers and their timing. Using a thermally active base catalyst results in sequential reactions, while using a photolatent base catalyst which generates a tertiary amine upon exposure to light results in simultaneous curing. In the first process the thiol—isocyanate precured in the presence of an externally added tertiary amine and the subsequent thiol—ene photopolymerization result in a quantitatively controlled sequential dual curing process. Simultaneous production of free radicals and tertiary amines by irradiating with UV light lead to simultaneous reactions of thiols with enes and isocyanates. Controlling the reaction sequence and timing provides an exciting opportunity for implementing a suitable strategy for fabricating photocurable materials for both thin films and thick cross-linked materials. In addition, the inclusion of thiourethane groups in thiol-ene networks offers numerous advantages such as enhanced physical and mechanical properties resulting from extensive hydrogen bonding. The relationships between the chemical composition and the physical/ mechanical properties of thiol-isocyanate-ene based ternary networks are established in terms of calorimetry, thermomechanical properties, refractive index, hardness, and tensile properties. The results reported are indicative of the vast range of properties achievable with thiolisocyanate-ene based ternary networks.

#### **Experimental Section**

Materials. Hexanethiol, butyl 3-mercaptopropionate, butyl thioglycolate, benzenethiol, hexyl isocyanate, phenyl isocyanate, cyclohexyl isocyanate, 1,5-diazabicyclo[4.3.0]-5-nonene (DBN), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,4-diazabicyclo[2.2.2]octane (DABCO), 4-dimethylaminopyridine (DMAP), triethylamine (TEA), tributylamine (TBA), 1,8-bis-(dimethylamino)naphthalene (proton sponge)), and 1,3,5-triallyl-1,3,5-triazine-2,4,6 (1H,3H,5H)-trione (TATAT) were purchased from Aldrich. Dithiol (glycol di-3-mercaptopropionate (GDMP)) and hexamethylene diisocyanate trimer (Desmodur N3600) were supplied by Bruno Bock Thio-Chemicals-S and Bayer Materials Science, respectively. Photoinitiators, 2,2-dimethoxy-2-phenyl acetophenone (DMPA) and isopropylthioxanthone (2 and 4-isomer mixture) (ITX), were obtained from Ciba Specialty Chemicals and Albemarle. The photogenerated amine (tributylamine · tetraphenylborate salt, TBA·HBPh<sub>4</sub>) was synthesized by reacting tributylamine and sodium tetraphenylborate in a hydrocholic acid (HCl) aqueous solution as reported in the literature.<sup>20</sup> The structures of all materials used are shown in Schemes 3 and 4. All materials were used as received.

Kinetics. Real-time infrared (RTIR) spectra were recorded on a modified Bruker 88 spectrometer to obtain kinetic profiles of thiol-isocyanate model reactions in dilute benzene solution as well as thiol-isocyanate-ene network formation. For thiol-isocyanate model reactions, all samples were prepared by adding isocyanates to the thiol solutions with catalyst present (for detailed concentration and measurement conditions see figure and table captions). Thin samples (25  $\mu$ m) between two salt plates sealed with silicon were placed immediately in the RTIR after mixing the samples. The conversion of thiol and isocyanate as a function of time were measured by monitoring the peaks at 2570 and 2250 cm<sup>-1</sup>, respectively. For stoichiometric reactions, the results measured from both peaks were identical; thus, only isocyanate conversions are reported here. It should be noted that there is some error in the measurements due to delay ( $\sim 10$  s) in initiating the RTIR measurements. For the sequential thiol-isocyanate/thiol-ene curing process, samples were prepared by dissolving the photoinitiator (DMPA, 1 wt %) and base catalyst (TEA, 0.1 wt %) into GDMP followed by the add-on of TATAT and N3600. Mixtures were immediately

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Scheme 3. Molecular Structures of Thiol, Ene, Isocyanate, Photointitiator, and Photo-Generated Amine Catalyst



#### Scheme 4. Molecular Structures of Tertiary Amine Catalysts



placed in the RTIR and retained for 20 min before irradiating with UV light to selectively induce the TEA catalyzed thiol-isocyanate coupling reactions. The thiol-ene free-radical reaction was subsequently initiated by irradiating with light  $(20.5 \text{ mW/cm}^2)$  from an Oriel lamp system equipped with a 200 W, high-pressure mercury-xenon bulb channeled through an electric shutter and optical fiber cable into the sample chamber. Samples for the simultaneous thiol-isocyanate/thiol-ene reactions were prepared by dissolving TBA  $\cdot$  HBPh<sub>4</sub> (0.61 wt %) and ITX (0.36 wt %) in GDMP followed by mixing the monomers, TATAT and N3600. Both thiol-isocyanate and thiol-ene reactions were triggered simultaneously by irradiating with UV light (1.41 mW/cm<sup>2</sup>) passed through a 365-nm filter. The conversions of GDMP, N3600, and TATAT as a function of time were measured during the sequential and simultaneous thiol-isocyanate and thiol-ene reactions by monitoring peaks at 2570, 2250, and 3080 cm<sup>-1</sup> for thiol, isocyanate, and ene, respectively.

**Characterization.** <sup>1</sup>H NMR spectra were obtained to confirm the dissociation of TBA  $\cdot$  HBPh<sub>4</sub> salt and generation of TBA before and after irradiation with light at 365 nm (1.5 mW/cm<sup>2</sup>) and full arc (10.2 mW/cm<sup>2</sup>) for 30 min in the presence and absence of ITX. All spectra were recorded on a Varian 300 MHz NMR for samples in CDCl<sub>3</sub> with tetramethysilane (TMS) as the internal reference.

The thiol-isocyanate-ene network films were prepared on glass plates using a 200  $\mu$ m draw down bar. For sequential thiol-isocyanate/thiol-ene reaction processes, cast films were precured at ambient temperature for 1 h to induce selectively GDMP-N3600 reactions followed by initiation of GDMP-TTT photopolymerization with a medium pressure mercury lamp (intensity =  $10.2 \text{ mW/cm}^2$  for 5 min). Thiol-isocyanate coupling reactions and thiol-ene photopolymerizations were performed at the same time for simultaneous reaction systems by irradiating with a medium pressure mercury lamp passed through a 365 nm optical filter (1.5 mW/cm<sup>2</sup>) for 30 min. All samples were postcured at 80 °C for 24 h to obtain approximately quantitative 100% conversion and remove any effects of the extent of reaction on the physical and mechanical properties. The same concentrations of TEA, DMPA, TBA·HBPh<sub>4</sub>, and ITX as used for RTIR measurements were employed in the preparation of films for mechanical and other testing.

Thermal properties of the thiol–isocyanate–ene films prepared by both sequential and simultaneous reaction systems were characterized by differential scanning calorimetry (DSC, TA Instruments Q 1000, equipped with RCS 90 as a refrigerated cooling system). Sample weights were  $8.0 \pm 1.0$  mg, and all experiments were carried out under nitrogen with a flow rate of 50 mL/min. DSC scans were conducted over a temperature range from -50 to 100 °C using 10 °C/min heating and cooling rates. On the first heating scan, samples were equilibrated at 100 °C (higher than the  $T_g$  of the thiourethane neat film (GDMP/TTT/N3600 = 100:0:100)) for 10 min to erase any thermal history, followed by cooling to -50 °C and subsequent heating to 100 °C. The second heating scans were recorded and used here for all thiol–isocyanate–ene network films.

Dynamic thermal mechanical properties of sequentially prepared thiol-isocyanate-ene samples were measured using a

Table 1. Second Order Rate	Constant $(k_2)$ of Amine	Catalyzed Thiourethane	<b>Reactions with Mono-Functional</b>	Thiols and Isocyanates in Benzene
	· -/	•		•

isocyanate	thiol (pKa)	catalyst (pKa)	$k_2 \times 10^2 (\mathrm{L} \cdot \mathrm{mol}^{-1} \cdot \mathrm{s}^{-1})$	
hexyl isocyanate	hexanethiol (10.53)	DBU (11.6) DBN (13.5) DABCO (8.2) DMAP (9.2) TEA (10.75) TBA (10.7) proton sponge (12.1)	$10700^{a} \\ 8300^{a} \\ 3.0^{b} \\ 0.6^{b} \\ 0.7^{b} \\ 0.3^{b} \\ slow^{b}$	
hexyl isocyanate	hexanethiol (10.53) butyl 3-mercaptopropionate (9.33) butyl thioglycolate (7.91) benzenethiol (6.43)	TEA (10.75)	$3.0^{c}$ 21.7 <sup>c</sup> 67.8 <sup>c</sup> 2097 <sup>c</sup>	
hexyl isocyanate cyclohexyl isocyanate phenyl isocyanate	benzenethiol (6.43)	DABCO (8.2)	$4.7^d$ $4.7^d$ $212^d$	

 $a^{'}$ [SH] = [NCO] = 570 mM, [Catalyst] = 0.24 mM.  $b^{'}$ [SH] = [NCO] = 730 mM, [Catalyst] = 80 mM.  $c^{'}$ [SH] = [NCO] = 730 mM, [TEA] = 2.3 mM.  $^{d}$ [SH] = [NCO] = 570 mM, [DABCO] = 0.12 mM.

DMTA (MK VI, Rheometrics). Measurements were conducted using the vertical tension mode on samples with dimensions of  $10 \times 8.0 \times 0.2$  mm (L  $\times$  W  $\times$  T) from -50 to 150 °C at a 5 °C/min heating rate and 1 Hz frequency with 0.05% strain.

Tensile property measurements were conducted with a mechanical testing machine (MTS, Alliance RT/10) according to ASTM D882 using a 100 N load cell with a specimen gauge length of 20 mm at a crosshead speed of 100 mm/min.

Refractive index was obtained using a Bausch&Lomb ABBE-3 L refractometer at 24 °C. 1-Bromonaphthalene was applied between the sample film and the prism shield.

Pencil and Persoz pendulum hardness (ASTM D-4366 using a BYK-Gardner pendulum hardness tester with a square frame pendulum) were measured. The results reported are the average of 10 tests.

## **Results and Discussion**

Model Kinetics for Tertiary Amine Catalyzed Thiol-Isocyanate Coupling Reactions. To enhance understanding of the thermally and photolytically induced tertiary amine catalyzed thiol-isocyanate polymerization reactions, extensive evaluation of reaction kinetics in model compounds was performed, and the results were evaluated in terms of the structures of the tertiary amine catalysts, thiols, and isocyanates. It is well-known that the reactions between hydrogen-containing compounds such as alcohols, thiols, and primary (or secondary) amines and isocyanates occur via a nucleophilic addition process such that the reactivity is generally proportional to the nucleophilicity of -OH, -SH, and -NH2 and the electron deficiency of the isocyanate carbon.<sup>12,21</sup>

The catalytic activity of tertiary amines results from the coordination of the nitrogen electron lone pair with both active hydrogen containing compounds and isocyanates, with the result being an increase in the nucleophilicity of hydrogen donors and a more electron susceptible carbon, respectively. The catalytic efficiency of tertiary amines is dependent upon the availability of the electron pair for complex formation as determined by both the basicity of the nitrogen and the steric hindrance.<sup>12,21-23</sup> The kinetic profiles of the thiol-isocyanate reactions of a monofunctional thiol (hexanethiol) and an aliphatic isocyanate (hexyl isocyanate) in dilute acetonitrile in the presence of different types of tertiary amines were obtained by realtime IR (see Supporting Information Figure S1 for kinetic plots), and the second order rate constants are summarized in Table 1. Note that the rate constants at the lower catalyst concentrations (Supporting Information Figure S1a) could only be given for DBU and DBN since the rates for the other catalysts were too slow to measure by real time IR. The rate constants for the 1,5-diazabicyclo[4.3.0]-5-nonene (DBN) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) catalyzed model system are significantly greater than for 1,4-diazabicyclo[2.2.2]octane (DABCO), 4-dimethylaminopyridine (DMAP), triethylamine (TEA), tributylamine (TBA), and 1,8-bis(dimethylamino)naphthalene (proton sponge). As stated above, this outcome is due to the higher basicity (see Table 1) of DBN and DBU as compared to DABCO, DMAP, TEA, TBA, and the proton sponge as determined by the  $pK_a$  values of the conjugate acids of each amine listed in Table 1. $^{24-26}$  Though a strong base catalyst, the proton sponge is effectively a noncatalyst for the thiol-isocyanate coupling reaction due to the significantly crowded environment of nitrogen atoms so that it is very difficult for electron lone pairs to take part in the thiol-isocyanate nucleophilic addition reactions.

It is well-known that the addition of thiols to electron deficient carbons depends on the acid dissociation constant  $(pK_a)$  of the thiol because this nucleophilic addition reaction proceeds through the thiolate anion chain process as shown in Scheme  $2^{12,27-30}$  In Table 1 the rate

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constants for the reaction of hexyl isocyanate with four different thiols in the presence of TEA (2.3 mM) are



**Figure 1.** Kinetic profiles for (a) thiol-ene (SH/C=C = 100:100; DMPA 1 wt %, intensity of high pressure mercury lamp: 20.5 mW/cm<sup>2</sup>) and (b) thiol-isocyanate networks (SH/NCO = 100:100; TEA 0.1 wt %).

shown (see Supporting Information Figure S2 for kinetic plots). The rate constants increase as the  $pK_a$  of the thiol decreases due to the increase in the formation rate of the corresponding thiolate anion, which is a strong nucleophile.

As discussed above, the reactivity of isocyanates with active hydrogen-containing compounds is affected by the electron deficiency of the carbon atom in isocyanates so that the substituents that stabilize positive character of the carbon atom enhance the isocyanate reactivity with the corresponding thiolate anion. Table 1 (see Supporting Information Figure S3 for kinetic plots) shows the isocyanate structural effect on the thiol–isocyanate coupling reaction. The reaction of the aromatic isocyanate (phenyl isocyanate) with benzenethiol is significantly faster than the reaction between the aliphatic isocyanates (hexyl and cyclohexyl isocyanate) and benzenethiol due to carbocation formation in the resonance structures of the aromatic isocyanate.<sup>21</sup>

Having established the relationship between structure and reactivity for the basic components (thiol, isocyanate, and catalyst) in thiol-isocyanate nucleophilic coupling reactions, results for the polymerization of a ternary mixture of thiol, isocyanate, and ene are evaluated. To demonstrate the efficiency of this ternary approach in



Figure 2. Kinetic profiles of thiol-isocyanate-ene ternary networks formed by the sequential curing process; SH/C=C/NCO = (a) 100:80:20, (b) 100:60:40, (c) 100:40:60, and (d) 100:20:80 (DMPA 1 wt %; TEA 0.1 wt %; intensity of high pressure mercury lamp: 20.5 mW/cm<sup>2</sup>).



**Figure 3.** <sup>1</sup>H NMR spectra (CHCl<sub>3</sub>-*d*) of (a) tributylamine (TBA) and TBA  $\cdot$  HBPh<sub>4</sub> (b) before, (c) after irradiation at 365 nm (1.5 mW/cm<sup>2</sup>), and (d) full are (10.2 mW/cm<sup>2</sup>) in CHCl<sub>3</sub>-*d* solution (5 wt %).



Figure 4. UV absorption spectra of ITX in acetonitrile (concentration:  $5.8 \times 10^{-5}$  M).

making networks highlighted by the presence of extensive thiourethane groups, we selected a dithiol based on the diester of mercaptopropionic acid and ethylene glycol, a triisocyanate which is the trimer (isocyanurate) of 1,6hexane diisocyanate, and a corresponding triallyl triene with the same isocyanurate cyclic ring structure as the triisocyanate.

Kinetics of Thiol–Isocyanate–Ene Ternary Systems. The kinetics of thiol–isocyanate–ene polymerizations were investigated by systematically varying the reactive composition and the reaction sequence. Figures 1 and 2 present the resultant functional group conversions as a function of reaction time for the separate and simultaneous thiol–isocyanate–ene ternary networks. In Figure 1a,b, results are presented for bulk polymerizations of each type. Here, it is seen that each reaction is relatively fast and essentially quantitative; the GDMP-TATAT photopolymerization occurs in a few seconds while the GDMP–N3600 coupling reaction takes approximately 20–30 min. These results on the distinct



**Figure 5.** <sup>1</sup>H NMR spectra (CHCl<sub>3</sub>-d) of (a) tributylamine (TBA) and TBA·HBPh<sub>4</sub> with ITX ((b) before and (c) after irradiation at 365 nm (1.5 mW/cm<sup>2</sup>) in CHCl<sub>3</sub>-d solution (5 wt %; ITX/TBA·HBPh<sub>4</sub> = 0.36:0.61)).

polymerization indicate that each reaction is independent of the other and can be controlled separately through the initial dark period, through light intensity, and through the catalyst and photoinitiator concentration. In Figure 2a-d, kinetic profiles are presented for thiolisocyanate-ene ternary mixtures in which the sequential dual curing process is performed on formulations with systematic variations of the relative thiol-ene to thiol-isocyanate ratio. The concentrations of TEA and DMPA were fixed at 0.1 and 1.0 wt % based on the total amount of the mixture. GDMP-N3600 coupling reactions forming thiourethane networks were allowed to proceed for 20 min in the dark followed by irradiation with UV light to trigger photopolymerization of GDMP and TATAT. N3600 conversions reached 90-91% in 20 min during selective TEA catalyzed thiol-isocyanate coupling reactions, and the corresponding GDMP conversions were 19, 36, 54, and 73% (~90% of theoretical conversion of thiols based on stoichiometry with NCO) as the N3600 molar ratio was increased (20, 40, 60, and 80%). TATAT and the remaining GDMP were reacted by photopolymerization, and nearly quantitative conversions were obtained in just a few seconds. It should be noted that, for all compositions, the final conversions of GDMP, N3600, and TATAT obtained by RTIR were not 100% due to molecular mobility restrictions at higher



**Figure 6.** Kinetic profiles of thiol-isocyanate-ene ternary networks formed by the simultaneous curing process; SH/C=C/NCO = (a) 100:100:0, (b) 100:80:20, (c) 100:60:40, (d) 100:40:60, (e) 100:20:80, and (f) 100:0:100 (ITX 0.36 wt %; TBA  $\cdot$  HBPh<sub>4</sub> 0.61 wt %; intensity of high pressure mercury lamp: 1.41 mW/cm<sup>2</sup> through 365-nm filter).

conversions. As shown in the model studies, the thiol-isocyanate reaction rate is controlled by both catalyst type and concentration while the thiol-ene photopolymerization can be initiated at any desired intensity and at any time prior to, during, or after the thiol-isocyanate coupling reactions. Consequently, the sequence of the thiol-isocyanate and thiol-ene reactions involving different reaction mechanisms is readily programmable based on whatever property requirements exist for the final polymers.

For simultaneous thiol—isocyanate—ene ternary network formation, both the thiol—isocyanate coupling and the thiol—ene free-radical reactions are triggered by UV light at 365 nm using the photogenerated amine, tributylamine · tetraphenylborate salt, (TBA · HBPh<sub>4</sub>, 0.61 wt %), and the photosensitizer, isopropylthioxanthone (ITX, 0.36 wt %), which generates both free-radicals and tributylamine catalyst upon photolytic decomposition.

First, considering photolysis of only TBA $\cdot$ HBPh<sub>4</sub> in solution, TBA $\cdot$ HBPh<sub>4</sub> absorbs UV light below 300 nm and upon direct photolysis at wavelengths less than 300

Table 2. Glass Transition Temperatures of Thiol–Isocyanate–Ene Ternary Networks through the Sequential and Simultaneous Dual Cure Systems Obtained by DSC

SH/C=C/NCO (molar ratio)	TEA + DMPA (°C)	$TBA \cdot HBPh_4 + ITX$ (°C)			
100:100:0	-6	-5			
100:80:20 100:60:40	4 10	8			
100:40:60	16	16			
100:20:80	30	28			
100:0:100	36	35			

nm gives TBA and other byproducts.<sup>20</sup> Accordingly, in Figure 3 are shown the NMR spectra of tributylamine and TBA·HBPh<sub>4</sub> before and after irradiation with UV light at 365 nm and broad spectrum of UV that contains wavelengths below 300 nm. The generation of TBA from TBA·HBPh<sub>4</sub> only occurs when TBA·HBPh<sub>4</sub> is photolyzed with the full arc of the unfiltered UV light. It is also well-known that ITX efficiently photosensitizes upon UV irradiation through photoexcitation and subsequent energy transfer to other molecules. The sensitization potential of ITX is highly dependent on the wavelength of the



**Figure 7.** DSC thermograms of thiol–isocyanate–ene hybrid networks formed by the sequential curing process; SH/C=C/NCO = (a) 100:100:0, (b) 100:80:20, (c) 100:60:40, (d) 100:40:60, (e) 100:80:20, and (f) 100:0:100 (DMPA 1 wt %; TEA 0.1 wt %; precure at room temperature for 1 h; intensity of medium pressure mercury lamp 10.2 mW/cm<sup>2</sup>; irradiation time, 5 min; postcure at 80 °C for 24 h).

irradiating UV light; that is, the higher extinction coefficient, the greater the amount of light absorbed as shown in Figure 4. Upon irradiation at 365 nm, ITX abstracts hydrogen from thiols (hydrogen donor) to produce thiyl radicals, thus initiating the radical thiol—ene photopolymerization. If ITX and TBA·HBPh<sub>4</sub> are both present and irradiated at wavelengths greater than 300 nm, the excited triplet state of ITX will also transfer energy to TBA·HBPh<sub>4</sub> which subsequently decomposes to give TBA, which catalyzes the thiol—isocyanate reaction and other byproducts. In Figure 5, the appearance of TBA is indeed confirmed by NMR with peaks at 2.6 ppm occurring following photolysis at 365 nm of a TBA·HBPh<sub>4</sub> solution containing ITX.

Ultimately, this combination results in the thiolisocyanate coupling reaction and thiol-ene free-radical photopolymerization being triggered simultaneously when ITX is used. Consequently, both the thiourethane and thiol-ene reactions will be initiated by ITX. In Figure 6, kinetic profiles of simultaneous thiol-isocyanate-ene ternary networks are presented as a function of the SH/C=C/ NCO ratio during UV irradiation at 365 nm in the presence of TBA·HBPh<sub>4</sub> and ITX. Both the thiol-isocyanate coupling reaction and thiol-ene photopolymerization are successfully initiated, and the conversion of GDMP, TA-TAT, and N3600 is nearly quantitative based on the stoichiometry; that is,  $Conversion_{SH} \sim Conversion_{C=C} + Con$ version<sub>NCO</sub>. However, it should be noted that the lower overall conversion of all components by the simultaneous process is due to the lower light intensity at 365 nm (1.41  $mW/cm^{2}$ ) as compared to the full arc (20.5 mW/cm<sup>2</sup>) for the sequential process. In addition, under these conditions, the thiol-ene photopolymerization proceeds more rapidly than the thiol-isocyanate coupling reaction. The different reaction rates can be synchronized either by changing the type of tertiary amine used to make the salt with the tetraphenyl



**Figure 8.** Dynamic mechanical behavior of thiol–isocyanate–ene ternary networks formed by the sequential curing process; SH/C=C/NCO = (a) 100:100:0, (b) 100:80:20, (c) 100:60:40, (d) 100:40:60, (e) 100:80:20, and (f) 100:0:100 (DMPA 1 wt %; TEA 0.1 wt %; precure at room temperature for 1 h; intensity of medium pressure mercury lamp 10.2 mW/cm<sup>2</sup>; irradiation time, 5 min; postcure at 80 °C for 24 h).

borate or by changing the relative amounts of the ITX and the TBA·HBPh<sub>4</sub>. Of course, the combined rate of both reactions is easily controlled simply by varying the amount of ITX.

Thermal Properties. DSC measurements were conducted to investigate the effect of the compositional ratio and reaction sequence of the thiourethane/thiol-ene hybrid networks on thermal properties. DSC thermograms of thiourethane/thiol-ene hybrid networks prepared by both sequential and simultaneous curing systems were almost identical. Glass transition temperatures obtained by DSC are summarized in Table 2, and a representative second heating scan of the thiourethane/ thiol-ene hybrid networks prepared by sequential curing system is shown in Figure 7. With an increase in the N3600 concentration,  $T_{\rm g}$  progressively increases due to the higher extent of hydrogen bonding resulting from the increase in the thiourethane linkages in the thiolisocyanate-ene ternary networks. In addition, as shown in Figure 7, the glass transition range  $(T_{g,e}-T_{g,i})$  is very narrow ( $\sim 5 \,^{\circ}$ C) for all compositions. It is clear that thiolisocyanate-ene ternary networks are highly uniform as

 Table 3. Glass Transition Temperatures and Rubbery Modulus (E' at 80 °C) of Thiol–Isocyanate–Ene Ternary Networks through the Sequential and Simultaneous Dual Cure Systems Obtained by DMTA

	TEA + DMPA			$TBA \cdot HBPh_4 + ITX$		
SH/C=C/NCO (molar ratio)	$T_{\rm g}  (^{\circ}{\rm C})^a$	E' (MPa) <sup>b</sup>	fwhm (°C)	$T_{\rm g}  (^{\circ}{\rm C})^a$	E' (MPa) <sup>b</sup>	fwhm (°C)
100:100:0	11	5.1	12	11	4.9	12
100:80:20	23	7.4	12	20	7.6	13
100:60:40	32	8.4	12	33	8.1	12
100:40:60	41	9.5	11	38	9.3	12
100:20:80	50	9.6	11	52	10.2	12
100:0:100	56	13.5	10	54	12.1	11

<sup>*a*</sup> The peak temperature of tan  $\delta$ . <sup>*b*</sup> The storage modulus (*E'*) at 80 °C.

Table 4. Mechanical Properties and Refractive Index of Thiol–Isocyanate–Ene Ternary Networks by the Sequential Dual Cure System

SH/C=C/NCO	pendulum	pencil	refractive index (sulfur
(molar ratio)	hardness	hardness	content, wt %)
100:100:0	30	3B	$\begin{array}{c} 1.5535  (15.8) \\ 1.5510  (14.4) \\ 1.5490  (13.2) \\ 1.5475  (12.2) \\ 1.5460  (11.3) \\ 1.5440  (10.6) \end{array}$
100:80:20	23	HB	
100:60:40	16	H	
100:40:60	18	2H	
100:20:80	82	4H	
100:0:100	220	8H	

found for typical thiol—ene based systems.<sup>1,31</sup> Also, the sequence of the thiol—isocyanate and thiol—ene reactions does not affect the uniformity or thermal transition of the network structure since both reactions are essentially independent of each other with no side products, resulting in homogeneous chemical structures as long as the conditions used ensure quantitative conversions for all components. This outcome would not be expected for highly glassy systems polymerized well below their  $T_g$  where diffusion limitations would limit the extent of reaction for the slower or last reaction.

Thermal Mechanical Properties. In addition to thermal properties, dynamic mechanical properties of thiourethane/thiol-ene hybrid networks are largely dictated by the compositional ratio. In Figure 8, the storage modulus and tan  $\delta$  of thiol-isocyanate-ene ternary networks are shown. The  $T_{\rm g}$  determined by tan  $\delta$  peak (see Table 3) increases as a function of the N3600 content due to increased hydrogen bonding consistent with DSC results. The rubbery plateau modulus (Table 3) also increases monotonically with increasing thiourethane content indicating that hydrogen bonding acts to physically cross-link the thiol-isocyanate-ene ternary networks so that the apparent network cross-linking density increases. The broadness of the glass transition determined by fwhm (full width at half-maximum) of the tan  $\delta$  plots is about 10 °C for all compositions (Table 3) implying that the distribution of relaxation times of thiol-isocyanate-ene ternary networks is narrow due to uniformity of the chemical structure. Consequently, the  $T_{g}$  of the thiol-isocyanate-ene ternary networks can be tuned simply by varying the composition over a wide temperature range without sacrificing the characteristic



**Figure 9.** Tensile properties of thiourethane/thiol-ene hybrid networks by sequential dual cure; SH/C=C/NCO = (a) 100:100:0, (b) 100:80:20, (c) 100:60:40, (d) 100:40:60, (e) 100:80:20, and (f) 100:0:100 (DMPA 1 wt %; TEA 0.1 wt %; precure at room temperature for 1 h; intensity of medium pressure mercury lamp 10.2 mW/cm<sup>2</sup>; irradiation time, 5 min; postcure at 80 °C for 24 h).

uniform network structure typically associated with thiol-ene based materials.

Mechanical Properties and Refractive Index. Tensile properties, pencil hardness, and pendulum hardness of thiourethane/thiol-ene hybrid networks prepared by the sequential curing process are shown in Figure 9 and Table 4. It is well-known that the mechanical properties of thiol-ene based materials may be enhanced by using (thio)urethane modified thiols or enes for the preparation of thiol-ene networks to improve hardness and increase  $T_{g}$ .<sup>18,19</sup> However, (thio)urethane linkages have strong hydrogen bonding and, if present in the thiol or ene monomers, increase the viscosity of the unpolymerized system. For thiol-isocyanate-ene ternary networks cured by both the sequential and the simultaneous curing methods, thiourethane linkages are formed during the curing process, thus eliminating the initial viscosity issues and promoting high functional group conversion. As seen in Figure 9, the Young's modulus and the stress at break are significantly improved by increasing the thiourethane content due to the large extent of hydrogen bonding in the hybrid networks, consistent with the DMA results (storage modulus at room temperature) in Figure 8 and Table 3. The elongation at break also increases from 50% for the thiol-ene neat network (Figure 9a) to 230% for

<sup>(31)</sup> Cramer, N. B.; Scott, J. P.; Bowman, C. N. Macromolecules 2002, 35, 5361.

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thiourethane-thiolene 60:40 hybrid network the (Figure 9d). Surface hardness was also measured using pencil hardness. As shown in Table 4, the pencil hardness increases with increases in the thiourethane content. The pendulum hardness, which simply measures energy damping, has a minimum for the thiourethane/thiol-ene at 40:60 composition, which has a glass transition temperature near ambient temperature. Finally, the refractive index is one of the most important physical properties of thiol based materials. It has been reported that the refractive index of thiol-ene, thiol-yne, and thiourethane systems is largely determined by the sulfur content although other factors related to additional components in the networks are also important.<sup>4,32</sup> The refractive indexes of the thiol-isocyanate-ene ternary networks shown in Table 4 are all relatively high and increase slightly with increasing sulfur content.

## Conclusions

In this study, thiol-isocyanate coupling and thiol-ene free radical step reactions, which are independent of each other, were sequentially and simultaneously employed to form thiourethane/thiol-ene hybrid networks with tunable network properties. A conventional base catalyst, TEA, and photoinitiator, DMPA, were used for sequential curing of thiourethane/thiol-ene hybrid networks. For simultaneous systems a photogenerated amine catalyst (TBA $\cdot$ HBPh<sub>4</sub>) was used in the presence of ITX to trigger the thiol-isocyanate coupling and the thiol-ene free radical reaction simultaneously by UV light. TBA was successfully generated by irradiating UV light at 365 nm due to the sensitization by ITX and efficiently catalyzed thiol-isocyanate coupling reaction. The thiol-ene free radical reaction was also initiated by ITX at 365 nm without any additional photoinitiator. Kinetic profiles clearly showed that both thiol-isocyanate and thiol—ene reactions are quantitative. Thermal properties of the hybrid network films prepared by both methods were identical regardless of the sequence. Consequently, thiourethane/thiol—ene hybrid systems can form the uniform and densely cross-linked network structure that is the characteristic of thiol click type reaction based materials. Very narrow glass transition temperature ranges were observed for all compositions as measured by DSC and DMA. Compositional variation of the ratio between polythiourethanes and thiol—ene networks enabled us to control the mechanical properties such as tensile, pencil, and pendulum hardness. Refractive index was more dependent on the sulfur content than the amount of hydrogen bonding in the hybrid networks.

The thiourethane/thiol—ene hybrid polymerization strategy offers many advantages in tailoring physical/ mechanical properties and in the manufacturing process for materials based on the thiol click reactions. Since thiols undergo various chemical reactions with corresponding reactants and initiators (or catalysts) associated with different mechanisms such as free-radical and anionic step reactions, it is possible to envision that many different combinations of thiol click type reactions will be appropriately used to form hybrid networks which meet varied requirements in chemistry, materials processing, and physical/mechanical properties.

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**Supporting Information Available:** Kinetic profiles (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

<sup>(32)</sup> Li, Q.; Zhou, H.; Wicks, D. A.; Hoyle, C. E.; Magers, D. H.; McAlexander, H. R. *Macromolecules* **2009**, *42*, 1824.