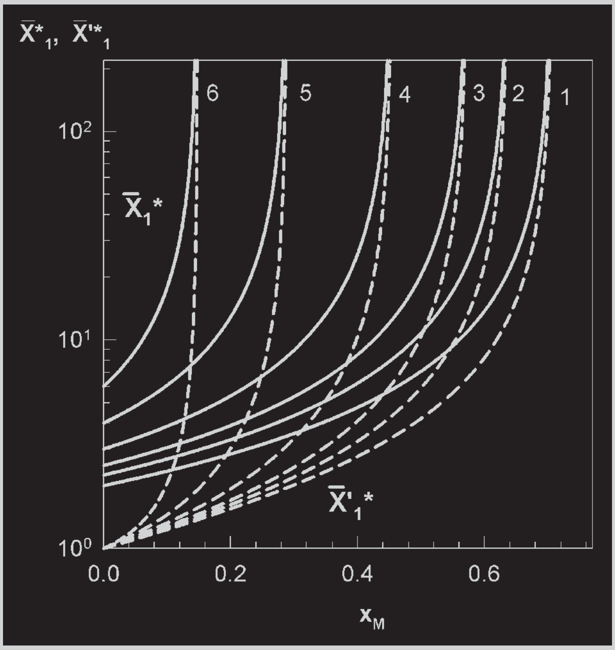
Summary: A kinetic model is presented for thiol-ene crosslinking photopolymerizations including the allowance for chain growth reaction of the ene, i.e., homopolymerization. The kinetic model is based on a description of the average chain lengths derived from differential equations of the type of Smoluchowski coagulation equations. The method of moments was applied to obtain average properties of thiol-ene reaction systems. The model predicts the molecular weight distribution of active and inactive species in the pre-gel regime of thiol-enes, as well as the gel points depending on the synthesis parameters. It is shown that, when no homopolymerization is allowed, the average molecular weights and the gel point conversion are given by the typical equations valid for the step-growth polymerization. Increasing the extent of homopolymerization also increases the average molecular weights and shifts the gel point toward lower conversions and shorter reaction times. It is also shown that the ratio of thiyl radical propagation to the chain transfer kinetic parameter (k_{p1}/k_{tr}) affects the gelation time, t_{cr}. Gelation occurs earlier as the k_{p1}/k_{tr} ratio is increased due to the predominant attack of thiyl radicals on the vinyl groups and formation of more stable carbon radicals. The gel point in thiol-ene reactions is also found to be very sensitive to the extent of cyclization, particularly, if the monomer functionalities are low.



Number-average chain length of carbon radicals $\bar{X}_1\bullet$ (solid curves) and thiyl radicals $\bar{X}'_1\bullet$ (dashed curves) plotted against the vinyl group conversion, x_M, during thiol-ene polymerization. Calculations were for six different k_p/k_{tr} ratios.

Kinetic Modeling of Thiol-Ene Reactions with Both Step and Chain Growth Aspects

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Introduction

Thiol-ene photopolymerizations are step-growth radical polymerizations involving a reaction between multifunctional thiol and ene (vinyl) monomers.[1–3] Previous work has demonstrated 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.

The step-growth nature of thiol-ene photopolymerizations was first suggested by Kharasch in 1938.[7] The polymerization reaction proceeds via propagation of a thiyl radical (–*S*•) 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 ($-\overset{\bullet}{C}H-$), thus formed, to the thiol functional group, regenerating a thiyl radical, i.e.,

$$-S\bullet + CH_2{=}CH- \xrightarrow{k_{p1}} -S{-}CH_2{-}\overset{\bullet}{C}H- \tag{1a}$$

$$-S{-}CH_2{-}\overset{\bullet}{C}H- + SH- \xrightarrow{k_{tr}} -S{-}CH_2{-}CH_2- + -S\bullet \tag{1b}$$

These successive propagation and chain transfer reactions serve as the basis for the step-growth nature of traditional thiol-ene polymerization. As a result, the gel formation dynamics of thiol-enes are quite different from the polymerization of multifunctional acrylate monomers. In a typical free-radical polymerization of multiacrylate monomers, high molecular weight polymers form at near-zero monomer conversion because of the chain-growth nature of the polymerization, leading to excessive cyclization, multiple cross-linking, microgelation, low gel point conversions, diffusion- and reaction diffusion-controlled reactions, and ultimately, the formation of inhomogeneous networks.[8–11] However, in thiol-ene systems, very low molecular weight species dominate the pre-gel regime, leading to higher gel point conversions and the formation of homogeneous networks.

Although the traditional free-radical reaction of a thiol and an ene proceeds via a step-growth process (Equation (1a)–(1b)), for some enes the propagation of a carbon radical via homopolymerization of the ene accompanies the traditional thiol-ene photopolymerization, i.e.,

$$\begin{aligned} &-S{-}CH_2{-}\overset{\bullet}{C}H- + CH_2{=}CH- \xrightarrow{k_p} \\ &\qquad -S{-}CH_2{-}CH_2{-}CH_2{-}\overset{\bullet}{C}H \end{aligned} \tag{1c}$$

This propagation step, referred to in the remaining of this manuscript as homopolymerization, is particularly important in thiol-acrylate polymerizations and leads to the formation of homopolymer groups in the copolymer.[4–6,12–14] One may expect that, at a high ratio of homopolymerization to chain transfer kinetic parameter k_p/k_{tr}, the reaction mechanism of thiol-enes changes from predominantly step-growth to predominantly chain-growth nature.

While thiol-ene polymerizations have been examined extensively in recent years, many fundamental aspects of these reactions, such as the molecular weight development during the pre and post-gel regimes, as well as the effect of the homopolymerization on the gelation process remain relatively unexplored. The aim of the present work is primarily to develop a kinetic model for prediction of the molecular weight averages of thiyl and carbon radicals as well as of polymer molecules during thiol-ene reactions with homopolymerization prior to the onset of gelation.

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 the average chain lengths derived from differential equations of the type of Smoluchowski coagulation equations.[15] The method of moments was applied to obtain average properties in the pre-gel period and to predict the gel point. In the kinetic treatment that follows, the main assumptions made are: (i) the steady-state approximation for each of the radical species in the system; (ii) the reactions are chemically controlled rather than diffusion controlled; and (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 pre-gel regime, while the validity of the third assumption (monoradical assumption) was previously demonstrated for free-radical cross-linking copolymerization systems.[16]

Kinetic Mechanism

Notation and Rate Equations

The dependent variables $S_r\bullet$, $R_r\bullet$, and P_r represent thiyl radicals, carbon radicals, and dead polymer or monomer molecules, respectively. The subscript r describes the total number of monomer units in the molecule. Thus, P_1 represents the unreacted monomers in the reaction system. The functionalities of the vinyl and thiol monomers are represented by f_1 and f_2, respectively, which denote the initial number of the functional groups of molecules. Furthermore, the symbols M_r and SH_r are used to represent the vinyl and thiol groups on molecules P_r, respectively. The total concentrations of carbon radicals $[R\bullet]$, thiyl radicals $[S\bullet]$, vinyl groups $[M]$ and thiol groups $[SH]$ in the reaction system are related to the variables defined above by the following equations:

$$[R\bullet] = \sum_{r=1}^{\infty} [R_r\bullet] \tag{2a}$$

$$[S\bullet] = \sum_{r=1}^{\infty} [S_r\bullet] \tag{2b}$$

$$[M] = \sum_{r=1}^{\infty} [M_r] \tag{2c}$$

$$[SH] = \sum_{r=1}^{\infty} [SH_r] \tag{2d}$$

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 four steps: initiation, propagation, chain

transfer, and termination. The reaction equations describing the steps of the polymerization can be written as follows:
Initiation:

$$I \xrightarrow{h\nu} A\bullet \tag{3a}$$

$$A\bullet + SH_r \xrightarrow{k_i} S_r\bullet \tag{3b}$$

$$A\bullet + M_r \xrightarrow{k_i} R_r\bullet \tag{3c}$$

Propagation:

$$S_j\bullet + M_{r-j} \xrightarrow{k_{p1}} R_r\bullet \tag{4a}$$

$$R_j\bullet + M_{r-j} \xrightarrow{k_p} R_r\bullet \tag{4b}$$

Chain Transfer:

$$R_r\bullet + SH_j \xrightarrow{k_{tr}} P_r + S_j\bullet \tag{5}$$

Termination:

$$S_j\bullet + S_{r-j}\bullet \xrightarrow{k_{tc}\text{ and/or }k_{td}} P_r \text{ and/or } P_j + P_{r-j} \tag{6a}$$

$$S_j\bullet + R_{r-j}\bullet \xrightarrow{k_{tc}\text{ and/or }k_{td}} P_r \text{ and/or } P_j + P_{r-j} \tag{6b}$$

$$R_j\bullet + R_{r-j}\bullet \xrightarrow{k_{tc}\text{ and/or }k_{td}} P_r \text{ and/or } P_j + P_{r-j} \tag{6c}$$

$$(r, j, r-j = 1, 2, 3, \ldots)$$

Decomposition of the initiator I according to Equation (3a) produces primary radicals $A\bullet$, which may react either with a thiol or vinyl group on $r$mers, denoted by SH_r and M_r, respectively (Equation (3b)–(3c)). Note that $r = 1, 2, 3, \ldots$, where $r = 1$ corresponds to the functional groups on monomers. The thiyl ($S_r\bullet$) and carbon radicals ($R_r\bullet$) thus formed may propagate according to Equation (4a) and (4b), respectively. Equation (4a) accounts for the propagation of a thiyl radical through the vinyl functional group, while Equation (4b) accounts for the homopolymerization reaction of carbon radicals. The chain transfer reactions represented by Equation (5) produce inactive polymer molecules of chain length r (P_r) during which carbon radicals $R_r\bullet$ become thiyl radicals $S_j\bullet$ of a different chain length. Finally, the termination reactions between thiyl and carbon radicals occur by coupling and/or by disproportionation mechanisms (Equation (6a)–(6c)). The rate constants k_i, k_{p1}, k_p, k_{tr}, k_{tc}, and k_{td} are for initiation, for the formation of carbon radicals from thiyl radicals, for propagation by homopolymerization, for chain transfer to thiol, and for termination by coupling and by disproportionation, respectively. For the sake of clarity and simplicity, we assume that the termination rate constant does not depend on the type of the radical.

In addition to the intermolecular reactions mentioned above, intramolecular reactions may also occur during the thiol-ene polymerization. These reactions are distinguished as cyclization and intramolecular chain transfer reactions, as schematically illustrated in Figure 1. Cyclization, that is intramolecular propagation, may occur by the attack of a thiyl or carbon radical center on one of the pendant vinyl groups on the same molecule and leads to the formation of

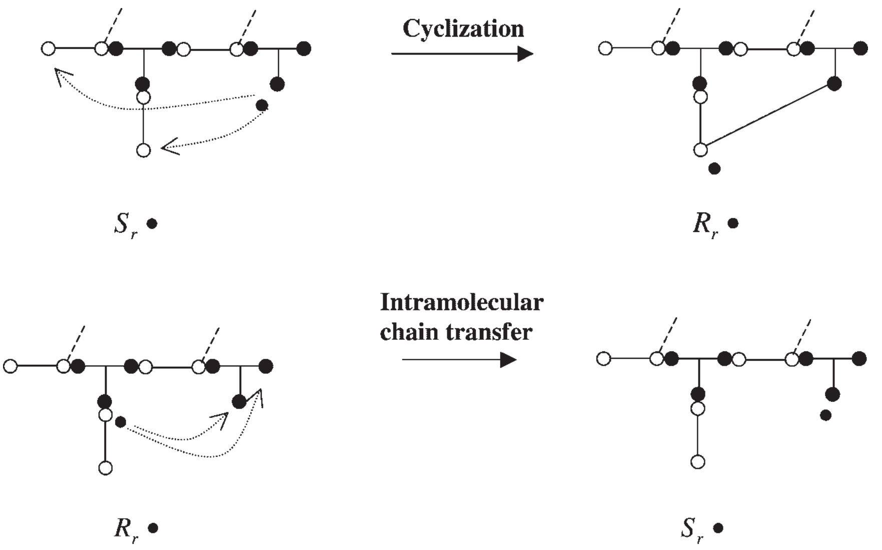

Figure 1. Schematic representation of cyclization and intramolecular chain transfer reactions in thiol-ene copolymerization of vinyl and thiol monomers ($f_1 = 2$, $f_2 = 3$). The filled and open circles represent thiol and vinyl groups, respectively. The dashed lines show the homopolymer blocks. The arrows show the possible routes for intramolecular reactions. Radical centers are indicated by the dots.

cycles. In typical thiol-ene reactions, the consumption rate of vinyl functional groups via propagation dominates over the consumption rate via homopolymerization.[4,5] Therefore, in the following analysis, cycles are assumed to form only by the attack of thiyl radicals on the pendant vinyl groups located on the same oligomer molecule. In contrast to cyclization, intramolecular chain-transfer reactions produce no cycles; they only convert carbon radicals into thiyl radicals (Figure 1). Since the intramolecular reactions occurring in similar molecules proceed in a similar micro-environment, it is reasonable to assume equal rates for both cyclization and intramolecular chain transfer reactions.

Neglecting functional group consumption by initiation relative to propagation or chain transfer, the rate equations for the concentrations of the functional groups and the monomer units are written as follows:

$$\frac{d[M_1]}{dt} = -f_1(k_{p1}[S\bullet] + k_p[R\bullet])[M_1] \quad [M_1](0) = [M]_0 \tag{7}$$

$$\frac{d[SH_1]}{dt} = -f_2 k_{tr}[R\bullet][SH_1] \quad [SH_1](0) = [SH]_0 \tag{8}$$

$$\frac{d[m_1]}{dt} = -f_1^{-1}\frac{d[M_1]}{dt} \quad [m_1](0) = 0 \tag{9}$$

$$\frac{d[m_2]}{dt} = -f_2^{-1}\frac{d[SH_1]}{dt} \quad [m_2](0) = 0 \tag{10}$$

where t is the reaction time, M_1 and SH_1 represent vinyl and thiol groups on unreacted monomers, and m_1 and m_2 represent the vinyl and thiol monomer units in the polymer. The initial conditions of the differential equations are indicated with the subscript zero. Equation (7) and (8) account for the consumption of the functional groups located on unreacted monomers. The prefactors f_1 and f_2 in these equations account for the fact that, if one of the functional groups on a monomer molecule has reacted, the others also disappear and become pendant functional groups on polymer molecules. Equation (9) and (10) describe the formation of vinyl and thiol monomer units in the polymer molecules, respectively. The accumulated mole fraction of vinyl monomer in the polymer, $\bar{F}_1$ is calculated from Equation (9)–(10) as:

$$\bar{F}_1 = \frac{[m_1]}{[m_1] + [m_2]} \tag{11}$$

Using Equation (3a)–(6c), the differential equations characterizing the population density distributions of the radicals $S_r\bullet$ and $R_r\bullet$, and the polymers P_r are given as follows:

$$\begin{aligned}\frac{d[S_r\bullet]}{dt} &= k_i[A\bullet][SH_r] + k_{tr}[R\bullet][SH_r] \\ &\quad - k_{p1}[S_r\bullet][M] - k_t([R\bullet] + [S\bullet])[S_r\bullet]\end{aligned} \tag{12}$$

$$\begin{aligned}\frac{d[R_r\bullet]}{dt} &= k_i[A\bullet][M_r] + k_{p1}\sum_{j=1}^{r-1}[S_j\bullet][M_{r-j}] + k_p\sum_{j=1}^{r-1}[R_j\bullet][M_{r-j}] \\ &\quad -(k_p[M] + k_{tr}[SH])[R_r\bullet] - k_t([R\bullet] + [S\bullet])[R_r\bullet]\end{aligned} \tag{13}$$

$$\begin{aligned}\frac{d[P_r]}{dt} &= k_{tr}[R_r\bullet][SH] - (k_{p1}[S\bullet] + k_p[R\bullet])[M_r] \\ &\quad - k_{tr}[R\bullet][SH_r] + k_{td}([R\bullet] + [S\bullet])([R_r\bullet] + [S_r\bullet]) \\ &\quad + 0.5k_{tc}\sum_{j=1}^{r-1}([R_j\bullet][R_{r-j}\bullet] + 2[R_j\bullet][S_{r-j}\bullet] + [S_j\bullet][S_{r-j}\bullet])\end{aligned} \tag{14}$$

where $k_t = k_{tc} + k_{td}$. The first and last rate expressions in Equation (12) and (13) account for the formation and consumption reactions of the radicals in the initiation and termination steps, respectively. Thiyl radicals $S_r\bullet$ also form by chain transfer, while they disappear by propagation, represented by the second and third rate expressions in Equation (12), respectively. Conversely, carbon radicals $R_r\bullet$ form by propagation and disappear by chain transfer, as shown by Equation (13). In addition, the homopolymerization reaction contributes to the formation and consumption of the carbon radicals $R_r\bullet$ in the reaction system. It should be noted that, since the rate of carbon radical formation by cyclization is assumed to be equal to its consumption rate by intramolecular chain transfer, the intramolecular rate expressions are excluded from Equation (12)–(13). Moreover, dead polymer molecules, P_r, form by the chain transfer reactions of $R_r\bullet$ 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_r (Equation (14)).

Moments of Polymer Distributions

The method of moments is then applied to the kinetic model of the reactions represented by Equation (12)–(14) to calculate the nth moment of the active polymer, inactive (dead) polymer, and functional group distributions, defined by:

$$Y_n \equiv \sum_{r=1}^{\infty} r^n [R_r\bullet] \tag{15a}$$

$$Y'_n \equiv \sum_{r=1}^{\infty} r^n [S_r\bullet] \tag{15b}$$

$$Q_n \equiv \sum_{r=1}^{\infty} r^n [P_r] \tag{15c}$$

$$W_n \equiv \sum_{r=1}^{\infty} r^n [M_r] \tag{15d}$$

$$W'_n \equiv \sum_{r=1}^{\infty} r^n [SH_r] \tag{15e}$$

$$(n = 0, 1, 2, \ldots)$$

From definitions, zeroth moments correspond to the total concentration of the species, i.e., $Y_0 \equiv [R\bullet]$, $Y'_0 \equiv [S\bullet]$, $W_0 \equiv [M]$, and $W'_0 \equiv [SH]$. From the moments of the polymer distributions, the nth average chain length of the carbon radical ($\bar{X}_n\bullet$), the thiyl radical ($\bar{X}'_n\bullet$), and the polymer ($\bar{X}_n$) are calculated as follows:

$$\bar{X}_n\bullet = Y_n / Y_{n-1} \tag{16a}$$

$$\bar{X}'_n\bullet = Y'_n / Y'_{n-1} \tag{16b}$$

$$\bar{X}_n = Q_n / Q_{n-1} \tag{16c}$$

$$(n = 1, 2, 3, \ldots)$$

where $n = 1$ and 2 correspond to the number- and weight-average chain lengths, respectively. Invoking the steady-state approximation to Equation (12)–(13), the moments of the active polymer distributions are evaluated as follows:
Thiyl radical moments:

$$\frac{dY'_n}{dt} = k_i[A\bullet][SH] + k_{tr}[R\bullet]W'_n - \{k_{p1}[M] + k_t(Y_0 + Y'_0)\}Y'_n \cong 0 \tag{17}$$

Carbon radical moments:

$$\frac{dY_n}{dt} = k_i[A\bullet][M] + k_{p1}\sum_{v=0}^{n}\binom{n}{v}Y'_v W_{n-v} + k_p\sum_{v=0}^{n}\binom{n}{v}Y_v W_{n-v} - \{k_p[M] + k_{tr}[SH] + k_t(Y_0 + Y'_0)\}Y_n \cong 0 \tag{18}$$

Assuming that the consumption of the functional groups by initiation is negligible relative to propagation, and since the radical termination rate in thiol-ene polymerizations is negligible compared to the rates of propagation or chain transfer,[12–14] from Equation (17)–(18), the moments of the active radicals are expressed as:

$$y_n = \sum_{v=0}^{n}\binom{n}{v}y'_v w_{n-v} + (\alpha - 1)\sum_{v=0}^{n-1}\binom{n}{v}y_v w_{n-v} \tag{19}$$

$$y'_n = w'_n \tag{20}$$

$$Y'_0 = (1 - \varphi)\left(\frac{R_I}{k_t}\right)^{0.5} \tag{21}$$

$$Y_0 = \varphi\left(\frac{R_I}{k_t}\right)^{0.5} \tag{22}$$

where $y'_n = Y'_n / Y'_0$, $y_n = Y_n / Y_0$, $w_n = W_n / W_0$, $w'_n = W'_n / W'_0$, R_I is the rate of initiation, $R_I = k_i[A\bullet]([M] + [SH])$, φ is the mole fraction of carbon radicals within the total radical species,

$$\varphi = \frac{k_{p1}[M]}{k_{p1}[M] + k_{tr}[SH]} \tag{23}$$

and α is the ratio of the consumption rates of vinyl to thiol functional groups,

$$\alpha \equiv \frac{d[M]}{d[SH]} = 1 + \frac{k_p[M]}{k_{tr}[SH]} \tag{24}$$

Note that the consumption of vinyl functional groups via homopolymerization does not occur in typical thiol-ene systems,[5] so that α remains unity throughout the reactions and the second term of the right hand side of Equation (19) vanishes. Homopolymerization occurs, however, for example in thiol-acrylate systems, which leads to higher vinyl group consumption relative to thiol consumption.[4] Furthermore, for monofunctional thiol monomers, the first term of the right hand side of Equation (19) is unity due to the fact that the chain length of the thiyl radicals cannot be greater than one ($y'_n = 1$).

Using the assumptions made above, the material balance for inactive molecules given by Equation (14) yields the rate equation for the nth moment of the polymer distributions as follows:

$$\frac{dQ_n}{dt} = k_{tr}[R\bullet][SH](y_n - \alpha w_n - w'_n); \quad Q_n(0) = [P_1]_0 \tag{25}$$

where $[P_1]_0$ is the initial monomer concentration, i.e., $[P_1]_0 = [M]_0/f_1 + [SH]_0/f_2$. Equation (25) describes the distribution of all species including the unreacted monomer molecules.

Moments of Functional Group Distributions

Let ΔM and ΔSH be the number of reacted vinyl and thiol groups at a given reaction time or functional group conversion. If there is no homopolymerization, that is, if $k_p \cong 0$, the $\Delta M/\Delta SH$ ratio remains unity during the entire polymerization (Equation (24)). Thus, under this condition, every treelike molecule, whatever its size, bears $(r - 1)$ reacted thiol and $(r - 1)$ reacted vinyl groups (Figure 2). However, if $k_p \neq 0$, the ratio of $\Delta M/\Delta SH$ becomes larger than unity; in this case, every molecule will still have $(r - 1)$ reacted vinyl groups, but the average number of reacted thiol groups is reduced to $(r - 1)/(\Delta M/\Delta SH)$. In addition, cyclization reactions may also occur during thiol-ene reactions, reducing further the number of pendant functional groups. Letting ξ be the fraction of reacted functional groups in cycles, the numbers of reacted vinyl and thiol

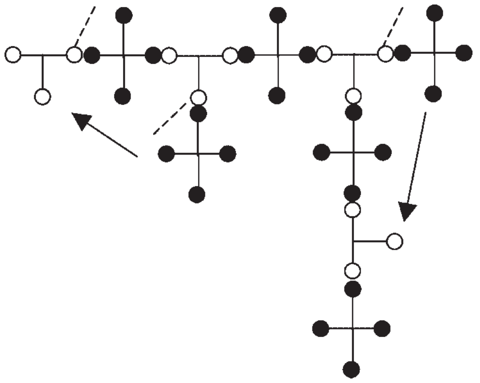

Figure 2. Schematic representation of a polymer molecule formed from tetrathiol and trivinyl monomer units. The total number of units is 10. If there is no homopolymerization, the number of reacted thiol or vinyl groups is 9. The dashed lines show the possible homopolymer blocks. The arrows show the cycle formation routes.

groups in a cyclic molecule become $(r-1)/(1-\xi)$ and $(r-1)/\{(1-\xi)(\Delta M/\Delta SH)\}$, respectively. Thus, the concentrations of pendant vinyl and thiol groups in $r$mers are given by:

$$[M_r] = r[P_r]F_{1,r}f_1 - (r[P_r] - [P_r])/(1-\xi) \tag{26}$$

$$[SH_r] = r[P_r](1-F_{1,r})f_2 - (r[P_r] - [P_r])/\{(1-\xi)(\Delta M/\Delta SH)\} \tag{27}$$

$(r > 1)$

where $F_{1,r}$ is the mole fraction of vinyl monomer in $r$mer molecules. Assuming a homogeneous distribution of the pendant functional groups along the polymer molecules, i.e., $F_{1,r} = \bar{F}_1$, the nth moment of the vinyl and thiol group distributions is written as follows:

$$W_n = \sum_{r=1}^{\infty} r^n [M_r] = [M]_0 + \bar{F}_1 f_1 (Q_{n+1} - Q_1) - (Q_{n+1} - Q_n)/(1-\xi) \tag{28}$$

$$W'_n = \sum_{r=1}^{\infty} r^n [SH_r] = [SH]_0 + (1-\bar{F}_1) f_2 (Q_{n+1} - Q_1) - (Q_{n+1} - Q_n)/\{(1-\xi)(\Delta M/\Delta SH)\} \tag{29}$$

It is worth noting that the cyclization parameter ξ in large molecules ($r \gg 1$) should scale with r by $r^{-3/2}$, while for small molecules ($r = 10^0 - 10^1$), it should mainly depend on the chemical nature of the functional groups.[17,18] Since in thiol-ene systems the chain length of the molecules is rather small ($\bar{X}_1 < 10^1$), we neglect the r dependence of ξ in the present analysis.

Conversion

Thiol and vinyl group conversions are defined as $x_{SH} = 1 - [SH]/[SH]_0$ and $x_M = 1 - [M]/[M]_0$, respectively. Using Equation (24)–(25) and (28), they can be calculated as follows:

$$\frac{dx_{SH}}{dt} = \frac{1}{(1-\xi)} k_{tr}[R\bullet](1 - x_{SH}) \tag{30}$$

$$\frac{dx_M}{dt} = \alpha r_0 \frac{dx_{SH}}{dt} \tag{31}$$

where r_0 is the stoichiometric imbalance for the reaction system,

$$r_0 = [SH]_0/[M]_0 \tag{32}$$

Chain Length Averages

Equation (25) together with Equation (28)–(29) give a general moment expression, which yields simple solutions for several of the moments. For example, the equation for the zeroth moment Q_0 corresponding to the total number of molecules is:

$$\frac{dQ_0}{dt} = -\alpha k_{tr}[R\bullet][SH] \qquad Q_0(0) = [P_1]_0 \tag{33}$$

while the first moment Q_1 equals the total number of monomer units in the reaction system, and it is time invariant:

$$\frac{dQ_1}{dt} = 0 \qquad Q_1(0) = [P_1]_0 \tag{34}$$

Moreover, the rate equation for the second moment Q_2 is obtained from Equation (25) as follows:

$$\frac{dQ_2}{dt} = 2(k_{p1}Y'_1 + k_p Y_1)W_1 \qquad Q_2(0) = [P_1]_0 \tag{35}$$

Solution of Equation (33)–(34) for the number-average chain length $\bar{X}_1$ gives:

$$\bar{X}_1 = \frac{1 + r_0}{1 + r_0 - x_M f_{\text{avr}}(1-\xi)} \tag{36}$$

where f_{avr} is the average functionality of the monomer mixture, i.e.,

$$f_{\text{avr}} = \frac{1 + r_0}{f_1^{-1} + r_0 f_2^{-1}} \tag{37}$$

Equation (36) is valid for all thiol-ene reactions with or without homopolymerization. The two extreme cases of Equation (36) are given by $\xi = 0$ and $\xi = 1$, corresponding to the ring-free and cyclo thiol-ene polymerizations, respectively. For the weight-average chain length $\bar{X}_2$, such a general equation cannot be derived from the moment equations of the kinetic model. However, for ring-free thiol-ene systems without homopolymerization ($k_p = 0$), one obtains from Equation (19)–(20), (28)–(29), (34)–(35):

$$\bar{X}_2 = \frac{1 + x_M r_0^{-0.5}}{1 - x_M r_0^{-0.5}\{(f_1 - 1)(f_2 - 1)\}^{0.5}} \tag{38}$$

Equation (36) and (38) are typical equations of step-growth polymerization.[19–21] Thus, neglecting homopolymerization reactions, that is, for $\alpha = 1$, the kinetic model derived for thiol-ene systems is identical to that of the step-growth reactions. However, if $\alpha > 1$, that is, if homopolymerization occurs, the differential equations of the kinetic model produce a different scenario. In this case, the primary molecules (that is the molecules, which would result if all cross-links were cut) with chain length $r \gg 1$ start to appear in the reaction system so that the kinetic model yields equations closer to those for chain-growth polymerizations.[22–24]

Calculations

To simulate the thiol-ene reactions with time as the independent variable, accurate prediction of the initiation rate, R_I, is necessary. Equation (39a) predicts the initiator concentration as a function of time, allowing R_I to vary as a function of time and assuming that each absorbed photon leads to the decomposition of one initiator molecule. Then, R_I is determined by Equation (39b).[25]

$$\frac{d[I]}{dt} = -2.303\varepsilon \frac{I_0 \lambda}{N_A h c}[I] \qquad [I](0) = [I]_0 \tag{39a}$$

$$R_I = -\phi \frac{d[I]}{dt} \tag{39b}$$

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 $\varepsilon = 150$ L/(mol · cm), $\lambda = 365$ nm, $\phi = 0.1$, $I_0 = 2$ mW/cm^2, and $[I]_0 = 0.02$ M.

Simultaneous solutions of the differential Equation (7)–(10) and (25) give the functional group concentrations and the moments of polymer distributions as a function of the reaction time. When the second moment or higher goes to infinity, the onset of gelation occurs. The independent variable time, t, can also be replaced with the fractional conversions of either vinyl or thiol groups by use of Equation (30) or (31). After this transformation, the system specific parameters required to solve the model are: a) initial concentrations and functionalities of the monomers, b) the ratio of homopolymerization to chain transfer rate constant k_p/k_{tr}, and c) the cyclization parameter ξ.

Results and Discussion

Data are presented first for the effect of the homopolymerization on the gelation kinetics in thiol-ene systems. This behavior is important in thiol-acrylate polymerizations where the ratio of the homopolymerization to the chain transfer kinetic constant (k_p/k_{tr}) is on the order of 1. Calculations in this section were for a reaction system consisting of divinyl and trithiol monomers with equivalent feed ratios of thiol and vinyl groups ($r_0 = 1$). Figure 3 shows the weight average chain length $\bar{X}_2$ vs. the reaction time and vinyl group conversion (x_M), when the k_p/k_{tr} ratio varies from 0 (curves 1) to 4 (curves 6). For

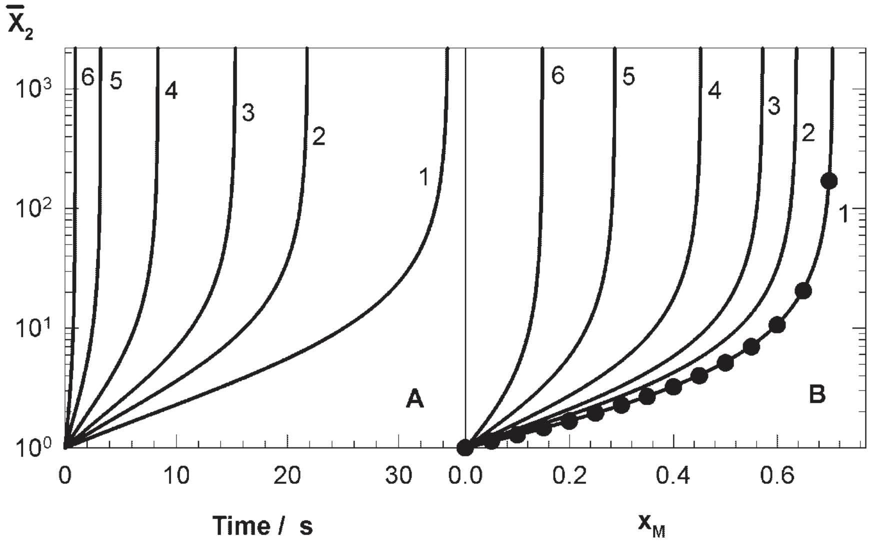

Figure 3. Weight-average chain length $\bar{X}_2$ in thiol-ene systems with $r_0 = 1$ plotted against the reaction time (A) and vinyl group conversion, x_M (B). $f_1 = 2$, $f_2 = 3$. Symbols were calculated using Equation (38). Calculations were for six different k_p/k_{tr} ratios: $k_p/k_{tr} = 0$ (1), ¼ (2), ½ (3), 1/1 (4), 2/1 (5), and 4/1 (6), $[I]_0 = 0.02$ M, $[M]_0 = 2$ M, $k_{p1} = k_{tr} = 5 \times 10^4$ L · mol^{-1} · s^{-1}, $k_{tc} = k_{td} = 10^6$ L · mol^{-1} · s^{-1}, $\xi = 0$.

calculations, typical values of the rate constants and concentrations were used:[12–14] $k_{p1} = k_{tr} = 5 \times 10^4\ \mathrm{L \cdot mol^{-1} \cdot s^{-1}}$, $k_{tc} = k_{td} = 1 \times 10^6\ \mathrm{L \cdot mol^{-1} \cdot s^{-1}}$, and $[M]_0 = 2$ M. These constants are typical for thiol-ene photopolymerization of dithiol – diallyl and tetrathiol-vinyl silazane comonomer pairs.[12–14] For $k_p/k_{tr} = 0$, i.e., when no homopolymerization was allowed, the dependence of $\bar{X}_2$ on x_M is predicted using Equation (38), as shown in the figure by the symbols. The asymptotic limit in $\bar{X}_2$ was used to predict the critical time, t_{cr}, and the critical conversion, x_{cr}, at the gel point. The gelation times decrease from 34.5 s to 0.9 s as the k_p/k_{tr} ratio is increased from 0 to 4. The critical conversion also decreases from 0.707 to 0.148 with increasing k_p/k_{tr} ratio. Thus, the gel point in particular is very sensitive to the value of k_p/k_{tr}, and it shifts toward lower conversions or shorter reaction times as k_p/k_{tr} is increased.

For the same reaction system, the solid curve in Figure 4A shows the number-average chain length $\bar{X}_1$ plotted against the vinyl group conversion, x_M. As predicted by Equation (36), $\bar{X}_1$ vs. x_M plots are independent of the k_p/k_{tr} ratio; $\bar{X}_1$ slightly increases with increasing conversion from 1 to 6. It should be noted that $\bar{X}_1$ is the average chain length of all molecules present in the reaction system, including the unreacted monomers. If the monomers are not taken into account, the resulting number-average chain length, $\bar{X}_{1,P}$, can be calculated from the moments of molecules with $r > 1$, denoted by Q_n^*. The rate equation for Q_n^* relates to Q_n using the following:

$$\frac{dQ_n^*}{dt} = \frac{dQ_n}{dt} - \frac{d[P_1]}{dt} \qquad Q_n^*(0) = 0 \tag{40}$$

The dashed curves in Figure 4A show $\bar{X}_{1,P}$ vs. x_M plots for various k_p/k_{tr} ratios. It is seen that $\bar{X}_{1,P}$ is k_p/k_{tr} dependent; the higher the k_p/k_{tr}, the higher the average chain length of the polymer molecules. Over the whole range of k_p/k_{tr} ratios presented here, the average chain lengths during the thiol-ene reactions remain below 10^1.

Figure 4B shows vinyl and thiol group conversions, x_M and x_{SH}, respectively, plotted against the reaction time up to the onset of gelation. Increasing the k_p/k_{tr} ratio also increases the conversion rate of the vinyl groups, while that of the thiol groups slightly decreases. This more rapid disappearance of vinyl groups is due to the increasing contribution of the homopolymerization reactions (Equation (4b)) to the gel forming system. The results as shown in Figure 4B have been observed experimentally in thiol-acrylate and thiol-methacrylate systems with and without photoinitiators.[4,5,26] The disadvantage of more rapid vinyl group consumption is the incomplete conversion of the thiol groups after the thiol-ene reactions. To obtain equivalent conversion of both functional groups, one has to alter the feed ratio of thiol and vinyl groups, r_0. The critical condition for obtaining equivalent conversions of both functional groups is obtained from Equation (30)–(31) as follows:

$$r_0 = 1 - \frac{k_p}{k_{tr}} \tag{41}$$

The dashed and dotted curves in the inset to Figure 4B are x_M and x_{SH} vs. time plots, respectively, for a reaction system with $r_0 = 1$ and $k_p/k_{tr} = 0.5$. It is seen that the vinyl groups are consumed much more rapidly than the thiol groups.

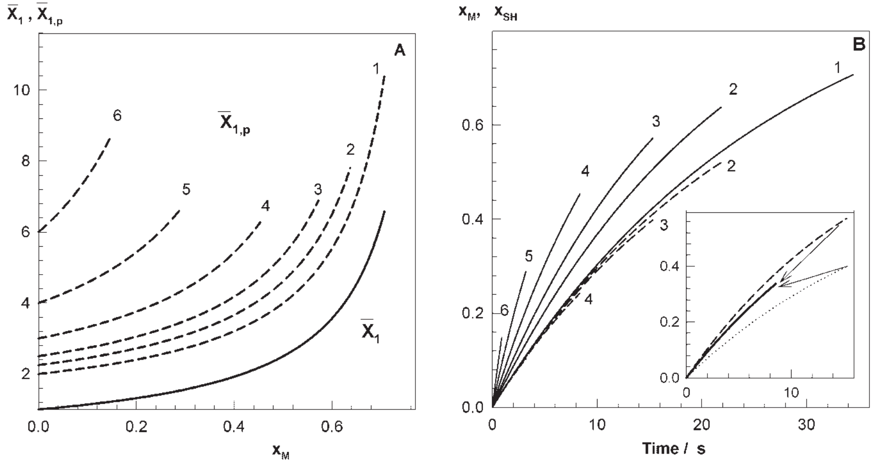

Figure 4. (A) Number-average chain length of all molecules $\bar{X}_1$ (solid curve) and, of those molecules with $r > 1$, $\bar{X}_{1,P}$ (dashed curves) plotted against the vinyl group conversion, x_M. (B): x_M (solid curves) and x_{SH} (dashed curves) vs reaction time plots. Calculations were for six different k_p/k_{tr} ratios: $k_p/k_{tr} = 0$ (1), ¼ (2), ½ (3), 1/1 (4), 2/1 (5), and 4/1 (6). All other kinetic parameters are the same as given in the caption for Figure 3. The dashed and dotted curves shown in the inset to Figure 4B are x_M and x_{SH} vs. reaction time plots, respectively, calculated for $r_0 = 1$ and $k_p/k_{tr} = 0.5$. Changing r_0 from 1 to 0.5, according to Equation (41), results in equivalent conversion rates of both functional groups, also shown in the inset by the solid curve.

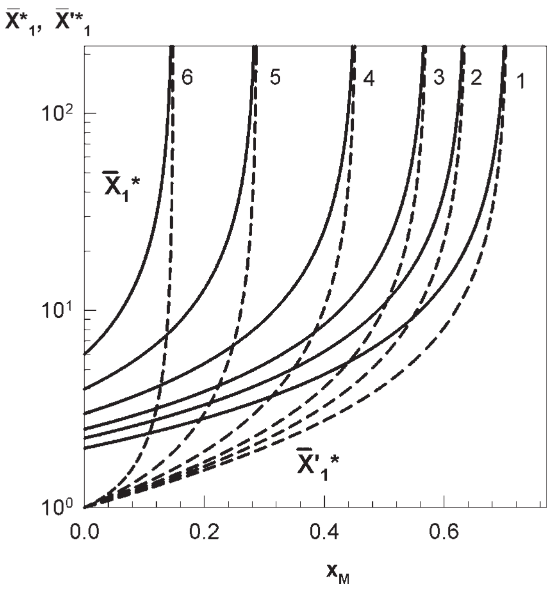

Figure 5. Number-average chain length of carbon radicals $\bar{X}_1\bullet$ (solid curves) and thiyl radicals $\bar{X}'_1\bullet$ (dashed curves) plotted against the vinyl group conversion, x_M. Calculations were for six different k_p/k_{tr} ratios: $k_p/k_{tr} = 0$ (1), ¼ (2), ½ (3), 1/1 (4), 2/1 (5), and 4/1 (6). All other kinetic parameters are the same as given in the Figure 3 caption.

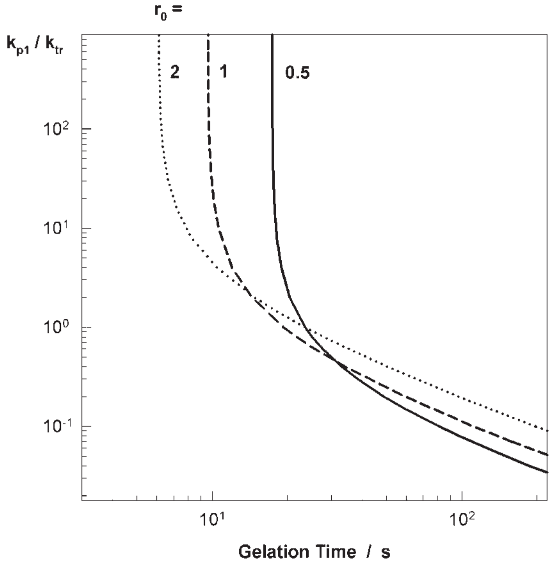

Figure 6. Effect of the k_{p1}/k_{tr} ratio on the gelation time in thiol-ene systems at three different feed ratios, r_0, of thiol and vinyl groups. $r_0 = 0.5$ (solid curve), 1 (dashed curve), and 2 (dotted curve).

However, according to Equation (41), if the same reaction is carried out at a feed ratio $r_0 = 0.5$, exactly equivalent conversion of both functional groups can be obtained, as seen by the solid curve in the figure.

Figure 5 shows number-average chain length of thiyl radicals, $\bar{X}'_1\bullet$ (dashed curves), and carbon radicals, $\bar{X}_1\bullet$ (solid curves), plotted against x_M for various k_p/k_{tr} ratios. When no homopolymerization was allowed (curves 1), $\bar{X}'_1\bullet \cong 1$ and $\bar{X}_1\bullet \cong 2$ over a wide range of conversions, indicating that the monomeric thiyl radicals together with the dimeric carbon radicals consisting of one thiol and one ene monomer units are active species in the pre-gel regime of thiol-ene systems. Increasing the extent of homopolymerization also increases the chain length of the active species. As the reaction system approaches the gel point, both $\bar{X}'_1\bullet$ and $\bar{X}_1\bullet$ diverge due to the formation of giant molecules with more than one radical center, as also reported for free-radical cross-linking copolymerizations.[16,22]

According to Equation (35) and (38), all the kinetic parameters of a thiol-ene system, except the homopolymerization rate constant, k_p, do not affect the gel point conversion. However, these parameters do affect the polymerization rate and thus, the gelation time. 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 more rapidly. An important kinetic parameter in thiol-ene systems is the ratio of the thiyl radical propagation constant to the chain transfer rate constant, k_{p1}/k_{tr}. The relative concentration of carbon radicals φ in the reaction system is proportional to this ratio and, for an equivalent feed ratio of thiol and vinyl groups, k_{p1}/k_{tr} is equal to the concentration ratio of carbon to thiyl radicals (Equation (23)). Figure 6 shows the variation of the gelation time, t_{cr}, with k_{p1}/k_{tr} at three different feed ratios of thiol and vinyl groups. Calculations were for $f_1 = f_2 = 3$, $\xi = 0$, and $k_p = 0$, which leads to, according to Equation (38), the gel point conversions $x_{SH,cr} = 0.707$, 0.500, and 0.354, for $r_0 = 0.5$, 1.0, and 2.0, respectively. Figure 6 shows that gelation occurs earlier as k_{p1}/k_{tr} is increased up to a critical value; thereafter, t_{cr} becomes nearly independent of k_{p1}/k_{tr}. One may explain this behavior with the predominant attack of thiyl radicals on the vinyl groups and formation of more stable carbon radicals as the k_{p1}/k_{tr} ratio is increased. The gelation times t_{cr}, in terms of the mole fraction of carbon radicals φ are calculated from Equation (22) and (30) as:

$$t_{cr} = \frac{t_{cr,\infty}}{\varphi} \tag{42}$$

where $t_{cr,\infty}$ is the limiting value of the gelation time at $\varphi = 1$, i.e.,

$$t_{cr,\infty} = \frac{-\ln(1 - x_{SH,cr})}{k_{tr}(R_I/k_t)^{0.5}} \tag{42a}$$

Thus, according to Equation (22) and (42), if $k_{p1}/k_{tr} \gg r_0$, the fraction of carbon radicals φ approaches to unity so that t_{cr} becomes independent of $k_{p1}\big/k_{tr}$. This condition is approached at $k_{p1}/k_{tr} > 10^0$ and 10^1 for $r_0 = 0.5$ and 1, respectively (Figure 6). However, if $k_{p1}/k_{tr} \ll r_0$, φ is much smaller than unity; no gel forms within a reasonable period of time.

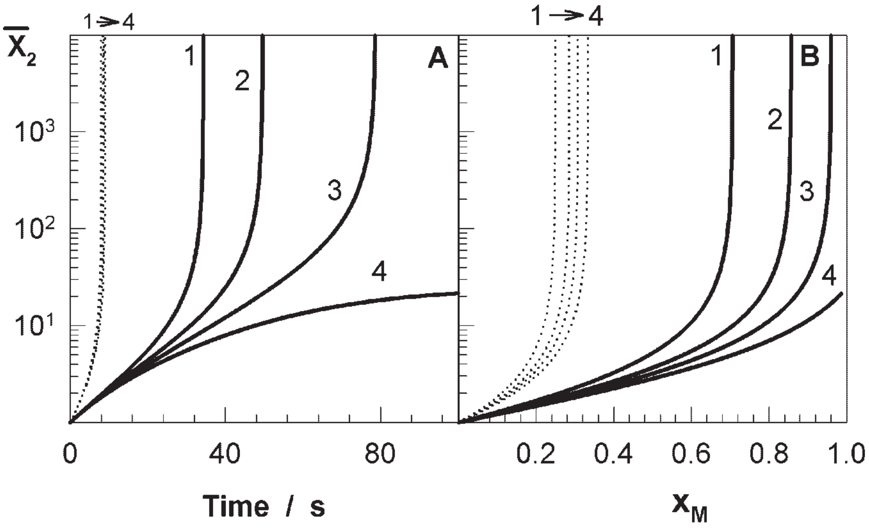

Figure 7. Weight- average chain lengths $\bar{X}_2$ in thiol-ene polymerizations with $f_1 = 2$ and $f_2 = 3$ (solid curves) and $f_1 = f_2 = 5$ (dotted curves) plotted against the reaction time (A) and vinyl group conversion, x_M (B). Calculations were for various cyclization parameters, ξ. The kinetic parameters used in the calculations are the same as given in the Figure 3 caption. $r_0 = 1$, k_p=0. $\xi = 0$ (1), 0.10 (2), 0.15 (3), and 0.20 (4).

Figure 7 shows the weight-average chain lengths $\bar{X}_2$ in thiol-ene reactions with $r_0 = 1$ plotted against the reaction time and vinyl group conversion, x_M. Calculations were for various values of the cyclization parameter, ξ. The functionalities of the monomers are taken as $f_1 = 2, f_2 = 3$ (solid curves) and $f_1 = f_2 = 5$ (dotted curves). The average molecular weights, $\bar{X}_2$, in the pre-gel regime are below 10^1 up to about 80% conversion. At a given reaction time or conversion, $\bar{X}_2$ slightly decreases with increasing ξ. The gel point is, however, very sensitive to ξ, particularly if the monomer functionalities are low; the gel point shifts toward higher conversions or longer reaction times as ξ is increased.

The dependence of the critical conversion x_{cr} on ξ is also illustrated in Figure 8A for the two thiol-ene systems. It is seen that, for $f_1 = f_2 = 5$, x_{cr} changes only slightly with ξ up to 0.4 due to the large number of pendant functional groups available in this system for gelation. However, for a reaction system with $f_1 = 2$ and $f_2 = 3$, even a small degree of cyclization rapidly increases the gel point conversion, x_{cr}. For $\xi > 0.16$ or $\xi > 0.60$, gelation is not attained for the comonomer pairs with $f_1 = 2, f_2 = 3$ and $f_1 = f_2 = 5$, respectively. The lack of gelation occurs because the concentration of pendant functional groups becomes insufficient to render all monomer units joined into a three-dimensional network. To illustrate the effect of the monomer functionality on the

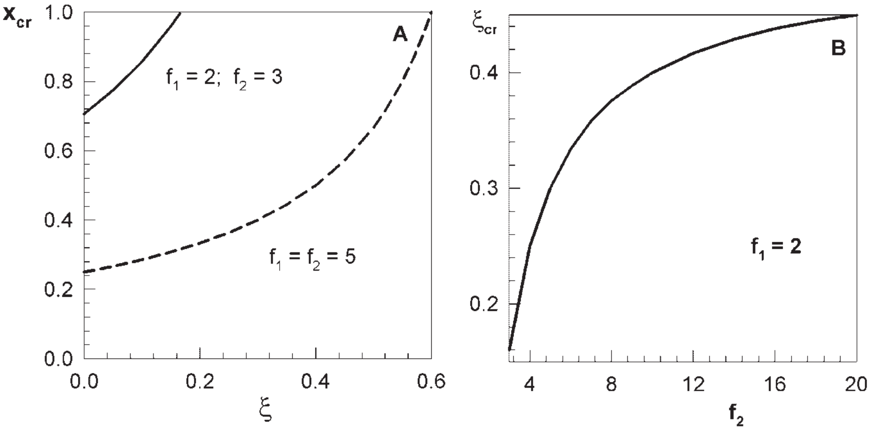

Figure 8. (A) The gel point conversions, x_{cr}, shown as a function of the cyclization parameter, ξ. The monomer functionalities are indicated in the figure. (B) The critical ξ value, ξ_{cr}, is shown as a function of f_2. $f_1 = 2$. The kinetic parameters used in the calculations are the same as given in the Figure 3 caption.

critical value of ξ (ξ_{cr}), in Figure 8B, ξ_{cr} is plotted against f_2 for a fixed vinyl monomer functionality f_1. ξ_{cr} is an increasing function of the monomer functionality. This result arises from the fact that, increasing functionality of the monomers also increases the concentration of the pendant functional groups in the reaction system. As a result, the effect of the functional groups lost in cycles on the onset of gelation becomes weaker at high monomer functionalities. For multifunctional thiol monomers with $f_2 \approx 10$, gelation occurs even after consumption of more than 40% of the functional groups by the cyclization reactions.

Conclusion

A kinetic model was developed for thiol-ene photopolymerization reactions. The model predicts the molecular weight distribution of active and inactive species in the pregel regime of thiol-enes, as well as the gel points depending on the synthesis parameters. It is shown that, when no homopolymerization is allowed, the average molecular weights and the gel point conversion are given by the typical equations valid for the step-growth polymerization. Increasing the extent of homopolymerization also increases the average molecular weights and shifts the gel point toward lower conversions or shorter reaction times. It is also shown that the ratio of thiyl radical propagation to the chain transfer kinetic parameter (k_{p1}/k_{tr}) affects the gelation times, t_{cr}. Gelation occurs earlier as k_{p1}/k_{tr} is increased up to a critical value; thereafter t_{cr} becomes insensitive to k_{p1}/k_{tr}. This behavior was explained with the predominant attack of thiyl radicals on the vinyl groups and formation of more stable carbon radicals as the k_{p1}/k_{tr} ratio is increased. It was also found that the gel point is very sensitive to the extent of cyclization. In particular, if the monomer functionalities are low, the gel point shifts toward significantly higher conversions or longer reaction times as the fraction of functional groups lost in cycles increases.

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