Macromolecules **2003,** *36,* 4631−4636

Mechanism and Modeling of a Thiol−Ene Photopolymerization

Neil B. Cramer,[†] Tanner Davies,[†] Allison K. O'Brien,[†] and Christopher N. Bowman*,[†,‡]

Department of Chemical Engineering, University of Colorado, Boulder, Colorado 80309-0424, and Department of Restorative Dentistry, University of Colorado Health Sciences Center, Denver, Colorado 80045-0508

Received January 21, 2003; Revised Manuscript Received April 8, 2003

ABSTRACT: Thiol−ene photopolymerizations proceed via a sequential radical propagation/chain transfer mechanism that leads to polymer and network formation much like a step growth polymerization. Here, the chain transfer step in this sequential reaction series is shown to be the rate-limiting step. A model has been developed that accurately predicts the observed polymerization kinetic behavior under a variety of circumstances. Chain transfer is modeled as a rate-limiting step with the rate parameter (k_p) for the propagation reaction being a factor of 10 greater than that for the chain transfer process (k_{CT}) ($k_p/k_{CT} = 10$). The polymerization rate is first-order overall with first-order dependence on thiol functional group concentration and independent of the ene functional group concentration; $R_p \propto [SH]^1[C{=}C]^0$. Polymerization rate behavior vs functional group concentration change is shown to be only a function of the ratio of propagation to chain transfer kinetic parameters.

Introduction

Thiol−ene photopolymerizations exhibit many of the same desirable properties as photopolymerizations of acrylic monomers. They polymerize rapidly and do not require solvents for processing, and their products are optically clear and have good mechanical properties.[1−6] In addition, thiol−ene polymers exhibit several unique aspects associated with their polymerization. They have the advantage of being relatively uninhibited by oxygen,[2,7,8] and they are rapidly polymerized with little or even no added photoinitiator.[8−10]

Thiol−ene photopolymerizations are radical reactions that proceed via a step growth mechanism. The basics of the step growth mechanism have been outlined and explored in several previous investigations.[1−3,9,11] As outlined below, the thiol−ene step growth mechanism involves the addition of a thiyl radical to a vinyl functional group (step 1), followed by radical transfer from the ensuing carbon radical to a thiol functional group (step 2). These successive propagation/chain transfer events serve as the basis for the thiol−ene polymerization reaction.

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

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

Thiol−ene polymerization reactivity has been well studied in a variety of systems;[1,2,12] however, the kinetic mechanisms and rate-limiting steps are acknowledged to be not well understood. Different theories have been raised about the dark reaction,[13−16] termination,[1−3,16] and even the overall reaction order.[1,3] It has been shown that the ratio of the propagation to the chain transfer kinetic parameters (k_p/k_{CT}) is the controlling parameter for conversions of thiol and (meth)acrylate functional groups in thiol−(meth)acrylate copolymerizations.[9,17]

In a step growth polymerization the nature of the product is heavily influenced by monomer functionality. Monofunctional monomers do not generate a polymer network, leading only to single adducts. Difunctional monomers polymerize to form linear polymers, whereas monomers with an average functionality greater than two form cross-linked polymer networks. Studying polymerization kinetics, particularly in network-forming polymer systems, is often complicated by factors such as diffusion-limited reactions and viscosity changes of several orders of magnitude as the reaction mixture changes from a liquid to a cross-linked polymer in a short time span.[18−20] These effects make accurate in situ determination of kinetic parameters and other system properties difficult. In cross-linking or linear thiol−ene systems, complicating kinetic factors from diffusion-controlled reactions or early gelation are not as significant as in typical chain growth systems since thiol−enes do not exhibit traditional autoacceleration behavior and do not gel until high conversions are obtained due to their step growth nature. However, monofunctional thiol−ene systems are still useful as tools to study the kinetics of thiol−ene reactions because they exhibit identical chemistry to thiol−ene polymerizations while reacting to form a nonpolymeric product. As a result, the material properties and diffusivities for reactions of monofunctional thiol−ene reactants do not change significantly during the reaction. Thus, studies with monofunctional materials can be used to focus solely on the radical addition and transfer reactions without the complexities typically added by polymer formation.

Thiol−ene polymerizations performed in dilute solutions have the additional advantage that the reactions can be studied while independently controlling the concentrations and stoichiometry of thiol and ene functional groups. Thus, studying thiol−ene systems in solution offers a unique method to study their reaction chemistry and kinetics. Note that although changes in

---

[†] University of Colorado.

[‡] University of Colorado Health Sciences Center.

* To whom correspondence should be addressed: phone 303-492-3247; fax 303-492-4341; e-mail christopher.bowman@colorado.edu.

10.1021/ma034072x CCC: $25.00

stoichiometry of thiol−ene systems would adversely impact material properties for network-forming reactions, they are a powerful tool for determining the mechanisms responsible for the desirable characteristics of thiol−ene photopolymerizations.

This work improves upon the understanding of thiol−ene polymerization kinetics by examining the overall reaction order for thiol−allyl ether polymerizations as well as the dependence of the polymerization rate on the individual concentrations of thiol and allyl ether functional groups. We have further complemented the kinetic investigation by developing a model for thiol−ene polymerization reactions. Modeling equations are developed using the established step growth mechanism for thiol−ene polymerizations. Simulations of the thiol−ene polymerizations aid in both understanding and predicting thiol−ene kinetics under a variety of different circumstances.

Experimental Section

Materials. The monomers 1-octanethiol, 1,6-hexanedithiol (dithiol), trimethylolpropane allyl ether (allyl ether), and trimethylolpropane diallyl ether (diallyl ether) and the solvent ethylene glycol diacetate (EGDAc) were purchased from Aldrich (Milwaukee, WI). The photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA), was purchased from Ciba-Geigy (Hawthorne, NY). The monomer pentaerythritol tetra(3-mercaptopropionate) (tetrathiol) was donated by Bruno Bock (Marschacht, Germany). All monomers and the photoinitiator were used as received.

Methods. FTIR studies were conducted using a Nicolet 750 Magna FTIR spectrometer with a KBr beam splitter and an MCT/A detector. Series scans were recorded, taking spectra at the rate of approximately 2.5 scans/s. The FTIR sample chamber was continuously purged with dry air. Samples were irradiated until the reaction was complete, as indicated by the functional group absorption spectra no longer decreasing. Thiol functional group conversion was monitored using the S−H absorption peak at 2570 cm^{-1}. Allyl conversions were monitored using the carbon−carbon double-bond absorption peak at 1636 cm^{-1}. Conversions were calculated using the ratio of peak areas to the peak area prior to polymerization. All reactions were performed under ambient conditions.

Monomer samples were placed between NaCl crystals in a horizontal transmission apparatus.[21] 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).

Differential scanning calorimetry (DSC) studies were conducted using a Perkin-Elmer DSC7 (Norwalk, CT). All DSC experiments were performed at 25 °C and purged with 20 sccm of nitrogen throughout the polymerization. Monomer samples were placed in aluminum pans (TA Instruments, New Castle, DE) inside the DSC chamber. Polymerizations were initiated via an EXFO Novacure light source (EXFO, Mississaugua, Ontario) with a 365 nm filter. Light intensity was experimentally verified with the DSC by monitoring the amount of heat absorbed from carbon disks (Perkin-Elmer, Norwalk, CT) placed in the sample holder.

Results and Discussion

The step growth propagation mechanism for thiol−ene polymerizations implies that the kinetics might be first order in both thiol and ene concentration and second order overall ($R_p \propto [SH]^1[C{=}C]^1$). However, preliminary photocalorimetry studies indicate that the polymerization rate is more heavily dependent on thiol monomer concentration than vinyl monomer concentration for thiol−allyl ether systems. To study this phenomenon in detail for thiol−allyl ether polymerizations, a series of experiments were performed to elucidate the overall reaction order as well as the reaction order for the individual thiol and ene components. Samples of monofunctional and difunctional thiol and ene monomers were polymerized in dilute solutions of EGDAc. The concentrations of thiol and ene functional groups were manipulated first by changing the concentrations of both functional groups and then independently manipulating the concentrations of thiol and ene functional groups.

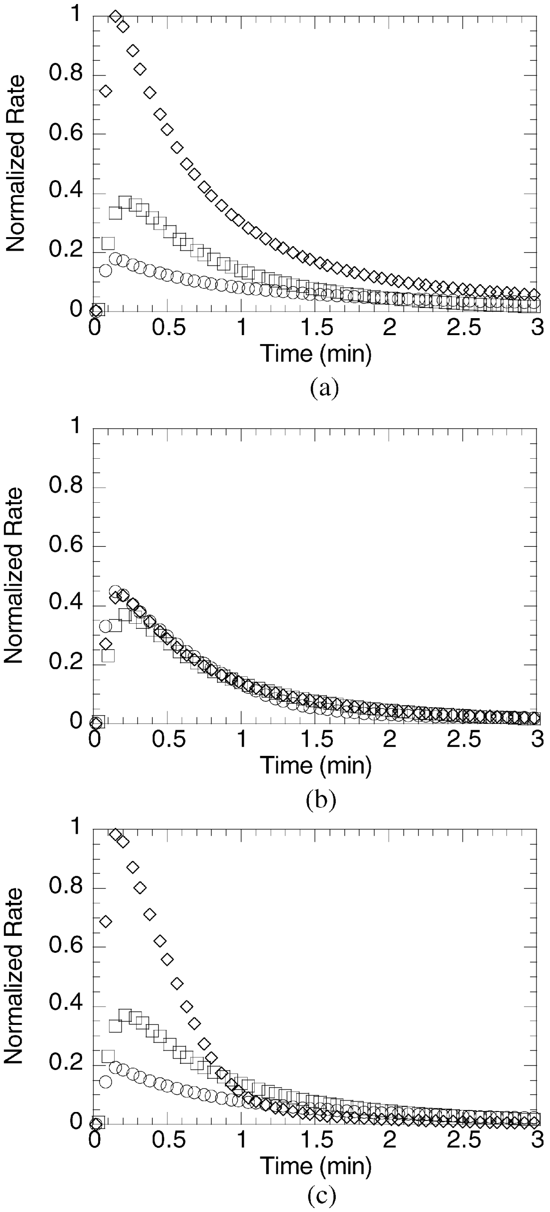


Figure 1. Normalized polymerization rate (R_p/R_{pmax}) for the dimerization of octanethiol and allyl ether in EGDAc. (a) 0.22 mol/L (○), 0.44 mol/L (◇), and 0.88 mol/L (□) thiol and allyl ether functional groups. (b) 0.44 mol/L thiol functional groups and 0.22 mol/L (○), 0.44 mol/L (◇), and 0.88 mol/L (□) allyl ether functional groups. (c) 0.44 mol/L allyl ether functional groups and 0.22 mol/L (○), 0.44 mol/L (◇), and 0.88 mol/L (□) thiol functional groups. R_{pmax} is determined from the maximum rate in the 0.88 mol/L thiol−ene sample. Samples contain 0.5 wt % DMPA and are irradiated with 365 nm light at 3.6 mW/cm^2.

Figure 1 shows the results for reactions of octanethiol and allyl ether in solutions of EGDAc. Systematically varying the concentrations of both thiol and ene functional groups equivalently demonstrates that the reaction occurs with roughly overall first-order behavior (Figure 1a). Holding the thiol functional group concentration constant, similar initial rate behavior is observed for three different concentrations of ene functional groups (Figure 1b). These results demonstrate that, in fact, the polymerization rate is independent of the concentration of ene functional groups. In contrast, the polymerization rate is shown to have a roughly first-order dependence on the concentration of thiol functional groups when the ene functional group concentration is held constant (Figure 1c). The results shown in Figure 1 clearly elucidate the surprising result that the thiol−ene reaction has a first-order dependence on the thiol functional group concentration and is independent of the ene functional group concentration.

In a similar manner, polymerizations were performed with difunctional thiol and ene monomers in dilute solutions of EGDAc. Polymerizations were carried out first by manipulating both the thiol and ene functional group concentrations in a stoichiometric polymerization (Figure 2a) and then independently manipulating the ene (Figure 2b) and then the thiol (Figure 2c) functional group concentrations. The observed polymerization reaction orders are nearly identical to those of the monofunctional system. The polymerization is first-order overall with first-order dependence on the thiol functional group concentration while being completely independent of the ene functional group concentrations. Hence, results from both monofunctional and difunctional thiol−ene polymerizations in solutions of EGDAc show that the polymerization rate is only a function of the concentration of thiol functional groups, e.g., $R_p \propto [\mathrm{SH}]^1[\mathrm{C{=}C}]^0$.

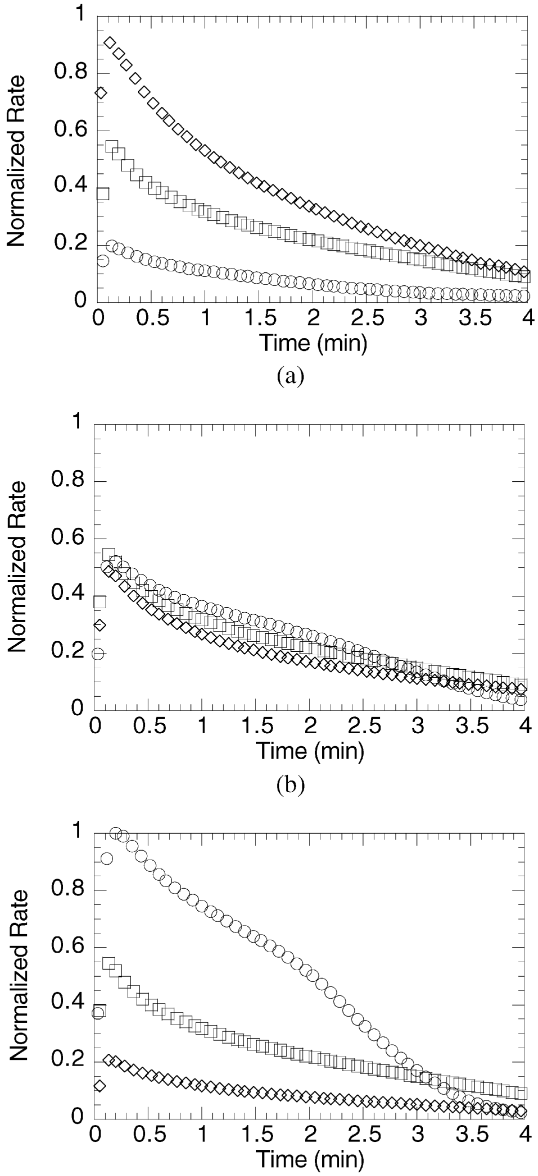
To aid in interpreting the observed polymerization results, we have developed a model for thiol−ene polymerizations. The model is based on the established step growth thiol−ene polymerization mechanism, containing four species balances on the concentration of thiol and ene functional groups as well as the concentrations of thiyl and carbon radicals. The governing equations for the model are shown in eqs 1−4.

$$\frac{\mathrm{d}[\mathrm{SH}]}{\mathrm{d}t} = -k_{\mathrm{CT}}[\mathrm{SH}][\mathrm{C}^\bullet] \tag{1}$$

$$\frac{\mathrm{d}[\mathrm{C{=}C}]}{\mathrm{d}t} = -k_{\mathrm{p}}[\mathrm{C{=}C}][\mathrm{S}^\bullet] \tag{2}$$

$$\frac{\mathrm{d}[\mathrm{S}^\bullet]}{\mathrm{d}t} = R_{\mathrm{i}} - R_{\mathrm{t}}(\mathrm{S}^\bullet) + k_{\mathrm{CT}}[\mathrm{SH}][\mathrm{C}^\bullet] - k_{\mathrm{p}}[\mathrm{C{=}C}][\mathrm{S}^\bullet] \tag{3}$$

$$\frac{\mathrm{d}[\mathrm{C}^\bullet]}{\mathrm{d}t} = R_{\mathrm{i}} - R_{\mathrm{t}}(\mathrm{C}^\bullet) - k_{\mathrm{CT}}[\mathrm{SH}][\mathrm{C}^\bullet] + k_{\mathrm{p}}[\mathrm{C{=}C}][\mathrm{S}^\bullet] \tag{4}$$



(a)

(b)

(c)

Figure 2. Normalized polymerization rate (R_p/R_{pmax}) for dithiol and diallyl ether monomers in EGDAc. (a) 0.22 mol/L (○), 0.44 mol/L (◇), and 0.88 mol/L (□) dithiol and diallyl ether functional groups. (b) 0.44 mol/L dithiol functional groups and 0.22 mol/L (○), 0.44 mol/L (◇), and 0.88 mol/L (□) diallyl ether functional groups. (c) 0.44 mol/L diallyl ether functional groups and 0.22 mol/L (○), 0.44 mol/L (◇), and 0.88 mol/L (□) dithiol functional groups. R_{pmax} is determined from the maximum rate in the 0.88 mol/L thiol−ene sample. Samples contain 0.5 wt % benzophenone and are irradiated with 365 nm light at 1.5 mW/cm^2.

Equation 1 accounts for the consumption of thiol functional groups by chain transfer with a carbon radical. Equation 2 accounts for consumption of ene functional groups via propagation of a thiyl radical. Consumption of ene functional groups via homopolymerization is not allowed here as it does not occur in thiol−allyl ether systems, though it clearly occurs in certain other types of thiol−ene polymerizations, particularly thiol−acrylate copolymerizations.[9] Equations 3 and 4 describe the concentrations of thiyl and carbon radicals, respectively, including contributions from initiation, termination, and either generation or consumption via propagation and chain transfer. Equations 1 and 2 assume that consumption of thiol and ene functional groups by initiation is negligible relative to propagation. The initiation rate (R_{i}) is denoted by eq 5 and is calculated on the basis of standard values for DMPA (f = efficiency, ϵ = molar absorptivity (150 L/(mol cm) for 365 nm light), [I] = initiator concentration, I_0 = light intensity, λ = wavelength, N_{Av} = Avogadro's number, h = Planck's constant, c = speed of light).[20,22] Rates of termination or consumption of thiyl and carbon radicals by radical−radical recombination are given in eqs 6 and 7, respectively. All kinetic parameters (k_{CT}, chain transfer; k_{p}, propagation; k_{t1}, k_{t2}, and k_{t3}, termination) are assumed to remain constant throughout the reaction. All radical−radical recombinations for termination are assumed to be equally likely, and thus the termination kinetic parameters (k_{t1}, k_{t2}, and k_{t3}) are all equal.

$$R_i = -\frac{d[I]}{dt} = \frac{2.303 f\epsilon[I]I_0\lambda}{N_{Av}hc} \tag{5}$$

$$R_t(S^\bullet) = 2k_{t1}[S^\bullet]^2 + k_{t2}[S^\bullet][C^\bullet] \tag{6}$$

$$R_t(C^\bullet) = k_{t2}[S^\bullet][C^\bullet] + 2k_{t3}[C^\bullet]^2 \tag{7}$$

These seven equations are numerically solved to model thiol−ene polymerization behavior. The experimentally observed rate behavior of Figures 1 and 2, $R_p \propto [SH]^1[C{=}C]^0$, is predicted by the model using chain transfer (eq 2) as the rate-limiting step in the polymerization. Modeling chain transfer as a rate-limiting step in the polymerization is accomplished using a ratio of propagation kinetic constant to the chain transfer kinetic constant of 10 ($k_p/k_{CT} = 10$). Using a value of $k_p/k_{CT} = 10$ (Figure 3), the model data predict the observed polymerization behavior for the dimerization of monofunctional thiol−enes in EGDAc. The kinetic parameters utilized are typical of propagation and termination kinetic parameters for acrylic photopolymerizations.[22,23]

An interesting result occurs due to the propagation kinetic parameter being 10 times the chain transfer kinetic parameter. The rates of propagation and chain transfer must be equivalent due to the step growth nature of the polymerization. Therefore, the steady-state concentration of carbon radicals is 10 times that of the thiyl radicals when concentrations of thiol and ene functional groups are equivalent.

$$\frac{k_p}{k_{CT}} = \frac{[C^\bullet]}{[S^\bullet]} = 10$$

It is also worthwhile to note that in Figure 3b,c model predictions of polymerization rates for initially 2:1 stoichiometric ratios of thiol to allyl functional groups show a rapid decrease in polymerization rate as the reaction nears completion. The polymerization rate in these systems is initially proportional to the thiol functional group concentrations. However, as the concentration of allyl functional groups approaches zero, the polymerization is no longer rate limited by the concentration of thiol functional groups, and despite an excess of thiol functional groups, the polymerization rate quickly falls off. This trend is also evident in the experimental results as seen in polymerization rates for initially 2:1 stoichiometric ratios in Figures 1c and 2c when compared to polymerization rates in 2:2 stoichiometric ratios of Figures 1a and 2a.

Typically, thiol−ene polymerizations are carried out in bulk without the use of solvents. In the case of bulk polymerizations, thiol and ene functional group concentrations cannot be independently manipulated. Increasing the thiol functional group concentration leads to a concomitant decrease in the ene functional group concentration. This coupling makes analysis of bulk polymerization rates in systems with varying functional group ratios more difficult. The linear thiol−ene system of dithiol and diallyl monomers was polymerized in bulk and monitored in real time with FTIR. Monomer solutions were polymerized with a 1:1 stoichiometric ratio of thiol and ene functional groups as well as initially 2:1 and 1:2 stoichiometric ratios of functional groups (Figure 4). The linear thiol−ene system with 1:1 stoichiometry achieves full conversion of both thiol and ene functional groups. In the 2:1 thiol−ene mixture, the thiol functional groups are the limiting reagent, reaching full conversion while ene functional groups achieve only 50% conversion and vice versa for the 1:2 stoichiometric mixture. It is clearly evident that polymerization of a 2:1 thiol−ene stoichiometric ratio of functional groups proceeds more rapidly than the 1:1 or 1:2 mixtures. The 1:1 and 1:2 stoichiometric mixtures have nearly equivalent curing times. Kinetic parameters identical to those that prevail for the monofunctional thiol−ene system in EGDAc are utilized to model the

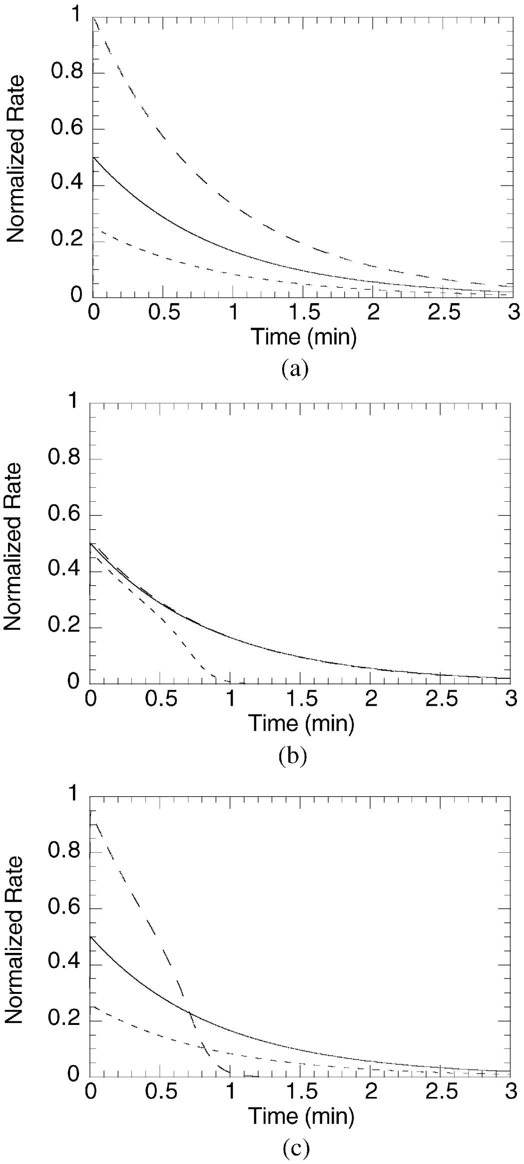


Figure 3. Modeling results using $k_p/k_{CT} = 10$. (a) 0.22 mol/L (- - -), 0.44 mol/L (—), and 0.88 mol/L (— —) thiol and ene functional groups. (b) 0.44 mol/L thiol functional groups and 0.22 mol/L (- - -), 0.44 mol/L (—), and 0.88 mol/L (— —) ene functional groups. (c) 0.44 mol/L ene functional groups and 0.22 mol/L (- - -), 0.44 mol/L (—), and 0.88 mol/L (— —) thiol functional groups. Normalized polymerization rate is determined from R_p/R_{pmax}, where R_{pmax} is determined from the maximum rate in the 0.88 mol/L thiol−ene system. Kinetic parameters are $k_p = 5 \times 10^4$ L/(mol s), $k_{CT} = 5 \times 10^3$ L/(mol s), k_{t1}, k_{t2}, $k_{t3} = 1 \times 10^6$ L/(mol s). Initiation efficiency (f) is assumed to be 0.1.

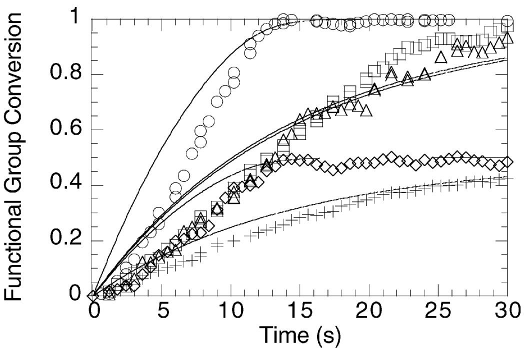


Figure 4. Model and experimental data for conversion vs time of dithiol and diallyl bulk linear polymerization with a 1:1 ratio of thiol and allyl functional groups (5.31 mol/L) (□), 2:1 ratio of thiol (◇), and allyl (○) functional groups (7.55:3.77 mol/L), and 1:2 ratio of thiol (△) and allyl (+) functional groups (3.32: 6.65 mol/L). Samples contain 0.5 wt % DMPA and are irradiated at 5 mW/cm^2 with a 320−500 nm filter. Kinetic parameters are $k_p = 5 \times 10^4$ L/(mol s), $k_{CT} = 5 \times 10^3$ L/(mol s), k_{t1}, k_{t2}, k_{t3} = 1×10^6 L/(mol s). Initiation efficiency (f) is assumed to be 1.

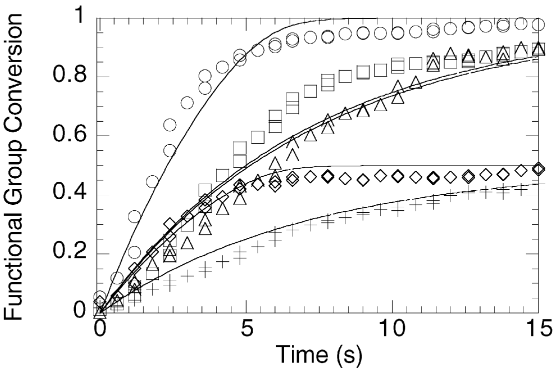
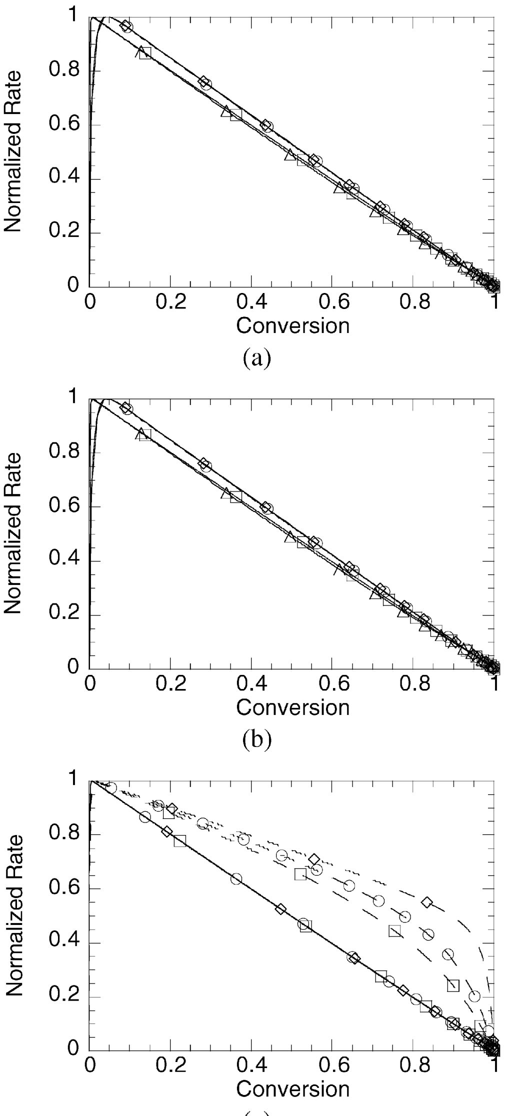


Figure 5. Model and experimental data for conversion vs time of tetrathiol and diallyl bulk cross-linking polymerization with a 1:1 ratio of thiol and allyl functional groups (4.82 mol/L) (□), 2:1 ratio of thiol (◇), and allyl (○) functional groups (6.6:3.3 mol/L) and 1:2 ratio of thiol (△) and allyl (+) functional groups (3.13:6.25 mol/L). Samples contain 0.5 wt % DMPA and are irradiated at 5 mW/cm^2 with a 320−500 nm filter. Kinetic parameters are $k_p = 1.4 \times 10^5$ L/(mol s), $k_{CT} = 1.4 \times 10^4$ L/(mol s), k_{t1}, k_{t2}, k_{t3} = 1×10^6 L/(mol s). Initiation efficiency (f) is assumed to be 1.



(a)

(b)

(c)

Figure 6. Normalized polymerization rate (R_p/R_{pmax}) as a function of ene functional group conversion for different kinetic parameters. Thiol and ene functional group concentrations are 0.44 mol/L for a 1:1 stoichiometric ratio of functional groups with baseline kinetic parameters $k_p = 5 \times 10^4$ L/(mol s), $k_{CT} = 5 \times 10^3$ L/(mol s) ($k_p/k_{CT} = 10$), k_{t1}, k_{t2}, $k_{t3} = 1 \times 10^6$ L/(mol s), initiation efficiency $f = 0.1$. (a) 1:1 stoichiometric ratio of thiol and ene functional groups with different individual kinetic parameters with k_p/k_{CT} constant. Baseline kinetic parameters (□), $k_p = 5 \times 10^5$ (◇), k_{t1}, k_{t2}, $k_{t3} = 1 \times 10^5$ (○), $f = 1$ (△). (b) 2:1 stoichiometric ratio of thiol to ene functional groups with different individual kinetic parameters with k_p/k_{CT} constant. Baseline kinetic parameters (□), $k_p = 5 \times 10^5$ (◇), k_{t1}, k_{t2}, k_{t3} = 1×10^5 (○), $f = 1$ (△) (c) 1:1 stoichiometric ratio of functional groups) with different ratios of propagation to chain transfer kinetic parameters. $k_p = 2.5 \times 10^4$ L/(mol s), $k_{CT} = 5 \times 10^3$ L/(mol s) ($k_p/k_{CT} = 5$) (□), $k_p = 5 \times 10^4$ L/(mol s), $k_{CT} = 5 \times 10^3$ L/(mol s) ($k_p/k_{CT} = 10$) (○), $k_p = 2.5 \times 10^5$ L/(mol s), $k_{CT} = 5 \times 10^3$ L/(mol s) ($k_p/k_{CT} = 50$) (◇). 2:1 stoichiometric ratio of functional groups) with different ratios of propagation to chain transfer kinetic parameters. $k_p/k_{CT} = 5$ (□), $k_p/k_{CT} = 10$ (○), $k_p/k_{CT} = 50$ (◇). R_{pmax} is determined from the maximum polymerization rate for each individual system.

bulk linear polymerizations with the exception that the initiation efficiency is assumed to be 1. The model results for the linear thiol−ene system, also shown in Figure 4, demonstrate that the polymerization kinetics for the bulk linear thiol−ene system are accurately predicted using chain transfer as the rate-limiting step ($k_p/k_{CT} = 10$).

Similar experiments are also performed with tetrathiol and diallyl monomers to form a cross-linked thiol−ene system. Polymerizations of initially 1:1, 2:1, and 1:2 stoichiometric ratios of thiol to ene functional groups are compared to model predictions in Figure 5. Experimental results are accurately predicted using the same ratio of propagation to chain transfer kinetic constants ($k_p/k_{CT} = 10$). Otherwise, results are similar to the linear system. The 2:1 ratio of thiol to ene functional groups clearly polymerizes faster than either the 1:1 or 1:2 ratios. The 1:1 and 1:2 ratios of thiol to ene functional groups exhibit almost equivalent curing times. Surprisingly, model results match experimental data very well throughout the entire polymerization. Even at conversions greater than the theoretical gel point, there is not a significant deviation between the model predictions and the experimental data. This result is to be expected for conversions below the gel point conversion (57% theoretically for this stoichiometric mixture) for a tetrathiol−diallyl system. Investigations by Saad[3] indicate that, as expected, the viscosity of the system begins to increase dramatically only near and following the gel point conversion. Apparently, even after gelation, diffusion-limited kinetics do not result in significant deviations for polymerization rates in this rubbery system until conversions are well above the gel point.

While the initiation, propagation, and termination kinetic parameters each have significant effects on overall polymerization rate behavior, the observed changes in rate with thiol and/or ene functional group concentrations are solely a function of the ratio of propagation to chain transfer kinetic constants (k_p/k_{CT}). This phenomenon is illustrated by plotting the normalized polymerization rate (R_p/R_{pmax}) as a function of conversion (Figure 6). Normalized rates are plotted utilizing the kinetic parameters from monofunctional thiol−ene reactions in solution (Figure 3). Subsequent rates are plotted with the propagation kinetic constant (k_p) and initiation rate (I_0) increased by a factor of 10 and the termination kinetic constants (k_{t1-3}) decreased by a factor of 10. The normalized rates are then plotted again for each of the four cases with the concentration of thiol functional groups increased by a factor of 2. Normalized rates are also plotted for both initially 1:1 and 2:1 stoichiometric ratios with values for the ratio of the propagation to chain transfer kinetic parameters of 5, 10, and 50. The results illustrate that the absolute values of the propagation (k_p) and termination (k_{t1-3}) kinetic parameters as well as the initiation rate have little effect on the normalized polymerization kinetics (Figure 6a,b). The experimentally observed change in polymerization behavior resulting from doubling the thiol functional group concentration is only a function of the ratio of propagation to chain transfer kinetic constants (k_p/k_{CT}) (Figure 6c).

Conclusions

Polymerizations of mono- and difunctional thiol and allyl ether monomers in solutions of EGDAc demonstrate that the polymerization kinetics are first order overall, first order in the thiol functional group concentration, and independent of the ene functional group concentration: $R_p \propto [SH]^1[C{=}C]^0$. The polymerization behavior is predicted utilizing a model based on the fundamental thiol−ene polymerization mechanism. The observed kinetic behavior is explained using chain transfer as the rate-limiting step in the polymerization by setting the ratio of propagation to chain transfer kinetic constants equal to 10 ($k_p/k_{CT} = 10$). Model predictions match both mono- and difunctional polymerization behavior in solutions of EGDAc. Bulk polymerizations of both linear and cross-linking thiol−ene systems are also accurately predicted. The ratio of the propagation kinetic constant to the chain transfer kinetic constant is the only adjustable parameter in the model affecting the observed rate behavior of $R_p \propto [SH]^1[C{=}C]^0$.

Acknowledgment. The authors acknowledge their funding sources for this work: the Fundamentals and Applications of Photopolymerizations NSF IUCRC, the NSF Ferroelectric Liquid Crystals Materials Research Center, a DOEd GAANN fellowship, and a Sloan Fellowship.

References and Notes

(1) Morgan, C. R.; Magnotta, F.; Ketley, A. D. *J. Polym. Sci., Part A: Polym. Chem.* **1977**, 627.
(2) Jacobine, A. F. In *Radiation Curing in Polymer Science and Technology III, Polymerisation Mechanisms*; Fouassier, J. D., Rabek, J. F., Eds.; Elsevier Applied Science: London, 1993; Vol. 3, p 219.
(3) Bor-Sen, C.; Saad, A. K. *Macromolecules* **1997**, *30*, 7322.
(4) Woods, J. G. *Radiation Curable Adhesives in Radiation Curing: Science and Technology*; Pappas, S. P., Ed.; Plenum Press: New York, 1992; p 333.
(5) Bor-Sen C.; Saad, A. K. *Photopolymerization Fundamentals and Applications*; Scranton, A., Bowman, C., Peiffer, R., Eds.; *ACS Symp. Ser.* **1996**, *No. 673*, 150.
(6) Gush, D. P.; Ketley, A. D. *Mod. Paint Coat.* **1978**, 58.
(7) Kharasch, M. S.; Nudenberg, W.; Mantell, G. J. *J. Org. Chem.* **1951**, *16*, 524.
(8) Cramer, N. B.; Scott, J. P.; Bowman, C. N. *Macromolecules* **2002**, *35*, 5361.
(9) Cramer, N. B.; Bowman, C. N. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3311.
(10) Hoyle, C.; Cole, M.; Bachemin, M.; Yoder, B.; Nguyen, C.; Kuang, W.; Bowman, C.; Cramer, N.; Jonsson, S.; Viswanathan, K. *RadTech Japan 2000 Technical Proceedings*, Tokyo, Japan, Dec 2000, p 211.
(11) Kharasch, M. S.; Read, J.; Mayo, F. R. *Chem. Ind. (London)* **1938**, *57*, 752.
(12) Davis, F. D.; Fettes, E. M. In *Polyethers*; Gaylord, N. G., Ed.; Interscience: New York, 1962; Part III.
(13) Szmant, H. H.; Mata, A. J.; Namis, A. J.; Panthananickal, A. M. *Tetrahedron* **1976**, *32*, 2665.
(14) D'Souza, V. T.; Nanjundiah, R.; Baeza, J.; Szmant, H. H. *J. Org. Chem.* **1987**, *52*, 1720.
(15) D'Souza, V. T.; Iyer, V. K.; Szmant, H. H. *J. Org. Chem.* **1987**, *52*, 1725.
(16) Sensfuss, S.; Friedrich, M.; Klemm, E. *Makromol. Chem.* **1991**, *192*, 2895.
(17) Lecamp, L.; Houllier, F.; Youssef, B.; Bunel, C. *Polymer* **2001**, *42*, 2727.
(18) Soh, S. K.; Sundberg, D. C. *J. Polym. Sci., Polym. Chem.* **1982**, *20*, 1299.
(19) Anseth, K. S.; Wang, C. M.; Bowman, C. N. *Macromolecules* **1994**, *27*, 650.
(20) Lovestead, T. M.; Berchtold, K. A.; Bowman, C. N. *Macromol. Theory Simul.* **2002**, *11*, 729.
(21) Lovell, L. G.; Berchtold, K. A.; Elliott, J. E.; Lu, H.; Bowman, C. N. *Polym. Adv. Technol.* **2001**, *12*, 335.
(22) Odian, G. *Principles of Polymerization*; John Wiley & Sons: New York, 1991.
(23) Anseth, K. S.; Wang, C. M.; Bowman, C. N. *Polymer* **1994**, *35*, 3243.

MA034072X