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Thiol−Allyl Ether−Methacrylate Ternary Systems. Polymerization Mechanism

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ABSTRACT: The polymerization mechanism of the ternary thiol−allyl ether−methacrylate monomer system has been investigated. The effects of various factors including the thiol concentration, functionality, and structure on the polymerization mechanism, the polymer network structure, and mechanical properties were examined. The thiol−allyl ether−methacrylate ternary system uniquely exhibits two different polymerization regimes: a methacrylate homopolymerization dominated regime coupled with chain transfer to thiol followed by a second thiol−ene polymerization dominated regime. This polymerization mechanism is primarily due to the chemical nature of the methacrylate and allyl ether double bonds. Because methacrylate homopolymerization with chain transfer reactions to thiols dominates the initial stage of polymerization (up to 60% of the methacrylate conversion), the concentration and structure of the thiol significantly affect the polymerization processes and polymer network structure. The methacrylate chain length significantly decreases from 20 to 1.5 with increasing thiol content, and the methacrylate conversion rate during the first polymerization regime depends linearly on the $[SH]_0$/$[\text{methacrylate}]_0$ ratio. The overall polymerization rates and glass transition temperature increase significantly with increasing thiol functionality, while the methacrylate final conversion decreases more than 20% due to the formation of the highly cross-linked network.

Introduction

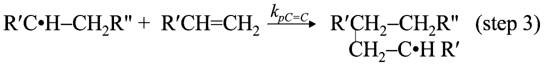
Thiol−ene reactions are a unique class of photopolymerization reactions that exhibit unique and often advantageous properties in regards to the polymerization processes and resulting polymer properties. The photopolymerization is a free-radical reaction that proceeds by a step growth mechanism involving free-radical addition (step 1) followed by a chain-transfer reaction (step 2).[1−4] In thiol−ene polymerizations a broad spectrum of physical properties are achieved because a wide variety of enes such as acrylate, vinyl ether, allyl ether, vinyl acetate, and alkene are used. Also, delayed gelation,[5] low polymerization shrinkage,[1,6,7] reduced oxygen inhibition,[1,2,8−10] photoinitiatorless polymerization,[11,12] and homogeneous polymer structures[1,2] of thiol−ene polymerizations promise thiol−ene polymers as high-performance materials. However, further improvements of mechanical properties of thiol−ene materials are highly desirable.

$$\mathrm{RS^{\bullet} + R'CH{=}CH_2 \xrightarrow{K_{psc}} R'C^{\bullet}H{-}CH_2SR} \quad \text{(step 1)}$$

$$\mathrm{R'C^{\bullet}H{-}CH_2SR + RSH \xrightarrow{k_{CT}} R'CH_2{-}CH_2SR + RS^{\bullet}} \quad \text{(step 2)}$$

One of the current drawbacks of thiol−ene materials is that hardness, toughness, and high glass transition temperature are not easily attainable properties. This limitation is primarily due to the unique cross-linked network structure of thiol−ene materials. In traditional thiol−ene systems where ene monomers do not undergo homopolymerization, the polymerization occurs by a stoichiometric reaction between thiol and ene monomers, a free-radical addition (step 1) followed by a chain-transfer reaction (step 2). In this case, multifunctional thiol−ene monomers produce cross-linked materials with relatively low cross-link density compared to the monomers polymerizing by a chain growth mechanism such as (meth)acrylates. In (meth)acrylate systems, each monomer is reacted with two other monomers at both ends of the double bond while in thiol−ene polymerization a thiol or ene functional group is reacted only one time with another functional group. In this case, the distance between cross-linking sites is much longer than (meth)acrylate systems. In addition, flexible thioether linkages are formed between the two cross-link sites. These characteristics generally result in low cross-link density, toughness, and glass transition temperature of thiol−ene polymers.

Utilization of thiol and ene monomers with rigid structure can produce rigid thiol−ene polymers. However, synthesis of new monomers is necessary due to limited availability of rigid thiol and nonhomopolymerizable ene monomer structures. To increase cross-link density and mechanical properties of thiol−ene polymers, thiol−ene systems containing ene monomers capable of homopolymerization such as thiol−acrylate and thiol−methacrylate system are designed. In this case, homopolymerization of the ene (step 3) is considered along with the thiol−ene step growth mechanism (steps 1 and 2), resulting in a mixed step-chain polymerization mechanism. However, because of the homopolymerization tendency of (meth)acrylates, only a relatively low concentration of thiol functional groups can be utilized while obtaining a high ene conversion.[13] This limitation frequently results in large amounts of extractable thiol monomers in cured products.



$$\mathrm{R'C{\bullet}H{-}CH_2R'' + R'CH{=}CH_2 \xrightarrow{k_{pC=C}} \underset{\textstyle |\atop\textstyle CH_2{-}C{\bullet}H\,R'}{R'CH_2{-}CH_2R''}} \quad \text{(step 3)}$$

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Another approach to develop hard thiol−ene polymers is to design thiol−vinyl−vinyl ternary systems. In thiol−vinyl−vinyl ternary systems, fundamental understanding of thiol−ene photopolymerization kinetics is more essential to design and control the polymerization processes and network structure as compared to binary thiol−ene systems. In fact, extensive research has been performed on the polymerization kinetics of various thiol−vinyl binary and thiol−vinyl−vinyl ternary systems.[11−19] In these studies, kinetic parameters of each propagation step (k_{psc}, k_{CT}, and $k_{pC=C}$) and rate-determining step of the polymerization are reported. These reports indicated that the extent of vinyl homopolymerization and the thiyl radical reactivity toward both vinyl groups determines the polymerization mechanism and network evolution of the thiol−vinyl−vinyl ternary systems. Hence, the polymerization processes and resultant network structure can be readily controlled by selecting different vinyl monomer structures. When two vinyl monomers undergoing no homopolymerization are used, the traditional thiol−ene reaction occurs. On the other hand, when one of the vinyl monomers undergoes homopolymerization, the polymerization proceeds by both step and chain growth mechanisms with high thiol conversion, unlike thiol−(meth)acrylate binary systems. In this case, a unique platform to design and control the polymerization kinetics, cross-linked network structure, and mechanical properties is achieved. Although several thiol−vinyl−vinyl ternary systems have been investigated, ternary systems containing methacrylate monomers have not been extensively examined. Because methacrylates exhibit an enhanced homopolymerization tendency and a different chemical nature of the double bonds relative to acrylates, the polymerization kinetics of ternary systems containing methacrylates are distinctly different from the thiol−vinyl−acrylate ternary systems. Also, because of the higher glass transition temperature of methacrylates as compared to acrylates, it is expected that methacrylates are a better candidate to design thiol−vinyl−vinyl polymers with enhanced mechanical properties.

Herein, we evaluate thiol−allyl ether−methacrylate ternary systems. A detailed polymerization mechanism is proposed for the multifunctional thiol−allyl ether−methacrylate systems, and the effect of monomer chemistry on the polymerization process is discussed. This work presents how the polymerization process and mechanical properties are altered by controlling polymerization kinetics. Understanding of the polymerization kinetics is used to develop the relationship between polymerization mechanism and mechanical properties.

Experimental Section

Materials. 1,6-Hexanediol dimethacrylate (HDDMA) and 1,6-hexanediol diacrylate (HDDA) were donated by Cytec Specialty Chemicals (Smyrna, GA). 1,6-Hexanedithiol (HDT), trimethylolpropane tris(3-mercaptopropionate) (TMPTMP), pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), triethylene divinyl ether (TEGDVE), and 1,3,5-triallyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (TATATO) were obtained from Aldrich. Glycol dimercaptopropionate (GDMP) was donated by Evans Chemetic Co. 2,2-Bis[4-(2-hyroxy-3-methacryloxyprop-1-oxy)phenyl]propane (BisGMA) was donated by Esstech. The photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA), was purchased from Ciba-Geigy. All monomers and the photoinitiator were used as received.

Methods. Kinetic profiles of the UV-induced polymerizations were studied using real-time FTIR, a Nicolet 750 Magna FTIR spectrometer with a KBr beam splitter and an MCT detector. Infrared spectra were recorded on a spectrometer designed to allow light to impinge on a horizontal sample using a fiber-optic cable. Monomer samples with thicknesses of about 25 μm were placed between two sodium chloride plates while the FTIR sample chamber was continuously purged with dry air. A series of infrared absorption spectra were obtained under continuous UV irradiation with 3.5 scans/s. The thiol functional group conversion was monitored at 2575 cm^{-1} (S−H stretching). The methacrylate and acrylate double bond conversions were calculated from 816 and 811 cm^{-1} (C═C−H out of plane bending), respectively. All IR absorption peaks of the allyl ether and vinyl ether double bonds (C═C−H stretching peak around 3100 cm^{-1}, C═C−H bending peak around 1640 cm^{-1}, and C═C−H out of plane bending around 900 cm^{-1}) are overlapped with methacrylate or acrylate peaks. However, the C═C−H stretching peaks of the allyl ether (3085 cm^{-1}) and vinyl ether (3117 cm^{-1}) are only partly overlapped with a methacrylate peak at (3105 cm^{-1}). Allyl ether and vinyl ether conversions were calculated by measuring the height of the C═C−H stretching peak shoulder of the allyl ether and vinyl ether peaks at 3081 and 3122 cm^{-1}, respectively. To ensure the accuracy of the allyl ether conversion calculated, a deconvolution technique was employed to separate an overlapping C═C stretching band of the allyl ether double bond at 3105 cm^{-1} from the methacrylate double bond at 3085 cm^{-1}. The allyl ether conversion obtained from peak height measurement was confirmed by comparing with the deconvolution results. The peaks separated by a deconvolution technique are shown in Figure 1. Conversions were calculated using the ratio of peak areas and/or height as a function of time to the peak areas and/or height prior to polymerization. All reactions were performed under ambient conditions. Polymerizations were initiated via an EXFO Acticure light source (EXFO, Mississauga, Ontario) with a 320−500 nm filter. Irradiation intensities were measured with an International Light, Inc., model IL1400A radiometer (Newburyport, MA).

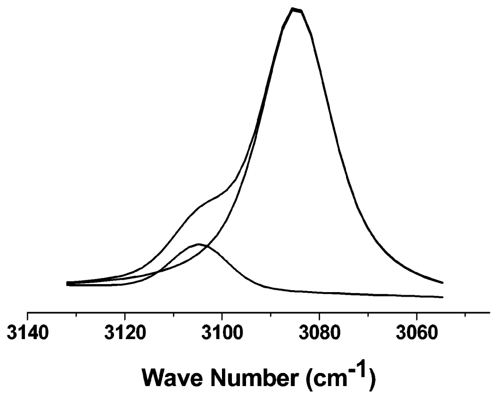

Figure 1. Deconvolution result of C═C−H stretching peaks of the allyl ether and methacrylate double bond at 3085 and 3105 cm^{-1}, respectively.

Results and Discussion

In thiol−vinyl−vinyl ternary systems polymerizing by mixed step and chain growth mechanisms, the polymerization kinetics are dominated by two factors. First is the reactivity of thiyl radicals toward vinyls which primarily depends on the electron density of the vinyl double bonds and the vinyl radical stability. Vinyls with high double bond electron density exhibit rapid addition of electrophilic thiyl radicals. If the vinyl radicals are stabilized by resonance and induction effects, the addition rate should increase further. Second is the chain transfer reaction rate for vinyl radicals to thiols. Vinyls with stabilized radicals exhibit a reduced chain transfer rate to thiol and enhanced homopolymerization tendencies. Therefore, the overall polymerization mechanism of thiol−vinyl−vinyl ternary systems can be altered on the basis of the nature of the two vinyl monomer structures. One example of a thiol−vinyl−vinyl-ternary system previously studied is the thiol−vinyl ether−norbornene system.[18] In this case, the reactivity of the thiyl radicals toward two nonhomopolymerizable enes is the same or slightly different and the stability of the ene radicals is low (no homo- and

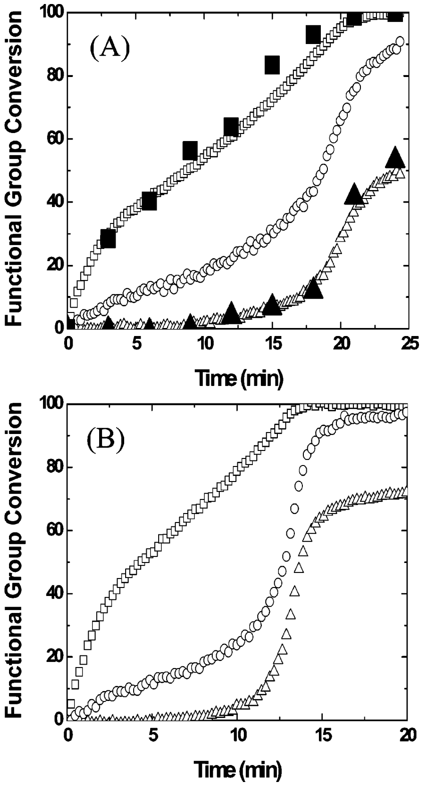

Figure 2. Functional group conversion vs time plots of HDT−TATATO−HDDMA ternary mixtures: methacrylate (□), thiol (○), and allyl ether (△) conversion. The conversion of methacrylate (■) and allyl ether (▲) double bonds calculated by the deconvolution technique. HDDMA content is (A) 50 and (B) 30 wt % while the TATATO/HDT functional group ratio is 1:1. Samples contain 0.1 wt % of DMPA and are irradiated at 15 mW/cm^2 using 320−500 nm light.

copolymerization between ene monomers). In this system, polymerization kinetics follow a traditional step growth thiol−ene reaction where thiol and ene functional groups are consumed in a nearly 1:1 stoichiometric ratio. Another example of a previously studied system is the thiol−vinyl ether−acrylate ternary system.[18] In this case, thiyl radicals preferentially react with the electron-rich vinyl ether double bonds and acrylate double bonds exhibit a homopolymerization tendency as well as chain transfer reaction to thiol functional groups. This results in both step and chain growth polymerization processes occurring simultaneously. The thiol−allyl ether−methacrylate might be expected to exhibit similar polymerization kinetics to the thiol−vinyl ether−acrylate case. However, as shown in this study, the higher electron density of the methacrylate double bonds and the increased stability of the methacrylate radicals compared to those of acrylates lead to a totally different polymerization mechanism.

Figure 2 presents the polymerization kinetics of hexanedithiol (HDT)−1,3,5-triallyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (TATATO)−1,6-hexanediol dimethacrylate (HDDMA) mixtures. The HDDMA content is 50 or 30 wt % while the allyl ether and thiol functional group ratio (TATATO/HDT) is 1:1 in both samples. In both cases, a very unique polymerization tendency is observed. During the initial polymerization stage (up to 60% methacrylate conversion), TATATO does not polymerize to any significant extent. However, the methacrylate conversion increases rapidly, and the thiol functional group conversion increases slowly. TATATO does not participate in the polymerization reaction during which ∼20% of the thiol functional groups are consumed, and the methacrylate double bond conversion reaches 60%. It is presumed that thiyl radicals produced by the chain transfer reaction of methacrylate radicals to thiol functional groups do not react significantly with allyl ether double bonds during this stage. At the latter stage of polymerization (after the methacrylate functional group conversion reaches 60%), the thiol−ene polymerization rate increases dramatically. This result indicates that two separate polymerization regimes occur in this ternary system: a methacrylate homopolymerization regime with chain transfer to thiol followed by a thiol−ene polymerization regime. This result is consistent with kinetic parameters for each propagation step in the thiol−allyl ether−methacrylate ternary system that were previously reported.[19] It is reported that the thiyl radical addition rate to a methacrylate double bond is 1.6×10^6 L/(mol s), which is ∼5 times faster than the rate constant for addition to an allyl ether double bond (3.4×10^5 L/(mol s)). Therefore, at the initial polymerization stage where the methacrylate concentration is high, there is very little thiyl radical addition to allyl ether double bonds, resulting in negligible allyl ether conversion. Only after significant consumption of methacrylate double bonds do the thiyl radicals react with allyl ether double bonds to any significant extent. Based on our previous report, the ratio of the methacrylate propagation rate parameter and chain transfer rate parameter of the methacrylate radical to the thiol is ∼1.7. This value is consistent with slower thiol consumption than methacrylate during the initial stage of polymerization.

The two separate polymerization regimes of these thiol−allyl ether−methacrylate systems—methacrylate chain polymerization followed by thiol−ene step growth polymerization—are unique and different from polymerization kinetics of other thiol−vinyl−vinyl ternary systems. Thiol−vinyl−vinyl ternary systems in which one of the vinyl groups homopolymerizes such as thiol−vinyl ether−acrylate and thiol−vinyl ester−acrylate ternary systems exhibit simultaneous consumption of both thiol and ene functional groups from the initial stage of polymerization.[13,18] For example, it is reported that in a thiol−vinyl ether−acrylate ternary system the thiyl radical addition rate to vinyl ether and acrylate double bonds is approximately the same.[18] Also, the ratio between the acrylate propagation rate through acrylate double bonds and the chain transfer rate of acrylate radicals to thiols is about 1.4, indicating a significant amount of chain transfer reaction to thiol. Therefore, in the thiol−vinyl ether−acrylate system, large amounts of thiyl radicals are produced and react with both vinyl ether and acrylate double bonds, resulting in all functional group conversions increasing from the initial stage of polymerization, and no distinct polymerization regimes are observed.

On the basis of these results, the two separate polymerization regimes are primarily due to the preferential addition of a thiyl radical to methacrylate double bonds. This preferential addition results from the chemical nature of the methacrylate and allyl ether double bonds. The addition rate of thiyl radicals to double bonds is strongly dependent on the electron density of the double bonds because of the electrophilic nature of the thiyl radicals. Methacrylate double bonds have higher electron density and radical stability than acrylate double bonds due to the presence of a methyl group on the β-carbon. These two characteristics increase the thiyl radical addition rate to methacrylate double bonds. It is also known that allyl ether double bonds exhibit a slower polymerization rate with thiols compared to vinyl ether, vinyl ester, and norbornene.[17−20] This result is primarily associated with lower electron density of allyl ether double bonds compared to the other monomers and suggests that a thiol−allyl ether−methacrylate system would have greater thiyl radical selectivity toward methacrylate double bonds than thiol−

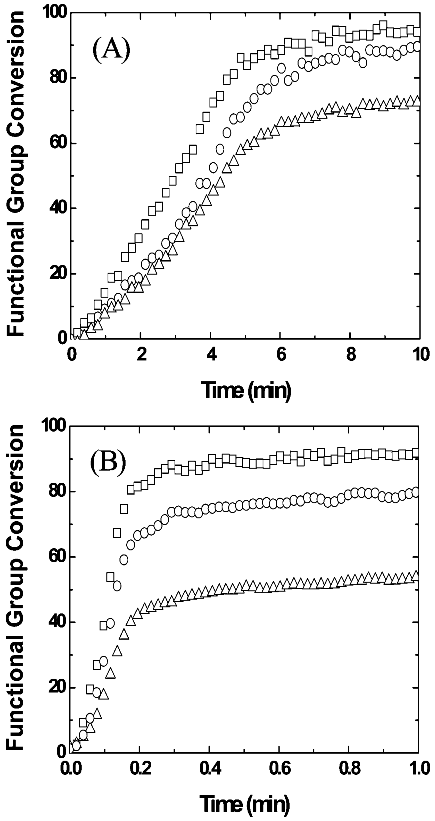

Figure 3. Functional group conversion vs time plots of (A) PETMP−TEGDVE−HDDMA and (B) PETMP−TATATO−HDDA ternary mixtures: methacrylate (□), thiol (○), and allyl ether (△) conversion. HDDMA content is 50 wt %, and the PETMP−TEGDVE(TATATO) functional group ratio is 1:1. Samples contain 0.1 wt % DMPA and are irradiated at 15 mW/cm^2 using 320−500 nm light.

vinyl ether−methacrylate or thiol−norbornene−methacrylate or thiol−allyl ether−acrylate systems. This expectation is supported by examining the polymerization kinetics of ternary systems in which the methacrylate is replaced by an acrylate. Figure 3 presents the polymerization kinetics of pentaerythritol tetrakis(3-mercaptopropionate) (PETMP)−triethylene divinyl ether (TEGDVE)−HDDMA and PETMP−TATATO−1,6-hexanediol diacrylate (HDDA) mixtures. HDDMA and HDDA content is 50 wt %, and the PETMP/TEGDVE (or TATATO) functional group ratio is 1:1 in the samples. In this study, the methacrylate is replaced with an identical acrylate (Figure 3B) which has lower electron density on the double bond compared to the methacrylate. Further, the allyl ether is replaced with a vinyl ether (Figure 3A), which has a higher electron density compared to the allyl ether. Therefore, in these two systems, thiyl radicals should exhibit less selectivity toward a specific double bond. The results of Figure 3 support this outcome as it is seen that the conversion of all functional groups increases from the initial stage of polymerization for both systems. This indicates that thiyl radicals readily propagate through both vinyl double bonds. These results demonstrate how the polymerization kinetics and network evolution of thiol−vinyl−vinyl ternary systems are readily controlled by selecting appropriate vinyl structures.

Methacrylate homopolymerization with a certain extent of a chain transfer to thiol dominates the initial stage of thiol−allyl ether−methacrylate polymerizations. Therefore, it is expected that concentration, functionality, and structure of the thiol monomer play an important role in the polymerization kinetics and the polymer network structure developed. The effect of thiol content on the polymerization rate of PETMP−TATATO−HDDMA ternary systems is shown in Figure 4. It is noted that PETMP−TATATO−HDDMA ternary systems also exhibit two separate polymerization steps as do HDT−TATATO−HDDMA ternary systems. The methacrylate conversion rate dramatically increases with increasing thiol content. This result can be explained by more rapid thiyl radical addition to methacrylate double bonds compared to the propagation rate of methacrylate radicals through methacrylate double bonds. We reported that the thiol addition rate to the methacrylate double bond (1.6×10^6 L/(mol s)) is much faster than the methacrylate propagation rate (0.95×10^5 L/(mol s)).[19] When the thiol content increases, it is expected that more methacrylate radicals undergo a chain transfer reaction to thiols followed by thiyl radical addition to methacrylate double bonds, resulting in a more rapid methacrylate conversion rate. To compare the degree of chain transfer with the enhanced methacrylate polymerization rate, it is important to measure how many methacrylate double bonds are consumed, on average, per chain transfer event.

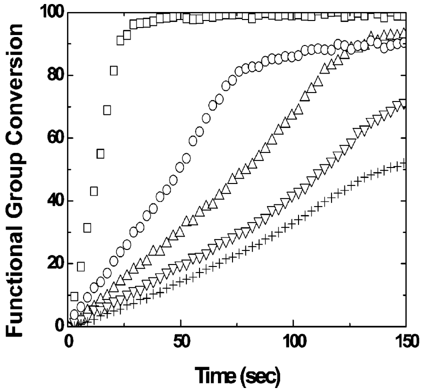

Figure 4. Methacrylate double bond conversion vs time plots of PETMP−TATATO−HDDMA as a function of thiol−ene content: 90 (□), 70 (○), 50 (△), 30 (▽), and 10 wt % (+). Samples contain 0.1 wt % DMPA and are irradiated at 15 mW/cm^2 using 320−500 nm light.

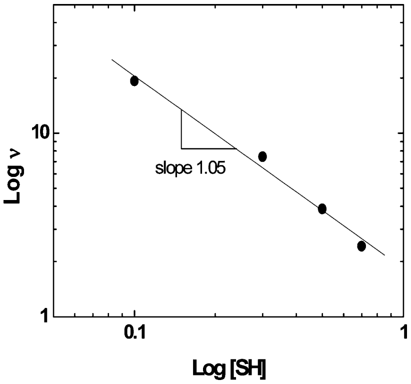

Figure 5. Methacrylate chain length (ν at 50% methacrylate conversion) of HDT−TATATO−HDDMA mixtures as a function of the thiol−ene content.

Figure 5 presents the methacrylate chain length (ν) at 50% methacrylate conversion of HDT−TATATO−HDDMA mixtures as a function of thiol−ene content (primarily methacrylate−thiol polymerization occurs before 50% methacrylate conversion). In this case, the methacrylate chain length is defined as the average number of methacrylate double bonds consumed prior to a chain transfer reaction to thiol. The methacrylate chain length is inversely proportional to [SH].[1] For the sample with 10 wt % thiol−ene ∼19 methacrylate double bonds are consumed per thiol group while the samples containing 50 and 30 wt % of thiol−ene have 4 and 2.5 methacrylate double bonds consumed per thiol, respectively.

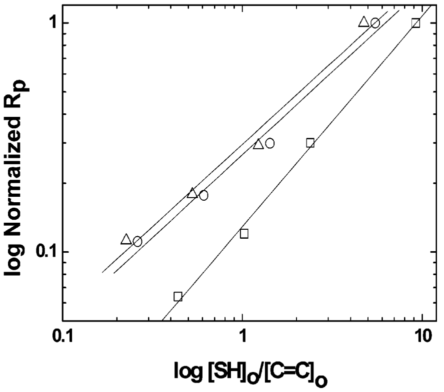

Figure 6. Log (R_p) vs log($[SH]_0/[C{=}C]_0$) plot of (□) PETMP−HDDMA binary mixtures along with (△) HDT−TATATO−HDDMA and (○) PETMP−TATATO−HDDMA ternary mixtures.

Examining the polymerization kinetics of thiol−methacrylate binary systems provides further information on the effect of thiol concentration on the methacrylate polymerization rate in thiol−allyl ether−methacrylate ternary systems. The mathematical expression for the steady-state polymerization rate has been derived previously, which is for traditional step growth thiol−ene systems where the propagation rate of vinyl homopolymerization ($k_{pC{=}C}$) is negligible. On the basis of the previously derived equation[17] and by considering homopolymerization of methacrylate monomers, the equation expressing the polymerization rate of the thiol−methacrylate system is given by

$$R_{p,SH} = \sqrt{\frac{R_i}{2k_t}}\frac{1}{\sqrt{\frac{1}{(k_{psc}[C{=}C])^2}+\frac{1}{(k_{CT}[SH])^2}+\frac{1}{(k_{psc}k_{CT}[C{=}C][SH])}}} \quad (1)$$

$$R_{p,C{=}C} = \sqrt{\frac{R_i}{2k_t}}\frac{1 + k_{pC{=}C}[C{=}C]/k_{CT}[SH]}{\sqrt{\frac{1}{(k_{psc}[C{=}C])^2}+\frac{1}{(k_{CT}[SH])^2}+\frac{1}{(k_{psc}k_{CT}[C{=}C][SH])}}} \quad (2)$$

where $R_{p,SH}$, $R_{p,C{=}C}$, k_{CT}, k_{psc}, and $k_{C{=}C}$ are R_p of the thiol functional group, R_p of the methacrylate functional group, the chain transfer, the thiyl radical propagation, and the carbon radical propagation kinetic parameters, respectively. These equations can be utilized in the polymerization kinetics of the first polymerization regime of the thiol−allyl ether−methacrylate systems where only the methacrylate−thiol polymerization occurs. On the basis of our previous report, the ratio of the thiol addition rate to the methacrylate double bond (k_{psc}) and the chain transfer rate to thiol (k_{CT}) is 25.[19] In this case $k_{psc} \gg k_{CT}$, the equations can be simplified. Thus, the monomer consumption rate of thiol and methacrylate functional groups is given by

$$\frac{dX_{SH}}{dt} = \sqrt{\frac{R_i}{2k_t}}k_{CT}\,(1 - X_{SH}) \quad (3)$$

$$\frac{dX_{C{=}C}}{dt} = \sqrt{\frac{R_i}{2k_t}}\left(k_{CT}\left(\frac{[SH]_0}{[C{=}C]_0} - X_{SH}\right) + k_{pC{=}C}(1 - X_{SH})\right) \quad (4)$$

Equation 3 indicates that the conversion rate of the thiol group is independent of both thiol and methacrylate concentration. Equation 4 indicates that the methacrylate conversion rate has a first-order dependence on the ratio of the initial concentration of thiol and methacrylate groups ($[SH]_0/[C{=}C]_0$). Figure 6 presents the log(R_p) vs log($[SH]_0/[C{=}C]_0$) plot of PETMP−HDDMA binary mixtures along with HDT−TATATO−HDDMA and PETMP−TATATO−HDDMA mixtures. The slope indicates the dependence of the methacrylate double bond conversion rate on monomer concentration. For the PETMP−HDDMA binary mixtures, the slope is 0.92 (standard deviation 0.035) and is consistent with the analytical expression of eq 4. This result indicates that in thiol−methacrylate binary systems the conversion rate of the methacrylate double bond has first-order dependence on thiol concentration while the thiol conversion rate is not affected by monomer concentration. However, for both ternary systems, the slope is 0.72 (standard deviation 0.065). It is expected that a small amount of thiyl radical addition to allyl ether double bonds and dilution effects caused by the allyl ether monomers might contribute to the deviation from eq 4.

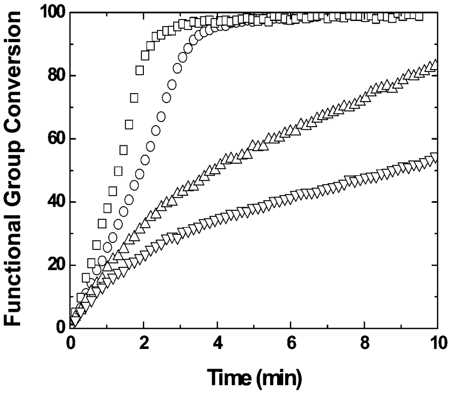

Figure 7. Methacrylate double bond conversion vs time plots of thiol−TATATO−HDDMA mixtures as a function of thiol functionality: PETMP (□), TMPTMP (○), EGMP (△), and HDT (▽). HDDMA content is 50 wt %, and the thiol−TATATO functional group ratio is 1:1. Samples contain 0.1 wt % DMPA and are irradiated at 15 mW/cm^2 using 320−500 nm light.

The functionality and structure of the thiol monomer affect the polymerization rate and network structure of ternary systems. Figure 7 shows the effect of functionality and structure of the thiol on the conversion rate of the methacrylate in thiol−TATATO−HDDMA ternary mixtures. The samples contain 50 wt % HDDMA, and the initial TATATO:thiol functional group ratio is 1:1 in all samples. The sample containing glycol dimercaptopropionate (GDMP) shows more rapid methacrylate consumption as compared to when HDT is used. This result is due to the mercaptopropionate having a more abstractable hydrogen compared to the aliphatic thiol, resulting in faster chain transfer to thiol.[1,2] It is reported that mercaptopropionates form six-membered intramolecular hydrogen bonding between thiol and ester groups, resulting in a weaker S−H bond.

Another interesting result is the effect of thiol functionality on the polymerization rate. Figure 7 also shows the methacrylate conversion rate of the ternary mixtures containing di-, tri-, and tetrafunctional thiol, GDMP, trimethylolpropane tris(3-mercaptopropionate) (TMPTMP), and PETMP. All thiols have identical thiol functional group structure. With increasing thiol functionality, the methacrylate polymerization rate increases dramatically. It is clearly shown that the sample containing PETMP takes just 2 min to reach 100% conversion while the sample containing GDMP takes more than 10 min. When PETMP was used and incorporated in methacrylate network structures, it is expected that the cross-link density and molecular size should be higher than when GDMP or TMPTA are used, as shown in Figure 8. Increased cross-link density reduces the mobility of the growing polymer radicals and the termination rate constant

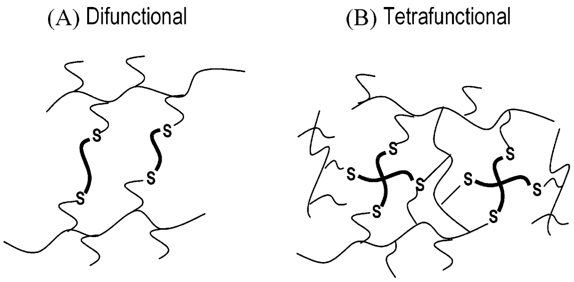

Figure 8. A diagram illustrating the effect of thiol functionality on cross-linked network structure of thiol−allyl ether−methacrylate ternary systems: (a) difunctional thiol and (b) tetrafunctional thiol.

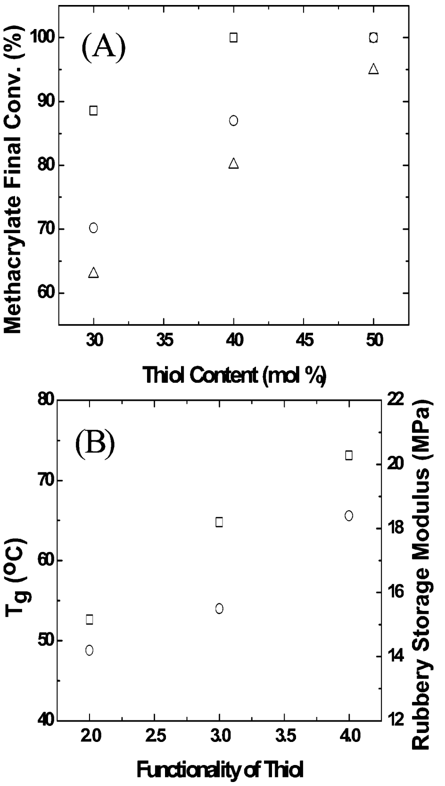

Figure 9. Effect of thiol functionality and content on (A) the final methacrylate conversion: GDMP (□), TMPTMP (○), PETMP (△). (B) T_g (□) and rubbery storage modulus (○) of the 50:50 molar BisGMA/thiol mixtures.

due to diffusion-controlled termination kinetics, resulting in the enhanced polymerization rate.[21−23]

Supporting evidence for the effect of thiol functionality on the polymerization kinetics of the thiol−allyl ether−methacrylate ternary systems is obtained by examining the final conversion, glass transition temperature, and rubbery modulus of methacrylate−thiol mixtures. Figure 9a shows the final conversion of 1:1 molar mixtures (based on a functional group) of BisGMA/thiol mixtures containing di-, tri-, and tetrafunctional thiols, GDMP, TMPTMP, and PETMP. It is clearly shown that final conversion of BisGMA/thiol mixtures decreases with increasing thiol functionality and decreasing thiol content, as shown in Figure 9a. Generally, final conversion of multifunctional monomers is related to various factors. One of the primary factors determining final conversion is the functionality of monomers. With increasing monomer functionality, cross-link density increases, resulting in vitrification at lower conversions. This result indicates that thiol molecules are incorporated into BisGMA networks, and the cross-link density of the resultant sample increases with thiol functionality, as illustrated in Figure 8. The other evidence supporting the effect of thiol functionality on cross-link network density includes glass transition temperature and rubbery storage modulus measurements. Modulus in the rubbery plateau region is used to estimate the molecular weight between cross-links using the equation $M_c = 3RT\rho/E'$, where M_c, R, T, ρ, and E' are the molecular weight between cross-links, gas constant, temperature, polymer density, and the storage modulus in the rubbery plateau, respectively.[24] Cross-link density increases with decreasing molecular weight between cross-links (M_c). Therefore, the equation indicates that cross-link density is proportional to the rubbery storage modulus. Because the BisGMA/thiol samples containing 50 mol % thiol show almost identical final conversion regardless of thiol functionality, T_g and storage rubbery modulus measured by DMA are compared as shown in Figure 9b. Because the BisGMA conversion is 100% and the thiol group conversion is approximately the same for all samples (25−30%, data not shown), it is expected that each sample has identical cross-link density, resulting in the same glass transition temperature and rubbery storage modulus. However, T_g and rubbery modulus increase with increasing thiol functionality. This result indicates that PETMP forms more highly cross-linked networks as compared to GDMP and TMPTMP. Two plots shown in Figure 9 clearly indicate that the higher thiol functionality produces a higher cross-linked network density. It is reasonable to expect that the observed increase in the polymerization rate of the thiol−allyl ether−methacrylate ternary mixtures with increasing thiol functionality is due to the decreased termination rate resulting from the highly cross-linked network structure.

Conclusion

The polymerization kinetics of thiol−allyl ether−methacrylate systems and the effect of polymerization kinetics on cross-linked network structure and mechanical properties have been evaluated. Two separate polymerization processes are observed in this thiol−vinyl−vinyl ternary system. In the initial polymerization stages, methacrylate homopolymerization with chain transfer to thiol occurs while thiol−allyl ether reactions dominate the later polymerization stage. The two-step polymerization process, chain polymerization of methacrylates followed by step growth polymerization of the thiol−ene, is primarily due to the combination of the chemical nature of the methacrylate and allyl ether double bonds. Because methacrylate homopolymerization with chain transfer reactions to thiols dominates the initial stage of polymerization, the content, concentration, and structure of the thiol significantly affect the polymerization processes.

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