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Synthesis, Thiol−Yne “Click” Photopolymerization, and Physical Properties of Networks Derived from Novel Multifunctional Alkynes

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ABSTRACT: Multifunctional alkynes (2, 3, or 4 ynes per monomer) were prepared utilizing the nucleophile-catalyzed thio−Michael addition reaction from commercially available multifunctional thiols (2, 3, or 4 thiols) and propargyl acrylate. Real-time FTIR (RTIR) and NMR spectroscopies indicate that the conjugate addition under these conditions proceeds to high conversions within seconds using the nucleophilic catalyst dimethylphenylphosphine, in the absence of solvent, at ambient temperature, and with no side products. A family of polymer networks was prepared by the photoinitiated thiol−yne reaction employing a 2:1 ratio of thiol to alkyne, which resulted in uniformly cross-linked materials of systematically increasing cross-link density. Photopolymerization kinetic profiles indicate that the thiol−yne reaction proceeded rapidly to high conversion with conversions decreasing with increasing functionality of the thiol and/or alkyne groups. Differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) results clearly indicate that the glass transition temperature increases as the overall cross-link density increases (from −10 to 42 °C by DMTA). An increase in the rubbery modulus (from 6 to 23 MPa at 70 °C) results as the functionality increases, with a concomitant decrease in the molecular weight between cross-links.

Introduction

The photoinitiated thiol−ene radical step-growth reaction in which a thiol adds across an electron-rich ene double bond proceeds rapidly to essentially complete conversion, with little-to-no side products, in the presence of oxygen or water, without photoinitiator, and in the absence of solvents.[1−21] This reaction has been recently employed in a wide variety of synthetic methods, highlighting its capabilities as a highly efficient process for chemical and materials synthesis and modification.[22−30] The thiol−ene reaction can be initiated using a photoinitiator (and light), with light and no distinct initiator, or through the use of thermal or redox initiators; all of these approaches can be used to generate primary radicals.

Cross-linked polymer networks may result from the polymerization when the thiol and ene monomers (or both) contain an average of more than two reactive functional groups. In a typical case where the thiol and ene are tri- or tetrafunctional, highly uniform densely cross-linked networks with few unreacted functional groups are formed.[2,4,5,12−14] One of the most desirable salient features of thiol−ene polymerization is the absence of any significant side product formation since typically the only undesirable side products are the result of radical coupling reactions. These networks are frequently characterized by dynamic mechanical thermal analysis (DMTA) which measures the tan δ versus temperature where thiol−ene networks have been found to have relatively low full width at half-maximum (fwhm) temperatures of ~10 °C.[2,4]

It has been reported that small molecule monofunctional alkyl thiols in solution undergo a two-step sequential reaction with terminal alkynes to produce 1,2-dithioethers via a process that is essentially identical to that reported for thiol−enes.[31−33] However, despite reports of the basic radical thiol−yne reaction, it was not used for materials synthesis until Fairbanks et al. reported that a tetrafunctional thiol readily copolymerizes with a dialkyne in a photoinduced radical step-growth polymerization process (Scheme 1).[34]

Each alkyne was reported to react with two thiol groups with the initial intermediate vinyl sulfide product being ~3 times more reactive than the alkyne toward thiol addition. The reaction proceeds at high rates under ambient humidity and atmospheric oxygen conditions to high conversion, thereby providing an extremely efficient methodology for fabricating high-performance cross-linked polymer networks and films in a facile and convenient fashion. Additionally, the thiol−yne reaction has recently been employed in the preparation of high refractive index materials comprised of only sulfur and hydrocarbon. In particular, Chan et al. reported that the reaction of a series of dialkynes and dithiols proceeds rapidly to produce highly cross-linked networks with the resulting refractive index values directly dependent on the sulfur content and nearly independent of cross-linking density.[35] Additionally, it was reported that the glass transition temperature (T_g) values increased significantly when a diyne was used to replace an analogous diene in stoichiometric thiol−yne/thiol−ene polymerizations. In addition

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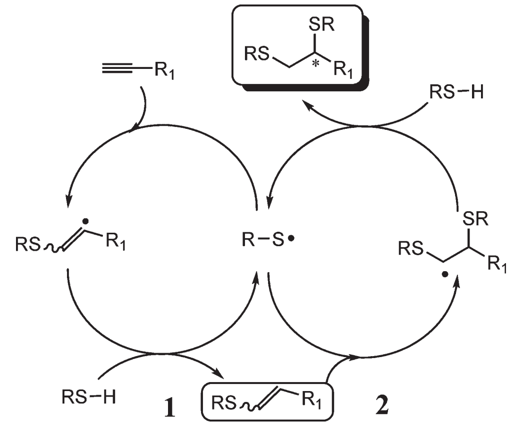
Scheme 1. Proposed Mechanism for the Radical Thiol−Yne Reaction



to the preparation of cross-linked materials the thiol−yne reaction has recently been employed as part of sequential syntheses of complex, branched molecules, as a means of preparing novel doubly end-functionalized polymers via a tandem thiol−ene/thiol−yne process, for preparing hyperbranched polymers, in the synthesis of dendrimers, and as a means of preparing highly functional polymer brushes.[36−41]

Here, we demonstrate the application of the thiol−yne reaction as a highly efficient process for creating high T_g, highly cross-linked networks. Further, these networks enable facile control and tunability of the T_g primarily associated with increasing the degree of cross-linking. Uniquely, these changes to the cross-linking density and T_g are achieved without significant changes to the chemical composition or network uniformity. We purport to build a series of highly uniform cross-linked networks that are comprised of starting materials containing nearly identical chemical compositions, which have similar degrees of backbone flexibility to ascertain the effects of cross-link density on mechanical and physical properties. These networks are formed in an efficient manner amenable to rapid fabrication under ambient conditions using light to initiate the process.

Experimental Section

Propargyl acrylate and dimethylphenylphosphine (Me_2PPh) were purchased from the Aldrich Chemical Co. at the highest available purity and used as received. Ethylene glycol di(3-mercaptopropionate), trimethylolpropane tris(3-mercaptopropionate), and pentaerythritol tetra(3-mercaptopropionate) were obtained from Bruno Bock Chemical Co. α,α-Dimethoxy-α-phenylacetophenone (Irgacure 651) was obtained from Ciba Chemical Co.

Synthesis of 2YNE. The target molecule (Figure 1) was prepared as follows: Ethylene glycol di(3-mercaptoprionate) (2THIOL) (2.38 g, 10 mmol) was mixed with 2×10^{-3} M Me_2PPh. To this mixture was added propargyl acrylate (2.20 g, 20 mmol). The solution was left for 1 h to ensure complete reaction. The kinetics were monitored as described below. ^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm)): δ 4.710−4.702 (4H), δ 4.308 (4H), δ 2.836−2.779 (m,8H), and δ 2.697−2.622 (m, 10H). ^{13}C NMR (300 MHz, $CDCl_3$, δ (ppm)): δ 170.70 ($CHCCH_2O(\mathit{C}{=}O)$), δ 170.14 ($SCH_2CH_2\mathit{C}{=}O$)), δ 77.10 ($CH\mathit{C}CH_2$), δ 74.77 ($CHC\mathit{C}H_2$), δ 61.57 ($\mathit{C}HCCH_2$), δ 51.36 ($(C{=}O)O\mathit{C}H_2CH_2$), δ 33.87 ($SCH_2\mathit{C}H_2(C{=}O)$), δ 33.82 ($O(C{=}O)\mathit{C}H_2$), δ 26.01 ($S\mathit{C}H_2CH_2(C{=}O)$), and δ 25.86 ($O(C{=}O)CH_2\mathit{C}H_2S$).

Synthesis of 3YNE. The target molecule (Figure 1) was prepared as follows: Trimethylolpropane tris(3-mercaptoprionate) (3THIOL) (2.98 g, 10 mmol) was mixed with 2×10^{-3} M Me_2PPh. To this mixture was added propargyl acrylate (3.30 g, 30 mmol). The reaction was left for 1 h to ensure complete reaction. The kinetics were monitored as described below. ^{1}H NMR (300 MHz, $CDCl_3$ δ (ppm)): δ 4.667 (6H), δ 4.006 (6H), δ 3.128 (3H), δ 2.713−2.610 (m, 24H), δ 1.439 (m, 2H), and δ 0.848 (m, 3H). ^{13}C NMR (300 MHz, $CDCl_3$, δ (ppm)): δ 170.52 ($CHCCH_2O(\mathit{C}{=}O)$), δ 170.09 ($SCH_2CH_2\text{-}\mathit{C}{=}O$)), δ 77.04 ($CH\mathit{C}CH_2$), δ 74.78 ($CHC\mathit{C}H_2$), δ 63.03 ($\mathit{C}HCCH_2$), δ 51.36 ($(C{=}O)O\mathit{C}H_2C$), δ 39.98 ($\mathit{C}(CH_2)_4$), δ 33.82 ($SCH_2\mathit{C}H_2(C{=}O)$), δ 33.72 ($O(C{=}O)\mathit{C}H_2$), δ 26.09 ($S\mathit{C}H_2CH_2(C{=}O)$), δ 25.84 ($O(C{=}O)CH_2\mathit{C}H_2S$), δ 18.92 ($CH_3\text{-}\mathit{C}H_2C$), and δ 6.66 ($\mathit{C}H_3CH_2C$).

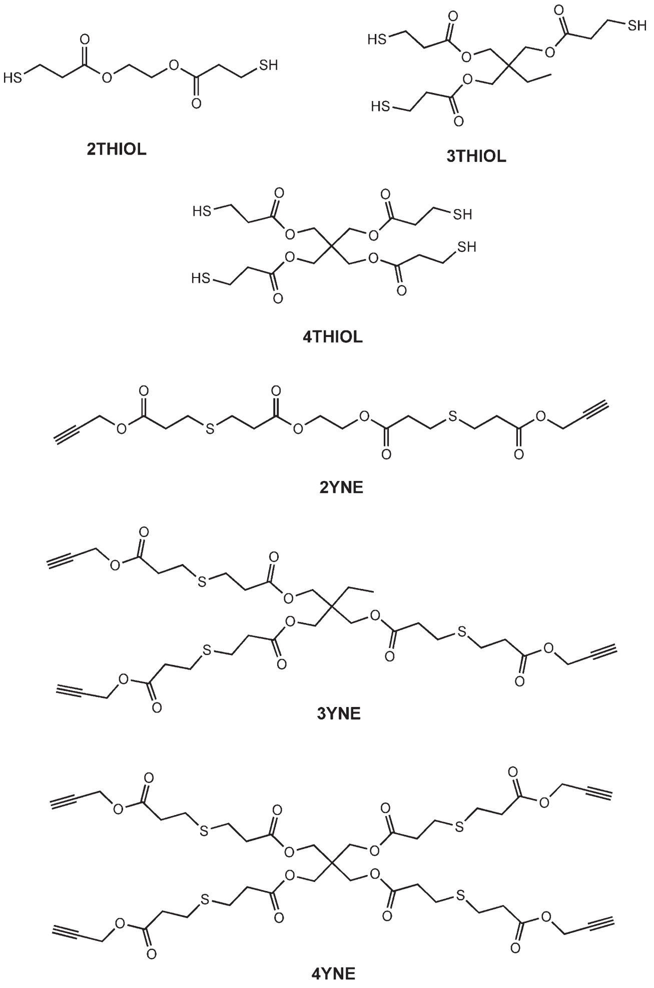


Figure 1. Structures and acronyms for multifunctional thiols and alkynes.

Synthesis of 4YNE. The target molecule (Figure 1) was prepared as follows: Pentaerythritol tetra(3-mercaptoprionate) (4THIOL) (2.44 g, 5 mmol) was mixed with 2×10^{-3} M Me_2PPh. To this mixture was added propargyl acrylate (2.20 g, 20 mmol). The reaction was left for 1 h to ensure complete reaction. The kinetics were monitored as described below. ^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm)): δ 4.676 (8H), δ 4.115 (8H), δ 3.333 (4H), and δ 2.721−2.621 (m, 32H). ^{13}C NMR (300 MHz, $CDCl_3$, δ (ppm)): δ 170.52 ($CHCCH_2O(\mathit{C}{=}O)$), δ 170.27 ($SCH_2CH_2\mathit{C}{=}O$)), δ 77.13 ($CH\mathit{C}CH_2$), δ 74.88 ($CHC\mathit{C}H_2$), δ 61.58 ($\mathit{C}HCCH_2$), δ 51.55 ($(C{=}O)O\mathit{C}H_2C$), δ 41.45 ($\mathit{C}(CH_2)_4$), δ 33.90 ($SCH_2\mathit{C}H_2(C{=}O)$), δ 33.85 ($O(C{=}O)\mathit{C}H_2$), δ 26.1909 ($S\mathit{C}H_2CH_2(C{=}O)$), and δ 26.02 ($O(C{=}O)CH_2\mathit{C}H_2S$).

Kinetic Measurements. Modifications of 2THIOL, 3THIOL, and 4THIOL with propargyl acrylate were formulated in a 1:1 molar ratio of thiol to acrylate with $\sim 2 \times 10^{-3}$ M Me_2PPh serving as the nucleophilic catalyst. Samples with thicknesses of 250 μm were sandwiched between NaCl plates with glass spacers. RTIR was used to monitor the loss of thiol and acrylate functional groups at 2570 cm^{-1} (−S−H stretch) and 1640 cm^{-1} (−C=C− stretch), respectively.

Film Synthesis and Kinetics. Samples were prepared with thicknesses of 250 μm sandwiched between NaCl plates with glass spacers with 2 wt % α,α-dimethoxy-α-phenylacetophenone (Irgacure 651) as the photoinitiator. RTIR was used to monitor the loss of thiol at 2570 cm^{-1} and alkyne at 2120 cm^{-1} ($-\text{C}{\equiv}\text{C}-$ stretch) functional groups. The light intensity of the high-pressure mercury lamp delivered to the sample via a light pipe was ~35.4 mW/cm^2 for the photoinduced reactions.

Film Preparation for Mechanical and Physical Testing. All samples were prepared in a 2:1 thiol to alkyne ratio and initiated with 1% Irgacure 651. Samples (500 μm thick) were cured in silicone molds with dimensions 25 mm × 5 mm × 0.5 mm and covered with glass slides. The samples were photocured on a Fusion curing line (12 passes) with a D bulb (belt speed of 10 feet/min, 3.1 W/cm^2 irradiance). All samples were allowed to remain at 60 °C for 72 h before any measurements were made.

Measurements and Instrumentation. NMR spectra were recorded on a Bruker 300 (53 mm) spectrometer. All spectra were recorded in CDCl_3 at 10% v/v unless noted otherwise. Real-time FTIR (RTIR) was used to monitor the kinetics of the reaction using a modified Bruker 88 spectrometer. UV light from an Oriel lamp system equipped with a 200 W high pressure mercury−xenon bulb was channeled through an electric shutter and fiber-optic cable in the sample chamber. Photopolymerizations were conducted using a light intensity of 35.4 mW/cm^2 measured with an IL-1400 calibrated radiometer from International Light. IR absorption spectra were obtained under continuous UV irradiation at a scanning rate of 5 scans/s. Thermal transitions were monitored using a TA Instruments DSC Q1000. All samples were heated to 120 °C for 5 min at 10 °C/min to erase thermal history. Samples were then cooled to −80 at 10 °C/min and then heated at 10 °C/min to 150 °C. DSC data from the second heating scan are reported in W/g. Modulus and tan δ measurements were performed on a Rheometric Scientific DMTA V at 2 °C/min from −60 to 100 °C. The T_g was determined as the temperature at the peak maximum in the tan δ curve. Storage moduli (E) are reported in Pa.

Results and Discussion

Synthesis and Kinetics of Multifunctional Alkynes. The multifunctional thiols 2THIOL, 3THIOL, and 4THIOL (Figure 1) were modified with propargyl acrylate, under bulk conditions, in a *nucleophile-initiated* reaction via a thio−Michael process yielding 2YNE, 3YNE, and 4YNE, respectively (Figure 1). While the base-catalyzed Michael addition (with for example triethylamine) of thiols to electron-deficient alkenes is a common reaction in organic synthesis, the use of the nucleophile-initiated process (with primary amines or trialkylphosphines) is less commonly employed.[36,42−44] Such nucleophile-initiated thio−Michael reactions require significantly less catalyst, can be easily performed in the absence of solvent (as conducted here), under a normal air atmosphere, exhibit rapid and quantitative conversions (in a little as a few seconds), and produce no side products.[36]

Kinetic Study of Networks Prepared from Multifunctional Thiols and Novel Multifunctional Alkynes. The newly prepared multifunctional alkynes, 2YNE, 3YNE, and 4YNE, and the multifunctional thiols 2THIOL, 3THIOL, and 4THIOL were used to prepare a series of nine networks with a systematic variation in network cross-link densities but nearly identical chemical compositions. Films were prepared by mixing a multifunctional alkyne (YNE) with a multifunctional THIOL and 1 wt % photoinitiator. The kinetics of each reaction were monitored by RTIR using 250 μm thick samples sandwiched between NaCl plates and irradiated with full arc UV light at 35.4 mW/cm^2. (Note the sample thickness and intensity of light of the RTIR films differ from those of films used for mechanical testing.) Figure 2 shows a representative photopolymerization kinetics plot for the reaction of 3THIOL with 3YNE initiated by 1% Irgacure 651.

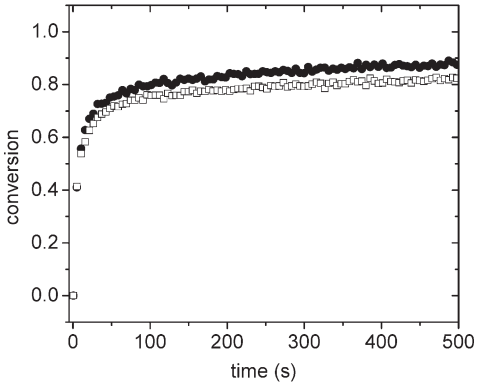


Figure 2. RT-FTIR-based percent conversion time plots for 2:1 molar ratios of (open square) thiol and (black circle) alkyne reactive groups for 3THIOL−3YNE thick film formulation (250 μm thick films, 1 wt % Irgacure 651, light intensity 53.4 mW cm^{-2}).

The data in Figure 2 illustrate the high conversion attained of thiol with yne (even only after a few minutes), with the final conversion reaching > 95% for both components. The data show a slight increase in yne conversion rate and final percent conversion (at 500 s). When an alkyne reacts with a thiyl radical in a typical photoinitiated network system, a vinyl sulfide radical is produced (Scheme 1). This radical then abstracts hydrogen from another molecule of thiol, yielding a vinyl sulfide intermediate that subsequently reacts in a typical thiol−ene reaction. The high reactivity of the intermediate vinyl sulfide toward further thiyl radical addition thus facilitates the formation of the double addition product. Fairbanks et al. determined that the rate of thiol addition to the vinyl sulfide is ~3 times greater than the reaction of the thiol with the parent alkyne in a stoichiometric formulation of 4THIOL with decadiyne.[34] The difference in reactivity of the alkyne and the intermediate vinyl sulfide was determined to be the cause of the difference in apparent rates of the thiol and alkyne conversions observed in this study.

The RTIR data in Figure 3 show a decrease in the rate of the thiol−yne polymerization reaction as the monomer functionality increases. This behavior is *inconsistent* with reports of model thiol−ene systems where there is no change in the polymerization rate when monomer functionality is increased beyond four.[2,43]

For example, Clark et al. report an initial decrease in apparent reaction rate upon increasing thiol functionality from 2 to 3 to 4, which is what is expected since the onset of vitrification occurs earlier as functionality increases.[43] The rates, however, plateau or seem unaffected in systems where the thiols have functionalities greater than 4 (i.e., 6, 9, or 12). Furthermore, the photoinitiated reaction of a hyperbranched 16-functional thiol and trifunctional ene (pentaerythritol triallylether) has been reported to have nearly the same polymerization rates and final conversion as a trithiol (trimethylolpropane tris(3-mercaptopropionate)) when polymerized with the same trifunctional ene.[2]

In Table 1, the theoretically calculated gel points for networks prepared in this study are listed using the classical equation (eq 1),[2,34] usually applied for thiol−ene systems:

$$p_c = \sqrt{\frac{1}{r(1-f_1)(1-f_2)}} \tag{1}$$

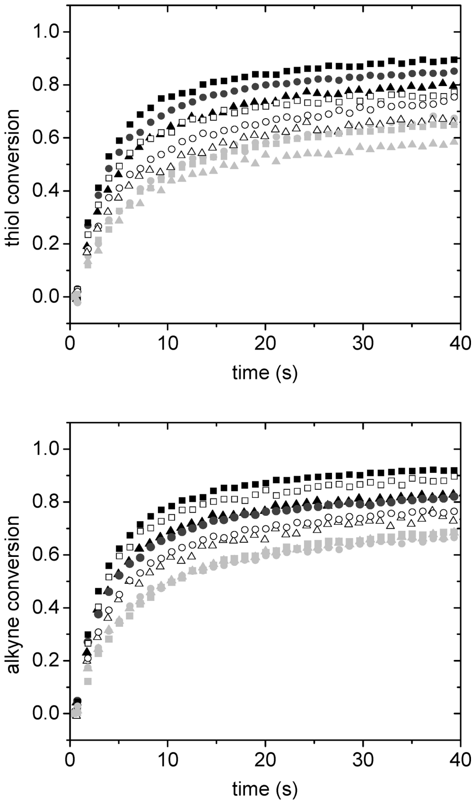


Figure 3. RTIR-based percent conversion time plots for 2:1 molar ratios of (top) thio and (bottom) alkyne reactive groups for (black square) 2THIOL−2YNE, (black circle) 3THIOL−2YNE, (black triangle) 4THIOL−2YNE, (open square) 2THIOL−3YNE, (open circle) 3THIOL−3YNE, (open triangle) 4THIOL−3YNE, (gray square) 2THIOL−4YNE, (gray circle) 3THIOL−4YNE, and (gray triangle) 4THIOL−4YNE thick film formulation (250 μm thick films, 1 wt % Irgacure 651, light intensity 53.4 mW cm^{-2}).

where p_c is the gel point, r is the ratio of thiol to ene, f_1 is the functionality of the thiol, and f_2 is the functionality of the ene. From the kinetic data shown in Figure 3 for the thiol−yne reactions, it is evident that the polymerization rate and conversion for the thiol−yne reaction decrease as the functionality of the monomers and cross-link density of the networks increases. The decrease in the maximum conversion achieved results from the increasing glass transition temperature of the polymer network. As the polymer network vitrifies at lower conversions, autodeceleration becomes prominent and limits the final conversion. It is not as clear why the initial polymerization rates are slowed as the monomer functionality increases. It is possible that the topological and steric limitations become more significant with increasing functionality.

Mechanical and Physical Properties of Networks Prepared from Multifunctional Thiols and Novel Multifunctional Alkynes. The mechanical and physical properties of networks prepared from multifunctional thiols and multifunctional alkynes were analyzed by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). All films were prepared at 500 μm in silicone molds and covered with glass slides while curing. Figure 4 shows the DSC scans of all nine films divided into sets grouped by the functionality of the thiol for clarity.

In each case as the number of ynes per monomer increases from 2 to 4, the T_g increases (Table 2). Additionally, the T_g range remains narrow for all systems even those with high glass transition temperatures, indicating that the highly desirable homogeneous network structure, common in thiol−ene systems, is retained regardless of cross-link density.

Table 1. Functionality of Monomers Measured Storage Modulus Reported at 70 °C and Cross-Link Density Calculated from Rubber Modulus

thiol	alkyne	f_1 (thiol)	f_2 (alkyne)	E' at 70 °C (MPa)	calcd cross-link density (M_c)
2THIOL	2YNE	2	4	6.3	0.74
	3YNE	2	6	13	1.52
	4YNE	2	8	13.7	1.60
3THIOL	2YNE	3	4	12.2	1.43
	3YNE	3	6	15.6	1.82
	4YNE	3	8	16.6	1.94
4THIOL	2YNE	4	4	14	1.64
	3YNE	4	6	16.7	1.95
	4YNE	4	8	23	2.69

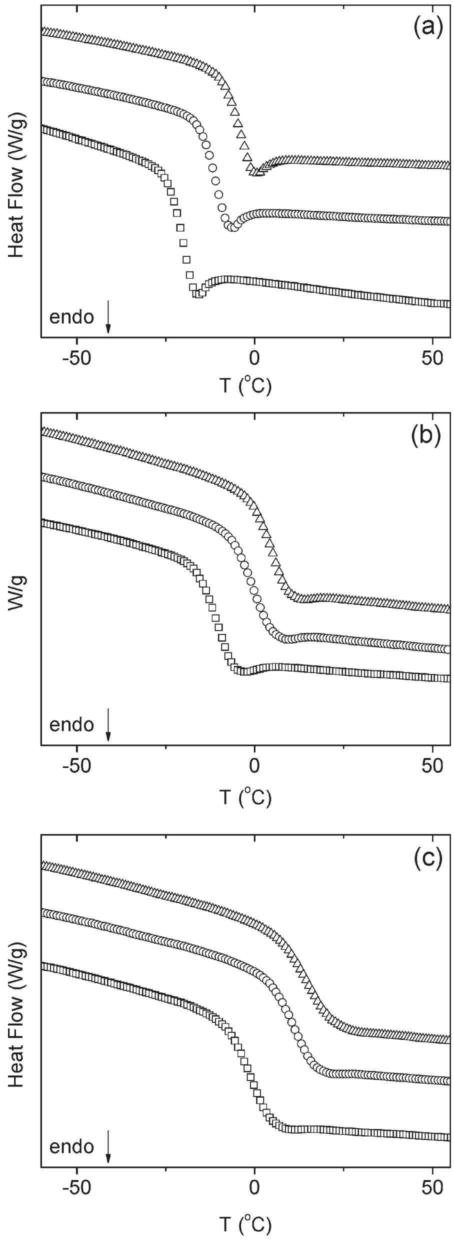


Figure 4. DSC vs temperature of DMA E' plots for photopolymerized networks formed from 2:1 thiol:alkyne mixtures: (a) 2THIOL with (square) 2YNE, (circle) 3YNE, and (triangle) 4YNE; (b) 3THIOL with (square) 2YNE, (circle) 3YNE, and (triangle) 4YNE; and (c) 4THIOL with (square) 2YNE, (circle) 3YNE, and (triangle) 4YNE.

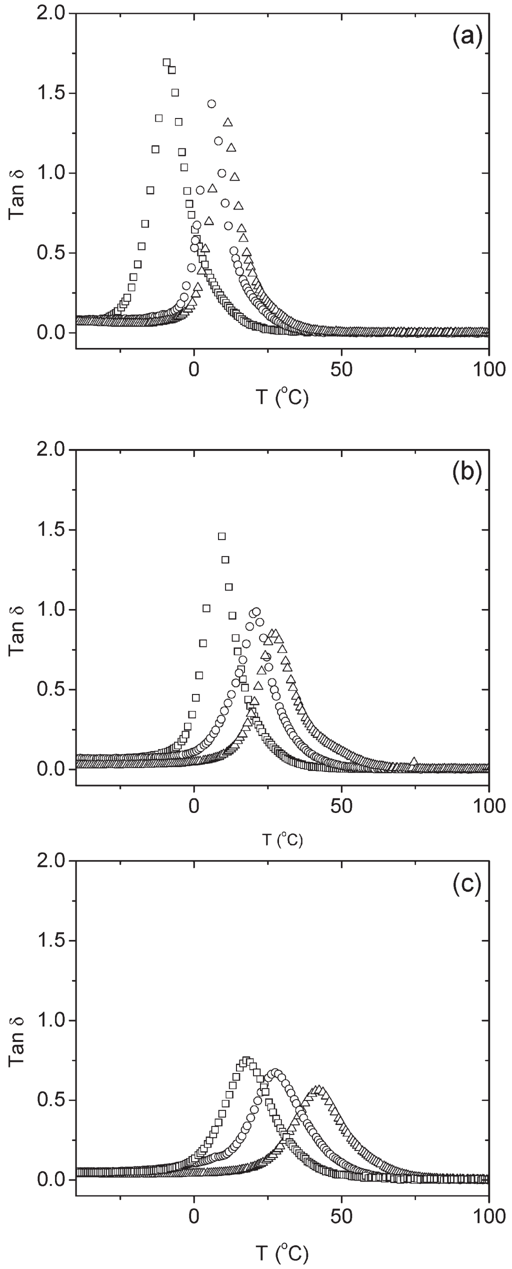


Figure 5. Tan δ plots vs temperature of DMA E' plots for photopolymerized networks formed from 2:1 thiol:alkyne mixtures: (a) 2THIOL with (square) 2YNE, (circle) 3YNE, and (triangle) 4YNE; (b) 3THIOL with (square) 2YNE, (circle) 3YNE, and (triangle) 4YNE; and (c) 4THIOL with (square) 2YNE, (circle) 3YNE, and (triangle) 4YNE.

By examining the DSC T_g data further, one notices an increase in T_g by ~10 °C as the thiol functionality increases from 2 to 3 to 4 when copolymerized with a given yne. For example, the T_gs of 2THIOL−2YNE, 3THIOL−2YNE, and 4THIOL−2YNE are −20, −10, and −1 °C, respectively. Additional evidence for the differences in the network structures of the nine thiol−alkyne systems is obtained by calculating heat capacity at constant pressure at T_g for the DSC heating scans in Figure 4. $c_{p,\text{glass}}$ is primarily determined by the vibrational degree of freedom component, which is a characteristic of solidlike below and at the T_g; $c_{p,\text{rubber}}$ is determined by the translational degree of freedom component, which is a characteristic of liquidlike behavior and is associated with network density. Thus, the jump in heat capacity at T_g (Δc_p at T_g) decreases as the cross-link density increases.

Table 2. T_g and Δc_p Values Determined by DSC; T_g and fwhm Values Determined by DMTA

thiol	alkyne	DSC T_g (°C)	Δc_p (J/g/°C) at T_g	DMTA T_g (°C)	DMTA fwhm (°C)
2THIOL	2YNE	−20	0.5456	−10	11
	3YNE	−11	0.4823	5	11
	4YNE	−3	0.4813	11	12
3THIOL	2YNE	−10	0.4236	9	12
	3YNE	0	0.4790	20	14
	4YNE	5	0.4716	27	16
4THIOL	2YNE	−1	0.4859	17	20
	3YNE	11	0.4654	25	20
	4YNE	14	0.4313	42	21

Figure 5 shows the temperature at which tan δ is a maximum for all multifunctional thiol and multifunctional alkyne network systems grouped according to the multifunctional alkyne. Tan δ maximum values, listed in Table 2, exhibit an increase in T_g as the cross-link density increases, consistent with the DSC measurements.

Additionally, the narrow fwhm values, which are expected of thiol−ene systems, slightly increase as the cross-link density of each system increases. Narrow fwhm values have been shown to correlate with homogeneity in network structure.[2] Systems with monomers of lower functionality such as those in Figure 5a exhibit very narrow fwhm values of ~11 °C. As the functionality of the systems increase, the fwhm value increases, indicating that there is a small reduction in homogeneity of the systems. Because the double addition of thiol to alkyne is a sequential reaction (thiol with alkyne and then thiol with vinyl sulfide), nonregiospecific products and the possibility of chain cyclization potentially increase the heterogeneous network structure formation.[31,34,35,45] However, fwhm values demonstrated with thiol−alkyne highly cross-linked networks are still very narrow compared to analogous multiacrylate systems that can span 100 °C.[2,34,35,43]

Storage moduli vs temperature plots are shown in Figure 6. This data shows an increase in the modulus (E') in the rubbery state based on cross-link density, which corresponds to the ideal rubber theory according to the equation[2,34]

$$E' = \frac{\rho R T}{M_c} \qquad (2)$$

where ρ is the polymer density, R is the ideal gas constant, T is the absolute temperature, and M_c is the molecular weight between cross-links. Data in Table 1 show the relationship between rubbery modulus and calculated cross-link density.

Summary and Conclusions

The nucleophile initiated thio−Michael addition reaction was used to prepare multifunctional alkynes, and the reaction proceeded to high conversions, rapidly, without any need for purification or isolation steps and with little if any side product formation. A series of networks with thioether linking groups were subsequently prepared by a rapid step-growth radical-mediated thiol−yne photopolymerization process between the novel multifunctional alkynes and three different multifunctional thiols. Based on the narrow thermal and mechanical transitions obtained by DSC and DMTA analysis, the network structures were uniform and homogeneously cross-linked. The fwhm values for tan δ versus temperature plots were greater than that observed for thiol−ene networks but were narrow compared to multiacrylate networks prepared by photopolymerization. Highly cross-linked networks were then tailored with increasing T_g, from −10 to 42 °C, as determined by DMTA and DSC. Additionally, the elastic moduli increased with increasing cross-link density

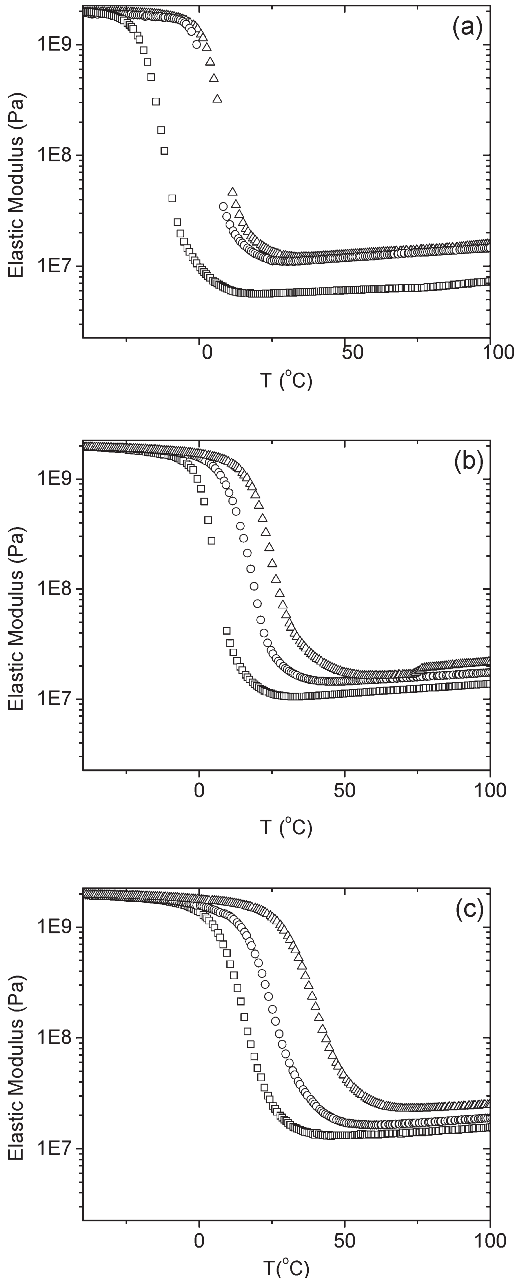


Figure 6. Elastic modulus plots vs temperature of DMA E' plots for photopolymerized networks formed from 2:1 thiol:alkyne mixtures: (a) 2THIOL with (square) 2YNE, (circle) 3YNE, and (triangle) 4YNE; (b) 3THIOL with (square) 2YNE, (circle) 3YNE, and (triangle) 4YNE; and (c) 4THIOL with (square) 2YNE, (circle) 3YNE, and (triangle) 4YNE.

from 6 to 23 MPa. The results presented herein demonstrate that thiol−yne chemistry can successfully be employed as a rapid high-throughput technique to prepare network materials to analyze structure−property relationships.

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