

Network Development in Mixed Step-Chain Growth Thiol–Vinyl Photopolymerizations

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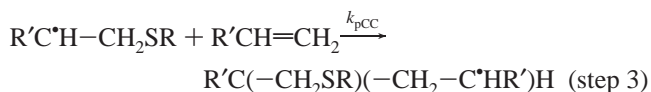
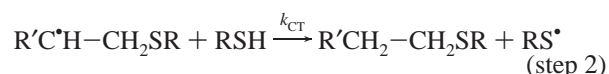
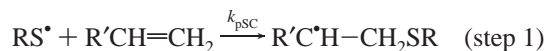
ABSTRACT: In this study, we develop a modeling framework based on combined kinetic and statistical modeling approaches to describe pregelation and postgelation network properties of polymerization kinetics dependent mixed step-chain growth polymerizations. Specifically, we utilize this modeling framework to predict the evolution of weight-average molecular weight, gel point conversion, and cross-linking density of binary and ternary thiol–vinyl systems, with simultaneous step and chain growth polymerizations. Conversion dependent kinetics and directionality of network structures are addressed in this study. We first determine polymerization kinetics driven probability parameters that define the nearest neighbor pairs. These probability parameters are then employed in a recursive statistical modeling framework to develop relationships that describe the network structure. The modeling predictions indicate that both thiol–acrylate and thiol–ene–acrylate systems provide a facile means to control network properties such as the gel point conversion and cross-linking density, with changes in monomer functionalities and their initial stoichiometric compositions. Thus, these novel thiol–vinyl systems provide a facile route to expand upon the property ranges that are available through either pure step growth or pure chain growth polymerizations.

Introduction

Thiol–vinyl polymerizations, which are reactions between thiol and vinyl monomers, exhibit several unique polymerization properties making them a primary focus of recent research. They exhibit all the advantages of typical acrylic photopolymerizations including solventless processing, rapid curing, and spatial and temporal control over polymerization. Furthermore, they exhibit several distinct advantages such as rapid curing in the presence of little or no added photoinitiator and relatively insignificant inhibition in the presence of oxygen.^{1–4} These dramatically attractive polymerization properties of thiol–vinyl systems make them suitable for a variety of applications that range from coatings to optoelectronics to biomedical applications.

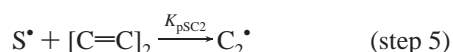
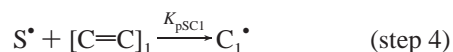
The thiol–vinyl polymerization reaction primarily proceeds via propagation of a thiyl radical through the vinyl functional group, followed by chain transfer of the vinyl radical to a thiol functional group to regenerate the thiyl radical. For the vinyl monomers such as vinyl ether and allyl ether, which do not undergo significant homopolymerization, the propagation and chain transfer steps form the basis for the step growth network evolution.^{5,6} However, in thiol–vinyl polymerizations wherein the vinyl monomer undergoes homopolymerization, the propagation mechanism includes carbon radical propagation (step 3) in addition to the thiyl radical propagation and chain transfer (steps 1 and 2), thereby leading to a simultaneous step-chain

growth network evolution. In this study, as a notation, we denote the vinyl monomers that do not homopolymerize as enes and those that do homopolymerize as acrylates.⁷



In ternary thiol–vinyl systems, the reaction mechanism is more complex.⁸ Steps 4–10 describe the propagation reaction mechanism of a general thiol–vinyl–vinyl system, wherein the vinyl monomers are able to both homopolymerize and copolymerize. These reactions are grouped according to the various activated radicals present in the system: propagation of a thiyl radical through either of the vinyl monomers (steps 4 and 5), homopolymerization (steps 6 and 9) and crosspolymerization (steps 7 and 10), and chain transfer to thiol monomers (steps 8 and 11). The general reaction mechanism presented here is readily simplified for both the thiol–ene–ene and thiol–ene–acrylate systems.

Events in which the thiyl radical is a reactant:



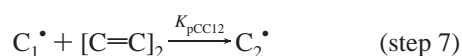
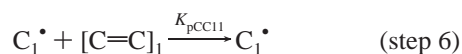
Events in which the vinyl radical-1, C^{\bullet} , is a reactant:

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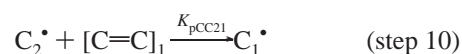
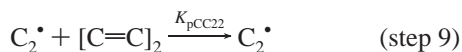
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Events in which the vinyl radical-2, C_2^\bullet , is a reactant:



While the reaction kinetics in binary thiol–ene systems do not influence the network structure, the network evolution in thiol–acrylate polymerizations and ternary thiol–vinyl systems is controlled by polymerization kinetics. For example, in mixed mode binary thiol–acrylate polymerizations, the network formation is a combination and competition of step and chain growth polymerizations, each of which leads to distinct network topologies. Furthermore, since the relative rates of these reactions are controlled by the ratio of chain transfer (step 2) to homopolymerization reactions (step 3),⁹ network architectures and resulting polymer properties in these systems are controlled by reaction kinetics. Similarly, due to the competitive nature of the reactions in which the radicals in ternary thiol–vinyl systems are involved, the network structural evolution in these systems is driven by polymerization kinetics. For these reasons, evaluation and knowledge of fundamental kinetics in these systems (binary mixed step-chain growth and ternary thiol–vinyl systems) is essential for the investigation of their network evolution.

Recently, a series of kinetic investigations was performed to evaluate the polymerization kinetics, reaction mechanisms, and rate-limiting steps of various binary thiol–vinyl systems.^{5,10} Furthermore, rotating sector-like unsteady-state experiments were performed on these binary thiol–vinyl systems to determine the absolute kinetic parameters.¹¹ A framework was then developed to utilize the knowledge of absolute rate parameters and reaction mechanisms in binary thiol–vinyl systems for predicting the polymerization kinetics of ternary thiol–vinyl systems.⁸

As the network structure in ternary thiol–vinyl systems and thiol–acrylate systems is controlled by polymerization kinetics, a combined kinetic and statistical modeling approach is necessarily to evaluate the network evolution. Here, this theory of combined kinetic and statistical modeling is based on both kinetic modeling and statistical modeling approaches.

Using statistical modeling approaches, several excellent works have addressed network evolution in both pure step growth and pure chain growth polymerizations.^{12–16} These modeling efforts enabled successful prediction of a polymer's pregelation and postgelation properties. However, pure statistical theories cannot predict network structures accurately for kinetically controlled polymerizations.^{17,18} Kinetic models, based on differential kinetic equations for every possible molecule in the system, successfully predict pregelation network properties for both the pure step and pure chain growth systems, even for the kinetically controlled systems.^{19–21} However, for the postgelation period, while the moment equations from simple kinetic models diverge, the complex kinetic models contain many kinetic parameters,

thereby making the comparison between model predictions and experimental data almost impossible.

The close similarity between kinetic and statistical modeling led to combined kinetic and statistical concepts in modeling of network systems.²² Such combination facilitates a good representation of kinetically controlled polymerizations as well as postgelation structural relations. This combined modeling is treated in a two-stage approach. In the first stage the nonrandom or kinetically controlled aspects are captured. Kinetic differential equations are solved to generate information about local structures termed as “superspecies”. These generated “superspecies” are then combined statistically in the second stage. Dusek and co-workers have utilized the concept of superspecies and random combinations in analyzing epoxy–amine resins and polyurethane systems with side reactions.^{14,23–25} Bokare and Gandhi utilized a combined approach to analyze the epoxy–amine systems which exhibit polyaddition reactions without any termination.²⁶ In these systems, living chainwise polymerization reactions occur in a predominantly stepwise polymerization environment. Investigations by other researchers have focused on the structural evolution in epoxy–amine systems, along with other similar systems with living polymerization, where both step growth and chain growth mechanisms are present.^{27–29}

In summary, while pure statistical modeling cannot capture kinetically controlled polymerization systems, the combined kinetic and statistical approach presents a novel means for capturing these effects. However, current work utilizing the kinetic and statistical approaches only examines systems like epoxy–amine, polyurethane, and other step growth systems with first shell substitution. In all these systems, either the polymerization is through pure step growth or through a living chain growth polymerization in a predominantly step growth environment. However, the thiol–vinyl polymerizations exhibit several unique features including: (a) significant step-chain growth, (b) formation of asymmetric structures, and (c) a polymerization mechanism that includes termination and chain transfer, therefore necessitating an extension of the current combined kinetic and statistical modeling approach. The model developed in this study is not only applicable to thiol–vinyl systems but is generalizable for copolymerization of any pure chain growth systems or mixed step and chain polymerizations.

Model Development

A network model is developed for general ternary thiol–vinyl–vinyl systems. The model will then be simplified for three special cases. As the polymerization in thiol–vinyl systems includes termination and chain transfer reactions, we utilize a variation of the typical two-stage approach of combined kinetic and statistical modeling. Here, instead of determining the concentration of superspecies (building blocks) in a separate kinetic step, the kinetically driven polymerization features are directly incorporated into the statistical model itself. First, the kinetically dependent probability parameters are determined utilizing the polymerization kinetics of the system. These kinetically dependent probability parameters are then utilized in a statistical framework to determine the network parameters. Before evaluating the probability parameters, we first look at the network structures of these systems.

Network Structures in Thiol–Vinyl–Vinyl Systems: In this work, SH_{f_1} represents the thiol monomer with f_1 functionalities. CC_{1,f_2} and CC_{2,f_3} depict the vinyl monomers $[CC]_1$ and $[CC]_2$ with f_2 and f_3 functionalities. While f_1 represents the actual functionality of the thiol monomer, f_2 and f_3 are twice the

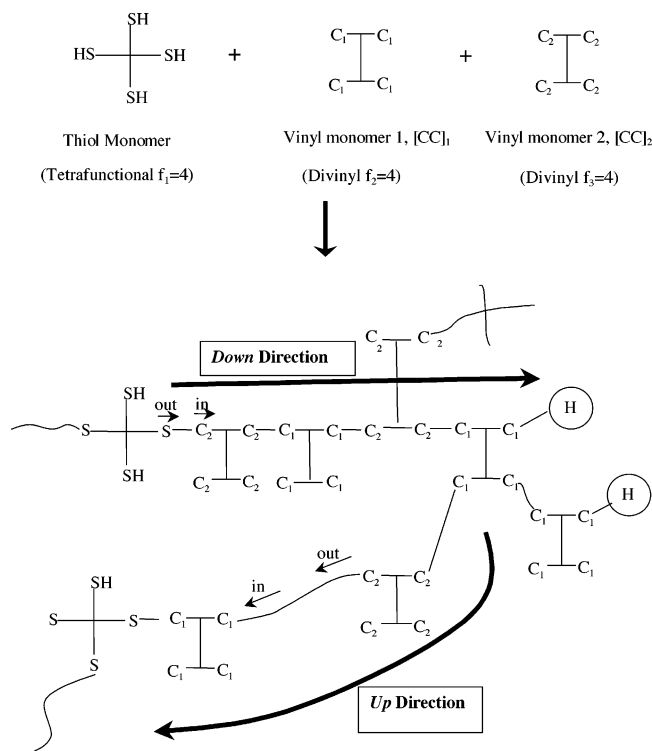


Figure 1. Schematic of a network formed from the polymerization of ternary thiol-vinyl-vinyl system.

number of vinyl groups on each of the monomers (Figure 1). Furthermore, M_{SH} , M_{CC1} , and M_{CC2} denote the molecular weights of the thiol, vinyl-1, and vinyl-2 monomers, respectively. This model also has the versatility to account for different functionalities of the monomers, from monofunctional to multifunctional.

For the generalized thiol-vinyl-vinyl case, wherein both the vinyl monomers can homopolymerize as well as cross-polymerize, a schematic representation of the formed network structure is presented in Figure 1. This network structure occurs due to the free radical based thiol-vinyl-vinyl reaction mechanism that includes initiation, propagation, chain transfer, and termination reactions. Initiation of kinetic chains in thiol-vinyl systems occurs due to initiator radicals and thiyl radicals.⁹ Therefore, to simplify model calculations, we consider here curing of these systems in the presence of type II initiators. In the presence of such initiators, the thiyl radicals are the primary initiating groups. The propagation mechanism of the generalized thiol-vinyl-vinyl system follows from steps 4–11. Furthermore, termination in these systems occurs either due to radical combination or disproportionation. However, to simplify model development, termination in these systems is assumed to occur only through disproportionation.

In Figure 1, the *down* direction on the kinetic chain indicates the direction of polymerization, and hence is directed toward the terminated end. The terminated end is a result of bimolecular radical-radical termination or chain transfer of a vinyl radical to a thiol monomer. The *up* direction refers to the direction opposite polymerization and is directed toward the initiation end of the kinetic chains.

The networks formed from thiol-vinyl-vinyl polymerizations are far more complicated than those formed from pure chain growth polymerizations. In polymerization of thiol-vinyl systems, even for the case of termination by disproportionation, the formed networks do not have symmetry; i.e., the weight of chains along the *up* and *down* directions is not equal. Looking

along the kinetic chain length of these systems, there is a directionality to them. For a propagating vinyl radical, chain transfer to thiol or termination by disproportionation effectively terminates the kinetic chain length, thereby making the weight added to the downside of a kinetic chain negligible. However, the initiating end of the kinetic chain consists of a multifunctional (f_i) thiol monomer, whose $f_i - 1$ arms lead into $f_i - 1$ kinetic chains and hence a nonnegligible mass in the *up* direction. Therefore, on any given unit, the mass attached in the *up* direction cannot be assumed to be equal to the mass in the *down* direction, thereby imparting directionality to the network. As previously demonstrated,²¹ the network properties of such asymmetrical kinetic chain are given by an average of network properties in its *up* and *down* directions.

To determine the network structure of a kinetic chain in the *down* direction, it is essential to know the likelihood of various monomers that would succeed a given monomer on the kinetic chain. Similarly, to determine the *upside* of a network, it is necessary to know the likelihood of various monomers that would precede a given monomer on the kinetic chain. Thus, a framework based on polymerization kinetics is developed to determine the probabilities (probabilistic kinetic parameters) of a given monomer to either precede or succeed another specific given monomer.

Probabilistic Kinetic Parameters. Parameters for Analyzing the Down Direction. In networks formed from free radical polymerization, the structural evolution in the polymerization direction of is a function of distinct pathways that a given propagating radical on a kinetic chain undertakes. For example, consider a thiyl radical on a polymeric chain. The thiyl radical propagates along either vinyl monomer-1 (step 4) or vinyl monomer-2 (step 5). Furthermore, it can also terminate with other radicals present in the system. Taking the propagation and termination steps into consideration, probability parameters are defined for the thiyl radical propagation along $[CC]_1$, a_1 , its propagation along $[CC]_2$, a_2 , and its termination with other radicals, a_3 . These probabilities are expressed as ratios of individual rates to the overall rate. Furthermore, these probabilities also represent the probabilities that monomers CC_{1f_2} , CC_{2f_3} , or a terminated end succeed a reacted thiol functionality. Equation 1, relates the probability parameter a_1 to the individual reaction rates. Similar equations are written for a_2 and a_3 .

$$a_1 = \frac{k_{pSC1}[S^*][CC]_1}{k_{pSC1}[S^*][CC]_1 + k_{pSC2}[S^*][CC]_2 + T_S'} = \frac{k_{pSC1}[CC]_1}{k_{pSC1}[CC]_1 + k_{pSC2}[CC]_2 + T_S} \quad (1)$$

T_S' represents the termination rate of the thiyl radicals and is given by $k_t(2[S^*]^2 + [C^*]_1[S^*] + [C^*]_2[S^*])$. Here, k_t represents the average termination parameter of the reacting system. T_S gives the normalized termination rate ($T_S'/[S^*]$) which is described by $k_t(2[S^*] + [C^*]_1 + [C^*]_2)$.

Similarly, considering all the vinyl radical-1's ($[C^*]_1$) propagation and termination events, we determine the probabilities for $[C^*]_1$ to homopolymerize (q_1), crosspolymerize with $[CC]_2$ vinyl groups (q_2), chain transfer to thiol (q_3), or terminate (q_4). Also, the probabilities q_1 and q_2 refer to the probabilities with which monomers CC_{1f_2} and CC_{2f_3} would succeed any given CC_{1f_2} monomer on a kinetic chain. Furthermore, mathematically, the sum of the probabilities q_3 and q_4 equals the probability that a given CC_{1f_2} group is the terminal end of the kinetic chain. Equation 2 relates q_1 to the individual rates of reactions and q_2 ,

q_3 , and q_4 can be represented in the same manner.

$$q_1 =$$

$$\frac{k_{\text{pCC11}}[\text{C}^*]_1[\text{CC}]_1}{k_{\text{pCC11}}[\text{C}^*]_1[\text{CC}]_1 + k_{\text{pCC12}}[\text{C}^*]_1[\text{CC}]_2 + k_{\text{CT1}}[\text{C}^*]_1[\text{SH}] + T_{\text{C1}}'} = \frac{k_{\text{pCC11}}[\text{CC}]_1}{k_{\text{pCC11}}[\text{CC}]_1 + k_{\text{pCC12}}[\text{CC}]_2 + k_{\text{CT1}}[\text{SH}] + T_{\text{C1}}} \quad (2)$$

As previously, T_{C1}' represents the termination rate of the vinyl radical.

For vinyl radical-2 ($[\text{C}^*]_2$), probabilistic parameters analogous to those defined for vinyl radical-1 are developed (not shown here) to describe its probabilities for homopolymerization (b_1), crosspolymerization (b_2), chain transfer to the thiol monomer (b_3), or termination (b_4).

Parameters for Analyzing the Kinetic Chains in the Up Direction. To describe the network in the *up* direction of a kinetic chain, it is essential to determine the probability of various monomers that would precede a given monomer in a kinetic chain. In other words, given a monomer on the kinetic chain, probability parameters must be developed to characterize the network in the direction opposite to polymerization.

First, consider a monomer CC_{1,f_2} on the polymer chain. Working backward, or looking into the history of the polymer chain, the monomer CC_{1,f_2} might have been incorporated into the chain because of the polymerization of a $[\text{CC}]_1$ vinyl group through a $[\text{C}^*]_1$ radical, through a $[\text{C}^*]_2$ radical, or through a $[\text{S}^*]$ radical. The probabilities of $[\text{CC}]_1$ polymerizing via the $[\text{C}^*]_1$ radical, via a $[\text{C}^*]_2$ radical, and through a thiyl radical are given by t_1 , t_2 , and t_3 , respectively. These probabilities are given by the ratio of the rate at which a radical attacks the $[\text{CC}]_1$ double bond to the overall rate at which all the possible radicals attack the $[\text{CC}]_1$ double bond. In other words, given a unit CC_{1,f_2} on a polymer chain, the probability parameters t_1 , t_2 , and t_3 , give the probabilities of monomers CC_{1,f_2} , CC_{2,f_3} , and SH_{f_1} of coming before the given CC_{1,f_2} unit. As before, we only present the relationship for parameter t_1 and the remaining parameters can be represented analogously.

$$t_1 = \frac{k_{\text{pCC11}}[\text{C}^*]_1[\text{CC}]_1}{k_{\text{pCC11}}[\text{C}^*]_1[\text{CC}]_1 + k_{\text{pCC21}}[\text{C}^*]_2[\text{CC}]_1 + k_{\text{pSC1}}[\text{S}^*][\text{CC}]_1} \quad (3)$$

Similar definitions are developed to describe the probabilities of the vinyl-2 monomer (r_1), vinyl-1 monomer (r_2), and thiol monomers (r_3) of being immediate preceding neighbors of CC_{2,f_3} monomers on a polymer chain. However, for the thiol monomer, due to its symmetry, we do not need different probabilistic parameters to describe both the upside and downside structure of a kinetic chain.

These probabilistic parameters are then utilized in a framework of the total law of probability to yield the network properties. The total law of probability, which is the fundamental basis for the recursive model, is given by eq 4. Let A_i , where $i = 1$ to n , be mutually exclusive and exhaustive events. Let Y be a random variable, $E(Y)$ its expected value (average value), $E(Y|A_i)$ its conditional probability given the event A_i has occurred. Then, the total law of probability states

$$E(Y) = \sum_{i=1}^n E(Y|A_i)P(A_i) \quad (4)$$

where $P(A_i)$ is the probability that event A_i has occurred.

Pregelation Properties. Here, we are primarily interested in deriving relationships for weight-average molecular weight in thiol–vinyl–vinyl systems. To derive the relationship for weight-average molecular weight, a random unit of mass on a polymer chain is chosen and the expected weight attached to it is evaluated. The average molecular weight is determined based on the polymeric portion of the reacting system, with unreacted monomers not being taken into account. In this work, “*” represents a unit that has been activated, i.e., a radical or a reacted unit. When choosing a unit of mass, the permissible choices are thiol monomers wherein m_1 functionalities have reacted, $\text{SH}_{f_1|m_1}^*$ (weight fraction: $w_{\text{SH}_{f_1|m_1}^*}$), vinyl monomer-1 wherein m_2 vinyl groups have reacted, $\text{CC}_{1,f_2|m_2}^*$ (weight fraction: $w_{\text{CC}_{1,f_2|m_2}^*}$), and vinyl monomer-2 in which m_3 vinyl groups have reacted, $\text{CC}_{2,f_3|m_3}^*$ (weight fraction: $w_{\text{CC}_{2,f_3|m_3}^*}$). The overall weight-average molecular weight, as previously treated¹² can then be represented by

$$\bar{M}_W = \sum_{m_1=1}^{f_1} w_{\text{SH}_{f_1|m_1}^*} E(W_{\text{SH}_{f_1|m_1}^*}) + \sum_{m_2=1}^{f_2/2} w_{\text{CC}_{1,f_2|m_2}^*} E(W_{\text{CC}_{1,f_2|m_2}^*}) + \sum_{m_3=1}^{f_3/2} w_{\text{CC}_{2,f_3|m_3}^*} E(W_{\text{CC}_{2,f_3|m_3}^*}) \quad (5)$$

where the weight fraction $w_{\text{SH}_{f_1|m_1}^*}$ is shown below and the weight fractions for vinyl monomer-1 and vinyl monomer-2 are represented in a similar manner. However, for writing equations for $w_{\text{CC}_{1,f_2|m_2}^*}$ and $w_{\text{CC}_{2,f_3|m_3}^*}$, it is important to realize that $f_2/2$ and $f_3/2$ are the number of functional groups on vinyl monomer 1 and 2, respectively.

$$w_{\text{SH}_{f_1|m_1}^*} = \frac{\left[\binom{f_1}{m_1} p_{\text{SH}}^{m_1} (1 - p_{\text{SH}})^{f_1 - m_1} M_{\text{SH}} \text{SH}_{f_1} \right]}{[(1 - (1 - p_{\text{SH}})^{f_1}) M_{\text{SH}} \text{SH}_{f_1} + (1 - (1 - p_{\text{CC}_1})^{f_2/2}) M_{\text{CC}_1} \text{CC}_{1,f_2} + (1 - (1 - p_{\text{CC}_2})^{f_3/2}) M_{\text{CC}_2} \text{CC}_{2,f_3}]} \quad (6)$$

Presented below are the expressions for the expected weights attached to the thiol, CC_{1,f_2} , and CC_{2,f_3} monomers on the polymer chains.

$$E(W_{\text{SH}_{f_1|m_1}^*}) = M_{\text{SH}} + m_1 E(\bar{W}_{\text{SH}}^{\text{out},*}) \quad (7)$$

$$E(W_{\text{CC}_{1,f_2|m_2}^*}) = M_{\text{CC}_1} + m_2 E(\bar{W}_{\text{CC}_1}^{\text{att},*}) \quad (8)$$

$$E(W_{\text{CC}_{2,f_3|m_3}^*}) = M_{\text{CC}_2} + m_3 E(\bar{W}_{\text{CC}_2}^{\text{att},*}) \quad (9)$$

$E(\bar{W}_{\text{SH}}^{\text{out},*})$ indicates the weight looking out from a thiyl radical. $E(\bar{W}_{\text{CC}_1}^{\text{out},*})$ and $E(\bar{W}_{\text{CC}_2}^{\text{out},*})$ are the weights attached per each of the reacted vinyl groups on CC_{1,f_2} and CC_{2,f_3} monomers, respectively. The above equations account for the number of groups reacted per monomer and the weight attached to each of the reacting groups. Because of the symmetry of the thiol monomer, $E(\bar{W}_{\text{SH}}^{\text{out},*})$, which describes the weight attached to an activated thiol radical, is enough to describe the network structure about a given thiol monomer unit. However, as the vinyl monomers on the kinetic chain have an asymmetry, it is essential to know the different weights looking in both directions, *up* and *down*. $E(\bar{W}_{\text{CC}_1}^{\text{out},*})$, which describes the overall weight associated with each of the reacted functional groups of the vinyl monomer-1, is expressed as below to relate to the weight attached in the *up* and *down* directions of the activated vinyl functional groups. Similar

equation can be written for $E(\bar{W}_{CC_2}^{out,*})$

$$E(\bar{W}_{CC_1}^{att,*}) = \frac{E(\bar{W}_{CC_1}^{att})}{p_{CC_1}} = \{E(\bar{W}_{CC_1}^{out,*}) + E(\bar{W}_{CC_1}^{out,*})\} \quad (10)$$

Therefore, using expressions based on eqs 5–10, and knowing the expected values of $E(\bar{W}_{SH}^{out,*})$, $E(\bar{W}_{CC_1}^{out,*})$, $E(\bar{W}_{CC_2}^{out,*})$, and $E(\bar{W}_{CC_1}^{out,*})$, we calculate the weight-average molecular weight of the ternary thiol–vinyl systems for any given conversion.

To compute the expected weights attached to a randomly chosen unit, a root monomer has to be chosen. The thiol monomer or either of the vinyl monomers is chosen at random as the root monomer, without affecting the model equations. In this study, for the sake of convenience, the thiol monomer is chosen as the root monomer and \bar{W}_{SH}^{out} , the weight attached to a thiol functional group looking out from its parent molecule, is calculated.

Since the thiol unit is picked at random, \bar{W}_{SH}^{out} is a random variable. \bar{W}_{SH}^{out} equals zero if the chosen thiol functionality is unreacted. However, if the thiol functionality is reacted, i.e., it becomes a radical, then \bar{W}_{SH}^{out} equals $\bar{W}_{SH}^{out,*}$, which is the weight attached to the thiyl radical.

$$E(\bar{W}_{SH}^{out}) = \begin{cases} E(\bar{W}_{SH}^{out,*}) & \text{if the thiol functionality has become a radical} \\ 0 & \text{if the thiol functionality has not become a radical} \end{cases} \quad (11)$$

Utilizing the total law of probability

$$\begin{aligned} E(\bar{W}_{SH}^{out}) &= E(\bar{W}_{SH}^{out}/SH - \text{reacts})P(SH - \text{reacts}) + \\ &E(\bar{W}_{SH}^{out}/SH - \text{does not react})P(SH - \text{does not react}) \\ &= p_{SH}E(\bar{W}_{SH}^{out,*}) + (1 - p_{SH}) \times 0 \end{aligned} \quad (12)$$

When a thiyl radical is randomly chosen and reacted, as above, it is essential to take into account the conversion at which this activated unit attaches to other moieties. This accounting is necessary as the probabilistic parameters which determine the polymer composition and hence the network of a given chain, change with extent of conversion (i.e., monomer composition). Furthermore, if the system is at a given conversion of p , it is possible that the growing chain has reacted at any given conversion up to p . Thus, the probability density of having a chosen unit reacted at any conversion \bar{p} less than p is $1/\bar{p}$. Thus,

$$E(\bar{W}_{SH}^{out,*}) = \frac{1}{p_{SH}} \int_0^{p_{SH}} E(\bar{W}_{SH}^{out,*}, \bar{p}_{SH}) d\bar{p}_{SH} \quad (13)$$

Similar relations, as of eq 13, are defined for the vinyl monomers.

The activated thiyl radical either propagates along the $[CC]_1$, with a probability of a_1 , propagates along $[CC]_2$ with a probability of a_2 , or terminates with a probability of a_3 . The various weights attached to a thiyl radical in each of the above cases are given by eq 14. Utilizing the total law of probability and eq 14, the expected weight looking out from the thiyl radical is related to the expected weight looking into vinyl monomers 1 and 2 (eq 15)

$$E(\bar{W}_{SH}^{out,*}, \bar{p}_{SH}) = \begin{cases} E(\bar{W}_{CC_1}^{in,*}, \bar{p}_{CC_1}) & \text{if thiyl radical reacts with } [CC]_1 \text{ functionality} \\ E(\bar{W}_{CC_2}^{in,*}, \bar{p}_{CC_2}) & \text{if thiyl radical reacts with } [CC]_2 \text{ functionality} \\ 0 & \text{termination by disproportionation} \end{cases} \quad (14)$$

$$E(\bar{W}_{SH}^{out,*}, \bar{p}_{SH}) = a_1 E(\bar{W}_{CC_1}^{in,*}, \bar{p}_{CC_1}) + a_2 E(\bar{W}_{CC_2}^{in,*}, \bar{p}_{CC_2}) + a_3 0 \quad (15)$$

$E(\bar{W}_{CC_1}^{in,*}, \bar{p}_{CC_1})$, the expected weight looking into vinyl monomer-1, is given by the sum of molecular weight of CC_{1f_2} (parent molecule) (M_{CC_1}) plus the weight looking out from the ensuing propagating radical, $[C^*]_1$, and the sum of expected weights on each of the remaining $(f_2 - 2)/2$ vinyl groups (eq 16). A similar equation is defined for $E(\bar{W}_{CC_2}^{in,*}, \bar{p}_{CC_2})$.

$$E(\bar{W}_{CC_1}^{in,*}, \bar{p}_{CC_1}) = M_{CC_1} + E(\bar{W}_{CC_1}^{out,*}, \bar{p}_{CC_1}) + \frac{(f_2 - 2)}{2} E(\bar{W}_{CC_1}^{att}) \quad (16)$$

The weight looking out from vinyl radicals can be easily expressed in terms of their probability parameters and the weights looking into other functional groups, thereby completing the recursive loop.

$$E(\bar{W}_{CC_1}^{out,*}, \bar{p}_{CC_1}) = q_1 E(\bar{W}_{CC_1}^{in,*}, \bar{p}_{CC_1}) + q_2 E(\bar{W}_{CC_2}^{in,*}, \bar{p}_{CC_2}) + q_3 0 + q_4 0 \quad (17)$$

$$E(\bar{W}_{CC_2}^{out,*}, \bar{p}_{CC_2}) = b_1 E(\bar{W}_{CC_2}^{in,*}, \bar{p}_{CC_2}) + b_2 E(\bar{W}_{CC_1}^{in,*}, \bar{p}_{CC_1}) + b_3 0 + b_4 0 \quad (18)$$

Equations 12–18 are solved to yield the weights looking out from the activated functional groups in the polymerization direction. i.e., $E(\bar{W}_{SH}^{out,*})$, $E(\bar{W}_{CC_1}^{out,*})$, and $E(\bar{W}_{CC_2}^{out,*})$. The final expressions for these weights are presented in the Supporting Information.

Equations are then developed for the *up* direction, i.e., the direction opposite to polymerization. For example, consider a vinyl group $[CC]_1$ on a polymer chain. This unit might have been incorporated into the polymer chain in any of the following manners: (a) propagation of another $[C^*]_1$ radical through the $[CC]_1$ group, (b) propagation of a $[C^*]_2$ radical through the $[CC]_1$ group, and (c) propagation of a $[S^*]$ radical through the $[CC]_1$ group. Using the respective probabilities and the total law of probability, the expected weight attached on the downside of the vinyl radical, looking away from it, is given by

$$E(W_{CC_1}^{out,*}, \bar{p}_{CC_1}) = t_1 E(W_{CC_1}^{in,*}, \bar{p}_{CC_1}) + t_2 E(W_{CC_2}^{in,*}, \bar{p}_{CC_2}) + t_3 E(W_{SH}^{in,*}, \bar{p}_{SH}) \quad (19)$$

where $E(W_{CC_1}^{in,*}, \bar{p}_{CC_1})$, $E(W_{CC_2}^{in,*}, \bar{p}_{CC_2})$, and $E(W_{SH}^{in,*}, \bar{p}_{SH})$ are the expected weights looking into activated vinyl monomer-1, vinyl monomer-2, and thiol monomer. A similar equation is derived for $E(W_{CC_2}^{out,*}, \bar{p}_{CC_2})$.

Relating the weight looking in to and out of a unit allows the development of recursive equations:

$$E(W_{SH}^{in,*}, \bar{p}_{SH}) = M_{SH} + (f_1 - 1)E(\bar{W}_{SH}^{out}) \quad (20)$$

$$E(W_{CC_1}^{in,*}, \bar{p}_{CC_1}) = M_{CC_1} + E(W_{CC_1}^{out,*}, \bar{p}_{CC_1}) + \frac{(f_2 - 2)}{2}E(\bar{W}_{CC_1}^{att}) \quad (21)$$

$$E(W_{CC_2}^{in,*}, \bar{p}_{CC_2}) = M_{CC_2} + E(W_{CC_2}^{out,*}, \bar{p}_{CC_2}) + \frac{(f_3 - 2)}{2}E(\bar{W}_{CC_2}^{att}) \quad (22)$$

Equation 20 relates the weight looking into a thiol functionality to the weight looking out from the remaining $f_1 - 1$ thiol monomer arms, which may or may not be reacted. Equations 21 and 22, which describe the weight looking into vinyl monomers in the *up* direction of polymerization, are similar to the equations in the *down* direction of polymerization.

Equations based on 19–22 are solved to obtain expressions for $E(W_{CC_1}^{out,*}, \bar{p}_{CC_1})$ and $E(W_{CC_2}^{out,*}, \bar{p}_{CC_2})$. Therefore, utilizing the above expressions as well as eqs 23 and 24, we obtain expressions for expected weights attached to the vinyl functional groups on the *downside* of a kinetic chain, i.e., $E(W_{CC_1}^{out,*})$ and $E(W_{CC_2}^{out,*})$. The detailed expressions for these expected weights are presented in the Supporting Information.

$$E(W_{CC_1}^{out,*}) = \frac{1}{p_{CC_1}} \int_0^{p_{CC_1}} E(W_{CC_1}^{out,*}, \bar{p}_{CC_1}) d\bar{p}_{CC_1} \quad (23)$$

$$E(W_{CC_2}^{out,*}) = \frac{1}{p_{CC_2}} \int_0^{p_{CC_2}} E(W_{CC_2}^{out,*}, \bar{p}_{CC_2}) d\bar{p}_{CC_2} \quad (24)$$

However, equations for the expected weights attached to activated radical functionalities both in the *up* direction (supplementary eqs 1–3) and *down* direction (supplementary eqs 4–5) of polymerization are not explicit. These equations are expressed in terms of $E(\bar{W}_{CC_1}^{att})$ and $E(\bar{W}_{CC_2}^{att})$. However, definitions for $E(\bar{W}_{CC_1}^{att})$ and $E(\bar{W}_{CC_2}^{att})$ (based on eq 10) can be utilized with these supplementary eqs 1–5 to determine either analytically or iteratively the explicit equations for expected weights in the *up* and *down* polymerization directions.

Values for the expected weights attached to thiol and vinyl functional groups when utilized along with eqs 7–9 determine the weight attached to the corresponding monomers. Furthermore, the determined expected weights attached to thiol and vinyl monomers when used with eq 5 and weight fractions ($w_{SH,f_1|m_1}^*$, $w_{CC_1,f_2|m_2}^*$, and $w_{CC_2,f_3|m_3}^*$) yield the weight-average molecular weight of the system. The average molecular weight of the polymer is then utilized to determine the gel point conversion of the system, which is defined as the conversion at which the weight-average molecular weight of the system diverges.

Postgelation Properties. To determine the postgel properties, it is essential to calculate the probability of finding a finite chain while looking out from a randomly chosen unit. Knowledge of this probability is employed for determining the various postgel properties of the network including sol fraction, gel fraction, and concentration of elastically effective chains. The probability of finding a finite chain varies according to whether we are looking *up* a chain or *down* a chain. Probability parameters, which are discussed earlier, are employed to determine both the probabilities of finding a finite chain as we look *up* and *down* the kinetic chain.

As previously, we first treat the downside of a network (i.e., along the direction of polymerization) and choose a thiol

monomer as the root monomer. Utilizing the total law of probability, the probability of finding a finite chain when looking out from a thiol functionality is given by eq 25. Here, \bar{F}_{SH}^{out} is the event that a chain looking out from a thiol functionality is a finite chain. The probability of finding a finite chain upon looking out from a thiol functionality is dependent on the probability of it being reacted or not. If it is reacted, then the probability of finding a finite chain while looking out from a thiol group ($P(\bar{F}_{SH}^{out})$) equals that of looking out from the radical ($P(\bar{F}_{SH}^{out,*})$). However, if the thiol group is unreacted, then the probability of finding a finite chain is unity. Using these relations

$$P(\bar{F}_{SH}^{out}) = p_{SH}P(\bar{F}_{SH}^{out,*}) + 1 - p_{SH} \quad (25)$$

Furthermore, as the reacted thiol functionality can react at any conversion below p_{SH} ,

$$P(\bar{F}_{SH}^{out,*}) = \frac{1}{p_{SH}} \int_0^{p_{SH}} P(\bar{F}_{SH}^{out,*}, \bar{p}_{SH}) d\bar{p}_{SH} \quad (26)$$

Similar conversion dependent equations can be assigned to vinyl monomers 1 and 2.

To expand eq 26, while the propagation of a thiyl radical through vinyl monomers leads to an extension of the kinetic chain, termination of the same would end the kinetic chain. Therefore, propagation of a thiyl radical through $[CC]_1$ would make $P(\bar{F}_{SH}^{out,*}, \bar{p}_{SH})$ equal to $P(\bar{F}_{CC_1}^{in,*}, \bar{p}_{CC_1})$, which is the probability of finding a finite chain when looking into functional group $[CC]_1$. Similarly, reaction of a thiyl radical with $[CC]_2$ would make $P(\bar{F}_{SH}^{out,*}, \bar{p}_{SH})$ equal to $P(\bar{F}_{CC_2}^{in,*}, \bar{p}_{CC_2})$. Finally, termination of a thiyl radical (through disproportionation) would make the probability of finding a finite chain equal to unity. Therefore,

$$P(\bar{F}_{SH}^{out,*}, \bar{p}_{SH}) = a_1 P(\bar{F}_{CC_1}^{in,*}, \bar{p}_{CC_1}) + a_2 P(\bar{F}_{CC_2}^{in,*}, \bar{p}_{CC_2}) + a_3 1 \quad (27)$$

Furthermore, the probabilities of finding a finite chain when looking into vinyl monomer-1 can be expressed as

$$P(\bar{F}_{CC_1}^{in,*}, \bar{p}_{CC_1}) = P(\bar{F}_{CC_1}^{out,*}, \bar{p}_{CC_1})P(E_{CC_1,f_2}) \quad (28)$$

Here, E_{CC_1,f_2} is the event that none of the remaining $(f_2 - 2)/2$ arms of vinyl monomer-1 leads to an infinite structure. As the arms of the vinyl monomer can react at any different conversion, this event is not conditioned by the conversion \bar{p}_{CC_1} . Also, each of the remaining arms of the vinyl monomer reacts independently. Thus, the probability that none of the arms leads to infinity is given by

$$P(E_{CC_1,f_2}) = \{p_{CC_1}P(\bar{F}_{CC_1}^{out,*})P(\bar{F}_{CC_1}^{out,*}) + 1 - p_{CC_1}\}^{f_2-2/2} \quad (29)$$

where $P(\bar{F}_{CC_1}^{out,*})$ is the probability of having a finite chain when looking *up* from reacted vinyl monomer-1. Equations similar to eqs 28 and 29 are also defined for finding a finite chain when looking into vinyl monomer-2.

Furthermore, recursive equations are developed by relating the probabilities of finding a finite chain when looking out from

a vinyl group to that of finding a finite chain when looking into another vinyl group.

$$P(\vec{F}_{CC_1}^{\text{out},*}, \vec{p}_{CC_1}) = q_1 P(\vec{F}_{CC_1}^{\text{in},*}, \vec{p}_{CC_1}) + q_2 P(\vec{F}_{CC_2}^{\text{in},*}, \vec{p}_{CC_2}) + q_3 1 + q_4 1 \quad (30)$$

$$P(\vec{F}_{CC_2}^{\text{out},*}, \vec{p}_{CC_2}) = b_1 P(\vec{F}_{CC_2}^{\text{in},*}, \vec{p}_{CC_2}) + b_2 P(\vec{F}_{CC_1}^{\text{in},*}, \vec{p}_{CC_1}) + b_3 1 + b_4 1 \quad (31)$$

Equations 25–31 are solved to yield the probabilities of finding a finite chain when looking out from $[S^*]$, $[C^*]_1$, and $[C^*]_2$ radicals. The detailed expressions for $P(\vec{F}_{CC_1}^{\text{out},*})$, $P(\vec{F}_{CC_2}^{\text{out},*})$, and $P(\vec{F}_{SH}^{\text{out},*})$ are presented in the Supporting Information.

Also, equations are developed for the *down* direction:

$$P(F_{CC_1}^{\text{out},*}) = \frac{1}{p_{CC_1}} \int_0^{p_{CC_1}} P(F_{CC_1}^{\text{out},*}, \vec{p}_{CC_1}) d\vec{p}_{CC_1} \quad (32)$$

$$P(F_{CC_2}^{\text{out},*}) = \frac{1}{p_{CC_2}} \int_0^{p_{CC_2}} P(F_{CC_2}^{\text{out},*}, \vec{p}_{CC_2}) d\vec{p}_{CC_2} \quad (33)$$

We first choose a vinyl monomer CC_{1,f_2} on a kinetic chain. Equations 12–14 give the probabilities of various pathways through which this monomer is incorporated into the kinetic chain. In other words, these equations give the probability of radicals $[C^*]_1$, $[C^*]_2$, and $[S^*]$ of propagating through CC_{1,f_2} . Also, as discussed earlier, these probabilities equal the likelihood of CC_{1,f_2} , CC_{2,f_3} , and SH_{f_1} monomers to precede a given vinyl monomer CC_{1,f_2} on a kinetic chain. For each of these possible states, the probability of finding a finite chain when looking out from CC_{1,f_2} equals the probability of looking into those corresponding monomers (eq 34)

$$P(F_{CC_1}^{\text{out},*}, \vec{p}_{CC_1}) = \begin{cases} P(F_{CC_1}^{\text{in},*}, \vec{p}_{CC_1}) & \text{If } [C^*]_1 \text{ reacts with } [CC]_1 \\ P(F_{CC_2}^{\text{in},*}, \vec{p}_{CC_2}) & \text{If } [C^*]_2 \text{ reacts with } [CC]_1 \\ P(F_{SH}^{\text{in},*}, \vec{p}_{SH}) & \text{If } [S^*] \text{ reacts with } [CC]_1 \end{cases} \quad (34)$$

Therefore, invoking the total law of probability gives

$$P(F_{CC_1}^{\text{out},*}, \vec{p}_{CC_1}) = t_1 P(F_{CC_1}^{\text{in},*}, \vec{p}_{CC_1}) + t_2 P(F_{CC_2}^{\text{in},*}, \vec{p}_{CC_2}) + t_3 P(\vec{F}_{SH}^{\text{out},*})^{(f_1-1)} \quad (35)$$

As before, equations are developed to relate the probabilities of looking in to and out of both the vinyl groups. Equation 36 gives the expression for $P(F_{CC_1}^{\text{in},*}, \vec{p}_{CC_1})$, a similar equation is defined for $P(F_{CC_2}^{\text{in},*}, \vec{p}_{CC_2})$.

$$P(F_{CC_1}^{\text{in},*}, \vec{p}_{CC_1}) = P(F_{CC_1}^{\text{out},*}, \vec{p}_{CC_1}) P(E_{CC_{1,f_2}}) \quad (36)$$

Furthermore, the probability of finding a finite chain looking into a thiol monomer, $P(F_{SH}^{\text{in},*}, \vec{p}_{SH})$, equals the probability that none of its remaining arms go to infinity and is given by eq 37.

$$P(F_{SH}^{\text{in},*}, \vec{p}_{SH}) = P(\vec{F}_{SH}^{\text{out},*})^{(f_1-1)} \quad (37)$$

Equations similar to those of 34–36 are also developed for determining the probability of having a finite chain preceding vinyl monomer-2. Equations 34–36 and the analogous equations

for vinyl monomer-2 are solved to yield the probability of having a finite chain in the *down* direction. The detailed expressions for $P(F_{CC_1}^{\text{out},*})$ and $P(F_{CC_2}^{\text{out},*})$ are presented in the Supporting Information.

In summary, expressions for $P(\vec{F}_{CC_1}^{\text{out},*})$, $P(\vec{F}_{CC_2}^{\text{out},*})$, and $P(\vec{F}_{SH}^{\text{out},*})$ {and hence $P(\vec{F}_{SH}^{\text{out},*})$ } give the probabilities of finding a finite chain when looking in the *down* direction from a randomly chosen unit on a polymer. Furthermore, equations for $P(F_{CC_1}^{\text{out},*})$ and $P(F_{CC_2}^{\text{out},*})$ describe the probabilities of finding a finite chain when looking in the *up* direction from a randomly chosen unit on a polymer chain. However, these equations are not explicit because of the presence of $P(E_{CC_{1,f_2}})$ and $P(E_{CC_{2,f_3}})$ (expressions based on eq 29), and are further coupled through them. Therefore, an iterative approach was utilized to obtain the solution for these systems. Upon determination of $P(\vec{F}_{CC_1}^{\text{out},*})$, $P(\vec{F}_{CC_2}^{\text{out},*})$, $P(\vec{F}_{SH}^{\text{out},*})$, $P(\vec{F}_{CC_1}^{\text{out},*})$, and $P(\vec{F}_{CC_2}^{\text{out},*})$, these probability values are employed for the determination of postgelation properties.³⁰

To determine cross-linking density, as previously treated by cascade theory, it is essential to calculate the probabilities (or fraction) of multifunctional monomer that would have a given number of paths going to infinity. Only those molecules that have at least three paths going to infinity act as cross-linkers. Knowledge of probability parameters ($P(\vec{F}_{CC_1}^{\text{out},*})$, $P(\vec{F}_{CC_2}^{\text{out},*})$, $P(\vec{F}_{SH}^{\text{out},*})$, $P(\vec{F}_{CC_1}^{\text{out},*})$, and $P(\vec{F}_{CC_2}^{\text{out},*})$) is utilized to determine the number of arms going to infinity in each of the functional monomers, and thereby to compute the overall cross-linking density of the system. A detailed evaluation of the cross-linking density of the system, based on the previous developments of cascade theory, is presented in the Supporting Information.

The framework developed here for determining various network properties such as the weight-average molecular weight, gel point conversion, and cross-linking density is utilized to analyze three different thiol–vinyl systems: (a) thiol–acrylate, (b) thiol–ene–acrylate, and (c) thiol–ene–ene systems (in the Supporting Information). As outlined previously, ene monomers refer to those vinyl monomer that do not homopolymerize, and acrylic monomers are those which readily undergo homopolymerization.

Thiol–Acrylate Systems. The general equations of pregelation and postgelation properties determined for the ternary thiol–vinyl–vinyl systems are simplified to obtain governing equations for thiol–acrylate systems. Simplification is carried out by setting acrylic monomers as $[CC]_1$ and equating the other vinyl monomer concentration, $[CC]_2$, to zero. Performing such a simplification transforms the probability parameters. Shown below are only those nonzero probability parameters that appear in network equations.

$$a_1 = \frac{k_{pSC1}[CC]_1}{k_{pSC1}[CC]_1 + T_s}; \quad q_1 = \frac{k_{pCC11}[CC]_1}{k_{pCC11}[CC]_1 + k_{pCT1}[SH] + T_{C1}}$$

$$t_1 = \frac{k_{pCC11}[C^*]_1}{k_{pCC11}[C^*]_1 + k_{pSC1}[S^*]}; \quad t_3 = \frac{k_{pSC1}[S^*]}{k_{pCC11}[C^*]_1 + k_{pSC1}[S^*]}$$

Furthermore, performing a balance on thiol radicals ($k_{pSC1}[S^*] - [CC]_1 = k_{CT1}[C^*]_1[SH]$), we can rearrange equations t_1 and t_3 as

$$t_1 = \frac{k_{pCC11}[CC]_1}{k_{pCC11}[CC]_1 + k_{CT}[SH]}; \quad t_3 = \frac{k_{CT}[SH]}{k_{pCC11}[CC]_1 + k_{CT}[SH]}$$

These simplifications, when used in the pregelation modeling

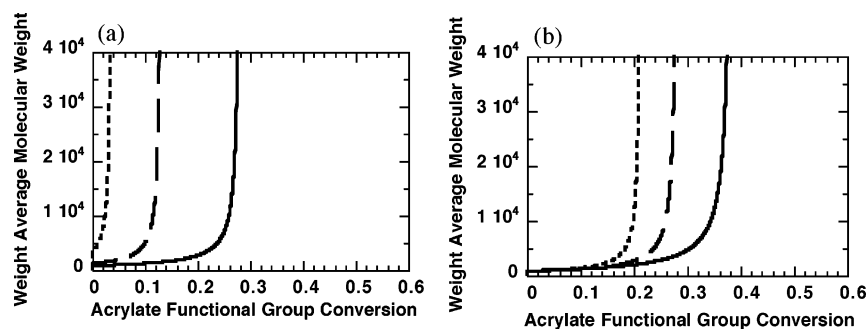


Figure 2. (a) Modeling predictions of average molecular weight as a function of acrylate functional group conversion in a thiol–acrylate system with tetrafunctional thiol ($f_1 = 4$) and difunctional acrylate monomers ($f_2 = 4$). Predictions are for (—) 50:50, (---) 30:70, and (· · ·) 10:90 thiol:acrylate mixtures. (b) Modeling predictions of average molecular weight as a function of acrylate functional group conversion in a thiol–acrylate system with varying thiol functionalities. Diacrylate monomers ($f_2 = 4$) are simulated in all the systems. Predictions are for (—) monofunctional thiol ($f_1 = 1$), (---) tetrafunctional thiol ($f_1 = 4$), and (· · ·) decafunctional thiol ($f_1 = 10$).

framework, lead to the following gelation condition:

$$1 - \frac{(f_2 - 2)}{2} \int_0^{p_{CC_1}} \left\{ \frac{q_1}{1 - q_1} + \frac{t_1}{1 - t_1} \right\} dp_{CC_1} - p_{CC_1}(f_1 - 1) \frac{(f_2 - 2)}{2} \int_0^{p_{SH}} \frac{a_1}{1 - q_1} dp_{SH} \rightarrow 0 \quad (38)$$

In this thiol–acrylate gelation equation, a_1 , q_1 , and t_1 are the only probability parameters that influence the network structure. Upon a rearrangement of these probability parameters, it is observed that they are primarily dependent on the ratios of propagation to chain transfer parameters (k_{pSC1}/k_{CT}) and the relative concentrations of thiol and acrylate functional groups. Previously, we have analyzed photopolymerization kinetics of thiol–acrylate systems and determined the ratio of propagation (k_{pSC1}) to chain transfer (k_{CT1}) kinetic parameters for many traditional thiol–acrylate systems to be around 1.5 ($=k_{pSC1}/k_{CT}$).¹⁰ Furthermore, the concentrations of the thiol and acrylate monomers, $[CC]_1$ and $[SH]$, which appear in the probability parameters are obtained using a very simple equation which gives relationships between relative conversions of thiol and acrylate functional groups. This analytical equation is described in detail elsewhere¹⁰ but is provided here for reference.

$$d[C=C]/d[SH] = 1 + (k_{p-c}/k_{CT}) * [C=C]/[SH] \quad (39)$$

Neglecting termination, the value of k_{pSC1}/k_{CT} and the relative concentrations of thiol and acrylate monomers (eq 39) are utilized to define completely the network structure of the thiol–acrylate polymer. This simplification is valid as termination in these systems does not greatly influence the network structure, primarily due to the large amount of chain transfer that occurs in these reactions. However, for the sake of completeness, in this study we take termination into consideration. For that purpose, kinetic equations for thiol–acrylate systems are solved to obtain T_{C1} and T_S , which are the product of the termination kinetic parameter and the radical concentrations.⁵ Utilizing the values of k_{pSC1}/k_{CT} , the relative conversions of monomer, and the termination parameters, the network properties of thiol–acrylate systems are evaluated by using eq 38.

Figure 2a plots the weight-average molecular weight evolution of thiol–acrylate systems with varying thiol concentrations. In this system, a tetrafunctional thiol monomer ($f_1 = 4$) is reacted with a divinyl acrylic monomer ($f_2 = 4$). The model predicts an increase in the gel point conversion with an increase in thiol concentration. This aspect can also be clearly examined from eq 38, wherein an increase in thiol concentration leads to a decrease in q_1 and t_1 , which thereby leads to an increase in the

conversion at which the gelation condition is reached. Mechanistically, the delayed gel point conversion of these systems with increasing thiol concentrations is caused by the increased contribution of the step growth mechanism.

To determine the predictive capability of the model, gel point experiments were performed on a tensometer,⁶ equipment based on cantilever beam technology. While the experimental gel points followed the same trend as the theoretical gel points, the differences between them were significant, primarily due to network nonideality: cyclization. Specifically, the experimental gel point conversions for the 30:70 thiol:acrylate system and 50:50 thiol:acrylate system were determined to be $20 \pm 5\%$ acrylate conversion and $44 \pm 8\%$ acrylate conversion, respectively. Upon incorporation of cyclization into the current modeling efforts, the model predictions match well with the experimental data: the theoretical gel point for the 30:70 system is 18% and for the 50:50 system is 35% conversion. However, this model development of cyclization is outside the scope of the current work and is presented elsewhere.³¹

The impact of thiol functionalities on the weight-average molecular weight evolution is presented in Figure 2b. This plot indicates that for a given thiol:acrylate stoichiometry, an increase in thiol functionality leads to a decrease in the gel point conversion. This aspect can also be clearly examined from eq 38 wherein an increase in thiol functionality leads to increase in the third term of the equation, which thereby leads to a decrease in the conversion at which the gelation condition is reached. Mechanistically, this decrease in the gel point conversion with higher thiol functionality is caused by the balance between thiol monomers serving as chain transfer agents and as multifunctional cross-link junctions. In a thiol–acrylate system with monofunctional thiol monomer, the thiol functional groups would serve only as a chain transfer agent. However, when a multifunctional thiol monomer is reacted with acrylic monomers, the thiol monomers not only serve as chain transfer agents but also increase the network connectivity and thereby decrease the gel point conversion.

In the reaction of tetrafunctional thiol monomers with diacrylate monomers, both the thiol and acrylic monomers function as cross-linkers. Figure 3 presents the impact of thiol monomer concentration on the ability of acrylic and thiol monomers to serve as cross-linkers. Assuming no cyclization, polymerization of difunctional acrylic monomers in the absence of thiol monomers results in all the acrylic monomers serving as cross-linking monomers. However, in the presence of the thiol monomers, the probability of acrylate monomers acting as a cross-linking agent decreases due to the chain transfer nature of the thiol monomer. Thus, while the cross-linking ability of

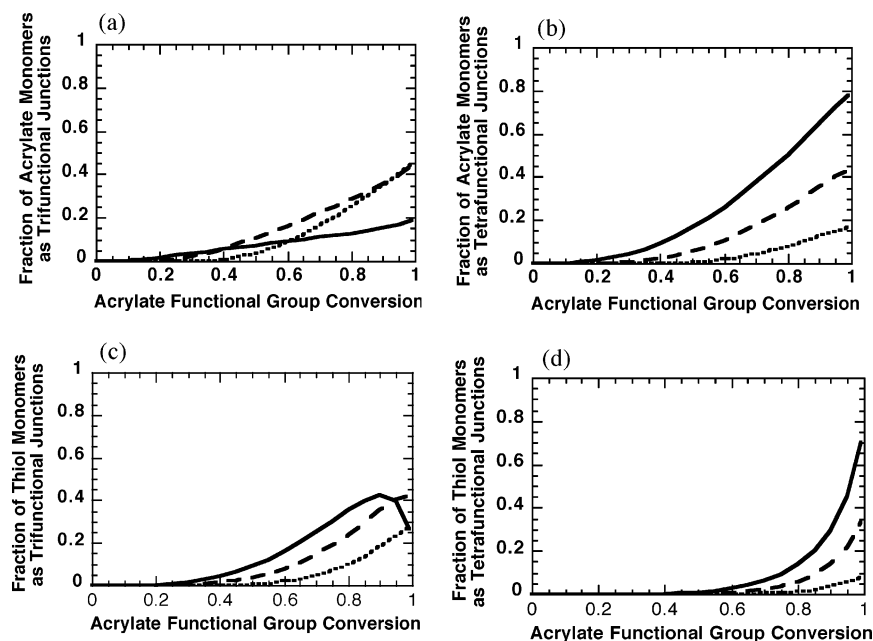


Figure 3. Modeling predictions of the fraction of acrylate monomers that serve as cross-linkers of degree (a) 3 and (b) 4 and thiol monomers that serve as cross-linker of degree (c) 3 and (d) 4 in thiol-acrylate systems of (—) 10:90, (---) 30:70, and (· · ·) 50:50 thiol:acrylate mixtures. In this system, tetrafunctional thiol monomer ($f_1 = 4$) is reacted with diacrylate monomer ($f_2 = 4$).

Table 1. Propagation Parameters That Are Employed for Predicting the Ternary Thiol-Vinyl Ether-Acrylate Network Structures⁸

k_{CT1}	2.1×10^6 L/mol·s	k_{CT2}	0.8×10^5 L/mol·s
k_{pSC1}	2.6×10^6 L/mol·s	k_{pSC2}	1.2×10^5 L/mol·s
k_{pCC11}	negligible	k_{pCC22}	1.15×10^5 L/mol·s
k_{pCC12}	1.0×10^5 L/mol·s	k_{pCC21}	0.30×10^5 L/mol·s

acrylate monomers in the 10:90 system is high, it decreases with increasing thiol monomer concentration. The decrease in the ability of the thiol monomer to cross-link with increasing initial thiol monomer concentration is primarily due to the decrease in thiol monomer conversion from a 10:90 system to a 50:50 system. For example, in a 10:90 system, the thiol functional groups reach nearly 90% conversion, while in a 50:50 monomer system, the thiol functional group reaches only around 55% conversion.¹⁰

Thiol-Ene-Acrylate Systems. In thiol-ene-acrylate systems, where the acrylic monomer readily homopolymerizes, the ene monomer does not homopolymerize. Furthermore, these vinyl monomers also undergo crosspolymerization. Determination of both the pregelation and postgelation properties requires knowledge of probability parameters. These probability parameters are strongly impacted by the various kinetic rate parameters and are also conversion dependent. Recently, we have investigated kinetic parameters of thiol-vinyl ether-acrylic systems, wherein the vinyl ether monomer does not participate in homopolymerization reactions.^{11,12} As the kinetic parameters of the thiol-vinyl ether-acrylate system are known, we utilize this system as a model for investigation of the network properties. Table 1 presents the kinetic propagation parameters that were utilized for this study. Furthermore, the termination parameters determined previously for this systems are also employed in this study.¹¹ Note, $[CC]_1$ and $[CC]_2$ represent vinyl ether and acrylate functional groups, respectively.

Other than the kinetic parameters, concentrations of thiol and vinyl functional groups as well as the thiol and vinyl radical concentrations strongly affect the probability parameters. Furthermore, these concentrations are all conversion dependent. For that reason, we utilize the polymerization kinetics model that we have developed earlier to determine the monomer and radical

Table 2. Experimental Data and Model Prediction of the Young's Modulus for the Thiol-Ene Polymers as a Function of the Percentage of Thiol Groups from Tetrathiol^a

% of thiols from tetrathiol	experimental modulus (MPa)	predicted modulus (MPa)
100	10.2	10.8
90	9.7	10
80	8.2	9
50	5.9	6
30	4	3.9
20	2.3	2.4

^a The remaining thiol groups are from dithiols added to a mixture of tetrathiol and divinyl ether.³²

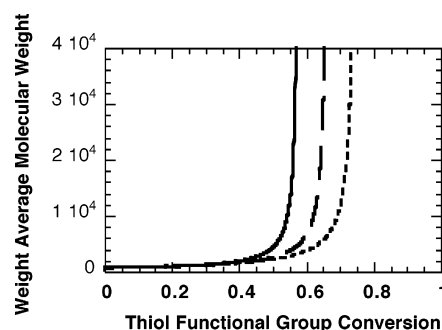


Figure 4. Modeling predictions of weight-average molecular weight as a function of thiol functional group conversion in a thiol-ene-acrylate system with tetrafunctional thiol, diene and monoacrylate monomers. Predictions are for (—) 1:1:0, (---) 1:1:0.4, and (· · ·) 1:1:1 thiol:ene:acrylate mixtures.

concentrations as a function of the reaction extent.¹² Probability parameters are then determined for a given reaction extent and hence facilitate the determination of the network structure. We investigate the theoretical modeling predictions of average molecular weight, gel point conversion, and cross-linking density of thiol-vinyl ether-acrylate systems, for varying monomer functionalities and their initial stoichiometries.

First, consider a thiol-vinyl ether-acrylate system in which tetrafunctional thiol monomer ($f_1 = 4$) is reacted with divinyl ether monomer (diene monomer) ($f_2 = 4$) and monoacrylate

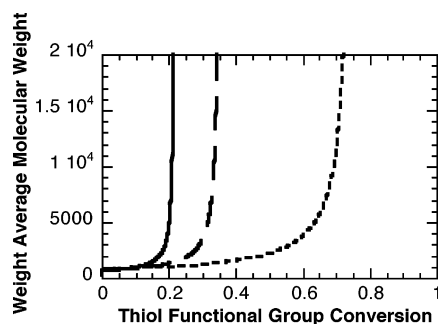


Figure 5. Modeling predictions of average molecular weight as a function of thiol functional group conversion in a 1:1:1 thiol–ene–acrylate system with varying acrylate functionalities. The thiol and ene monomers in all the systems are tetrafunctional and difunctional, respectively. Predictions are for (—) triacrylate ($f_3 = 6$), (---) diacrylate ($f_3 = 4$), and (- -) monoacrylate ($f_3 = 2$).

monomer ($f_3 = 2$). Figure 4 plots the average molecular weight evolution as a function of thiol conversion for initially stoichiometric ratios of 1:1:0, 1:1:0.4, and 1:1:1 thiol:vinyl ether:acrylate functional groups. The average molecular weight of the 1:1:0 system, which is a pure step growth reaction between tetrafunctional thiol monomers and diene monomers, diverges at the same conversion (57.6%) predicted by the classical Flory–Stockmayer equation. However, an increase in the concentration of monofunctional acrylate monomer in the reaction mixture leads to a slower evolution of the molecular weight and ultimately delays the gel point conversion in these systems.

To understand this phenomenon, consider the network structures formed from the pure step growth thiol–ene reaction and that from the thiol–monoacrylate system (steps 1–3). In a thiol–ene photopolymerization reaction, as indicated in the reaction mechanism, a thiol functional group is added across an ene functional group (of the diene monomer), thereby rendering each arm of the thiol monomer an elastically active chain. However, polymerization of the thiol and monoacrylate system results only in branched oligomers. Thus, when a thiol

monomer is reacted with the diene and monoacrylate monomers, the thiyl radical is in a competition to react with either the ene monomer or the acrylic monomer. The relative reactivity of thiyl radicals with vinyl ether and acrylic double bonds is equal to $k_{\text{PSCl}}[\text{CC}]_1/k_{\text{PSCl}}[\text{CC}]_2$. Therefore, increasing monoacrylate concentrations leads to elastically inactive thiol groups, due to their reactivity with non-cross-linking monoacrylate monomers. This loss of elastically active chains leads to delayed gelation in systems with higher acrylate concentrations.

Figure 5 investigates the impact of acrylic monomer functionality on the gel point conversions of 1:1:1 thiol:vinyl ether:acrylate systems. This figure compares the weight-average molecular weight evolution of thiol–vinyl ether–acrylate systems using acrylic monomers of functionality 2 (monovinyl monomer), 4 (divinyl monomer), and 6 (trivinyl monomer). Clearly, increasing the functionality of the acrylic monomers increases the network connectivity and thereby leads to a more rapid evolution of molecular weight and hence decreases the gel point conversion.

Changes in monomer concentrations and their functionalities also impact postgelation properties, most significantly the cross-linking density. Incorporation of acrylic monomers into thiol–ene systems facilitates formation of materials with a wide range of elastomeric properties. A tetrafunctional thiol monomer is reacted with a difunctional vinyl monomer, and a monoacrylate monomer in a 1:1:1 stoichiometric system of thiol:vinyl ether:acrylate functional group concentrations. In this system, only the thiol and vinyl ether monomers have the potential to serve as cross-linking agents. Presented in Figure 6, parts a and b are the probabilities of thiol monomer and ene monomers, respectively, of being cross-links of degree 3 (trifunctional cross-linker) and 4 (tetrafunctional cross-linker).

While a diene monomer in a step-growth thiol–ene reactions cannot serve as a cross-link, in these ternary systems even the diene monomers can serve as cross-linkers. This interesting phenomena occurs as the vinyl ether monomer copolymerizes

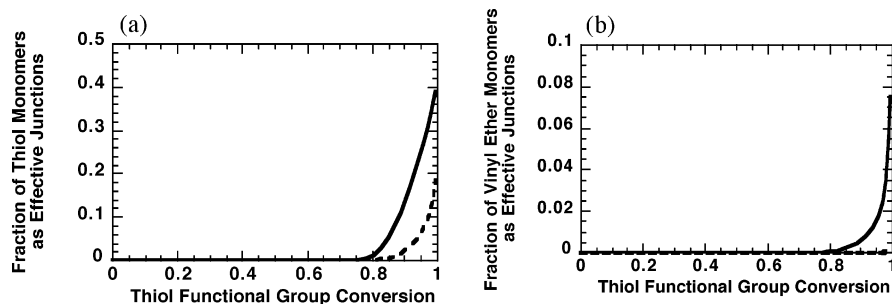


Figure 6. Modeling predictions of the fraction of (a) thiol and (b) vinyl ether monomers that serve as effective junctions of degree 3 (---) and degree 4 (—) in a 1:1:1 thiol:ene:acrylate system. In this system tetrafunctional thiol monomers ($f_1 = 4$) are reacted with difunctional ene ($f_2 = 4$) and monofunctional acrylate monomers ($f_3 = 2$).

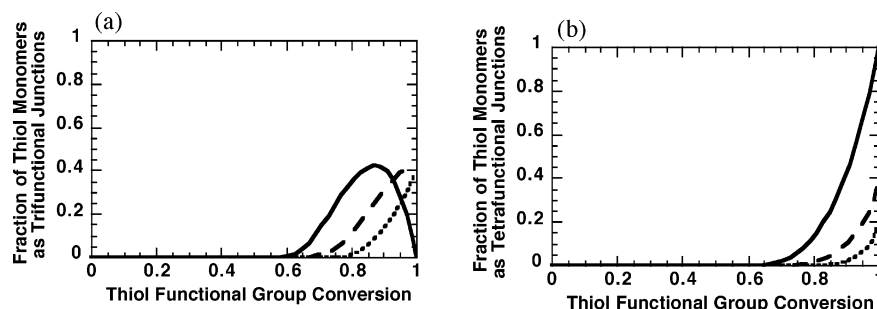


Figure 7. Modeling predictions of the fraction of thiol monomers that serve as cross-linker of degree (a) 3 and (b) 4 in thiol–ene–acrylate systems of (—) 1:1:0, (---) 1:1:0.4, and (···) 1:1:1 thiol:ene:acrylate mixtures. In this system tetrafunctional thiol monomers ($f_1 = 4$) are reacted with diene ($f_2 = 4$) and monoacrylate monomers ($f_3 = 2$).

with acrylic monomers in the thiol–ene–acrylate reaction mechanism, thereby, effectively increasing the diene functionality.

The impact of monoacrylate concentration on the cross-linking densities of a tetrafunctional thiol–diene–monoacrylate mixture is shown in Figure 7. In the 1:1:0 systems, trifunctional cross-links are formed first which then give way to tetrafunctional cross-linkers. At the completion of the reaction, in the assumption of no cyclization, all the arms of the tetrathiol go to infinity. That is, every tetrafunctional thiol monomer acts as a cross-linker. However with increasing monoacrylate concentration, fewer arms on the thiol monomer lead to infinity, thereby reducing the cross-linking density.

Conclusions

A network model was developed to describe the structural evolution in the pregelation and postgelation regimes of the mixed mode thiol–vinyl photopolymerizations. A combined kinetic and statistical modeling approach was utilized to capture the network evolution in these kinetically controlled polymerizing systems, which also show conversion dependence and directionality of network structures. The general network model developed for ternary thiol–vinyl–vinyl systems was then simplified for thiol–acrylate and thiol–ene–acrylate systems. As the probability parameters are controlled by polymerization kinetics, we utilize fundamental polymerization kinetic mechanisms that we have developed earlier for these systems.

In the thiol–ene–acrylate systems where a thiol monomer was reacted with vinyl ether and acrylate monomers, the gel point conversion and cross-linking density were easily modified with changes in the monomer functionalities and their initial stoichiometric ratios. Furthermore, even in the thiol–acrylate systems, controlling the monomer functionalities and their stoichiometries provides a facile means to adjust the network properties. As the shrinkage stress in network forming polymers is developed only after the gel point conversion, the delayed gelation aspect of thiol–vinyl systems facilitates reductions in shrinkage stresses. In summary, this work highlights the control over network evolution through adjustment of polymerization kinetics.

Furthermore, the modeling framework developed here can be employed for determining the network properties of any kinetically controlled copolymerization system, with no restriction on the relative rates of step and chain growth contributions or living nature of polymerizations.

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Appendix

Pure Step Growth Systems. The general equations of pregelation and postgelation properties determined for the ternary thiol–vinyl–vinyl systems are simplified to obtain governing equations for pure step growth systems. As the network evolution in thiol–ene systems occur by pure step growth,^{1–11} model simplifications are performed for this case to test predictive abilities of the model. Simplification is carried out by setting ene monomer as $[CC]_1$ and equating the other vinyl monomer concentration, $[CC]_2$, to zero. Shown below are only those nonzero probability parameters that appear in network equations.

$$a_1 = \frac{k_{pSC1}[CC]_1}{k_{pSC1}[CC]_1 + T_s}; \quad t_3 = 1$$

Pregelation: These simplifications, when used in the pregelation modeling framework, lead to the following gelation condition:

$$1 - p_{SH}p_{CC_1}(f_1 - 1)\frac{(f_2 - 2)}{2} \rightarrow 0$$

As in thiol–ene reaction, the thiol and ene monomers are consumed in stoichiometric proportions, p_{SH} or p_{CC_1} can be eliminated by using the ratio r of all $[SH]$ groups to all $[CC]_1$ groups. Specifically, substituting $p_{SH} = r \times p_{CC_1}$ into the above equation yields

gel point ene conversion = $p_{CC_1} =$

$$\frac{1}{\left\{r\left(1 - (f_1 - 1)\left(\frac{f_2}{2} - 1\right)\right)\right\}^{1/2}}$$

which is the Flory–Stockmayer theory of gelation for step-growth systems. For example, for a stoichiometric mixture of tetrathiol ($f_1 = 4$) and triene ($f_2 = 6$) monomers, the above equation predicts a gel point of 40.8% conversion. Previous experimental investigations using tetrathiol and triene monomers have experimentally observed a gel point conversion of around 40% conversion.⁶

Postgelation: Using the above simplifications of a_1 and t_3

$$P(\vec{F}_{CC_1}^{out,*}) = 1; P(\vec{F}_{CC_1}^{out,*}) = P(\vec{F}_{SH}^{out,*})^{f_1-1}; P(\vec{F}_{SH}^{out,*}) = \frac{1}{p_{SH}} \int_0^{p_{SH}} P(E_{CC_{1/2}}) d\bar{p}_{SH}$$

Using the above equations along with eqs 25 and 29, yields

$$P(\vec{F}_{SH}^{out}) = p_{SH}[P(\vec{F}_{SH}^{out})^{f_1}p_{CC_1} + (1 - p_{CC_1})]^{(f_2/2)} - 1 + (1 - p_{SH})$$

These equations were previously utilized³² to successfully predict the modulus of various thiol–ene systems, thereby demonstrating the productiveness of the model.

Supporting Information Available: Text giving final equations for weights looking out from the activated functional groups in the polymerization direction and final equations for weights looking out from the activated functional groups in the down direction of polymerization and a discussion of the determination of cross-linking density. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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