

## Thiol–Enes: Chemistry of the Past with Promise for the Future

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Received 8 June 2004; Accepted 18 June 2004

DOI: 10.1002/pola.20366

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The photopolymerization of mixtures of multifunctional thiols and enes is an efficient method for the rapid production of films and thermoset plastics with unprecedented physical and mechanical properties. One of the major obstacles in traditional free-radical photopolymerization is es-

sentially eliminated in thiol–ene polymerizations because the polymerization occurs in air almost as rapidly as in an inert atmosphere. Virtually any type of ene will participate in a free-radical polymerization process with a multifunctional thiol. Hence, it is possible to tailor materials with virtually any

combination of properties required for a particular application. © 2004 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 42: 5301–5338, 2004

**Keywords:** photopolymerization; coatings; plastics; thiol–ene



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*Journal of Polymer Science: Part A: Polymer Chemistry*, Vol. 42, 5301–5338 (2004)  
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Charles E. Hoyle received a B.S. degree in Chemistry from Baylor University in Texas in 1972. He subsequently obtained Masters and Doctorate degrees in Chemistry under the direction of Professor Fred Lewis at Northwestern University, concentrating on small molecule photochemistry. After spending almost two years at the University of Toronto in Jim Guillet's lab dealing with polymer photophysics, he joined Armstrong World Industries in Lancaster, PA in 1978 where he investigated polymer photodegradation and photoinitiated polymerization. In 1983, he came to the University of Southern Mississippi, where he obtained dual appointments in Polymer Science and Chemistry. During his 20-plus years at the University of Southern Mississippi, he has focused on all aspects of polymer photochemistry and photophysics including photopolymerization, photodegradation, polymer luminescence, and laser flash photolysis. He has had the distinct opportunity to work with outstanding colleagues at USM, developing collaborative efforts that have opened up many exciting possibilities that continue to drive his research efforts. Participation in two National Science Foundation sponsored conferences early in his academic career, one between polymer photochemists from the United States and Sweden and the other involving polymer photochemists from the United States and Australia, provided a conduit for meeting many of the scientists that he still collaborates with today. Most of the work on thiol-ene polymerization in his lab has been made possible by 3M Corporation, Fusion UV Systems, and the National Science Foundation.

## INTRODUCTION

Descriptions of the use of thiols in chemical reactions extend well over 100 years, encompassing a number of fields ranging from biochemistry to polymer science. Early work on thiol-ene free-radical chemistry dates from the late 1930s to the early 1950s.<sup>1-23</sup> An excellent review of thiol chemistry was published in 1974 covering all of the work on thiols to the mid 1970s.<sup>4</sup> A review of thiol-ene free-radical photoinitiated polymerization was published in 1993.<sup>5</sup> This review focuses on all aspects of thiol-ene photopolymerization. After a brief historical perspective of the emergence of the science and chemistry of thiol-ene polymerization, sections are presented that deal successively with the processes for initiating thiol-ene polymerization, the basic thiol-ene polymerization mechanism and structural features that affect the polymerization rate and kinetics, gelation, the role of oxygen in the polymerization process, and a physicomachanical consideration of basic network film

properties. Practical considerations dealing with thiol odor, the storage and shelf-life stability of thiol-ene monomer mixtures, and the stability of networks formed from thiol-ene polymerizations follow. Next, several examples of interesting and emerging thiol-ene systems are covered, followed by a concluding description of applications that take advantage of the rapid polymerization process in air to yield matrices with highly uniform crosslink density, which is characteristic of thiol-ene photopolymerization. Our review is selective, rather than exhaustive, in its coverage of the literature before 1992.

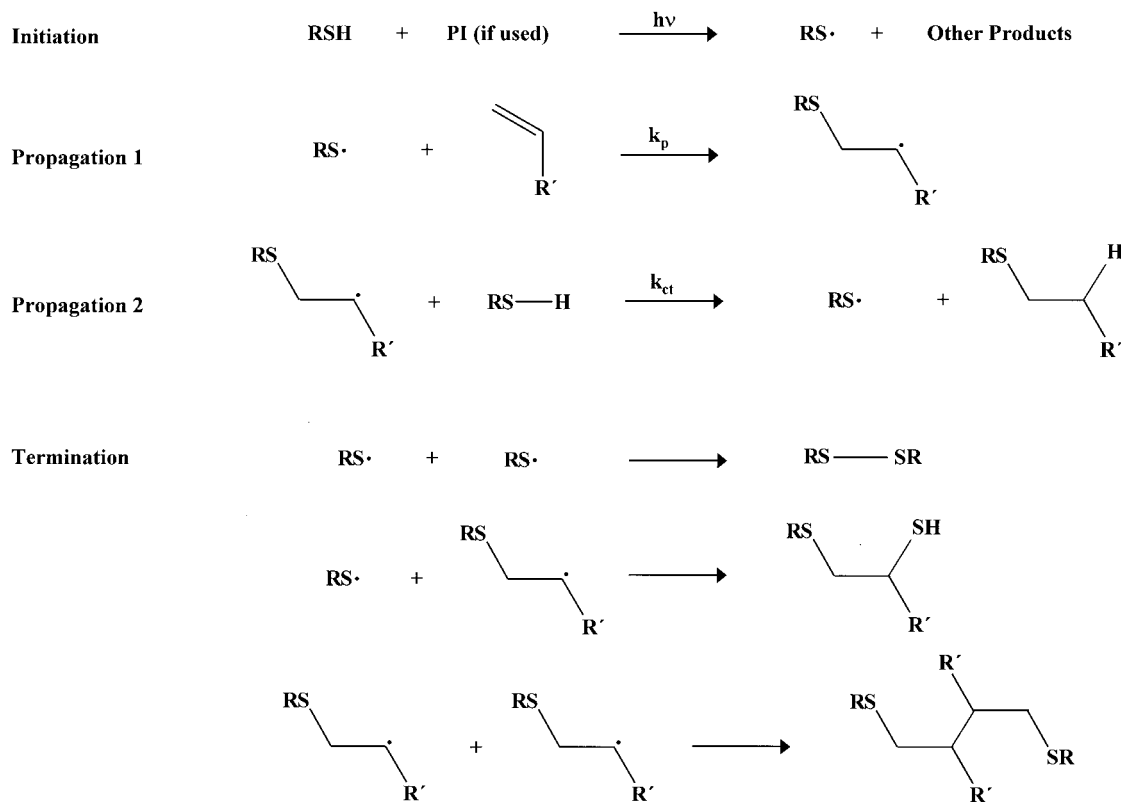
## HISTORICAL PERSPECTIVE

The brilliant work at W. R. Grace on the photopolymerization of thiol-enes by Morgan, Ketley, and their coworkers<sup>6-11</sup> led to applications involving the fabrication of relief printing plates (called the Letterflex process) and conformal coatings on electronics. In collaboration with W. R. Grace,

Armstrong developed wear layers for floor tiles based on thiol-ene photocuring.<sup>12</sup> These successes with the photo-initiated polymerization of thiol-enes by W. R. Grace and Armstrong led to the first really large-scale uses of radiation curing in the United States, ensuring the expanding future of this green technology. For a wide variety of reasons, both economic and technical, thiol-ene photocuring gave way to acrylate-based photocurable systems. Objections at the time to thiol-ene-based ultraviolet (UV)-curable resins included odor, as well as the incorrect perception that all thiol-ene coatings were subject to rapid yellowing and discoloration upon weathering. Unfortunately, benzophenone (BP) was used in rather large quantities in these systems as a photoinitiator, giving rise to significant light stability problems of the cured networks associated with colored byproducts formed upon exposure to interior and exterior light. As new low-cost acrylate multifunctional monomers and oligomers of high purity became available at prices that allowed for widespread applications, the use of thiol-ene chemistry was severely curtailed. The abandonment of the widespread use of thiol-ene chemistry in industrial applications for these reasons was unfortunate because Ketley and coworkers<sup>6,8</sup> demonstrated in the late 1970s that it was possible to use conventional cleavage-type photoinitiators to initiate thiol-ene polymerization and that thiols could be effec-

tively incorporated into acrylate formulations to reduce oxygen inhibition and enhance final film properties.

There have been several efforts since the late 1970s to revive the use of thiol-ene photopolymerization in industrial applications, including those of Klemm and coworkers<sup>13-22</sup> in Germany and early and mid 1990s, Jacobine, Woods, and coworkers<sup>23-35</sup> in the United States in the early 1990s, and Toh and coworkers<sup>36-42</sup> in Australia beginning in the mid 1990s. Perhaps the most successful industrial use of thiol-ene photopolymerization since the 1970s era has been by Norland Products, which has successfully marketed photocurable thiol-ene optical and electronic adhesives for a number of years (the details of their use in technical applications is discussed later). In addition, recent efforts led by Bowman, Cramer, and coworkers<sup>43-56</sup> and Hoyle, Jonsson, and coworkers,<sup>57-72</sup> spurred in part by National Science Foundation funded efforts involving Industrial University Cooperative Research Centers in Coatings at the University of Southern Mississippi and in Photopolymerization at the University of Colorado, have led to a resurgence of interest in thiol-ene photopolymerization highlighted by new chemistry and potential applications. Results from this work, some of it still unpublished, are incorporated into this review of thiol-ene photopolymerization. As mentioned in the introduction, for an extensive account of thiol-ene photopolymerization before 1992, the



**Scheme 1.** General thiol-ene photopolymerization process.

reader is referred to the outstanding comprehensive review by Jacobine.<sup>5</sup>

## BASIC KINETICS OF THIOL-ENE POLYMERIZATION

In general, as shown in Scheme 1, thiol-ene systems polymerize by a free-radical chain mechanism involving



Morgan et al.<sup>7</sup> conducted an extensive investigation of the effects of both the thiol and ene structures on the overall rate of the thiol-ene addition process. Their detailed work established two very basic rules about thiol-ene free-radical chain reactions. First, the overall conversion rate of the thiol-ene reaction is directly related to the electron density on the ene, with electron-rich enes being consumed much more quickly than electron-poor enes. The basic exception to this rule is that highly conjugated double bonds copolymerize very slowly with thiols, presumably because of the stability of the carbon-centered allylic radical formed upon the addition of the thiyl radical to the carbon-carbon double bond. Second, in several cases, thiols based on mercaptopropionate esters copolymerize with a given ene more quickly than mercaptoacetate esters, which in turn react more quickly than simple alkyl thiols. We next elaborate on these two basic observations of Morgan et al.<sup>7</sup>

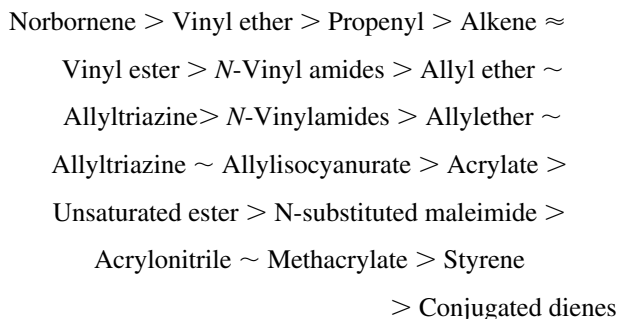
### Ene Structure

The most salient feature of thiol-ene photopolymerization is that almost any type of ene (including those whose structures are shown in Chart 1) can participate. Most results in the literature corroborate the original observations of Morgan et al.<sup>7</sup> with respect to the relationship between the chemical structures of the ene and thiol and the reactivity. The following order for the reaction of a wide variety of enes with three thiol types (alkyl 3-mercaptopropionates, alkylthioglycolates, and alkylthiols, as shown in Chart 2) is based on our assessment of literature reports<sup>5,43</sup> as corroborated by results in our laboratory. Some questions still exist about the exact order because of differences in the experimental conditions under which the ene reactivities were evaluated. The ordering may change slightly with the thiol structure. Also, when two enes are evaluated in competitive reactions with a single thiol, it is not possible to extrapolate the results to

two steps:<sup>5</sup> an initial addition of the thiyl radical to the carbon of an ene functionality (labeled propagation 1) and a subsequent hydrogen abstraction of a thiol group by a carbon-centered radical to give a thiyl radical (labeled propagation 2). Termination occurs by radical-radical coupling.

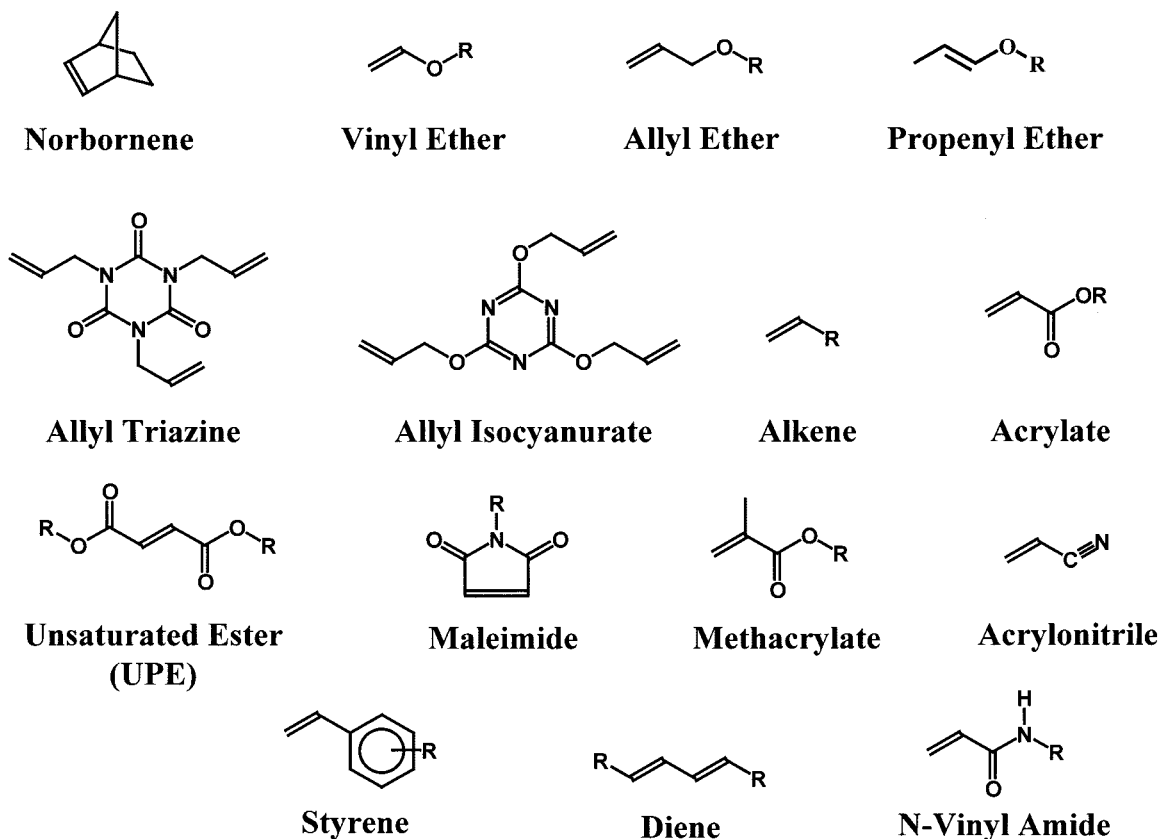
The two-step process in Scheme 1 results in the addition of a thiol group across an ene double bond:

noncompetitive reactions between the individual enes and thiols. This arises because the basic thiol-ene free-radical reaction is a two-step sequence:



Except for the first entry and the last three entries, the ene reactivity decreases, for the most part, with decreasing electron density of the carbon-carbon double bond. Norbornene, methacrylate, styrene, and conjugated dienes are special cases. The rates of free-radical addition of thiols to norbornene are exceptionally rapid because of a combination of the significant relief of ring strain resulting from the addition of the thiyl radical across the double bond and the subsequent rapid hydrogen-abstraction rate of a thiol hydrogen by the carbon-centered radical. The carbon-centered radicals that form when the thiyl radical is added to a methacrylate, styrene, or conjugated diene carbon-carbon bond are very stable and produce radicals (methacrylic, benzylic, or allylic) that have inherently low hydrogen-abstraction rate constants. Incidentally, in contrast to the conjugated dienes, nonconjugated dienes undergo thiol-ene reactions quite rapidly according to the exact position of the enes.

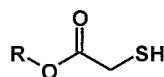
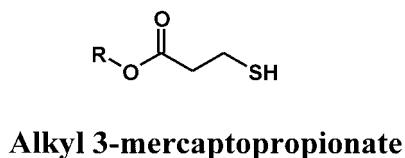
To determine which of the two propagation steps in Scheme 1 is rate-determining, Cramer et al.<sup>45</sup> recorded plots of the conversion percentage versus the time for four types of ene monomers with pentaerythritol tetra(3-mercaptopropionate) (TetraThiol1; see Chart 3). The



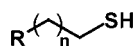
**Chart 1.** General structures of typical enes used in thiol–ene polymerizations.

enes that they evaluated were multifunctional, with only the acrylate being capable of homopolymerizing and copolymerizing with the thiol. By consecutively holding

the thiol and ene concentrations constant and varying the concentration of the second component, they were able to determine the order of the reaction (see eq 2) with respect to both the thiol- and ene-functional groups. Table 1 shows the respective values for exponents  $n$  and  $m$  (which relate the polymerization rate to the thiol and ene concentrations, respectively) and the ratios of the rate constant for propagation ( $k_p$ ) to the rate constant for chain transfer ( $k_{ct}$ ) for four enes (see structures and acronyms in Chart 3) that were evaluated.<sup>45</sup> The results for  $k_p/k_{ct}$  for the addition of 1-butanethiol (see Chart 3) to two other monofunctional enes (styrene and pentene; see Chart 3) are also given in Table 1:



Alkylthioglycolate

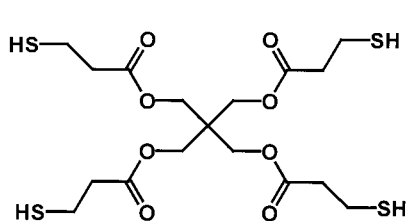
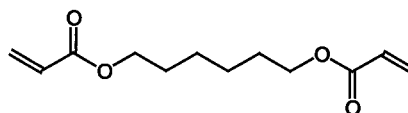
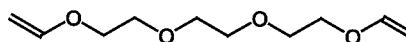
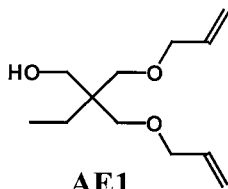
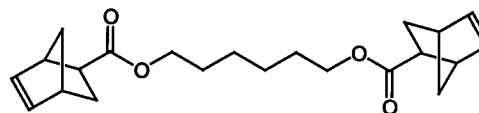
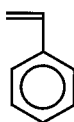
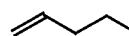


Alkyl thiol

**Chart 2.** General structures of three basic types of thiols used in thiol–ene polymerizations.

$$R_{\text{polymerization}} \propto [\text{RSH}]^n [\text{C}=\text{C}]^m \quad (2)$$

where  $R_{\text{polymerization}}$  is the rate of polymerization. Although the respective  $k_p$  and  $k_{ct}$  values for N1 (where N represents norbornene) and TEGDVE (divinylether) were approximately equal, indicating that neither the propagation step nor the chain-transfer step were rate-determining,  $k_p$  values for HDDA (diacrylate), AE1

**TetraThiol1****HDDA****TEGDVE****AE1****N1****Styrene****Pentene****Chart 3.** Structures of thiol and enes used in rate-constant analysis.

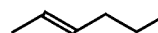
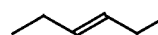
(where AE represents allyl ether), and pentene were reported to be at least an order of magnitude greater than  $k_{ct}$ . This indicated that the chain-transfer hydrogen-abstraction process is the slow step for thiol-acrylate, thiol/allyl ether, and thiol-alkene copolymerizations. A particularly interesting case arises for the photoinitiated polymerization of a mixture of a thiol and acrylate because the acrylate can homopolymerize and copolymerize with thiols: the results in Table 1 are only for the copolymerization process. Although the results in Table 1 are important in determining the limiting reaction in

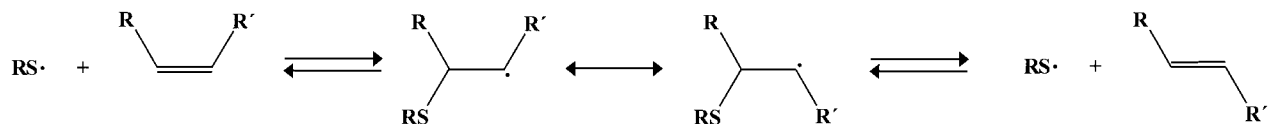
the free-radical addition of thiols to enes, additional work is needed before a complete understanding of the role that the ene structure has in defining the slow step in thiol-ene reactions and ultimately the overall rate of the copolymerization process.

The reactivity of the ene in a thiol-ene free-radical chain reaction is dependent on the extent of substitution.<sup>5,59,72,74</sup> Model studies from our laboratory have shown that highly substituted alkenes are less reactive than singly substituted alkenes. A conversion-time plot

**Table 1.** Kinetic-Rate-Constant Ratios for  $k_p$  and  $k_{ct}$  and Exponents  $n$  and  $m$ 

Ene	$k_p/k_{ct}$	$n$	$m$
HDDA	13 <sup>a</sup>	0.4 <sup>a</sup>	0.6 <sup>a</sup>
N1	1.0 <sup>a</sup>	1/2 <sup>a</sup>	1/2 <sup>a</sup>
TEGDVE	1.2 <sup>a</sup>	1/2 <sup>a</sup>	1/2 <sup>a</sup>
AE1	10 <sup>a</sup>	1 <sup>a</sup>	0 <sup>a</sup>
Styrene	800,000 <sup>b</sup>	—	—
Pentene	43 <sup>b</sup>	—	—

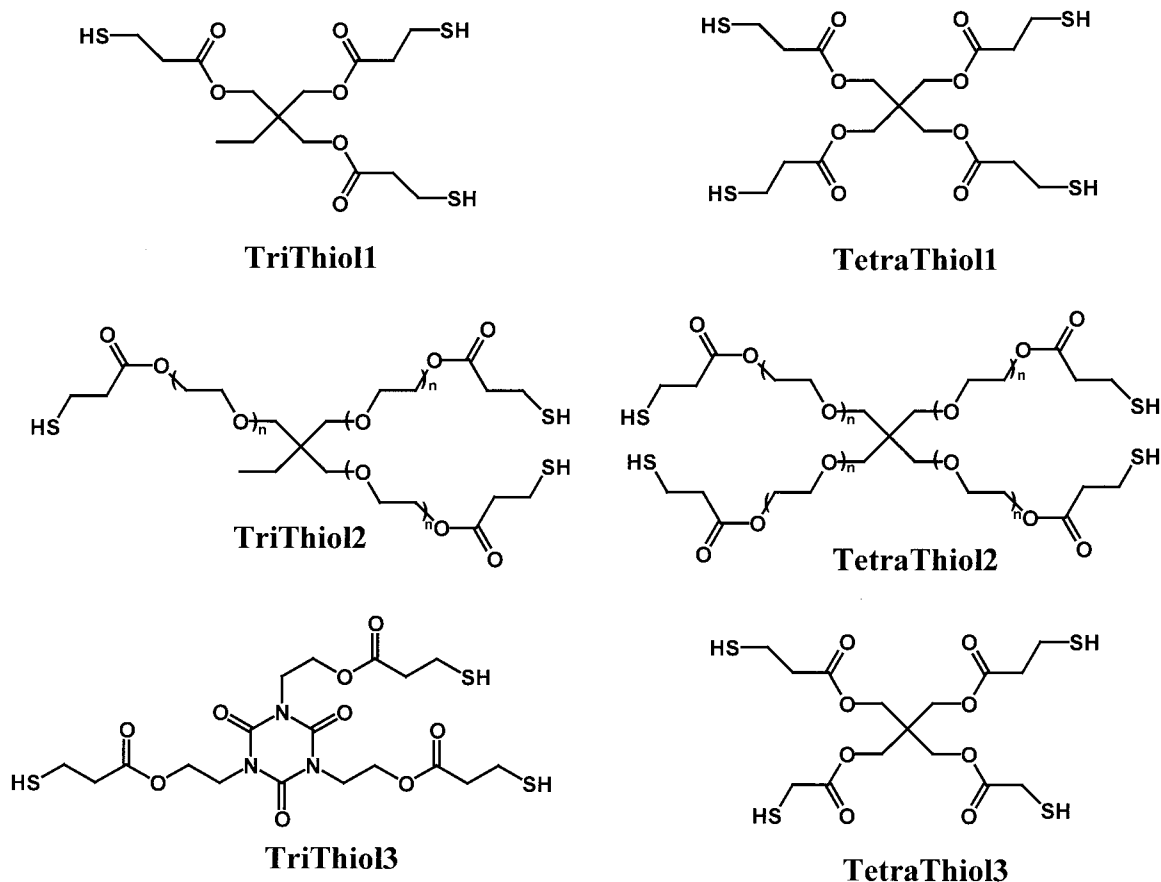
<sup>a</sup> Reference 45.<sup>b</sup> Reference 73.**1-hexene****trans-2-hexene****trans-3-hexene****Chart 4.** Structures of hexenes.



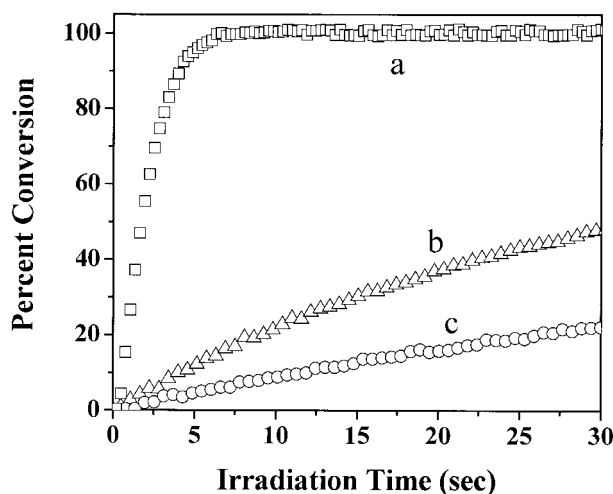
**Scheme 2.** Reversible addition of the thiyl radical to the disubstituted ene.

obtained from the real-time infrared (RTIR) analysis of the ene and thiol loss in Figure 1 illustrates the effect that the double-bond position can have on the conversion rate of three hexenes (see the structures in Chart 4) copolymerized with a monofunctional thiol.<sup>59,72</sup> The results for the 1:1 molar mixtures show that 1-hexene is 8 times more reactive than *trans*-2-hexene and 18 times more reactive than *trans*-3-hexene, both of which have internal double bonds. This suggests that steric hindrance is important in the two-step propagation sequence involved in the thiol–ene free-radical polymerization process, most assuredly because of a reversible equilibrium in the propagation step in Scheme 2. We have found that when attempting to carry out rapid thiol–ene free-radical chain reactions involving multifunctional enes, we must ensure that the ene groups are located at terminal positions.

Johansson et al.<sup>75,76</sup> pointed out that the addition of the thiyl radical (propagation step 1 in Scheme 1) to *cis*-ene bonds, as shown in Scheme 2, is reversible with efficient isomerization, and this leads to the less reactive *trans* structure. The *trans*-ene structure has been reported to react with the thiyl radical in an efficient addition step, although the reaction is reversible and still not as fast as that with terminal enes. The reversibility of thiyl radical addition to internal enes has been reported previously.<sup>77–79</sup> In summary, although reaction orders with respect to thiol and ene concentrations have been determined, and there is published information on the reactivity of some thiol and ene combinations, there is little or no reliable information on individual rate constants. Additionally, in some systems in which highly abstractable hydrogens are on the enes, the mechanism in



**Chart 5.** Structures of basic multifunctional thiols.



**Figure 1.** Conversion–time plots from RTIR of the photopolymerization of 1:1 molar mixtures of ethyl 3-mercaptopropionate and (a) 1-hexene, (b) 2-hexene, and (c) 3-hexene. The samples contained 1.0 wt % DMPA (photoinitiator). The light intensity was 3.0 mW/cm<sup>2</sup> with 365-nm light.

Scheme 1 may not be accurate. The free-radical chemistry of thiols and enes has been investigated for over 50 years, and yet there are significant and critical voids in our understanding of the basic kinetics and rate processes involved.

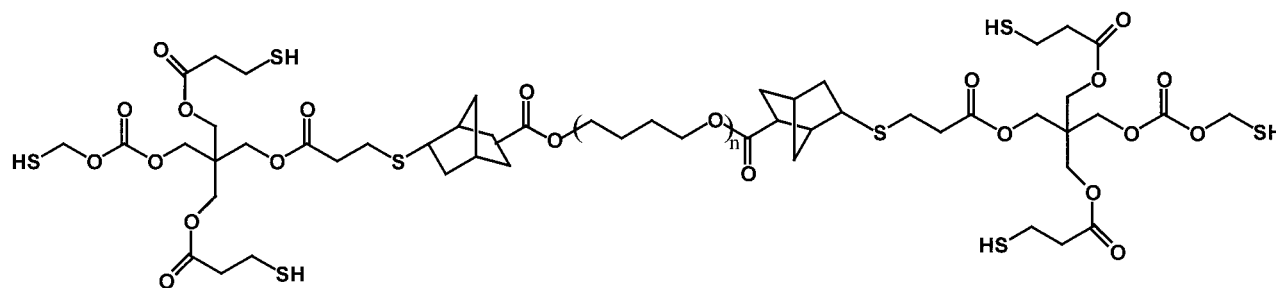
### Thiol Structure

Three types of multifunctional thiols used in thiol–ene photoinitiated polymerization have been reported: alkyl thiols, thiol glycolate esters, and thiol propionate esters, as shown in Chart 2. It has been reported in at least one case that thiols based on propionate esters and glycolate esters result in greater reaction rates because of a weakening of the sulfur–hydrogen bond by hydrogen bonding of the thiol hydrogen groups with the ester carbonyl.<sup>80</sup> Rates of addition almost 6 times greater have been found for the free-

radical addition of methyl mercaptopropionate to 1-heptene than for 1-pentanethiol to 1-heptene. It is expected that similar results might be found for thiol addition to other types of enes; however, no additional results have been reported to date other than for addition to enes other than 1-heptene. It might be expected that in cases in which the chain-transfer step is not rate-limiting that there would be no dependence of the rate on the thiol structure.

Structures, formal names, and acronyms for several of the commercially available multifunctional thiols traditionally used in thiol–ene polymerizations are shown in Chart 5: in the case of mercapto esters, only the mercaptopropionate esters are shown, with the understanding that the corresponding mercaptoglycolate esters are also readily synthesized and have indeed been made and evaluated in thiol–ene polymerizations. The two most widely used and commercially available thiols, TetraThiol1 (see Chart 3 and Chart 5 for reference) and trimethylolpropane tri(3-mercaptopropionate) (TriThiol1; see Chart 5) are based on the reactions of mercaptopropionic acid with trimethylol propane and pentaerythritol, respectively. TriThiol2 and TetraThiol4 (also shown in Chart 5), based on reactions of mercaptopropionic acid with ethoxylated trimethylol propane and ethoxylated pentaerythritol, are also available commercially, as is TriThiol3 (Chart 5). TriThiol2, TetraThiol2, and TriThiol3 have been touted as low-odor thiols.<sup>61,81</sup> TetraThiol3 (Chart 5) is a four-functional thiol containing two 3-mercaptopropionate groups and two 2-mercaptopropionate groups with different reactivities,<sup>82</sup> which could provide an avenue for the formation of crosslinked networks with novel molecular architectures.

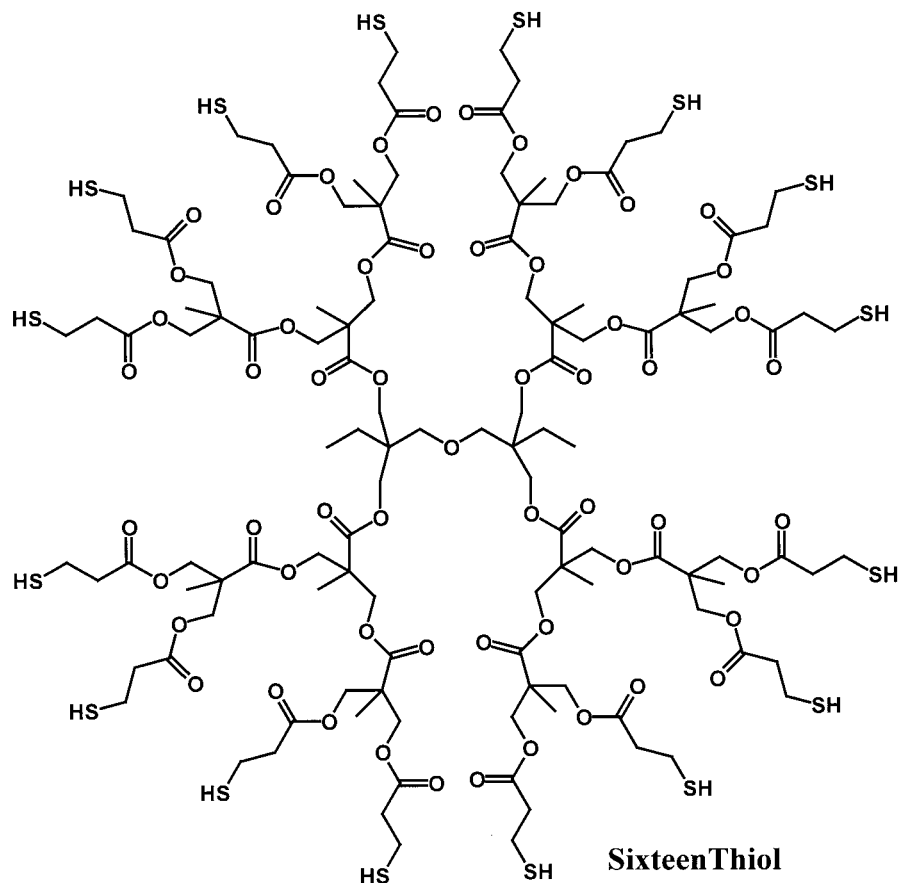
In addition to the more traditional multifunctional thiols (shown in Chart 5), others have been reported that may well be useful in a variety of applications. Wood et al.<sup>27</sup> reported the synthesis of thiols via a process in which an excess of thiol was added to a dinorbornene by a free-radical chain process. In the presence of an azo thermal initiator that produced free radicals, the thiol was added to the dinorbornene and yielded a six-functional thiol (SixThiol; see Chart 6).<sup>27</sup> The synthesis of SixThiol



**SixThiol**

**Chart 6.** Structure of SixThiol.





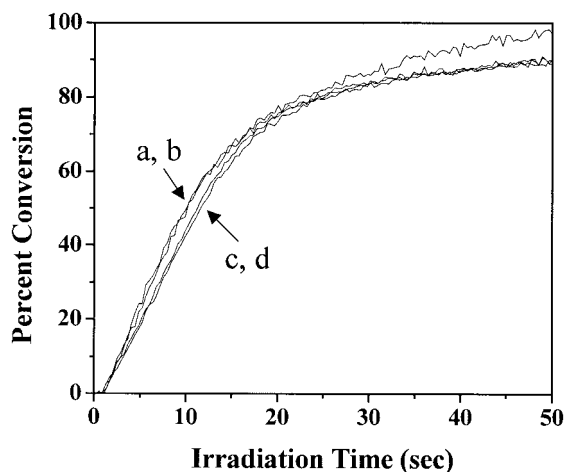
**Chart 7.** Structure of SixteenThiol.

is particularly interesting because it provides a rationale for the general synthesis of highly functional thiols by a thermal free-radical chain process. For example, the tetrafunctional thiol could be added to the trifunctional and tetrafunctional norbornenes synthesized by Woods et al.<sup>27</sup> to yield 9- and 12-functional thiols. Also, this method is not limited to norbornenes because it should be possible to also use multifunctional allyl ethers, vinyl ethers, and other multifunctional monomers. This would provide for the synthesis of an abundant number of multifunctional thiols with a wide variance in the chemical structure of the backbone separating the thiol groups. Woods et al.<sup>27</sup> reported that HexaThiol and similar multifunctional thiols could be mixed with virtually any multifunctionality monomer with which it was miscible to adjust the gel point of the polymerization process. Such higher functional thiols might be expected to give some unusual architectures. Because the choices of enes to copolymerize with these new multifunctional thiols are essentially endless, it should be possible to tailor the molecular composition of films in a way previously impossible.

Finally, a recently synthesized hyperbranched 16-functional thiol (SixteenThiol; see Chart 7) was described by workers at Perstorp.<sup>83–85</sup> Figure 2 shows polymerization exotherms and a conversion–time plots for a 1:1 mixture of SixteenThiol and AE2 as well as a 1:1 mixture of TriThiol1 and AE2 (given in Chart 8 along with several other allyl ethers that can be readily copolymerized with either SixteenThiol or TriThiol1). The ene and thiol rates and conversions for both mixtures are surprisingly almost identical, even though the polymerization gel points are predicted to be at 50% and approximately 18% for AE2 with TriThiol1 and SixteenThiol, respectively. The high conversion may not be too surprising because of the high conversions obtained for the free-radical polymerization of dendrimeric (meth)acrylates.<sup>86,87</sup>

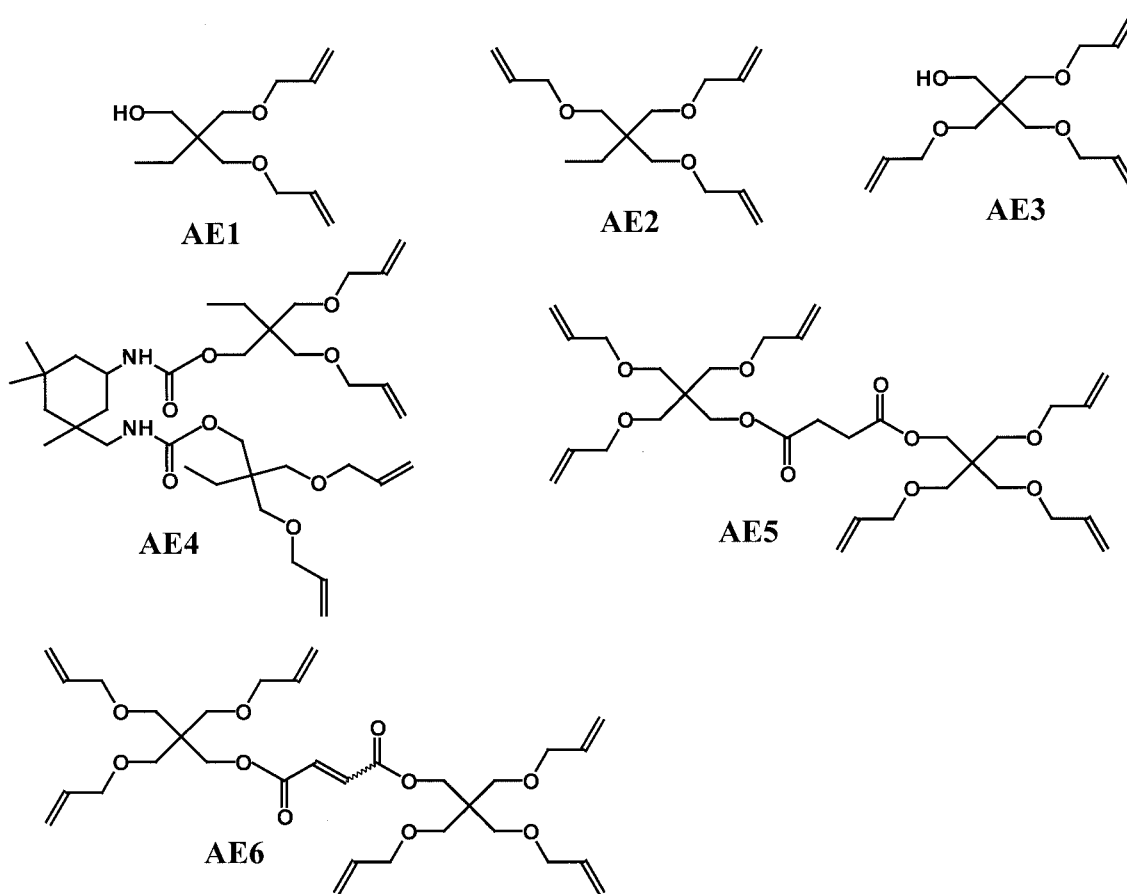
### Initiation

As with any free-radical polymerization process, there are a number of ways of initiating thiol–ene polymerization, including the excitation of a diarylketone fol-

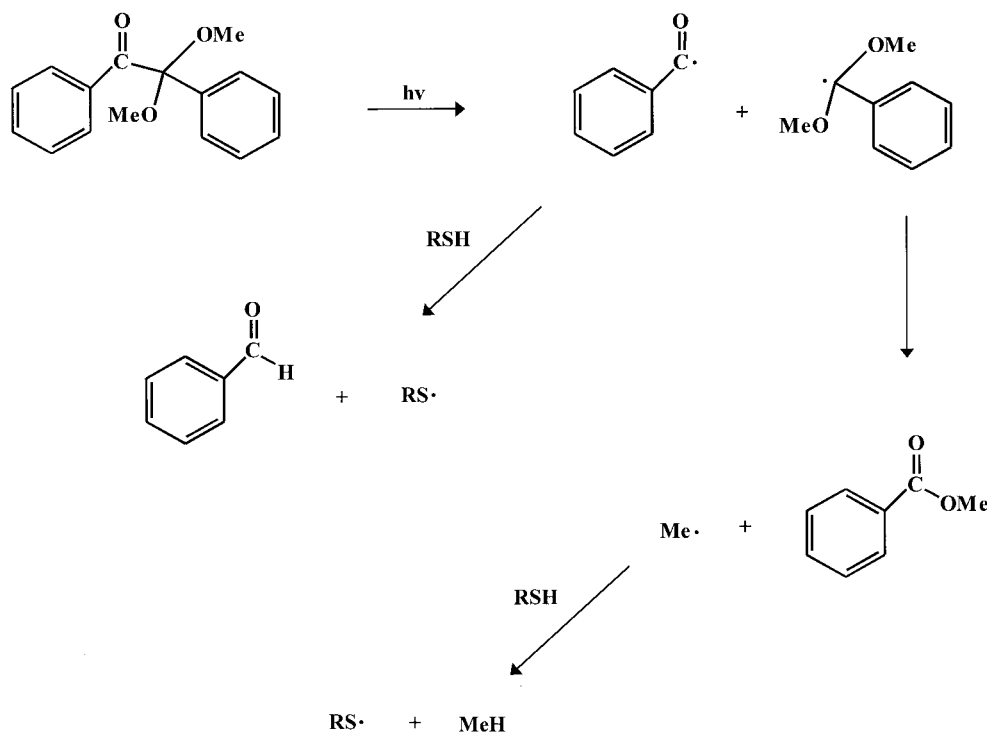


**Figure 2.** Conversion-time plots from RTIR of the photopolymerization of 1:1 molar mixtures of Sixteen-Thiol and AE2 [(a) thiol conversion and (b) allyl ether ene conversion] and TriThiol1 and AE2 [(c) thiol conversion and (d) allyl ether ene conversion] with 0.05 wt % DMPA. The light intensity was 5.0 mW/cm<sup>2</sup>.

lowed by hydrogen transfer,<sup>6</sup> the excitation of an aryl aliphatic ketone followed by  $\alpha$ -bond cleavage,<sup>6,8</sup> and the direct excitation of the thiol followed by a lysis of the sulfur-hydrogen bond.<sup>46</sup> Each of these processes is discussed separately. Per eq 3, a diarylketone, such as BP, can be excited to its singlet state, upon irradiation with UV light of sufficient energy, and this can be followed by an efficient intersystem crossing to the triplet state.<sup>6</sup> In the presence of thiols, there is an efficient hydrogen transfer from the thiol to the excited triplet state of the diarylketone, resulting in the formation of a thiyl radical and a semipinacol radical. Such an efficient hydrogen-abstraction process does not occur for aliphatic alcohols and triplet-state BP; instead, there is hydrogen abstraction involving the hydrogen on the  $\alpha$ -carbon.<sup>88</sup> Once formed, the thiyl radical in eq 3a initiates the polymerization process by inserting into the carbon-carbon double bond of the ene to give a carbon-centered radical, thus initiating the two-step radical-chain process shown in Scheme 1. This process of initiation, although quite inefficient because of the inability of the semipinacol radical



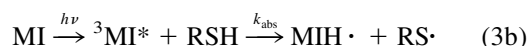
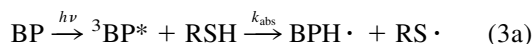
**Chart 8.** Structures of allyl ethers.



**Scheme 3.** Mechanism for the photoinitiation of thiol-ene free-radical polymerization with a cleavage-type photoinitiator.

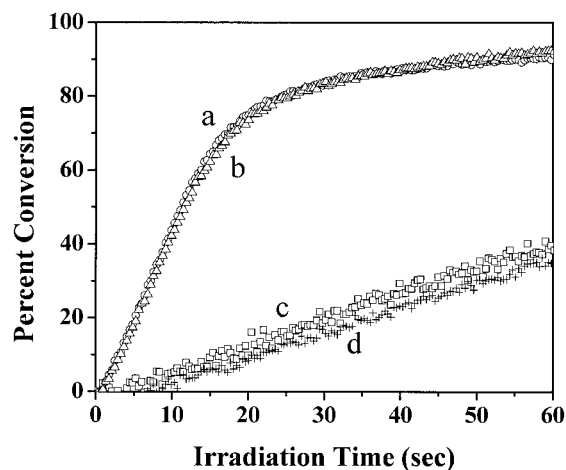
either to insert into the carbon-carbon double bond or to abstract hydrogens efficiently, does result in reasonable polymerization rates because of the rapid propagation rates for thiol-ene polymerizations. Unfortunately, if BP or some other diarylketone is used to initiate thiol-ene polymerization, most of the diarylketone remains unconsumed at the end of the polymerization and remains in the film as a plasticizer and photoreactive species. This can severely hinder the long-term stability of films exposed to sunlight or even certain types of room light. One way of circumventing this problem is to use an *N*-substituted maleimide as the excited-state triplet species,<sup>60</sup> which abstracts a hydrogen from the labile thiol group, as shown in eq 3b. The rate constant for hydrogen abstraction ( $k_{\text{abs}}$ ) of a thiol hydrogen by an *N*-alkyl maleimide in eq 3b is about 10 times greater than  $k_{\text{abs}}$  by BP in eq 3a ( $\sim 10^8$  vs  $\sim 10^7$  L mol<sup>-1</sup> s<sup>-1</sup>, as measured by laser flash photolysis quenching in our laboratory). Because maleimides are quite reactive in free-radical processes, they are consumed by the radical chain process that they initiate and hence do not remain in the film after exposure. Although this adequately eliminates the problem of residual photoinitiator in the final films, *N*-substituted maleimides, at least the simple ones, are toxic, and this limits their use unless care is taken in

selecting a low-toxicity, multifunctional *N*-alkylmaleimide:



In a particularly fascinating study,<sup>89</sup> Belfield and Schafer initiated the free-radical polymerization of a traditional thiol-ene mixture by exciting isopropylthioxanthone (ITX) at 775 nm in the near-infrared with the output of a 120-fs pulsed laser source. The two photon absorption processes resulted in the formation of the ITX excited state, which subsequently abstracted a hydrogen from a thiol to initiate the thiol-ene polymerization of thin and thick (>2 cm) samples by the two-step propagation sequence in Scheme 1.

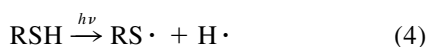
Thiol-ene polymerization can also be initiated by the excitation of cleavage photoinitiators, which give a benzoyl radical and a tertiary carbon radical upon the absorption of a photon of light, as depicted in Scheme 3 for dimethoxyphenyl acetophenone (DMPA).<sup>8</sup> A rearrangement of the tertiary carbon radical occurs, yielding a methyl radical and methyl benzoate. The methyl and



**Figure 3.** Conversion–time plots from RTIR of the photopolymerization of 1:1 molar mixtures of TriThiol1 and AE2 with 0.05 wt % DMPA [photoinitiator; (a) thiol conversion and (b) allyl ether ene conversion] and without DMPA [(c) thiol conversion and (d) allyl ether ene conversion]. The light intensity was 5.0 mW/cm<sup>2</sup>.

benzoyl radicals may insert into a carbon–carbon bond directly or abstract a hydrogen from a thiol group. In either case, the two-step process characteristic of the thiol–ene free-radical chain reaction in Scheme 1 is initiated. Initiation with the cleavage photoinitiator is more efficient than hydrogen-transfer (abstraction) photoinitiators such as BP because the quantum yield for the production of reactive radicals is higher.

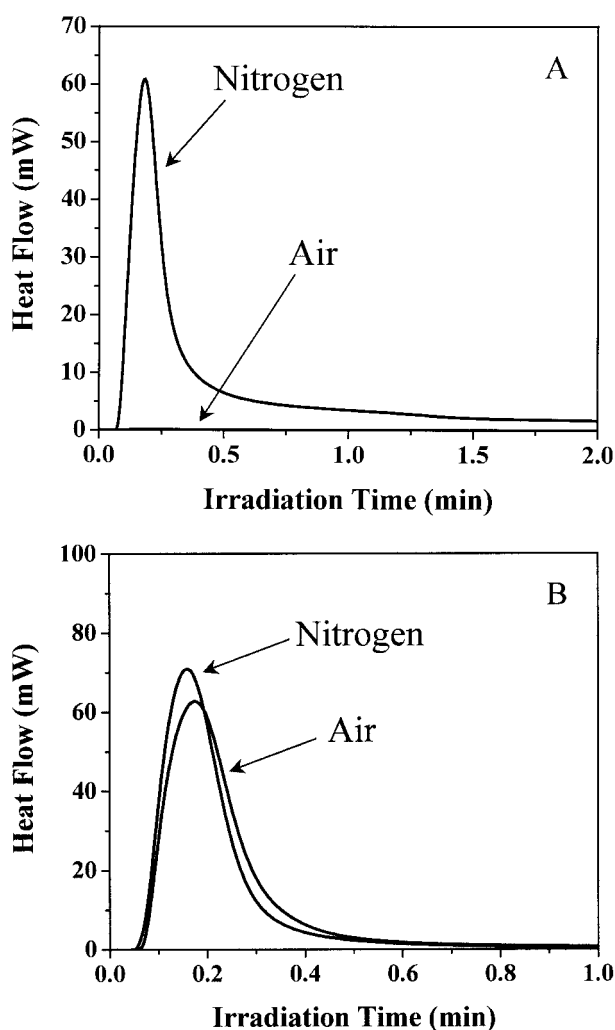
Although not as efficient as initiation by either hydrogen-abstraction or  $\alpha$ -cleavage processes, it is still possible to excite directly the thiol and induce the cleavage of the labile sulfur–hydrogen bond. In the early 1950s, it was reported that the photolysis of thiols in the gas phase resulted in an efficient lysis of the sulfur–hydrogen bond that generated the thiyl and hydrogen radicals (see eq 4).<sup>90,91</sup> The equivalent process, the cleavage of a hydrogen–oxygen bond, is not efficient for the photolysis of alcohols because the oxygen–hydrogen bond energy is much higher. Hence, the direct excitation of thiol–ene mixtures with an unfiltered high-pressure mercury lamp source in the absence of an added photoinitiator leads to an efficient polymerization process.<sup>46</sup> The conversion versus the exposure time, obtained by RTIR analysis and shown in Figure 3, for the excitation of a 1:1 molar mixture of the ene AE2 and the thiol TriThiol1 in the absence of a photoinitiator is high, but not as high as when a cleavage-type initiator is used, as shown in Figure 3 for comparison:



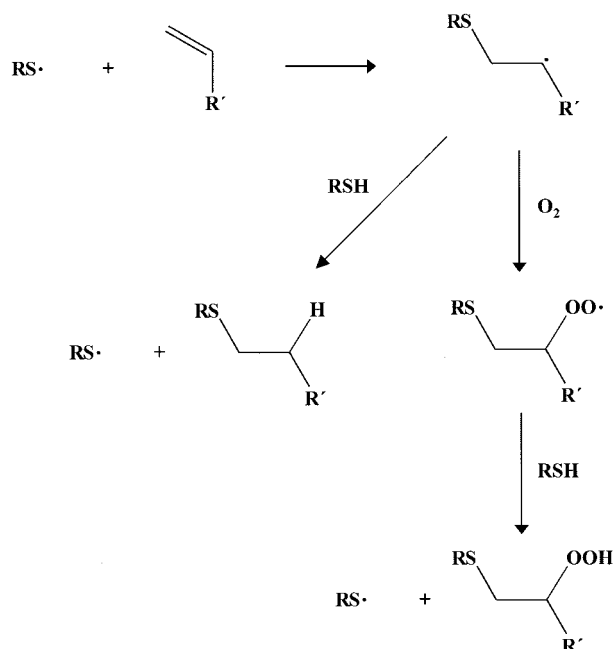
By measuring the dependence of the polymerization rate on the concentrations of both the thiol- and ene-functional groups in a 1:1 molar mixture of traditional thiol–ene combinations, researchers showed that the dependence of the initiation process is proportional to the square root of the thiol concentration (see eq 5) when the excitation light source has a frequency corresponding to the direct absorption of the thiol group.<sup>92</sup> This supports the proposition that the direct excitation of the thiol groups results in the generation of the thiyl and hydrogen radical initiating species:

$$R_{\text{initiation}} \propto [\text{RSH}]^{1/2} \quad (5)$$

where  $R_{\text{initiation}}$  is the rate of initiation.



**Figure 4.** Photo-DSC exotherms in nitrogen and air of (A) HDDA and (B) a 1:1 molar mixture of TriThiol1 and AE2 with 1 wt % DMPA. The light intensity was 1.0 mW/cm<sup>2</sup>.



**Scheme 4.** Oxygen-scavenging mechanism for free-radical polymerization in the presence of aliphatic thiols.

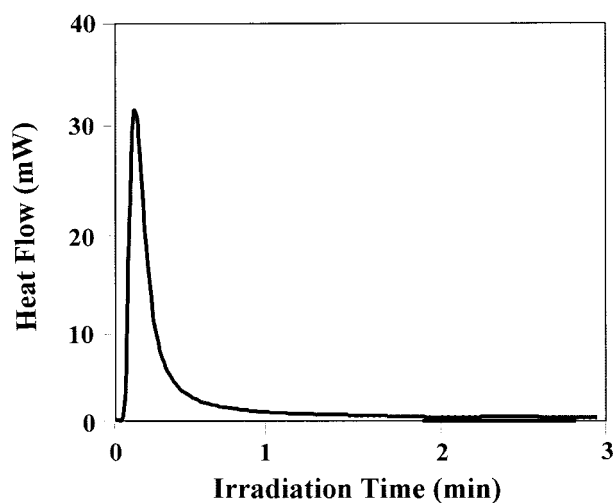
### Gelation

If multifunctional enes and thiols have a combined functionality of at least five, with each component having a minimum functionality of two, polymerization occurs by the free-radical chain reaction shown in Scheme 1. The crosslinked network will form with mechanical properties dependent on the chemical structure of the parent thiols and

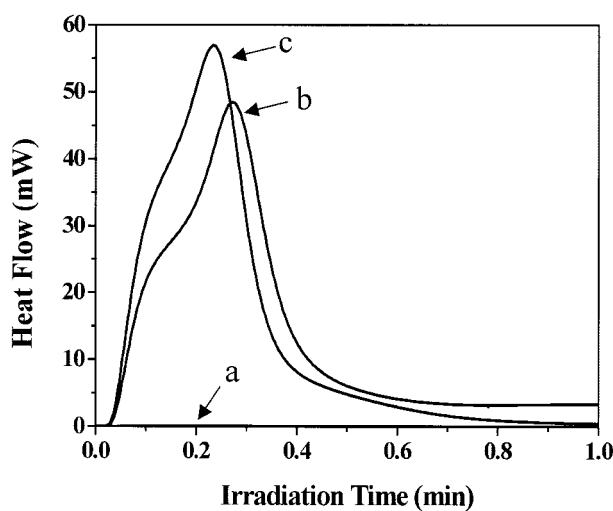
enes, their functionality, and the extent of conversion of each functional group. The interesting point about the thiol-ene free-radical polymerization is the delayed onset of gel formation in comparison with traditional acrylates. Until the gel point, the medium is low-viscosity and consists primarily of low-molecular-weight species. The gel point for the curing of thiol-enes by light, by which a crosslinked network is formed and the system diffusion rates are reduced drastically, can be obtained as follows:<sup>28</sup>

$$\alpha = [1/r(f_{\text{thiol}} - 1)(f_{\text{ene}} - 1)]^{1/2} \quad (6)$$

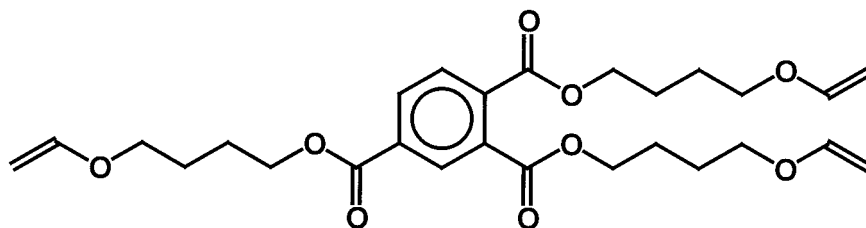
where  $r$  is the thiol-ene molar ratio based on functional groups,  $f_{\text{thiol}}$  is the thiol functionality, and  $f_{\text{ene}}$  is the ene functionality. The gel point can thus be controlled by the variation in the functionality of the thiol and ene. For instance, gelation takes place at 50% conversions of both thiol and ene groups for a mixture in which both components are trifunctional and after about 33% conversions when both components are tetrafunctional. With a combination of Fourier transform mechanical spectroscopy and RTIR spectroscopy, and with the gel point defined as the conversion at which the loss tangent becomes frequency-independent, Chiou and coworkers<sup>93-95</sup> in a series of rheological reports on thiol-ene photopolymerization made several important observations. They found that the elastic modulus, which could be used to represent the buildup of a network during the photopolymerization of TriThiol1 and ene AE2, began to increase at about 65–66% conversion of thiol-functional groups (at slightly lower conversions than the gel point, which was found to occur at ca. 71% thiol-functional-



**Figure 5.** Photo-DSC exotherm of a 1:1 molar mixture of TriThiol1 and TVE with 1 wt % 2-hydroxy-2,2'-dimethyl acetophenone in sunlight.



**Figure 6.** Photo-DSC exotherms in air of HDDA with 0.1 wt % DMPA and (a) 0, (b) 25, or (c) 40 mol % TriThiol1. The light intensity was 3.2 mW/cm<sup>2</sup>.



## TVE

**Chart 9.** Structure of TVE.

group conversion). This result is very different from other typical free-radical polymerizations of multifunctional monomers such as acrylates, for which the conversion at which gelation occurs actually supercedes increases in the elastic modulus. Also, for thiol–ene photopolymerization, networks are formed at much higher conversions than for multifunctional acrylate monomer polymerization, in which gels form at very low conversions, typically after only a few percent. A direct benefit of shrinkage occurring in the liquid phase is that the final crosslinked films ultimately obtain have a higher conversion of functional groups, and there is less stress built into the network that is eventually formed than for crosslinked networks based on the polymerization of traditional (meth)acrylate monomers. Combined with the high affinity of thioether linkages to adhere to a variety of substrates, including metals, the reduced stress of thiol–ene films makes them especially attractive in applications for which adhesion is particularly critical.

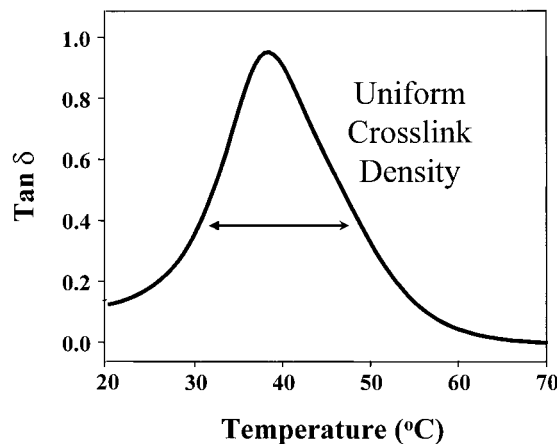
Chiou et al.<sup>96</sup> also investigated the photocuring of a 1:1 molar mixture of TriThiol2 and AE2 with colloidal fumed silica fillers as viscosity and rheology modifiers. *In situ* rheological measurements along with real-time Fourier transform infrared (FTIR) analysis showed that the filled thiol–enes could, with the right type of silica particle, form a physical gel of fumed silica particles before chemical crosslinking of the thiol–ene by the copolymerization process. For all of the fumed silica fillers investigated, the crosslinking mechanism was not altered, although the polymerization rate was diminished.

## OXYGEN INHIBITION

One of the particularly important aspects of the thiol–ene photoinitiated free-radical polymerization is its relative insensitivity to oxygen inhibition, a problem that generally plagues free-radical polymerization processes. Figure 4(A,B) shows exotherms for the photopolymerization

of pure HDDA (see Chart 3) and a 1:1 molar mixture of TriThiol1 and AE2 in air and nitrogen: unlike the acrylate polymerization of HDDA, oxygen inhibition is negligible for the thiol–ene free-radical polymerization. This insensitivity to oxygen inhibition is shared by virtually all thiol–ene combinations. The mechanism for the reduction of oxygen inhibition in the thiol–ene polymerization given in Scheme 4 is based on the hydrogen abstraction of a thiol hydrogen by peroxy radicals that are formed by the reaction of carbon-centered propagation radicals with molecular oxygen.<sup>8</sup> The thiyl radicals thus formed simply add into carbon–carbon double bonds to continue the main propagation step(s).

To illustrate graphically how insensitive thiol–ene polymerization is to oxygen inhibition, we have recorded the exotherm in Figure 5 of a 1:1 molar mixture of TriThiol2 and trivinyl ether (TVE; Chart 9) initiated by sunlight in a photo-DSC instrument open to air. The polymerization, which used a low concentration of the photoinitiator to initiate polymerization, was essentially



**Figure 7.** Tan  $\delta$  versus the temperature of a film made from the photopolymerization of a 1:1 molar mixture of TriThiol1 and AE2 with 1 wt % DMPA.

complete in a few seconds! This result is particularly noteworthy because it opens up the way for rapid curing in sunlight in the presence of air without the need of laminating the resin during sunlight exposure. Another interesting observation is that the film can be cured in sunlight in just a few minutes even if no photoinitiator is used, because, as already explained, thiol–ene systems self-initiate without the need of any additional photoinitiator. The rate of curing can thus be adjusted by how much photoinitiator is used to initiate the polymerization in air by sunlight from times as short as 3–5 s to several hundred seconds of exposure to sunlight. Finally, although the system whose polymerization exotherm is depicted in Figure 5 is a particularly reactive thiol–ene mixture, virtually any thiol–ene mixture can be cured in air in sunlight under nonlamine conditions, although there will certainly be variations in the polymerization rate depending on the exact structure of the ene used.

It is also possible to add thiol to other monomers that are prone to oxygen inhibition and increase the polymerization rate. Figure 6 shows that the addition of even 25 or 40 mol % TriThiol1 to HDDA results in rapid polymerization in air in comparison with pure HDDA. This shows that the addition of thiols to formulated acrylates typically used in photocuring applications for thin films and coatings can result in increases in the polymerization rate, providing for a significant reduction in the amount of the photoinitiator required to attain an acceptable rate of cure in a particular application.

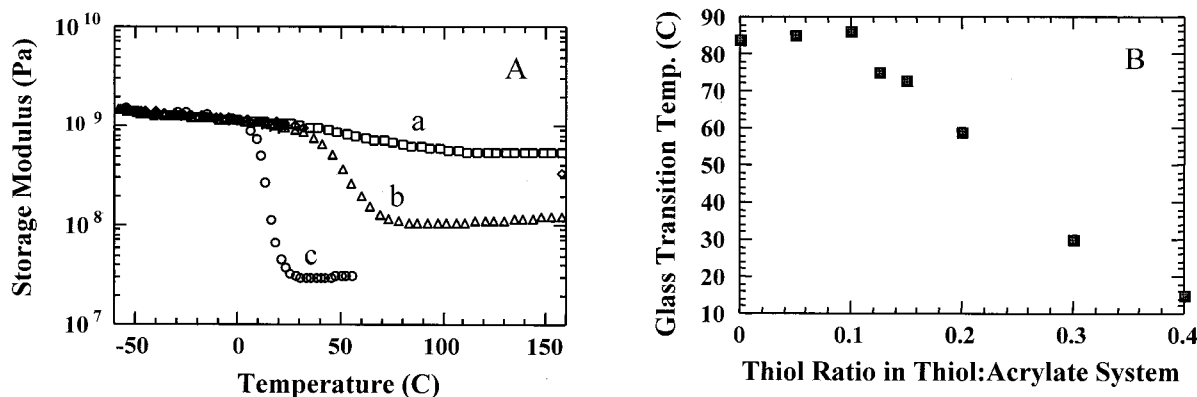
## MECHANICAL AND PHYSICAL PROPERTIES OF THIOL–ENE-BASED FILMS AND NETWORKS

There are several very important features of the physical and mechanical performance parameters of thiol–ene-based networks that are related to the chemical structure of the matrix and the high uniformity of crosslinking. As already pointed out, because thiol–ene polymerization proceeds by a free-radical step-growth process (Scheme 1) with gelation defined by eq 6, the buildup of stress in the films, typical of other multifunctional-monomer free-radical-based polymerizations such as acrylates that gel at low conversions,<sup>97,98</sup> is minimized. The reduction in stress leads to an increase in the adhesion of the film to a given substrate.

Probably the most salient feature of thiol–ene-based films is the uniformity in the network crosslink density. This is best illustrated by the rather narrow glass-transition region in a typical film produced by the polymerization of a 1:1 molar mixture of TriThiol1 and triallyl-1,3,5-triazine-2,6,6(1H, 3H, 5H) trione (Allyl Triazine; see Chart 1), as shown by a plot of  $\tan \delta$  versus the temperature derived from dynamic mechanical analysis

(DMA) in Figure 7. This film is formed between an ene (Allyl Triazine) that does not homopolymerize and a trifunctional thiol (TriThiol1). There are important implications of the uniformity in the crosslink density of thiol–ene-based networks on physical properties that should not be overlooked. For example, when a 1:1 mixture of TriThiol1 and Allyl Triazine is exposed in a Rayonet reactor with 300-nm lamps in a round-bottom flask, in either the absence or presence of a small amount of a photoinitiator, extremely hard and round spheres about 7–8 cm in diameter are formed that are resistant to extremely high impact without shattering or severe stress cracking. These hard and round spheres, which have peak maxima in the  $\tan \delta$  values derived from DMA about 10 °C above room temperature, are glassy in nature and are very hard at room temperature. Round spheres made by the curing of 1:1 mixtures (we have made them up to ~30 cm in diameter) of TriThiol1 and flexible monomers such as TEGDVE (Chart 3) or AE2 (Chart 8) have glass transitions below room temperature and exhibit unusually high storage moduli. These thiol–ene-based materials, which owe their unusual properties to the highly uniform crosslinked network formed by the high conversion of the thiol–ene systems, are in stark contrast to acrylate-based photocured crosslinked networks, which are very heterogeneous in nature and do not exhibit the same physicomechanical properties. In contrast to a film produced by the photopolymerization of a difunctional acrylate such as HDDA, which has a glass transition, as shown in Figure 8(a), from DMA storage modulus plots extending over about 100 °C, the narrow  $\tan \delta$  DMA plot in Figure 7 for the film produced from a pure thiol–ene polymerization indicates a very uniform crosslink density with few dangling chain ends. Cramer and Bowman<sup>44</sup> showed that the addition of TetraThiol1 to HDDA results in a film with an increasingly lower and much narrower glass transition, as shown by the DMA storage modulus plots in Figure 8 for various concentrations of the tetrathiol. The polymerization of such thiol–acrylate mixtures is characterized by a dual polymerization process with both acrylate homopolymerization and thiol–acrylate copolymerization sequences. Apparently, the resultant networks produced when as little as 15 mol % thiol is incorporated with acrylates are much more uniform than networks formed from pure acrylate resins. This suggests that the physical and mechanical properties of photopolymerized acrylate networks can be altered dramatically by the addition of multifunctional thiols.

In the most vivid demonstration to date of the effect of the uniformity of thiol–ene crosslinked networks, Natarajan et al.<sup>99</sup> reported that holographic polymer-dispersed liquid crystals (HPDLCs) formed by the photopolymerization of a 1:1 molar mixture of TriThiol1 and the monomer designated AE1 (Chart 8) with a nonpolymerizable liquid-crystalline component yielded phase-sepa-



**Figure 8.** (A) Storage modulus versus the temperature of films made from the photopolymerization of 1,6-hexanedioldiacrylate with (a) 0, (b) 20, or (c) 40 mol % TetraThiol1 and (B)  $T_g$  versus the molar ratio of thiol to acrylate.

rated liquid-crystal regions that were spherical and quite uniform in size. The low shape and size dispersity of the phase-separated liquid-crystal-rich regions have their origins in the uniform crosslink density of the thiol-ene matrix. These authors demonstrated that the uniform thiol-ene networks are also mechanically stable at room temperature over long time periods, whereas acrylate-based polymer-dispersed liquid-crystal (PDLC) films lock in nonthermodynamically equilibrated structures that relax over time; this results in undesirable changes in the phase structure of the liquid-crystal networks. The work by Natarajan and Bunning on HPDLCs<sup>99</sup> and other work on traditional phase-separated structures in thiol-ene-based PDLCs (discussed in a separate section) shows the potential of ultrauniform crosslinked networks in the development of modulatable optical components.

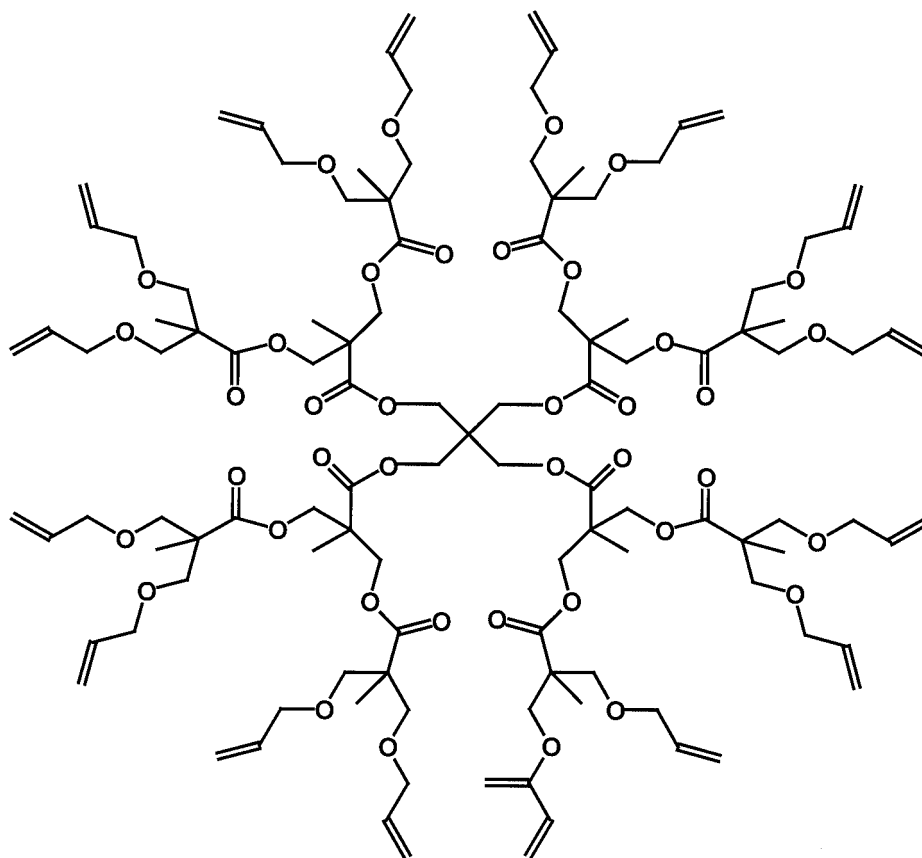
In detailed accounts of thiol-ene-based network physical property performance, Rhenberg and coworkers<sup>100,101</sup> investigated the hardness, chemical resistance, and mechanical and thermal stability of several thiol/allyl ether networks. Five thiols and five allyl ethers (see Chart 8 for the designated ene structures) were synthesized, and various combinations were polymerized with the same initiator concentration and light exposure. For a given thiol (e.g., TriThiol1), the glass-transition temperature ( $T_g$ ) of the final films ranged from about  $-26$  to approximately  $2$  °C, being dependent on the chemical structure of allyl ether. Both AE2 and AE6 polymerized efficiently with TriThiol1. Interestingly, the network that formed from TriThiol1 and AE6 had a higher, narrower glass transition than that of films made from lower functionality allyl ethers. This is potentially an important consideration that may be exploited in the future. In general, it was reported that the  $T_g$ 's of the thiol-ene networks did not change upon aging for time periods of up to 1 month, and this indicated that at least for this time period, the films were thermally and oxida-

tively stable. This was, of course, expected because of the inherent stabilization resulting from the thiol-ether group, which acted as an antioxidant.<sup>102-104</sup> In work corroborated in our laboratory, Carlsson et al.<sup>100</sup> reported that the thiol-ene films were stable via thermogravimetric analysis up to approximately 300 °C or more.

Rhenberg et al.<sup>105,106</sup> also reported that a thiol-ene mixture based on TriThiol1 and a dendrimeric allyl ether (see AE7 in Chart 10) readily polymerized upon exposure to light (BP was used as a photoinitiator). This is significant because it indicates the propensity of even highly functional enes to participate in efficient thiol-ene copolymerizations. The film produced had a relatively narrow glass-transition range of about 25–30 °C (in comparison with what was obtained for films formed from multifunctional acrylates) and a peak maximum in a plot of  $\tan \delta$  versus the temperature of 11 °C.

One particularly important aspect of any photopolymerized crosslinked network is its inherent ability to adhere to a variety of surfaces. The low stress built into the thiol-ene crosslinked network results from much of the polymerization occurring before gelation, while the thiol-ene mixture is still a low-molecular-weight, viscous liquid. Consequently, there is good adhesion to most substrates. In addition, the thioether linkages formed during the addition of a thiol across the ene double bond are flexible and adhere to a variety of surfaces, including metals, to which they have particularly good adhesion.<sup>30</sup> Woods and coworkers reported the synthesis, copolymerization kinetics with thiols, film properties, and stabilization of multifunctional norbornenes for use in a variety of applications, including coatings for optical fibers, adhesives,<sup>23-34</sup> and PDLCs.<sup>35</sup> Examples of norbornene monomers made through the reaction of cyclopentadiene with the corresponding multifunctional acrylate via a Diels-Alder reaction are shown in Chart 11 (N1–N4). These monomers were stabilized by





AE7

**Chart 10.** Structures of a 16-functional allyl ether.

treatment with amphoteric molecules<sup>29</sup> such as magnesium hydroxide for the removal of chloride ions. The resultant norbornene monomers copolymerized with a given multifunctional thiol at rates faster than those of any other thiol-ene photopolymerizations reported to date because of the alleviation in ring strain upon the addition of the thiol radical to the norbornene group to form a carbon-centered radical that readily abstracted thiol hydrogens. As previously mentioned, the thiol-ene systems with norbornene derivatives exhibit excellent adhesive properties.

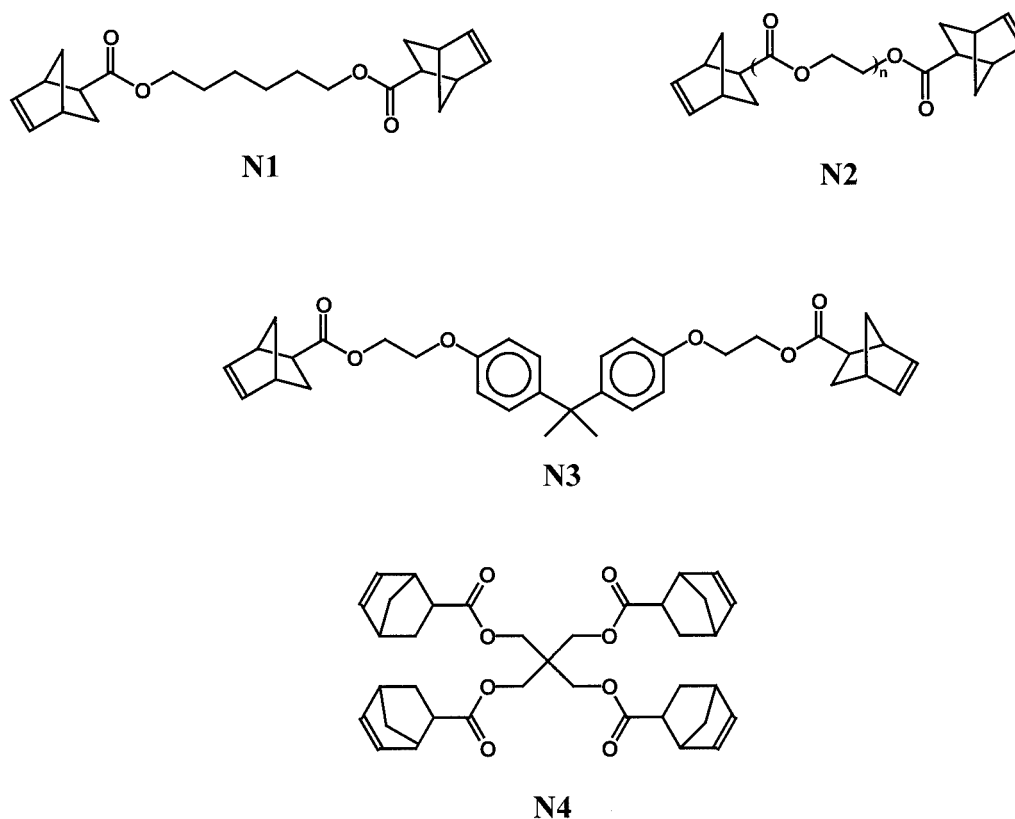
## ODOR

Of course, thiols have an odor like most organic molecules. Nonetheless, thiols, because of their ability to produce crosslinked networks rapidly in air with reduced stress shrinkage problems and with exceptional network uniformity, a wide range of mechanical and physical properties, high optical clarity, and a thioether linkage that is a flexible antioxidant, should not be excluded on the basis of odor

alone. Masking agents can be used for applications for which there may be serious objections to the odor of thiol. Also, as pointed out by Davidson and coworkers,<sup>107,108</sup> there are a number of available thiols (TriThiol2, TetraThiol2, and TriThiol3) that reputedly have little odor because of improved synthetic procedures. Apparently, eliminating the thioglycolic acid or mercaptopropionic acid from which multifunctional thiols are generally synthesized can aid in reducing the odor of commercial multifunctional thiols. Indeed, TriThiol<sup>3</sup> from Yodo Chemicals has essentially no thiol odor and copolymerizes as rapidly with enes as other trifunctional thiols, as shown in Figure 9.

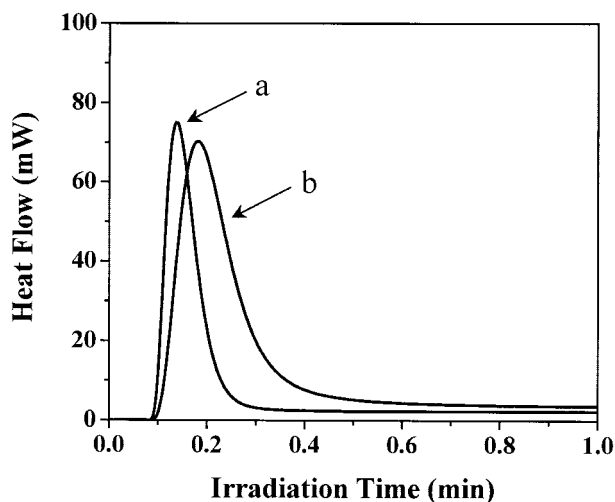
## THERMAL SHELF-LIFE STABILITY OF THIOL-ENE MIXTURES

Although thiol-enes are very reactive when exposed to light, certain thiol-ene mixtures are quite unstable thermally at room temperature. This could potentially limit their use in certain applications for which it is required



**Chart 11.** Structures of several multifunctional norbornenes.

that samples be stored for long periods of time before curing. Presumably, the limited shelf-life stability of thiol-enes may be due to a variety of reasons depending



**Figure 9.** Photo-DSC exotherms in air of 1:1 molar mixtures of (a) TriThiol1 and AE2 with 1 wt % DMPA and (b) TriThiol3 and AE2 with 1 wt % DMPA. The light intensity was approximately 65 mW/cm<sup>2</sup>.

on the particular system: (1) thiol-ene reactions due to a base-catalyzed addition of thiol to the ene double bond,<sup>108</sup> (2) the decomposition of peroxide impurities and subsequent initiation of a thermal free-radical reaction, (3) the reaction of hydroperoxide impurities to form thiyl radical intermediates that initiate polymerization, or (4) the spontaneous initiation of polymerization via the generation of radicals through a ground-state charge-transfer complex formed between the thiol and ene components in the mixture.<sup>19,20</sup> In a recent account, which basically sums up the problem of shelf-life stability of thiol-ene systems in general, Christmas et al.<sup>109</sup> reported that the addition of as little as 5 pph TriThiol1 to a model acrylate formulation consisting of a mixture of an acrylated urethane oligomer and a combination of three low-molecular-weight acrylate monomers reduced the shelf life of the formulation from more than 30 days to about 12 h. An extension of this work showed that the shelf-life stability of an acrylate-thiol mixture was inversely proportional to the average acrylate functionality, and the stability of a TriThiol1/trifunctional acrylate mixture could be enhanced at the expense of reactivity by the addition of monofunctional acrylate.<sup>110</sup> In agreement with this report, we have found that, depending on the chemical structure of the ene, the shelf-life stability of

unstabilized thiol–enes can range from a few hours to much greater than a month. The thiol/vinyl ether mixtures seem to be the most unstable, with other mixtures having somewhat greater stability. Interestingly, the shelf-life stability is dependent to an extent on the exact chemical structure of the backbone separating ene-functional groups, the storage protocol, and the synthetic approach used to make the ene.<sup>108,109</sup> Possible contaminants that can lead to shelf-life problems include groups that easily oxidize at room temperature to produce peroxides, chloride ions,<sup>29</sup> and certain base–amine catalysts.<sup>107</sup>

Because of the immense importance of the shelf-life stability of thiol–ene mixtures with respect to end-use applications, a number of investigations have been conducted dealing with various strategies for extending the shelf life of thiol–ene mixtures and eliminating premature polymerization at room temperature. In 1971, Stahly<sup>111</sup> described the use of several vinyl radical scavengers, including triallyl phosphates. Subsequently, Guthrie and Rendulic<sup>112</sup> reported the use of phosphorous acid and hindered phenolic antioxidant stabilizers. In the early 1990s, Klemm and coworkers<sup>19,20</sup> conducted an extensive program to evaluate thermal stabilizers such as pyrogallol, hydroquinone, catechol, and 1,2,3-trihydroxybenzene as inhibitors of the premature gelation of thiol–ene mixtures at room temperature. Of these thermal stabilizers, pyrogallol was the most successful in thermal stabilization. Other measures used to prevent thermal polymerization at ambient temperatures have included the addition of sulfur,<sup>31</sup> potassium iodine–iodine mixtures,<sup>31</sup> hindered phenolics,<sup>32,113,114</sup> an alkenyl-substituted phenolic combined with a free-radical scavenger,<sup>33</sup> the aluminum or ammonium salt of *N*-nitrosophenylhydroxylamine,<sup>34</sup> phosphines and triarylphosphites,<sup>107</sup> phosphoric acid,<sup>115</sup> 3-propenylphenol,<sup>31</sup> and a combination of an alkenylphenol and a salt of *N*-nitrosophenylhydroxylamine.<sup>34</sup> To determine which is the best stabilizer for a given thiol–ene system, we must evaluate each stabilizer type on a case-by-case basis. For example, Davidson and Mead<sup>107</sup> reported that triphenyl phosphite was extremely effective in stabilizing mixtures consisting of TetraThiol1, TriThiol2, and TriThiol3 with several multifunctional allyl ethers. Additionally, we have found that the simple addition of the aluminum salt of a particular *N*-nitrosophenylhydroxylamine provides adequate stabilization against early gelation for acrylate–thiol mixtures for up to 1 week at 60 °C. Also, Christmas et al.<sup>109</sup> showed that unstable acrylate mixtures containing thiols can be stabilized for longer than 30 days with the aluminum salt of *N*-nitroso-*N*-phenylhydroxyl amine. These results certainly substantiate the work by Rakas and Jacobine.<sup>34</sup>

In the case of very thermally unstable thiol/vinyl ether mixtures, we have found that the shelf-life stability can be extended by the simple addition of methacrylates, styrene derivatives, and even conjugated 1,3-dienes. The addition of thiyl radicals to these ene stabilizers is rapid and selective, but the subsequent hydrogen-abstraction reactions of thiol hydrogens are very slow. The overall results are relatively stable systems.

## OXIDATIVE, THERMAL, PHOTO, AND CHEMICAL STABILITY OF THIOL–ENE-BASED NETWORKS

One of the intriguing aspects of films made through the photopolymerization of thiol–ene mixtures is their oxidative stability. Woods et al.<sup>25</sup> reported that films made through the photopolymerization of thiol–enes had good water absorption resistance and oxidative stability, with essentially no weight loss for films held at 200 °C in air for 40 min. Interestingly, the onset of thermal decomposition for these films was reported to be greater than 250 °C upon scanning at 10 °C/min.<sup>25</sup> Why should these films be so thermally stable in air? Interestingly, there is a thioether group formed for each addition of a thiol group across an ene double bond in the polymerization of thiol–ene systems. It is well known that thioether groups serve as antioxidant stabilizers for many commodity polymers when used in combination with radical scavengers.<sup>102–104</sup> As for long-term thermal stability, Norland Optical literature<sup>116</sup> indicates that photopolymerizable thiol–ene optical and electronic adhesives show little loss in performance or discoloration upon exposure to 50 °C for 3 years! This would translate into extremely long-term stability (>20 years) at room temperature. In a limited investigation, we found that several thiol–ene-based films exhibited excellent color stability (low yellowing) upon exposure to simulated weathering: as long as no aromatic groups are included in the thiols or enes, there is no reason to suspect any problems with long-term weathering. However, other than these limited studies, as far as we are aware, there have been no long-term thermal stability or photostability reports of any photopolymerized thiol–ene networks.

The chemical stability of photopolymerized thiol–ene-based networks has been investigated to a limited extent. In one case from Norland,<sup>116</sup> after the exposure of a film of a thiol–ene-cured adhesive to a wide variety of chemicals for 1 h, relatively good stability was reported. Only an aqueous sodium hydroxide solution resulted in film degradation. Extensive investigations have not been reported to date for the hydrolytic stability of thiol–ene films. However, a personal communication from Woods and Jacobine suggested that under certain conditions, the

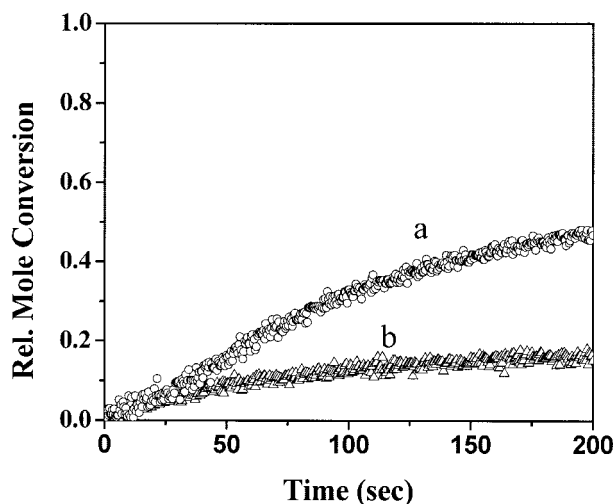
laminating adhesive properties of thiol–ene networks may deteriorate upon aging. A thorough investigation of this phenomenon awaits.

### SPECIFIC NOVEL THIOL–ENE COMBINATIONS

As mentioned in the section on the kinetics and polymerization mechanism for thiol–ene polymerizations, thiols have been reported to undergo free-radical chain reactions with a wide variety of ene monomers. Although the thiol–ene reactions are the fastest with electron-rich enes are still rapid enough for applications for which absolute speed is not the only factor. In recent years, we have conducted a fairly extensive search of new multifunctional ene monomers for use in thiol–ene polymerization. In this section, we present results for these systems as well as others reported in the literature.

#### Thiols and Acrylates

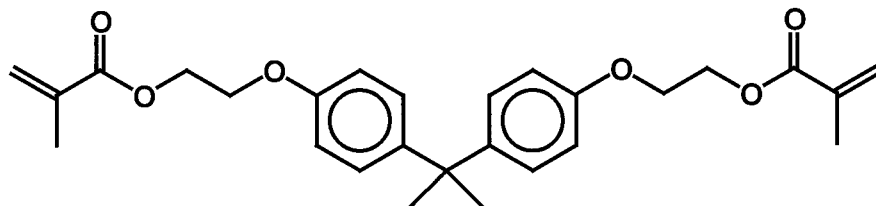
As first introduced in the late 1970s,<sup>8</sup> but essentially ignored for a long period of time, thiol–acrylate mixtures undergo rapid polymerization processes because the acrylate copolymerizes with the thiol (thiyl addition to the acrylate bond followed by the hydrogen abstraction of thiol hydrogen) and homopolymerizes (acrylate group propagation). This unique combination of two types of free-radical polymerization processes provides an opportunity to use a wide variety of acrylates with various chemical structures that combine the features of acrylate networks with thiol–ene networks.<sup>8</sup> Figure 6 shows exotherms for the photopolymerization of a typical difunctional acrylate (HDDA) with 0, 25, or 40 mol % TriThiol1 (based on functional groups) with a low concentration of the cleavage photoinitiator DMPA in air. The rate is accelerated in air by the addition of thiol because of a chain mechanism, as shown in Scheme 3. The plot of the molar conversion versus time in Figure 10 for a 1:3 molar mixture (based on functional groups) of TriThiol1 and HDDA indicates that the acrylate is consumed at a much faster rate than the thiol because the acrylate undergoes both homopolymerization and copolymerization with the thiol. This combination is especially interesting because, as we have already pointed out, Bowman and Cramer<sup>44</sup> showed that the glass-transition region (shown in Fig. 8) is lowered and narrowed dramatically by the addition of TetraThiol1 to HDDA. This clearly indicates that the inhomogeneities in the matrix produced by the polymerization of pure HDDA are to a great extent reduced by the addition of thiol. The exact structure of the network produced by the thiol–acrylate polymeriza-



**Figure 10.** Conversion–time plots of (a) acrylate and (b) thiol from RTIR of the photopolymerization of HDDA with 25 mol % TriThiol1 in the absence of a photoinitiator. The light intensity was 5.0 mW/cm<sup>2</sup>.

tion is not known, but it is obvious that it is quite different from that produced by the polymerization of only the difunctional acrylate: it is more homogeneous with respect to the crosslink density, and as already indicated, this can have far-reaching ramifications for the design of films with tailored physical properties.

Recently, Lecamp et al.<sup>117</sup> conducted a thorough investigation of the photopolymerization of a dimethacrylate polyether oligomer containing an aromatic ether (see MACBPA in Chart 12) and TetraThiol1. They investigated the effect of the light intensity, photoinitiator concentration, and polymerization temperature on the rate by a combination of photo-DSC and real-time FTIR, and they concluded, as with the thiol–acrylate photopolymerization discussed already, that the methacrylate groups are consumed by a combination of homopolymerization and copolymerization, with the methacrylate conversion approximately three times greater than the thiol conversion. The ratio of the rate constant for the hydrogen abstraction of the hydrogen on the thiol group by the carbon-centered radical on the methacrylate radical chain end to the reaction to the rate constant for methacrylate homopolymerization was estimated to be 0.26. The matrix  $T_g$  was highly dependent on the amount of thiol in the mixture, decreasing from approximately 50 °C for the film produced by the polymerization of pure MACBPA to approximately 8 °C for the film obtained by the polymerization of a 1:1 molar functional group mixture of TetraThiol1 and MACBPA. Because of the effect of the thiol in providing a type of plasticizing effect, the conversion of the methacrylate functional groups increased from 62% for the pure dimethacrylate to 95% for the mixture.



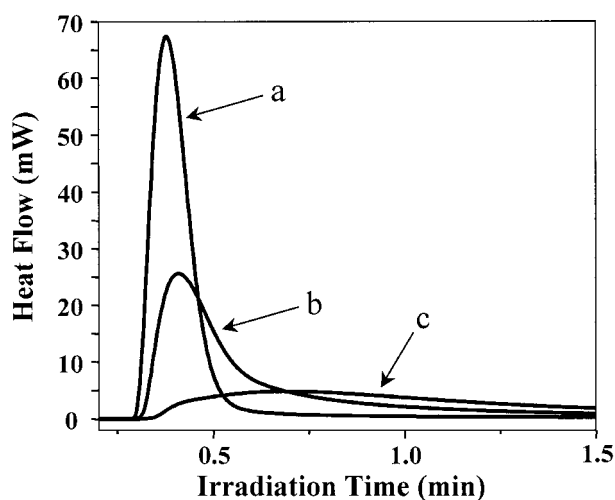
### MAcBPA

**Chart 12.** Structure of a difunctional methacrylate (MAcBPA).

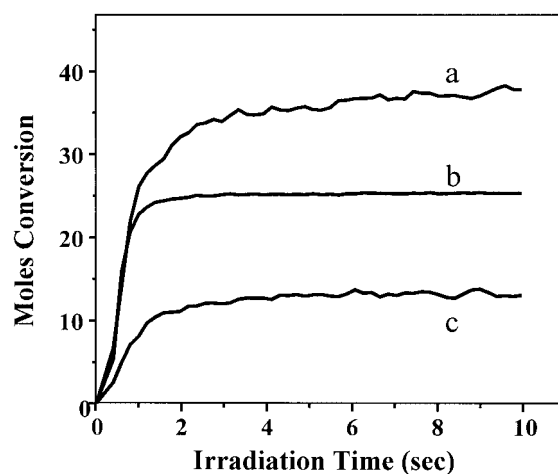
#### Thiols and Unsaturated Ester (UPE)/Vinyl Ether

UPEs with styrene are extensively used as components in thermally cured matrix composites with filler reinforcements. In an attempt to extend the use of thiol-ene polymerization in the context of the photocuring of UPEs (see Chart 1), increasing amounts of the electron-rich ene TEGDVE (Chart 3) were added to a mixture of TriThiol1 and UPE. The photo-DSC results for the photopolymerization of these three component mixtures are shown in Figure 11. As might be expected, as the electron-rich monomer TEGDVE is added to the TriThiol1 and UPE mixture, the rate of polymerization increases dramatically. These results agree with those of Morgan and Ketley,<sup>6</sup> who showed that thiols add rather rapidly to electron-rich monomers such as vinyl ethers. The RTIR results for the polymerization of a 2:1:1 molar mixture of TriThiol1, UPE, and TEGDVE are plotted in Figure 12 with

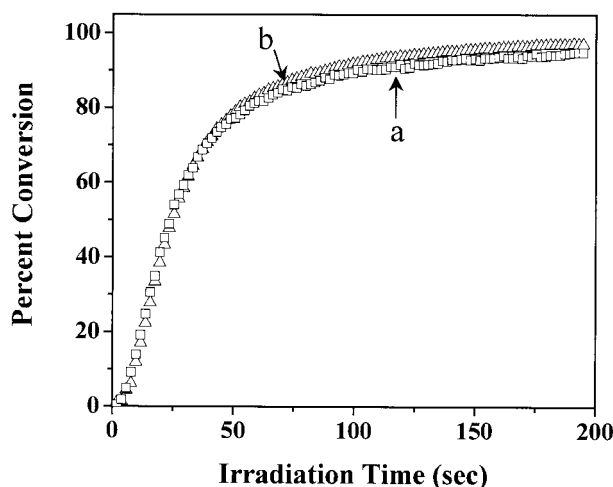
normalization to 100 mol of total functional groups. The results in Figure 12 show that the conversion rate of the vinyl ether groups [Fig. 12(b)] is much faster than that of the UPE groups [Fig. 12(c)] and that the vinyl ether groups are essentially converted before any substantial conversion of the UPE groups. The kinetics of the vinyl and UPE group reactions are mirrored by the thiol conversion in Figure 12(a), which exhibits a very rapid initial loss of thiol groups (reaction with vinyl ether) followed by a much slower conversion (reaction with UPE). Interestingly, the relative number of thiol-functional-group moles converted and the total number of the relative moles of vinyl ether and UPE groups converted are identical, and this indicates that no copolymerization involving vinyl ether and UPE takes place. Because it is well known that vinyl ethers and UPEs readily copolymerize when initiated with a photoinitiator,<sup>118</sup> it can be concluded that the



**Figure 11.** Photo-DSC exotherms of (a) 2:1:1, (b) 1:0.8:0.2, and (c) 1:1:0 TriThiol1–UPE–TEGDVE functional group mixtures in air with 1 wt % 2-hydroxy-2,2-dimethyl acetophenone. The light intensity was 3 mW/cm<sup>2</sup>.



**Figure 12.** Plots of the molar conversion versus the time from RTIR of the photopolymerization of 2:1:1 TriThiol1–UPE–TEGDVE molar functional group mixtures for (a) thiol, (b) vinyl ether, and (c) UPE in nitrogen with 1 wt % 2-hydroxy-2,2-dimethyl acetophenone. The light intensity was 27 mW/cm<sup>2</sup>.

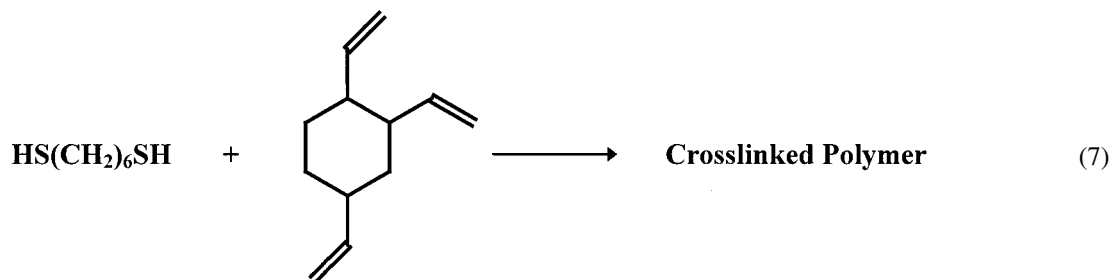


**Figure 13.** RTIR thiol and ene conversion for 1:1 functional group mixtures of (a) 1,2,4-trivinyl cyclohexane and (b) HDDA. The photoinitiator was 1 wt % DMPA. The light intensity was 2.7 mW/cm<sup>2</sup> with 365-nm light.

thiol/vinyl ether copolymerization is much faster than the copolymerization of the vinyl ether and UPE. The kinetics for these three-component systems clearly illustrate that both of the ene components are incorporated into the films by a reaction with the thiol. There is no doubt that the use of multiple enes with different reactivities provides significant leverage in developing physical and mechanical properties in the final cured films.

### Thiols and Difunctional and Trifunctional Olefins

As previously discussed, the reactions of thiols with simple alkenes are quite rapid as long as the ene is not disubstituted. In this context, one of the most intriguing and interesting reactions of thiols is the reaction between alkane dithiols and simple polyenes bearing no heteroatoms. For example, 1,6-hexanedithiol reacts rapidly with a trifunctional ene, as shown in the following reaction, yielding a crosslinked network with thioether heterolinkages in an otherwise hydrocarbon crosslinked network:

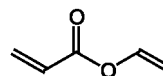


Although the properties of the films produced by this polymerization have not been evaluated to date, Figure 13 shows that the polymerization proceeds to a high conversion quite rapidly. It might be expected that such a film would be thermally, oxidatively, and photochemically stable; however, additional work is required to substantiate this speculation.

### Thiols and Multifunctional Norbornenes

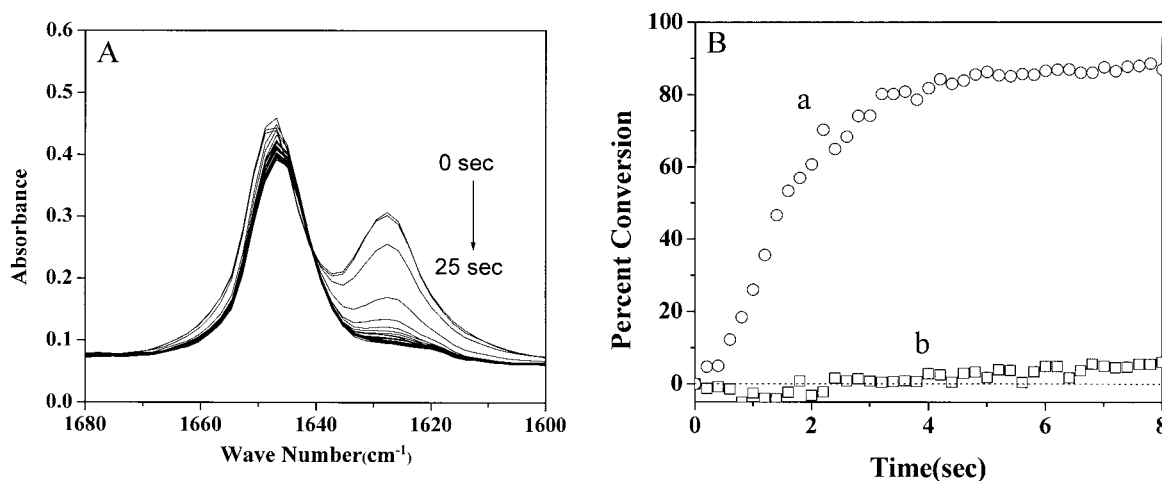
In what has now become a classic work in the field, Jacobine, Woods, and coworkers<sup>23–35</sup> from Loctite authored a series of articles and patents dealing with thiol-ene photopolymerization involving multifunctional norbornenes as the ene component. They synthesized several of the basic norbornene structures (N1–N4 in Chart 11). Although Jacobine<sup>5</sup> summarized their work before 1991 in his review article on thiol-ene photopolymer-

ization, several additional publications subsequently appeared.<sup>23–35</sup> They basically found ultrarapid copolymerization rates attributed to the relief of strain in a highly irreversible addition of the thiyl radical to the norbornene ene groups. The formed radicals undoubtedly abstract thiol hydrogens efficiently. Because of the ease of synthesis of multifunctional norbornenes, such as the simple reaction of multifunctional acrylates with cyclopentadiene, norbornene derivatives with a wide range of chemical structures and numbers of functional groups



**Vinyl Acrylate**

**Chart 13.** Structure of VA.



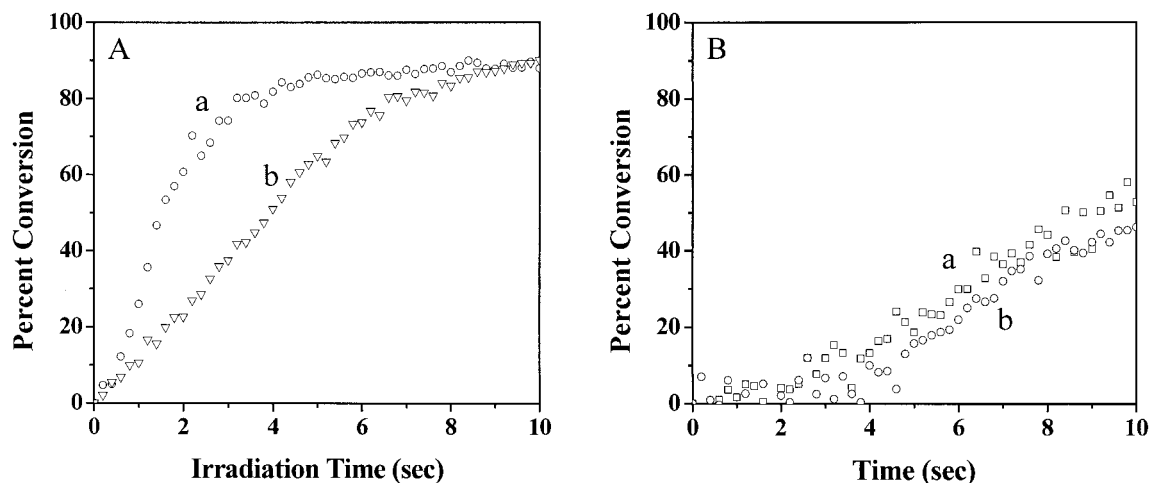
**Figure 14.** (A) IR absorption spectrum change and (B) conversion–time plot of (a) acrylate and (b) vinyl groups in VA photopolymerization without added photoinitiator. The light intensity was 35 mW/cm<sup>2</sup>.

can be synthesized. This allows the tailoring of the final structure of the cured thiol–norbornene mixtures to exhibit a wide range of physical and mechanical properties. For example, they reported films formed from the polymerization of thiol–norbornene mixtures with glass transitions ranging from  $-39$  to  $71$  °C. Higher fractional conversions were obtained when the difunctional norbornenes had a flexible spacer between the two norbornene groups because of the higher mobility afforded by the flexible spacer after the gel-point conversion was reached.<sup>31</sup> The more flexible dinorbornene N2 required a much higher total energy dose ( $17$  mJ/cm<sup>2</sup>) to attain a given conversion than either N1 ( $75$  mJ/cm<sup>2</sup>) or N3 ( $407$  mJ/cm<sup>2</sup>).<sup>31</sup> Shrinkages of less than 5% were reported for these systems.<sup>33</sup> In addition to the fact that most of this shrinkage occurred in the liquid phase, few problems resulting from stress-induced shrinkage during polymerization that occurs during the free-radical polymerization of other multifunctional crosslinking monomers were found. It was even reported that samples could be polymerized to depths greater than  $1.5$  cm.<sup>33</sup> Physical, mechanical, optical, and chemical properties including the refractive index, tensile strength, elongation, hardness, tear resistance, adhesion, aging, oxidative stability, hydrolytic stability, and oxidative stability were reported for selected samples.<sup>25,30,33</sup> The electrical and thermal conductivity and other critical properties were reported in an earlier publication.<sup>26</sup> In a particularly revealing piece of information, the in-phase component of the modulus from DMA was reported to be much greater than  $10^8$  dyn/cm<sup>2</sup>, and as mentioned previously for other thiol–ene-based crosslinked films, the glass-transition regions were very narrow (ca.  $15$ – $20$  °C full width at half-maximum). This was indicative of films with a

highly uniform crosslink density.<sup>34</sup> Readers should consult the original references for complete details on the synthesis, curing rates, and property analysis of films and adhesives made from multifunctional norbornenes and thiols.<sup>23–35</sup>

### Thiols and Vinyl Acrylate (VA)

VA (see Chart 13) also photopolymerizes with multifunctional thiols in the presence or absence of an added photoinitiator. Interestingly, the acrylate group polymerizes by a free-radical homopolymerization, while concurrently the thiol adds to the vinyl ester group in a very rapid free-radical copolymerization process according to the mechanism in Scheme 1. Not only does the curing of mixtures of TriThiol1 and VA constitute interesting possibilities for making multistructured film networks, it is also one of the few examples of two free-radical chain propagation processes occurring simultaneously and independently.<sup>119,120</sup> This unique photopolymerization can be examined in greater detail with RTIR to record the disappearance of all the components (vinyl ester, acrylate, and thiol). Figure 14(A,B), which depicts IR absorbance changes and the resulting conversion plots for the acrylate and vinyl groups during neat VA polymerization with no external photoinitiator, indicates a much faster polymerization rate for the acrylate group than for the vinyl group. The conversion of the acrylate group reaches 80% in about 3–4 s, whereas little of the vinyl functionality is converted. The results in Figure 14(B) indicate that a linear acrylate polymer with vinyl pendant groups is formed until a conversion much greater than 80% is attained. Figure 15(A,B) shows that the addition of 30 mol % TriThiol1 to VA to form a 7:7:6 acrylate/



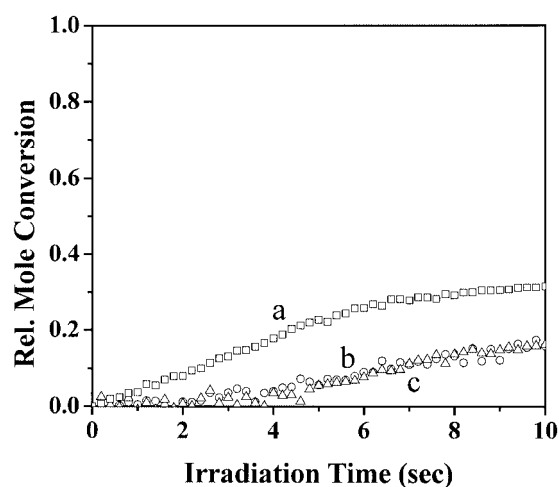
**Figure 15.** Conversion–time plots of (A) acrylate groups with (a) 0 and (b) 30% TriThiol1 and (B) (a) vinyl and (b) thiol groups of a 7:3 VA–TriThiol1 molar mixture without a photoinitiator. The UV light intensity was 35 mW/cm<sup>2</sup>.

vinyl ester/thiol molar functional group mixture results in a large increase in the photoinitiated conversion of the vinyl ester groups, in addition to the rapid acrylate conversion. Converting the results in Figure 15 to relative moles of thiol, vinyl ester, and acrylate versus time and including the results for thiol conversion, we find in Figure 16 that the vinyl ester and thiol groups polymerize at the same conversion rate, whereas the acrylate converts more quickly. An NMR analysis of the polymer clearly shows that the thiol adds exclusively to the vinyl ester, whereas the acrylate undergoes a simultaneous homopolymerization. The exclusive addition of the thiol to the vinyl ester is a result of the very rapid acrylate homopolymerization and the rapid rate of addition of the thiol to the relatively electron-rich vinyl ester. Probably the most interesting aspect of this polymerization process is the distinct rate acceleration of all species when the acrylate conversion is about 20%. At that point, a high enough acrylate conversion is attained to generate enough high-molecular-weight polymer with vinyl ester side groups to react with the multifunctional thiol and form a gel according to eq 5. The resultant network is a unique acrylate homopolymer crosslinked by virtue of the reaction of the vinyl ester side groups with the multifunctional thiol. The interesting aspect of this polymerization is that initially the vinyl ester ene groups are not multifunctional. Only after the acrylate homopolymerizes does a multifunctional vinyl ester form, which then reacts with the multifunctional thiol to form a crosslinked network.

### Thiols and Polymeric Enes

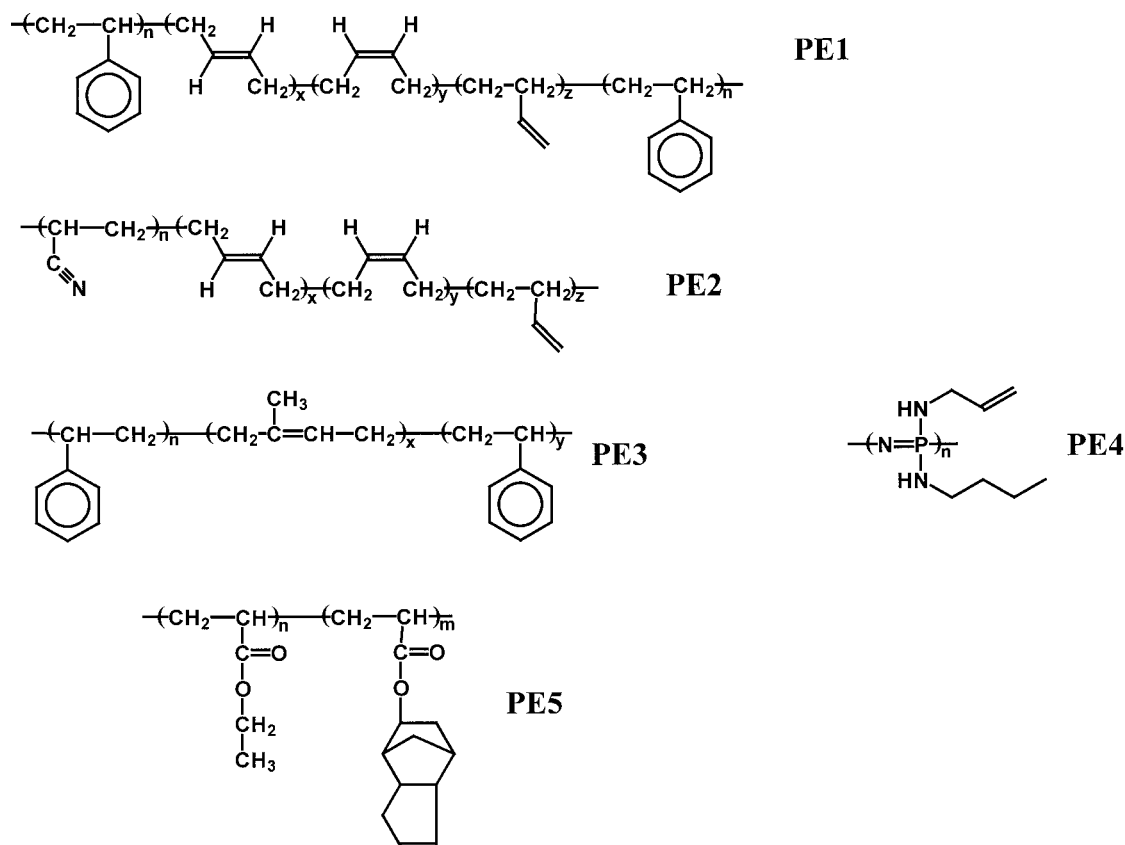
The photopolymerizable mixtures described in this section have polymers with reactive ene-functional side

groups present in the initial mixture along with multifunctional thiols. In essence, these systems work by a free-radical addition of thiols to the available enes attached as pendant side groups to the polymer backbone. The gelation in traditional thiol–ene systems is determined by eq 5, and so if  $f_{\text{ene}}$  is as large as it would be for a polymer with side-chain ene-functional groups, then gelation will occur at a relatively low conversion for thiol and ene groups. The five polymers in Chart 14 have been reported to react with trifunctional or tetrafunctional thiols to induce crosslinking via the thiol–ene free-radical chain process. Each is discussed. The first of these block copolymers, the styrene–butadiene–styrene



**Figure 16.** Relative molar conversion versus time for a 7:3 VA–TriThiol1 molar mixture without a photoinitiator: (a) acrylate, (b) vinyl, and (c) thiol. The light intensity was 35 mW/cm<sup>2</sup>.



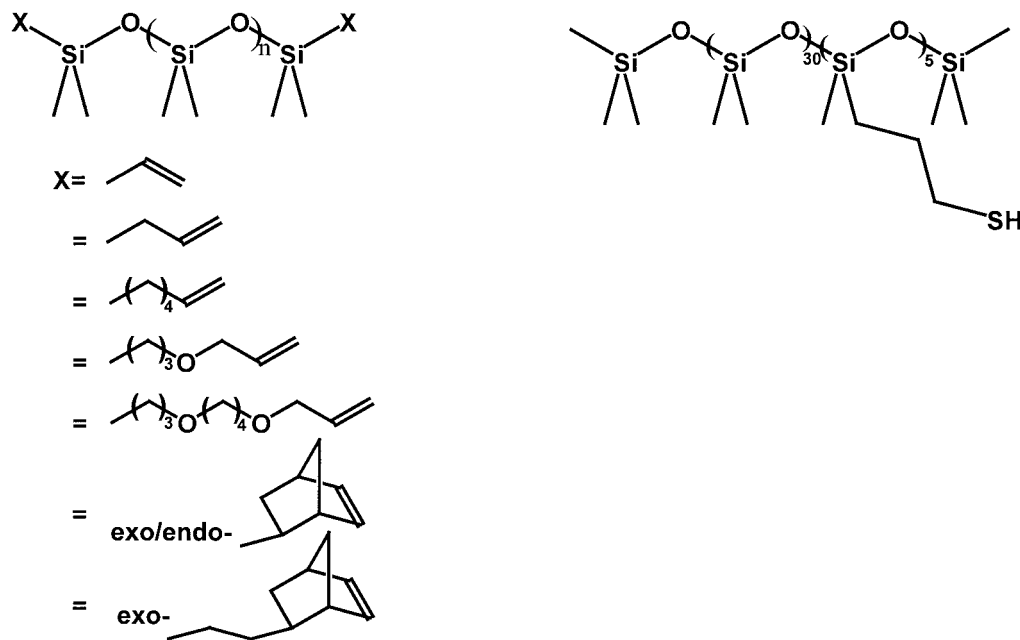


**Chart 14.** Structures of polymers with pendant and internal enes.

block copolymer PE1, consists of three types of functional enes: 1,2-vinyl, 1,4-cis, and 1,4-trans. These polymers typically must be crosslinked to be used as elastomers. Although it is possible to accomplish crosslinking with azides or multifunctional acrylates to produce hard, impact-resistant materials, these processes are relatively inefficient and slow. Several reports<sup>121–127</sup> from a number of laboratories have shown that multifunctional thiols (difunctional, trifunctional, or tetrafunctional) add to the vinyl- and 1,4-*trans*-enes to produce lightly crosslinked elastomers with improvements in the hardness and impact resistance. As discussed,<sup>75–79</sup> the thiyl radical adds to *cis* internal alkenes, inducing an isomerization to the *trans*-ene, as shown in Scheme 2. Per Figure 1, the *trans* structure, once formed, will react with a thiyl radical and thus induce the thiol–ene propagation/chain-transfer sequence of reaction steps. The crosslinking reactions of PE1 and PE2 with multifunctional thiols were reported<sup>121–124</sup> to be much more effective in increasing the crosslink density and gel content than when a difunctional acrylate was used as the crosslinking agent. Acrylates create a very inhomogeneous network in comparison with the thiol–ene crosslinking reaction and do not copolymerize with alkene bonds efficiently.

Decker and coworkers<sup>123,124</sup> also investigated the photochemical crosslinking of a PE1 block copolymer with multifunctional thiols. The rapid crosslinking process was complete in approximately 1 s in air upon exposure to a high-intensity light when a cleavage-type photoinitiator was used. Similar results would also be obtained if a diaryl ketone or no photoinitiator were used, only a longer exposure time would be required. In agreement with Klemm and Gorski,<sup>18</sup> who investigated the free-radical addition of an alkylmonothiol to polybutadiene and model compounds, Decker and coworkers<sup>121–124</sup> reported that the external pendant vinyl bonds were approximately 10 times more reactive than the main-chain butene groups. However, increasing the vinyl group concentration above 8% did not enhance crosslinking because intramolecular polymerization of the pendant vinyl groups with other pendant vinyl groups or main-chain butene groups occurred at these concentrations.

Decker and Viet reported that an elastomeric styrene–isoprene–styrene (PE3) triblock copolymer (shown in Chart 14), which had no external vinyl double bonds, also reacted efficiently with the trifunctional thiol; however, the process did not occur as rapidly as that for the PE1 triblock elastomer with thiol.<sup>121</sup> Interestingly, al-



**Chart 15.** Structures of siloxane-based thiol and enes.

though the diacrylate was not as efficient in crosslinking PE3 as the trithiol, the combination of the trithiol and diacrylate-crosslinked PE3 proceeded much more quickly than either of the individual components alone. This is a case of using mixtures of multiple ene types and structures for a synergistic rate enhancement of the thiol-ene copolymerization reactions.

In other work, Ahn et al.<sup>125</sup> found that allylaminophosphazene hexafunctional monomers and functionalized polymers (PE4; see the structure in Chart 14) readily photopolymerized with various multifunctional thiols. Also, an 80:20 copolymer of dicyclopentenyl acrylate and ethyl acrylate (designated PE5) reacted in a thiol-ene photopolymerization process with the mercaptoglycolate analogue of thiol TriThiol1 with both DMPA and BP as photoinitiators to give crosslinked films.<sup>126</sup> Multicomponent mixtures consisting of PE5 combined with low concentrations of a trifunctional and tetrafunctional acrylate mixture and the tetrafunctional thiol were also photopolymerized to give highly crosslinked gels. In other work, vinyl ether side groups attached to a polymer chain made by the polymerization of phthalic anhydride and glycidyl ether were also crosslinked with a multifunctional thiol upon exposure to light. Finally, Nishikubo et al.<sup>127</sup> reported that this polymer with pendant vinyl ether groups could be readily crosslinked by the addition of 1,4-phenylenedi(methylthiol) and photolysis.

#### Siloxane-Functionalized Thiols and $\alpha,\beta$ -Siloxane Enes

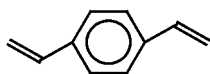
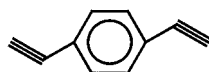
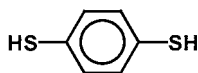
Networks based on crosslinked siloxane polymers are interesting and have received considerable attention in

the literature because they are particularly attractive as low-dielectric, hydrophobic materials with potential applications in optics and electronics as both structural components and adhesives. Several approaches to creating linear siloxane-based films and networks involving thiol-ene chemistry have been reported. As described in Jacobine's review article,<sup>5</sup> which was followed by an extensive investigation by Muller and Kuntze,<sup>128</sup> mixtures of difunctional  $\alpha,\omega$ -siloxanes (see Chart 15 for the structures of several siloxane difunctional enes) and a linear dithiol-terminated silicone as well as a multifunctional thiol siloxane (see Chart 15 for structure) were photopolymerized to produce films with excellent mechanical and physical properties characterized by high tensile strength and elongations of greater than 500%. The following dependence of the polymerization rate on the structure, generally consistent with the electron density of the ene, was reported:

Vinyl > Norborneyl

> Vinyloxyalkyl Alkene > Allyloxyalkyl

In work closely related to thiol-ene photopolymerization processes, siloxane-based crosslinked networks were formed by the water-catalyzed crosslinking of butadiene oligomers functionalized by the photolysis of a monofunctional thiol attached to a trialkoxy silane group: the thiol was added via a radical chain process to pendant 1,2-vinyl groups as well as internal *cis*- and *trans*-ene groups in the backbone of the oligomer.<sup>17</sup> The resultant

**1,4-Divinyl benzene****1,4-Diethynylbenzene****1,4-Benzenedithiol**

**Chart 16.** Structures of an aromatic alkene, an aromatic alkyne, and an aromatic dithiol.

trialkoxysilane modified butadiene oligomer could readily form a siloxane network in the presence of an acid catalyst. The result was a thermally stable, transparent organic-inorganic hybrid network (essentially a modified ceramic material) that had the physical and optical properties associated with a glass-modified organic structure. These materials have potential use as high-performance, abrasion-resistant coatings. A trialkoxysilane with an attached thiol has also been used as an adhesion promoter for photocurable thiol-ene primer coatings on traditional optical lenses.<sup>129</sup>

#### Aromatic Difunctional and Multifunctional Aliphatic Thiols with Divinylbenzenes and Diethynylbenzenes

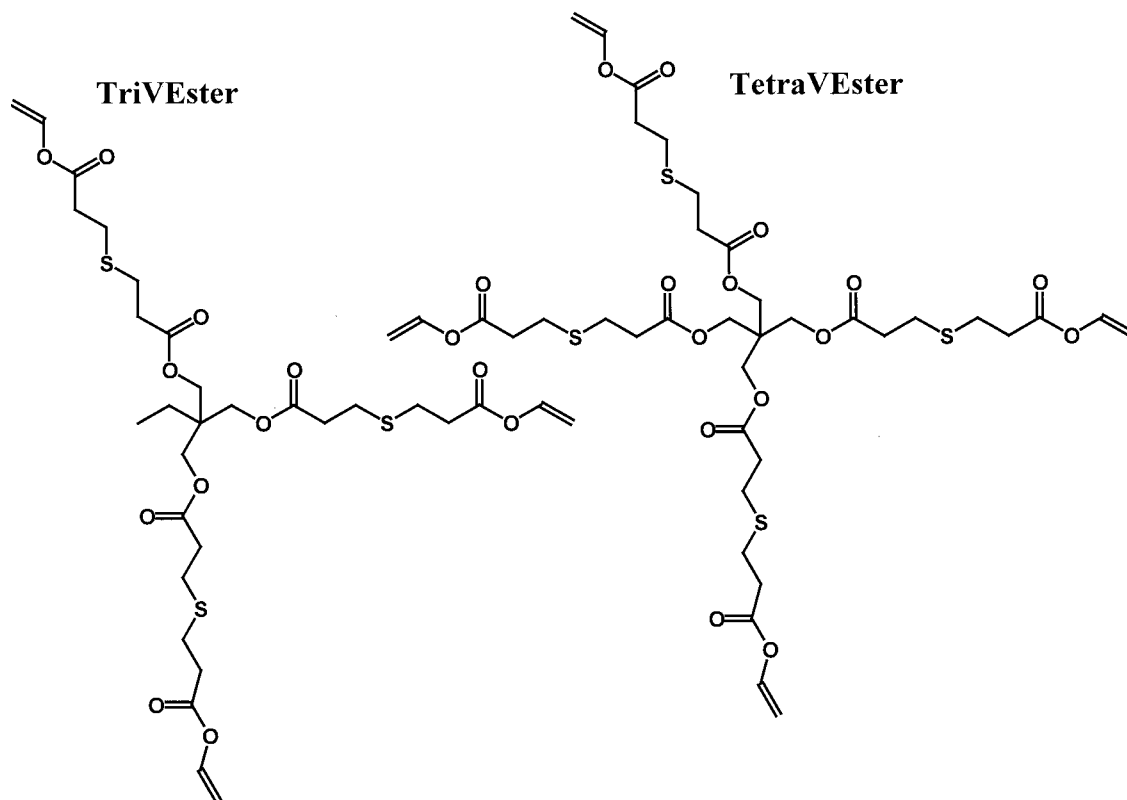
In 1989, Kobayashi et al.<sup>130</sup> reported the photoinitiated polymerization of 1,4-divinylbenzene and 1,4-benzenedithiol (see the structures in Chart 16), which yielded a linear polymer with a refractive index of 1.8. Subsequently, patents were issued dealing with the photopolymerization of 1,4-divinylbenzene and various polythiols for producing crosslinked materials for the fabrication of optical components.<sup>131,132</sup> Since then, a large number of patents describing photocurable resins consisting of multifunctional aliphatic thiols and 1,4-divinylbenzene have appeared.<sup>36-42</sup> In several cases, 1,4-benzenedithiol was copolymerized with acrylates or allyl ethers with high-refractive-index spacer groups. To provide a stable network,

multifunctional acrylates were added to the multifunctional thiol mixture with divinylbenzene, and the total mixture [photoinitiator, meth(acrylates), 1,4-divinylbenzene, and multifunctional thiol] was photopolymerized.<sup>37-42</sup> Although the kinetics and contributions of each of the free-radical reactions involved in the curing process are unknown [1,4-divinylbenzene and 1,4-benzenedithiol copolymerization, 1,4-benzenedithiol and meth(acrylate) copolymerization, meth(acrylate) homopolymerization, 1,4-divinylbenzene and meth(acrylate) copolymerization, and 1,4-divinylbenzene homopolymerization], the final matrix generally had a high glass transition (90 °C) while maintaining the high refractive index found for divinylbenzene-multifunctional thiol-based networks. The resultant crosslinked polymers exhibited a high refractive index (>1.55) and a high Abbe number (>35): an Abbe number reflects the dispersity of different light frequencies passing through an optical lens. These highly rigid materials make excellent optical lenses.

The free-radical photopolymerization of 1,4-diethynylbenzene with 1,4-benzenedithiol (see the structures in Chart 16) in solid<sup>36</sup> and solution<sup>37</sup> phases produced linear polymers, with the *cis*-ene structure being dominant in the polymers formed. Unlike the free-radical polymerization reaction of 1,4-benzenedithiol with 1,4-divinylbenzene, the slow step among the two-step propagation sequence (Scheme 1) was reported to be the addition of the arylthiyl radical to the alkyne triple bond, not the chain-transfer hydrogen-abstraction process. Obviously, the hydrogen-abstraction process for this polymerization is relatively simple in comparison with the reaction of the thiyl radical with the triple bond.

#### Thiols and Multifunctional Vinyl Esters

Chart 17 depicts two multifunctional vinyl ester monomers recently synthesized in the pure form by an amine-catalyzed addition of trifunctional and tetrafunctional thiols to the acrylate group of VA.<sup>88</sup> These monomers copolymerize rapidly with thiols in the presence or absence of a cleavage-type photoinitiator. As shown in Figure 17 for a mixture of a trifunctional vinyl ester (TriVEster) with TriThiol1 and DMPA, very rapid polymerization rates in air can be achieved; similar results were obtained for a mixture of the tetrafunctional vinyl ester (TetraVEster) and TriThiol1. We reiterate that it is also possible to polymerize the mixtures in Figure 17 without the addition of a photoinitiator. Presumably, initiation in this case occurs by the direct excitation of thiol groups, which produce thiyl and hydrogen radicals by the cleavage of the hydrogen-sulfur (HS) bond, as described previously.

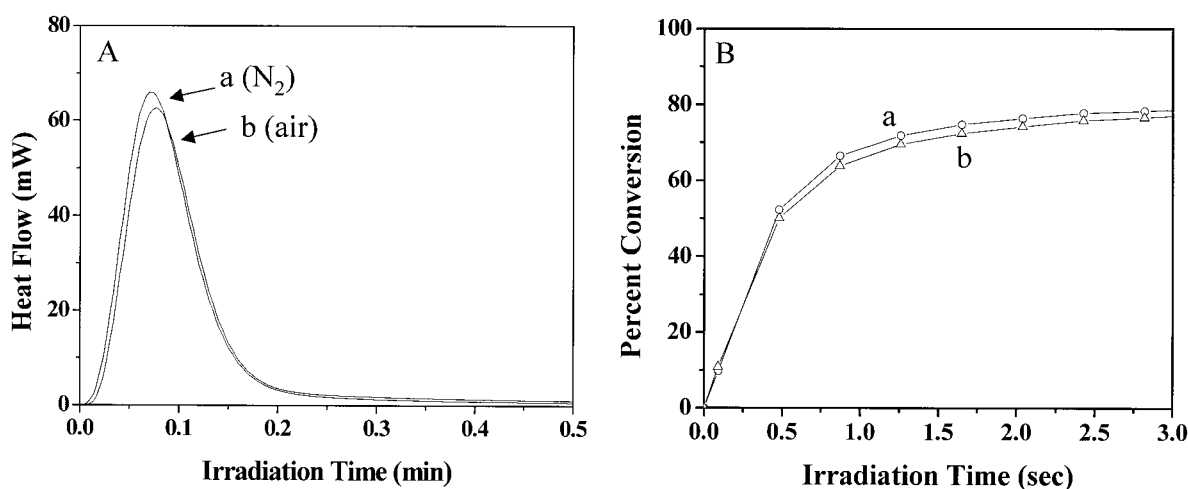


**Chart 17.** Structures of multifunctional vinyl esters.

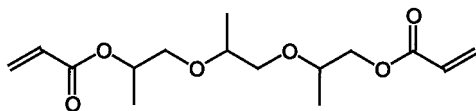
## EXAMPLES OF THIOL-ENE APPLICATIONS

Although thiol-ene formulations have been touted for a large number of applications, it is not clear how wide-

spread their use is currently. Applications reported by Jacobine<sup>5</sup> include protective coatings on floors, conformal coatings on electronic components and printed circuit boards, adhesives, wire coatings, optical fibers, and



**Figure 17.** (A) Photo-DSC exotherms in (a) nitrogen and (b) air and (B) conversion-time plots in (a) nitrogen and (b) air of 1:1 molar mixtures of TriThiol1 and TriVEster with 1.0 wt % DMPA. The light intensities were (A) 2.15 and (B) 14 mW/cm<sup>2</sup> with 365-nm light.



### TPGDA

**Chart 18.** Structure of a difunctional acrylate.

protective coatings on plastics, images, and PDLs. Here, literature examples of some of these applications are updated, and potential new applications introduced since 1992 are added.

### Clear Protective Coatings

Although the use of thiol-ene in protective clear coats has been discussed in the past thoroughly by numerous authors, because of the tremendous potential for a resurgence in applications, it is instructive to reiterate the potential for the use of thiol-ene in photocuring applications of thin films. As we have already pointed out, the choice of enes to use in thiol-ene polymerization ranges from electron-rich vinyl ethers to electron-poor acrylates and UPEs. The almost unlimited choice of enes, combined with the ready availability of a variety of multifunctional thiols, provides formulators with tremendous latitude in selecting a combination of components that can balance demanding requirements. The following is a list of attributes associated with the photocuring process and the resultant properties of the network films that make thiol-ene chemistry particularly attractive for use in protective clear coats:

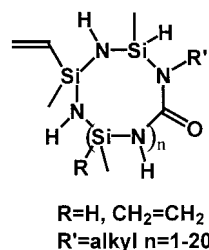
1. They photopolymerize very rapidly in air in comparison with traditional acrylates.
2. They can be photocured without the addition of a photoinitiator, although the rates are much faster when a conventional cleavage photoinitiator is used.
3. The rheology of the initial unpolymerized resin as well as the properties of the final film can be easily modified with a wide variety of enes.
4. The films have highly uniform crosslink density that ensures optimum mechanical performance.
5. The thioether linkages formed during the polymerization process are flexible and serve as efficient antioxidants for the crosslinked network.
6. The films exhibit excellent weatherability.
7. The adhesion of thiol-ene based clear coatings to a large variety of substrates, including plastics, metals, glass, and wood, is outstanding because

of the late gelation process (in comparison with multifunctional acrylates that gel early during the cure process), which allows a significant conversion to be attained while the resin is in the liquid state, and the nature of the thioether group, which promotes adhesion.

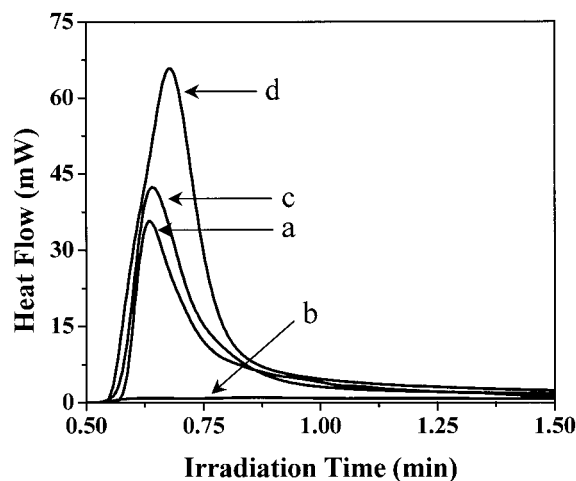
All of these items, the technical aspects of which have been mentioned throughout this review, serve to make thiol-ene chemistry an exceptional choice for use in clear-coat applications.

### Pigmented Coatings

Photopolymerizable pigmented coatings (inks) are typically thin, and because of the light blocking effect of the dispersed pigments, high photoinitiator concentrations are required to obtain acceptable cure rates. The addition of multifunctional thiols to typical acrylate-based pigmented coatings can increase polymerization rates dramatically.<sup>65,71</sup> RTIR results examining the effect of 30 mol % trithiol on the conversion rate of a typical acrylate, tripropyleneglycoldiacrylate (TPGDA; see Chart 18), containing 5 wt % calcium lithol rubine (a typical pigment) in air are shown in Figure 18.<sup>71</sup> The homopolymerization of pigmented TPGDA in air results in little or no conversion because of oxygen inhibition. However, once 30 mol % trithiol is added, the polymerization rate increases significantly, and a final conversion that is slightly greater than that obtained for TPGDA with 5 wt % calcium lithol rubine in nitrogen is achieved. Although the initial rate of conversion is slower for the pigmented thiol-acrylate polymerized in air than for the pigmented TPGDA system polymerized in nitrogen, because of delayed network formation due to the effect of the thiol (even in the case of acrylates for which both acrylate homopolymerization and acrylate-thiol copolymerization occur), generally higher conversions are achieved with reduced overall stress-induced shrinkage problems. This simple example clearly demonstrates that the addition of a thiol to a pigmented



**Chart 19.** Structure of poly(urea silazane) monomers.



**Figure 18.** Photo-DSC exotherms of TPGDA samples in air containing (a) 1 wt % DMPA, (b) 1 wt % DMPA and 5 wt % red pigment, (c) 7 wt % DMPA and 5 wt % red pigment, and (d) 1 wt % DMPA, 5 wt % red pigment, and 35 mol % triethanolamine. The light intensity was 9.98 mW/cm<sup>2</sup> at 365 nm.

photocurable resin will not only enable polymerization to occur in air but also result in higher conversions, which can significantly influence the physical properties of ink coatings. In an extensive investigation in our laboratory, we have found that the use of thiols in highly pigmented and otherwise opaque coatings can greatly enhance polymerization rates and conversions while producing films with improved flexibility and mechanical and physical properties. Cured pigmented thin-film networks are expected to have better substrate adhesion than typical ink formulations. The increase in the rate and the promise of enhanced flexibility, substrate adhesion, and mechanical and physical performance inherent to thiol-ene cured systems should provide the impetus for formulators to develop thiol-ene ink systems. The disadvantages of odor and shelf-life stability can be readily overcome with masking agents or low-odor thiols and thermal stabilizers. There is little question that the use of thiols in photocurable ink applications represents an area for growth and a distinct opportunity for those willing to invest the time and effort.

### Ceramics

In a particularly interesting application for thiol-ene photopolymerization, Bowman and coworkers<sup>45,51,55,56</sup> showed that two poly(urea silazane) monomers (see Chart 19) containing multiple vinyl silane groups effectively underwent rapid copolymerization with multifunctional thiols to high conversions to form a crosslinked

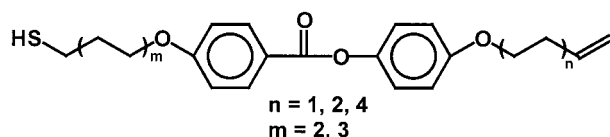
network when a cleavage-type photoinitiator was used to initiate the polymerization (see Scheme 3 for the initiation mechanism with DMPA as the photoinitiator). By controlling the concentration of the photoinitiator, they could produce structures several millimeters thick. Upon the pyrolysis of the films, a uniform shrinkage of the object occurred to give a three-dimensional ceramic material that retained dimensional stability. Such pyrolyzed films open up the way for fabricating microfluidic devices and new optical components.

### Natural Oil Coatings onto Metals

The coating of vegetable oils onto metal aluminum substrates was accomplished by the binding of a silane coupling agent with a mercapto group to aluminum sheets in a collaborative effort between Johansson and Sundell.<sup>75,76</sup> A thin vegetable oil film was then applied and was followed by a subsequent photoinduced attachment of the thiol to unsaturation in the vegetable oil. An isomerization from *cis*- to *trans*-enes was followed by the typical thiol-ene free-radical addition process with the thiol. The whole process was quite slow, but it was nonetheless reported that films of 25 Å or less could be effectively bound to the aluminum substrate. This important result clearly indicates how thiols can be used to bind very thin films to metal substrates (in this case, an environmentally friendly natural oil). The result is illustrative of the type of unique application of thin films that can be accomplished with thiol-ene free-radical chain reactions.

### Liquid-Crystalline Structural Materials

In a series of articles, Broer and coworkers<sup>133–138</sup> described the photoinitiated polymerization of liquid-crystalline monomers with both a terminal thiol group and a terminal ene group on the same molecule (see the structures in Chart 20 with  $n = 1, 2$ , or 4 and  $m = 2$  or 3). These inherently thermotropic liquid-crystalline comonomers, having a *p,p'*-alkoxy substituted on a phenyl benzoate mesogenic unit, readily polymerized via a photoinitiated thiol-ene radical process to yield linear liquid-crystalline polymers. The photopolymerization, initiated with a conventional cleavage photoinitiator, was conducted in three media: a lyotropic bulk phase, an isotropic solvent,<sup>137</sup> and an anisotropic (liquid-crystalline) solvent.<sup>137,138</sup> An almost quantitative conversion of both thiol and ene groups was obtained when the polymerization was conducted at temperatures greater than 100 °C in bulk. The resultant polymers, as expected, were liquid-crystalline with a reasonably wide nematic temperature range. Although not reported, such liquid-crystalline polymers are expected to exhibit higher order parameters than attainable for films or networks formed by chain



**Chart 20.** Structures of liquid-crystalline thiol-ene monomers with both thiol- and ene-functional groups on the same molecule ( $n = 1, 2, \text{ or } 4$  and  $m = 2 \text{ or } 3$ ).

growth polymerization. The authors pointed out that it should be possible to pattern liquid-crystalline structured thiol-ene polymers by lithographic processes at a given temperature. However, no examples of the patterning and formation of specific liquid-crystalline organizational structures were reported. The resultant linear polymers aggregated into a threadlike structure that was formed by phase separation during polymerization.<sup>137</sup> The reports by Broer and coworkers<sup>133–138</sup> point out the potential for using liquid-crystalline thiols and enes to form structured polymers with unusual architectures, and this should be an interesting area for future development.

#### Adhesives and Pressure-Sensitive Adhesives

Woods<sup>139</sup> wrote a comprehensive review of the use of thiol-ene chemistry in adhesives before 1992. He pointed out that in general thiols can be used as chain-transfer agents to limit and control the molecular chain growth of monomers used in formulating pressure-sensitive and laminating adhesives. Besides being useful as components that can alter the performance properties of photocured adhesives, thiols have the added advantage of promoting rapid free-radical polymerization in air (see Scheme 4). As a chain-transfer agent, monofunctional thiols reduce the molecular weights of free-radical polymerizing monomers (e.g., acrylates) and produce tacky polymers that can aid in adhesion. As described by Woods,<sup>139</sup> photocurable adhesives were first described in patents in the early 1970s and since have been used in a variety of situations, many in critical optical applications for which rapid curing to yield materials with good substrate adhesion is paramount. In 1991, Klemm and Sensfuss<sup>14</sup> described optical adhesives made from the copolymerization of divinyl ethers and diallyl ethers with multifunctional thiols. Likewise, Woods, Jacobine, and coworkers<sup>30,34,35,139</sup> reported the use of mixtures of multifunctional norbornenes and multifunctional thiols as laminating adhesives. A large number of adhesives based on thiol-ene photopolymerization by Norland Products have been reported to be suitable for use in a wide variety of both optical and electronic

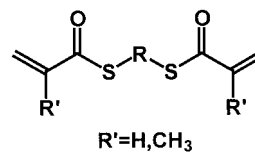
applications: Their base properties are reported in Norland technical literature.<sup>116</sup>

#### Optical Components

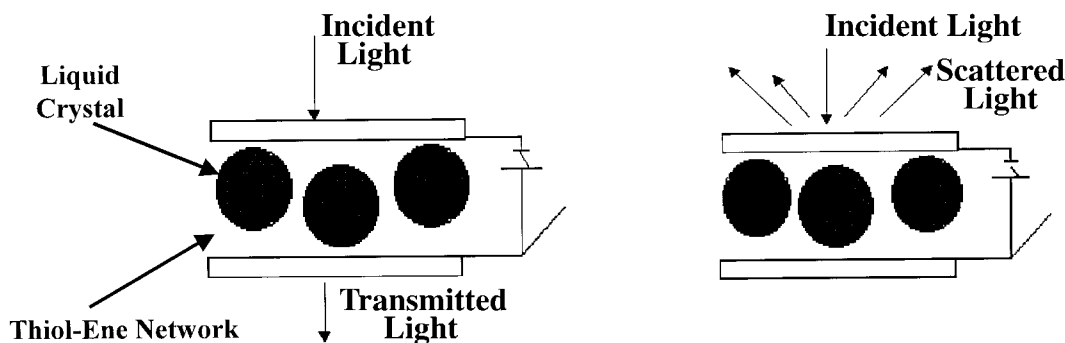
We first focus on a description of thiol-ene applications in optics for which thiol-ene polymerization is likely to have its greatest impact in the future. Several patents filed by SOLA describe the use of photocurable thiol-ene formulations.<sup>36–42,129</sup> The addition of multifunctional thiols to divinylbenzene, as described previously, produces a clear high-refractive-index glassy material with a correspondingly high Abbe number ( $>35$ ). The final networks generally have high glass transitions ( $>90\text{ }^{\circ}\text{C}$ ) and retain the high refractive index found for divinylbenzene-multifunctional thiol-based networks. These highly rigid materials make excellent optical lenses. Characteristic of the thiol-ene copolymerization between a multifunctional thiol and divinylbenzene is the relatively low rate for the chain-transfer step (propagation step 2 in Scheme 1). The resultant slow copolymerization rate results from the low hydrogen-abstraction (chain-transfer) step. In at least one case, Toh and coworkers<sup>37,40–42</sup> describe the use of a second polymerizable component that polymerizes thermally and acts as a stabilizing network. This crosslinked matrix is a hard interpenetrating network and serves to add dimensional stability to the thiol-ene network. The combination is a clear, highly refractive material that is useful as an optical lens.

Toh et al.<sup>40</sup> also reported photocurable optical casting materials consisting of several meth(acrylate) monomers in which at least one of the multifunctional meth(acrylates) had a thioacrylate structure (see the general structure type in Chart 21). These thioacrylates, when polymerized with traditional meth(acrylate) monomers, produced crosslinked networks that did not require components with aromatic groups, which are generally used in the fabrication of high-refractive-index materials.

Dynamic optical components that switch in electrical fields have also been made from thiol-ene systems. These PDLCs are crosslinked networks with liquid-crystal-rich domains that are phase-separated (dispersed).<sup>140–144</sup> The phase-separated nematic liq-



**Chart 21.** Structure of a difunctional thioacrylate.



**Figure 19.** Light scattering in PDLCs.

liquid-crystal molecules in the phase-separated regions align when an electric field is applied. The extraordinary refractive index, which is perpendicular to the propagation vector of the electric field, is chosen to be equal (or almost equal) to the refractive index of the crosslinked network (see Fig. 19 for a layout of a PDLC between two conductive glass plates). Upon the application of the electric field, the film is transformed from an opaque film into an optically transparent film as the directors of the liquid-crystalline domains are oriented in the direction of the applied field. To date, the liquid crystals are mixtures of several cyanobiphenyl molecules, and the crosslinked networks are formed by the copolymerization of a thiol-ene mixture (Norland 65 or a related thiol-ene system, or another similar thiol-ene mixture from Norland Optical Adhesives, Inc.) and a critical concentration of the nonreactive small-molecule liquid crystal. A very large number of publications (several hundred) have appeared since 1991 dealing with every aspect of the phase-separation process, morphology, and optical switching performance of many types of PDLCs based on multifunctional thiol-enes, virtually all from Norland Optical Products, and we only list a few of the references in this review to provide lead references to the interested reader.<sup>140–211</sup> In traditional PDLCs, the photocurable resin, initially optically clear because of the mixing of the liquid crystal with the thiol-ene, which yields a homogeneous solution, becomes opaque as the polymerization proceeds upon illumination with a nontemporally and nonspatially coherent light source, eventually resulting in a crosslinked network with phase-separated liquid-crystal-rich regions and a crosslinked network matrix that has a much smaller impurity concentration of liquid-crystal molecules in the network. The uniformity of the phase-separated liquid-crystal regions is due to the uniformity of the thiol-ene matrix and the sudden gelation during polymerization defined by the gel point equation (eq 6), as discussed previously. NOA65, the thiol-

ene mixture typically used in PDLC applications, is reputed<sup>140</sup> to consist of AE4, which is a tetrafunctional allyl ether formed from the reaction of trimethylolpropane diallyl ether and isophorone diisocyanate, Tri-Thiol1, and 5 wt % BP as a photoinitiator. In films formed by the photopolymerization of NOA65 with a liquid-crystal component,<sup>140–171</sup> the switching efficiency of the film is no doubt dictated by the nature of the basic crosslinked network. As we have stated previously, the uniform crosslink density of the film formed by the polymerization of multifunctional thiol-ene mixtures is characterized by very well-defined phase-separated liquid-crystal-rich regions with relatively narrow dispersity in the shape and size of the liquid-crystalline regions. The unique structure of the thiol-ene networks is a key to success in switching performance for PDLCs based on thiol-ene polymerization. Also, the sudden gelation due to the step-growth nature of thiol-ene polymerization leads to uniform phase separation because the liquid-crystal phase separation occurs well below conversions at which gelation begins. The reaction products present before gelation are low-molecular-weight dimers, trimers, and so forth. When the gelation takes place, the phase-separated liquid-crystal domains are locked in by the crosslinked network. The potential use of virtually any ene to copolymerize with the thiol affords the possibility of creating a network matrix whose chemical structure is tailored to maximize phase separation of the liquid crystal from the crosslinked matrix. In addition to NOA65, there have been several additional reports for other thiol-ene-based photocurable mixtures from Norland Products used in PDLC applications, a few of which are cited here.<sup>172–181</sup>

Recently, there has been a strong interest in HPDLCs and their formation with multifunctional thiol-enes to form a crosslinked matrix. HPDLCs require a high-intensity visible laser for processing and a photoinitiator suitable for excitation by the laser source. Typically, as with traditional thiol-ene-based PDLCs, work has been



conducted with off-the-shelf mixtures from Norland Optical Products.<sup>182–191</sup>

Finally, as we have already indicated, there are many references to optical and electronic applications other than PDLs and HPDLs of the thiol–ene-based resins from Norland Products; only a few representative references are given.<sup>192–206,208–211</sup> Interestingly, these systems have been used off the shelf and in a wide variety of optic and photonic applications. The cured thiol–ene adhesives, with refractive indices ranging from 1.52 to 1.56, are touted for use in optical applications, including bonding associated with prisms, mounting components, the fabrication of light guides, lenses, mirrors, optical fiber splices, the bonding of optical components to plastics and metals, the lamination of polarized film to glass, and the lamination of solar cells, holographic plates, flat-panel displays, and touch screens. They are also useful in applications requiring plastic-to-plastic bonding and metal-to-plastic bonding. The basic thiol–ene optical and electronic adhesive resins are reputed to have excellent shelf-life stability, apparently because of thermal inhibitors added to the mixture. There is no question that the enormous popularity of multifunctional thiol–enes in the optics industry arises from a variety of features inherent to thiol–ene photopolymerization, including the ability to polymerize rapidly in air, the uniformity of the crosslinked network, the resistance of the network to chemical, oxidative, and UV degradation, and the high clarity of the cured matrices.

### Thermosets

Probably the most interesting and potentially important future application of thiol–ene chemistry may well involve the photoinitiated polymerization of very thick thermoset materials that exhibit ultraelastic properties. As already pointed out in a previous section, it is possible to photocure extremely thick (up to a meter or greater) thiol–ene samples through the simple exposure of samples with little or no photoinitiator to low light intensities: the low light intensities are required because heat released by the polymerization can cause severe distortions in the final cured objects. The fascinating aspect of these thermosets is the wide variation in the mechanical properties obtainable. The unprecedented uniformity of the thiol–ene networks and the lack of dangling chain ends produce some extremely unusual properties that are essentially unequalled by conventional polymer materials. As we have mentioned previously, as elastomers, the energy storage modulus upon large deformations is unusually high and unequalled by any other type of elastomer. The glassy thiol–ene-based materials exhibit high storage moduli even when subjected to large deforma-

tions that would literally shatter most glassy materials. The machineability of the thiol–ene elastomers is superior to that of virtually every type of polymer material, offering precision cuts and high tolerances.

Recently, thiol–enes have been used in thermally and photolytically initiated frontal polymerizations to produce thick thiol–ene thermosets.<sup>212,213</sup> Frontal polymerization involves polymerization that, once initiated by light or heat, self-propagates by the diffusion of an exothermic reaction zone. It was reported that thiol–ene plastics 12.5 cm thick could be formed by the frontal polymerization of TriThiol1–HDDA mixtures or TriThiol1–AE2 mixtures that had been degassed and initiated by a thermal point source.<sup>212</sup> More recently, various thiol–acrylate mixtures initiated by UV light have been shown to produce thick thermosets even in air, and this dramatically increases the potential for this novel technology to be used in future applications.<sup>213</sup>

### CONCLUSIONS

Thiol–ene polymerizations have been extensively studied over the last century and are known to proceed via a free-radical step-growth mechanism. Multifunctional thiols will copolymerize with almost any multifunctional ene, and the reaction mechanism affords delayed gelation, low shrinkage, high conversion, and uniform crosslink densities; this results in the ability to produce products with unique physical and mechanical properties. As evidenced by the large number of recent publications and patents highlighted in this review, the use of thiol–ene technology continues to grow as traditionally perceived disadvantages have been dispelled. New synthetic methods for monomer synthesis and various stabilizers have been developed to alleviate issues such as thiol odor and shelf-life stability. The formation of flexible thioether linkages during thiol–ene polymerization results in networks with excellent adhesion, high refractive index, heat resistance, low oxidation, and low water absorption. The ability to achieve thick section cure, the insensitivity to oxygen, fast polymerization rates, low UV degradation, and reactive formulations that can achieve almost 100% functional group conversion provide new opportunities in such diverse areas as machineable plastic construction materials, *in situ* mold compounding, and electrooptic components. Thiol–ene chemistry continues to be used in critical applications for which high performance is required, and as scientists from diverse fields continue to learn about the advantageous characteristics that thiol–ene systems offer, as outlined in this review, there is no

reason not to expect new applications of this technology to be developed throughout the 21st century.

The authors would like to thank Fusion UV Systems, 3M Corporation, and the National Science Foundation (grant 0120943) for finding our basic research on thiolene polymerization.

## REFERENCES AND NOTES

1. Kharasch, M. S.; Mayo, F. R. *Chem Ind* 1938, 57, 752.
2. Marvel, C. S.; Chambers, R. R. *J Am Chem Soc* 1948, 70, 933.
3. Marvel, C. S.; Caesar, P. D. *J Am Chem Soc* 1951, 73, 1097.
4. *The Chemistry of the Thiol Group*; Patai, S., Ed.; Wiley: New York, 1974.
5. Jacobine, A. F. In *Radiation Curing in Polymer Science and Technology III*; Fouassier, J. D.; Rabek, J. F., Eds.; Elsevier: London, 1993; Chapter 7, pp 219–268.
6. Morgan, C. R.; Ketley, A. D. *J Radiat Cur* 1980, 7, 10.
7. Morgan, C. R.; Magnotta, F.; Ketley, A. D. *J Polym Sci Polym Chem Ed* 1977, 15, 627.
8. Gush, D. P.; Ketley, A. D. *Mod Paint Coat* 1978, November, 58.
9. Bush, R. W.; Ketley, A. D.; Morgan, C. R.; Whitt, D. G. *J Radiat Cur* 1980, April 20.
10. Morgan, C. R.; Ketley, A. D. *J Polym Sci Polym Lett Ed* 1978, 16, 75.
11. Morgan, C. R. U.S. Patent 3,784,524, 1974.
12. Ross, J. S.; Leininger, L. W.; Sigel, G. A.; Tian, D. *RadTech NA Tech Conf Proc* 2000, Vol. I, 241.
13. Klemm, E.; Gorski, U. *Angew Makromol Chem* 1995, 224, 125.
14. Klemm, E.; Sensfuss, S. *J Macromol Sci Chem* 1991, 28, 885.
15. Klemm, E.; Beil, U.; Martin, R. *Acta Polym* 1991, 42, 20.
16. Klemm, E.; Beil, U. *Angew Makromol Chem* 1991, 188, 189.
17. Gorski, U.; Klemm, E. *Angew Makromol Chem* 1998, 254, 11.
18. Klemm, E.; Gorski, U. *Angew Makromol Chem* 1993, 207, 187.
19. Klemm, E.; Sensfuss, S.; Holfter, U.; Flammersheim, H. J. *Angew Makromol Chem* 1993, 212, 121.
20. Kuhne, G.; Diesen, J. S.; Klemm, E. *Angew Makromol Chem* 1996, 242, 139.
21. Klemm, E.; Sensfuss, S.; Holfter, U.; Schutz, H. *Makromol Chem* 1990, 191, 2403.
22. Klemm, E.; Bellstodt, K.; Kuse, A.; Martin, R.; Riesenberger, E.; Wolf, H. German Patent DD 301155, 1992.
23. Jacobine, A. F.; Glaser, D. M.; Nakos, S. T. In *Radiation Curing of Polymeric Materials*; Hoyle, C.; Kinstle, J., Eds.; ACS Symposium Series 417; American Chemical Society: Washington, DC, 1990; pp 160–175.
24. Jacobine, A. F.; Woods, J. G.; Rakas, M. A. U.S. Patent 5,516,455, 1996.
25. Woods, J. G.; Rakas, M. A.; Alberino, L. M.; Kropp, P. L.; Sutkaitis, D. M.; Nakos, S. T. WO 95/00869, 1995.
26. Jacobine, A. F.; Glaser, D. M.; Nakos, S. T.; Masterson, M.; Grabek, P. J.; Rakas, M. A.; Mancini, D.; Woods, J. G. In *Radiation Curing of Polymers II*; Randell, D. R., Ed.; RSC Special Publication 89; Royal Society of Chemistry: Cambridge, England, 1991; pp 342–356.
27. Woods, J. G.; Rakas, M. A.; Jacobine, A. F.; Alberino, L. M.; Kropp, P.; Sutkaitis, D. M.; Glaser, D. M.; Nakos, S. T. U.S. Patent 5,459,175, 1995.
28. Jacobine, A. F.; Glaser, D. M.; Grabek, P. J.; Mancini, D.; Masterson, M.; Nakos, S. T.; Rakas, M. A.; Woods, J. G. *J Appl Polym Sci* 1992, 45, 471.
29. Glaser, D. M.; Jacobine, J. F.; Grabek, P. J. U.S. Patent 5,399,624, 1995.
30. Moszner, N.; Schoeb, W.; Rheinberger, V. *Polymer Bulletin* 1996, 37(3), 289.
31. Woods, J. G.; Jacobine, A. F. *RadTech NA Tech Conf Proc* 1992, Vol. I, 173.
32. Glaser, D. M.; Jacobine, J. F.; Grabek, P. J. U.S. Patent 5,459,173, 1995.
33. Dowling, J. P.; Richardson, S. C.; Quigley, K. U.S. Patent 5,358,976, 1994.
34. Rakas, M. A.; Jacobine, A. F. *J Adhes* 1992, 36, 247.
35. Salamon, P. A.; Jacobine, A. F.; Glaser, D. M. *RadTech NA Tech Conf Proc* 1992, Vol. I, 239.
36. Diggins, D. R.; Toh, H. K. European Patent AU PL5865, 1992.
37. Toh, H. K.; Bateman, I. R.; Diggins, D. R.; Cielinski, B. G. U.S. Patent 5,977,276, 1999.
38. Toh, H. K.; Fang, C. WO 00/64956, 2000.
39. Chen, F.; Toh, H. K. U.S. Patent 6,153,663, 2000.
40. Toh, H. K.; Chen, F.; Kok, C. M. U.S. Patent 6,172,140, 2001.
41. Toh, H. K.; Bateman, I. R.; Diggins, D. R.; Cielinski, B. G. U.S. Patent 6,313,251, 2001.
42. Bateman, I. R.; Toh, H. K.; Diggins, D. R.; Kloubek, H. U.S. Patent 6,391,983, 2002.
43. Cramer, N. B.; Bowman, C. N. *J Polym Sci Part A: Polym Chem* 2001, 39, 3311.
44. Cramer, N. B.; Bowman, C. N. *Polym Prepr (Am Chem Soc Div Polym Chem)* 2003, 44(1), 17.
45. Cramer, N. B.; Reddy, S. K.; O'Brien, A. K.; Bowman, C. N. *Macromolecules* 2003, 36, 7964.
46. Cramer, N. B.; Scott, J. P.; Bowman, C. N. *Macromolecules* 2002, 35, 5361.
47. Cramer, N. B.; Davies, T.; O'Brien, A. K.; Bowman, C. N. *Macromolecules* 2003, 36, 4631.

48. Cramer, N. B.; Beckel, E.; Harant, A. W.; Davies, T.; Williamson, D. L.; Bowman, C. N. *Liq Cryst* 2002, 29, 1291.
49. Cramer, N. B.; Bowman, C. N. *Polym Prepr (Am Chem Soc Div Polym Chem)* 2001, 42(2), 699.
50. Beckel, E.; Cramer, N. B.; Harant, A. W.; Bowman, C. N. *Polym Prepr (Am Chem Soc Div Polym Chem)* 2002, 43(2), 530.
51. Reddy, S. K.; Cramer, N. B.; Cross, T.; Raj, R.; Bowman, C. N. *Polym Prepr (Am Chem Soc Div Polym Chem)* 2003, 44(2), 543.
52. Reddy, S. K.; Cramer, N. B.; Cross, T.; Raj, R.; Bowman, C. N. *Chem Mater* 2003, 15, 4257.
53. Cramer, N. B.; Davies, T.; O'Brien, A. K.; Bowman, C. *Polym Prepr (Am Chem Soc Div Polym Chem)* 2003, 44(1), 23.
54. Cramer, N.; Beckel, E.; Harant, A.; Bowman, C. *Proc Int Waterborne High-Solids Powder Coat Symp* 2003, 30, 311.
55. Reddy, S. K.; Cramer, N. B.; O'Brien, A. K.; Cross, T.; Raj, R.; Bowman, C. N. *Macromol Symp* 2004, 206, 361.
56. Cramer, N. B.; Reddy, S. K.; Lu, H.; Cross, T.; Raj, R.; Bowman, C. N. *J Polym Sci Part A: Polym Chem* 2004, 42, 1752.
57. Hoyle, C. E.; Cole, M.; Bachemin, M.; Kuang, W.; Yoder, B.; Nguyen, C.; Jonsson, E. S. *Polym Prepr (Am Chem Soc Div Polym Chem)* 2001, 42(2), 697.
58. Lee, T. Y.; Lowery, K. A.; Guymon, A. C.; Jonsson, E. S.; Hoyle, C. E. *Polym Prepr (Am Chem Soc Div Polym Chem)* 2003, 44(1), 21.
59. Roper, T. M.; Hoyle, C. E.; Guymon, A. C. *Polym Prepr (Am Chem Soc Div Polym Chem)* 2003, 44(1), 111.
60. Clark, S. C.; Hoyle, C. E.; Jonsson, S.; Morel, F.; Decker, C. *Polymer* 1999, 40, 5063.
61. Hoyle, C. E.; Cole, M.; Bachemin, M.; Kuang, W.; Jonsson, S. *RadTech NA Tech Conf Proc* 2002, 675.
62. Cole, M.; Bachemin, M.; Nguyen, C.; Viswanathan, K.; Hoyle, C. E.; Jonsson, S.; Hall, H. K. *RadTech NA Tech Conf Proc* 2002, 211.
63. Hoyle, C. E.; Cole, M.; Bachemin, M.; Kuang, W.; Jonsson, S. *RadTech NA Tech Conf Proc* 2002, 675.
64. Nason, C.; Cole, M.; Hoyle, C. E.; Jonsson, S.; Viswanathan, K. *RadTech NA Tech Conf Proc* 2002, 687.
65. Roper, T. M.; Rhudy, K. L.; Chandler, C. M.; Hoyle, C. E.; Guymon, C. A. *RadTech NA Tech Conf Proc* 2002, 697.
66. Lee, T. Y.; Hoyle, C. E.; Roper, T. M.; Guymon, C. A.; Jonsson, S.; Kudryakov, I. *RadTech NA Tech Conf Proc* 2002, 705.
67. Hoyle, C. E.; Roper, T. M.; Pan, B.; Nason, C.; Lee, T. Y.; Turner, T.; Jonsson, S. *RadTech Eur Tech Conf Proc* 2003, Vol. I, 571.
68. Hoyle, C. E.; Lee, T. Y.; Nason, C.; Roper, T.; Pan, B.; Clark, T.; Guymon, A. C.; Jonsson, S. *RadTech Asia Tech Conf Proc* 2003, 267.
69. Hoyle, C. E.; Cole, M.; Bachemin, M.; Kuang, W.; Kalyanaraman. In *Photoinitiated Polymerization*; Belfield, K. D.; Crivello, J. V., Eds.; ACS Symposium Series 847; American Chemical Society: Washington, DC, 2003; pp 52–64.
70. Pojman, J. A.; Varisli, B.; Perryman, A.; Edwards, C.; Hoyle, C. *Macromolecules* 2004, 37, 691.
71. Roper, T. M.; Guymon, A. C.; Hoyle, C. E. *Polymer* 2004, 45, 2921.
72. Roper, T. M.; Chandler, C.; Guymon, C. A.; Hoyle, C. E.; Jonsson, S. E. *RadTech NA Tech Conf Proc* 2004, 4, 3.
73. Sivertz, C. *J Phys Chem* 1959, 63, 34.
74. Oswald, A. A.; Naegle, W. *Makromol Chem* 1966, 97, 258.
75. Johansson, M.; Samuelsson, J.; Sundell, P. E.; Bexell, U.; Olsson, M. *Polym Prepr (Am Chem Soc Div Polym Chem)* 2003, 44(1), 19.
76. Bexell, U.; Olsson, M.; Johansson, M.; Samuelsson, J.; Sundell, P. E. *Surf Coat Technol* 2003, 166, 141.
77. Walling, C.; Helmreich, W. *J Am Chem Soc* 1959, 81, 1144.
78. Chatgililoglu, C.; Altieri, A.; Fischer, H. *J Am Chem Soc* 2003, 124, 12816.
79. Altieri, C.; Samadi, A.; Sassatelli, F.; Landi, L.; Chatgililoglu, C. *J Am Chem Soc* 2004, 126, 1063.
80. Cole, M. C. Dissertation, University of Southern Mississippi, 2001.
81. Rhenberg, N.; Annby, U.; Sjogreen, C.-A.; Davidson, R. S. WO 01/14300 A1, 2001.
82. Peterson, P. M.; Harlan, R. D.; Schoenberg, J. E. U.S. Patent 6,201,099, 2001.
83. Sangermano, M.; Bongiovanni, R.; Malucelli, G.; Priola, A.; Harden, A.; Rehnberg, N. *J Polym Sci Part A: Polym Chem* 2002, 40, 2583.
84. Wan, Q.; Schrick, S. R.; Culbertson, B. M. *J Macromol Sci Pure Appl Chem* 2000, 37, 1301.
85. Wan, Q.; Schrick, S. R.; Culbertson, B. M. *J Macromol Sci Pure Appl Chem* 2000, 37, 1317.
86. Johansson, M.; Hult, A. *J Coat Technol* 1995, 67, 35.
87. Hult, A.; Johansson, M.; Malmstrom, E. *Macromol Symp* 1995, 98, 1159, 2004.
88. Hoyle, C. E. University of Southern Mississippi, Hattiesburg, MS. Unpublished results, 2004.
89. Belfield, K. D.; Schafer, K. J. In *Photoinitiated Polymerization*; Belfield, K. D.; Crivello, J. V., Eds.; ACS Symposium Series 847; American Chemical Society: Washington, DC, 2003; pp 464–481.
90. Carlson, D. D.; Knight, A. R. *Can J Chem* 1973, 51, 1410.
91. Skerrett, N. P.; Thompson, N. W. *Trans Faraday Soc* 1938, 34, 1238.

92. Hoyle, C. E.; Bowman, C. N. University of Southern Mississippi, Hattiesburg, MS. Unpublished results, 2004.
93. Chiou, B.; English, R.; Khan, S. *Macromolecules* 1996, 29, 5368.
94. Chiou, B.; Khan, S. *Macromolecules* 1997, 30, 7322.
95. Chiou, B.; Khan, S. In *Photopolymerization Fundamentals and Applications*; Scranton, A.; Bowman, C.; Peiffer, R., Eds.; ACS Symposium Series 673; American Chemical Society: Washington, DC, 1997; pp 150.
96. Chiou, B.; Raghaven, S.; Khan, S. *Macromolecules* 2001, 34, 4526.
97. Kloosterboer, J. G.; Van de Hei, G. M. M.; Boots, H. M. J. *Polym Commun* 1984, 25, 354.
98. Bowman, C. N.; Anseth, K. S. *Macromol Symp* 1995, 93, 269.
99. Natarajan, L. V.; Shepherd, C. K.; Brandelik, D. M.; Sutherland, R. L.; Chandra, S.; Tondiglia, V. P.; Tomlin, D.; Bunning, T. J. *Chem Mater* 2003, 15, 2477.
100. Carlsson, I.; Harden, A.; Lundmark, S.; Manea, A.; Rehnberg, N.; Svensson, L. In *Photoinitiated Polymerization*; Belfield, K. D.; Crivello, J. V., Eds.; ACS Symposium Series 847; American Chemical Society: Washington, DC, 2003; pp 65–75.
101. Rehnberg, N.; Harden, A.; Lundmark, S.; Manea, A.; Svensson, L. *Polym Prepr (Am Chem Soc Div Polym Chem)* 2001, 42(2), 701.
102. Scott, G. *Dev Polym Stab* 1981, 4, 1–21.
103. Scott, G. *Dev Polym Stab* 1983, 6, 29–71.
104. Shelton, J. R. *Dev Polym Stab* 1981, 4, 23–69.
105. Sangermano, M.; Bongiovanni, R.; Malucelli, G.; Priola, A.; Harden, A.; Rehnberg, N. *Polym Prepr (Am Chem Soc Div Polym Chem)* 2002, 43(2), 1013.
106. Sangermano, M.; Bongiovanni, R.; Malucelli, G.; Priola, A.; Harden, A.; Rehnberg, N. *J Polym Sci Part A: Polym Chem* 2002, 40, 2583.
107. Davidson, S.; Mead, C. *RadTech Eur Tech Conf Proc* 2003, Vol. I, 579.
108. Rehnberg, N.; Annby, U.; Sjorgreen, C. A.; Davidson, R. S. *PCT Pat. Appl. WO* 2001044377, 2001.
109. Christmas, B. K.; Ho, H.; Ngo, T.; Brenes, D. *Proc RadTech NA Tech Conf Proc* 2002, Vol. I, 712.
110. Christmas, B. K.; Lam, M.; Dilber, J. M.; Vo, M.; Shakati, S. *Proc Radtech NA Tech Conf Proc* 2004, 3, 2.
111. Stahly, E. E. U.S. Patent 3,619,393, 1971.
112. Guthrie, J. L.; Rendulic, F. J. U.S. Patent 3,855,093, 1974.
113. Kehr, C. L.; Wszolek, W. R. U.S. Patent 3,661,744, 1992.
114. Kehr, C. L.; Wszolek, W. R. *Proc Am Chem Soc Div Org Coat Plast Chem* 1973, 33, 295.
115. Hoyle, C. E.; Hensel, R. D.; Grubb, M. B. *Polym Photochem* 1984, 4, 69–80.
116. Norland Optical Products Literature. <http://www.norlandproducts.com>, accessed March 2004.
117. Lecamp, L.; Houllier, F.; Youssef, B.; Bunel, C. *Polymer* 2001, 42, 2727.
118. Decker, C.; Decker, D. *Polymer* 1997, 38, 2229.
119. Lee, T. Y.; Hoyle, C. E.; Roper, T. M.; Guymon, C. A.; Jonsson, E. S.; Kudryakov, I. *RadTech NA Tech Conf Proc* 2002, Vol. I, 705.
120. Lee, T. Y.; Roper, T. M.; Jonsson, E. S.; Guymon, A.; Hoyle, C. E. *Macromolecules* 2004, 37, 3606.
121. Decker, C.; Trieu Nguyen, T. V. *Macromol Chem Phys* 1999, 200, 1965.
122. Decker, C.; Trieu Nguyen, T. V. *J Appl Polym Sci* 2000, 77, 1902.
123. Decker, C.; Trieu Nguyen, T. V. *Polymer* 2000, 41, 3905.
124. Decker, C.; Trieu Nguyen, T. V. *Macromol Chem Phys* 1999, 200, 358.
125. Ahn, K.; Kim, U. Y.; Kim, C. L. *J Macromol Sci Chem* 1986, 23, 169.
126. Eisele, G.; Fouassier, J. P.; Reeb, R. *J Polym Sci Part A: Polym Chem* 1997, 35, 2333.
127. Nishikubo, T.; Kameyama, A.; Sasano, K.; Swaada, M. *J Polym Sci Part A: Polym Chem* 1993, 31, 91.
128. Muller, U.; Kunze, A. *J Macromol Sci Pure Appl Chem* 1996, 33, 439.
129. Weissman, P. U.S. Patent 6,310,161, 2001.
130. Yagi, T.; Morishita, T.; Kobayashi, E. *Zairyo Gijyutsu* 1989, 7, 272.
131. Yoshida, H.; Takenoshita, Y. *Jpn. Kokai Tokkyo Koho* 11, 1988.
132. Kawaki, T.; Kobayashi, M.; Aoki, O.; Yamazaki, Y.; Iwai, T. *Jpn. Kokai Tokkyo Koho* 4, 1989.
133. Lub, J.; Broer, D.; Antonio, M. *Liq Cryst* 1998, 24(3), 375.
134. Lub, J.; Broer, D.; VandenBroek, N. *Liebigs Ann/Recl* 1997, 11, 2281.
135. Lub, J.; Broer, D. J.; Allan, J. F. *Mol Cryst Liq Cryst Sci Tech Sect A: Mol Cryst Liq Cryst* 1999, 332, 2769.
136. Wilberbeek, H. T. A.; Goosens, J. G. P.; Bastiaansen, C. W. M.; Broer, D. J. *Macromolecules* 2002, 35, 8962.
137. Wilberbeek, H. T. A.; van der Meer, M. G. M.; Bastiaansen, C. W. M.; Broer, D. J. *J Phys Chem B* 2002, 106, 12874.
138. Wilberbeek, H. T. A.; van der Meer, M. G. M.; Jansen, M. A. G.; Nelissen, L.; Fisher, H. R.; van Es, J. J. G. S.; Bastiaansen, C. W. M.; Lub, J.; Broer, D. J. *Liq Cryst* 2003, 30, 93.
139. Woods, J. G. In *Radiation Curing*; Pappas, S. P., Ed.; Plenum Press: New York, 1992; p 333.
140. Smith, G. W. *Mol Cryst Liq Cryst* 1991, 196, 89.
141. Bhargava, R.; Wang, S. Q.; Koenig, J. L. *Macromolecules* 1999, 32, 2748.
142. Bhargava, R.; Wang, S. Q.; Koenig, J. L. *Macromolecules* 1999, 32, 8982.

143. Bhargava, R.; Wang, S. Q.; Koenig, J. L. *Macromolecules* 1999, 32, 8989.
144. Bhargava, R.; Levin, I. W. *Macromolecules* 2003, 36, 92.
145. Challa, S. R.; Wang, S. Q.; Koenig, J. L. *Appl Spectrosc* 1996, 50, 1339.
146. Challa, S. R.; Wang, S. Q.; Koenig, J. L. *Appl Spectrosc* 1997, 51, 10.
147. Rafferty, D. W.; Koenig, J. L. *J Phys D: Appl Phys* 2002, 35, 284.
148. Lucchetti, L.; Simoni, F. *J Appl Phys* 2000, 88, 3934.
149. Lucchetta, D. E.; Francescangeli, O.; Lucchetti, L.; Simoni, F. *Liq Cryst* 2001, 28, 1793.
150. Nwabunma, D.; Kim, K. J.; Lin, Y.; Chien, L. C.; Kyu, T. *Macromolecules* 1998, 31, 6806.
151. Nwabunma, D.; Kyu, T. *Macromolecules* 1999, 32, 664.
152. Nwabunma, D.; Chiu, H.-W.; Kyu, T. *Macromolecules* 2000, 33, 1416.
153. Nwabunma, D.; Kyu, T. *Polymer* 2000, 42, 801.
154. Russell, G. M.; Paterson, B. J. A.; Imrie, C. Y. *Chem Mater* 1995, 7, 2185.
155. Korner, W.; Scheller, H.; Beck, A.; Fricke, J. *J Phys D: Appl Phys* 1994, 27, 2145.
156. Nicoletta, F. P.; Santangelo, M.; Hakemi, H.-A.; Caruso, C.; Chidichimo, G. *Mol Cryst Liq Cryst* 1997, 299, 353.
157. Whitehead, J. B.; Gill, N. L.; Adams, C. *Proc SPIE* 2000, 4107, 189–197.
158. Gill, N. L.; Whitehead, J. B.; Woullard, N. *PMSE Book Abstr* 1998, 112.
159. Karapinar, R.; O'Neill, M.; Hird, M. *J Phys D: Appl Phys* 2002, 35, 900.
160. Zheng, W.; Milburn, G. H. *Liq Cryst* 2000, 27, 1423.
161. Lovinger, A. J.; Amundson, K. R.; Davis, D. D. *Chem Mater* 1994, 6, 1726.
162. Caputo, R.; Sukhov, A. V.; Tabiryan, N. V.; Umeton, C. *Chem Phys* 1999, 245, 463.
163. Margerum, J. D.; Yamagishi, F. G.; Lackner, A. M.; Sherman, E.; Miller, L. J.; Van Ast, C. I. *Liq Cryst* 1993, 14, 345.
164. Lackner, A. M.; Margerum, J. D.; Sherman, E. *Liq Cryst* 1995, 261, 593.
165. Parbhakar, K.; Jin, J. M.; Nguyen, H. M.; Dao, L. H. *Chem Mater* 1996, 8, 1210.
166. Doane, J. W.; Yang, D. K.; Chien, L. C. U.S. Patent 5,691,795, 1991.
167. Amundson, K. *Phys Rev E: Stat Phys Plasmas Fluids Relat Interdiscip Top* 1996, 53, 2412.
168. Smith, G. W. *Mol Cryst Liq Cryst* 1994, 239, 63.
169. Smith, G. W. *Mol Cryst Liq Cryst* 1994, 241, 37.
170. Smith, G. W. *Mol Cryst Liq Cryst* 1994, 241, 77.
171. Montgomery, G. P.; Vaz, N. A.; Smith, G. W. *Mol Cryst Liq Cryst* 1993, 225, 131.
172. Takeda, H.; Yoshino, K. *J Appl Phys* 2002, 92, 5658.
173. Kim, J. H.; Lee, K.; Lee, S. D. *Mol Cryst Liq Cryst* 1997, 302, 1067.
174. Miller, S. A.; Huffman, W. A.; Gilbert, L. R.; Vesley, G. F. U.S. Patent 5,876,238, 1999.
175. Klosowicz, S. J.; Piecek, W.; Czuprynski, K. L. *Opt Appl* 2002, 32, 797.
176. Cairns, D. R.; Genin, G. M.; Wagoner, A. J.; Briant, C. L.; Crawford, G. P. *Appl Phys Lett* 1999, 75, 1872.
177. Sixou, P.; Gautier, C.; Villanova, H. *Mol Cryst Liq Cryst* 2001, 364, 679.
178. Matsumoto, S.; Houlbert, M.; Hayashi, T.; Kubodera, K. *Appl Phys Lett* 1996, 69, 1044.
179. Ren, H.; Fan, Y.; Wu, S. *Appl Phys Lett* 2003, 83, 1515.
180. Ren, H.; Fan, Y.; Wu, S. *Appl Phys Lett* 2002, 81, 3537.
181. Matsumoto, S.; Sugiyama, Y.; Sakata, S.; Hayashi, T. *Liq Cryst* 2000, 27, 649.
182. Lucchetti, L.; Di Bella, S.; Simoni, F. *Liq Cryst* 2002, 29, 515.
183. Date, M.; Takeuchi, Y.; Tanaka, K.; Kato, S. *J Soc Inf Display* 1998, 6, 37.
184. Date, M.; Takeuchi, Y.; Tanaka, K.; Kato, S. *J Phys D: Appl Phys* 1999, 32, 3164.
185. Date, M.; Takeuchi, Y.; Tanaka, K.; Kato, S. *J Phys D: Appl Phys* 1999, 31, 2225.
186. Pinto-Iguanero, B.; Olivares-Perez, A.; Fuentes-Tapia, I. *Opt Mater* 2002, 20, 225.
187. Natarajan, L. V.; Shepherd, C. K.; Brandelik, D. M.; Sutherland, R. L.; Chandra, S.; Tondiglia, V. P.; Tomlin, D.; Bunning, T. J. *Chem Mater* 2003, 15, 2477.
188. Park, S. H.; Xia, Y. *Langmuir* 1999, 15, 266.
189. Fuh, A. Y. G.; Ko, T. C.; Tsai, M. S.; Huang, C. Y.; Chien, L. C. *Mol Cryst Liq Cryst* 1998, 321, 809.
190. Fuh, A. Y. G.; Tsai, M. S.; Huang, C. Y.; Ko, T. C.; Chien, L. C. *Opt Quant Electron* 1996, 38, 1535.
191. He, G. S.; Lin, T. C.; Hsiao, V. K. S.; Cartwright, A. N.; Prasad, P. N.; Natarajan, L. V.; Tondiglia, V. P.; Jakubiak, R.; Vaia, R. A.; Bunning, T. J. *Appl Phys Lett* 2003, 83, 2733.
192. Singh, P. K.; Lakshmikumar, S. T. *Semicond Sci Technol* 2002, 17, 1123.
193. Ozaki, M.; Shimoda, Y.; Kasano, M.; Yoshino, K. *Adv Mater* 2002, 14, 514.
194. Montechhi, M.; Ingram, Q. *Nucl Inst Methods Phys Res Sect A* 2001, 465, 329.
195. Tang, H.; Cao, G.; Taboada, J. M.; Chen, R. T. J. *Polym Sci Part B: Polym Phys* 1997, 35, 2385.
196. Ahn, S. W.; Shin, S. Y. *IEEE J Sel Top Quant Electron* 2001, 7, 819.
197. Odom, T. W.; Love, C. J.; Wolfe, D. B.; Paul, K. E.; Whitesides, G. M. *Langmuir* 2002, 18, 5314.
198. Rogers, J. A. *J Appl Phys* 1999, 86, 2959.
199. Park, B.; Eom, S. Y.; Suh, S. W.; Lim, M.; Lee, W. K.; Lee, S. D. *Mol Cryst Liq Cryst* 1995, 267, 21.

200. Ventura, M. J.; Straub, M.; Gu, M. *Appl Phys Lett* 2003, 82, 1649.
201. Galajda, P.; Ormos, P. *Appl Phys Lett* 2002, 80, 4653.
202. Hsu, Y. Y. U.S. Patent 6,120,701, 2000.
203. Hsu, Y. Y. U.S. Patent 6,174,467, 2001.
204. Hsu, Y. Y. U.S. Patent 6,203,723, 2001.
205. Lackritz, H. S.; Kowalczyk, T. C.; Lee, Y. C.; Deacon, D. A. G. U.S. Patent 6,236,774, 2000.
206. Lackritz, H. S.; Kowalczyk, T. C.; Lee, Y. C.; Deacon, D. A. G. U.S. Patent 6,724,968, 2004.
207. Debe, M. K. U.S. Patent 5,336,558, 1994.
208. Tanaka, K.; Kato, K.; Tsuru, S.; Sakai, S. U.S. Patent 5,751,452, 1998.
209. Wu, S.-T.; Mo, T.-S.; Fuh, A. Y.-G.; Wu, S.-T.; Chien, L.-C. *Jpn J Appl Phys Part 1: Reg Pap Short Notes Rev Pap* 2001, 40, 6441.
210. Ren, H.; Wu, S.-T. *Appl Phys Lett* 2002, 81, 3537–3539.
211. Ren, H.; Fan, Y.-H.; Wu, S.-T. *Appl Phys Lett* 2003, 83, 1515.
212. Pojman, J. A.; Varisli, B.; Perryman, A.; Edwards, C.; Hoyle, C. *Macromolecules* 2004, 37, 691–693.
213. Nason, C.; Hoyle, C. E.; Pojman, J. A. *Polym Prepr (Am Chem Soc Div Polym Chem)* 2004, 45(2).