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Monomer Functionality and Polymer Network Formation

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ABSTRACT: In free radical polymerizations multivinyl monomers are used to create cross-linked polymeric materials. By utilizing a kinetic model, the relative effectiveness of divinyl and trivinyl cross-linking agents was investigated in copolymerizations with monovinyl monomers where the cross-linking potential was equivalent. The trivinyl cross-linking agent was found to yield more cross-links and less cycles than the divinyl cross-linking agent. Interestingly, prior to complete reaction, increased cross-linking as a function of conversion is also observed when no cyclization occurs. Here, the trivinyl cross-linking agent produced more elastically active cross-links than the divinyl cross-linking agent as a function of conversion until 100% conversion when the number of cross-links is the same, because cyclization is not present. Differences between divinyl and trivinyl cross-linkers are also observed experimentally in the reaction kinetics of these copolymerizations. With equal cross-linking potential, the trivinyl copolymerization reacted more rapidly than the divinyl copolymerization because the increased cross-linking led to more dramatic autoacceleration.

Introduction

Cross-linked polymers formed by free radical polymerization are used in many current and emerging applications, including dental materials, protective and decorative coatings, contact lenses, superabsorbent materials, and hydrogels for biomaterials.[1−6] When designing a cross-linked polymer for a specific application, it is important to understand the network formation and the resulting material properties as each application has specific material requirements. Multifunctional monomers, such as divinyl and trivinyl cross-linking agent, are frequently used in free radical polymerizations to form cross-linked networks. The manner in which the cross-linking agent's double bonds react and incorporate into the network in a bulk or copolymerization will determine the cross-link density of the ultimate polymer produced. The material properties, such as the molecular weight between cross-links, swelling, and diffusion of a solute within its mesh, are all determined by the extent of cross-linking in the network.[7−10]

Over the past decades much research has been devoted to examining the factors that control the cross-linking rate and final cross-link density. The cross-linking agent concentration, final conversion, and extent of primary cyclization all influence the extent of cross-linking. Clearly, a lower concentration of cross-linking monomer and lower final conversion will both yield less densely cross-linked networks. In addition, primary cyclization, where a pendant double bond reacts with the radical on its own propagating chain, will reduce the cross-linking density. As a result of the reduction in cross-linking density, primary cyclization decreases the material strength and increases swelling and diffusion. It also results significant heterogeneity, formation of microgels, and delays in the gel point.[11−13] Unlike the concentration of cross-linking agent and conversion, the extent of cyclization is difficult to measure.

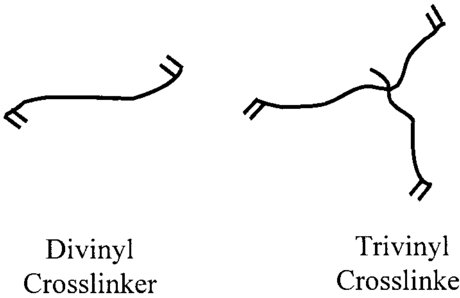

Figure 1. Schematic of divinyl and trivinyl cross-linking agents.

Many factors affect the extent of primary cyclization such as monomer size, monomer stiffness, comonomer ratio, and solvent concentration.[11,14−19] The focus of this work will be to address the question of how monomer functionality, specifically the number of reactive double bonds, affects the network formation and the extent of cross-linking during free radical polymerization. Divinyl and trivinyl cross-linking agents (Figure 1) are commonly used in photopolymerization applications to form cross-linked polymers. A few prominent examples include the use of diethylene glycol dimethacrylate (DEGDMA) copolymerized with hydroxyethyl methacrylate (HEMA) in contact lenses and other hydrogels and trimethylolpropane trimethacrylate (TMPTMA) copolymerized with acrylic acid to form superabsorbent materials. The goal of this work is to provide a basis on which to choose a divinyl or trivinyl cross-linking agent based on the extent of cyclization and cross-linking in the two systems. Our approach is to use a kinetic model to analyze the network formation in both divinyl and trivinyl copolymerizations. Using this model, the effect of monomer functionality is seen when divinyl and trivinyl copolymerizations are compared, where each cross-linking agent is copolymerized with a monovinyl monomer such that they have the same equivalent ultimate cross-linking potential, i.e., at 100% conversion

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in the absence of primary cyclization. Specifically, there are the same total number of divinyl or trivinyl double bonds in their respective copolymerizations. Divinyl monomers have two double bonds that can contribute to the cross-linking reaction, while trivinyl monomers have three double bonds that may engage in cross-linking reactions. If all pendant double bonds react equivalently, polymerization systems with two-thirds as much divinyl as trivinyl monomers will have the same ultimate cross-linking density. Cross-linked polymers are already known to have microgels regions as the double bonds do not react homogeneously, and pendant double bonds frequently form primary cycles. This work investigates the cross-linking reactivity of trivinyl monomers relative to divinyl monomers.

The kinetic model used for this work accounts for the varying pendant reactivity during the polymerization and predicts the rate of pendant cyclization and cross-linking. To validate the model, simulation data was compared to experimental results for the molecular weight between cross-links ($\overline{M_c}$). For these experiments copolymerizations of octyl methacrylate (OcMA) with diethylene glycol dimethacrylate (DEGDMA) or trimethylolpropane trimethacrylate (TMPTMA) were used.[20] The rate of cyclization and cross-linking will depend on the molecular structure of the cross-linking agent. Factors such as chain stiffness and the length between double bonds on the cross-linking agent will play an important role in facilitating or encumbering cyclization. In this work the two cross-linking agents (DEGDMA and TMPTMA) were selected to have similar chain lengths between the double bonds and similar flexibility so the results could be attributed to the effect of monomer functionality. OcMA was used as the monovinyl monomer because it is rubbery at room temperature, which facilitates its polymerization to complete conversion. It is important to compare divinyl and trivinyl data as well as model and experimental data at the same conversion, because the $\overline{M_c}$ decreases dramatically with conversion. All OcMA samples acheived nearly 100% conversion. Additionally, Fourier transform infrared spectroscopy (FT-IR) experiments were performed to observe how differences in cross-linking affect the diffusion-controlled kinetics of divinyl and trivinyl polymerizations. For these experiments DEGDMA and TMPTMA were copolymerized with methoxyethyl methacrylate (MEMA). MEMA was chosen because it reacts more rapidly than OcMA, and unlike more commonly used HEMA, it does not dimerize to form a cross-linking agent.

Background

In comparing the network structure of copolymers created with divinyl and trivinyl cross-linking agents, the extent of cross-linking must be quantified. One way to measure the cross-linking density is to determine the molecular weight between cross-links, $\overline{Mc}$. The number-average molecular weight between cross-links is defined as the density, ρ (total weight of polymer/volume), divided by the concentration of cross-linked chains, ν, as shown in eq 1

$$\overline{Mc} = \frac{\rho}{\nu} \tag{1}$$

$\overline{Mc}$ can be determined experimentally using dynamic mechanical analysis (DMA) to measure the storage modulus in the rubbery region.[21]

It is of interest to be able to calculate the theoretical $\overline{Mc}$ for an ideal cross-linked network with complete conversion and no cyclization. The concentration of cross-linked chains equals the number of double bonds (ndb) of the cross-linking agent times the concentration of cross-linking molecules, $[M_{\mathrm{xl}}]$.[22]

$$\nu = ndb[M_{\mathrm{xl}}] \tag{2}$$

Thus, the same cross-linking density will be achieved for a divinyl and trivinyl copolymerization when the same total numbers of cross-linking agent double bonds are present. For example, when the divinyl monomer concentration in its copolymerization is 0.2 M and the trivinyl monomer concentration in the trivinyl copolymerization is 0.133 M, both monomer mixtures will have 0.4 M cross-linkable double bonds.

For a very loosely cross-linked system, the concentration of cross-linking agent is much less than the concentration of monovinyl monomer. The polymer density is calculated as the initial monovinyl concentration times the molecular weight of the monovinyl monomer. For a more highly cross-linked system when the weight of the cross-linking agent should not be neglected, the density of the polymer network will be the initial double bond concentration, $[DB_0]$, times the average molecular weight of a repeat unit on a double bond basis, $\overline{Mr}$. Thus, the theoretical $\overline{Mc}$ for a copolymerization system will be the following:

$$\overline{Mc}_{\mathrm{theor}} = \frac{\overline{Mr}[DB_0]}{ndb[M_{\mathrm{xl}_0}]} \tag{3}$$

With the kinetic model we are also able to calculate the molecular weight between cross-links as a function of conversion and cyclization rate. Using differential balances, the model tracks at each time step how many monomers are incorporated into the network and what fraction of the pendant double bonds react by cyclization and cross-linking. To determine the $\overline{Mc}$ as a function of conversion, X, the density of growing polymer in eq 1 is calculated on the basis of the concentration of double bonds that have been incorporated into the network, $[DB_0]X$. This result assumes that the concentration of cross-linking agent is low and that all monomers with at least one double bond reacted are part of the network and contributing to the network density. Thus, this analysis is most accurate at high conversion. The concentration of cross-links, ν, will be a function of both conversion and extent of cross-linking. For a divinyl copolymerization, noncyclized fully reacted divinyl molecules will contribute two cross-linked chains as shown in Figure 1a. Divinyl molecules that either cycle or have an unreacted pendant will form a linear structure and will not contribute any cross-linked chains. The concentration of cross-linked chains formed for the divinyl copolymerization will then be twice the concentration of pendants that react in cross-linking reactions, $[Pen_{\mathrm{xl}}]$, and $\overline{Mc}$ is calculated as follows.

$$\overline{Mc}_{\mathrm{Di}} = \frac{\overline{Mr}[DB_0]X}{2[Pen_{\mathrm{xl}}]} \tag{4}$$

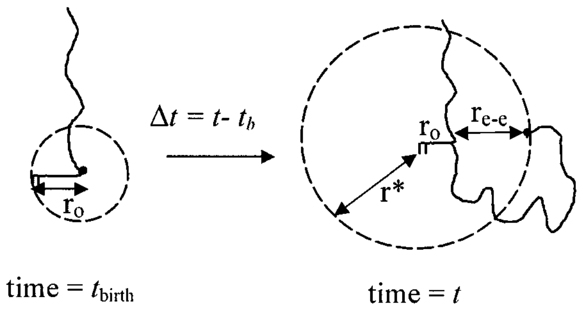

Figure 2. Radius containing the local radical for a particular pendant.

For trivinyl polymerizations, a fully reacted trivinyl with both pendants cross-linking, $[Pen_{\text{xl-xl}}]$, will contribute three cross-linked chains (Figure 1b). Trivinyl cross-linking molecules with one pendant that cross-links and the other pendant that cycles, $[Pen_{\text{xl-cyc}}]$, or is unreacted, $[Pen_{\text{xl}}]$, will form two cross-linked chains. Trivinyl monomers where both pendants are unreacted or undergo cyclization reactions will form a linear chain and not contribute to the number or cross-linked chains. The equation for calculating $\overline{Mc}$ for a trivinyl polymerization is thus

$$\overline{Mc}_{\text{Tri}} = \frac{\overline{Mr}[DB_0]X}{3[Pen_{\text{xl-xl}}] + 2([Pen_{\text{xl}}] + [Pen_{\text{xl-cyc}}])} \qquad (5)$$

Model

The simulation utilized for this work is a kinetic model that accounts for the varying reactivity of pendant double bonds in cyclization and cross-linking reactions. It has been described in detail in previous work.[13,18,23] The model captures the kinetic behavior of multifunctional monomer polymerizations where monomeric and pendant double bonds do not react equivalently. It includes the local dynamics around pendant double bonds where the pendant can react by cyclization with the radical in close proximity to it on the same propagating chain. Divinyl monomers have one pendant double bond that reacts to form a cycle or cross-link while trivinyl monomers have two pendants. Inclusion of this varying reactivity between monomeric and pendant double bonds is important for accurately comparing the network formation of divinyl and trivinyl copolymerization systems. Assuming second-order bimolecular kinetics, differential species balances are used to account for all of the double bonds. For the consumption of monomeric double bonds and pendant double bonds in cross-linking reactions, the important radical concentration in the kinetic expression is the concentration of radicals in the bulk solution. This bulk radical concentration is calculated assuming a constant rate of initiation and making the pseudo-steady-state assumption. For pendant double bonds reacting in cyclization reactions, the important radical concentration is the apparent radical concentration of the radical on the same propagating chain seen by the pendant double bond. For each pendant this local radical concentration is determined by how far the radical on the same chain has propagated.

To calculate the local radical concentration, a spherical volume is assumed with the pendant double bond in the center and the radical on the surface of the sphere (Figure 2). The distance between the radical and pendant double bond, the radius of the sphere, is the length of the cross-linking agent (r_0) plus the distance the radical has propagated, the polymer end-to-end distance ($r_{\text{e-e}}$), calculated for an unperturbed chain using the characteristic ratio,[24] the number of carbon–carbon bonds added, and the length of the carbon–carbon bond. The model tracks how far, on average, the radical propagates away from pendant double bonds created at each birth time. For the trivinyl monomer when the first double bond on the cross-linking agent reacts, two pendant double bonds are created. The local radical concentration is calculated identically for both pendants. When one of the two pendants reacts by cross-linking or cyclization, the radical is again close to the remaining pendant, and the distance the radical has propagated, $r_{\text{e-e}}$, is set to zero again. Using this method, the rate of pendant double bond cross-linking and cyclization is calculated. The model utilizes eqs 4 and 5 to calculate the $\overline{Mc}$ for divinyl and trivinyl polymerizations as a function conversion.

Several parameters are input into the model to specify the monomer system to be simulated. The length of the cross-linking molecule, r_0, and the characteristic ratio, C_n, for calculating the end-to-end distance must be defined for the determination of the local radical concentration. For the comparison of the divinyl and trivinyl polymerizations a value of 5.0 Å was used for the cross-linking molecule length, and the characteristic ratio was 7.0. The parameters were kept the same for the divinyl and trivinyl polymer so that the differences in cross-linking could be attributed to the effect of functionality and not differences in cross-linking agent single or chain flexibility. For the simulations that were compared to experimental data the values of r_0 and C_n were specific to the monomers used. Molecular dynamic simulations work on DEGDMA was used to provide the distance between the two double bonds as 4.7 Å. Using this value for r_0, the value of C_n, the characteristic ratio, was fit to the experimental data for DEGDMA/OcMA and determined to be 8.1. Since both the divinyl and trivinyl copolymers studied were loosely cross-linked and mainly consist of OcMA, the characteristic ratio, C_n, should be equivalent for both copolymers. Using C_n equal to 8.1, r_0 for TMPTMA was fit to the experimental data and determined to be 9.8 Å. Additionally, the kinetic parameters must be specified for the polymerization. For the simulations in this work the kinetic parameters, k_{p}, k_{t}, k_{cyc}, and k_{xl}, all remain constant throughout the simulation. The rate constant for cyclization (k_{cyc}) and cross-linking (k_{xl}) are assumed to be equivalent to the kinetic constant for propagation (k_{p}), as the varying pendant reactivity is captured in the radical concentrations. The chemical reactivity of the monovinyl and divinyl or trivinyl cross-linking agent is assumed to be equivalent. The values of the kinetic parameters for k_{p} and k_{t} were taken from experimental data for HEMA for all simulations.[25] Previous work has shown that the extent of cross-linking vs cyclization is not dependent on the values of the kinetic parameters.[13,26]

Experimental Methods

The monomers for the experimental studies are octyl methacrylate (OcMA; Polysciences Inc., Warrington, PA), diethylene glycol dimethacrylate (DEGDMA; Sartomer, West Chester, PA); and trimethylolpropane trimethacrylate (TMPTMA; Polysciences Inc., Warrington, PA). All monomers were used as received without further purification. Samples were

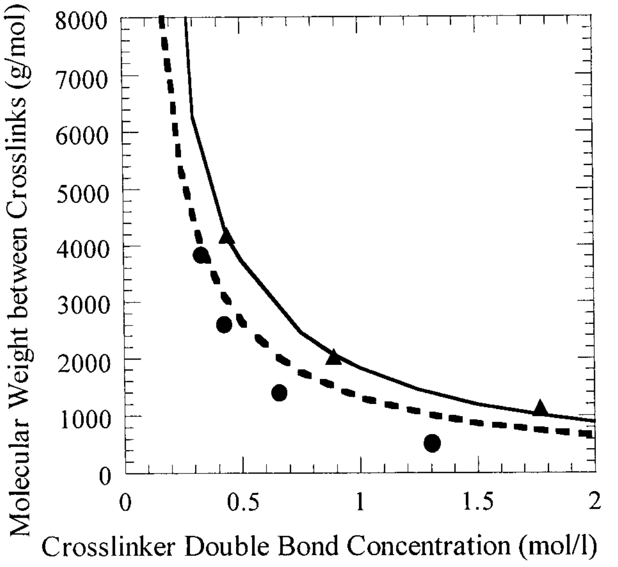

Figure 3. Average molecular weight between cross-links for OcMA copolymerizations with divinyl or trivinyl cross-linking agents. Simulation data for DEGDMA (—) and TMPTMA (- - -). Experimental data for DEGDMA (▲) and TMPTMA (●).[20]

made with different concentrations of cross-linking agent (DEGDMA or TMPTMA) copolymerized with OcMA. All samples were cured to 100% conversion by photopolymerization with 0.1 wt % 2,2-dimethoxy-2-phenylacetophenome (DMPA; Ciba Geigy, Hawthorne, NY) at approximately 600 mW/cm^2 using a 365 nm wavelength fiber-optic light source (EFOS, Canda). The dynamic mechanical analysis (DMA) experiments to determine the $\overline{Mc}$ of these OcMA copolymer with TMPTMA or DEGDMA were published previously and the experimental methods were described therein.[20] For the kinetic experiments, DEGDMA and TMPTMA were copolymerized with methoxyethyl methacrylate (MEMA). The photopolymerizations were initiated with 0.1 wt % 2,2-dimethoxy-2-phenylacetophenone (DMPA; Ciba Geigy, Hawthorn, NY) and a UV light source (Ultracure 100SS Watt Hg sort-arc lamp, EFOS, Missississaugua, Ontario, Canda) at a light intensity of 13.4 mW/cm^2. The C=C (stretch) peak at 1637 cm^{-1} was monitored by real-time infrared (IR) spectroscopy (Magna 750, series II, Nicolet Instrument, Madison, WI) to determine the conversion as a function of time for each polymerization reaction.[27,28]

Results and Discussion

To investigate the effect of monomer functionality, divinyl and trivinyl copolymerization are compared using both modeling and experimental techniques. The kinetic model predicts the degree of cross-linking and primary cyclization as a function of conversion. The simulation results of DEGDMA and TMPTMA copolymerized with OcMA are compared to the experimental results to validate the model. Measurement of the molecular weight between cross-links ($\overline{Mc}$) is a method to characterize the network structure and can be performed both with the model and experimentally. Using dynamic mechanical analysis, the modulus in the rubbery region was measured and $\overline{Mc}$ calculated for OcMA copolymers with DEGDMA or TMTPMA cross-linking agents that have reacted nearly 100% conversion. The results of the $\overline{Mc}$ measurement at various concentrations of cross-linking double bonds are shown in Figure 3. The model predictions at 100% conversion are consistent with the trend of the experimental data. For both the experimental and simulation data, the $\overline{Mc}$ is smaller for the trivinyl than divinyl, indicating that there is a higher cross-linking density when the cross-linking potential is the same. The trivinyl cross-linking agent is thus more efficient than the divinyl at cross-linking. The difference between the trivinyl and divinyl can be explained by the extent of cyclization in the polymerization. At 100% conversion all monomeric and pendant double bonds have reacted; therefore, the difference in $\overline{Mc}$ must be explained by the trivinyl copolymerization having less pendant double bonds reacted by cyclization than in the divinyl copolymerization. Primary cyclization causes an increase in the $\overline{Mc}$ and will correspondingly change other important material properties. Table 1 shows the predicted integral fraction of pendants that cycle for the polymerization with a divinyl or trivinyl cross-linking agent. In the copolymerization with the trivinyl cross-linking agent, the fraction of primary cyclization is always less than for the equivalent divinyl copolymerization. The experimental results show that the trivinyl polymerization cross-links even more efficiently than the model predicts. This result may be due in part to the fact that TMTPMA is sterically limited from having both pendants cycle. This idea will be discussed in further detail later in the text. The results show clearly the trivinyl and divinyl polymerization are not equivalent even when their cross-linking potential is identical.

Table 1.

cross-linking agent double bond concn (M)	integral fraction of pendants that cycle with divinyl cross-linking agent	integral fraction of pendants that cycle with trivinyl cross-linking agent
0.5	0.4253	0.2694
0.75	0.4195	0.2657
1.0	0.4139	0.2622
1.5	0.4032	0.2555
2.0	0.3934	0.2492

To investigate further the differences between divinyl and trivinyl polymerizations, ideal network formation in the absence of cyclization is analyzed. For comparison, the concentration of elastically active cross-linked chains is calculated as a function of conversion. For divinyl copolymerizations without cyclization, every fully reacted divinyl monomer contributes two cross-linked chains to the network structure. Partially reacted or unreacted divinyl molecules do not add to the number of cross-linked chains. The probability that the divinyl cross-linking monomer is fully reacted is simply X^2, where X is the conversion, so the concentration of cross-linked chains can be predicted by eq 6, where $[M_{\mathrm{xl0}}]$ is the initial cross-linking agent concentration.

$$[\nu_{\mathrm{e-di}}] = 2X^2[M_{\mathrm{xl0}}] \tag{6}$$

For trivinyl polymerizations, assuming no cyclization, a fully reacted trivinyl monomer will contribute three cross-linked chains. The probability that a trivinyl monomer will be fully reacted will be X^3. Trivinyl monomers that have one reacted pendant and one unreacted pendant will form two cross-linked chains like the divinyl monomer. The probability that this will occur is $3X^2(1 - X)$ as there are three possible ways to have two double bonds reacted and one unreacted. Trivinyl monomers where both pendants are unreacted will not contribute to the number of cross-linked chains. Thus, the concentration of cross-linked chains is the number of chains produced by each reacted monomer species

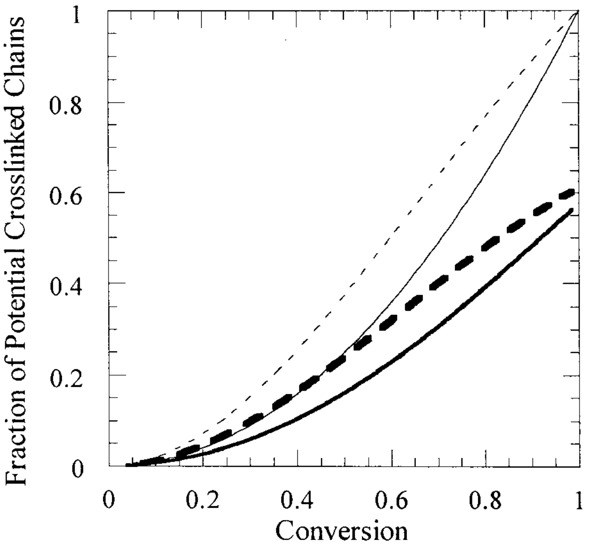

Figure 4. Evolution of real network formation predicted by simulation compared to the ideal network formation. Fraction of potential cross-linked chains that form as a function of conversion for copolymerizations with 0.2 M divinyl cross-linking agent predicted by the model (—) and 0.13 M trivinyl cross-linking agent predicted by the model (— — —), 0.2 M divinyl cross-linking agent for an ideal network (—), and 0.13 M trivinyl cross-linking agent for an ideal network (- - -).

times the probability of that conformation, as shown in eq 7:

$$[\nu_{\mathrm{e-tri}}] = \{3X^3 + 6X^2(1 - X)\}[M_{\mathrm{xl0}}] \qquad (7)$$

The normalized concentration of elastically active cross-linked chains is plotted vs conversion for divinyl and trivinyl polymerizations in Figure 4. For a 0.2 M divinyl and 0.133 M trivinyl copolymerization, the concentration of cross-linking double bonds is equivalent and should yield the same cross-link density in the absence of cyclization. Examining the statistical predictions of the network formation assuming no cyclization shows that these reactions are not equivalent until 100% conversion is reached. In fact, the ratio of elastically active cross-links for trivinyl to divinyl cross-linking agents (without cyclization) is $2 - X$. The trivinyl monomer produces more cross-linked chains until the end of the reaction. At the low double bond conversion the trivinyl is twice as effective as a cross-linking agent. This result demonstrates that even in an ideal network, the trivinyl monomer is a more effective cross-linking agent than a divinyl monomer with equivalent cross-link potential at incomplete conversions. This phenomenon can be explained by the fact that every trivinyl monomer has two pendants that can react by cross-linking. If either pendant cross-links, the first double bond of the cross-linking agent incorporated into network and the cross-linked pendant will together act as a cross-link in the network. In contrast, the divinyl has only one pendant that can cross-link, if the pendant reacts by cyclization or not at all, it will not contribute to the cross-linking of the network at all.

In a real network the situation is complicated by the existence of primary cyclization. Figure 4 show the normalized concentration of cross-linked chains predicted by the model compared to the ideal case in the absence of cyclization. For both the trivinyl and the divinyl, fewer elastically active cross-linked chains are produced because cyclization is consuming a significant fraction of the pendants. In the network formation predicted by the model, the ratio of trivinyl to divinyl cross-linked chains is slightly higher than predicted for the ideal network. Figures 5 and 6 provide more details about how the pendants double bonds react. In Figure 5 the concentration of pendants that cross-link normalized by the number of pendants is shown as a function of conversion. Figure 5 shows how the trivinyl pendants react by cross-linking at a higher rate until almost 80% conversion. Cyclization reactions are also occurring at higher rates in the trivinyl (Figure 6). It may at first appear to be a contradiction that the cumulative fraction of trivinyl pendants that cross-link is less (cycle is more) than the divinyl at the end of the reaction, and still the trivinyl produces more elastically active cross-linked chains (Figure 4). The values plotted in Figures 6 and 7 are normalized by the total number of potential pendants. In the equal cross-linking case with 0.2 M divinyl and 0.133 M trivinyl, there are actually more potential trivinyl pendants. This fact explains why it is

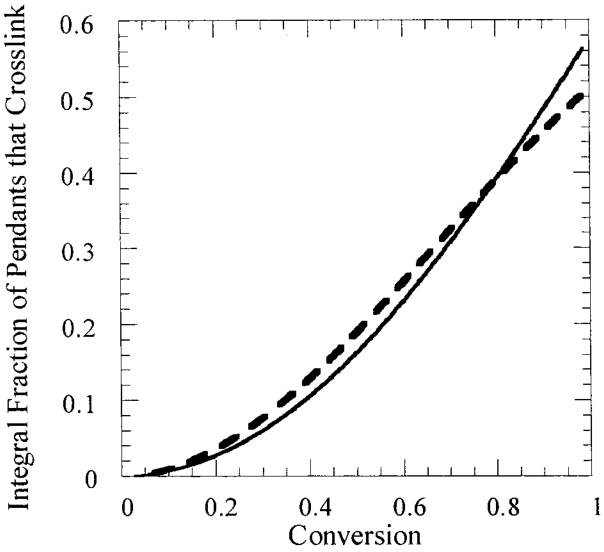

Figure 5. Normalized fraction of pendants that react by cross-linking for copolymerization with 0.2 M divinyl cross-linking agent (—) and 0.13 M trivinyl cross-linking agent (— — —).

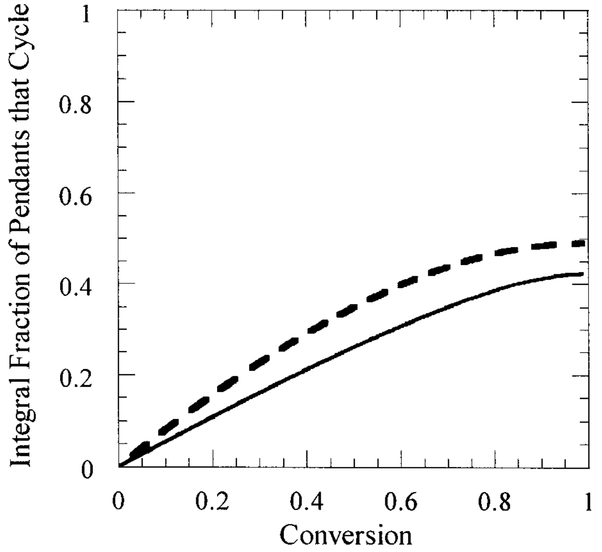

Figure 6. Normalized fraction of pendants that react by cyclization for copolymerization with 0.2 M divinyl cross-linking agent (—) and 0.13 M trivinyl cross-linking agent (— — —).

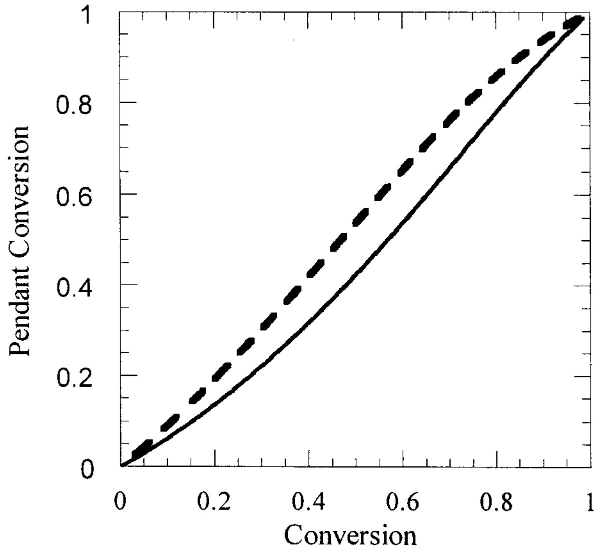

Figure 7. Pendant conversion vs double bond conversion for 0.2 M divinyl (—) and 0.13 M trivinyl (— — —) copolymerizations.

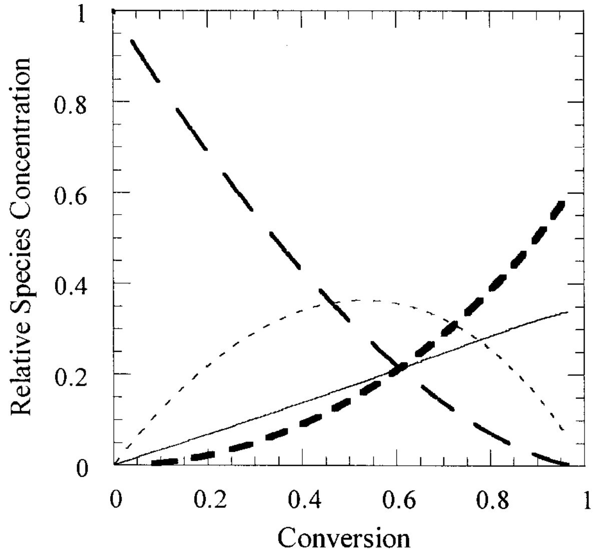

Figure 8. Relative species concentration of divinyl cross-linking molecules as a function of conversion: unreacted (— — —); monomer incorporated into network (- - -); one pendant cross-links (— — —); one pendant cycles (—).

possible to have more pendant cycle in a trivinyl copolymerization (Figure 5) and still produce more cross-linkages in the polymer (Figure 4). It is also interesting to note that since for the trivinyl there is a higher degree of both cyclization and cross-linking occurring initially, the trivinyl pendants are reacting faster as a function of conversion than the divinyl (Figure 7). Many polymerization reactions, especially cross-linking polymerizations, will not achieve 100% conversion,[29] and the earlier cross-linking of the trivinyl in the reaction further enhances its effectiveness as a cross-linking agent.

The model is also able to provide information about how the divinyl and trivinyl monomers react throughout the polymerization. As shown in Figure 8 for the bulk polymerization of a divinyl monomer, there are four possible states the monomer can be in: unreacted ($P_{0,0}$), one double bond reacted and incorporated into the network ($P_{1,0}$), having the second (pendant) double bond cycle ($P_{2,0}$), or cross-link ($P_{2,1}$). The plot in Figure 8 shows the relative species concentration of monomers

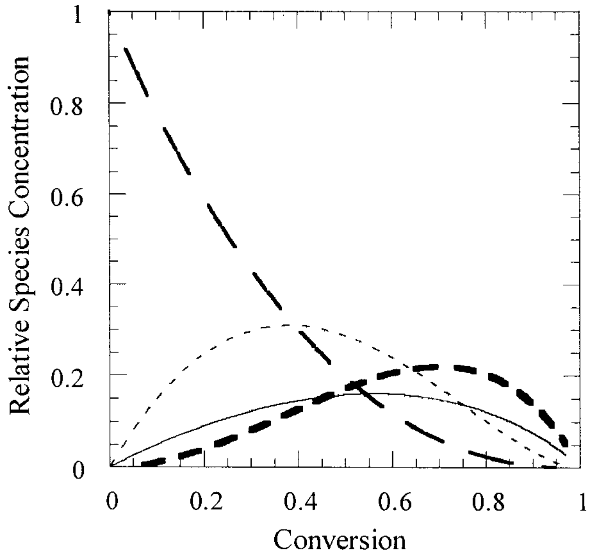

Figure 9. Relative species concentration of partly or unreacted trivinyl molecules as a function of conversion: unreacted (— — —); monomer incorporated into network (- - -); one pendant cross-links (— — —); one pendant cycles (—).

($P_{i,j}$) with *i* double bonds reacted and *j* pendants form cross-links as a function of conversion. Obviously, initially all the monomer species are unreacted and the concentration decreases with conversion. The concentration of incorporated monomers that have one unreacted pendant double bond builds up in the first half of the reaction and then declines as pendants are consumed. More interestingly, the first pendant double bonds react by cyclization at a greater rate than by cross-linking as seen in the higher concentration of $P_{2,0}$ relative to $P_{2,1}$. Only after 60% conversion does the cross-linking species ($P_{2,1}$) dominate. Cyclization is a significant reaction where at 100% conversion about one-third of the potential cross-linking reactions are lost to cyclization.

For the trivinyl case there are even more permutations of how the monomer can react as shown in Figure 9. There are four partially unreacted species ($P_{0,0}$, $P_{1,0}$, $P_{2,1}$, and $P_{2,0}$) and three different fully reacted species ($P_{3,2}$, $P_{3,1}$, and $P_{3,0}$). Figure 9 shows the fraction of monomers that are partially reacted and unreacted as a function of conversion. At 0% conversion all double bonds are unreacted. Next, species with one double bond incorporated into the network are created. Similar to the divinyl polymerization, the first pendants react by cyclization at a higher rate than by cross-linking until approximately 50% conversion. At that point the fraction of incorporated monomer species with one pendant reacting by cyclization ($P_{2,0}$) is less than with one pendant reacting by cross-linking ($P_{2,1}$). Figure 10 shows the species distribution of fully reacted monomers. Having all double bonds react by cross-linking ($P_{3,2}$) may be the most desirable, but it is not the most frequent outcome. Having one cycled and one cross-linked pendant ($P_{3,1}$) is the most common. Finally, the least desirable species with both pendants forming cycles $P_{3,0}$ is the fate of about 7% of the monomers. In this conformation the cross-linking agent will simply add loops as a part of the polymer chain.

It is conceivable that the existence of these species with two cycles ($P_{3,0}$) may not be sterically possible for some cross-linking agents. The cross-linking monomer may not be flexible enough to have both pendants react

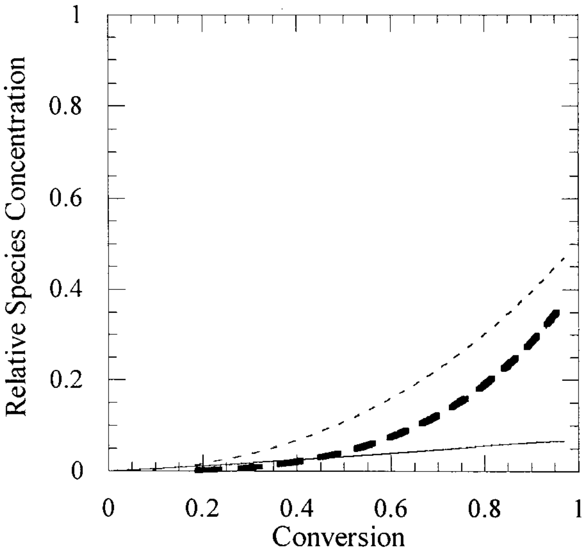

Figure 10. Relative species concentration of fully reacted trivinyl molecules as a function of conversion: one pendant cycles and one pendant cross-links (- - -); both pendants cross-link (— — —); both pendants cycle (—).

with the same propagating chain to form two primary cycles. This possibility was proposed in the work by Matsumoto on TMPTMA.[30] With the restriction that a trivinyl monomer cannot have both its pendants react in cyclization reactions, the network structure created would be even more cross-linked. There would be an increased number of species with one pendant cycling and one pendant cross-linking, ($P_{2,1}$) and both pendants cross-linking ($P_{3,2}$). To look at how the polymer network may evolve in this case, the equal cross-linking copolymerization with 0.2 M divinyl or 0.13 M trivinyl can be reexamined when no double cyclization is restricted. In this case the normalized integral fraction of pendants that reacts by cross-linking is higher for the trivinyl throughout the reaction (unlike Figure 6 where double cyclization was allowed). The higher degree of pendant cross-linking has a significant effect on the number of elastically active chains produced as seen in Figure 11. This plot is analogous to Figure 5 and shows the fraction of elastically active cross-linked chains produced as a function of conversion when no double cyclization is assumed. Here, the trivinyl and divinyl diverge as they approach 100% conversion with the trivinyl becoming an even more effective cross-linking agent. The modeling and mechanical properties results clearly assert that the trivinyl cross-linking agent acts as a more effective cross-linking agent than the divinyl cross-linking agent. To further verify the increased cross-linking rate during the trivinyl copolymerization the overall kinetics of the system were studied. Differences in cross-linking density can be observed in rate of polymerization. The kinetics of free radical polymerizations are marked by a phenomenon known as autoacceleration or the gel effect where termination of radical chains becomes diffusion-limited and the polymerization rate increases due to an increased radical concentration.[29,31] These diffusion limitations set in as the free volume of the system is decreased by the transformation of mobile monomer units into polymer chains. The creation of cross-linked polymer chains further decreases the mobility of the system. When more cross-linking occurs during the polymerization, the network will form more rapidly, and mobility restrictions leading to diffusion and reaction diffusion-controlled termination will occur at a lower conversion. Thus, it is expected that autoacceleration will occur at lower conversion in the polymerization that undergoes more cross-linking. Using FTIR, the double bond conversion vs time was measured for polymerization of methoxyethyl methacrylate (MEMA) with equal double bond concentrations of either DEGDMA or TMPTMA (Figure 12). Two mol % DEGDMA and 1.34 mol % TMPTMA copolymerized with MEMA will both have a cross-linking double bond concentration of 0.27 M and total double bond concentration of 6.7 M, more than 95% of which is MEMA. Polymerized at the same light intensity and initiator concentration, the kinetics of the systems should be identical if the cross-linking is equivalent. The results show that the trivinyl system reacts more rapidly than the divinyl. The maximum rate of the trivinyl polymerization is 1.3×10^{-3} mol/(L s), and the maximum rate of the divinyl polymerization is 1.1×10^{-3} mol/(L s). The increased

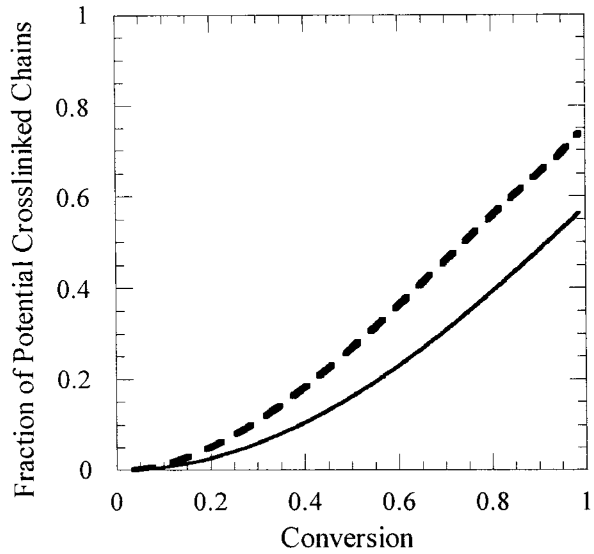

Figure 11. Evolution of real network formation predicted by simulation with no double cyclization allowed for the trivinyl. Fraction of potential cross-links that form as a function of conversion with 0.2 M divinyl cross-linking molecules (—) and 0.13 M trivinyl cross-linking molecules (— — —).

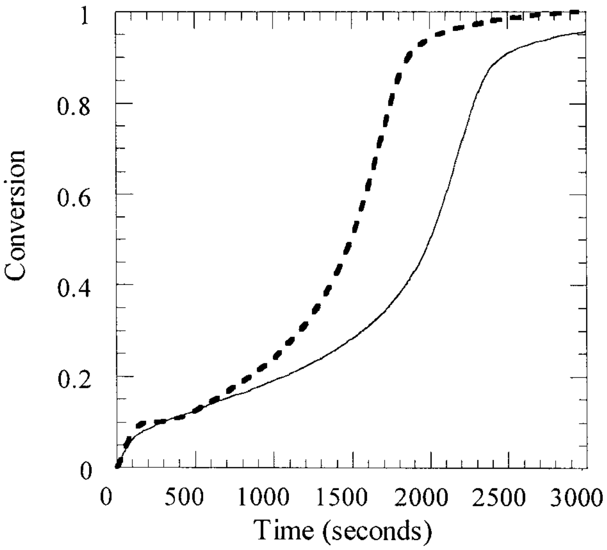

Figure 12. Conversion vs time for equal cross-linking potential systems of 2.0 mol % DEGDMA (—) and 1.33 mol % TMPTMA (— — —) copolymerized with MEMA.

autoacceleration of the trivinyl further collaborates that it is a more effective cross-linking agent than the divinyl.

Conclusions

It has been found through modeling and experimental results that trivinyl copolymerizations produce more cross-links than divinyl copolymerizations with equivalent cross-linking potential. Several conclusions can be made regarding the difference between trivinyl and divinyl cross-linking agents. Even in an ideal network, it was shown that, prior to complete conversion, the trivinyl would be a more effective cross-linking agent than the divinyl monomer. When the kinetic model is used to predict the extent of cross-linking and cyclization in a real network, the trivinyl copolymerization forms a more cross-linked network than the divinyl copolymerization throughout the reaction and at 100% conversion. In some cases, the trivinyl cross-linking agent may not be flexible enough to have both its pendants react in primary cyclization reactions. If cyclization of both pendant double bonds were not possible, then the trivinyl cross-linking agent would have an additional advantage and be even more efficient than a divinyl cross-linking agent. Finally, differences between divinyl and trivinyl cross-linkers can be observed experimentally in the reaction kinetics of these copolymerizations. With equal cross-linking potential, the trivinyl copolymerization reacts more rapidly than the divinyl copolymerization because increased cross-linking causes enhances autoacceleration.

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