

Photopolymerization of Thiol-Alkynes: Polysulfide Networks

Justin W. Chan,[†] Hui Zhou,[†] Charles E. Hoyle,^{*,†,‡} and Andrew B. Lowe^{*,†}

School of Polymers and High Performance Materials, Department of Polymer Science, 118 College Drive #10076, The University of Southern Mississippi, Hattiesburg, Mississippi 39406-10076, Department of Chemistry & Biochemistry, 118 College Drive #5043, The University of Southern Mississippi, Hattiesburg, Mississippi 39406-5043

Received November 26, 2008. Revised Manuscript Received February 12, 2009

A series of photoinitiated reactions involving radical chain addition of dithiols across the triple bonds of dialkynes results in quantitative loss of all of the thiol and alkyne groups in 1:1 molar functional group neat mixtures. The reactions proceed rapidly to give uniform networks with relatively narrow differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) glass transition ranges. The glass transitions of the network films are directly related to the network structure and range from below 0 °C to about 40 °C as determined by DMA. The thiol-alkyne based hydrocarbon networks with sulfide linking groups have refractive index values which extend as high as 1.66. There is a linear relationship between the density and the refractive index, both of which increase linearly with weight percent sulfur.

Introduction

The radical step growth reaction for thiol addition across ene double bonds proceeds rapidly in the presence of oxygen or water with few side products.^{1–19} Recently, the efficiency

* Corresponding author. E-mail: andrew.lowe@usm.edu (A.B.L.); charles.hoyle@usm.edu (C.E.H.).

[†] Department of Polymer Science, The University of Southern Mississippi.

[‡] Department of Chemistry & Biochemistry, The University of Southern Mississippi.

- (1) Jacobine, A. F. In *Radiation Curing in Polymer Science and Technology III, Polymerisation Mechanisms*; Fouassier, J. D., Rabek, J. F., Eds.; Elsevier Applied Science: London, 1993; Vol. 3, p 219.
- (2) Hoyle, C. E.; Lee, T. Y.; Roper, T. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5301.
- (3) Reddy, S. K.; Cramer, N. B.; Kalvaitas, M.; Lee, T.; Bowman, C. N. *Aust. J. Chem.* **2006**, *59*, 586.
- (4) Senyurt, A. F.; Wei, H.; Hoyle, C. E.; Piland, S. G.; Gould, T. E. *Macromolecules* **2007**, *40*, 4901.
- (5) Bowman, C. N.; Carioscia, J.; Lu, H.; Stansbury, J. W. *PCT Int. Appl.* **2005**, 34 pp.
- (6) Carioscia, J. A.; Lu, H.; Stansbury, J. W.; Bowman, C. N. *Dent. Mater.* **2005**, *21*, 1137.
- (7) Reddy, S. K.; Cramer, N. B.; Bowman, C. N. *Macromolecules* **2006**, *39*, 3681.
- (8) Wei, H. Y.; Li, Q.; Ojelade, M.; Madbouly, S.; Otaigbe, J. U.; Hoyle, C. E. *Macromolecules* **2007**, *40*, 8788.
- (9) Cook, W. D.; Chausson, S.; Chen, F.; Le Pluart, L.; Bowman, C. N.; Scott, T. F. *Polym. Int.* **2008**, *57*, 469.
- (10) Johnson, P. M.; Stansbury, J. W.; Bowman, C. N. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 1502.
- (11) Nilsson, C.; Simpson, N.; Malkoch, M.; Johansson, M.; Malmstrom, E. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 1339.
- (12) White, T. J.; Natarajan, L. V.; Tondiglia, V. P.; Lloyd, P. F.; Bunning, T. J.; Guymon, C. A. *Polymer* **2007**, *48*, 5979.
- (13) Senyurt, A. F.; Hoyle, C. E.; Wei, H. Y.; Piland, S. G.; Gould, T. E. *Macromolecules* **2007**, *40*, 3174.
- (14) Carioscia, J. A.; Stansbury, J. W.; Bowman, C. N. *Polymer* **2007**, *48*, 1526.
- (15) Wei, H. Y.; Senyurt, A. F.; Jonsson, S.; Hoyle, C. E. *Macromolecules* **2007**, *40*, 822.
- (16) Sangermano, M.; Gross, S.; Priola, A.; Rizza, G.; Sada, C. *Macromol. Chem. Phys.* **2007**, *208*, 2560.
- (17) Carioscia, J. A.; Schneidewind, L.; O'Brien, C.; Ely, R.; Feeser, C.; Cramer, N.; Bowman, C. N. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 5686.
- (18) Cook, W. D.; Chen, F.; Pattison, D. W.; Hopson, P.; Beaujon, M. *Polym. Int.* **2007**, *56*, 1572.

and quantitative nature of the thiol-ene reaction has been used in a variety of synthetic processes that delineate and define its use as a highly efficient reaction for chemical and materials synthesis.^{20–27} The thiol-ene reaction is generally initiated by using either a photoinitiator (and light) or a thermal initiator (and heat) to generate radicals. Alternatively, light alone can be used to produce a lysis of the sulfur–hydrogen bond to produce thiy radical capable of initiating the chain growth process. Linear polymers are produced if the thiol and enes have functionalities of 2, and network polymers are produced if the average functionalities of the thiol and ene are greater than 2. In the typical case where the thiol and ene are tri- or tetrafunctional, densely linked networks are formed that are highly uniform with few unreacted functional groups. These networks are characterized by dynamic mechanical tan δ versus temperature plots at the network glass transition that have full width half-maximum (fwhm) temperatures of 10–15 °C,^{2,4} depending upon the actual structure of the thiol and ene components. This means that the networks are extremely uniform because such fwhm values are typically characteristic of linear polymers with low polydispersity. The corresponding DSC

- (19) Ortiz, R. A.; Urbina, B. A. P.; Valdez, L. V. C.; Duarte, L. B.; Santos, R. G.; Valdez, A. E. G.; Soucek, M. D. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 4829.
- (20) Killops, K. L.; Campos, L. M.; Hawker, C. J. *J. Am. Chem. Soc.* **2008**, *13*, 5062.
- (21) Campos, L. M.; Killops, K. L.; Sakai, R.; Paulusse, J. M. J.; Damiron, D.; Drockenmuller, E.; Messmore, B. W.; Hawker, C. J. *Macromolecules* **2008**, *41*, 7063.
- (22) Voets, I. K.; de Keizer, A.; Stuart, M. A. C.; Justynska, J.; Schlaad, H. *Macromolecules* **2007**, *40*, 2158.
- (23) Lutz, J. F.; Schlaad, H. *Polymer* **2008**, *49*, 817.
- (24) Gress, A.; Volk, A.; Schlaad, H. *Macromolecules* **2007**, *40*, 7928.
- (25) Hordyjewicz-Baran, Z.; You, L. C.; Smarsly, B.; Sigel, R.; Schlaad, H. *Macromolecules* **2007**, *40*, 3901.
- (26) Brummelhuis, N.; Diehl, C.; Schlaad, H. *Macromolecules* **2008**, *41*, 9946.
- (27) Dondoni, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 8995.

scans of thiol-ene networks are characterized by extremely narrow glass transition ranges, consistent with the DMA results.

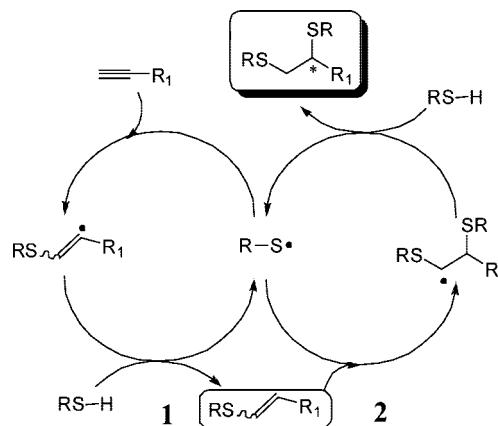
One of the salient kinetic features of thiol-ene polymerization is the absence of any significant side product formation because the only real side products are a result of radical coupling processes. The networks are held together by sulfide linkages that connect the chemical structures associated with the thiol and ene monomers. To date, most of the thiols used in forming thiol-ene networks have ester linkages comprising carbon and oxygen carboxylate esters. There have been reports of multifunctional (e.g., trifunctional) alkenes used to make thiol-ene networks.²⁸ However, because of limited availability of alkyl thiols and hydrocarbon enes with functionalities greater than 2, thiol-ene polymerizations that lead to networks with only carbon, hydrogen, and sulfur are limited.

One of the factors that has not been explored to any great extent in thiol-ene systems is the tailoring of network films that have high refractive index and density while maintaining network structures with high uniformity. This is unfortunate because the inclusion of sulfur in a variety of molecular formats into polymer matrices continues to attract a significant amount of attention.^{29–33} Many potential applications exist for relatively high refractive index materials, where the refractive index can be controlled over a range of values. Because sulfur has a high atomic refraction³³ compared to typical organic atoms such as oxygen, carbon, nitrogen, and hydrogen, there is interest in being able to incorporate sulfur into hydrocarbon networks while maintaining control over the mechanical and thermal properties. Toward this end, consider first a hypothetical uniform thermoset hydrocarbon network comprising only hydrogen and carbon. The refractive index of such networks would be very low and independent of how the network structure was linked because the inherent refraction of saturated molecular structures containing only carbon and hydrogen is very low. Starting from this consideration, we purport to build a family of uniform hydrocarbon thermoset networks that would contain sulfide linkages that are formed by an efficient manner amenable to rapid fabrication under ambient conditions using light to initiate the process. This would of course lend itself to photocuring of thin network films or thick thermoset plastics, opening a whole array of potential applications in the optics field. Such networks will be designed to contain a variation in sulfur content and cross-link density to allow for a clear correlation between sulfur weight percent and the network refractive index.

Herein, we report the use of difunctional alkynes and a series of end functionalized dithiolalkanes. It will be shown

- (28) Roper, T. M.; Guymon, C. A.; Jonsson, E. S.; Hoyle, C. E. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 6283.
- (29) Matsuda, T.; Funae, Y.; Yoshida, M.; Yamamoto, T.; Takaya, T. *J. Appl. Polym. Sci.* **2000**, *76*, 45.
- (30) Okutsu, R.; Ando, S.; Ueda, M. *Chem. Mater.* **2008**, *20*, 4017.
- (31) Okutsu, R.; Suzuki, Y.; Ando, S.; Ueda, M. *Macromolecules* **2008**, *41*, 6165.
- (32) Berti, C.; Pilati, F.; Manaresi, P.; Guaita, M.; Chiantore, O. *Polymer* **1994**, *35*, 1564.
- (33) Matsumoto, K.; Costner, E. A.; Nishimura, I.; Ueda, M.; Willson, C. G. *Macromolecules* **2008**, *41*, 5674.

Scheme 1. Proposed Thiol-yne Chain Reaction Mechanism



that the use of thiol-yne chemistry to fabricate materials represents a sister process to the thiol-ene reactions already discussed.^{1–27} Indeed, in the past, it has been reported that small molecule monofunctional alkyl thiols in solution undergo a two-step sequential reaction with terminal alkynes to give high yields of 1,2-dithioethers essentially identical to that reported for thiol-enes.^{2,34–36} The radical reaction of thiol-enes originally reported in 1905³⁷ received considerable attention in the chemical literature up until 1975 when Morgan and Ketly introduced the first photoinitiated thiol-ene radical processes for industrial films and coating applications.^{1,2} To date thiol-yne reactions have not been used for making new materials. Moreover, from the conditions originally reported for the thiol-yne reactions, it was not possible to tell how fast and efficient they really were, and if they could be employed for materials synthesis.^{34–36} In other words, although the thiol-yne reactions were reported more than 50 years ago to be facile processes, there has been little effort to capitalize on what could be an exceptional opportunity for materials fabrication. Just as the Huisgen reaction involving the alkyne-azide 1,3-dipolar cycloaddition reaction process, originally reported in 1967,³⁸ had new life for materials synthesis breathed into it by the recognition by Kolb, Finn, and Sharpless³⁹ that the reaction possessed exceptional qualities including rapid, high-yield reactions that proceeded under ambient conditions, the potential for the thiol-yne radical reaction sequence purports to be a facile method for the rapid fabrication of new materials. Toward this end, Bowman et al. recently showed (Scheme 1) that a tetrafunctional thiol readily polymerizes with dialkynes via a photoinduced radical step growth process identical to that for traditional thiol-enes.⁴⁰ The reaction was reported to proceed at high rates under ambient humidity and atmospheric oxygen conditions to high conversion, thereby providing for an extremely efficient methodology for fabricating high performance networks and films. By extending

- (34) Blomquist, A. T.; Wolinsky, J. J. *Org. Chem.* **1958**, *23*, 551.
- (35) Griesbaum, K. *Angew. Chem., Int. Ed.* **1965**, *9*, 273.
- (36) Behringer, H. *Annalen* **1949**, *564*, 219.
- (37) Posner, T. *Ber. Chem. Ges.* **1905**, *38*, 646.
- (38) Huisgen, R.; Szeimes, G.; Möbius, L. *Chem. Ber.* **1967**, *100*, 2494.
- (39) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed. 2001*, *40*, 2004.
- (40) Fairbanks, B. D.; Scott, T. F.; Kloxin, C. J.; Anseth, K. S.; Bowman, C. N. *Macromolecules* **2008**, *42*, 211.

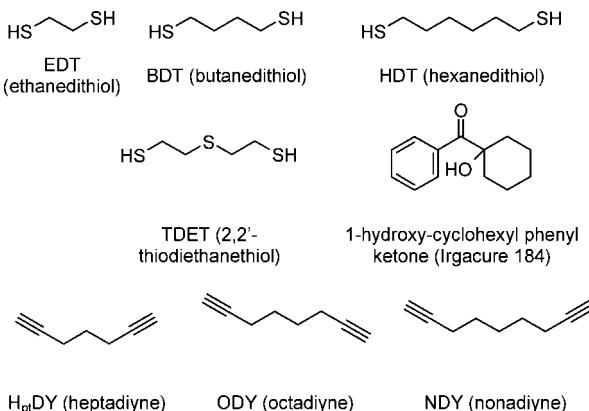


Figure 1. Structures and acronyms for alkyl dithiols and dialkynes.

this to the reaction of difunctional alkane thiols with dialkynes, which are technically tetrafunctional with respect to the addition of thiols, we have produced highly cross-linked hydrocarbon networks comprising only carbon, hydrogen, and sulfur with relatively high refractive indices. The reactions are rapid, proceed to essentially quantitative conversion and by choice of the methylene chain length separating the yne and thiol end groups, it is possible to systematically vary the sulfur content in the network and the cross-link density. Herein, it will be demonstrated that there is a linear relationship between not only the sulfur weight percent in the network and the refractive index, which can be as high as 1.66, but also the network density; note that we discuss both the network density (g/mL) and the network cross-link density as two separate items.

The synthetic approach presented herein demonstrates the ability to prepare in a rapid one step synthetic approach polymer cross-linked networks composed of only sulfur and hydrocarbon exhibiting relatively high refractive indices with commercially available starting materials. It produces no side products, has no other heteroatoms than sulfur, requires no material clean up, and does not use solvents or high temperatures to process films.

Experimental Section

Materials. All thiols and alkynes, whose structures and names are given in Figure 1, were purchased from Aldrich Chemical Co. and used as received. The photoinitiator, 1-hydroxy-cyclohexyl-phenyl-ketone or Irgacure 184, was obtained from Ciba Specialty Chemicals.

Kinetics. All samples were 2:1 thiol to alkyne molar ratios, or 1:1 functional group ratios, taking the dialkyne to be tetrafunctional using 2 wt % 1-hydroxy-cyclohexyl phenyl ketone (Irgacure 184). Sample thicknesses were approximately 200 μm . Real-time FTIR was used to monitor the loss of thiol (2570 cm^{-1}) and yne (2120 cm^{-1}) functional groups. The light intensity of the high pressure mercury lamp delivered to the sample via a light pipe was $\sim 20\text{ mW/cm}^2$.

Network Preparation for Mechanical, Thermal, and Optical Property Analysis. Samples $\sim 1\text{ mm}$ thick were placed between glass plates and irradiated using a medium pressure Hg lamp (light intensity 9.25 mW/cm^2) for 30 min. All samples were prepared from nominally 1:1 molar functional group ratios and allowed to remain at room temperature for at least 2 days before any measurements were made.

Measurements and Instrumentation. Thermal transitions were monitored by a TA Instrument DSC Q1000 DSC. All samples were heated to $150\text{ }^\circ\text{C}$ for 5 min at $10\text{ }^\circ\text{C/min}$ to erase thermal history. Samples were then cooled to $-75\text{ }^\circ\text{C}$ at $5\text{ }^\circ\text{C/min}$ and then heated at $10\text{ }^\circ\text{C/min}$. DSC data are reported in W/g from the second heating scan. Modulus and tan delta measurements were monitored by a Rheometric Scientific DMTA V. Storage moduli (E') are reported in Pa. Refractive index measurements were recorded on a Bausch and Lomb Abbe 3 L Refractometer at $\sim 25\text{ }^\circ\text{C}$ using bromonaphthalene and an unfiltered white light source. The refractive index values are essentially comparable to isolated 589 nm D line values. Density measurements were recorded using the XS104 Mettler Toledo microbalance equipped with a density determination kit at $\sim 22\text{ }^\circ\text{C}$ in water.

Results and Discussion

The four dithiols and three dialkynes in Figure 1 were used to prepare a series of networks that contain only sulfur, carbon, and hydrogen. These networks, in addition to having variation in the network cross-linking density, are characterized by an increasing sulfur content. The results will first focus on a brief consideration of the polymerization profiles of the thiol-yne systems followed by an evaluation of the physical, mechanical, and optical properties of the resulting films.

Kinetics. In the kinetic analysis, each terminal yne group is considered to be difunctional, making each dialkyne tetrafunctional with respect to the radical reaction with thiol. As an example of the kinetic results that were obtained for all of the possible combinations of the dithiols and dialkynes in Figure 1, the real-time infrared-based conversions for the thiol (2570 cm^{-1}) and yne (2120 cm^{-1}) peaks for 1:1 functional group molar mixtures of ODY and HDT are shown in Figure 2a for the first 50 s of exposure to the unfiltered output of a high pressure mercury lamp. The disappearance of both the thiol and yne groups is rapid under the conditions employed ($200\text{ }\mu\text{m}$ and 20 mW/cm^2), with the percent conversion of functional groups at a given photolysis time being slightly greater for the yne than the thiol. This is reflective of the reaction of the alkyl vinyl sulfide that was formed by the initial thiol-yne reaction (Scheme 1). According to Bowman et al.,⁴⁰ the slower reaction is the addition of thiol to yne, i.e., the thiol-yne reaction leading to formation of the vinylsulfide is slower than the reaction between thiol and vinylsulfide. The overall result is to have a low concentration of the vinylsulfide intermediate product forming but disappearing as thiol reacts with the alkyl vinyl sulfide. For a detailed kinetic analysis of the thiol-alkyne radical step-growth process in Scheme 1, the interested reader is referred to reference.⁴⁰ The results for the EDT-ODY photopolymerization in Figure 2b show a trend similar to that for the EDT-ODY photopolymerization, i.e., the yne percent conversion rate is greater than that of the thiol. Although not shown, the conversion rate for the thiol and yne components for the BDT-ODY photopolymerization is intermediate between the HDT-ODY and EDT-ODY photopolymerizations. This is consistent with the restriction in mobility as the alkane unit length becomes shorter, resulting in a reduction in the reaction rate. Such observations have been made for thiol-ene systems where

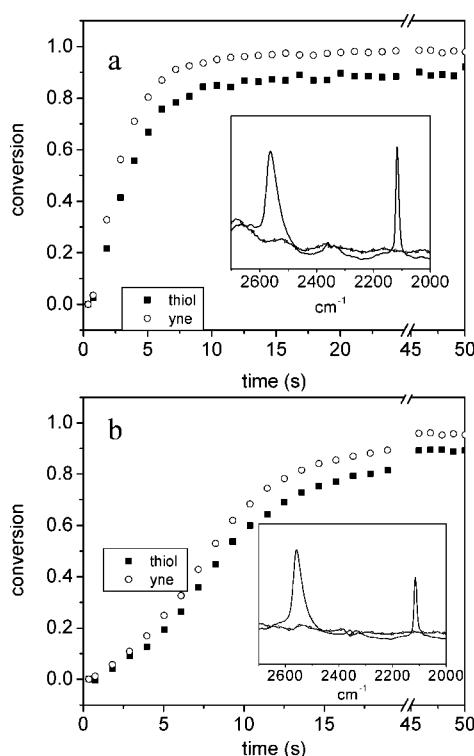


Figure 2. RT-FTIR-based percent conversion time plots for 2:1 molar ratios of thiol:alkyne reactive groups for (a) hexanedithiol-octadiyne and (b) ethanedithiol-octadiyne.

the rates decreased modestly as the thiol and ene functionalities increased.² Similar results (not shown) obtained for the other dithiol-dialkyne combinations exhibit the same trends with respect to thiol-alkyne conversions, i.e., lower rates for the EDT systems compared to the HDT systems under the same exposure conditions.

Summarizing, rapid rates and conversions approaching 100% of each functional group are achieved under the relatively mild photolysis and ambient conditions used for the real-time IR measurements. Actually, real-time IR-based conversions for all combinations in Figure 2 for several minutes have been recorded, and all achieve essentially 100% conversions within our ability to record IR peaks at the high conversions. As shown in Table 1, the weight percent of sulfur in the network, calculated from the weight of the individual thiol and ene components, approaches 46% in the case of the photopolymerized H_{pt}DY and EDT system. Questions dealing with the mechanical and thermal properties and relationship between the refractive index of the polymerized network and the sulfur content will be evaluated next.

Thermal and Dynamic Mechanical Analysis. Having demonstrated that the thiol and alkyne components in the 1:1 thiol-alkyne molar functional group mixtures are effectively photopolymerized to high conversion, DSC scans and DMA storage modulus and $\tan \delta$ plots for all nine of the thiol-alkyne networks are given in Figures 3–5. To ensure high conversion of all samples, as we have already mentioned in the previous section and as detailed in the Experimental Section, samples were exposed to high light intensities and doses. Consider first the DSC scans. In each case for a given dialkyne, the resulting network glass transition temperature increases as the dithiol molecular

weight decreases. This is consistent with an expected increase in the glass transition temperature with an increase in network cross-link density. The DSC glass transition temperatures from Figure 2 recorded in Table 1 extend from -15 to 14 °C depending on the particular dithiol-dialkyne combination used to prepare the network. It is noted that the samples prepared from EDT have consistently greater DSC or DMA glass transition values than the samples prepared from BDT and HDT because the number of methylene spacer groups doubles and triples on going from EDT to BDT to HDT. One particularly important point about all of the networks is the rather narrow range for the glass transition region, which is typical of thiol-ene networks.^{2,4} The supposition that the dithiol-dialkyne networks are uniform is confirmed by the DMA results in Figures 4 and 5 where the storage modulus, E' , and the $\tan \delta$ energy damping exhibit narrow temperature transitions. The transitions in Figures 4 and 5, as quantified by the fwhm values of the $\tan \delta$ versus temperature plots in Figure 4 listed in Table 1, are clearly very narrow compared to fwhm values for photopolymerized multifunctional (meth)acrylate transitions, which can be up to 200 °C.² This indicates that the dithiol–dialkyne networks are relatively uniform. However, the fwhm values for thiol-yne reactions (Table 1) are ~ 20 – 25 °C, whereas the thiol-ene networks evaluated under the same conditions are typically near 10 °C.^{2,4} The kinetics of the sequential polymerization process no doubt effects the size distribution of cyclic rings that form. Specifically, it has been reported that the formation of cyclic rings in thiol-ene polymerization results from the intramolecular addition of thiyl radicals to ene double bonds on the same oligomeric molecule.⁴¹ The resulting ring structures vary in size, and hence their distribution influences the mechanical properties of the thiol-ene network. Accordingly, the ring structure size distribution in thiol-yne networks might be expected to be different from that of traditional thiol-enes because of the two sequential regiospecific reactions, yielding two nonidentical sulfide linkage, which comprise the overall thiol-yne reaction process.³⁴

Density and Refractive Index. Two important physical and optical properties associated with the dithiol-dialkyne networks, density and refractive index, were measured. The results in Table 1 clearly show that the dithiol–dialkyne networks have high refractive index values spanning a 0.08 range from approximately 1.58 to 1.66. These very high refractive indices are the direct result of incorporating sulfur into the hydrocarbon network in the form of sulfide linkages as seen by comparing the refractive index values with the percentage of sulfur in the network (the last column in Table 1). Concomitantly, as shown in Table 1, the densities of the networks also increase with sulfur content. The plots in Figures 6 and 7 show that both the refractive index and the density increase linearly with the sulfur content. This is certainly expected from the high atomic refraction and density inherent to sulfur. Figure 8 shows structures and acronyms of several traditional thiol and ene components used to form thiol-ene networks for comparison with the

(41) Okay, O.; Bowman, C. N. *Macromol. Theory Simul.* **2005**, *14*, 267.

Table 1. Physical and Optical Data for Thiol-Alkyne Networks

dithiol	diyne	density (g/mL)	RI	DSC T_g (°C)	DMA T_g (°C)	DMA fwhm (°C)	wt % S
TEDT	H _{pt} DY	1.280	1.6575	-14	16	15	48.00
	H _{pt} DY	1.250	1.6540	14	38	21	45.72
	ODY	1.210	1.6381	9	33	19	43.54
	NDY	1.202	1.6265	9	30	21	41.56
BDT	H _{pt} DY	1.172	1.6081	-5	15	21	38.1
	ODY	1.147	1.6024	-4	20	24	36.57
	NDY	1.139	1.5995	-5	22	20	35.17
HDT	H _{pt} DY	1.105	1.5820	-15	5	23	32.66
	ODY	1.096	1.5792	-11	5	20	31.53
	NDY	1.089	1.5755	-10	10	19	30.48

dithiol–dialkyne networks in Table 1. The densities and refractive index values for the photopolymerized thiol-ene networks produced from the components in Figure 8 are given in Table 2. A comparison of refractive index for the thiol-ene networks and thiol-yne networks cannot be made based strictly on sulfur content, since the thiol-ene systems have other heteroatoms present including oxygen and nitrogen. Nonetheless, it is interesting to compare the

refractive index values of the dithiol–dialkyne networks to those for the traditional thiol-ene networks. Of course, both the thiol-ene and thiol-yne networks have high densities because of the high cross-link density that results from the step-growth nature of the thiol-ene and thiol-yne reactions. The refractive index values for these thiol-ene systems, where there are other heteroatoms present (oxygen and nitrogen) but the sulfur contents are relatively small, exhibit lower

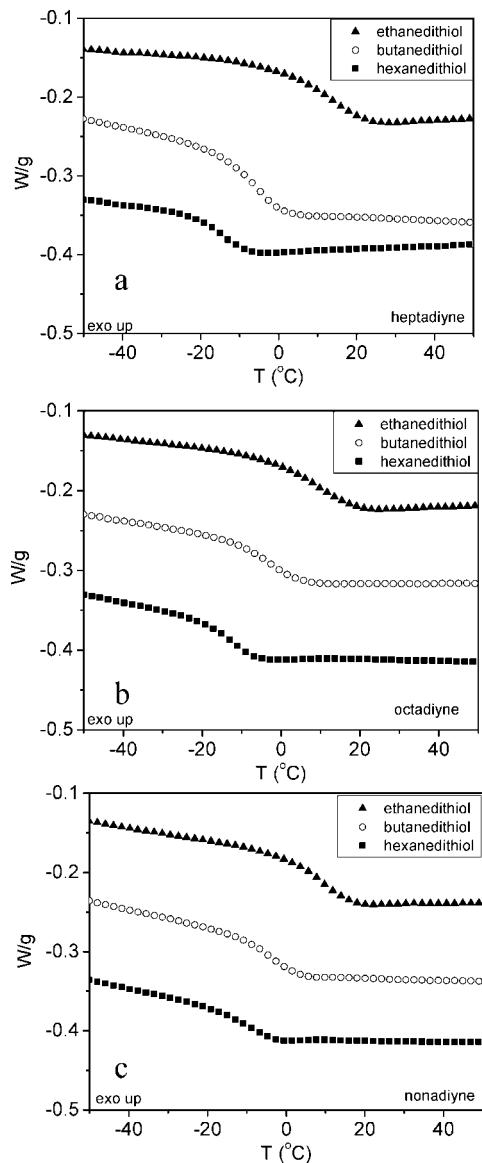


Figure 3. DSC scans for photopolymerized networks formed from 2:1 thiol: alkyne mixtures: (a) heptadiyne-dithiol, (b) octadiyne-dithiol, and (c) nonadiyne-dithiol.

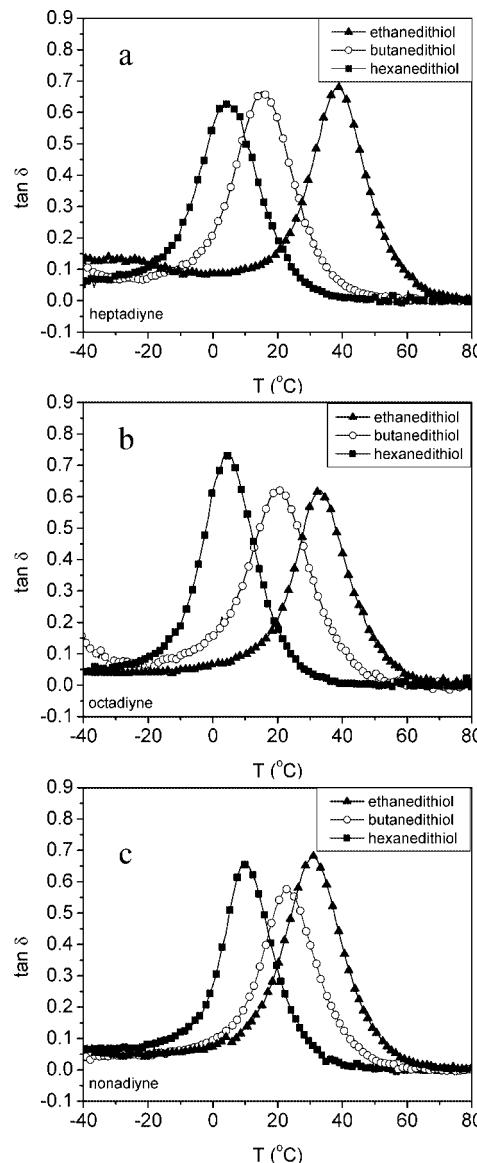


Figure 4. DMA tan δ plots for photopolymerized networks formed from 2:1 thiol: alkyne mixtures: (a) heptadiyne-dithiol, (b) octadiyne-dithiol, and (c) nonadiyne-dithiol.

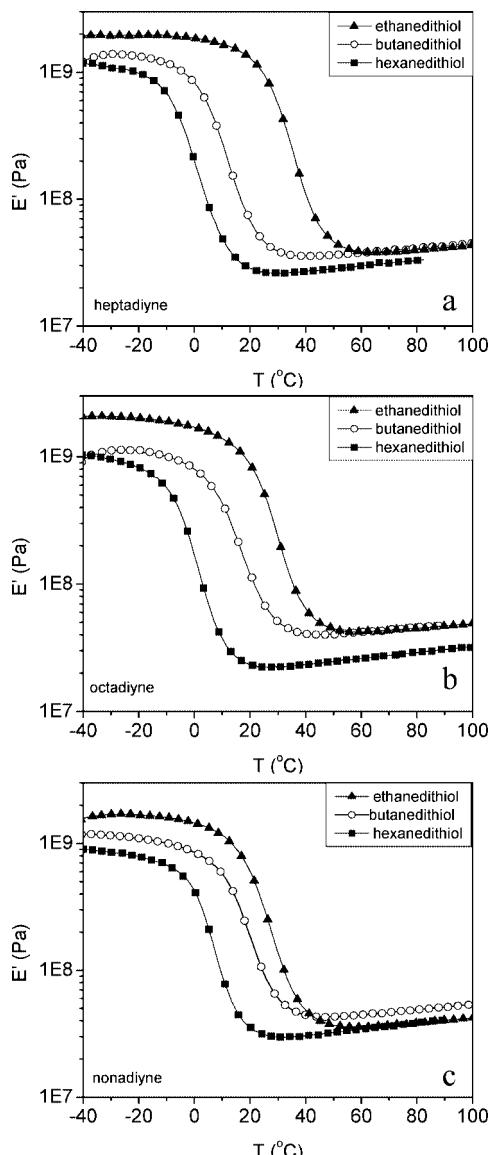


Figure 5. DMA E' plots for photopolymerized networks formed from 2:1 thiol:alkyne mixtures: (a) heptadiyne-dithiol, (b) octadiyne-dithiol, and (c) nonadiyne-dithiol.

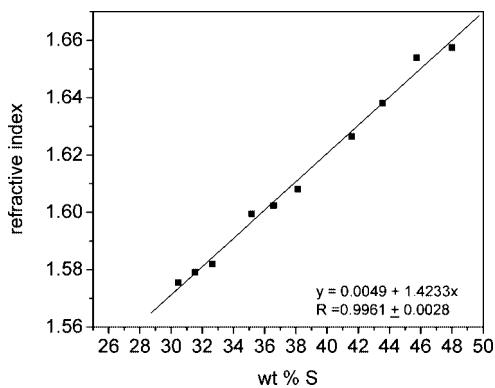


Figure 6. Refractive index versus weight percent sulfur plots for photopolymerized networks formed from 2:1 thiol:alkyne mixtures.

refractive index values than for any of the thiol-yne-based networks because of the latter's high sulfur content. The refractive index is obviously influenced heavily by the percent sulfur in the network. Note that even the 4T-TTT-

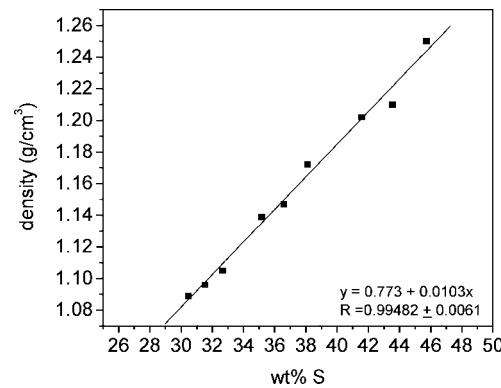


Figure 7. Density versus weight percent sulfur for photopolymerized networks formed from 2:1 thiol:alkyne mixtures.

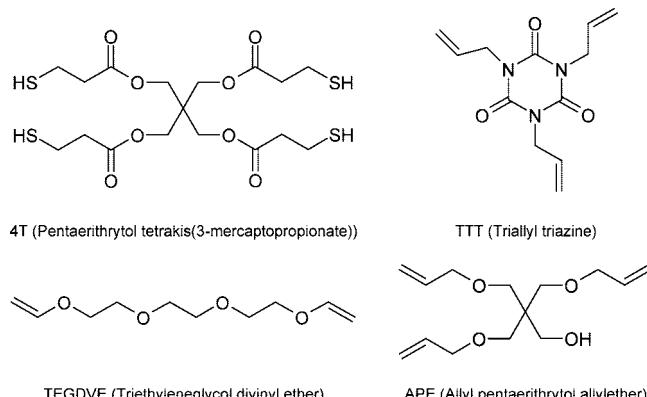


Figure 8. Structures and acronyms for tetrathiol and multialkenes.

Table 2. Refractive Index Values and Densities of Several Thiol-ene Networks

thiol	ene	density (g/mL)	RI	wt % S
4T	APE	1.261	1.5350	15.44
	TEGDVE	1.252	1.5215	14.36
	TTT	1.382	1.5622	15.62

based network with the highest network density only has a refractive index of ~ 1.56 .

Finally, to delineate the effect of cross-link density versus sulfur content on all of the parameters including thermal/mechanical transitions density and refractive index, films were made using the dithiol TEDT (see Figure 1) and $H_{pt}DY$. This network is particularly interesting since the molecular weight of the linking chain between the two terminal thiols is greater than for EDT and approximately equivalent to that for HDT. The result is a decrease in the cross-link density of the network film compared to the EDT- $H_{pt}DY$ film with corresponding decrease in the glass transitions measured by both DSC and DMA (see Table 1). Nonetheless, both the density and the refractive index increase with the percent increase in sulfur obtained when TEDT is used. Importantly, both the refractive index and density for the TEDT- $H_{pt}DY$ network in Figures 6 and 7 clearly fit on the linear plots versus sulfur weight percent for the other dithiol-dialkyne networks, in agreement with the well-known high atomic refraction and density of sulfur.

Conclusions

Ten hydrocarbon networks with sulfur linking groups were made by a rapid step-growth radical photopolymerization process. According to narrow thermal and mechanical transitions obtained by DSC and DMA analysis, the network structures were very uniform. However, the fwhm values for $\tan \delta$ versus temperature plots are somewhat greater than for thiol-ene networks. High weight percentages of sulfide linkages approaching 50% were incorporated into the network. It was found that both the refractive index and the density are linearly proportional to the sulfur content in

the network. The results presented herein demonstrate that high concentrations of sulfur can be incorporated into highly uniform hydrocarbon thermoset networks by a rapid photopolymerization process under ambient conditions. This demonstrates the importance of the two regioselective thiol-ene reactions as a useful reaction bearing many of the characteristics of, and providing an interesting correlation between, the thiol-ene²⁰⁻²⁷ and alkyne-azide^{38,39} type reactions.

Acknowledgment. Fusion UV Systems is acknowledged for providing the high-intensity lamp source.

CM803262P