



## KINETIC GELATION MODEL PREDICTIONS OF CROSSLINKED POLYMER NETWORK MICROSTRUCTURE

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**Abstract**—A kinetic gelation model was used to predict the complex network structures that arise in the high crosslinking regime of homopolymerizations and copolymerizations of multifunctional monomers. In particular, network inhomogeneities, relative functional group reactivities, and cyclization vs crosslinking tendencies were studied for a variety of systems as a function of the reaction conditions. Since the network structure strongly influences the physical and mechanical properties of the polymer, the objective of this work was to predict and study the effects of reactions conditions on this structure to provide insight for developing better materials. The following work presents the results from a kinetic gelation simulation, and when available, compares these results to experimental values.

### INTRODUCTION

Free radical polymerization of multifunctional monomers produces crosslinked networks with structures that are extremely complex. In addition to this microstructural complexity, the general crosslinked nature of the system requires that the material be suitable for application immediately after curing. For example, not only is the microstructure (i.e. crosslinks and cycles) unalterable after polymerization, but the system is insoluble and essentially fixed in macroscopic structure. Since the physical and mechanical properties of the network are strongly dependent on the network structure, characterizing and simulating the structural evolution of the network becomes increasingly important to provide a basis for developing structure-property relationships.

In many applications, copolymerizations of difunctional monomers with relatively small amounts of a multifunctional monomer have been used to produce rather loosely crosslinked networks. These applications include areas such as superabsorbents (Brannon-Peppas and Harland, 1990) and controlled release systems (Mack *et al.*, 1987; Brunstedt and Anderson, 1992). Typically, less than 1% of the multifunctional monomer is added in these systems. In contrast, highly crosslinked networks are produced when the amount of multifunctional monomer is increased or the multifunctional monomer is homopolymerized. These densely crosslinked networks have material properties that make them suitable for applications such as dental restorative materials (Watts, 1992), abrasion resistant coatings (Oshima *et al.*, 1976), nonlinear optical materials (Eich *et al.*, 1989), and aspherical lenses (Zwiers and Dortant, 1985; Kloosterboer, 1988). As the applications for crosslinked polymer networks continue to expand,

characterizing the network microstructure becomes imperative to produce networks with the desired physical and mechanical properties for the application.

Although the properties of the polymer system are strongly dependent on the network structure, multifunctional monomer polymerizations and the resulting polymer structures are extremely difficult to characterize experimentally or with models and simulations. This difficulty arises primarily from the structural heterogeneity that develops in the polymer during the polymerization of multifunctional monomers (Kloosterboer, 1988). Since these monomers have more than one functional group, each group may possess a different reactivity. In general, this functional group reactivity is not only unequal but changes with conversion in the system. Any polymerization involving multifunctional monomers has this added complexity of possible varying reactivity of functional groups on the same molecule. The primary result is the formation of microgel regions early in the reaction (because of high pendant double-bond reactivity) (Bastide and Leibler, 1988; Funke, 1989; Matsumoto *et al.*, 1989), which can lead to a significant reduction in the mechanical properties of the polymer when compared with a homogeneous network.

Microgels are regions in the system of higher average crosslinking density than the overall system manifested from the strong spatial correlation between pendant group reactivity and the radical location. For example, several researchers (Soper *et al.*, 1972; Dušek and Ilavský, 1975a,b; Shah *et al.*, 1978; Matsumoto *et al.*, 1987; Mikos *et al.*, 1987; Landin and Macosko, 1988) have studied the effect of the chain length and flexibility between double bonds in divinyl monomers on the extent of cyclization in the system. In general, as the chain flexibility was increased, the reactivity of the pendant functional groups was enhanced which

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led to extensive cyclization at low conversions. Landin and Macosko (1988) also studied the effect of the relative amount of the divinyl monomer in a vinyl-divinyl copolymerization on cyclization tendencies.

For clarification, when characterizing these polymer networks the following definitions will apply (Dotson *et al.*, 1992). When a radical on a polymer chain propagates through a pendant double bond (i.e. a double bond from a monomer with one double bond already reacted), a crosslink, secondary cycle, or primary cycle can be formed. A crosslink forms when the radical reacts with a pendant double bond on a different kinetic chain. When the radical reacts with a pendant double bond on its own kinetic chain, a primary cycle results. Finally, if the radical reacts with a pendant double bond on a different kinetic chain with which it is already crosslinked, a secondary cycle forms. These definitions will be applied throughout this paper in characterizing polymer network structures.

The elegant theory of Flory (1953) and Stockmayer (1943, 1944) has traditionally been used to predict gel point conversions in systems that have a relatively low density of crosslinks. In this regime, the system is assumed homogeneous, and all functional groups are assumed to possess equal reactivity. In contrast, when the fraction of crosslinking monomer is increased, several researchers (Dušek, 1982; Boots, *et al.*, 1985; Li, *et al.*, 1989) have experimentally measured conversions at the gel point which are significantly greater than those predicted by the classical Flory-Stockmayer theory. Walling (1945) was among the first to point out this deviation from ideality for the copolymerization of vinyl acetate and divinyl adipate, as well as the copolymerization of methyl methacrylate and ethylene glycol dimethacrylate.

The primary explanation for this non-ideal network behavior lies in the unequal reactivity of the functional groups and the ensuing competition between cyclization and crosslinking. For example, the earlier works of Dušek and Ilavský (1975a,b) showed that the dominant reaction of the pendant functional groups at low conversion was primary cyclization. Considering that primary cyclization does not contribute to the formation of an overall network, systems with extensive primary cyclization will have higher conversions at their gel points. In terms of heterogeneity, a microgel region is formed in the proximity of each radical initiation site, and these submicron regions are extensively cycled and crosslinked. But the macroscopic gel point is dependent on the formation of an infinite network, and the system does not gel until the microgel regions are connected macroscopically through a network of crosslinks.

As stated previously, the formation of microgels results primarily from the unequal reactivity of functional groups, where the pendant functional group has an enhanced reactivity because of its spatial proximity to the propagating radicals. This behavior dominates at low conversions, and as the conversion

is increased, the reactivity of the functional groups changes. In particular, the reactivity of the monomeric functional group approaches, and in some cases surpasses, the reactivity of the pendant functional group. Several researchers (Minnema and Staverman, 1958; Dušek and Spěváček, 1980; Galina *et al.*, 1980; Kloosterboer, 1988) have proposed that the microgel regions formed at the beginning of the reaction act to shield the pendant functional groups from further reaction at higher conversions. In essence, the unreacted pendant functional groups become shielded in the core of the highly crosslinked microgel regions. Thus, at higher conversions, the concentration of accessible pendant functional groups is drastically decreased, and the overall reactivity of the pendant functional groups decreases.

Summarizing, the reactions of multifunctional monomers and the crosslinked networks that they produce are extremely complex. This complexity arises mainly from the unequal reactivity of the functional groups and spatial heterogeneity. At low conversions, the enhanced reactivity of the pendant functional groups leads to higher cyclization rates, the formation of microgel regions, and a delay in the onset of gelation. As conversion is increased, the reactivity of the pendant functional group is significantly decreased as the microgel regions act to shield the reacted pendant groups within. These tendencies lead to the formation of a heterogeneous network and add to the tremendous difficulties in characterizing and modeling these systems.

Three different approaches have been used to model these systems. The first method considers a statistical approach (Macosko and Miller, 1976; Dotson *et al.*, 1988; and Scranton and Peppas, 1990) whereby polymer structures evolve according to certain probabilistic rules for the formation of bonds between smaller monomer molecules. The second approach is kinetic based (Mikos *et al.*, 1986; Tobita and Hamielec, 1988, 1989) and involves solving the differential equations that describe the concentration of each reacting species. Finally, the third approach involves simulation of the structure in space using a percolation-type simulation called a kinetic gelation model (Manneville and de Seze, 1981; Boots and Pandey, 1984; Simon *et al.*, 1989). While statistical and kinetic methods are useful in modeling lightly crosslinked networks of relatively homogeneous nature, they are limited by their mean-field nature and are incapable of predicting the heterogeneities that arise in the high crosslinking regime. In contrast, kinetic gelation models can be used to predict and model spatial heterogeneities that arise during polymerization of multifunctional monomers. While limited by their fixed lattice structure and the difficulty in introducing realistic mobility of reacting species, kinetic gelation models are presently the method of choice for modeling reactions of high crosslinking density. This work presents the results of a kinetic gelation simulation of the network microstructure during the homopolymerization of tetrafunctional

monomers and the copolymerization of tetrafunctional and difunctional monomers.

### SIMULATION

A kinetic gelation model was used to study the structural evolution of polymer networks that form during the polymerization of multifunctional monomers. The model was based on a face centered cubic lattice with 12 nearest-neighbor sites, rather than the traditional simple cubic lattice which only has six. The lattice was periodic and not closed. Also, monomer molecules were allowed to occupy multiple sites instead of a single site, which enables us to study the effects of increased chain length between functional groups. For example, the differences between the networks produced from ethylene glycol dimethacrylate (EGDMA) and tetraethylene glycol (TeEGDMA) dimethacrylate can be determined. The effects of monomer size on the structure of the network can be quite significant, particularly for polymerizations occurring in the high crosslinking regime. Here, the reaction is primarily diffusion controlled from the onset, and the high localized concentration of pendant double bonds leads to increased primary cyclization. The distance between the functional groups in the monomer is one of the factors that will control this rate of primary cyclization.

Initiator molecules occupy two lattice sites and decay with a first-order rate constant. This first-order decay of the initiator provides a more realistic and variable representation of the polymerization as compared to simulations that use "fast" initiation (i.e. generating all radicals at the start) or "slow" initiation (i.e. allowing a single radical to propagate and become trapped before initiating a second). Secondly, when the initiator molecule decays, it generates two radicals each occupying its own site. The radicals can recombine and become inactive or propagate. In this manner, the efficiency of the initiator is introduced, since a "pseudo-cage effect" is introduced from the close proximity of the two radicals upon decay.

Finally, void sites were incorporated into the model to represent free volume or solvent. The primary function of the void volume is to control the mobility of the system, as all species are allowed to move through a crankshaft-type motion. Movement occurs between propagation steps, as a certain fraction of sites are randomly chosen and allowed to move if all bonds are preserved. This movement allows trapped radicals the possibility of becoming active later in the reaction depending on the localized mobility, rather than being permanently trapped. By varying the void site fraction, the effects of mobility on the polymer structure can be elucidated.

Monomer molecules, initiator molecules, and void sites were placed on the lattice in an ordered fashion. The exact void site fraction was slightly varied to accommodate the incorporation of entire monomer and initiator molecules. Once all molecules were placed on the lattice, the system was randomized by allowing species to move before starting the reaction.

The minimum randomization time (or minimum number of sites that must be checked for movement) was established by running several simulations which had different prereaction movement times. When plots of all of the simulation results no longer varied with increasing movement, this initial movement time was set as the minimum time for randomization. This kinetic gelation model's development is discussed further elsewhere (Bowman and Peppas, 1992).

While maintaining the basic setup, reaction mechanism, and mobility mechanism, modifications to the previous simulation include the ability to predict molecular weights, fraction of primary and secondary cycles vs crosslinks, initiator efficiencies, and kinetic chain lengths. In addition to these changes, the present simulation is also able to model copolymerizations of difunctional and tetrafunctional monomers, whereas the previous model was restricted to homopolymerizations of tetrafunctional monomers. Although the simulation is still restricted to a lattice, we believe these changes will improve the general understanding of network microstructural evolution. In particular, we will study the effects of rates of polymerization (by varying the initiator concentration and decay constant), system mobility, monomer size, and copolymer composition on the microstructure of the polymer network.

### RESULTS AND DISCUSSION

Typical simulations were run on a  $40 \times 40 \times 40$  lattice with 15% void volume and 1% initiator. The void volume of 15% was selected to allow reasonable mobility of the monomer molecules and chain segments. The minimum size of the lattice was determined by running the simulation on various lattice sizes and plotting the molecular weight as a function of conversion. No significant change in the gel point conversion was observed for lattice sizes larger than  $40 \times 40 \times 40$ . Therefore, this size was established as the minimum lattice size for the homopolymerization of 3-site monomer molecule with a minimum initiator decay time of 1/5000 (longest kinetic chains). The initiator decay time was inversely related to a characteristic parameter,  $\tau$ , which has units of simulation time.

In addition, most of the figures shown are the results from a single simulation. Bowman and Peppas (1992) demonstrated in earlier works that the network properties as a function of conversion were highly reproducible with only slight simulation to simulation deviations. We have found the same to be true in simulating structural aspects of the network such as crosslinking and cyclization tendencies. In only a few cases, the simulation noise required runs to be averaged.

Initiator decay constants ranged from 1/50 to 1/5000, leading to relatively short kinetic chains, modeling a relatively fast polymerization such as a photopolymerization. Photopolymerizations are predominant in many of the applications for highly

crosslinked networks such as dental materials, aspherical lenses, and coatings. Mobility of all species was introduced between propagation steps by randomly checking 10% of the sites for movement. A more thorough discussion of the exact mobility mechanism is presented elsewhere (Bowman and Peppas, 1992). Finally, the standard size for a tetrafunctional monomer was 3-sites and for a difunctional monomer, 1-site.

Figure 1 plots the weight average molecular weight and the weight average molecular weight excluding the largest chain, essentially the sol fraction after gelation, vs conversion of double bonds for a homopolymerization of a 3-site tetrafunctional monomer. These molecular weights were calculated assuming each lattice site had a molecular weight of one. The initiator decay constant was 1/500. Considering the gel point to occur where the weight average molecular weight diverges, the gel point conversion is between 4% and 8% double-bond conversion. During the homopolymerization of multifunctional monomers, most of the systems will gel at extremely low conversions, and in fact, slower rates of polymerization (e.g. thermally initiated polymerizations) of these monomers can gel at less than 1% conversion. This dependence of the gel point conversion on the rate of initiation will be discussed later.

Looking at the weight average molecular weight minus the largest chain, a gradual increase in the molecular weight is seen as chains of comparable size exist even when the largest chain is subtracted. As the system gels and the largest molecule is essentially an infinite network, the sol fraction molecular weight decreases as only small chains exist independent of the network. These small chains arise primarily as new radicals are generated near monomer pools where the radicals can propagate through monomer only a few steps before encountering a pendant double bond on the network. This analysis provides a second method for defining and determining the gel point conversion in these systems.

Figure 2 shows the dramatic effect of the size of the monomer molecule on the weight average molecular weight and gel point conversion. The initiator decay

constant chosen was 1/50 to magnify the differences between the gel points of the two systems. As the monomer size is decreased from a 5-site molecule to a 3-site molecule (e.g. like the difference between TeEGDMA and EGDMA), the conversion at the gel point is increased. This difference in gel point conversion is attributed mainly to the inefficient use of the pendant double bond in the polymerization of the smaller, 3-site monomer. Before the gel point, the dominating reaction of the pendant double bond in a smaller monomer molecule is primary cyclization rather than crosslinking. Consequently, smaller monomer molecules will have higher conversions with a greater fraction of primary cycles at the gel point, as compared to larger monomer molecules which will have a lower conversion with a relatively higher fraction of crosslinks.

When a radical on a polymer chain propagates through a pendant double bond (i.e. a double bond from a monomer with one double bond already reacted), a crosslink, secondary cycle, or primary cycle is formed. Since each of these pendant double-bond reactions will affect the material properties differently, it is important to characterize the reaction tendencies. The following definitions have been applied throughout this paper. When a radical reacts with a pendant double bond on its own kinetic chain, a primary cycle results. These primary cycles do not contribute to the formation of an overall network, and thus, primary cyclization might be viewed as an undesirable side reaction. When a radical reacts with a pendant double bond on a different kinetic chain, a crosslink is formed. Since crosslinks connect different kinetic chains, they are the desired reaction for network formation. Finally, if the radical reacts with a pendant double bond on a different chain with which it is already crosslinked, a secondary cycle forms. Like primary cycles, secondary cycles do not contribute to the overall formation of the network and may be viewed as undesirable from this standpoint. In the most general sense of structure-property relationships, crosslinks enhance the mechanical properties most, followed by secondary cycles and then primary cycles. This statement is obviously simplified in its

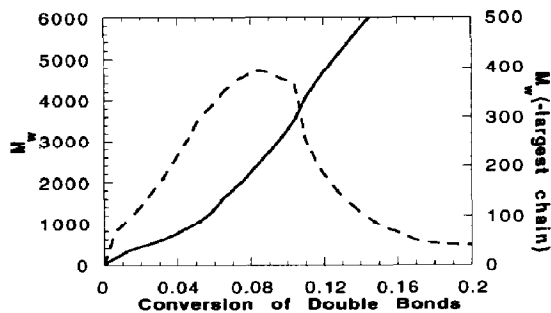


Fig. 1. The weight average molecular weight (—) and the weight average molecular weight excluding the largest chain (---) vs double-bond conversion.

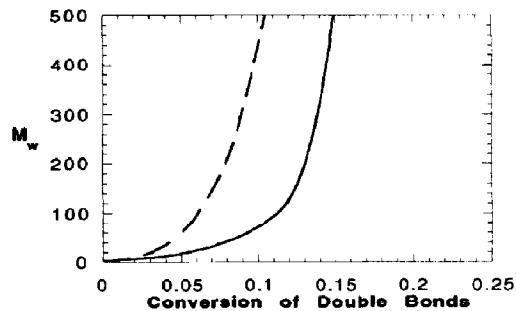


Fig. 2. The weight average molecular weight as a function of double-bond conversion for a 3-site (—) and 5-site (---) monomer.

viewpoint (strictly speaking, the elastic activity of the cycles and crosslinks must be established to determine its contribution to the mechanical properties), yet useful.

Figure 3 shows the relative fraction of crosslinks, primary cycles, and secondary cycles as a function of double-bond conversion for two different size monomer molecules for a homopolymerization of tetrafunctional monomer. Initially, primary cyclization dominates crosslinking and secondary cyclization, as the pendant double bonds have an increased reactivity in the localized region of the free radical. This behavior accounts for the formation of microgel regions and the heterogeneity of the network. As conversion and polymer concentration increase, crosslinking and secondary cyclization begin to increase and a network forms. Finally, a transition region is reached where secondary cyclization and primary cyclization cross-over. The trend is now towards a more homogeneous network structure with a very high degree of cyclization.

Figure 3 also illustrates the effects of monomer size on the competition between crosslinking, primary cyclization, and secondary cyclization. For the 3-site monomer molecule, the trend is towards a much higher fraction of primary cycles for an extended conversion. These primary cycles are formed at the expense of remaining unreacted, as in larger monomer molecules, where they might react later in the polymerization with a higher probability of becoming crosslinks or secondary cycles which generally have a greater influence on the mechanical properties of the network. This initial high degree of primary cyclization also leads to a more heterogeneous network. Finally, the transition region where secondary cyclization dominates the primary cyclization occurs much later for the 3-site monomer (62% conversion). Compare this value to the 5-site molecule where secondary cyclization dominates as early as 20% double-bond conversion.

The tendency of increasing primary cyclization with decreasing size of the monomer molecule seems rather intuitive. However, Shah *et al.* (1978) and

Landin and Macosko (1988) have reported just the opposite. An increase in the cyclization tendency was seen with an increase in the bridge length between methacrylate groups. Where the present kinetic gelation model places no restriction on the flexibility or minimum length of primary cycles, these restrictions obviously are important for molecules that have relatively short lengths between the functional groups. These simulation results are more appropriate for molecules with longer bridges between double bonds and relatively flexible molecules. To study the polymerizations of stiffer molecules and molecules with shorter chain lengths between the functional groups, a minimum length for primary cycle loops must be introduced, and a flexibility or stiffness of the pendant group must be incorporated into the simulation.

Considering the enhanced reactivity of the pendant functional groups, Fig. 4 shows the fraction of monomer molecules with both double bonds reacted as a function of double-bond conversion for the homopolymerization of a 3-site, 5-site, and 10-site tetrafunctional monomer. Also plotted is the theoretical prediction for a completely homogeneous system with equal reactivity of functional groups. As the size of the monomer molecule is decreased from 10-sites to 3-sites, the reactivity of the pendant double bond is significantly increased. This enhanced reactivity is primarily the result of the close proximity of the pendant double bond to the active radical site. Recall that at lower total double-bond conversions this behavior leads to a higher degree of primary cyclization and loops that generally contribute little to the overall mechanical stability of the network. As the size of the monomer is increased, the local concentration of pendant double bonds begins to approach that of the bulk concentration, which leads to a more equal reactivity of the functional groups. In particular, the 10-site monomer curve begins to approach the homogeneous curve where both double bonds are equally reactive, and a more homogeneous network is formed.

To further illustrate the difference in reactivity of the pendant and monomeric double bonds, the reactivity ratio of the pendant functional groups to the

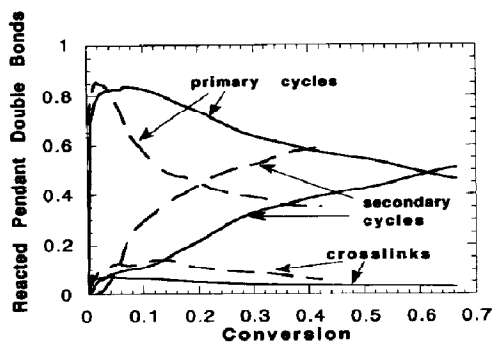


Fig. 3. The fraction of pendant double bonds that become crosslinks, primary cycles, and secondary cycles as a function of double-bond conversion for a 3-site (—) and 5-site (---) monomer.

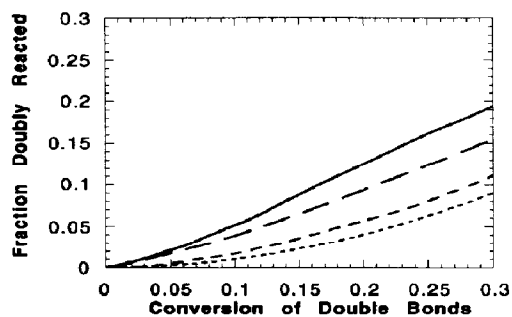


Fig. 4. The fraction of monomers with both functional groups reacted vs double-bond conversion for a 3-site (—), 5-site (---), and 10-site (· · ·) monomer as compared to the homogeneous case (- · - ·).

monomeric functional groups,  $R$ , was calculated from the known concentration of pendant functional groups,  $[P]$ , as a function of the monomeric functional groups,  $[M]$  by

$$R = \frac{2[M]}{[P]} \left( 1 + \frac{d[P]}{d[M]} \right). \quad (1)$$

This equation was derived from the differential species balances on the monomeric and pendant double bonds. The factor of two arises from the stoichiometry since each monomer molecule that reacts decreases the number of monomeric double bonds by two while only increasing the number of pendant double bonds by one. Figure 5 plots this reactivity ratio as a function of the double-bond conversion for different size monomer molecules. Initially, the reactivity of the pendant functional group is one or two orders of magnitude greater than the monomeric functional group, depending on the size of the monomer molecule. In particular, the 3-site monomer has a significantly higher reactivity ratio compared to the 5-site and 10-site monomers illustrating the greater tendency for cyclization and heterogeneity when polymerizing monomer molecules with shorter distances between the functional groups.

In all cases as the reaction proceeds to higher conversions, the reactivity ratio dramatically decreases and approaches or drops below 1. The 10-site monomer's reactivity ratio decreases first, followed by the 5-site and then the 3-site monomers. This decrease in the reactivity ratio results from the inaccessibility of the pendant functional groups to the free radicals as they become embedded and trapped in the microgel regions. Finally, as higher conversions are reached, the concentration of unshielded pendant double bonds becomes so low that the reactivity ratio drops below 1 and the monomeric double-bond reactivity exceeds that of the pendant groups. Polymerization continues until all functional groups, both monomeric and pendant, are essentially embedded in the network and inaccessible to the radicals. A maximum functional group conversion is reached despite the pre-

sence of continued initiation and unreacted functional groups.

In addition to studying the effects of monomer size on the network structure, the rate of polymerization was varied by changing the initiator decay constant to determine the resulting effects on the microstructure. Recall, most homopolymerizations of multifunctional monomers are photoinduced, so the initiator decay constants were chosen to reflect relatively fast initiation rates. Figure 6 illustrates the dependence of the weight average molecular weight on the rate of initiation for the homopolymerization of a 3-site monomer molecule. As the rate of initiation is increased, the average kinetic chain length correspondingly decreases which leads to higher conversions at the gel point. This trend is shown in Fig. 6 as the fastest initiation rates, lowest  $\tau$ 's, have significantly delayed gel point conversion compared to the slower initiation rates. Here,  $\tau$  is the inverse of the initiator decay constant. This data also provides a comparison for some of the earlier kinetic gelation model predictions for the gel point conversion which used "fast" initiation (Hermann *et al.*, 1982; Bansil *et al.*, 1984). "Fast" initiation decays all of the initiator molecules in the initial time step (i.e.  $\tau = 0$ ), which can accurately describe some radiation polymerizations such as initiation by a high-intensity laser pulse. In general, most fast initiation models will predict higher gel point conversions than those predicted by slow initiation because of the differences in the kinetic chain lengths in the network.

In addition to the effect of the initiation rate on the gel point, one should consider how a slow or fast polymerization rate might affect the resulting polymer structure. Figure 7 contains data from four different simulations conducted with initiator decay constants ranging from 1/50 to 1/10000. The fate of the reacted pendant double bond, whether it becomes a crosslink, secondary cycle, or primary cycle, is plotted as a function of double-bond conversion. In Fig. 7, no general trends existed in the curves as a function of the initiation rate, and the differences seen in the curves were merely simulation to simulation variations. The conclusion is that the differences in these systems lie

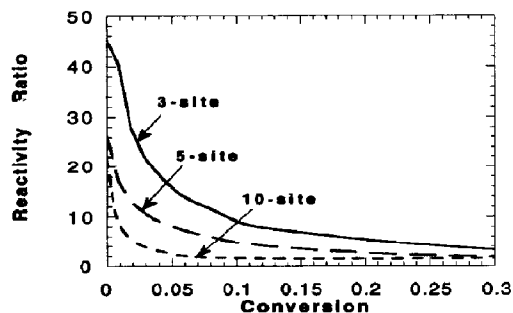


Fig. 5. The relative reactivity of the pendant functional group to the monomeric functional group as a function of double-bond conversion for different sized monomer molecules: 3-site (—), 5-site (---), and 10-site (···).

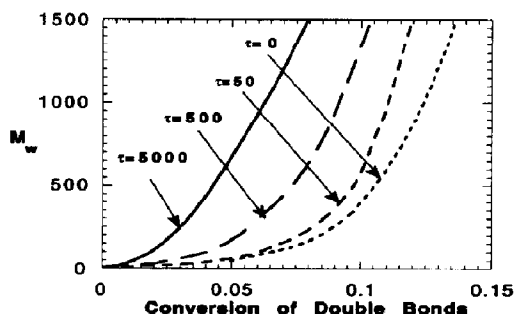


Fig. 6. The weight average molecular weight vs conversion of double bonds for various initiator decay times.

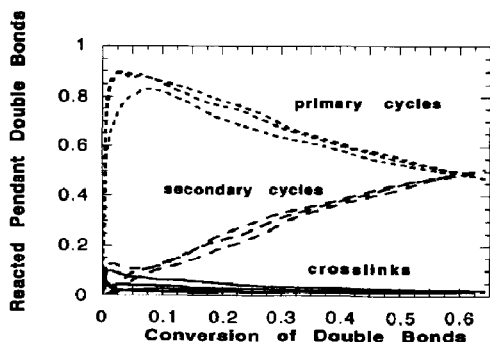


Fig. 7. The fraction of reacted pendant double bonds that become primary cycles (· · · · ·), secondary cycles (---), and crosslinks (—) as a function of double-bond conversion for different initiator decay times.

mainly in the number and size of the microgel regions, but the microgel regions themselves will have generally the same structure, regardless of size. Thus, faster initiation rates will produce smaller and many more microgel regions as compared to slower initiation rates, but the microgels will be similar in structure.

Finally, to conclude the studies for the homopolymerizations, the effects of void volume (e.g. free volume or solvent) on the network microstructure were determined. In general, the mobility of the system was increased or decreased by controlling the fraction of void sites in the matrix. As the void volume was increased, the relative reactivity of the pendant double bond increased, and the fraction of doubly reacted monomers increased. This trend is shown in Fig. 8 for a 3-site monomer molecule where the fraction of doubly reacted monomer is plotted vs double-bond conversion for five different void volume fractions, 0, 0.15, 0.45, 0.70, and 0.90. For the case of 90% void volume, the system approaches the highly heterogeneous limit where for every monomeric functional group that reacts, a pendant functional group also reacts. Whereas when the void volume is decreased, the trend is towards equal reactivity of the functional groups. Hence, when polymerizing multifunctional monomers, the most homogeneous networks will be formed from a solvent-free system or a system with a lower average free volume. Additionally, the solvent-monomer compatibility, though not included in this simulation, would affect the network homogeneity.

Figure 9 emphasizes the differences in the reactivities of the functional groups by plotting the reactivity ratio as a function of double-bond conversion for different void volumes. Again, we see the two orders of magnitude difference between the pendant functional group and the monomeric functional group at the beginning of the reaction. In general, systems with higher void volume fractions have higher reactivity ratios and a delay in the decrease of the reactivity ratio. Many of the effects of increased void volume

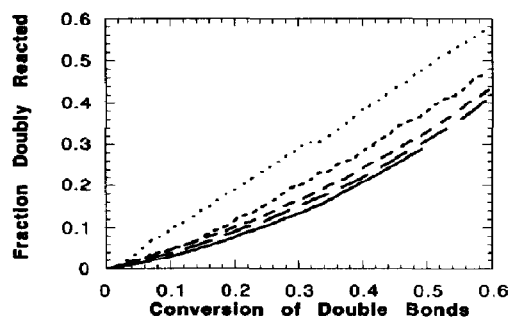


Fig. 8. The fraction of monomers with both functional groups reacted as a function of double-bond conversion for void volume fractions of 0.90 (· · · · ·), 0.70 (---), 0.45 (- · - · -), 0.15 (—), and 0 (—).

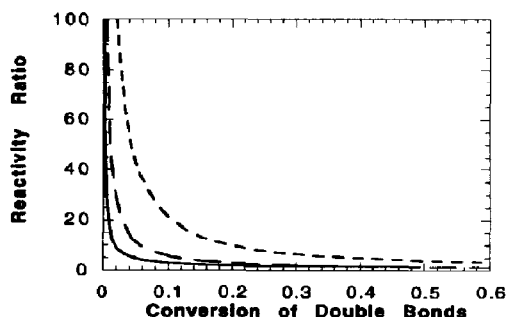


Fig. 9. The relative reactivity of the pendant functional group to the monomeric functional group vs conversion of double bonds for void volume fractions of 0.45 (---), 0.15 (—), and 0 (—).

depicted in the reactivity ratio in Fig. 9 can be explained in a manner analogous to the size effects described in Fig. 5. As the size of the monomer molecule is decreased, the local concentration of the pendant functional group is effectively increased which leads to a higher reactivity ratio. Similarly, by introducing a greater void volume, a higher local concentration of the pendant functional group results along with an enhanced reactivity of the pendant group.

Figure 10 compares the experimental data of Kloosterboer *et al.* (1984) photopolymerizing 1,6-hexanediol diacrylate with the simulation results for the fraction of reacted monomer in the polymer with both functional groups reacted vs the conversion of monomer. The predictions are plotted for two different void volume fractions, 0.15 and 0.45, and the homogeneous, theoretical curve derived from equal reactivity of the functional groups is also shown. The kinetic gelation model appears to predict quite accurately the early reactivity of the pendant functional groups as the ratio of doubly reacted monomer to reacted monomer rapidly rises to a value of 0.20 and remains relatively constant. The homogeneous curve, however, significantly underestimates the reactivity of

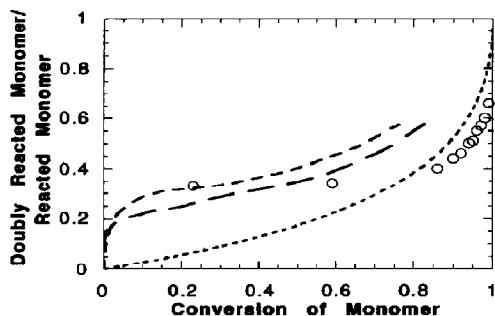


Fig. 10. Fraction of reacted monomer in the polymer with both functional groups reacted vs conversion of monomer for two different void volume fractions 0.45 (---) and 0.15 (—). The open circles represent the experimental data of Kloosterboer *et al.* (1984) photopolymerizing 1,6-hexanediol diacrylate. The theoretical curve for equal reactivity of the functional groups is also plotted (-----).

the pendant functional groups from the beginning of the reaction up to 80% conversion of the monomer. Whereas at higher conversions, the kinetic gelation model seems to underpredict the effect of shielding on the reactivity of the pendant double bonds. The model tends to overestimate somewhat the reactivity of the pendant double bonds at these higher conversions, where shielding becomes more significant. Another explanation is the inability of the kinetic gelation model to account for consumption of volume during the polymerization. If some mechanism for volume shrinkage could be incorporated into the model, we might see a shifting in the curve as illustrated by the differences in the 0.45 and 0.15 void site fraction simulations. Even with this limitation, the kinetic gelation model certainly provides a good approximation of the functional group reactivity in the high crosslinking regime where the homogeneous assumption is clearly invalid.

In addition to homopolymerizations of tetrafunctional monomers, the copolymerizations of tetrafunctional and difunctional monomers were studied to determine the effects of relative composition of the monomers on the network structure. For these simulations, tetrafunctional monomers occupied 3-sites, whereas the difunctional monomers occupied only 1 lattice site. First, the dependence of the gel point conversion on the concentration of the tetrafunctional monomer in the comonomer feed was predicted for 1%, 10%, 25%, and 75% of tetrafunctional monomer. Figure 11 shows this dependence by plotting the weight average degree of polymerization as a function of double-bond conversion for an initiator decay constant of  $1/500$ . Comparing the 75% tetrafunctional monomer system to the homogeneous system in Fig. 1, the systems gel at approximately the same conversion and the molecular weight development is nearly identical, as one might expect since both systems are in the high crosslinking regime.

Looking at the effect of composition on the gel point, the gel point is significantly shifted to higher

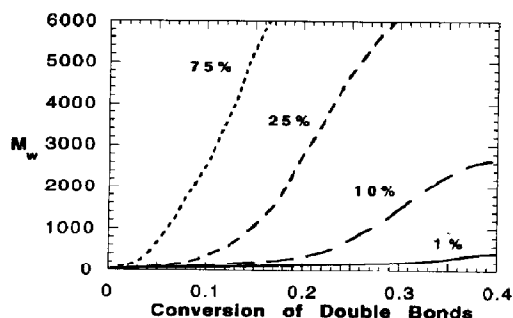


Fig. 11. The weight average molecular weight as a function of double-bond conversion for different amounts of tetrafunctional monomer in the comonomer feed.

conversions as the amount of tetrafunctional monomer is decreased. In the case of 1% crosslinker, the system is just approaching the gel point at 0.35–0.40 conversion of the double bonds. This behavior agrees with our physical intuition that as the amount of tetrafunctional monomer is decreased, the formation of an infinite network will be delayed because the number of molecules that can act as crosslinks is significantly reduced. We do not wish to imply that a kinetic gelation is the best model for the case of the copolymerization with only 1% tetrafunctional monomer. Clearly, for this low crosslinking density, kinetic and statistical models would be more appropriate. Here, we have included the 1% case only as a basis for comparison to higher crosslinking densities.

A further point of interest lies in the "efficiency" of crosslinking of the tetrafunctional monomer. The number of pendant double bonds that forms crosslinks was normalized by the number of tetrafunctional monomers, and thus the maximum possible number of crosslinks. This fraction and the absolute number of crosslinks (on a  $40 \times 40 \times 40$  lattice) vs conversion of the tetrafunctional monomer is plotted in Fig. 12 for different comonomer compositions. As the concentration of the tetrafunctional monomer is increased, an overall decrease in the fraction of crosslinks that are formed from the reacted pendant double bonds occurs. In other words, lowering the concentration of the tetrafunctional monomer in the system seems to lead to a higher "efficiency" of crosslinking for the pendant double bonds that react. Recalling from Figs 3 and 7 that the primary reaction of the pendant double bonds at low conversions is primary cyclization, systems with less crosslinker will have a reduced fraction of pendant double bonds that form primary cycles and an increased fraction of crosslinks.

Also plotted in Fig. 12 is the absolute number of crosslinks vs conversion of tetrafunctional monomer. These curves are to emphasize that the mechanical properties of the system are largely determined by the absolute number of crosslinks and secondary cycles in the system. Hence, increasing the fraction of tetrafunctional monomer enhances the mechanical properties of the network because a greater absolute number of

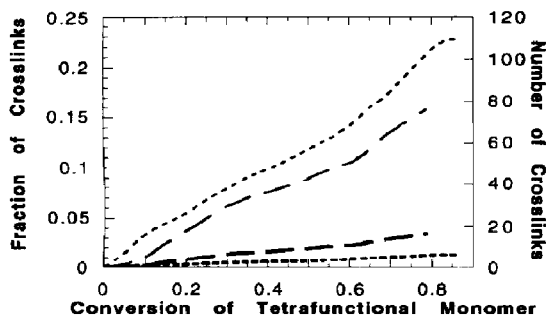


Fig. 12. The fraction of reacted pendant double bonds that form crosslinks normalized by the number of tetrafunctional monomers vs conversion of tetrafunctional monomer for 10% (---) and 75% (····) tetrafunctional monomer in the comonomer mixture. In addition, the absolute number of crosslinks vs conversion of tetrafunctional monomer for 10% (---) and 75% (····) tetrafunctional monomer.

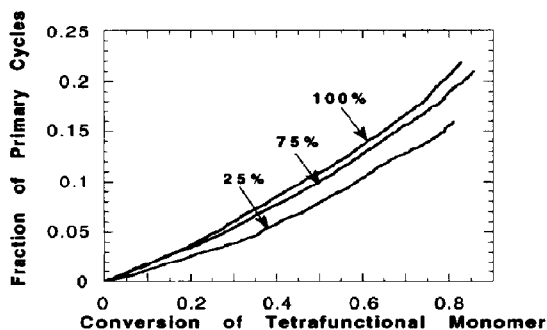


Fig. 13. The fraction of reacted pendant double bonds that form primary cycles normalized by the number of tetrafunctional monomers vs conversion of tetrafunctional monomer for various comonomer compositions. The percentages represent the relative amount of the tetrafunctional monomer in the mixture.

crosslinks results, but the efficiency of the mechanical enhancement is significantly reduced because of primary and secondary cyclization. Figure 13 shows the number of primary cycles normalized by the number of tetrafunctional monomers as a function of conversion of tetrafunctional monomer for the cases of 100%, 75%, and 25% tetrafunctional monomer. As expected, an increase in the relative amount of crosslinker, and likewise pendant double bonds, leads to higher rates of primary cyclization in the more cross-linked networks.

Figure 14 compares simulation results to some of the experimental data of Landin and Macosko (1988) polymerizing methyl methacrylate and ethylene glycol dimethacrylate. Their experimental data were primarily in the low functional group conversion regime (i.e. less than 7% double-bond conversion). The simulated curve shown is for the copolymerization of 99% 1-site difunctional monomer and 1% 3-site tetrafunctional monomer with an initiator con-

centration of 0.003 and a decay constant of  $1/500$ . The model seems to predict reasonably well the consumption of pendant double bonds and the trends in the gel point conversion.

So far, only a fixed size (3 sites) of the tetrafunctional monomer has been considered. Figure 15 illustrates the effect of size of the crosslinker on the structure of the polymer network for a copolymerization of 75% difunctional and 25% tetrafunctional monomer. The fraction of reacted pendant double bonds that form crosslinks is plotted as a function of conversion of the tetrafunctional monomer. As the size of the tetrafunctional monomer is increased, the pendant double bond is further removed from the immediate location of the propagating radical. As with the homopolymerization of the tetrafunctional monomer, this distance greatly reduces the probability of the formation of the small primary cycles that result when the propagating radical reacts with the pendant double bond on the same monomer molecule after only a few or one propagation steps.

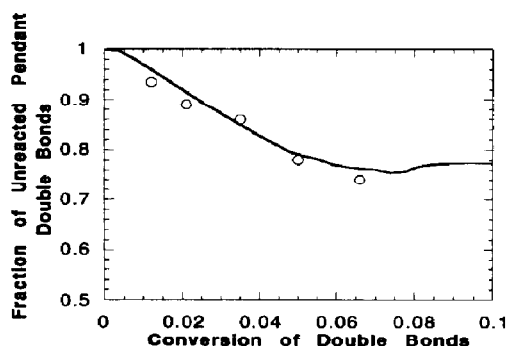


Fig. 14. The fraction of unreacted pendant double bonds as a function of double-bond conversion comparing the experimental data (o) of Landin and Macosko (1988) copolymerizing 1.13 wt% ethylene glycol dimethacrylate in methyl methacrylate to simulated results (—).

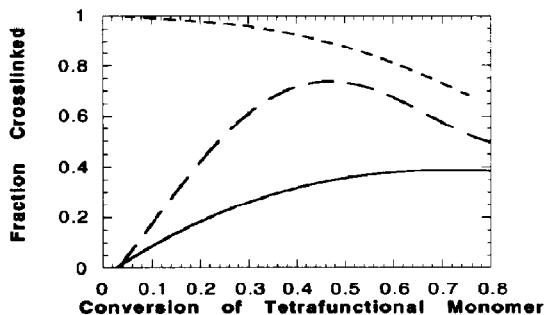


Fig. 15. The fraction of pendant double bonds reacted that form crosslinks vs conversion of tetrafunctional monomer for a copolymerization of 25/75 tetrafunctional/difunctional monomer varying the size of the tetrafunctional monomer. 10-site (---), 5-site (— — —), and 3-site (—) tetrafunctional monomers.

The differences between a 10-site crosslinker and 3-site crosslinker are quite dramatic when looking at the differences between the fraction of crosslinks that are formed. The 10-site tetrafunctional monomer has its pendant double bonds consumed primarily in the crosslinking reaction, whereas the 3-site tetrafunctional monomer has its pendant double bonds consumed mainly in primary cyclization. To produce the most highly crosslinked network, a balance exists between increasing the efficiency of crosslinking by increasing the size of the tetrafunctional monomer and the greater molecular weight between crosslinks caused by the larger tetrafunctional monomer molecules.

### CONCLUSIONS

Results have been presented from a new kinetic gelation simulation. These results are provided as a way of obtaining insight into the heterogeneity during polymerizations involving large amounts of tetrafunctional monomer. The dependence of the pendant double bond reactivity, i.e. the heterogeneity, was ascertained as a function of reaction conditions such as monomer size, fraction of tetrafunctional monomer, conversion, amount of free volume/solvent, and initiation rate. These results indicate that pendant double bonds will be most reactive in systems with smaller monomer molecules at low double-bond conversion in the presence of a large amount of solvent and no difunctional monomer. Unfortunately, it was also shown that the increase in reactivity of these pendant double bonds was due entirely to the formation of primary cycles. That is, the pendant double bonds that react form a large amount of primary cycles that generally do not contribute significantly to the mechanical strength or network development. This effect was evidenced by many factors including a significant increase in the gel point conversion as monomer size was decreased or as the amount of free volume was increased. The effect of initiation rate was found to be primarily an effect on the microgel size rather than the microgel structure. The structure of the microgels remained unchanged as the initiation rate was changed over more than an order of magnitude; however, a delay in the gel point conversion was seen at higher initiation rates because of the shorter kinetic chains. With respect to copolymerization behavior, simulation results agreed with experimental observations in predicting that as the amount of tetrafunctional monomer is decreased, the crosslinking efficiency of the pendant double bond increases. Despite the increased efficiency, the absolute number of crosslinks continues to drop as the fraction of tetrafunctional monomer is decreased.

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### NOTATION

[P]	concentration of pendant functional groups
[M]	concentration of monomeric functional groups
R	relative reactivity of the pendant functional groups to the monomeric functional groups

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