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# Thiol−Vinyl Mechanisms. 1. Termination and Propagation Kinetics in Thiol−Ene Photopolymerizations

**Sirish K. Reddy,**[†] **Neil B. Cramer,**[†] **and Christopher N. Bowman***[,†,‡]

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

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ABSTRACT: In this work, termination and propagation kinetics of thiol−ene photopolymerizations are investigated via unsteady-state analysis, and termination is shown to occur though bimolecular radical−radical recombinations. The termination rate is too rapid to be resolved by standard differential scanning calorimetry (DSC) or Fourier transform infrared spectroscopy (FTIR) unsteady-state techniques. However, a modified rotating sector technique is demonstrated to be a viable technique for the quantification of the average radical lifetimes in thiol−ene systems. The application of the rotating sector technique to thiol−ene polymerizations requires extensive theoretical developments and analysis that are also presented here. Kinetic parameters in thiol−ene systems are determined by utilizing the experimental knowledge of average radical lifetimes and analytical expressions for steady-state and unsteady-state polymerizations. Knowledge of individual rate parameters in binary thiol−ene systems, rather than ratios of rate parameters, is essential for the prediction of polymerization kinetics in complex thiol−ene systems.

## Introduction

Thiol−ene photopolymerizations are reactions between multifunctional thiol and ene monomers that exhibit several unique polymerization properties. They exhibit all the advantages of typical acrylic photopolymerizations including solventless processing, rapid curing, and spatial and temporal control over polymerization. Further, they exhibit several distinct advantages such as rapid curing in the presence of little or no added photoinitiator and relatively insignificant inhibition in the presence of oxygen.

The thiol−ene photopolymerization reaction is based on the addition of a thiol functional group to an ene functional group as outlined in the following schematic. The reaction proceeds via addition of a thiyl radical through the ene functional group to form a carbon radical (step 1). Chain transfer of the carbon radical to another thiol functional group follows the addition step, regenerating the thiyl radical and forming the thiol−ene addition product (step 2). Because of this unique step growth polymerization mechanism, the molecular weight evolution in thiol−ene systems occurs slowly, thereby leading to delayed gelation and polymer films that have reduced shrinkage stress.

$$\mathrm{RS^{\bullet} + R'CH{=}CH_2 \xrightarrow{k_{pSC}} R'C^{\bullet}H - CH_2SR} \qquad \text{step 1}$$

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

Several researchers have studied and characterized polymerization reactivities of thiol−ene systems with a wide variety of different monomer chemistries.[1−9] Previous evaluations of thiol−ene reactivities are all presented as normalized reactivity comparisons, as the polymerization mechanism and kinetics of thiol−ene systems were not well understood.[1] It was shown previously that the polymerization rate in thiol−ene systems scales with the initiation rate to the $^1/_2$ power, indicative of a bimolecular termination mechanism. However, the termination rate and its importance in thiol−ene systems have been extensively debated.[1,23,24] Theories ranging from slow and unimportant termination, no termination, or termination by impurities have all been proposed.

We recently developed a comprehensive model for thiol−ene photopolymerization kinetics. Utilizing experimental kinetics and model predictions, several aspects of thiol−ene photopolymerization kinetics were investigated. The propagation kinetics in these systems were shown to be strongly controlled by the ratio of the propagation to the chain transfer parameter ($k_p/k_{ct}$). It was determined from the model that for a thiol−allyl ether system, in which the ratio of $k_p/k_{ct}$ is very high, the polymerization rate is independent of the ene monomer concentration and that chain transfer is the rate-limiting step. It was also shown that in a thiol−vinyl silazane ($k_p/k_{ct} \ll 1$) system, propagation is the rate limiting step and the polymerization rate is first order in ene monomer concentration and nearly independent of thiol monomer concentration. Further, the polymerization rate was shown to be nearly equivalently affected by both thiol and ene monomer concentrations in thiol−vinyl ether and thiol−norbornene systems, which have $k_p/k_{ct} \approx 1$. However, knowledge of individual rate parameters rather than the ratios of these rate parameters is essential to have the ability to predict polymerization kinetics in more complex thiol−ene systems. For that purpose, this work attempts to evaluate absolute kinetic constants in thiol−vinyl systems as well as to investigate the termination mechanism in these systems. The development of an analytical model for thiol−ene systems[2,10] allows for just such a quantitative study of the kinetic parameters to be undertaken.

Differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR) are commonly utilized techniques for determining kinetic parameters in cross-linking

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* To whom correspondence should be addressed. Telephone: 303-492-3247. Fax: 303-492-4341. E-mail: christopher.bowman@colorado.edu.

[†] Department of Chemical and Biological Engineering, University of Colorado.

[‡] Department of Restorative Dentistry, University of Colorado Health Sciences Center.

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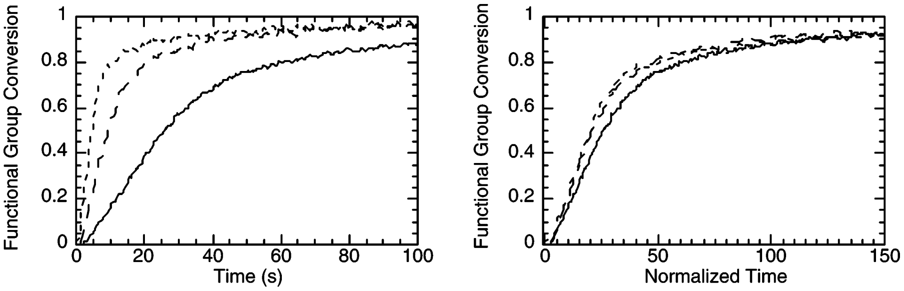

(a) (b)

**Figure 1.** (a) Conversion vs time results for thiol−allyl ether polymerizations with a 1:1 ratio of thiol to ene functional groups. (b) Results where time is normalized by light intensity to the $^1/_2$ power. Samples contain 0.1 wt % DMPA and are irradiated at 1 (—), 5 (— —), and 20 (- - -) mW/cm$^2$.

free radical polymerizations using unsteady-state experiments.[11−15] To determine kinetic parameters utilizing DSC and FTIR in after-effect experiments, the light is extinguished during the polymerization, and the polymerization is monitored in the dark.[11−13]

Other techniques for determining kinetic parameters utilize pulsed laser or rotating sector experiments. These techniques are based on the analysis of continuous unsteady-state kinetics with alternating light and dark periods or cycles.[16−18] For the rotating sector method the irradiating light is shuttered on and off, generating regular intervals of light and dark periods. The steady-state average propagating radical lifetime ($\tau_s$) is determined by monitoring the average polymerization rate as a function of cycle time. $\tau_s$ is defined as the average time from the creation of a radical to its ultimate termination, disregarding possible chain transfer steps. The ratio of the average polymerization rate in the system exposed to intermittent exposure to its steady-state polymerization rate for continuous exposure is determined as a function of the intermittent exposure time. The experimental data is then superimposed onto a theoretical curve for $\tau_s$, and $\tau_s$ is determined by calculating a best fit of the experimental data to the theoretical curves.[19−21] Analytical expressions for initiation, termination, and polymerization rate are utilized to derive expressions for the termination and propagation kinetic parameters as a function of $\tau_s$.

In this work, experiments are performed to clarify the termination mechanism and its importance in thiol−ene photopolymerizations. We investigate two thiol−ene systems, a thiol−norbornene system, in which both the propagation and chain transfer steps occur equally rapidly, and a thiol−allyl system, in which the chain transfer step is known to be the rate-limiting step. A general analytical approach for average radical lifetimes ($\tau_s$) in unsteady-state thiol−ene polymerizations is developed for both systems. Utilizing rotating sector experiments and analytical expressions for $\tau_s$ and steady-state polymerization rates, we quantify the propagation, chain transfer, and termination kinetic parameters in these thiol−ene systems. The experimentally determined kinetic parameters are then used to predict steady-state and complex thiol−ene polymerization kinetics accurately.

## Experimental Section

**Materials.** The monomer trimethylolpropane diallyl ether (allyl) was purchased from Aldrich (Milwaukee, WI). The photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA), was purchased from Ciba-Geigy (Hawthorne, NY). The monomers pentaerythritol tetra(3-mercaptopropionate) (thiol) and 1,6-hexanediol di(*endo*,*exo*-norborn-2-ene-5-carboxylate) (norbornene) were donated by Bruno Bock (Marschacht, Germany) and Henkel Loctite Corporation (Rocky Hills, CT), respectively.

**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 scans per second. The FTIR sample chamber was continuously purged with dry air, and the thiol functional group conversion was monitored using the S−H absorption peak at 2570 cm$^{-1}$. Norbornene and allyl ether conversions were monitored with double bond absorption peaks at 713 and 1636 cm$^{-1}$, respectively. Conversions were calculated using the ratio of peak areas to the peak area prior to polymerization. All reactions were performed under ambient conditions.

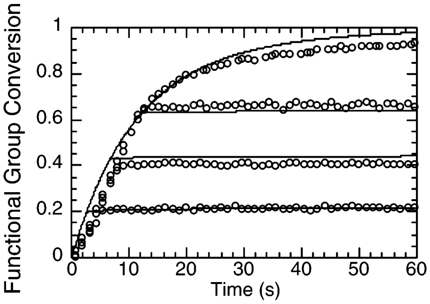

**Figure 2.** Model and experimental data for conversion vs time of tetrathiol and diallyl polymerizations with a 1:1 ratio of thiol and allyl functional groups (4.82 mol/L). Polymerizations are for a full cure, as well as 5, 7.5, and 12 s of irradiation time. Samples contain 0.1 wt % DMPA and are irradiated at 10 mW/cm$^2$. Modeling kinetic parameters utilized are $k_p = 1.4 \times 10^5$ L/mol·s, $k_{CT} = 1.4 \times 10^4$ L/mol·s, and $k_{t1}$, $k_{t2}$, and $k_{t3} = 1 \times 10^6$ L/mol·s.

Monomer samples were laminated between sodium chloride windows in a horizontal transmission apparatus.[25] Polymerizations were initiated via an EXFO Acticure light source (EXFO, Mississauga, Ontario) with a 320−500 nm filter, and irradiation intensities were measured with an International Light, Inc. Model IL1400A radiometer (Newburyport, MA).

Rotating sector experiments were performed with a Uniblitz model VMM-T1 Shutter Driver/Timer (Uniblitz Electronic, Rochester, NY) adaptation to the Acticure light source. The shuttering system (VS14S2ZM1R1) is in a cased configuration, equipped with reflective blade coatings, and has the R1 modification to enable its use under the intense heat produced by the light source.

## Results and Discussion

Utilizing FTIR experiments, polymerization rates are shown to scale with initiation rates to the $^1/_2$ power ($R_p \propto R_i^{1/2}$) for the thiol−allyl ether system (Figure 1). This result indicates that termination occurs via bimolecular radical−radical recombination and thereby undermines other theories of slow and unimportant termination, no termination, or termination by impurities. Further, termination by bimolecular radical−radical recombination show here is also in agreement with previous investigations.[3]

In Figure 2, unsteady-state experiments for the thiol−allyl ether system are presented. The unsteady-state results for the thiol−allyl system and the thiol−norbornene system (not shown) demonstrate that termination in thiol−ene systems is extremely rapid. To calculate kinetic parameters with FTIR, the polymerization reaction must be accurately monitored for a reasonably finite period of time after illumination has ceased. As seen in Figure 2, the polymerization rate decays too rapidly to resolve the kinetics accurately in the dark with FTIR. The time between when the light is extinguished and when the polymerization rate has ceased is not distinguishable within the time resolution offered by FTIR. The data also indicates that DSC experiments, which have an even longer response time of 3−5 s, could also not be used to monitor unsteady-state kinetics accurately. Modeling predictions for unsteady-state experiments are also presented in Figure 2. The rate parameters for modeling the unsteady-state experiments are taken from previous modeling work on thiol−allyl systems.[2] Modeling predictions match the unsteady-state experimental data extremely well. These results do not indicate that the modeling parameters represent actual values for kinetic parameters, it only reconfirms that the ratio of the propagation to the termination kinetic parameters, or a lumped kinetic parameter ($R_p \propto k'[\mathrm{SH}]$), is correct. The results also indicate that the extremely rapid termination observed in thiol−ene systems is reasonable for typical termination kinetics where diffusion-limited kinetics do not dominate because of the lower molecular weights associated with the step growth mechanism.

As the polymerization kinetics in the after effect experiments were too rapid to be resolved experimentally by FTIR, rotating sector experiments were performed in an effort to determine the kinetic parameters. The shutter frequencies for all of the experiments were chosen so as to keep the ratio of dark to light illumination of 3:1. When the shutter frequencies for light and dark times are large relative to $\tau_s$, the polymerization rate during illumination will be identical to the steady-state polymerization rate and negligible during the dark cycle. Thus, for shutter frequencies of 3:1, the average polymerization rate will be 1/4 of the steady-state value. For all shutter cycle times above this critical shutter speed, the average polymerization rates will be $^1/_4$ of the steady-state rate. For shutter frequencies where the light and dark cycles are less than the critical shutter speed, the average polymerization rates will be greater than $^1/_4$ of the steady-state value.[16] To determine the experimental values of $\tau_s$, shutter speeds higher than the critical speeds are used.

The shutter in our rotating sector equipment permits a minimum cycle time of 0.4 ms, with a illumination time of 0.1 ms and $r$ (length of dark period to the length of light period) value of 3. Hence, this experimental technique can be utilized, theoretically, to measure average radical lifetimes as small as 0.0001 s. This result is in contrast to typical FTIR unsteady-state experiments that can measure average radical lifetimes only on the order of tenths of a second or greater.

The average radical lifetime, $\tau_s$, is defined as the concentration of radicals divided by their termination rate.[16] In a system with radicals $\mathrm{M}^\bullet$,

$$\tau_s = \frac{[\mathrm{M}^\bullet]_s}{2k_t[\mathrm{M}^\bullet]_s^{\,2}} = \frac{1}{2k_t[\mathrm{M}^\bullet]_s} \tag{1}$$

where $k_t$ is the average termination kinetic parameter and $[\mathrm{M}^\bullet]_s$ is the steady-state radical concentration. In thiol−ene systems, termination occurs through two types of radicals: carbon based radicals and sulfur based (thiyl) radicals. The termination of radicals in these systems is due to bimolecular recombination and is given by eqs 2−4. By setting the total radical concentration to $\mathrm{M}^\bullet$ ($[\mathrm{M}^\bullet] = [\mathrm{C}^\bullet] + [\mathrm{S}^\bullet]$) and the total termination rate to $2k_t[\mathrm{M}^\bullet]^2$, the unsteady-state kinetics in these systems are described by the same equations that have been used previously to describe those in traditional homopolymerization systems. Hence, the average radical lifetime in these systems is equal to the total radical concentration divided by their termination rate and is given by eq 5.

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

$$R_t(\mathrm{C}^\bullet) = k_{t2}[\mathrm{S}^\bullet][\mathrm{C}^\bullet] + 2k_{t3}[\mathrm{C}^\bullet]^2 \tag{3}$$

$$R_t = R_t(\mathrm{C}^\bullet) + R_t(\mathrm{S}^\bullet) = 2k_{t1}[\mathrm{S}^\bullet]^2 + 2k_{t2}[\mathrm{S}^\bullet][\mathrm{C}^\bullet] + 2k_{t3}[\mathrm{C}^\bullet]^2 \tag{4}$$

$$\tau_s = \frac{[\mathrm{M}^\bullet]_s}{2k_t[\mathrm{M}^\bullet]_s^{\,2}} = \frac{[\mathrm{S}^\bullet]_s + [\mathrm{C}^\bullet]_s}{2k_{t1}[\mathrm{S}^\bullet]_s^{\,2} + 2k_{t2}[\mathrm{S}^\bullet]_s[\mathrm{C}^\bullet]_s + 2k_{t3}[\mathrm{C}^\bullet]_s^{\,2}} \tag{5}$$

where $[\mathrm{C}^\bullet]_s$ and $[\mathrm{S}^\bullet]_s$ are the steady-state radical concentrations of the carbon and thiyl radicals and $k_{t1}$, $k_{t2}$, and $k_{t3}$ are the bimolecular termination rate parameters for thiyl−thiyl, thiyl−carbon, and carbon−carbon radical recombinations, respectively. Further, by relating the polymerization rate ($R_p$) to individual radical concentrations (eq 6), the overall average radical lifetime is expressed as a function of monomer concentrations and kinetic parameters (eq 7).

$$R_p = k_{ct}[\mathrm{C}^\bullet][\mathrm{SH}] = k_p[\mathrm{S}^\bullet][\mathrm{CC}] \tag{6}$$

$$\tau_s = \frac{[\mathrm{M}^\bullet]_s}{2k_t[\mathrm{M}^\bullet]_s^{\,2}} = \frac{1}{R_{p,s}} \frac{\dfrac{1}{k_p[\mathrm{CC}]} + \dfrac{1}{k_{ct}[\mathrm{SH}]}}{\dfrac{2k_{t1}}{(k_p[\mathrm{CC}])^2} + \dfrac{2k_{t2}}{(k_{ct}k_p[\mathrm{CC}][\mathrm{SH}])} + \dfrac{2k_{t3}}{(k_{ct}[\mathrm{SH}])^2}} \tag{7}$$

where $k_{ct}$ is the chain transfer kinetic parameter, $k_p$ is the propagation kinetic parameter, and [CC] and [SH] are the concentrations of the ene and thiol functional groups, respectively. The analytical expression for the steady-state polymerization rate ($R_{p,s}$) in thiol−ene systems has been derived previously[2] and is given by

$$R_{p,s} = \sqrt{\frac{R_i}{2}} \frac{1}{\sqrt{\dfrac{k_{t1}}{(k_p[\mathrm{C{=}C}])^2} + \dfrac{k_{t2}}{(k_pk_{ct}[\mathrm{C{=}C}][\mathrm{SH}])} + \dfrac{k_{t3}}{(k_{ct}[\mathrm{SH}])^2}}} \tag{8}$$

Equations 7 and 8 depict the average radical lifetimes and steady-state polymerization rate for any thiol−ene system. To utilize these equations for quantification of the rate parameters in specific thiol−ene systems, these equations have to be simplified based on the specific kinetics of the system studied.

Initiation rates in free radical photopolymerizations are calculated from the expression[16,22]

$$R_i = \frac{2.303 f\epsilon[I]I_0\lambda}{N_{AV}hc} \tag{9}$$

where $f$ is the lumped efficiency, $\epsilon$ is the molar absorptivity (150 L/mol·cm for DMPA and 365 nm light), [I] is the initiator concentration, $I_o$ is the light intensity, $\lambda$ is the initiation

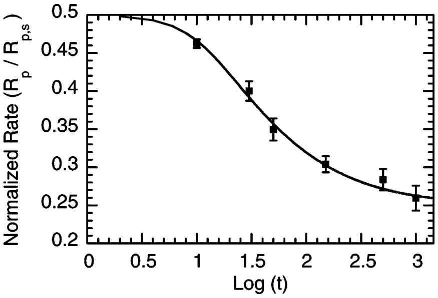

**Figure 3.** Rotating sector results for a 1:1 stoichiometric ratio of thiol and norbornene polymerizations (■). Samples contain 0.1 wt % DMPA and are irradiated at 2 mW/cm$^2$. *t* is the irradiation time in ms for one shutter cycle. Normalized rates are the steady-state polymerization rate divided by the polymerization rate during unsteady-state rotating sector polymerizations. The theoretical curve is for $\tau = 0.01$ s (—).

wavelength, $N_{AV}$ is Avogadro's number, *h* is Planck's constant, and *c* is the speed of light. In this work, the initiation rates are based on standard values for DMPA.[22]

Rotating sector experiments were performed with a 1:1 stoichiometric mixture of the thiol–norbornene system. The normalized rates as a function of illumination time are presented in Figure 3. Also presented is the theoretical curve for $\tau_s$ equal to 0.01 s. The experimental data of normalized polymerization rates were fitted to the theoretical curve by performing a nonlinear regression on the experimental data. On the basis of this analysis $\tau_s$ was determined to be 0.01 s with a 95% confidence interval for $\tau_s$ of $0.01 \pm 0.0014$ s.

Before solving for the kinetic parameters with analytical expressions for $\tau_s$ and $R_{p,s}$ (eqs 7 and 8), it is essential to simplify the analytical equations. These simplifications are based on the polymerization characteristics of the individual system. In our previous work on the steady-state kinetics of thiol–norbornene systems, it was experimentally shown that the overall polymerization rate is equivalently affected by both thiol and norbornene functional group concentrations. It was further shown that by assuming all three termination parameters to be equal ($k_{t1} = k_{t2} = k_{t3}$), the thiol–norbornene polymerizations are predicted accurately by setting the propagation kinetic parameter equal to the chain transfer parameter ($k_p = k_{ct}$). Apart from the quantification of rate parameters in the thiol–norbornene system, this study also aims to investigate the validity of the assumption of equal termination parameters. For that purpose, we consider the other possible modes of termination and attempt to understand or describe the termination mode in thiol–ene systems.

Three possible modes of termination are (i) only thiyl–thiyl radical termination is important ($k_{t1} \gg k_{t2}$ and $k_{t3}$), (ii) only carbon–carbon radical terminations is important ($k_{t3} \gg k_{t2}$ and $k_{t1}$), and (iii) only thiyl–carbon radical terminations is important ($k_{t2} \gg k_{t1}$ and $k_{t3}$). The expression for the steady-state polymerization (eq 8) is simplified for each of the above cases and further analysis described for those cases that are consistent with the previously observed experimental polymerization kinetics.

Setting $k_p = k_{ct}$ for this thiol–norbornene system, a condition imposed to account for the experimentally observed equivalent dependence of rate on both thiol and ene concentrations, evaluation of eq 8 reveals that the only other termination mode (apart from $k_{t1} = k_{t2} = k_{t3}$) in which the polymerization rate is equivalently affected by both the thiol and ene monomer concentrations is when carbon–thiyl radical termination dominates the termination rate, i.e., $k_{t2} \gg k_{t1}$ and $k_{t3}$. In all other cases, the polymerization rate would not vary nearly equivalently with both thiol and ene monomer concentrations. For example, when $k_{t1} \gg k_{t2}$ and $k_{t3}$, the steady-state polymerization rate expression (eq 8) simplifies such that the polymerization rate is dependent only on the ene monomer concentration and is independent of thiol monomer concentration, $R_p \propto$ [CC]. This result is not in accordance with the experimentally observed kinetics, thereby negating the possibility of only thiyl–thiyl radical termination being important. For the case when only carbon–carbon radical termination is considered, the steady-state polymerization rate expression (eq 8) simplifies such that the polymerization rate is dependent only on the thiol monomer concentration and is independent of the ene monomer concentration, $R_p \propto$ [SH]. Hence, the only possible modes of termination in which the rate expression corresponds to the experimentally observed polymerization kinetics are when all the radical–radical recombinations are equally likely ($k_{t1} = k_{t2} = k_{t3}$) and when the thiyl–carbon radical termination dominates the termination mechanism ($k_{t2} \gg k_{t1}$ and $k_{t3}$). We first consider the case of $k_{t1} = k_{t2} = k_{t3}$ and then consider the case corresponding to $k_{t2} \gg k_{t1}$ and $k_{t2} \gg k_{t3}$.

To solve for the kinetic parameters in a thiol–norbornene system, the experimental values of $\tau_s$ and $R_{p,s}$ are coupled with their corresponding analytical equations. For this purpose the analytical equations of $\tau_s$ and $R_{p,s}$ (eqs 7 and 8) described for a general thiol–ene system are simplified for the specific case of the thiol–norbornene system. Considering first the possibility of equal likelihood of all radical–radical recombinations, eqs 7 and 8 are simplified by assuming $k_{t1} = k_{t2} = k_{t3}$ and setting the ratio of propagation to chain transfer parameters to one ($k_p = k_{ct}$). Employing these simplifications, equations for $\tau_s$ and $R_{p,s}$ for a thiol–norbornene system are represented by eqs 10 and 11.

$$\tau_s = \frac{k_p}{2k_t R_{p,s}} \frac{\dfrac{1}{[\mathrm{CC}]} + \dfrac{1}{[\mathrm{SH}]}}{\dfrac{1}{([\mathrm{CC}])^2} + \dfrac{1}{([\mathrm{CC}][\mathrm{SH}])} + \dfrac{1}{([\mathrm{SH}])^2}} \qquad (10)$$

$$R_{p,s} = \sqrt{\frac{R_i}{2k_t}} \frac{k_p}{\sqrt{\dfrac{1}{([\mathrm{C{=}C}])^2} + \dfrac{1}{([\mathrm{C{=}C}][\mathrm{SH}])} + \dfrac{1}{([\mathrm{SH}])^2}}} \qquad (11)$$

The kinetic parameters are determined by utilizing these simplified analytical equations and the experimental values of $\tau_s$ (=0.01 s) and $R_{p,s}$ for the 1:1 stoichiometric system.

$$k_{t1} = k_{t2} = k_{t3} = \frac{2}{3R_i{\tau_s}^2} = 3.5 \times 10^8 \text{ L/mol·s}$$

$$k_p = k_{ct} = \frac{2}{R_i\tau_s}\frac{R_{p,s}}{[\mathrm{C{=}C}]} = \frac{2}{R_i\tau_s}\frac{R_{p,s}}{[\mathrm{SH}]} = 3.1 \times 10^6 \text{ L/mol·s}$$

Experimental data for the polymerization of thiol–norbornene systems are presented in Figure 4 along with the model predictions using the above determined kinetic parameters. As the thiol–norbornene system represents a true step growth polymerization, the limiting reagents in 1:2 and 2:1 stoichiometric systems reach nearly 100% conversion, while the functional group in excess achieves only 50% conversion. The 1:2 and 2:1 stoichiometric systems have an excess of unreacted monomer, thereby leading to polymerization systems that do not encounter significant diffusion limitations. At high conversions the 1:1 system encounters significant diffusion limitations due to the network forming a glassy polymer. In our kinetic modeling, we assume the rate parameters to be independent of

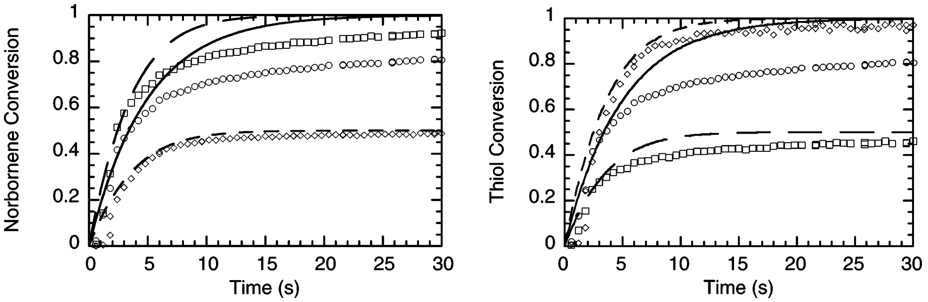

**Figure 4.** Model predictions and experimental data for conversion vs time of thiol and norbornene photopolymerizations. Modeling predictions are based on the assumption that $k_{t1} = k_{t2} = k_{t3}$. Norbornene functional group conversions are shown for initially 1:1 (3.88 mol/L) (○, —), 2:1 (5.66:2.83 mol/L) (□, − −), and 1:2 (2.38:4.76 mol/L) (◇, - -) ratios of thiol to norbornene functional groups. Thiol functional group conversions and model predictions are shown for initially 1:1 (○, —), 2:1 (□, − −), and 1:2 (◇, - -) ratios of functional groups. Samples contain 0.1 wt % DMPA and are irradiated at 4 mW/cm$^2$. The kinetic parameters for modeling are experimentally determined by rotating sector experiments and are given by $k_{t1} = k_{t2} = k_{t3} = 3.5 \times 10^8$ L/mol•s and $k_{ct} = k_p = 3.1 \times 10^6$ L/mol•s.

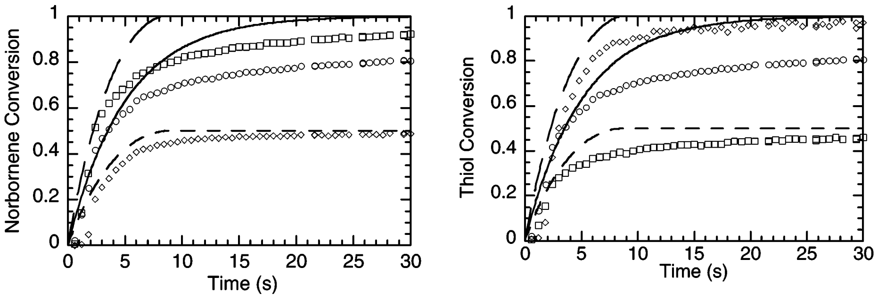

**Figure 5.** Experimental data and model predictions for conversion vs time of thiol and norbornene photopolymerizations. Modeling predictions are based on the assumption that $k_{t2} \gg k_{t1}$ and $k_{t2} \gg k_{t3}$. Norbornene functional group conversions are shown for initially 1:1 (3.88 mol/L) (○, —), 2:1 (5.66:2.83 mol/L) (□, − −), and 1:2 (2.38:4.76 mol/L) (◇, - -) ratios of thiol to norbornene functional groups. Thiol functional group conversions and model predictions are shown for initially 1:1 (○, —), 2:1 (□, − −), and 1:2 (◇, - -) ratios of functional groups. Samples contain 0.1 wt % DMPA and are irradiated at 1 mW/cm$^2$. The kinetic parameters for modeling are experimentally determined by rotating sector experiments and are given by $k_{ct} = k_p = 2.8 \times 10^6$ L/mol-s and $k_{t2} = 8.7 \times 10^8$ L/mol•s.

conversion, thereby leading to discrepancies in modeling predictions and experimental data at high conversions for the 1:1 stoichiometric system. However, for the 1:2 and 2:1 stoichiometric systems, which do not have significant diffusional limitations, the model predictions portray experimental kinetics well throughout the entire polymerization.

In the second possible case, i.e., when thiyl−carbon termination dominates the termination rate ($k_{t2} \gg k_{t1}$ and $k_{t3}$), the steady-state polymerization rate (eq 8) is expressed as

$$R_{p,s} = \sqrt{\frac{R_i}{2k_{t2}}}k_p\sqrt{[\mathrm{C{=}C}][\mathrm{SH}]} \tag{12}$$

The average radical lifetime (eq 7) for this case simplifies as

$$\tau_s = \frac{k_p}{2k_{t2}R_{p,s}}([\mathrm{CC}] + [\mathrm{SH}]) \tag{13}$$

The above equations are solved for the 1:1 thiol−norbornene system utilizing the experimental values for $\tau_s$ (=0.01 s) and $R_{p,s}$.

$$k_{t2} = \frac{2}{R_i{\tau_s}^2} = 1.05 \times 10^9 \text{ L/mol•s}$$

$$k_p = k_{ct} = \frac{2}{R_i\tau_s}\frac{R_{p,s}}{[\mathrm{C{=}C}]} = \frac{2}{R_i\tau_s}\frac{R_{p,s}}{[\mathrm{SH}]} = 3.1 \times 10^6 \text{ L/mol•s}$$

These kinetic parameters are then utilized to predict the polymerization kinetics of the thiol−norbornene systems. Figure 5 compares model predictions with the experimental polymerization kinetics. Comparing the modeling predictions from Figures 4 and 5, while the modeling predictions in Figure 4 show a good match between experimental kinetics and predictions, the predictions in Figure 5 do not match well with the experimental kinetics. These differences are very evident for the 1:2 stoichiometric systems, which do not exhibit diffusion limited kinetics. Thus, it is evident that model parameters obtained from the assumption of equal radical−radical combinations for all radicals accurately predicts the experimental polymerization kinetics for the nondiffusional limited regimes. However, model predictions from kinetic parameters obtained by assuming only carbon−thiyl radical termination fail to predict experimental polymerizations accurately. These results indicate that the assumption of equal importance of all kinetic parameters might be valid. However, more experiments have to be performed to confirm/clarify the above feature.

To demonstrate further the validity of the assumption that all termination parameters are equally important, off-stoichiometry rotating sector experiments were performed. For this purpose, rotating sector experiments were conducted with 1:4 and 4:1 stoichiometric mixtures of thiol−norbornene systems. A comparison of the average radical lifetimes for these nonstoichiometric systems with that of the 1:1 stoichiometric system confirms the termination mode in these systems. Results for the nonstoichiometric rotating sector experiments along with the theoretical curves are presented in Figure 6. Performing a nonlinear regression on the experimental data, the $\tau_s$ values for the 1:4 and 4:1 thiol−norbornene systems are found to be 0.0011 and 0.009, respectively. Analysis on confidence limits of the $\tau_s$ parameter in these systems yielded 95% confidence limits of 0.011 ± 0.0015 and 0.009 ± 0.0014 for the 1:4 and 4:1 systems.

To understand the termination mode in these systems, eqs 7 and 8 are solved to relate the theoretical $\tau_s$ values for the

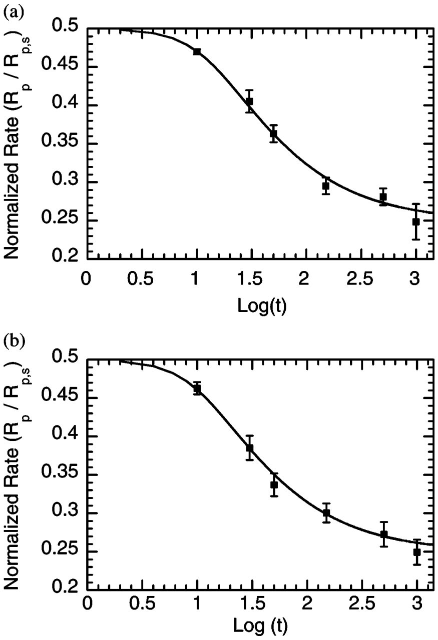

**Figure 6.** Rotating sector results for thiol−norbornene systems having an initial functional group composition of (a) 1:4 and (b) 4:1 stoichiometric ratios of thiol and norbornene functional groups (■). Samples contain 0.1 wt % DMPA and are irradiated at 2 mW/cm$^2$. *t* is the irradiation time in ms for one shutter cycle. Normalized rates are the steady-state polymerization rate divided by the polymerization rate during unsteady-state rotating sector polymerizations. Theoretical curves for the 1:4 and 4:1 systems are given by $\tau = 0.011$ s (−) and $\tau = 0.009$ s (−), respectively.

nonstoichiometric systems with that of a 1:1 stoichiometric system. This analysis is performed for both termination possibilities. For the first case when all the termination events are equally likely ($k_{t1} = k_{t2} = k_{t3}$), eq 10 is simplified, and the theoretical $\tau_s$ values for nonstoichiometric systems are expressed as a function of $\tau_s$ values for the 1:1 system.

$$\frac{\tau_{s,1:1}}{\tau_{s,1:4}} = \frac{14}{5}\frac{R_{p,s,1:4}/[\mathrm{C{=}C}]_{1:4}}{R_{p,s,1:1}/[\mathrm{C{=}C}]_{1:1}} \tag{14}$$

$$\frac{\tau_{s,1:1}}{\tau_{s,4:1}} = \frac{7}{10}\frac{R_{p,s,4:1}/[\mathrm{C{=}C}]_{4:1}}{R_{p,s,1:1}/[\mathrm{C{=}C}]_{1:1}} \tag{15}$$

where $\tau_{s,1:1}$, $\tau_{s,1:4}$, and $\tau_{s,4:1}$, indicate the average radical lifetimes for the 1:1, 1:4, and 4:1 stoichiometric ratios of the thiol:norbornene systems. Similar notations are utilized to denote the polymerization rates ($R_{p,s}$) and the double bond concentrations ([CC]) for each of the three thiol−norbornene systems.

In the second case when only the carbon−thiyl radical termination is important ($k_{t2} \gg k_{t1}$ and $k_{t3}$), eq 13 is solved to yield relationships between the $\tau_s$ values for stoichiometric and nonstoichiometric cases:

$$\frac{\tau_{s,1:1}}{\tau_{s,1:4}} = \frac{8}{5}\frac{R_{p,s,1:4}/[\mathrm{C{=}C}]_{1:4}}{R_{p,s,1:1}/[\mathrm{C{=}C}]_{1:1}} \tag{16}$$

$$\frac{\tau_{s,1:1}}{\tau_{s,4:1}} = \frac{2}{5}\frac{R_{p,s,4:1}/[\mathrm{C{=}C}]_{4:1}}{R_{p,s,1:1}/[\mathrm{C{=}C}]_{1:1}} \tag{17}$$

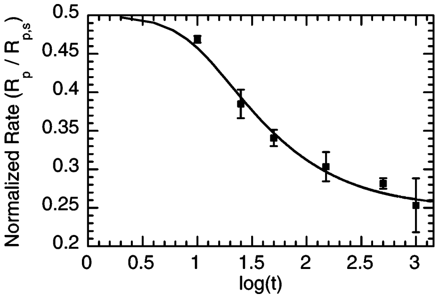

**Figure 7.** Rotating sector results for tetrathiol and diallyl polymerizations (■). Samples contain 0.2 wt % DMPA and are irradiated at 2 mW/cm$^2$. *t* is the irradiation time in ms for one shutter cycle. Normalized rates are the steady-state polymerization rate divided by the polymerization rate during unsteady-state rotating sector polymerizations. Theoretical curves are shown for $\tau = 0.0085$ s (−).

Utilizing the experimental values of steady-state polymerization kinetics, the above expressions (eqs 14−17) can be simplified to relate the average radical lifetimes for the nonstoichiometric systems to those for stoichiometric systems. Such an analysis is performed for both possible termination modes and is presented below.

$$\text{If } k_{t1} = k_{t2} = k_{t3} \qquad \frac{\tau_{s,1:1}}{\tau_{s,1:4}} = 0.98 \quad \text{and} \quad \frac{\tau_{s,1:1}}{\tau_{s,4:1}} = 0.9$$

$$\text{If } k_{t2} \gg k_{t1} \text{ and } k_{t3} \qquad \frac{\tau_{s,1:1}}{\tau_{s,1:4}} = 0.55 \quad \text{and} \quad \frac{\tau_{s,1:1}}{\tau_{s,4:1}} = 0.52$$

From the experimental results, the ratio of $\tau_{s,1:1}$ to $\tau_{s,1:4}$ is found to be 0.9 and the ratio of $\tau_{s,1:1}$ to $\tau_{s,4:1}$ is approximately 1.1. Hence, the ratios of $\tau_s$ values for the 1:4 and 4:1 thiol:norbornene systems with that of 1:1 systems match much more closely to the first case (of equal $k_t$'s) rather than to the second case (of unequal $k_t$'s). Thus, the rotating sector experiments further demonstrate that the case of equal likelihood of all radical−radical recombinations is the correct case.

Experiments were also performed to investigate the kinetic parameters in thiol−allyl systems. In thiol−allyl systems the polymerization kinetics were previously shown to vary first order in thiol functional group concentration and independent of ene monomer concentration (i.e., $R_p \propto [\mathrm{SH}]^1[\mathrm{CC}]^0$).[10] This first order dependence of rate on thiol monomer concentration was explained with chain transfer as the rate-limiting step. The polymerization kinetics were predicted by setting a high ratio of the propagation kinetic parameter to the chain transfer kinetic parameter. Utilizing this knowledge of kinetic parameters, equations for the steady-state polymerization rate and average radical lifetime (eqs 7 and 8) are determined to be

$$\tau_s = \frac{1}{R_{p,s}}\frac{k_{ct}[\mathrm{SH}]}{2k_{t3}} \tag{18}$$

$$R_{p,s} = \sqrt{\frac{R_i}{2k_{t3}}}k_{ct}[\mathrm{SH}] \tag{19}$$

where $k_{t3}$ represents the termination parameter for carbon−carbon radical termination. As the concentration of carbon radicals to thiyl radicals is proportional to the ratio of the propagation kinetic parameter to the chain transfer kinetic parameter, and as $k_p > k_{ct}$ in the thiol−allyl system, the radicals present in the system are predominantly carbon radicals. Because of this shift of radical concentration to carbon radicals, the carbon−carbon radical termination ($k_{t3}$) kinetic parameter is the only termination parameter appearing in eqs 18 and 19. Figure 7 presents the experimental data for the unsteady-state kinetics of the 1:1 thiol−allyl system. Performing a nonlinear regression on the experimental data, the average radical lifetime for this

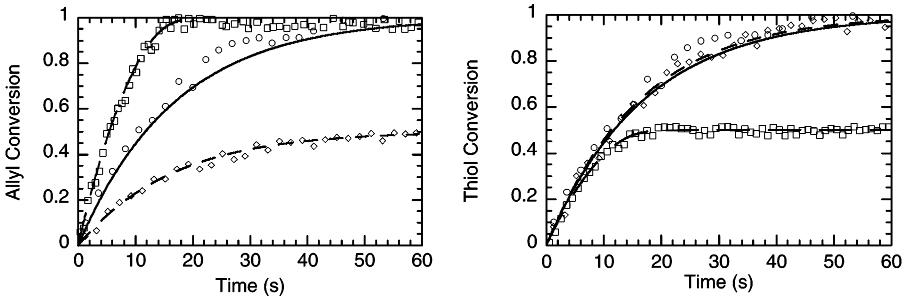

**Figure 8.** Model predictions and experimental data for conversion vs time of thiol and allyl photopolymerizations. Key: (a) allyl functional group conversions for initially 1:1 (4.82 mol/L) (○, —), 2:1 (6.6:3.3 mol/L) (□, − −), and 1:2 (3.13:6.25 mol/L) (◇, - -) ratios of thiol to allyl ether functional groups; (b) thiol functional group conversions and model predictions for initially 1:1 (○, —), 2:1 (□, − −), and 1:2 (◇, - -) ratios of functional groups. Samples contain 0.1 wt % DMPA and are irradiated at 4 mW/cm$^2$. Kinetic parameters for modeling are experimentally determined by a combination of rotating sector and steady-state experiments to be $k_{CT} = 2.1 \times 10^5$, $k_p = 2.1 \times 10^6$, $k_{t1} = 3.5 \times 10^8$ L/mol•s, $k_{t2} = 2.6 \times 10^8$ L/mol•s, and $k_{t3} = 1.9 \times 10^8$ L/mol•s.

system was found to be 0.0085 s. Furthermore, the 95% confidence limits for the average radical lifetime were found to be 0.0085 ± 0.0017 s. Utilizing experimental values for average radical lifetime and steady-state polymerization kinetics, equations for $\tau_s$ and $R_{p,s}$ (eqs 18 and 19) are solved to yield kinetic parameters.

$$k_{t3} = \frac{1}{2R_i{\tau_s}^2} = 1.9 \times 10^8 \text{ L/mol•s}$$

$$k_{ct} = \frac{1}{R_i\tau_s}\frac{R_{p,s}}{[\text{C=C}]} = \frac{1}{R_i\tau_s}\frac{R_{p,s}}{[\text{SH}]} = 2.1 \times 10^5 \text{ L/mol•s} \qquad (20)$$

The rotating sector technique for the thiol−allyl system quantifies only the carbon−carbon termination kinetic parameter ($k_{t3}$). However, as the same thiol monomer is employed in this system and in the thiol−norbornene system, the thiyl−thiyl radical termination parameter from the thiol−norbornene system is employed here ($k_{t1} = 3.5 \times 10^8$ L/mol•s). For the cross termination parameter, we replace the termination rate parameter between the thiyl and carbon radicals, $k_{t2}$, by the geometric mean approximation of the termination parameters for the carbon−carbon and thiyl−thiyl radicals.[26]

$$k_{t2} = \sqrt{k_{t1}k_{t3}} = 2.6 \times 10^8 \text{ L/mol•s} \qquad (21)$$

Experimental steady-state polymerization kinetics of thiol−allyl systems with initial compositions of 1:1, 2:1, and 1:2 stoichiometric ratios of thiol to ene functionalities are presented in Figure 8 along with the model predictions. Polymerization kinetics of these systems are successfully predicted by utilizing the above determined rate parameters. The propagation parameter that was utilized for model predictions was found by assuming the ratio of propagation to chain transfer parameter to be approximately 10, as determined in previous work.

For the thiol−norbornene system solving for the 95% confidence intervals of $\tau_s$, yields the termination kinetic parameters in the range $2.7 \times 10^8$ to $4.7 \times 10^8$ L/mol•s and the propagation parameter in the range $2.7 \times 10^6$ to $3.6 \times 10^6$ L/mol•s. For the thiol−allyl system the 95% confidence limits for $\tau_s$ yield the carbon−carbon radical termination parameter ($k_{t3}$), in the range $1.4 \times 10^8$ to $2.9 \times 10^8$ L/mol•s and the chain transfer parameter ranges from $1.6 \times 10^5$ to $2.3 \times 10^6$ L/mol•s.

A similar analysis was also performed for the thiol−vinyl ether system, and solving for the 95% confidence interval of $\tau_s$ (0.0094 ± 0.0011) yielded the termination parameters in the range $3.4 \times 10^8$ to $5.4 \times 10^8$ L/mol•s, the propagation parameter in the range $2.4 \times 10^6$ to $3.05 \times 10^6$ L/mol•s, and the chain transfer parameter in the range $1.9 \times 10^6$ to $2.4 \times 10^6$ L/mol•s. The termination kinetic parameter in all these systems is on the order of $10^8$ L/mol•s. These high termination kinetic parameters of thiol−ene systems account for the rapid decrease in the polymerization rates in aftereffect experiments (Figure 2). Typical (meth)acrylate systems, at very low monomer conversions (<5% conversion), also exhibit such high termination kinetic parameters (on the order of $10^7$−$10^9$ L/mol•s).[26] However, these termination kinetic parameters in (meth)acrylate systems rapidly decrease due to diffusion limited kinetics associated with the formation of high molecular weight polymers. As the thiol−ene systems exhibit a step-growth evolution, the molecular weight evolution and the concomitant increase in viscosity in these systems occurs more slowly as compared to the typical chain growth polymerizing systems. Therefore, diffusion-limited kinetics are not observed until very high conversions in thiol−ene systems. In all the rotating sector experiments performed in this study, the unsteady-state polymerization rates were computed by monitoring the first 40% of conversion. The $\tau_s$ values or the kinetic parameters do not change significantly even if we consider only the initial 10% conversion. This feature indicates that the kinetic parameters in thiol−ene systems are relatively constant until high conversions.

## Conclusions

Termination in thiol−ene photopolymerizations is shown to occur by radical−radical recombinations. Furthermore, the termination rates are demonstrated to be extremely rapid, such that unsteady-state kinetics cannot be accurately monitored with FTIR or DSC techniques. The rotating sector method is shown to be a technique by which termination and propagation kinetic parameters can be quantified for thiol−ene systems. Utilizing rotating sector theory, analytical equations are developed for the average radical lifetime ($\tau_s$) in thiol−ene systems. The experimental values and analytical equations for $\tau_s$ and steady-state polymerization are used to quantify the rate parameters. In the thiol−norbornene system, the propagation and chain transfer parameters are determined to be $3.1 \times 10^6$ L/mol•s, while the termination parameter is shown to be $3.5 \times 10^8$ L/mol•s.

Rotating sector experiments were performed on the off-stoichiometric compositions to investigate the importance of all the radical−radical termination routes in thiol−norbornene systems. By using both the experimental values of $\tau_s$ and the theoretical relations between the $\tau_s$ values for the stoichiometric and off-stoichiometric systems, this study has demonstrated that all the radical−radical recombinations are likely.

In the thiol−allyl system, the chain transfer kinetic parameter was determined to be 2.1 × $10^5$ L/mol·s and the termination kinetic parameter as 1.9 × $10^8$ L/mol·s. In both the thiol−norbornene and the thiol−allyl system, the experimentally determined rate parameters successfully predict the polymerization kinetics of both stoichiometric and off-stoichiometric systems.

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