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Thiol−Vinyl Mechanisms. 2. Kinetic Modeling of Ternary Thiol−Vinyl Photopolymerizations

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ABSTRACT: A framework is developed to understand and predict the photopolymerization kinetics of ternary thiol−vinyl systems: thiol−ene−ene and thiol−ene−acrylate. Ternary thiol−vinyl photopolymerization systems of thiol−allyl ether−norbornene, thiol−vinyl ether−norbornene, and thiol−vinyl ether−acrylate monomer mixtures are experimentally characterized and successfully modeled. The kinetic rate parameters employed for modeling are experimentally obtained from rotating sector unsteady-state analysis and rate mechanisms of the corresponding binary mixtures. In thiol−ene−ene systems, the relative consumption of the ene functional groups is shown to be proportional to the respective propagation kinetic parameters of the ene monomers and independent of the chain transfer kinetic parameters. In the thiol−ene−acrylate systems that exhibit a mixed step-chain growth mechanism, the relative conversion of monomers is shown to depend on both the propagation and chain transfer kinetic parameters.

Introduction

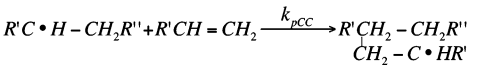
Thiol−vinyl reactions are a unique class of photopolymerization reactions, which have several distinct advantages over typical acrylic polymerization systems.[1−4] The advantageous curing kinetics of thiol−vinyl systems affords them several unique properties relative to other photopolymerization processes.[5,6] The fundamental monomer chemistry, polymerization kinetics, and resultant material properties of these systems have been extensively investigated.[1,7−13] Due to their ability to participate in chain transfer events, the thiol monomer rapidly participates in a radical mediated polymerization reaction with both homopolymerizable and nonhomopolymerizable vinyl monomers. In this study, the vinyl monomers that do not homopolymerize are denoted as ene monomers.

Thiol−ene photopolymerizations are addition reactions between multifunctional thiol and ene monomers. For thiol−ene photopolymerizations, the alternation of propagation and chain transfer steps forms the basis for step growth network evolution.[14,15] The step growth polymerization mechanism of thiol−ene reactions involves propagation of a thiyl radical through an ene functional group to form a carbon radical (step 1). The carbon radical, upon chain transfer to a thiol functional group, regenerates the thiyl radical and forms the thiol−ene addition product (step 2).

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

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

In thiol−vinyl polymerizations wherein the vinyl monomer undergoes homopolymerization, the reaction mechanism is a combination of step and chain growth polymerizations.[8] The propagation mechanism for these thiol−acrylate systems includes a carbon radical propagation step (step 3) in addition to the thiyl radical propagation and chain transfer steps (steps 1 and 2).



$$R'C\bullet H-CH_2R''+R'CH=CH_2 \xrightarrow{k_{pCC}} \begin{array}{l} R'CH_2-CH_2R'' \\ \;\;|\\ \;CH_2-C\bullet HR' \end{array} \qquad \text{Step 3}$$

We recently developed a model for thiol−vinyl photopolymerization kinetics detailing the photopolymerization kinetics, mechanisms, and rate-limiting steps for various thiol−vinyl systems.[9,10,16] The model contains specie balances on the thiol, [SH], and vinyl, [C═C], functional group concentrations as well as on the thiyl, $S^{\bullet}$, and carbon, $C^{\bullet}$, radicals. The governing specie balances for the model are given in eqs 1−4.

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

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

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

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

where k_{CT}, k_{pSC}, and k_{pCC} are chain transfer, thiyl radical propagation, and carbon radical propagation kinetic parameters, respectively. Consumption of thiol functional groups by chain transfer is accounted for by eq 1. Equation 2 accounts for consumption of vinyl functional groups via propagation of thiyl and carbon radicals. For traditional thiol−ene systems the homopolymerization kinetic constant (k_{pCC}) is negligible. Equations 3 and 4 describe the concentrations of thiyl and carbon radicals, including contributions from initiation, termination, and either generation or consumption by thiyl radical propagation and chain transfer. The initiation rate (R_{i}), shown in eq 5, is

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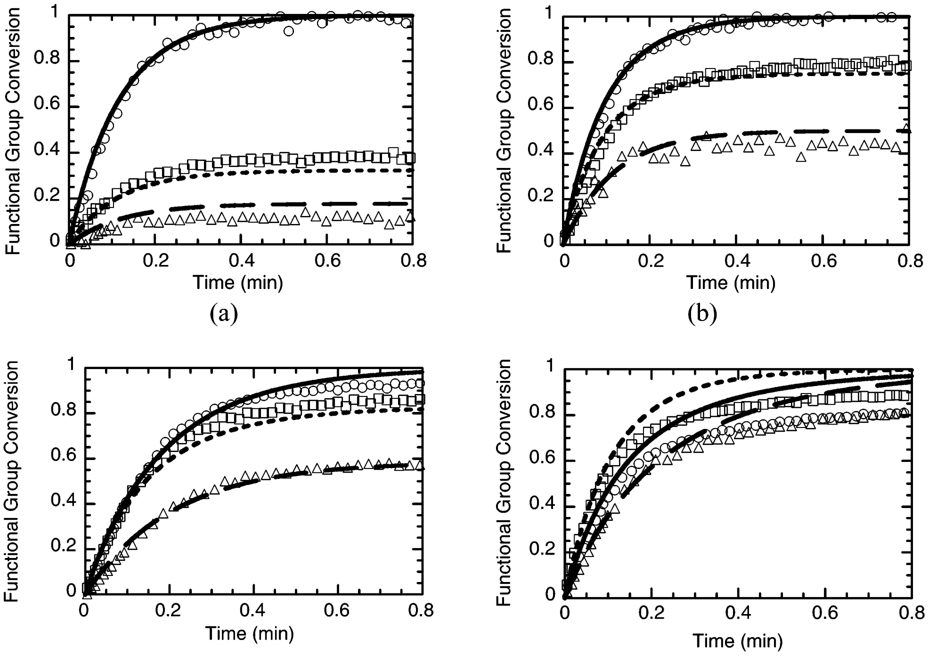


(a) (b)

(c) (d)

Figure 1. Model predictions and experimental data for conversion vs time of ternary thiol−allyl−norbornene photopolymerizations. Thiol (○, —), allyl (ρ, — —),and norbornene (□, - - -) conversions were performed for initially (a) 0.5:1:1 (1.57:3.14:3.14 mol/L), (b) 1:0.5:1 (3.20:1.60:3.20 mol/L), (c) 1:1:0.5 (3.51:3.51:1.75 mol/L), and (d) 2:1:1 (4.33:2.16:2.16 mol/L) stoichiometric ratios of thiol−allyl−norbornene functionalities. Samples contain 0.1 wt % DMPA and are irradiated at 2 mW/cm^2. Kinetic parameters for modeling are given in Table 1.

calculated based on standard values for 2,2-dimethoxy-2-phenylacetophenone (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]

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

Utilizing experimental kinetic measurements and model predictions, several aspects of thiol−vinyl polymerization kinetics were investigated. Further, unsteady-state rotating sector experiments were also conducted on various thiol−vinyl systems to quantify their absolute kinetic parameters. These absolute kinetic parameters were then employed to predict successfully the experimentally observed polymerization kinetics.[17] Elucidation of these absolute kinetic parameters was not only helpful for gaining a fundamental understanding of the reaction mechanism of these binary systems, but this knowledge is extremely critical and essential for our current study of successful predictions of ternary thiol−vinyl systems.

Ternary thiol−vinyl systems (thiol−ene−ene and thiol−ene−acrylate systems) are unique formulations, as they offer several distinct additional advantages for thiol−vinyl photopolymerizations. These advantages are primarily due to enhanced control and tailorability of polymerization kinetics and polymeric material properties. Introduction of a third component to binary thiol−vinyl systems dramatically improves the ability to design the monomer formulations to obtain desired material properties in the cured film. Further, ternary thiol−vinyl systems, in contrast to binary thiol−vinyl polymerizations, offer a consistency in their mechanical properties with variations in monomer stoichiometry.

Ternary thiol−vinyl formulations also provide a unique framework through which control over curing kinetics transforms into control over polymer network architecture. Because of the pure step growth nature of the polymerization, the polymerization kinetics in binary thiol−ene systems do not influence the network structure. However, the network evolution in ternary thiol−vinyl systems is dictated by the reaction kinetic parameters, which control the relative polymerization rates of the vinyl monomers.[18] Therefore, ternary thiol−vinyl systems give a distinct ability to control the network evolution and hence the polymer properties by controlling the relative curing rates of the multiple vinyl monomers. To control the relative consumption of individual components in ternary systems and thereby impact network properties, it is essential to be able to predict the polymerization kinetics in these systems. In this study, we utilize rate parameters from binary thiol−ene systems[17] for predicting the ternary polymerization kinetics. This ability would lead to improved monomer chemistry variation, in which we are able to control the network properties of the formed networks.

In essence, this study expands upon our understanding of reaction mechanisms of binary thiol−ene systems, rate-limiting steps, and knowledge of their absolute kinetic parameters. Experimental and modeling techniques are utilized to study and predict the polymerization kinetics in ternary thiol−ene−ene and thiol−ene−acrylate systems.

Experimental Section

Materials. The photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA), was purchased from Ciba-Geigy (Hawthorne, NY). The monomers trimethylolpropane diallyl ether (allyl ether) and pentaerythritol tetra(3-mercaptopropionate) (tetrathiol) were purchased from Aldrich (Milwaukee, WI). The monomers hexyl acrylate (acrylate), triethylene glycol divinyl ether (vinyl ether), and 1,6-hexanediol di(endo,exo-norborn-2-ene-5-carboxylate) (norbornene) were donated by UCB Chemicals (Smyrna, GA), ISP Technologies Inc. (Wayne, NJ), and Henkel Loctite Corporation (Rocky Hills, CT), respectively. All the 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

CDV

detector. Series scans were recorded, taking spectra at the rate of approximately two 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 spectra no longer decreasing. Thiol functional group conversion was monitored using the S−H absorption peak at 2570 cm^{-1}. Vinyl ether and acrylate conversions were monitored using the carbon−carbon double bond absorption peak at 1636 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. As both the vinyl ether and acrylate functionalities have absorption peaks at 1636 cm^{-1}, it is essential to monitor another peak for double bond absorption in systems composed of both vinyl ether and acrylate monomers. Double bonds in acrylates also absorb at 1415 cm^{-1}. Therefore, the acrylate double bond conversion can be calculated by monitoring the peak area at 1415 cm^{-1}. The vinyl ether conversion is then calculated by subtracting the peak contribution due to the acrylate double bonds at 1636 cm^{-1}.

Samples were placed in a horizontal transmission apparatus within the FTIR chamber. 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

To predict the polymerization kinetics of thiol−ene−ene and thiol−ene−acrylate systems, a modeling approach was developed for ternary thiol−vinyl photopolymerization reactions. The model is an extension of the model utilized for binary thiol−vinyl systems and can be utilized to predict photopolymerization kinetics between a thiol functional group and two independently homopolymerizable or nonhomopolymerizable vinyl groups. The model consists of six specie balances on thiol, [SH], and the two vinyl functional groups, [C═C]$_1$ and [C═C]$_2$, as well as the concentration of thiyl radicals, [S]$^\bullet$, and two different carbon radicals, [C]$_1^\bullet$ and [C]$_2^\bullet$. The governing equations for the model are shown in eqs 6−11.

$$\frac{d[SH]}{dt} = -k_{CT1}[C^\bullet]_1[SH] - k_{CT2}[C^\bullet]_2[SH] \tag{6}$$

$$\frac{d[C{=}C]_1}{dt} = -k_{PSC1}[S^\bullet][C{=}C]_1 - k_{pCC11}[C^\bullet]_1[C{=}C]_1 - k_{pCC21}[C^\bullet]_2[C{=}C]_1 \tag{7}$$

$$\frac{d[C{=}C]_2}{dt} = -k_{PSC2}[S^\bullet][C{=}C]_2 - k_{pCC12}[C^\bullet]_1[C{=}C]_2 - k_{pCC22}[C^\bullet]_2[C{=}C]_2 \tag{8}$$

$$\frac{d[S^\bullet]}{dt} = \frac{R_i}{3} - R_t(S^\bullet) + k_{CT1}[C^\bullet]_1[SH] + k_{CT2}[C^\bullet]_2[SH] - k_{PSC1}[S^\bullet][C{=}C]_1 - k_{PSC2}[S^\bullet][C{=}C]_2 \tag{9}$$

$$\frac{d[C^\bullet]_1}{dt} = \frac{R_i}{3} - R_t(C^\bullet)_1 - k_{CT1}[C^\bullet]_1[SH] - k_{PCC12}[C^\bullet]_1[C{=}C]_2 + k_{PSC1}[S^\bullet][C{=}C]_1 + k_{PCC21}[C^\bullet]_2[C{=}C]_1 \tag{10}$$

$$\frac{d[C^\bullet]_2}{dt} = \frac{R_i}{3} - R_t(C^\bullet)_2 - k_{CT2}[C^\bullet]_2[SH] - k_{PCC21}[C^\bullet]_2[C{=}C]_1 + k_{PSC2}[S^\bullet][C{=}C]_2 + k_{PCC12}[C^\bullet]_1[C{=}C]_2 \tag{11}$$

Equation 6 accounts for the consumption of thiol functional groups by chain transfer reactions with carbon radicals (C$_1^\bullet$ and C$_2^\bullet$). Equations 7 and 8 account for the consumption of [C═C]$_1$ and [C═C]$_2$ functional groups via propagation with thiyl radical as well as carbon radicals (C$_1^\bullet$ and C$_2^\bullet$). Equations 9−11 describe the concentrations of thiyl and carbon radicals based on the contributions from initiation, termination, and either generation or consumption by thiyl radical propagation, chain transfer, and cross-polymerization between vinyl functional groups. The initiation reaction in these systems is assumed to occur with equal likelihood through the thiol or the vinyl monomers. In this model k_{CT1} and k_{CT2} depict the chain transfer kinetic parameters for the chain transfer of the carbon radicals, C$_1^\bullet$ and C$_2^\bullet$, respectively, to the thiol monomer. k_{pSC1} and k_{pSC2} denote the propagation kinetic parameters for the addition of thiyl radical to the vinyl monomers [C═C]$_1$ and [C═C]$_2$, respectively. The homopolymerization propagation kinetic parameters for the two vinyl monomers, [C═C]$_1$ and [C═C]$_2$, are represented by k_{pCC11} and k_{pCC22}. Also, k_{pCC12} and k_{pCC21} denote the cross-polymerization kinetic parameters for the propagation of a carbon radical C$_1^\bullet$ through [CC]$_2$ and the propagation of a carbon radical C$_2^\bullet$ through [CC]$_1$.

The overall initiation rate in ternary systems is given by eq 5. The individual initiation rates of each of the three different radicals, S$^\bullet$, C$_1^\bullet$, and C$_2^\bullet$, are calculated by utilizing the overall initiation rate and assuming the individual initiation rates to be proportional to monomer concentrations. Termination rates for thiyl and carbon radicals by radical−radical recombination are given in eqs 12−14.

$$R_t(S^\bullet) = 2k_{t1}[S^\bullet]^2 + k_{tSC1}[S^\bullet][C^\bullet]_1 + k_{tSC2}[S^\bullet][C^\bullet]_2 \tag{12}$$

$$R_t(C^\bullet)_1 = 2k_{tCC11}[C^\bullet]_1^{\,2} + k_{tSC1}[S^\bullet][C^\bullet]_1 + k_{tCC12}[C^\bullet]_1[C^\bullet]_2 \tag{13}$$

$$R_t(C^\bullet)_2 = 2k_{tCC22}[C^\bullet]_2^{\,2} + k_{tSC2}[S^\bullet][C^\bullet]_2 + k_{tCC12}[C^\bullet]_1[C^\bullet]_2 \tag{14}$$

where k_{tSS}, k_{tSC1}, k_{tSC2}, k_{tCC11}, k_{tCC12}, and k_{tCC22} represents the termination kinetic parameters between thiyl−thiyl, thiyl−carbon 1, thiyl−carbon 2, carbon 1−carbon 1, carbon 1−carbon 2, and carbon 2−carbon 2 radicals, respectively. All kinetic parameters are assumed to remain constant throughout the reaction.

Thiol—Ene—Ene Systems. We first consider a ternary thiol−allyl−norbornene system as a model of thiol−ene−ene reactions. In thiol−allyl−norbornene systems, neither the allyl nor norbornene monomers undergoes any significant homopolymerization (k_{pCC11}, $k_{pCC22} \approx 0$). Further, the allyl and norbornene monomers do not undergo any significant cross-polymerization (k_{pCC21}, $k_{pCC12} \approx 0$). The lack of any cross-polymerization in the thiol−allyl−norbornene systems is validated by experimental results shown later in Figure 1. Therefore, the consumption of both the allyl and the norbornene monomers occurs primarily through propagation by thiyl radicals. The polymerization rates for the ene monomers, eqs 7 and 8, are simplified, and the relative conversions of ene monomers are obtained by dividing their individual polymerization rates:

$$\frac{d[C{=}C]_1}{d[C{=}C]_2} = \frac{k_{PSC1}[S^\bullet][C{=}C]_1}{k_{PSC2}[S^\bullet][C{=}C]_2} = \frac{k_{PSC1}[C{=}C]_1}{k_{PSC2}[C{=}C]_2} \tag{15}$$

Observing expression 15, the relative consumption of ene monomers is proportional to the ratio of their respective

Table 1. Propagation and Termination Parameters for the Thiol−Allyl Ether and Thiol−Norbornene Systems That Are Obtained from the Unsteady-State Experiments of Corresponding Binary Systems[17]

thiol−allyl		thiol−norbornene	
k_{CT1}	2.1×10^5 L/mol·s	k_{CT2}	3.1×10^6 L/mol·s
k_{pSC1}	2.1×10^6 L/mol·s	k_{pSC2}	3.1×10^6 L/mol·s
k_{tCC11}	1.9×10^8 L/mol·s	k_{tCC22}	3.5×10^8 L/mol·s
k_{tSC1}	2.6×10^8 L/mol·s	k_{tSC2}	3.5×10^8 L/mol·s
k_{tSS}	3.5×10^8 L/mol·s	k_{tSS}	3.5×10^8 L/mol·s

Table 2. Propagation and Termination Kinetic Parameters for Thiol−Vinyl Ether and Thiol−Norbornene Systems Obtained from Binary Unsteady-State Experiments[17]

thiol−vinyl ether		thiol−norbornene	
k_{CT1}	2.1×10^6 L/mol·s	k_{CT2}	3.1×10^6 L/mol·s
k_{pSC1}	2.7×10^6 L/mol·s	k_{pSC2}	3.1×10^6 L/mol·s
k_{tCC11}	4.2×10^8 L/mol·s	k_{tCC22}	3.5×10^8 L/mol·s
k_{tSC1}	4.2×10^8 L/mol·s	k_{tSC2}	3.5×10^8 L/mol·s
k_{tSS}	4.2×10^8 L/mol·s	k_{tSS}	3.5×10^8 L/mol·s

propagation kinetic parameters. Furthermore, it is evident that the values of chain transfer parameters, k_{CT1} and k_{CT2}, do not influence the relative conversions of the functional groups. However, the values of chain transfer kinetic parameters do impact the overall polymerization rate of the system.

The specie balance equations along with the expression for initiation rate (eqs 5−14) are numerically solved to model polymerization kinetics in thiol−allyl−norbornene systems. As the allyl and norbornene monomers do not cross-polymerize, all the propagation parameters for the ternary thiol−allyl−norbornene systems are gathered from previous investigations of binary thiol−allyl and thiol−norbornene systems. The propagation and termination parameters that were previously determined from binary investigations are given in Table 1. The allyl monomer is denoted by $[C{=}C]_1$, and the norbornene monomer is denoted by $[C{=}C]_2$.

The only other kinetic parameter that is needed to model the ternary thiol−allyl−norbornene system is the termination kinetic parameter of allyl−norbornene radicals. For simplicity, the root-mean-square of allyl−allyl and norbornene−norbornene radical termination is used for this termination kinetic parameter.[20]

$$k_{tCC12} = \sqrt{k_{tCC11} \times k_{tCC22}} = 2.6 \times 10^8 \text{L/mol·s} \quad (16)$$

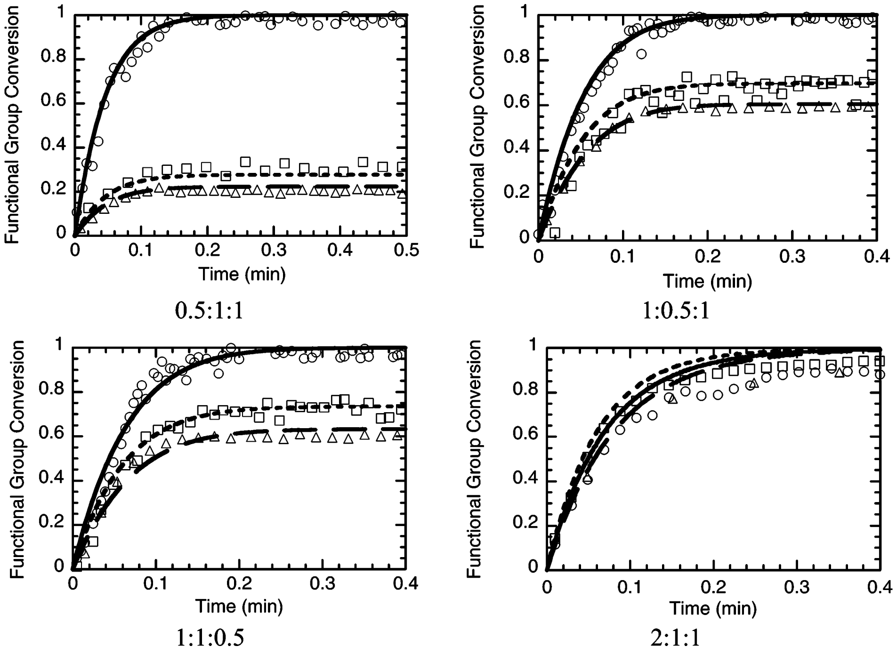
Utilization of these kinetic parameters enables us to predict the polymerization kinetics in ternary thiol−allyl−norbornene systems. Experimental steady-state polymerization kinetics along with model predictions of thiol−allyl−norbornene systems with initial composition of 0.5:1:1, 1:0.5:1, 1:1:0.5, and 2:1:1 of thiol−allyl−norbornene functional groups are presented in Figure 1. It is evident from Figure 1 that the polymerization kinetics of all of the components within the thiol−allyl−norbornene system are predicted successfully utilizing kinetic parameters determined from unsteady-state experiments of binary systems. Discrepancies in modeling predictions and experimental data occur at high conversions for the stoichiometric system of 2:1:1 composition of thiol−vinyl ether−norbornene. These discrepancies are due to the diffusion limitations associated with the cross-linked network, which forms a glassy polymer at high conversion.

For all the stoichiometric combinations of the thiol, allyl, and norbornene monomers presented in Figure 1, the overall consumption of the ene monomers (allyl and norbornene functionalities) is in equivalence with the consumption of thiol monomers. For example, consider the system that has an initial stoichiometric ratio of 0.5:1:1 for the thiol−allyl−norbornene functionalities. In this system, the thiol monomer, which is the limiting reagent, reaches 100% conversion, and the allyl and norbornene monomers achieve a final conversion of 15% and 35%, respectively. Considering the initial monomer stoichiometries and final functional group conversions, 0.5 mol of thiol monomer is consumed for every 0.15 mol of allyl and 0.35 mol of norbornene groups. Therefore, the sum total of ene functional groups consumed equals the total thiol functional groups consumed. This aspect of equivalent consumption of thiol and ene monomers, which also holds for other stoichiometric ratios of this particular ternary system, is in compliance with the step growth nature of the polymerization. These aspects also demonstrate and validate our assumption of negligible cross-polymerization of allyl−norbornene functional groups.

Understanding of polymerization kinetics of ternary thiol−ene−ene systems is not only attractive from a fundamental perspective, but this knowledge also provides a route to form networks with varied gel point conversion and shrinkage stresses while maintaining constant final material properties. For example, while the propagation kinetic parameter for the thiyl−norbornene system is 3.1×10^6 L/mol·s (Table 1), the propagation kinetic parameter for the thiyl−allyl is 2.1×10^6 L/mol·s (Table 1). Consequently, in a ternary system with an initial stoichiometric ratio of 1:1 allyl: norbornene functional groups, consumption of norbornene functional groups, for small monomer conversions, is approximately 1.5 times higher than the allyl functional group. Therefore, by keeping the overall average functionality constant and increasing the functionality of the monomer with lower reactivity (allyl ether) and decreasing the functionality of the faster reacting monomer (norbornene), network connectivity is decreased at lower conversions, delaying the gel point conversion. As the shrinkage stress developed in network forming films primarily occurs only after the gelation point, the delayed gelation aspect of these systems leads to films with reduced shrinkage stresses. A detailed discussion of kinetically induced network control phenomena is beyond the scope of current work and is treated elsewhere.[21]

We next consider photopolymerization kinetics of ternary thiol−vinyl ether−norbornene systems. Here, the propagation kinetic parameter of vinyl ether functional groups is much greater than that of allyl ether functional groups and is comparable to that of the norbornene. As such, the thiol−norbornene−vinyl ether is a much faster reacting system. As in the previous case, the ene monomers in thiol−vinyl ether−norbornene systems do not undergo either homopolymerization or cross-polymerization. Therefore, the relative consumption of ene monomers in this system is again nearly proportional to their respective propagation kinetic parameters (eq 15). The propagation kinetic parameters are similarly determined from the propagation kinetic parameters for the corresponding binary thiol−vinyl ether and thiol−norbornene systems. These kinetic parameters were previously determined and are presented in Table 2.

The termination kinetic parameter for the thiyl−thiyl radical termination is slightly different for the thiol−vinyl ether and thiol−norbornene systems. However, as the same thiol monomer is utilized in both these systems, the differences in the termination kinetic parameters may be due to the differences in the viscosities or chemical environment of the individual thiol−ene systems. As a simplification, the thiyl−thiyl radical termination parameter for the thiol−vinyl ether−norbornene system is approximated as the geometric mean of the termination



0.5:1:1

1:0.5:1

1:1:0.5

2:1:1

Figure 2. Model predictions and experimental data for conversion vs time of thiol−vinyl ether−norbornene photopolymerizations. Thiol (○, −), vinyl ether (△,− −),and norbornene (□, - - -) conversions were performed for initially (a) 0.5:1:1 (5.06 mol/L), (b) 1:0.5:1 (6.82:3.41 mol/L), (c) 1:1:0.5 (6.82:3.41 mol/L), and (d) 2:1:1 (6.82:3.41 mol/L) stoichiometric ratios of thiol−vinyl ether−norbornene functionalities. Samples contain 0.1 wt % DMPA and are irradiated at 2 mW/cm^2. Propagation kinetic parameters for modeling are taken from Table 2. The termination kinetic parameters are utilized from eqs 17−19.

parameters for the binary thiol−vinyl ether and thiol−norbornene systems.

$$k_{\mathrm{tSS}} = \sqrt{k_{\mathrm{tSS(thiol-vinyl\ ether)}} k_{\mathrm{SS(thiol-norbornene)}}} = \sqrt{4.2 \times 10^8 \times 3.5 \times 10^8} = 3.8 \times 10^8 \text{ L/mol·s} \quad (17)$$

The termination kinetic parameter of eq 17 lies well within the 95% confidence intervals of thiyl−thiyl termination parameter determined from rotating sector experiments (2.7×10^8 L/mol·s $< k_{\mathrm{tSS}} < 4.7 \times 10^8$ L/mol·s).[17] The termination kinetic parameters for the thiyl−carbon and carbon−carbon radicals are equal to that of thiyl−thiyl radicals in both the binary thiol−norbornene and thiol−vinyl ether systems. Therefore, to maintain uniformity all other termination parameters in the ternary system are set equal to the thiyl−thiyl termination parameter of eq 17. Performing this operation ensures standardization of viscosity changes for all the termination kinetic parameters.

$$k_{\mathrm{tCC11}} = k_{\mathrm{tCC22}} = k_{\mathrm{tSC1}} = k_{\mathrm{tSC2}} = k_{\mathrm{tCC12}} = k_{\mathrm{tSS}} = 3.8 \times 10^8 \text{ L/mol·s} \quad (18)$$

Also, the termination parameter for the vinyl−norbornene radicals is approximated by the geometric mean approximation for the termination parameters of vinyl ether−vinyl ether and norbornene−norbornene radicals.

$$k_{\mathrm{tCC12}} = \sqrt{k_{\mathrm{tCC11}} \times k_{\mathrm{tCC22}}} = 3.8 \times 10^8 \text{ L/mol·s} \quad (19)$$

The model and kinetic parameters (Table 2 and eqs 17−19) are employed for predicting the kinetics of thiol−vinyl ether−norbornene systems. Figure 2 presents the experimental polymerization kinetics and model predictions for 0.5:1:1, 1:0.5:1, 1:1:0.5, and 2:1:1 initial stoichiometric compositions of thiol−vinyl ether−norbornene systems. The model accurately predicts the polymerization kinetics of the nonstoichiometric systems, in which at least one of the monomers does not achieve complete conversion. For the stoichiometric system with a 2:1:1 composition of thiol−vinyl ether−norbornene, significant diffusion limitations are encountered at high conversions due to the cross-linked network forming a glassy polymer. In the kinetic modeling it is assumed that the rate parameters are to be independent of conversion, thereby causing discrepancies in modeling predictions and experimental data at high conversions for the 2:1:1 stoichiometric system. Further, as in the thiol−allyl−norbornene systems, the overall ene monomer consumption in the thiol−vinyl ether−norbornene systems equals the thiol monomer consumption. Equivalent consumption of thiol and both ene monomers validates the assumption of negligible cross-polymerization between the vinyl ether and norbornene monomers. Additionally, as both the vinyl ether and norbornene monomers exhibit similar reactivity toward the thiyl radical, $k_{\mathrm{pSC2}}/k_{\mathrm{pSC1}} \approx 1.1$, the consumption of functional groups at low monomer conversions is nearly equivalent to the initial monomer composition.

Thiol—Ene—Acrylate Systems. Thiol−ene−acrylate systems offer yet further control and opportunities for materials properties that are not possible through conventional thiol−ene or acrylic systems. However, the polymerization kinetics are more complex: unlike in thiol−ene−ene systems, wherein the vinyl monomers do not homopolymerize, the acrylic monomers in thiol−ene−acrylate systems readily homopolymerize. Further, vinyl ether and acrylate monomers readily copolymerize in free radical photopolymerization reactions. These features complicate the predictions of polymerization kinetics in ternary thiol−vinyl ether−acrylate systems. To characterize the kinetic parameters and reaction mechanisms completely in thiol−vinyl ether−acrylate systems, it is essential to investigate the polymerization kinetics of acrylate−vinyl ether systems in addition to the kinetics of thiol−vinyl ether and thiol−acrylate systems.

To understand the rate mechanisms and copolymerization relations between the vinyl ether and acrylate monomers, polymerization kinetics were studied for vinyl ether−acrylate systems. When a mixture of vinyl ether ($[\mathrm{C{=}C}]_1$) and acrylate monomers ($[\mathrm{C{=}C}]_2$) is polymerized through a radical mecha-

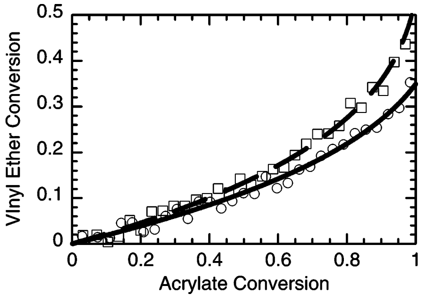


Figure 3. Comparison of model predictions and experimental data for vinyl ether−acrylate polymerizations with various stoichiometric ratios of vinyl ether and hexyl acrylate: 1:1 acrylate−vinyl ether (○, −) and 4:1 acrylate−thiol (□, − −). All samples were polymerized with 1 wt % DMPA and a light intensity of 2 mW/cm^2.

nism, there are two possible reactions in which the acrylic monomer participates: propagation across another acrylic monomer (step 1) or addition to a vinyl ether monomer (step 2). The vinyl ether functional group does not participate in homopolymerization, and therefore the vinyl ether radical only participates in one reaction, propagation through the acrylic double bonds (step 3).

$$C_2^\bullet + [\mathrm{C{=}C}]_2 \xrightarrow{k_{\mathrm{pCC22}}} C_2^\bullet \qquad \text{(Step 1)}$$

$$C_2^\bullet + [\mathrm{C{=}C}]_1 \xrightarrow{k_{\mathrm{pCC21}}} C_1^\bullet \qquad \text{(Step 2)}$$

$$C_1^\bullet + [\mathrm{C{=}C}]_2 \xrightarrow{k_{\mathrm{pCC12}}} C_2^\bullet \qquad \text{(Step 3)}$$

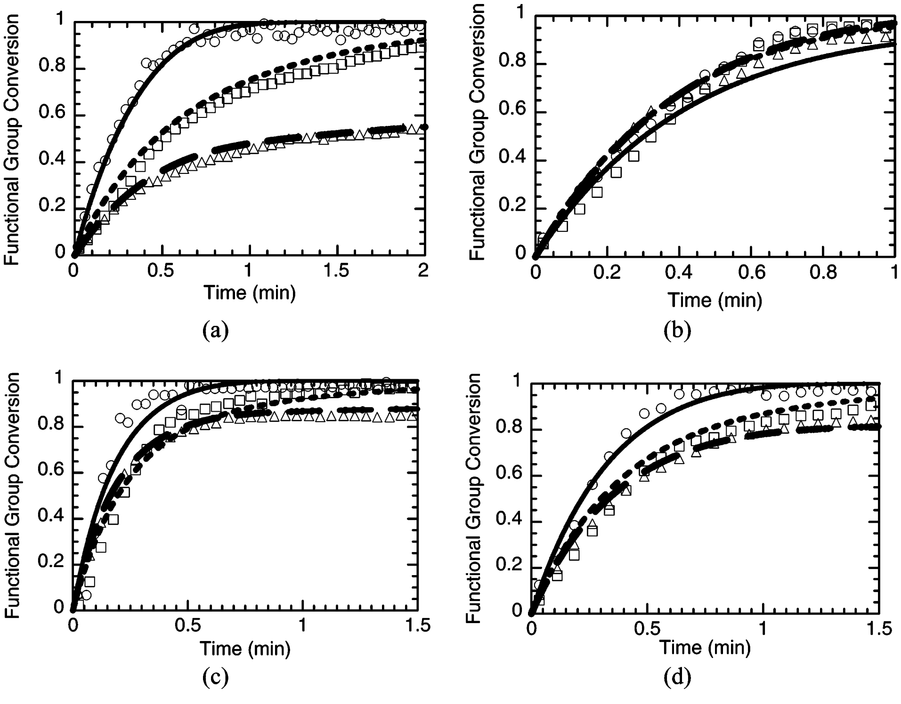
The rate of vinyl ether radical consumption by addition to acrylic double bonds (step 3) must equal the rate of its generation by the addition of an acrylic radical to a vinyl ether monomer (step 2), neglecting the effects of termination. Setting the rates of steps 2 and 3 equal, the theoretical relative consumption of vinyl ether and acrylate functional groups is expressed as

$$\frac{d[\mathrm{C{=}C}]_2}{d[\mathrm{C{=}C}]_1} = 1 + \frac{k_{\mathrm{pCC22}}[\mathrm{C{=}C}]_2}{k_{\mathrm{pCC21}}[\mathrm{C{=}C}]_1} \qquad (20)$$

To deconvolute the experimental conversions of acrylate and vinyl ether functionalities, absorption of the acrylic double bonds under both 1415 and 1636 cm^{-1} peaks was measured and the ratio was found to be 1.5. Utilization of this information along with the methodology described in Experimental Section allowed us to determine the vinyl ether and acrylate monomer conversions. Presented in Figure 3 are the experimental conversions and theoretical predictions of eq 20 for the 1:1 and 1:4 stoichiometric compositions of vinyl ether: acrylate systems. The value for $k_{\mathrm{pCC22}}/k_{\mathrm{pCC21}}$ is found by fitting the theoretical relative conversions (based on eq 20) to the experimental data. The kinetic parameters are assumed to remain constant throughout the reaction. The ratio of propagation kinetic parameters ($k_{\mathrm{pCC22}}/k_{\mathrm{pCC21}}$) was found to be approximately 3.8. Thus, in a 1:1 vinyl ether−acrylate system, an acrylic radical homopolymerizes approximately 3.8 times before reacting with a vinyl ether double bond.

From the analysis of vinyl ether−acrylate binary systems, the cross-polymerization kinetic parameter of an acrylic radical with a vinyl ether double bond is related to its homopolymerization kinetic parameter. In other words, $k_{\mathrm{pCC21}} = k_{\mathrm{pCC22}}/3.8$. The same applies to thiol−acrylate systems as discussed in previous studies, where $k_{\mathrm{CT2}} = k_{\mathrm{pCC22}}/1.5$,[8] and $k_{\mathrm{pSC2}} = 13{*}k_{\mathrm{CT2}} = (13/1.5)k_{\mathrm{pCC22}}$.[10] Therefore, the kinetic parameter for the acrylate homopolymerization would determine the kinetic parameters for all other reactions in which an acrylic radical participates. The propagation and termination parameters of thiol−vinyl ether binary systems are presented in Table 2.

The kinetic parameter for propagation of vinyl ether radicals through acrylate functional groups (k_{pCC12}) is unknown as is the termination parameter for acrylic−acrylic radicals, k_{tCC22}.



(a) (b) (c) (d)

Figure 4. Model predictions and experimental data for conversion vs time of ternary thiol−vinyl ether−acrylate photopolymerizations. Thiol (○, −), vinyl ether (△, − −), and acrylate (□, - - -) conversions were performed for initially (a) 0.5:1:1 (1.9:3.82:3.82 mol/L), (b) 1:0.5:1 (3.87:1.93:3.87 mol/L), (c) 1:1:0.5 (3.94:3.94:1.97 mol/L), and (d) 2:1:1 (3.23:3.23:3.23 mol/L) stoichiometric ratios of thiol−vinyl ether−acrylate functionalities. Samples contain 0.1 wt % DMPA and are irradiated at 2 mW/cm^2. Kinetic parameters for modeling are tabulated in Table 3.

Table 3. Propagation and Termination Parameters that Are Employed for Predicting the Ternary Thiol−Vinyl Ether−Acrylate Polymerization Kinetics

	Propagation Parameters		
k_{CT1}	2.1×10^6 L/mol·s	k_{CT2}	0.8×10^5 L/mol·s
k_{pSC1}	2.6×10^6 L/mol·s	k_{pSC2}	1.2×10^6 L/mol·s
k_{pCC11}	negligible	k_{pCC22}	1.1×10^5 L/mol·s
k_{pCC12}	1.0×10^5 L/mol·s	k_{pCC21}	0.30×10^5 L/mol·s
	Termination Parameters		
k_{tSS}	4.2×10^8 L/mol·s	k_{tCC11}	4.2×10^8 L/mol·s
k_{tCC12}	3.1×10^8 L/mol·s	k_{tCC22}	2.2×10^8 L/mol·s
k_{tSC1}	4.2×10^8 L/mol·s	k_{tSC2}	3.1×10^8 L/mol·s

Adjusting these kinetic parameters along with the homopolymerization kinetic parameter (k_{pCC22}), facilitates the prediction of ternary thiol−vinyl ether−acrylate kinetics. While all the kinetic parameters for the thiol−ene−ene systems are experimentally determined, these kinetic parameters for the thiol−ene−acrylate systems are adjusted to fit the experimental data. The termination parameters for vinyl ether−acrylic radicals and thiyl−acrylic radicals are estimated by the geometric mean approach, as discussed earlier. The propagation and termination parameters employed for model predictions of thiol−ene−acrylate systems are tabulated in Table 3. Previous work[20] utilizing pulsed laser experiments found the propagation and termination parameters of typical chain growth polymerizing acrylic systems at very low conversions (<1%) to be on the order of 1.0×10^5 L/mol·s and 1.0×10^8 L/mol·s, respectively. Values of the homopolymerization kinetic parameter (k_{pCC22}) and the termination kinetic parameter (k_{tCC22}) that are utilized for the model predictions are representative of these rate parameters.

The propagation and termination kinetic parameters of Table 3 are utilized for the prediction of polymerization kinetics in thiol−vinyl ether−acrylate systems. Figure 4 presents the model predictions and experimental polymerization kinetics for initially 1:1:1, 0.5:1:1, 1:0.5:1, and 2:2:1 stoichiometric ratios of thiol: vinyl ether: acrylate systems. As observed in thiol−ene−ene systems, the model successfully predicts the polymerization kinetics for the off-stoichiometric systems, while exhibiting small discrepancies at higher monomer conversions for the 2:1:1 stoichiometric system.

The propagation kinetic parameters employed for model predictions exhibit several interesting features. For example, while vinyl ether radicals have a chain transfer kinetic parameter of 2.1×10^6 L/mol·s, they propagate along the acrylic monomers with a propagation kinetic constant of 1.0×10^5 L/mol·s. This dramatic difference between chain transfer (k_{CT1}) and propagation (k_{pCC12}) kinetic parameters indicates that vinyl ether radicals predominantly chain transfer to thiol monomer rather than extend the kinetic chain by propagating through an acrylic functional group. Further, from the relative ratio of k_{pSC1} and k_{pSC2}, a thiyl radical propagates through vinyl ether functional groups twice as readily as it propagates through acrylic functional groups. These kinetic features significantly impact the network of the formed polymers.

Conclusions

A framework has been developed for understanding and predicting photopolymerization kinetics of ternary thiol−vinyl systems based on experimental observation of the corresponding binary systems. This framework is utilized to examine network evolution and to tailor polymer properties. Specifically, photopolymerization kinetics are characterized and successfully modeled for varying stoichiomeric ratios of thiol−allyl ether−norbornene, thiol−vinyl ether−norbornene, and thiol−vinyl ether−acrylate systems. The thiol−allyl ether−norbornene and thiol−vinyl ether−norbornene systems are shown to polymerize through a step growth mechanism, where the ene monomers do not participate in either homo or cross polymerizations. Thiol−vinyl ether−acrylate systems polymerize through a mixed step-chain growth mechanism, due to the presence of step growth reaction between the thiol and the vinyl monomers and chain growth reaction of the acrylic units. The kinetic parameters employed for modeling ternary thiol−ene−ene systems are obtained from absolute rate parameters experimentally determined from the corresponding binary systems. In the thiol−ene−ene systems, the relative conversion of ene monomers is dictated by the ratio of propagation kinetic parameters of the thiyl radical through the corresponding functional groups. Chain transfer kinetic parameters for the ene radicals impact the overall polymerization rate but do not influence the relative monomer conversions. In the thiol−ene−acrylate systems, which exhibit a mixed step-chain growth mechanism, the relative conversion of monomers depends on both the propagation and chain transfer kinetic parameters.

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