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Thiol−Ene Photopolymerization Mechanism and Rate Limiting Step Changes for Various Vinyl Functional Group Chemistries

Neil B. Cramer,[†] **Sirish K. Reddy,**[†] **Allison K. O'Brien,**[†] **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, CO, 80045-0508

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ABSTRACT: The mechanism and kinetics of thiol−ene photopolymerizations utilizing a tetrafunctional thiol monomer copolymerized with acrylate, norbornene, vinyl ether, and vinyl silazane functionalized ene monomers are successfully modeled and experimentally characterized. Modeling predictions demonstrate that the reaction orders in thiol−ene systems are controlled by the ratio of thiyl radical propagation to chain transfer kinetic parameters (k_p/k_{CT}). Ratios of kinetic parameters (k_p/k_{CT}) were found to vary significantly with the ene functional group chemistry and to have a dramatic impact on polymerization kinetics. For high ratios of k_p/k_{CT}, polymerization rates are first order in thiol functional group concentration and nearly independent of ene functional group concentration. For k_p/k_{CT} values near unity, polymerization rates are approximately $^1/_2$ order in both thiol and ene functional group concentrations. When k_{CT} is much greater than k_p, polymerization rates are first order in ene functional group concentration and nearly independent of the thiol functional group concentration. In thiol−allyl ether and thiol−acrylate systems, the step growth polymerization rates are first order in thiol functional group concentration ($R_p \propto [SH]$). For thiol−norbornene and thiol−vinyl ether systems, polymerizations are nearly $^1/_2$ order in both thiol and ene functional group concentrations ($R_p \propto [SH]^{1/2}[C{=}C]^{1/2}$). In thiol−vinyl silazane systems, polymerization rates are approximately first order in ene functional group concentration ($R_p \propto [C{=}C]$) and independent of thiol functional group concentration. A theory is proposed which states that the effect of functional group chemistry on k_p/k_{CT} is controlled primarily by ene functional group electron density (k_p) and carbon radical stability (k_{CT}).

Introduction

Thiol−ene photopolymerizations exhibit several unique properties that have made them the recent focus of considerable investigation. They exhibit all of the advantages of typical photopolymerizations in that they polymerize rapidly, do not require solvents for processing, are optically clear, and have excellent mechanical properties.[1−6] In addition, thiol−ene polymerizations have the advantages of being relatively uninhibited by oxygen,[2,7,8] exhibit delayed gelation,[3] and enable radical polymerization of a wide range of thiol and vinyl functional group chemistries.[1,2]

The radical thiol−ene step growth polymerization mechanism was first proposed in 1938.[9] Since then, thiol−ene reactions have undergone considerable investigation to determine monomer effects on polymerization rates,[1,10−16] effects of oxygen,[7,8,17] effects of a thiol−olefin charge-transfer complex and the co-oxidation reaction,[18−21] thiol−(meth)acrylate copolymerizations,[6,22,23] initiatorless polymerizations,[8,22,24] and applications to polymer stabilized liquid crystals.[25−28] However, several aspects of thiol−ene polymerizations, including reaction order and kinetics,[2,3] initiation without photoinitiators,[8,22,24] and the dark reaction[19,20,29,30] are still not well understood.

Thiol−ene photopolymerizations are based on the radical catalyzed addition of a thiol to a vinyl functional group. When multifunctional monomers with an average functionality greater than two are utilized, highly cross-linked polymer networks are formed via a step growth mechanism. As outlined below, the thiol−ene step growth mechanism involves propagation of a thiyl radical through a vinyl functional group (step 1), followed by chain transfer from the resulting carbon radical to a thiol functional group, regenerating the thiyl radical (step 2). These successive propagation/chain transfer steps serve as the basis for the step growth thiol−ene photopolymerization reaction.

propagation

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

chain transfer

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

Initiation of radical centers is typically achieved via standard radical photoinitiators. This work utilizes the cleavage photoinitiator 2,2-dimethoxy-2-phenyl acetophenone (DMPA), and termination is assumed to occur via bimolecular radical recombination.[1,2]

Through calorimetry and FTIR experiments it was determined that thiol−ene photopolymerization rates utilizing thiol−allyl ether monomers vary with the first order of the thiol functional group concentration, independent of the allyl ether functional group concentration ($R_p \propto [SH]^1[C{=}C]^0$).[31] A model was developed for thiol−ene polymerizations to explain these results. The model contains four species balances on the thiol, [SH], and ene, [C=C], functional groups as well as material balances on the thiyl, [S•], and carbon, [C•], radicals. The governing equations for the model are given in eqs 1−4.

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

[†] University of Colorado.

[‡] University of Colorado Health Sciences Center.

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$$\frac{d[SH]}{dt} = -k_{CT}[SH][C^\bullet] \quad (1)$$

$$\frac{d[C{=}C]}{dt} = -k_{pSC}[C{=}C][S^\bullet] \quad (2)$$

$$\frac{d[S^\bullet]}{dt} = R_i - R_t(S^\bullet) + k_{CT}[SH][C^\bullet] - k_{pSC}[C{=}C][S^\bullet] \quad (3)$$

$$\frac{d[C^\bullet]}{dt} = R_i - R_t(C^\bullet) - k_{CT}[SH][C^\bullet] + k_{pSC}[C{=}C][S^\bullet] \quad (4)$$

Equation 1 accounts for the consumption of thiol functional groups via hydrogen abstraction by the carbon radical. Equation 2 accounts for consumption of ene functional groups by propagation of the thiyl radical through the vinyl functional group. Because of the step growth nature of the polymerization and the large average number of reactions per radical that is formed, steps 1 and 2 must occur at nearly equivalent rates. 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 their consumption by propagation.

The initiation rate (R_i), as calculated by eq 5, is calculated based on standard values for DMPA (f, efficiency; ϵ, molar absorptivity 150 L/mol·cm for 365 nm light; [I], initiator concentration; I_O, light intensity; λ, wavelength; N_{AV}, Avogadro's number; h, Planck's constant; c, speed of light).[32,33] Termination rates for thiyl and carbon radicals by radical−radical recombination are given in eqs 6 and 7, respectively. All kinetic parameters (k_{CT}, chain transfer; k_{pSC}, 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 are assumed to be equal. Though this assumption of equal termination is clearly not likely to be correct, little or no other information is available. Hence, to maintain simplicity and focus on the propagation mechanisms, we have assumed equivalent termination rates for the various possible recombinations.

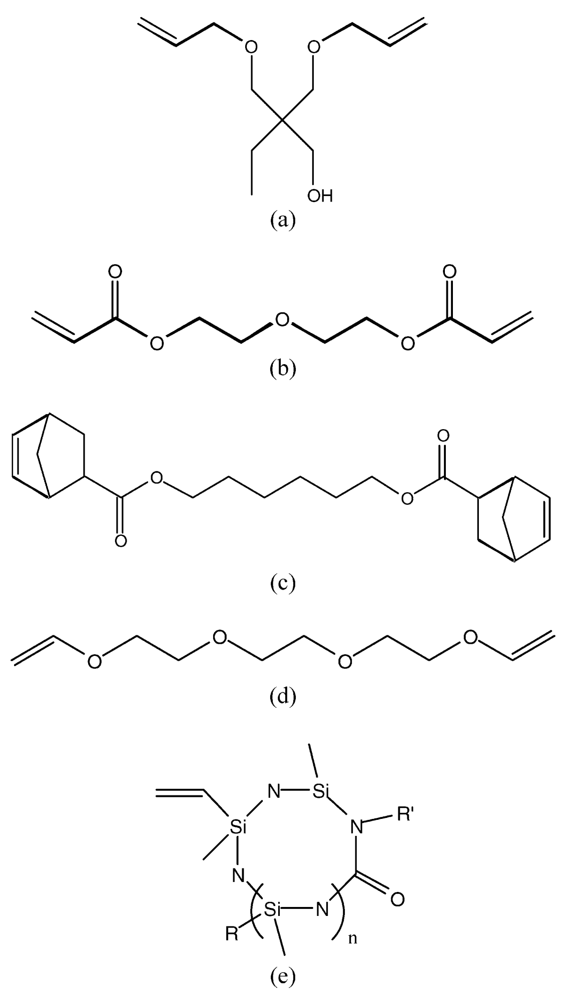
$$R_i = -\frac{d[I]}{dt} = \frac{2.303 f\epsilon[I]I_0\lambda}{N_{AV}hc} \quad (5)$$

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

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

Previously, for thiol−allyl ether systems, the kinetic phenomenon of first-order rate dependence on thiol functional group concentration was explained using chain transfer as the rate-limiting step for the polymerization.[31] Modeling chain transfer as a rate-limiting step in the polymerization is accomplished by using a ratio of the propagation kinetic parameter to the chain transfer kinetic parameter of 10 ($k_{pSC}/ k_{CT} = 10$).

Here, we expand upon this previous kinetic evaluation of thiol−ene systems by examining the kinetics and reaction orders for a range of vinyl functional group chemistries. The thiol−ene kinetics were studied utilizing allyl ether, acrylate, norbornene, vinyl ether, and vinyl silazane monomers, all in conjunction with the same thiol monomer. The monomers associated with these different vinyl functional groups are shown in Figure 1.



(a)

(b)

(c)

(d)

(e)

Figure 1. Monomer chemistry of (a) allyl ether (trimethylolpropane diallyl ether), (b) acrylate (1,6-hexanediol diacrylate), (c) norbornene (1,6-hexanediol di(endo,exo-norborn-2-ene-5-carboxylate), (d) vinyl ether (triethylene glycol divinyl ether), and (e) vinyl silazane (VL20) functional groups, where R = H or $CH_2{=}CH_2$ and $n = 1-20$.

Experimental Section

Materials. The photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA), was purchased from Ciba-Geigy (Hawthorne, NY). The monomers pentaerythritol tetra(3-mercaptopropionate) (tetrathiol), 1,6-hexanediol diacrylate (acrylate), triethylene glycol divinyl ether (vinyl ether), and 1,6-hexanediol di(*endo*,*exo*-norborn-2-ene-5-carboxylate) (dinorbornene), and VL20 (vinyl silazane) were donated by Bruno Bock (Marschacht, Germany), UCB Chemicals (Smyrna, GA), ISP Technologies Inc. (Wayne, NJ), Loctite Corp. (Rocky Hills, CT), and Kion International (Columbus, OH), respectively. 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 scans per second. 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 peak no longer decreasing. Thiol functional group conversion was monitored using the S−H absorption peak at 2570 cm^{-1}, while the vinyl ether and acrylate conversions were monitored using the carbon−carbon double bond absorption peak at 1636 cm^{-1}. Norbornene and vinyl silazane conversions were monitored with double bond absorption peaks at 713 and 1600 cm^{-1}, respectively. Conversions were calculated using the ratio of peak areas to the peak area prior to polymerization.

Samples were placed in a horizontal transmission apparatus.[34] All reactions were performed under ambient conditions as a laminate between two sodium chloride windows. Photopolymerizations 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).

Results and Discussion

In thiol−ene polymerizations, the ratio of propagation to chain transfer kinetic parameters significantly impacts the polymerization kinetics and the rate limiting step. To understand this effect better, the overall polymerization rate in thiol−enes is presented by analytically solving the four species balances (eqs 1−4) on thiol and ene functional groups, and thiyl and carbon radical concentrations. Consumption rates of thiol and ene functional groups (eqs 1 and 2) are set equal and the pseudo-steady-state assumption (i.e., eqs 3 and 4 = 0) is also invoked, for which the solution is given in eq 8. Here, two limiting cases are presented to illustrate reaction order dependence on the ratio of propagation to chain transfer kinetic parameters (k_{pSC}/k_{CT}). In case 1, the propagation kinetic parameter is much greater than the chain transfer kinetic parameter ($k_{pSC} \gg k_{CT}$). For this case, the polymerization rate expression (eq 8) simplifies such that the polymerization rate is first order, dependent only on the thiol functional group concentration (eq 9). In other words, chain transfer is the rate limiting step of the reaction, as was previously shown for thiol−allyl ether systems. In the second case, the chain transfer kinetic parameter is much greater than the propagation kinetic parameter ($k_{CT} \gg k_p$), implying that propagation is the rate limiting step here. The polymerization rate expression now simplifies such that the polymerization rate depends only on the vinyl functional group concentration to the first power (eq 10). For the final case when $k_p \approx k_{CT}$, the polymerization rate is approximately equally dependent on both the thiol and ene functional group concentrations as presented in eq 11.

$$R_p = \sqrt{\frac{R_i}{2k_t}} \times \frac{1}{\sqrt{\dfrac{1}{(k_{pS-C}[C{=}C])^2} + \dfrac{1}{(k_{CT}[SH])^2} + \dfrac{1}{(k_{pS-C}k_{CT}[C{=}C][SH])}}} \tag{8}$$

$$R_p = \sqrt{\frac{R_i}{2k_t}}k_{CT}[SH] \quad \text{for } k_{pSC} \gg k_{CT} \tag{9}$$

$$R_p = \sqrt{\frac{R_i}{2k_t}}k_{pSC}[C{=}C] \quad \text{for } k_{CT} \gg k_{pSC} \tag{10}$$

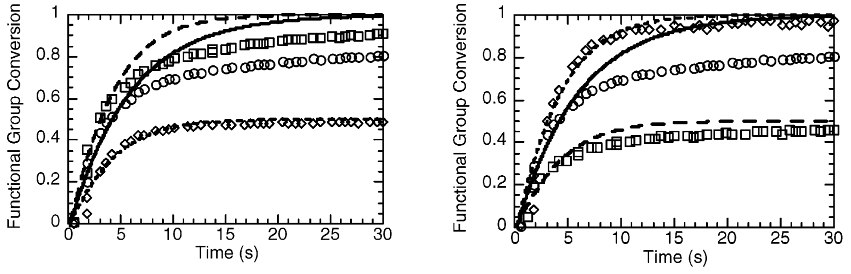
$$R_p = \sqrt{\frac{R_i}{2k_t}}k^*[SH]^{1/2}[C{=}C]^{1/2} \quad \text{for } k_{pSC} \approx k_{CT} \text{ and } [SH] = [C{=}C] \tag{11}$$

Polymerization kinetics in thiol−acrylate systems are also influenced by the ratio of propagation and chain transfer kinetic parameters. In these cases, the relative conversions of thiol and acrylate functional groups have been shown to be dependent on the ratio of the homopolymerization and chain transfer kinetic parameters.[22,23] For the case of thiol−acrylate systems, the model must be amended to include homopolymerization of the vinyl, i.e., acrylate, functional groups. The material balances on the thiol functional groups, as well as those for thiyl and carbon radicals (eqs 1, 3, and 4) are unaffected. The species balance on ene functional groups is amended such that it includes consumption of ene functional groups by thiyl radical and carbon radical propagation or homopolymerization (eq 12), where k_{pCC} is the homopolymerization kinetic parameter. All remaining assumptions are the same. These equations are valid for any thiol−ene system in which the ene functional group undergoes a significant amount of homopolymerization. However, chain transfer must still occur as a prominent feature in the polymerization such that effects from diffusion limited kinetics are not significantly pronounced until high conversions.

$$\frac{d[C{=}C]}{dt} = -k_{pSC}[C{=}C][S^\bullet] - k_{pCC}[C{=}C][C^\bullet] \tag{12}$$

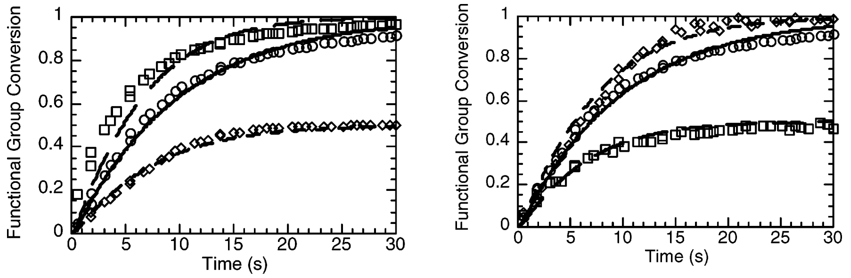
A series of experiments was performed to investigate the effects of the different vinyl functional group chemistries on thiol−ene photopolymerizations. In addition to the previously studied thiol−allyl ether system, the tetrathiol monomer was polymerized with acrylate, norbornene, vinyl ether, and vinyl silazane monomers. All of the systems were polymerized with initially 1:1, 2:1, and 1:2 stoichiometric ratios of thiol to ene functional groups. Polymerization kinetics were both measured with FTIR and then predicted using the appropriate modeling equations. The ratio of the propagation to the chain transfer kinetic parameters was previously determined to be the only parameter that affects polymerization rate differences as the initial stoichiometric thiol to ene functional group ratios are varied.[31] Therefore, differences in polymerization rates of systems with different stoichiometric ratios (i.e., 1:1, 2:1, and 1:2) are fit using the ratio of propagation to chain transfer kinetic parameters (k_p/k_{CT}). Overall polymerization rates are then estimated by fitting the absolute values of k_p and k_{CT} while holding the ratio (k_p/k_{CT}) constant. Initiation rates are calculated from the photoinitiator concentration, [I], and the irradiating light intensity, I_0, which are held constant for all systems. Termination kinetic parameters are assumed to be identical for all of the different systems. Again, the assumption of equivalent termination is made to maintain simplicity, due to a lack of available information on termination kinetics. Experimental and modeling results for thiol−norbornene, thiol−vinyl ether, and thiol−vinyl silazane systems are shown in Figures 2−4, respectively.

For the norbornene, vinyl ether, and vinyl silazane systems, the polymerization is representative of a true step growth polymerization with nearly equivalent consumption of the two functional groups. Therefore, in the initially 2:1 and 1:2 stoichiometric ratio systems, the limiting reagent reaches nearly 100% conversion, while the functional group in excess reaches approximately 50% conversion. Because of excess monomer in the 2:1 and 1:2 stoichiometric systems, the reactions do not become strongly diffusion limited. The 1:1 system



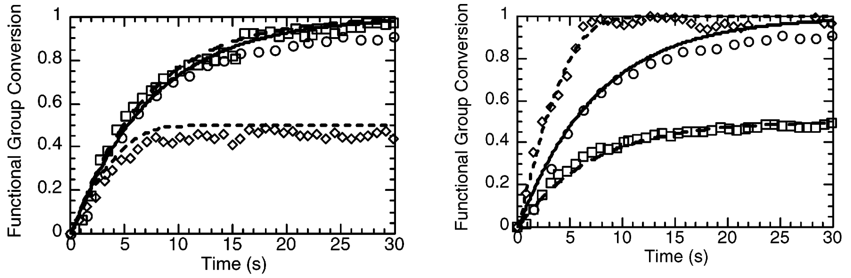
(a) norbornene (b) thiol

Figure 2. Model predictions and experimental data for functional group conversion vs time of tetrathiol and dinorbornene photopolymerizations. (a) Norbornene conversion 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. (b) Thiol conversion 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 1.0 mW/cm^2. Kinetic parameters for modeling are $k_p = 1 \times 10^5$ L/mol·s, $k_{CT} = 1 \times 10^5$ L/mol·s, and k_{t1}, k_{t2}, $k_{t3} = 1 \times 10^6$ L/mol·s.



(a) vinyl ether (b) thiol

Figure 3. Model predictions and experimental data for functional group conversion vs time of tetrathiol and divinyl ether photopolymerizations. (a) Vinyl ether conversion for initially 1:1 (5.06 mol/L) (○, —), 2:1 (6.82:3.41 mol/L) (□, — —), and 1:2 (3.34: 6.67 mol/L) (◇, - - -) ratios of thiol to vinyl ether functional groups. (b) Thiol conversion 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 0.5 mW/cm^2. Kinetic parameters for modeling are $k_p = 1.3 \times 10^5$ L/mol·s, $k_{CT} = 1.1 \times 10^5$ L/mol·s, and k_{t1}, k_{t2}, $k_{t3} = 1 \times 10^6$ L/mol·s.



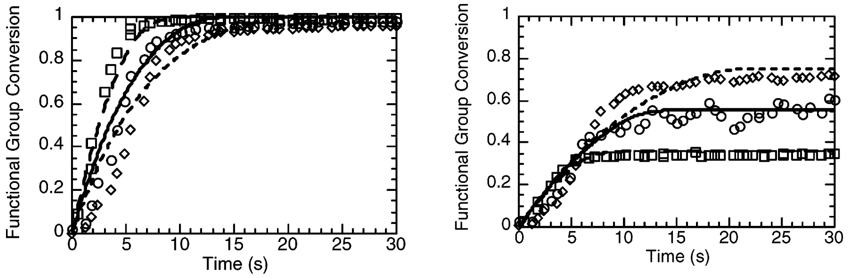
(a) vinyl silazane (b) thiol

Figure 4. Model predictions and experimental data for functional group conversion vs time of tetrathiol and vinyl silazane photopolymerizations. (a) Vinyl silazane conversion for initially 1:1 (2.35 mol/L) (○, —), 2:1 (3.84:1.92 mol/L) (□, — —), and 1:2 (1.33:2.65 mol/L) (◇, - - -) ratios of thiol to vinyl silazane functional groups. (b) Thiol conversion for initially 1:1 (○, —), 2:1 (□, — —), and 1:2 (◇, - - -) ratios of functional groups. Samples contain 0.1 wt % DMPA and are irradiated at 2.0 mW/cm^2. Kinetic parameters for modeling are $k_p = 5.0 \times 10^4$ L/mol·s, $k_{CT} = 2.5 \times 10^5$ L/mol·s, and k_{t1}, k_{t2}, $k_{t3} = 1 \times 10^6$ L/mol·s.

likely encounters significant diffusional restrictions at high conversions, and diffusion control is known to have a dramatic effect on kinetic parameters.[35] As such, there is inherent discrepancy in modeling predictions and experimental data at high conversions, particularly for the 1:1 stoichiometric systems as the modeling kinetic parameters are assumed to be independent of conversion.

Thiol−norbornene polymerizations are predicted with a ratio of propagation to chain transfer kinetic parameters of unity. In this case, polymerization rates are equivalently affected by both thiol and norbornene functional groups (eq 8), or as seen in Figure 2, polymerization rates are slightly and equivalently increased with both the 2:1 and 1:2 ratios of thiol to norbornene functional groups. Thiol−vinyl ether polymerizations are also predicted with a ratio of propagation to chain transfer kinetic parameters near unity; the value determined was 1.2. Here, the polymerization rate increases for both the 2:1 and 1:2 ratios of thiol to vinyl ether functional groups (Figure 3), with a slightly greater increase for the 2:1 system where the thiol concentration is higher (Figure 3b). In the thiol−vinyl silazane system the polymerization rate is significantly increased only for the 1:2 system. This result is modeled by the ratio of propagation to chain transfer kinetic parameters being significantly less than unity; the value determined was 0.2. The polymerization rate scales approximately with the first order of the ene functional group concentration in a manner consistent with eq 10, where propagation is identified as the rate-limiting step.

Kinetic features of the thiol−norbornene, thiol−vinyl ether, and thiol−vinyl silazane systems are all accurately predicted by fitting the ratio of propagation to chain transfer kinetic parameters. Experimental and modeling results for the thiol−acrylate system are



(a) acrylate (b) thiol

Figure 5. Model predictions and experimental data for functional group conversion vs time of tetrathiol and acrylate photopolymerizations. (a) Acrylate conversion for initially 1:1 (4.82 mol/L) (○, —), 2:1 (6.6:3.3 mol/L) (□, − −), and 1:2 (6.26:3.13 mol/L) (◇, - - -) ratios of thiol to acrylate functional groups. (b) Thiol conversion 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 10 mW/cm^2. Kinetic parameters for modeling are $k_{\mathrm{PS-C}} = 2.2 \times 10^5$ L/mol·s, $k_{\mathrm{CT}} = 1.7 \times 10^4$ L/mol·s, $k_{\mathrm{PC-C}} = 2.5 \times 10^4$ L/mol·s, and k_{t1}, k_{t2}, $k_{\mathrm{t3}} = 1 \times 10^6$ L/mol·s.

Table 1. Ratio of Propagation to Chain Transfer Kinetic Parameters, Polymerization Rate Scaling with Thiol and Ene Functional Group Concentrations, and Maximum Polymerization Rates for Acrylate, Allyl Ether, Vinyl Ether, Norbornene, and Vinyl Silazane Monomers Polymerized with Tetrathiol[a]

		$R_p \propto [\mathrm{SH}]^x[\mathrm{C{=}C}]^y$		
functional group	k_p/k_{CT}	x	y	R_{pmax}
acrylate	13	0.4	0.6	2.1
allyl ether	10	1	0	1.0
vinyl ether	1.2	0.5	0.5	4.8
norbornene	1	0.5	0.5	6.0
vinyl silazane	0.2	0	1	3.3

[a] Values for polymerization rate scaling are only valid for stoichiometric systems.

shown in Figure 5. The relative conversions of thiol and acrylate functional groups are determined by the ratio of acrylate homopolymerization to chain transfer kinetic parameters ($k_{\mathrm{pCC}}/k_{\mathrm{CT}} = 1.5$), as previously described.[22] Differences in polymerization rates with varying initial functional group ratios are then determined by fitting the ratio of thiyl radical propagation to chain transfer kinetic parameters ($k_{\mathrm{pSC}}/k_{\mathrm{CT}}$). The polymerization rate increases with increasing concentration of thiol functional groups. This observation is modeled using a ratio of thiyl radical propagation to chain transfer kinetic parameters of 13. The polymerization would scale with the first order of the thiol concentration, consistent with eq 9 ($R_p \propto [\mathrm{SH}]$), if not for contributions from homopolymerization of the acrylate. As such, the initial polymerization rate scales approximately as $R_p \propto [\mathrm{SH}]^{0.4}[\mathrm{C{=}C}]^{0.6}$ for stoichiometric mixtures. Assuming that the termination kinetic constants are all 1×10^6, the homopolymerization kinetic parameter determined is 2.5×10^4 L/mol·s. This value is in reasonable agreement with the experimentally determined value of 1×10^4 L/mol·s for bulk HDDA polymerizations at low conversions.[36]

A summary of the propagation to chain transfer kinetic parameters, polymerization rate scaling with functional group concentrations, and maximum polymerization rates is presented in Table 1. The ratio of propagation to chain transfer kinetic parameters and subsequent reaction order dependence on thiol and ene functional groups varies significantly with the vinyl functional group chemistry. Acrylate and allyl ether functional groups have the highest ratios of propagation to chain transfer kinetic parameters and step growth polymerization rates scale with the first order of the thiol functional group concentration. In the case of the acrylate system, scaling is proportional to acrylate functional group concentration to the $^3/_5$ power due to contributions from homopolymerization. Norbornene and vinyl ether functional groups exhibit roughly equivalent kinetic parameters, such that polymerization rates scale with approximately the $^1/_2$ order for both the thiol and ene functional group concentrations. Vinyl silazane has a greater chain transfer kinetic parameter, and the polymerization rates scale approximately with the first order in ene functional group concentration. The relative polymerization rates for stoichiometric, bulk monomer systems are norbornene > vinyl ether > vinyl silazane > acrylate > allyl ether. These results are similar to previous polymerization rate relationships determined for thiol−ene systems.[1,10]

The thiol monomer, and thus the thiyl radical, is identical across all of the systems that were studied. Therefore, the differences in the ratio of propagation to chain transfer kinetic parameters and polymerization rates must lie primarily with the vinyl functional groups. A trend between monomer chemistry, polymerization rates, and reaction orders is not immediately apparent. Previous studies on polymerization rates and reaction enthalpies[10] show no trend toward reactivity and similarly here show no relationships for the rate-determining step. A general trend between polymerization rates and electron density has been previously described.[1] Low polymerization rates from monomers such as allyl ether are explained from a stable allylic radical. Fast polymerization rates of norbornene are explained by alleviation of ring strain.[2]

We propose that the rate of thiyl radical propagation (k_{psc}) is primarily controlled by electron density and that the rate of chain transfer (k_{CT}) is primarily controlled by carbon radical stability. Specifically, the electron density of the vinyl functional group is correlated to k_p, and the carbon radical stability is correlated to k_{CT}. Therefore, the ratio of k_p/k_{CT} is related to the electron density of the vinyl group and carbon radical stability, where increased electron densities lead to greater values of k_p and increased radical stability leads to lower values of k_{CT}. Polymerization rates would be directly related to the electron density of the vinyl group and inversely related to carbon radical stability. Acrylates, which have a low electron density, exhibit a high ratio of k_p/k_{CT} as does the allyl ether, which exhibits a stable allylic radical or low value of k_{CT}. Both vinyl ether and norbornene functional groups have radicals without any significant stabilization. Vinyl ethers have a high electron density, and thus, exhibit ratios of k_p/k_{CT} near unity with rapid polymerization rates. High reactivities of norbornene functional groups are explained by reduction of ring strain, and thus, they also exhibit ratios of k_p/k_{CT} near unity and rapid polymerization rates. The electron density of the vinyl silazane is relatively high, however, reactivities and radical stability are not well understood due to complexities associated with silicon chemistry.

Conclusions

Thiol−ene photopolymerization kinetics and rate limiting steps are successfully modeled and experimentally characterized for a variety of ene functional group chemistries. Analytical solutions to the governing equations for thiol−ene polymerizations demonstrate reaction orders for thiol and ene functional group concentrations that are dependent on the ratio of propagation to chain transfer kinetic parameters (k_p/k_{CT}). Reaction orders are shown to vary significantly with functional group chemistry. Thiol−allyl ether and thiol−acrylate systems exhibit the highest ratios of propagation to chain transfer kinetic parameters and, as such, the step growth polymerization rates scale with the first order in thiol functional group concentration ($R_p \propto [SH]$). Thiol−norbornene and thiol−vinyl ether systems have roughly equivalent ratios of propagation to chain transfer kinetic parameters and polymerization rates scale roughly with the $^1/_2$ order in both thiol and ene functional group concentrations ($R_p \propto [SH]^{1/2}[C{=}C]^{1/2}$). Thiol−vinyl silazane systems exhibit a propagation to chain transfer kinetic parameter ratio significantly less than one, and polymerization rates scale approximately with the first order in ene functional group concentration ($R_p \propto [C{=}C]$). We postulate that the ratio of propagation to chain transfer kinetic parameters (k_p/k_{CT}) and polymerization rates are correlated to the electron density of the vinyl groups and the carbon radical stability.

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