

Molecular Weight Development during Thiol–Ene Photopolymerizations

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ABSTRACT: A kinetic model is presented for the pregelation period of thiol–ene photopolymerizations utilizing multifunctional thiol and ene monomers. The model involves the moment equations for thiyl radicals, carbon radicals, and polymers, and it predicts the chain length averages as a function of the reaction time or functional group conversion. Cyclization reactions are taken into account with the assumption that the probability of cyclization is proportional to the number of local pendant vinyl groups connected to the thiyl radical center. The cyclization reaction is arbitrarily truncated at a critical size, N , in that only cycles with sizes less than N are allowed during gelation. The relative rate constant of cyclization with respect to propagation was calculated using the kinetic model and the experimental gelation data obtained for a thiol–ene system consisting of divinyl and trithiol monomers. It was shown that if the functional group conversion is taken as the independent variable, the reaction kinetics of the ring-free thiol–ene system is identical to that of usual step-growth reactions. In the time scale of the reactions, however, the rate expressions for intermolecular reactions in thiol–enes are first-order reactions overall, and the reaction rates as well as the gelation times can easily be manipulated by the kinetic parameters. The cyclization rate in thiol–ene reactions is slower compared to that in step-growth reactions. This result arises from intramolecular chain transfer reactions reducing the probability of favorable intramolecular collisions between the functional groups.

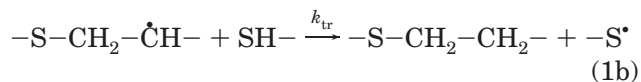
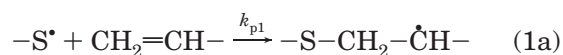
Introduction

Cross-linking copolymerization reactions are typical systems that incorporate chain-growth mechanism involving a monovinyl monomer reacted with a multifunctional vinyl monomer (cross-linker). Of particular interest here; however, are step-growth reactions that occur between multifunctional thiol and ene (vinyl) monomers, generally known as thiol–ene polymerization reactions.^{1–3} Previous work shows significant polymerization advantages of thiol–ene systems, including a rapid reaction,^{4,5} low shrinkage, little or no oxygen inhibition,^{1,5,6} self-initiation,⁵ accessibility of a large number of thiol–ene comonomer pairs,³ and the formation of highly cross-linked networks having good physical, optical, and mechanical properties. Cross-linked materials obtained as a result of thiol–ene polymerizations are widely used in electronic and other coating applications as well as optical materials.

As first reported in the early 1940s, the reaction of a near-stoichiometric mixture of a difunctional thiol and a divinyl monomer results in the formation of a linear polymer, while use of monomers with a higher functionality leads to the formation of an infinite network, often at intermediate to high monomer conversions, depending on the monomer functionality.⁷ Gel formation for thiol–enes is quite different from the polymerization of multifunctional acrylate monomers. In the more typical acrylate system, high molecular weight polymers form at near-zero monomer conversion because of the

chain-growth nature of the polymerization, leading to excessive cyclization, microgelation, low gel point conversions, diffusion- and reaction-controlled reactions, and ultimately, the formation of inhomogeneous networks.^{8–11} However, in thiol–ene systems, very low molecular weight species dominate the pregel regime, leading to higher gel point conversions and the formation of homogeneous networks.

Kharasch first proposed in 1938 the step-growth nature of thiol–ene photopolymerizations.¹² The polymerization reaction proceeds via propagation of a thiyl radical ($-S^{\bullet}$) through the vinyl functional group. Rather than being followed by additional propagation, this propagation step is continually followed by chain transfer of the carbon radical ($-\dot{C}H-$), thus formed, to the thiol functional group, regenerating a thiyl radical, i.e.,



These successive steps of propagation and chain transfer serve as the basis for the step-growth nature of thiol–enes. Recently, a detailed investigation of the mechanism and the kinetics of thiol–ene photopolymerization utilizing multifunctional monomers was reported.^{13–15} It was shown that the reaction order in thiol–enes is controlled by the ratio of thiyl radical propagation to chain transfer kinetic parameters, i.e., by the k_{p1}/k_{tr} ratio. This ratio was found to vary significantly depending on the chemistry of the monomers and has a dramatic impact on the polymerization kinetics.¹⁴

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While thiol–ene polymerizations have been examined extensively, many fundamental aspects of these reactions, such as the molecular weight development during the pre and postgel regimes, the magnitude of intramolecular cross-linking reactions (i.e., primary and secondary cyclization) as well as the degree of spatial inhomogeneity in the final materials remain relatively unexplored. The aim of the present work is primarily to develop a kinetic model for prediction of the molecular weight averages of thiol and carbon radicals as well as of polymer molecules during thiol–ene photopolymerizations up to the onset of gelation. It was also of inherent interest to investigate the factors responsible for the transition of the polymerization mechanism from chain-growth to step-growth in thiol–ene systems.

Here, we report a kinetic model for thiol–ene photopolymerizations utilizing multifunctional thiol and ene monomers. The kinetic model is based on a description of evaluation of the average chain lengths and chain composition by means of differential equations of the type of Smoluchowski coagulation equations.¹⁶ Cyclization reactions are taken into account with the assumption that the probability of cyclization is proportional to the number of pendant vinyl groups connected to the thiol radical centers. Furthermore, the cyclization reaction is arbitrarily truncated at a critical cycle size defined by N , in that only cycles with sizes less than N are allowed to form during gelation. The method of moments was applied to obtain average properties in the pregel period and to predict the gel point.

In the kinetic treatment that follows, the main assumptions made are as follows: (i) the steady-state approximation is used for each of the radical species in the system; (ii) the reactions are chemically controlled rather than diffusion-controlled; (iii) active (radical) species contain only one radical center. The second assumption is reasonable for thiol–ene systems due to the very low molecular weight of polymers over a large range of the pregel regime, while the validity of the third assumption (monoradical assumption) was demonstrated before in free-radical cross-linking copolymerization systems.¹⁷ Furthermore, consumption of ene functional groups via homopolymerization is not allowed here as it does not occur in traditional thiol–ene systems, such as in thiol–vinyl ether, thiol–allyl polymerizations. Simple relations between the synthesis parameters and the pregel properties of thiol–ene systems were also derived for practical calculations.

Kinetic Mechanism

Notation and Constraints. The application of kinetic equations to polymerization processes has been a subject of many studies.¹⁶ In the present work, a notation was used, similar to that used by Mikos et al.¹⁸ and Timm et al.^{19,20} for chain-growth and step-growth reactions, respectively. The dependent variables $S_{x,y,c}$, $R_{x,y,c}$, and $P_{x,y,c}$ represent thiol radicals, carbon radicals, and dead polymer or monomer molecules, respectively. Three subscripts are used to describe the composition of the molecules; they correspond to the number of thiol monomer units (x), vinyl monomer units (y), and intramolecular links, i.e., cycles (c). Thus, $P_{1,0,0}$ and $P_{0,1,0}$ denote the unreacted thiol and vinyl monomers, respectively. The functionalities of the vinyl and thiol monomers are represented by f_1 and f_2 , respectively, which denote the initial number of functional groups per molecule. Furthermore, the symbols $M_{x,y,c}$ and $SH_{x,y,c}$ are

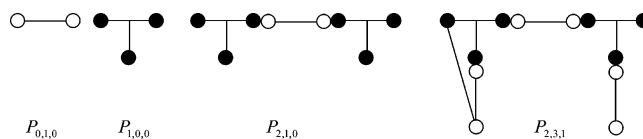


Figure 1. Examples for vinyl monomer ($f_1 = 2$), thiol monomer ($f_2 = 3$), and oligomers in a thiol–ene reaction system. The filled and open circles represent thiol and vinyl groups, respectively.

used to represent the vinyl and thiol group functionalities of the polymer molecules $P_{x,y,c}$, respectively. From the bonding constraints of the monomer links, $M_{x,y,c}$ and $SH_{x,y,c}$ relate to the chemical composition of the polymer molecules by the equations:

$$M_{x,y,c} = (f_1 - 1)y - (x - 1) - c \quad (2a)$$

$$SH_{x,y,c} = (f_2 - 1)x - (y - 1) - c \quad (2b)$$

where $x, y, c = 0, 1, 2, \dots$. Examples of several monomer and oligomer molecules for a trithiol-divinyl comonomer system ($f_1 = 2$ and $f_2 = 3$) and the notation used are presented in Figure 1.

The total concentrations of carbon radicals $[R^*]$, thiol radicals $[S^*]$, vinyl groups $[M]$ and thiol groups $[SH]$ in the reaction system relate to the variables defined above by

$$[R^*] = \sum_x \sum_y \sum_c [R_{x,y,c}^*] \quad (3a)$$

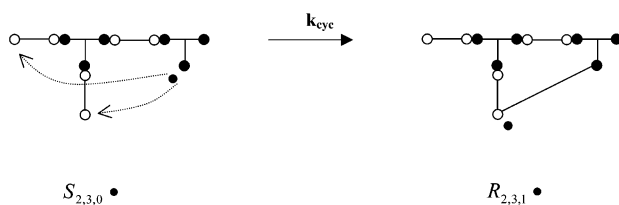
$$[S^*] = \sum_x \sum_y \sum_c [S_{x,y,c}^*] \quad (3b)$$

$$[M] = \sum_x \sum_y \sum_c M_{x,y,c} [P_{x,y,c}] \quad (3c)$$

$$[SH] = \sum_x \sum_y \sum_c SH_{x,y,c} [P_{x,y,c}] \quad (3d)$$

where the triple summations occur over all permissible values of x , y , and c . Parts c and d of eq 3 neglect the functional group concentration on the radical species due to the low radical concentration during the reactions. For each radical or polymer molecule, the bonding constraints restrict the permissible number of x , y , and c . The constraints for the monomer links can be summarized as $M_{x,y,0} \geq 0$ and $SH_{x,y,0} \geq 0$ or 1. Thus, the lower limit for the number of the vinyl monomer units (y) in a molecule occurs when all pendant vinyl groups have reacted intermolecularly, that is when $M_{x,y,0} = 0$. On the other hand, the upper limit for y occurs when all thiol groups in the molecule have reacted intermolecularly, that is, when $SH_{x,y,0} = 0$. This upper limit condition is valid for carbon radicals and polymer molecules; however, for thiol radicals, since at least one unreacted thiol group is needed to locate the thiol radical center, the requirement for the upper limit of y becomes $SH_{x,y,0} = 1$. Furthermore, existence of a thiol or a carbon radical requires at least one thiol or vinyl monomer unit in the molecule, respectively. Thus,

Cyclization:



Intramolecular chain transfer:

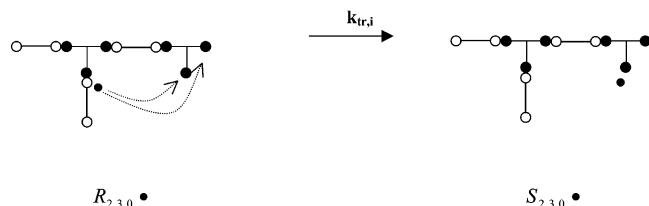


Figure 2. Schematic representation of cyclization and intramolecular chain transfer reactions in thiol-ene copolymerization of vinyl and thiol monomers ($f_1 = 2$, $f_2 = 3$). The filled and open circles represent thiol and vinyl groups, respectively. The arrows show the possible routes for intramolecular reactions. Radical centers are indicated by the dots.

using eq 2, parts a and b, the bonding constraints for the monomer links can be formulated as follows:

$$y = 1 \quad (\text{for } x = 0) \quad (4a)$$

$$\text{int}\left(\frac{x-1}{f_1-1}\right) + \gamma \leq y \leq (f_2-1)x + \gamma' \quad (\text{for } x = 1, 2, 3, \dots) \quad (4b)$$

$$x > 0 \quad (\text{for } S_{x,y,c} \cdot) \quad (4c)$$

$$y > 0 \quad (\text{for } R_{x,y,c} \cdot) \quad (4d)$$

where $\gamma = 1$ and 0 for noninteger and integer values of the first term in the parenthesis of eq 4b, respectively, and $\gamma' = 1$ for carbon radicals and polymer molecules, while $\gamma' = 0$ for thiol radicals.

Furthermore, the lower limit for the number of cycles c in a molecule is zero (ring-free molecules), while its upper limit depends on the number of the limiting functional group. Thus, the bonding constraint for cycles c is

$$0 \leq c \leq \min \{M_{x,y,0}; SH_{x,y,0}\} \quad (4e)$$

where $\min\{M_{x,y,0}; SH_{x,y,0}\}$ is the minimum number of the thiol and vinyl functional groups on $P_{x,y,c}$. For example the upper limits for c in the molecules $P_{2,1,0}$ and $P_{2,3,1}$ illustrated in Figure 1 are 0 and 2, respectively.

The initial conditions of the reacting species in the polymerization system are denoted by the subscript 0. For example, the initial concentrations of the vinyl and thiol functional groups are given by $[M]_0 \equiv f_1[P_{0,1,0}]_0$ and $[SH]_0 \equiv f_2[P_{0,1,0}]_0$, respectively.

Reaction Kinetics. A set of kinetic mechanisms is presented for thiol-ene photopolymerizations of multifunctional thiol and ene monomers having symmetric functional groups. The mechanism consists of five steps: initiation, propagation, chain transfer, termination, and the intramolecular reactions. The reaction

Table 1. Reaction Equations for Thiol-ene Photopolymerization of Multifunctional Monomers

initiation:



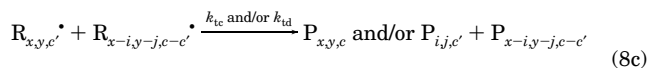
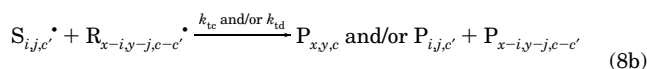
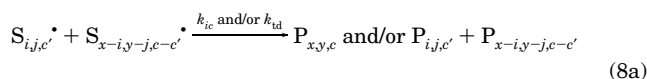
propagation:



chain transfer:



termination:



intramolecular reactions:

(A) cyclization



(B) intramolecular chain transfer



equations describing all possible steps of the polymerization are listed in Table 1.

Decomposition of the initiator I according to eq 5a produces primary radicals $A \cdot$, which may react either with a thiol or vinyl group on monomer or polymer molecules (eq 5b and 5c). Equation 6 accounts for the propagation of a thiyl radical $S_{i,j,c'} \cdot$ thus formed through the vinyl functional group. The chain transfer reactions represented by eq 7 produce polymer molecules $P_{x,y,c}$ during which the carbon radical $R_{x,y,c} \cdot$ becomes a thiyl radical $S_{i,j,c'} \cdot$ with a different composition. The termination reactions (eq 8a–c) between thiyl and carbon radicals may occur by coupling and/or by disproportionation mechanisms. For the sake of clarity, we assume that the termination rate constants by coupling and disproportionation (k_{tc} and k_{td} , respectively) do not depend on the type of the radical end. Intramolecular reactions are distinguished as cyclization and intramolecular chain transfer reactions. These reactions are schematically illustrated in Figure 2. Cyclization, that is intramolecular propagation, may occur by the attack of a thiyl radical center on one of the pendant vinyl groups on the same molecule and leads to formation of cycles (eq 9). In contrast, intramolecular chain-transfer reactions produce no cycles; they convert carbon radicals into thiyl radicals without changing the chemical composition of the species (eq 10).

There are several theoretical approaches to the treatment of intramolecular reactions in linear and nonlinear polymerizations.^{19–28} As shown in Figure 2, in thiol-ene cross-linking polymerizations, the rate of cycle formation reactions is a function of the local pendant vinyl group concentration around the radical center.

Thus, the cyclization reactions occurring in thiyl radicals $S_{x,y,c}^{\bullet}$ are governed by the rate expression:

$$\text{rate}_{\text{cyc}(S_{x,y,c})} = k_{\text{cyc}} [S_{x,y,c}^{\bullet}] M_{x,y,c} \quad (11a)$$

where k_{cyc} is the rate constant for cyclization. According to eq 11a, the actual rate constant of cyclization for a thiyl radical $S_{x,y,c}^{\bullet}$ is equal to the product of the kinetic constant k_{cyc} and the local concentration of pendant vinyls; thus, it increases with increasing number of pendant vinyl groups connected to the radical center. It must be noted that, in small molecules ($x \approx 1$) the pendant vinyl group may have an enhanced reactivity for intramolecular reactions because of its close proximity to the thiyl radical center. In large molecules, however, its reactivity may be diminished by steric limitations and increasing distance from the radical center. In the present model, it is assumed that cycles up to a critical size dominate the gel formation reactions, that is, the cyclization reaction described by eq 11a is truncated at a critical value of x . This assumption crudely takes into account the size dependent reactivity of the pendant vinyl groups for intramolecular reactions, that is, in large molecules, the pendant vinyl group reactivity is so low that intermolecular reactions predominate over cyclization. Similarly, the rate of intramolecular chain transfer reactions in $R_{x,y,c}$ radicals is governed by the equation

$$\text{rate}_{\text{tr},i(R_{x,y,c})} = k_{\text{tr},i} [R_{x,y,c}] SH_{x,y,c} \quad (11b)$$

where $k_{\text{tr},i}$ is the rate constant for intramolecular chain transfer reactions. Since the intramolecular reactions occurring in similar molecules proceed in a similar microenvironment, it is reasonable to assume that the rate of cyclization in $S_{x,y,c}^{\bullet}$ radicals is equal to the rate of intramolecular chain transfer reactions involving $R_{x,y,c}$ radicals, i.e.,

$$\text{rate}_{\text{cyc}(S_{x,y,c})} = \text{rate}_{\text{tr},i(R_{x,y,c})} \quad (12)$$

On the basis of the reaction scheme in Table 1, the differential equations characterizing the population density distributions of the radicals $S_{x,y,c}^{\bullet}$ and $R_{x,y,c}^{\bullet}$ and the polymers $P_{x,y,c}$ are given in Table 2. Here, t is the reaction time, k_i is the rate constant for initiation, and $k_t = k_{tc} + k_{td}$. The first and last rate expressions in eqs

13 and 14 account for the formation and consumption reactions of the radicals in the initiation and termination steps, respectively. Thiyl radicals $S_{x,y,c}^{\bullet}$ also form by inter- and intramolecular chain transfer reactions, represented by the second and third rate expressions, respectively, while they disappear by the propagation and cyclization reactions represented by the fourth rate expression in eq 13. Conversely, carbon radicals $R_{x,y,c}^{\bullet}$ form by propagation and cyclization reactions and they disappear by chain transfer reactions, as shown by eq 14. Moreover, dead polymer molecules $P_{x,y,c}$ form by intermolecular chain transfer reactions of $R_{x,y,c}^{\bullet}$ radicals as well as by the termination reactions, while they disappear by the attack of thiyl and carbon radicals on the pendant functional groups on $P_{x,y,c}$ (eq 15).

Introducing the steady-state approximation for all radicals and assuming that the consumption of the functional groups by initiation is negligible relative to propagation, eqs 12–14 give the normalized concentrations of the thiyl and carbon radicals with x units of thiol monomer, y units of vinyl monomer, and c cycles, $\phi''_{x,y,c}$ and $\phi'_{x,y,c}$, respectively, as follows:

$$\phi''_{x,y,c} \equiv \frac{[S_{x,y,c}^{\bullet}]}{[S^{\bullet}]} = \frac{SH_{x,y,c} [P_{x,y,c}]}{[SH]} \quad (16)$$

$$\phi'_{x,y,c} \equiv \frac{[R_{x,y,c}^{\bullet}]}{[R^{\bullet}]} = \frac{\sum_{i=1}^x \sum_{j=0}^y \sum_{c'=0}^c \phi''_{i,j,c'} \frac{M_{x-i,y-j,c-c'} [P_{x-i,y-j,c-c'}]}{[M]} + \frac{k_{\text{cyc}}}{k_{p1}} \left(\phi''_{x,y,c-1} \frac{M_{x,y,c-1}}{[M]} - \phi''_{x,y,c} \frac{M_{x,y,c}}{[M]} \right)}{1} \quad (17)$$

$$\varphi = \frac{[R^{\bullet}]}{[R^{\bullet}] + [S^{\bullet}]} = \left(1 + \frac{k_{\text{tr}} [SH]}{k_{p1} [M]} \right)^{-1} \quad (17a)$$

$$[R^{\bullet}] = \varphi (R_i/k_t)^{0.5} \quad (17b)$$

$$[S^{\bullet}] = (1 - \varphi) (R_i/k_t)^{0.5} \quad (17c)$$

where R_i is the initiation rate, $R_i = k_i [A^{\bullet}] ([M] + [SH])$ and φ is the mole fraction of carbon radicals within the total radical species. Note that, since the radical termination rate in thiol–ene polymerizations is negligible

Table 2. Rate Equations for Thiol–Ene Photopolymerization of Multifunctional Monomers

$$\frac{d[S_{x,y,c}^{\bullet}]}{dt} = k_i [A^{\bullet}] SH_{x,y,c} [P_{x,y,c}] + k_{\text{tr}} [R^{\bullet}] SH_{x,y,c} [P_{x,y,c}] + k_{\text{tr},i} SH_{x,y,c} [R_{x,y,c}^{\bullet}] - (k_{p1} [M] + k_{\text{cyc}} M_{x,y,c}) [S_{x,y,c}^{\bullet}] - k_t ([R^{\bullet}] + [S^{\bullet}]) [S_{x,y,c}^{\bullet}] \quad (x \geq 1, y \geq 0) \quad (13)$$

$$\frac{d[R_{x,y,c}^{\bullet}]}{dt} = k_i [A^{\bullet}] M_{x,y,c} [P_{x,y,c}] + k_{p1} \sum_i \sum_j \sum_{c'} [S_{i,j,c'}^{\bullet}] M_{x-i,y-j,c-c'} [P_{x-i,y-j,c-c'}] + k_{\text{cyc}} M_{x,y,c-1} [S_{x,y,c-1}^{\bullet}] - (k_{\text{tr}} [SH] + k_{\text{tr},i} SH_{x,y,c}) [R_{x,y,c}^{\bullet}] - k_t ([R^{\bullet}] + [S^{\bullet}]) [R_{x,y,c}^{\bullet}] \quad (x \geq 1, y \geq 1) \quad (14)$$

$$\frac{d[P_{x,y,c}]}{dt} = k_{\text{tr}} [R_{x,y,c}^{\bullet}] [SH] - k_{p1} [S^{\bullet}] M_{x,y,c} [P_{x,y,c}] - k_{\text{tr}} [R^{\bullet}] SH_{x,y,c} [P_{x,y,c}] + k_{td} ([R^{\bullet}] + [S^{\bullet}]) ([R_{x,y,c}^{\bullet}] + [S_{x,y,c}^{\bullet}]) + 0.5 k_{tc} \sum_i \sum_j \sum_{c'} ([R_{i,j,c'}^{\bullet}] [R_{x-i,y-j,c-c'}^{\bullet}] + 2 [R_{i,j,c'}^{\bullet}] [S_{x-i,y-j,c-c'}^{\bullet}] + [S_{i,j,c'}^{\bullet}] [S_{x-i,y-j,c-c'}^{\bullet}]) \quad (x \geq 1, y \geq 1) \quad (15)$$

compared to the rates of propagation or chain transfer,^{13–15} these reactions are neglected in the derivation of eqs 16 and 17. The candidate limits for the triple summation of eq 17 were determined by satisfying bonding constraints for each radical molecule. For example, the radical species $R_{1,1,1}^{\bullet}$ may only form by the cyclization reaction of the thiyl radicals $S_{1,1,0}^{\bullet}$ so that the first term of the right-hand side of eq 17 is zero, while $R_{2,2,1}^{\bullet}$ radicals may form by the propagation reactions of $S_{1,0,0}^{\bullet}$ and $S_{1,1,1}^{\bullet}$ radicals with $M_{1,2,1}$ and $M_{1,1,0}$ pendant vinyl groups, respectively, as well as by cyclization of $S_{2,2,0}^{\bullet}$ radicals.

Using eq 15, the rate equation for polymer molecules $P_{x,y,c}$ can now be rewritten as follows:

$$\frac{d[P_{x,y,c}]}{dt} = k_{tr}[R^{\bullet}][SH] \left\{ \phi'_{x,y,c} - P_{x,y,c} \left(\frac{M_{x,y,c}}{[M]} + \frac{SH_{x,y,c}}{[SH]} \right) \right\};$$

$$[P_{x,y,c}](0) = 0 \quad (18)$$

where $x \geq 1, y \geq 1$. The rate equations for the monomer molecules $P_{1,0,0}$ and $P_{0,1,0}$ are

$$\frac{d[P_{1,0,0}]}{dt} = -f_2 k_{tr}[R^{\bullet}][P_{1,0,0}]; \quad [P_{1,0,0}](0) = [P_{1,0,0}]_0 \quad (19)$$

$$\frac{d[P_{0,1,0}]}{dt} = -f_1 k_{p1}[S^{\bullet}][P_{0,1,0}]; \quad [P_{0,1,0}](0) = [P_{0,1,0}]_0 \quad (20)$$

Moments of Polymer Distributions. The method of moments is applied to the kinetic model of the reactions to calculate the moments of the molecular weight distribution of the radical and polymer molecules, defined as follows:

$$\psi_{n,m,l} \equiv \sum_x \sum_y \sum_c x^n y^m c^l [P_{x,y,c}] \quad (21a)$$

$$\psi'_{n,m,l} \equiv \sum_x \sum_y \sum_c x^n y^m c^l [R_{x,y,c}^{\bullet}] \quad (21b)$$

$$\psi''_{n,m,l} \equiv \sum_x \sum_y \sum_c x^n y^m c^l [S_{x,y,c}^{\bullet}] \quad (21c)$$

$$(n, m, l = 0, 1, 2, \dots)$$

where the summations incorporate all molecules including the unreacted monomers, i.e., $x, y, c \geq 0$. From definitions, $\psi'_{0,0,0} \equiv [R^{\bullet}]$ and $\psi''_{0,0,0} \equiv [S^{\bullet}]$. In terms of the moments, the number-average chain length of carbon radicals $\bar{X}_n^{\bullet}$ and thiyl radicals $\bar{X}_n^{\bullet}$ are given by

$$\bar{X}_n^{\bullet} = \frac{\psi'_{1,0,0} + \psi'_{0,1,0}}{\psi'_{0,0,0}} \quad (22a)$$

$$\bar{X}_n^{\bullet} = \frac{\psi''_{1,0,0} + \psi''_{0,1,0}}{\psi''_{0,0,0}} \quad (22b)$$

It is also possible to calculate the number- and the weight-average chain length of polymer molecules, $\bar{X}_n$ and $\bar{X}_w$, respectively, as follows:

$$\bar{X}_n = \frac{\psi_{1,0,0} + \psi_{0,1,0}}{\psi_{0,0,0}} \quad (23a)$$

$$\bar{X}_w = \frac{\psi_{2,0,0} + 2\psi_{1,1,0} + \psi_{0,2,0}}{\psi_{1,0,0} + \psi_{0,1,0}} \quad (23b)$$

The gel point corresponding to the incipient formation of an infinite network is calculated by use of eq 23b at the point at which $\bar{X}_w$ goes to infinity.

To generate an expression descriptive of the moments of the polymer distribution, the differential eqs 18–20 were multiplied by the weight factor $x^n y^m c^l$ and then summed, which leads to

$$\frac{d\psi_{n,m,l}}{dt} =$$

$$k_{tr}[R^{\bullet}][SH] \left\{ \frac{\psi'_{n,m,l}}{\psi'_{0,0,0}} - \sum_x \sum_y \sum_c x^n y^m c^l [P_{x,y,c}] \left(\frac{M_{x,y,c}}{[M]} + \frac{SH_{x,y,c}}{[SH]} \right) \right\}$$

$$+ \delta \frac{d[P_{1,0,0}]}{dt} + \delta' \frac{d[P_{0,1,0}]}{dt} \quad (x, y > 0) \quad (24)$$

where δ and δ' equal unity when $m = l = 0$, and $n = l = 0$, respectively; otherwise they equal zero. Solution of eq 24 requires the moments of carbon radicals $\psi'_{n,m,l}$. By substitution of eq 16 into eq 17, and summing over all x, y , and c values satisfying the bonding constraints for $S_{x,y,c}^{\bullet}$ and $R_{x,y,c}^{\bullet}$, $\psi'_{n,m,l}$ was evaluated as follows:

$$\frac{\psi'_{n,m,l}}{\psi'_{0,0,0}} =$$

$$\sum_x \sum_y \sum_c \frac{SH_{x,y,c} [P_{x,y,c}]}{[SH]} \sum_i \sum_j \sum_{c'} (x+i)^n (y+j)^m (c+c')$$

$$c'^l \frac{M_{i,j,c'} [P_{i,j,c'}]}{[M]} + \frac{k_{cyc}}{k_{p1}} \sum_x \sum_y \sum_c \{ (c+1)^l -$$

$$c^l \} \frac{x^n y^m M_{x,y,c} SH_{x,y,c} [P_{x,y,c}]}{[M][SH]} \quad (25)$$

Equation 24 together with eq 25 give a general moment expression, which yields simple solutions for several of the moments. For example, the equation for the zeroth moment $\psi_{0,0,0}$ corresponding to the total number of molecules is

$$\frac{d\psi_{0,0,0}}{dt} = -k_{tr}[R^{\bullet}][SH] =$$

$$-k_{p1}[S^{\bullet}][M]; \quad \psi_{0,0,0}(0) = [P_{1,0,0}]_0 + [P_{0,1,0}]_0 \quad (26)$$

while the first moments $\psi_{1,0,0}$ and $\psi_{0,1,0}$ equal the total number of thiol and vinyl monomer units, respectively, and they are time invariant:

$$\frac{d\psi_{1,0,0}}{dt} = 0; \quad \psi_{1,0,0}(0) = [P_{1,0,0}]_0 \quad (27)$$

$$\frac{d\psi_{0,1,0}}{dt} = 0; \quad \psi_{0,1,0}(0) = [P_{0,1,0}]_0 \quad (28)$$

Furthermore, the first moment $\psi_{0,0,1}$ corresponding to the total number of cycles is obtained from eq 24 as

$$\frac{d\psi_{0,0,1}}{dt} = -\frac{k_{\text{cyc}}}{k_{\text{p1}}} \frac{d\psi_{0,0,0}}{dt} \sum_x \sum_y \sum_c \frac{\text{SH}_{x,y,c} \text{M}_{x,y,c} [\text{P}_{x,y,c}]}{[\text{M}][\text{SH}]}; \quad \psi_{0,0,1}(0) = 0 \quad (29)$$

Conversion. Vinyl and thiol group conversions are defined by x_{M} and x_{SH} , respectively. Using eqs 2a, 2b, 27, and 28, they are calculated as follows:

$$\frac{dx_{\text{SH}}}{dt} = \frac{1}{[\text{SH}]_0} \left(\frac{d\psi_{0,0,1}}{dt} - \frac{d\psi_{0,0,0}}{dt} \right) \quad (30)$$

$$x_{\text{M}} = r_0 x_{\text{SH}} \quad (31)$$

where r_0 is the stoichiometric imbalance for the reaction system,

$$r_0 = [\text{SH}]_0/[\text{M}]_0 \quad (31a)$$

Note that the first and the second terms of eq 30 account for the consumption of the functional groups by intra- and intermolecular reactions, respectively.

Chain Length Averages. Using eqs 23a and 30, the number-average chain length of polymer molecules $\bar{X}_n$ can be calculated as

$$\bar{X}_n = \frac{1 + r_0}{1 + r_0 - x_{\text{M}} f_{\text{avr}} (1 - \xi)} \quad (32)$$

where f_{avr} is the average functionality of the monomers

$$f_{\text{avr}} = \frac{[\text{M}]_0 + [\text{SH}]_0}{[\text{P}_{1,0,0}]_0 + [\text{P}_{0,1,0}]_0} \quad (33)$$

and ξ is the fraction of reacted functional groups in cycles

$$\xi = \frac{\psi_{0,0,1}}{[\text{M}]_0 x_{\text{M}}} \quad (34)$$

Equation 32 is valid for all thiol-ene reactions with or without cyclization and, is a typical equation for step-growth polymerizations.^{29–31} The two extreme cases of eq 32 are given by $\xi = 0$ and $\xi = 1$, corresponding to the ring-free and purely cyclic thiol-ene polymerizations, respectively. For the weight-average degree of polymerization $\bar{X}_w$, such a general equation cannot be derived from the moment equations of the kinetic model. $\bar{X}_w$ is calculated numerically from the following moment equations together with eq 29:

$$\frac{d\psi_{2,0,0}}{d\psi_{0,0,0}} = -2 \sum_x \sum_y \sum_c \frac{x \text{SH}_{x,y,c} [\text{P}_{x,y,c}]}{[\text{SH}]} \sum_x \sum_y \sum_c \frac{x \text{M}_{x,y,c} [\text{P}_{x,y,c}]}{[\text{M}]}; \quad \psi_{2,0,0}(0) = [\text{P}_{1,0,0}]_0 \quad (35a)$$

$$\frac{d\psi_{0,2,0}}{d\psi_{0,0,0}} = -2 \sum_x \sum_y \sum_c \frac{y \text{SH}_{x,y,c} [\text{P}_{x,y,c}]}{[\text{SH}]} \sum_x \sum_y \sum_c \frac{y \text{M}_{x,y,c} [\text{P}_{x,y,c}]}{[\text{M}]}; \quad \psi_{0,2,0}(0) = [\text{P}_{0,1,0}]_0 \quad (35b)$$

$$\frac{d\psi_{0,0,2}}{d\psi_{0,0,0}} = -2 \sum_x \sum_y \sum_c \frac{c \text{SH}_{x,y,c} [\text{P}_{x,y,c}]}{[\text{SH}]} \sum_x \sum_y \sum_c \frac{c \text{M}_{x,y,c} [\text{P}_{x,y,c}]}{[\text{M}]} - \frac{k_{\text{cyc}}}{k_{\text{p1}}} \sum_x \sum_y \sum_c \frac{(2c + 1) \text{M}_{x,y,c} \text{SH}_{x,y,c} [\text{P}_{x,y,c}]}{[\text{SH}][\text{M}]}; \quad \psi_{0,0,2}(0) = 0 \quad (35c)$$

$$\frac{d\psi_{1,1,0}}{d\psi_{0,0,0}} = - \sum_x \sum_y \sum_c \frac{x \text{SH}_{x,y,c} [\text{P}_{x,y,c}]}{[\text{SH}]} \sum_x \sum_y \sum_c \frac{y \text{M}_{x,y,c} [\text{P}_{x,y,c}]}{[\text{M}]} - \sum_x \sum_y \sum_c \frac{y \text{SH}_{x,y,c} [\text{P}_{x,y,c}]}{[\text{SH}]} \sum_x \sum_y \sum_c \frac{x \text{M}_{x,y,c} [\text{P}_{x,y,c}]}{[\text{M}]}; \quad \psi_{1,1,0}(0) = 0 \quad (35d)$$

$$\frac{d\psi_{1,0,1}}{d\psi_{0,0,0}} = - \sum_x \sum_y \sum_c \frac{x \text{SH}_{x,y,c} [\text{P}_{x,y,c}]}{[\text{SH}]} \sum_x \sum_y \sum_c \frac{c \text{M}_{x,y,c} [\text{P}_{x,y,c}]}{[\text{M}]} - \sum_x \sum_y \sum_c \frac{c \text{SH}_{x,y,c} [\text{P}_{x,y,c}]}{[\text{SH}]} \sum_x \sum_y \sum_c \frac{x \text{M}_{x,y,c} [\text{P}_{x,y,c}]}{[\text{M}]} - \frac{k_{\text{cyc}}}{k_{\text{p1}}} \sum_x \sum_y \sum_c \frac{x \text{M}_{x,y,c} \text{SH}_{x,y,c} [\text{P}_{x,y,c}]}{[\text{SH}][\text{M}]}; \quad \psi_{1,0,1}(0) = 0 \quad (35e)$$

$$\frac{d\psi_{0,1,1}}{d\psi_{0,0,0}} = - \sum_x \sum_y \sum_c \frac{y \text{SH}_{x,y,c} [\text{P}_{x,y,c}]}{[\text{SH}]} \sum_x \sum_y \sum_c \frac{c \text{M}_{x,y,c} [\text{P}_{x,y,c}]}{[\text{M}]} - \sum_x \sum_y \sum_c \frac{c \text{SH}_{x,y,c} [\text{P}_{x,y,c}]}{[\text{SH}]} \sum_x \sum_y \sum_c \frac{y \text{M}_{x,y,c} [\text{P}_{x,y,c}]}{[\text{M}]} - \frac{k_{\text{cyc}}}{k_{\text{p1}}} \sum_x \sum_y \sum_c \frac{y \text{M}_{x,y,c} \text{SH}_{x,y,c} [\text{P}_{x,y,c}]}{[\text{SH}][\text{M}]}; \quad \psi_{0,1,1}(0) = 0 \quad (35f)$$

Calculations. Solution of eq 29 for the concentration of cyclic structures requires the molar concentration of all individual polymer molecules $\text{P}_{x,y,c}$, which are given

by eqs 18–20. The infinite set of eqs 18–20, and 29 is truncated since the model assumes that cycles up to a critical size dominate the gel formation reactions. Thus, eq 29 is replaced with the following equation:

$$\frac{d\psi_{0,0,1}}{dt} = - \frac{k_{\text{cyc}}}{k_{\text{p1}}} \frac{d\psi_{0,0,0}}{dt} \sum_{x=1}^N \sum_{y=1}^{(f_2-1)x+1} \sum_{c=0}^{\min\{M_{x,y,c}, \text{SH}_{x,y,c}\}} \frac{\text{SH}_{x,y,c} M_{x,y,c} [\text{P}_{x,y,c}]}{[\text{M}][\text{SH}]}; \quad \psi_{0,0,1}(0) = 0 \quad (36)$$

where N is the truncation point, i.e., the number of thiol monomer units in the largest cycle. According to eq 36, formation of cycles up to a certain value of N is allowed; all others are forbidden. For example, if $N = 10$, the largest cycle consists of 10 thiol and $\{10(f_2 - 1) + 1\}$ vinyl monomer units (eq 4a). Thus, to calculate the number of cycles in the reaction system, eqs 18–20 and 36 are coupled; taking N as a model parameter, they are numerically integrated up to the onset of gelation. Note that the number of the differential equations for polymer molecules $\text{P}_{x,y,c}$ represented by eq 18 drastically increases as N is increased. For example, for a divinyl–trithiol comonomer system, the number of equations for $\text{P}_{x,y,c}$ increases from 62 to 607 as N is increased from 5 to 15.

The average chain lengths of molecules were calculated by coupling the above equations with the moment equations given by eqs 26–28 and 35a–f. The triple summation terms in eq 35a–f were evaluated in terms of the corresponding moments, i.e.

$$\sum_x \sum_y \sum_c x M_{x,y,c} [\text{P}_{x,y,c}] = (f_1 - 1) \psi_{1,1,0} - \psi_{2,0,0} + \psi_{1,0,0} - \psi_{1,0,1} \quad (37a)$$

$$\sum_x \sum_y \sum_c y M_{x,y,c} [\text{P}_{x,y,c}] = (f_1 - 1) \psi_{0,2,0} - \psi_{1,1,0} + \psi_{0,1,0} - \psi_{0,1,1} \quad (37b)$$

$$\sum_x \sum_y \sum_c c M_{x,y,c} [\text{P}_{x,y,c}] = (f_1 - 1) \psi_{0,1,1} - \psi_{1,0,1} + \psi_{0,0,1} - \psi_{0,0,2} \quad (37c)$$

The independent variables time t or $\psi_{0,0,0}$ in the model equations can be replaced with the limiting functional group conversion x_{M} or x_{SH} using eqs 26, 30, and 31. After this transformation, the system specific parameters required to solve the model are as follows: (a) the initial concentration of the functional groups, represented by $[\text{M}]_0$ and r_0 ; (b) the functionalities f_1 and f_2 of the vinyl and thiol monomers, respectively; (c) the ratio of cyclization to propagation rate constants $k_{\text{cyc}}/k_{\text{p1}}$.

Results and Discussion

Thiol–ene vs Step-Growth Polymerizations. Neglecting cyclization and transforming the independent variable time t with the limiting conversion x_{SH} or x_{M} , the kinetic model derived for the thiol–ene system becomes identical to that of the usual step-growth polymerization.^{19,20} Thus, all the kinetic parameters of a thiol–ene system do not affect the molecular weight development and the gel point conversion during the reactions. However, in the time scale of the reactions, thiol–ene reactions exhibit characteristic features. This

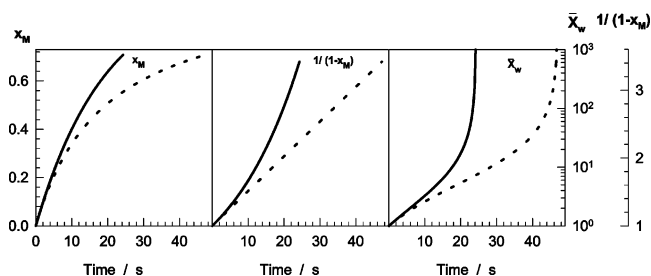


Figure 3. Functional group conversion x_{M} , $1/(1 - x_{\text{M}})$, and the weight-average chain length $\bar{X}_{\text{w}}$ plotted as a function of the reaction time for ring-free thiol–ene (solid curves) and step-growth polymerizations (dashed curves). $f_1 = 2$, $f_2 = 3$, $r_0 = 1$. Rate constants and concentrations used in the calculations are given in the text.

is due to the fact that, in thiol–enes, only the molecules and the radicals can react with each other, while any two molecular species can react in step-growth polymerizations

In a typical step-growth reaction, each favorable collision between one type of functional group with the another type produces a chemical bond, so that the rate expression for the zeroth moment is proportional to the product of the functional group concentrations, that is, using the current notation, it can be written as $d\psi_{0,0,0}/dt \propto [\text{M}][\text{SH}]$. In thiol–ene reactions, however, only collisions between the thiol radicals and pendant vinyl groups may lead to a bond formation, i.e., $d\psi_{0,0,0}/dt \propto [\text{S}^*][\text{M}] \propto [\text{R}^*][\text{SH}]$ (eq 26). Thus, the rate equation for the zeroth moment in thiol–ene reactions is first-order overall. The type of the functional group determining the rate of the reactions depends on the $k_{\text{p1}}/k_{\text{tr}}$ ratio. For example, using eqs 17a, 17b, and 26, one may show that $d\psi_{0,0,0}/dt \propto [\text{SH}]$ and $d\psi_{0,0,0}/dt \propto [\text{M}]$ for $k_{\text{p1}}/k_{\text{tr}} \gg 1$ and $k_{\text{p1}}/k_{\text{tr}} \ll 1$, respectively. Both of these limits have been observed experimentally, depending on the thiol and ene selected.^{4,5,13–15}

To simulate the thiol–ene reactions with time as the independent variable, accurate prediction of the initiation rate R_1 is necessary. Equation 38a predicts the initiator concentration as a function of time, allowing R_1 to vary as a function of time and assuming that each absorbed photon leads to the decomposition of one initiator molecule. Then, R_1 was determined by eq 38b.³²

$$\frac{d[\text{I}]}{dt} = -2.303 \epsilon \frac{I_0 \lambda}{N_A h c} [\text{I}]; \quad [\text{I}](0) = [\text{I}]_0 \quad (38a)$$

$$R_1 = -\phi \frac{d[\text{I}]}{dt} \quad (38b)$$

where ϕ is the number of radicals formed per absorbed photon that initiate polymerization, i.e., the initiator efficiency, ϵ is the molar absorptivity coefficient, I_0 is the incident light intensity, λ is the wavelength, h is the Planck's constant, and c is the speed of light. For calculations, we set $\epsilon = 150$ L/mol-cm, $\lambda = 365$ nm, $\phi = 0.1$, $I_0 = 2$ mW/cm², and $[\text{I}]_0 = 0.02$ M.

In Figure 3, the solid curves show the functional group conversion x_{M} , $1/(1 - x_{\text{M}})$, and the weight-average chain length $\bar{X}_{\text{w}}$ plotted as a function of the reaction time for a ring-free thiol–ene photopolymerization consisting of divinyl and trithiol monomers ($f_1 = 2$, $f_2 = 3$) and for the case where one has stoichiometric amounts of the two functional groups ($r_0 = 1$). For calculations, the usual values of the rate constants and concentrations were

used,^{13–15} $k_{p1} = k_{tr} = 5 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$, $k_t = 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$, $[M]_0 = 2 \text{ M}$. For comparison, the kinetic features of a usual step-growth reaction are also shown in Figure 3 by the dotted curves. These calculations were performed using the model equations except that the rate expression for the zeroth moment is replaced with the following equation:

$$\frac{d\psi_{0,0,0}}{dt} = -k_1[M][SH] \quad (39)$$

where k_1 is the rate constant for intermolecular reactions. k_1 was set to $k_{tr}[R]_0/[M]_0$ in order to obtain the same initial rates for both of the reactions.

Figure 3 shows that the thiol–ene photopolymerization is governed by a first-order reaction kinetics compared to the second-order kinetics of the usual step-growth reactions. For example, $1/(1 - x_M)$ increases exponentially with reaction time in the thiol–ene system, while it is linear in time for the step-growth reaction. Furthermore, the gel point, at which $\bar{X}_w$ goes to infinity, occurs in shorter times in the thiol–ene system compared to the step-growth reactions. The results also show that the rate of polymerization as well as the gelation times can easily be manipulated in thiol–ene systems by changing one of the several kinetic parameters appearing in eq 38a and 38b. For example, increasing the initiation rate, R_i , or decreasing the termination rate constant, k_t , increases the total concentration of the radicals so that gelation occurs in much shorter reaction times.

Another distinction between the thiol–ene and step-growth reactions appears in the rate of cyclization reactions. In step-growth reactions, all intramolecular collisions between different types of functional groups may lead to cycle formation. However, in thiol–ene systems, intramolecular collisions within the carbon radicals as well as between the functional groups produce no cycle. This effect decreases the cyclization probability in thiol–ene reactions.

Cyclization. Data are presented first of the effect of the cycle size on the gelation kinetics in thiol–ene polymerizations. Calculations allowing formation of cycles up to a critical size were performed by truncating the cyclization rate expression at a critical value of N , which is the number of thiol monomer units in the largest cycle. The solid curves in Figure 4A show the number- and weight-average chain lengths, $\bar{X}_n$ and $\bar{X}_w$, respectively, plotted against the functional group conversion x_M for various values of N . Calculations are for a divinyl and trithiol comonomer pair with equivalent feed ratio of thiol and vinyl groups ($r_0 = 1$). The k_{cyc}/k_{p1} ratio is set to 0.1. The filled symbols are results of calculations of $\bar{X}_w$ using the equation

$$\bar{X}_w = \frac{1 + x_M r_0^{-0.5}}{1 - x_M r_0^{-0.5} \{(f_1 - 1)(f_2 - 1)\}^{0.5}} \quad (40)$$

which was derived for ring-free step-growth polymerizations.^{29,30,33} It is seen that the prediction of the model equations for $N = 0$, that is, for neglecting cyclization ($k_{cyc}/k_{p1} = 0$) reduces to that given by eq 40. The asymptotic limit in $\bar{X}_w$ was used to predict the critical conversion x_{cr} at the gel point. In Figure 4B, the critical conversion x_{cr} and the fraction of functional groups wasted in cycles ξ are plotted as a function of N . For $N = 0$, gelation occurs at $x_{cr} = 0.707$, as predicted by eq

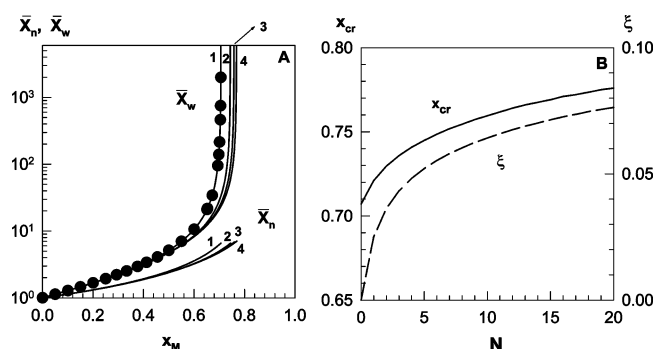


Figure 4. (A) Number- and weight-average chain lengths, $\bar{X}_n$ and $\bar{X}_w$, respectively, during thiol–ene polymerizations plotted against the functional group conversion x_M for various values of N , the number of thiol monomer units in the largest cycle. The solid curves were calculated using the model equations while the filled symbols are results of calculations of $\bar{X}_w$ using eq 40. $[M]_0 = 2 \text{ M}$, $r_0 = 1$, $f_1 = 2$, $f_2 = 3$, $k_{cyc}/k_{p1} = 0.1$. $N = 0$ (1), 5 (2), 10 (3), and 15 (4). (B) Critical conversion, x_{cr} , (solid curve) and the fraction of functional groups wasted in cycles, ξ (dashed curve), shown as a function of N .

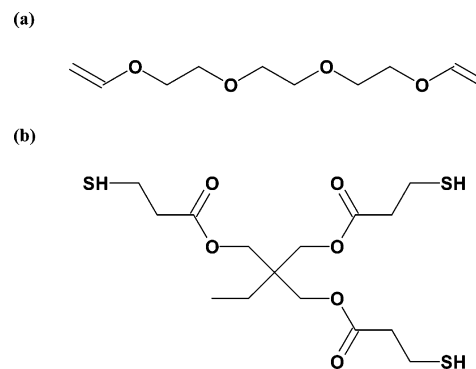


Figure 5. Chemical structures of monomers utilized in this work: (a) tri(ethylene glycol) divinyl ether; (b) trimethylolpropane tris(3-mercaptopropionate).

40. As N is increased, both x_{cr} and ξ increase, first rapidly up to about $N = 5$ but then, they increase only slightly with N . Results such as those in Figure 4B were also calculated for various k_{cyc}/k_{p1} ratios as well as for various monomer concentrations and comonomer functionalities. Thus, the gel point conversion and the total number of cycles are very sensitive to the cycle size of less than five thiol monomer units while larger cycles do not significantly affect the gelation kinetics. One may explain this behavior with the predominant role of the short chains in the pregel regime of thiol–enes. As seen in Figure 4A, the average chain lengths remain below 10^1 up to about 60% functional group conversion, indicating that the molecules containing less than 10 monomer units are the dominant species in the reaction system. As a result, cycles formed in such molecules determine the pregel properties of the reaction system. On the basis of this analysis, for all following calculations, N was set to 10.

In order for the results of the simulations to be meaningful, realistic values of the cyclization rate constant k_{cyc} are to be used in the calculations. The relative rate constant k_{cyc}/k_{p1} was therefore determined experimentally for a thiol–ene system at different initial monomer concentrations. Gelation experiments were performed using tri(ethylene glycol) divinyl ether ($f_1 = 2$) and trimethylolpropane tris(3-mercaptopropionate) ($f_2 = 3$) monomers (Figure 5). This comonomer pair is a traditional thiol–ene system in that the ene

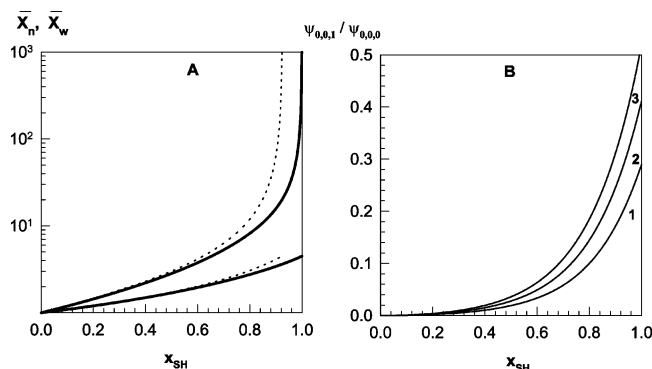


Figure 6. (A) Number- and weight-average chain lengths, $\bar{X}_n$ and $\bar{X}_w$, respectively, during divinyl-trithiol polymerization plotted against the limiting functional group conversion x_{SH} . $c = 100$ wt %. $r_0 = r_{0,cr} = 0.585$. $k_{cy}/k_{p1} = 0$ (dotted curves) and 0.073 (solid curves). (B) Average number of cycles per molecule, $\psi_{0,0,1}/\psi_{0,0,0}$, plotted against the limiting conversion x_{SH} . $c = 100$ (1), 67 (2), and 30 wt % (3).

Table 3. Values of k_{cy}/k_{p1} and ξ in Thiol–Ene Reactions of Tri(ethylene glycol) Divinyl Ether and Trimethylolpropane Tris(3-mercaptopropionate) in Dichloromethane at Various Concentrations c (g of Monomers/100 g of Solution), Where Standard Deviations Are Given in Parentheses

$[M]_0$ (M)	c (wt %)	$r_{0,cr}$	k_{cy}/k_{p1}	$\xi \times 10^2$
1.50	100	0.585 (0.007)	0.073 (0.007)	7.6 (0.6)
1.39	67	0.618 (0.007)	0.094 (0.006)	9.9 (0.5)
0.50	30	0.645 (0.005)	0.043 (0.001)	11.7 (0.2)

does not homopolymerize via a radical mechanism.^{13–15} Due to the very rapid polymerizations when using either photo or thermal initiators, an accurate determination of the critical conversion x_{cr} by using Fourier transform infrared studies^{4,5} was not possible. Therefore, instead of x_{cr} , we determined the critical value of r_0 ($r_{0,cr}$) at which no gel forms, i.e., at which x_{cr} becomes unity. For this purpose, we varied the ratio of the initial concentrations of thiol-to-vinyl groups, r_0 , in small steps until no gel is obtained. Gelation experiments were carried out using 2,2'-azobis(isobutyronitrile) (AIBN) as the thermal initiator at 50 °C. The reaction time was 1 day. The concentration of AIBN was varied between 0.17 and 1 wt % (0.067–0.01 M). As expected, $r_{0,cr}$ was found to be independent of the initiator concentration. Gelation experiments were carried out at three different concentrations of the monomers in dichloromethane, which is a good solvent for the polymer.

In the first two columns of Table 3, the initial concentration of the monomers and the experimentally determined values of $r_{0,cr}$ are collected. Figure 6A shows the molecular weight development during the bulk thiol–ene polymerization at $r_0 = r_{0,cr}$. The dotted curves are simulation results for $k_{cy}/k_{p1} = 0$. It is seen that, assuming no cyclization, gelation should occur before the complete conversion of the limiting functional group. The solid curves in Figure 6A were obtained by adjusting the relative rate constant k_{cy}/k_{p1} of the model until the asymptotic limit in $\bar{X}_w$ fits $x_{cr} = 1$. The values of k_{cy}/k_{p1} and ξ thus evaluated for bulk as well as for solution polymerizations are collected in the third and fourth columns of Table 3. The relative rate constant for cyclization is 0.073 for the bulk reaction; as expected, it increases to 0.094 with decreasing monomer concentration from 100 to 67 wt %. At 30% monomer concentration, however, k_{cy}/k_{p1} decreases again to 0.043. It

should be noted that the gel point for this dilute reaction system was a point at which gel particles in the lower part of the reactor start to appear. This result is likely caused by the high degree of dilution of the gelling system so that the gel molecule cannot occupy the entire polymerization system. The decrease in k_{cy}/k_{p1} may thus be attributed to the heterogeneity of the system. The relative rate constants tabulated in Table 3 are 2-fold smaller than those reported for cross-linking urethane polymerization of a triol and diisocyanate, carried out under similar feed ratios and monomer concentrations.²⁰ This deviation could be due to the intramolecular chain transfer reactions in thiol–enes, which reduce the probability of favorable collisions responsible for cycle formation.

Table 3 also shows that ξ in bulk system is about 0.08 at the gel point, indicating that about 8% of the potential cross-links (pendant vinyls and thiol radical centers) are lost to cyclization reactions. The fraction of functional groups wasted in cycles increases from 0.08 to 0.12 as the degree of dilution is increased. The ξ values thus found for the thiol–ene system are much smaller compared to the typical free-radical systems. For example, in acrylate systems, it was reported that more than 50% of the cross-linker molecules are consumed in cyclization reactions.¹⁰ The degree of cyclization changes over the course of the reaction. To get a picture of how cyclization rates change over the reaction, the average number of cycles per molecule, $\psi_{0,0,1}/\psi_{0,0,0}$, is plotted. In Figure 6B, $\psi_{0,0,1}/\psi_{0,0,0}$ as a function of the limiting conversion x_{SH} is shown for the three reaction systems studied. Cycles start to form mainly at moderate to high conversions. For example $\psi_{0,0,1}/\psi_{0,0,0}$ for the bulk system is below 0.1 up to about 80% conversion; thereafter, they increase rapidly and become 0.29, at the gel point. Decreasing the monomer concentration from 100 to 30% increases the $\psi_{0,0,1}/\psi_{0,0,0}$ ratio at the gel point to 0.52. The results thus found completely differ from the free-radical cross-linking copolymerization reactions, where cyclization starts at nearly zero monomer conversions.¹⁰ Another interesting point is that, since each propagation event is followed by a chain transfer reaction, secondary cyclization (multiple cross-linking) reactions do not readily occur during the thiol–ene reactions, which are well-known, dominant reactions in free-radical cross-linking copolymerizations.

For the same reaction system ($f_1 = 2$, $f_2 = 3$), Figure 7A shows the number-average chain length of thiol radicals $\bar{X}_n^*$ (solid curves) and carbon radicals $\bar{X}_n^{\bullet}$ (dotted curves) plotted against the limiting conversion x_{SH} for various k_{cy}/k_{p1} ratios between 0 and 0.3. Figure 7B shows the variation of the weight-average chain length $\bar{X}_w$ of polymers with the conversion x_{SH} . The feed ratio of thiol and vinyl groups r_0 is 0.65 for these calculations. Over a wide range of conversion, $\bar{X}_n^* \approx 1$ and $\bar{X}_n^{\bullet} \approx 2$, indicating that the monomeric thiol radicals together with the dimeric carbon radicals consisting of one thiol and one ene monomer units are active species in the reaction system. Increasing the extent of cyclization further decreases the molecular weight of both active and inactive species. As the reaction system approaches the gel point, both $\bar{X}_n^*$ and $\bar{X}_n^{\bullet}$ diverge due to the formation of giant molecules with more than one radical center, as also reported for free-radical cross-linking copolymerizations.^{17,34} As expected, the gel point is shifted to higher conversions by

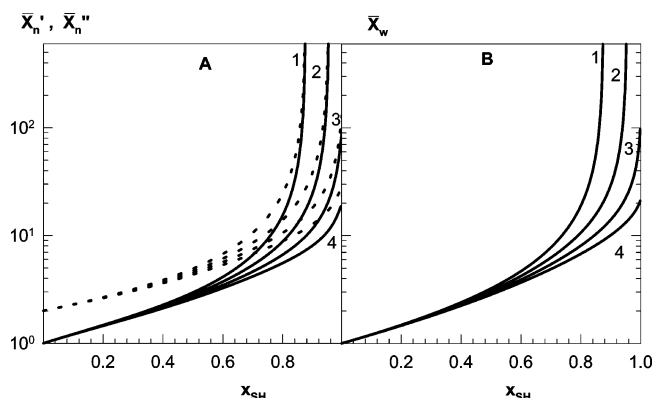


Figure 7. (A) Number-average chain length of thiol radicals, $\bar{X}_n''$ (solid curves), and carbon radicals, $\bar{X}_n'$ (dotted curves), plotted against the limiting conversion x_{SH} for various k_{cyc}/k_{p1} ratios. (B) Variation of the weight-average chain length $\bar{X}_w$ of polymers with the conversion x_{SH} . $f_1 = 2$, $f_2 = 3$, $[M]_0 = 2$ M, $r_0 = 0.65$. $k_{cyc}/k_{p1} = 0$ (1), 0.1 (2), 0.2 (3), and 0.3 (4).

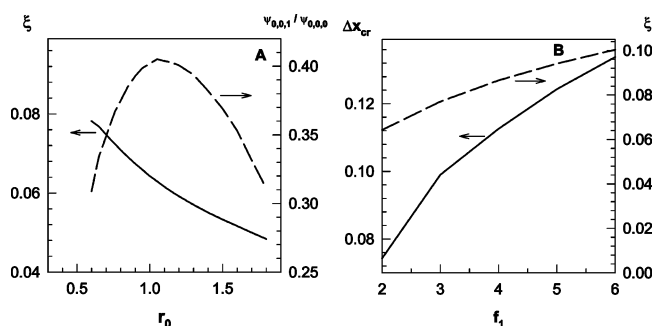


Figure 8. (A) Fraction of functional groups wasted in cycles, ξ (solid curve) and the average number of cycles per molecule, $\psi_{0,0,1}/\psi_{0,0,0}$ (dashed curve) shown as a function of the feed ratio of the functional groups r_0 . $[M]_0 = 2$ M, $f_1 = 2$, $f_2 = 3$, $k_{cyc}/k_{p1} = 0.1$. (B) Shift of the gel point due to cyclization, Δx_{cr} (solid curve) and the fraction of functional groups wasted in cycles, ξ (dashed curve) plotted against the functionality of the vinyl monomer f_1 . $k_{cyc}/k_{p1} = 0.1$, $[M]_0 = 2$ M, $r_0 = 1$, $f_2 = 3$.

cyclization, or gelation does not occur at all for $k_{cyc}/k_{p1} > 0.2$.

Figure 8A shows the effect of the feed ratio of thiol and vinyl groups r_0 on the extent of cyclization during thiol–ene reactions. Here, the fraction of functional groups wasted in cycles ξ (solid curve) and the average number of cycles per molecule $\psi_{0,0,1}/\psi_{0,0,0}$ (dashed curve) are plotted against r_0 for $k_{cyc}/k_{p1} = 0.1$ and for a divinyl-trithiol reaction system. ξ decreases continuously as r_0 is increased starting from $r_{0,cr}$, indicating that the cyclization reactions can be suppressed if an excess of the thiol monomer is used in the reaction. This unique behavior is due to the decreasing concentration of pendant vinyl groups on the molecules available for cyclization. In contrast, the average number of cycles per molecule $\psi_{0,0,1}/\psi_{0,0,0}$ exhibits a maximum at about $r_0 = 1$ while $\psi_{0,0,1}/\psi_{0,0,0}$ decreases as the feed ratio deviates from unity. This maxima happens because the concentration of unreacted monomer molecules increases as r_0 deviates from unity, which reduces the average number of cycles per molecule. Calculations indeed show that the number of cycles per polymer molecule, $\psi_{0,0,1}/(\psi_{0,0,0} - P_{1,0,0} - P_{0,1,0})$, decreases monotonically as the feed ratio r_0 is increased. Figure 8B shows the effect of the functionality of the monomers on the extent of cyclization during thiol–ene reactions. Here, the shift of the gel point due to cyclization is plotted against the functionality of the vinyl monomer

f_1 . Δx_{cr} is defined as $\Delta x_{cr} = (x_{cr} - x_{cr,0})/x_{cr,0}$, where $x_{cr,0}$ is the gel point conversion for the ring-free polymerization. It is seen that, the higher the functionality of the vinyl monomer, the higher the extent of cyclization and thus, the larger is the shift of the gel point toward higher conversions. Similar results were also found if the thiol group functionality f_2 is varied at a fixed value of f_1 . The results in Figure 8 thus found suggest that the experimentally determined degree of cyclization at $r_0 = r_{0,cr}$ is the largest value for this reaction system and, it would decrease as the feed ratio r_0 approaches to unity. Moreover, increasing functionality of the monomers used in the cross-linking polymerization would also increase the degree of cyclization during the reactions.

Conclusions

The molecular weight development and the process of cyclization during thiol–ene photopolymerizations utilizing multifunctional thiol and ene monomers are successfully modeled up to the onset of gelation. Modeling predictions demonstrate that the molecular weight development and the gel point conversions in ring-free thiol–ene reactions are identical to those in step-growth reactions. Deviations appear due to the first-order reaction kinetics of thiol–ene systems as well as due to the cyclization reactions. The cyclization rate constant in thiol–ene polymerization is smaller than that in traditional step-growth reactions due to the intramolecular chain transfer reactions, which reduce the probability of cycle formation.

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