Control of network structure in free-radical crosslinking copolymerization

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A kinetic model which describes the network structure development during free-radical crosslinking copolymerization is proposed. The model was successfully applied to various batch copolymerization systems such as methyl methacrylate/ethylene glycol dimethacrylate, styrene/*p*-divinylbenzene, styrene/ethylene glycol dimethacrylate, and acrylamide/*N*,*N*′-methylene-bis-acrylamide. The model calculations suggest that polymer networks synthesized by free-radical copolymerization are, in general, inhomogeneous at least on a microscopic scale. This model can be used to control the network structure, and a semi-batch policy to produce homogeneous polymer networks is proposed.

(Keywords: crosslinking; gels; copolymerization; cyclization; mathematical model; crosslinking density distribution)

INTRODUCTION

Recently, the polymeric network has become a very attractive research area simultaneously combining fundamental and applied topics of great interest. The synthesis of network polymers with controlled structure may permit the development of a whole range of useful new polymer products. This has been motivated in part by the phenomenal success achieved by superabsorbent polymers, which can absorb as much as 1000 g of water per gram of polymer.

Since the physical properties of polymeric networks strongly depend on the polymerization kinetics, an understanding of the kinetics of network formation is essential. As for the modelling of network formation, various models have been proposed[1–6] since the pioneering work of Flory[7–11] and Stockmayer[12,13]. Quite often, basic theories have been developed for step-growth polymerization as the simplest mechanism of network formation in which an equilibrium system can be assumed, and these theories have been applied to other mechanisms of network formation with minor modifications. Generally, an *f*-functional polycondensation system may be well described by these statistical approaches, however, agreement with data for free-radical copolymerization is usually poor. This is partly attributed to the characteristic reaction scheme of free-radical polymerization, namely, the system is a non-equilibrium one and crosslinkage is formed only through a polymer radical whose concentration is fairly low and whose lifetime is very short, and therefore, the existence of other chains of different ages during its growth has a significant effect on the kinetics of network formation.

On the other hand, in order to describe the kinetic features of the reaction systems, the percolation theory[14–19], which is considered to be equivalent to a non-mean-field theory, has been applied to polymeric gelation[20–26]. These approaches may work well to describe the behaviour near the critical threshold p_c(gel point) where system-specific features are not important. However, present percolation models are far from simulating actual network formation, since the bonds are too rigid, the movement of molecules is too suppressed and chemical rules of bond formation are quite often ignored.

Recently, a new kinetic theory based on a mean-field theory for free-radical copolymerization with long chain branching and crosslinking has been proposed[27–33]. This kinetic model accounts for the history of the generated network structure and can be used for calculations of various important properties such as onset of gelation, weight fraction of gel and sol, number- and weight-average chain length of sol fraction, crosslinking density in sol and gel fractions, etc. In this paper, we focus on the network structure development during crosslinking copolymerization. An important feature of this kinetic model is that it proves the existence of and permits the calculation of the crosslinking density distribution. At present, the statistical models based on a mean-field theory cannot be used for these kinds of calculations since they inevitably employ the assumption that the crosslinking density is the same for all polymer chains. The existence of a crosslinking density distribution with a significant variance implies that the polymer network is inhomogeneous at least on a microscopic scale. For example, polyacrylamide gels have been shown to be

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inhomogeneous in various experimental studies[34]. In this paper, a kinetic model for network structure development is derived, and after discussing the applicability of the present model to a real copolymerization system, a semi-batch policy to produce homogeneous polymer networks is proposed.

MODEL DEVELOPMENT

Kinetics of crosslinking

The primary polymer molecule[11] is used to observe the history of the generated network structure. The primary polymer molecule is a rather imaginary molecule which would exist if all crosslinks connected to it were severed, thus the primary polymer molecule itself is a linear polymer. For the formation of primary polymer molecules, the pseudo-kinetic rate constant method[27,31–33,35] in which the kinetic treatment of a multi-component polymerization reduces to that of a homopolymerization is used. The crosslinking density ρ^{f} is defined as the fraction of units which are crosslinked.

$$\rho^{\mathrm{f}} = \frac{(\text{number of crosslinked units})}{(\text{total number of units bound in the polymer chain})} \tag{1}$$

The crosslinked unit is a unit which bears a tri-branching point[11]. Let us consider the simple example shown in *Figure 1*. Linear polymer molecules A and B are primary polymer molecules. The crosslinking densities for each primary polymer molecule are given by $\rho^{\mathrm{f}}_{\mathrm{A}} = 1/4$ and $\rho^{\mathrm{f}}_{\mathrm{B}} = 1/5$. The overall (accumulated) crosslinking density $\bar{\rho}^{\mathrm{f}}$ is 2/9. From the point of view of physical properties of a polymer network, ρ^{f} is important. However, once a divinyl monomer unit is bound in the polymer chain, its reactivity may not be the same as for the monomeric double bonds due to chemical effects and/or physical effects such as steric hindrance known as the 'shielding effect'[36] and the excluded volume effect[37]. In such cases it is important to know which primary polymer molecule the crosslinked divinyl monomer originally belonged to. In order to facilitate the derivation of a mathematical expression, we define another crosslinking density ρ which is defined with respect to the number of monomeric units.

$$\rho = \frac{(\text{number of crosslinked units})}{(\text{total number of } \textit{monomeric units} \text{ bound in the polymer chain})} \tag{2}$$

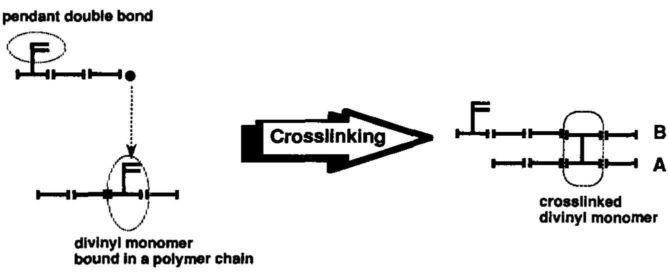

Figure 1 Simple example of crosslinked polymer formation. The primary polymer molecule A consists of four units and has four monomeric units, thus $\rho^{\mathrm{f}}_{\mathrm{A}} = 1/4$ and $\rho_{\mathrm{A}} = 1/4$. The primary polymer molecule B consists of five units but has four monomeric units, since one of the units was originally a pendant double bond on A, and therefore $\rho^{\mathrm{f}}_{\mathrm{B}} = 1/5$ and $\rho_{\mathrm{B}} = 1/4$

In the simple molecule shown in *Figure 1*, since the crosslinked divinyl monomer was originally bound in the primary polymer molecule A, the crosslinking densities for each primary polymer molecule are given by $\rho_{\mathrm{A}} = 1/4$ and $\rho_{\mathrm{B}} = 1/4$. The overall crosslinking density is $\bar{\rho} = 2/8 = 1/4$. When the crosslinking density is much smaller than unity, there is virtually no difference between the two definitions for crosslinking density. However, if a high mole fraction of divinyl monomer is used, one needs to carefully distinguish these definitions as has been done in this simple example. The relationship between these definitions will be shown later.

Now, let us consider the history of a primary polymer molecule. In free-radical copolymerization, each primary polymer molecule experiences a different history of crosslinking and cyclization, and therefore, the crosslinking densities of primary polymer molecules whose time of formation is different may not be the same. Let us assume that the primary polymer molecule C shown in *Figure 2* was formed at time t_b when the accumulated number of moles of monomers bound in polymer chains is b. At time t_n when the accumulated number of moles of monomers bound in polymer chains is n ($n > b$), the primary polymer molecule D adds to a pendant double bond on the primary polymer molecule C, which results in crosslinkage between two primary polymer molecules. In this case from the point of view of primary polymer molecule D, this crosslinkage is formed during its growth, so let us call the density of this type of crosslinking the 'instantaneous crosslinking density', $\rho_{\mathrm{i}}(n)$, which is solely the function of the time of formation. On the other hand, from the point of view of the primary polymer molecule C, the identical crosslinkage is formed but after it was formed, so let us call this type of crosslinking density 'additional crosslinking density', $\rho_{\mathrm{a}}(b, n)$, which is a function of both the time of formation and the present time. Here, $\rho_{\mathrm{a}}(b, n)$ is the additional crosslinking density experienced in the time interval t_b to t_n. At time t_n, the crosslinking density of the primary polymer molecules which were formed at t_b is given by the sum of the two types of crosslinking density:

$$\rho(b, n) = \rho_{\mathrm{i}}(b) + \rho_{\mathrm{a}}(b, n) \tag{3}$$

To calculate the additional crosslinking density, one can formulate the following equation assuming a homogeneous system:

$$N_b[\rho_{\mathrm{a}}(b, n + \Delta n) - \rho_{\mathrm{a}}(b, n)] = k_{\mathrm{p}}^{*0}(n)[F_2(b) - \rho_{\mathrm{a}}(b, n) - \rho_{\mathrm{c}}(b, n)]N_b[\mathrm{R}^{\cdot}]_n \Delta t \tag{4}$$

where N_b is the total number of monomeric units bound in the primary polymer molecule formed at t_b, $F_2(b)$ is the instantaneous mole fraction of divinyl monomer bound in the polymer chains formed at t_b, $\rho_{\mathrm{c}}(b, n)$ is the mole fraction of pendant double bonds wasted by

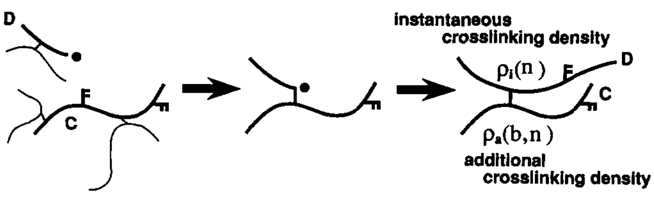

Figure 2 Schematic drawing of the crosslinking process

cyclization reactions for the primary polymer molecules which were formed at t_b, $[\mathrm{R}^{\cdot}]_n$ is the total polymer radical concentration at t_n, and k_p^{*0} is defined by:

$$k_p^{*0} = k_{p13}^{*}\phi_1^{\cdot} + k_{p23}^{*}\phi_2^{\cdot} + k_{p33}^{*}\phi_3^{\cdot} \tag{5}$$

where k_{pi3}^{*} is the kinetic rate constant for crosslinking reaction in which radical of type i reacts with the pendant double bond, and $\phi_i^{\cdot}$ is the mole fraction of polymer radical of type i. Subscript 1 is used to designate monovinyl monomer, 2 is used for divinyl monomer and 3 is used for pendant double bonds.

Strictly, the rate constant for crosslinking reaction should be considered chain length and structure dependent due to steric hindrance and/or excluded volume effects between large molecules. However, since smaller polymer radicals with high mobility exist in greater numbers, it may be reasonable to neglect the effect of the decreased reaction rate between large molecules. (The decrease in reaction rate between large molecules would have a significant effect on the delay of the gel point, however.)

From equation (4), it is straightforward to derive the fundamental equation for the additional crosslinking density as follows:

$$\frac{\partial \rho_a(b,n)}{\partial n} = \frac{k_p^{*0}(n)[F_2(b) - \rho_a(b,n) - \rho_c(b,n)]}{k_p(n)[\mathrm{M}]_n V(n)} \tag{6}$$

where $[\mathrm{M}]_n$ is the total monomer concentration at t_n, $V(n)$ is the reaction volume at t_n and $k_p(n)$ is the pseudo-kinetic rate constant for propagation which is defined as follows[27,31–33,35]:

$$k_p = (k_{11}f_1 + k_{12}f_2)\phi_1^{\cdot} + (k_{21}f_1 + k_{22}f_2)\phi_2^{\cdot} + (k_{31}f_1 + k_{32}f_2)\phi_3^{\cdot} \tag{7}$$

where k_{ij} is the propagation rate constant in which the radical of type i reacts with the double bond of type j, and f_i is the mole fraction of monomer of type i.

Since all additional crosslinking points need to have their own partners, namely, instantaneous crosslinking points, the instantaneous crosslinking density is given by the integration over all formation time. Therefore, the crosslinking density of the primary polymer molecules which are formed at time t_u is given by the following equation (see *Figure 3* for details):

$$\rho_i(u)\,\Delta u = \int_0^u [\rho_a(b, u + \Delta u) - \rho_a(b,u)]\,\mathrm{d}b \tag{8'}$$

$$\rho_i(u) = \int_0^u \frac{\partial \rho_a(b,u)}{\partial u}\,\mathrm{d}b = \frac{k_p^{*0}(u)u}{k_p(u)[\mathrm{M}]_u V(u)}[\bar{F}_2(u) - \bar{\rho}_a(u) - \bar{\rho}_c(u)] \tag{8}$$

where all superscript bars are used to designate accumulated values, and, for example, $\bar{\rho}_a(u)$ is given by:

$$\bar{\rho}_a(u) = \frac{1}{u}\int_0^u \rho_a(b,u)\,\mathrm{d}b \tag{9}$$

and $\bar{\rho}(u)$, $\bar{\rho}_i(u)$ and $\bar{\rho}_a(u)$ can be related as follows:

$$\bar{\rho}(u) = \bar{\rho}_i(u) + \bar{\rho}_a(u) = 2\bar{\rho}_i(u) = 2\bar{\rho}_a(u) \tag{10}$$

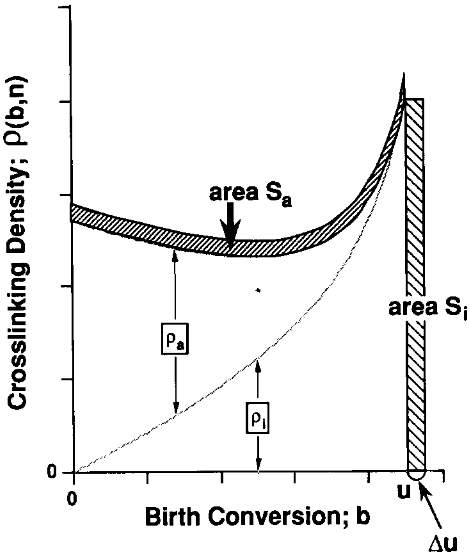

Figure 3 Schematic drawing showing the fundamental concept for the derivation of the instantaneous crosslinking density. Since all additional crosslinking points need to have their own partners, the area S_i must be equal to the area S_a, and therefore equation (8′) can be derived

Crosslinking densities given above are defined with respect to the number of monomeric units, however, from the physical point of view the crosslinking density defined with respect to the number of units, $\rho^f(b,n)$, may be more important. The relationship between $\rho(b,n)$ and $\rho^f(b,n)$ is given by:

$$\rho^f(b,n) = \frac{\rho(b,n)}{1 + \rho_i(b)} \tag{11}$$

Using equations (3), (6), (8) and (11) it is possible to calculate the crosslinking density distribution as a function of the time of formation of the primary polymer molecule. Some of the model calculations can be found elsewhere[28–33,38]. The existence of a crosslinking density distribution is a very important feature of polymer networks synthesized in a kinetically controlled reaction system. Models for network formation in which an equilibrium system is assumed inevitably employ the assumption that the crosslinking density is the same for all polymer chains. However, this assumption is not strictly valid for a batch free-radical crosslinking copolymerization except under Flory's simplifying assumptions[11], namely: (1) the reactivities of all types of double bonds are equal; (2) all double bonds react independently of one another; and (3) there are no intramolecular reactions in finite molecules. For these limiting conditions in a batch reactor, all primary polymer molecules possess equal crosslinking densities independent of t_b as was proven earlier[30,33]. However, in free-radical crosslinking copolymerization, the following non-ideal effects are important, namely: (1) differences in the reactivities of monomeric double bonds; (2) differences in the reactivity of pendant double bonds relative to the monomeric double bond in a divinyl monomer; and (3) the effect of cyclization. The more significant the above effects are, the larger is the variance of the crosslinking density distribution. The existence of a crosslinking density distribution shows that polymer networks synthesized by free-radical crosslinking copolymerization are inhomogeneous at least on a microscopic scale.

Kinetics of cyclization

One of the important features of cyclization is that it is controlled not by the conventional rate law using average concentrations of functional groups, but by conformational statistics of the sequence of bonds. In our formalism, it is convenient to divide the cyclization reactions into two groups, namely, primary and secondary cyclization (*Figure 4*). With primary cyclization the cycle forms within one primary polymer molecule, while with secondary cyclization it is formed between two or more primary polymer molecules. The mathematical importance of the difference between primary and secondary cyclization is that primary cyclization is solely a function of t_b, while secondary cyclization is a function of both t_b and the present time.

Primary cyclization. Now we are to assume that the molecular conformation of a primary polymer molecule is not affected by the bondings formed between primary polymer molecules as well as by those within the primary polymer molecule. This assumption may be applicable for lightly crosslinked polymer systems. If a radical centre on a primary polymer molecule is located at the origin of coordinates, the probability that a randomly selected monomeric unit bound on the identical primary polymer molecule resides in the volume $\mathrm{d}V$ at a distance R is given by the following Gaussian distribution:

$$p(R)\,\mathrm{d}V=\left(\frac{3}{2\pi\langle R^2\rangle}\right)^{3/2}\exp\left[-\frac{3}{2}\left(\frac{R^2}{\langle R^2\rangle}\right)\right]\mathrm{d}V \qquad (12)$$

where $\langle R^2\rangle$ is the average square of the end-to-end distance. $\sqrt{\langle R^2\rangle}$ follows the following scaling law[39,40].

$$\sqrt{\langle R^2\rangle}=cN^{\alpha} \qquad (13)$$

where N is the number of monomeric units, and c and α are constants. The prefactor c depends on the detailed monomer structure and on the solvent chosen, while the exponent α shows a universal feature. The exponent α is close to $3/5$ in a good solvent, and is $1/2$ in a θ-solvent.

In order for the primary cyclization to be formed, $R=0$.

$$p(0)\,\mathrm{d}V=\left(\frac{3}{2\pi}\right)^{3/2}\left(\sqrt{\langle R^2\rangle}\right)^{-3\alpha}\mathrm{d}V$$
$$=AN^{-3\alpha}\,\mathrm{d}V \qquad (14)$$

where A is a constant.

Equation (14) shows that smaller cycles have a better chance of formation than larger ones. The probability of forming a cycle for the primary polymer radical with chain length s is given by:

$$P_{\mathrm{c},s}=\sum_{N=1}^{s}k'_{\mathrm{cp}}F_2N^{-3\alpha} \qquad (15)$$

where F_2 is the instantaneous mole fraction of divinyl monomer bound in the polymer chain.

Therefore, the expectation of the number of cycles formed for a primary polymer molecule with chain length r is given by:

$$E(n_{\mathrm{c}})=\sum_{s=1}^{r}\sum_{N=1}^{s}k'_{\mathrm{cp}}F_2N^{-3\alpha}$$
$$\cong\int_1^r\int_1^s k'_{\mathrm{cp}}F_2y^{-3\alpha}\,\mathrm{d}y\,\mathrm{d}s$$
$$=\frac{k'_{\mathrm{cp}}F_2}{1-3\alpha}\left(\frac{r^{2-3\alpha}-1}{2-3\alpha}+1-r\right) \qquad (\alpha\neq 1/3, 2/3) \qquad (16)$$

The primary cyclization density, ρ_{cp}, for the primary polymer molecule with chain length r is given by:

$$\rho_{\mathrm{cp}}=E(n_{\mathrm{c}})/r$$
$$=\frac{k'_{\mathrm{cp}}F_2}{1-3\alpha}\left[\frac{r^{2-3\alpha}-1}{(2-3\alpha)r}+\frac{1}{r}-1\right] \qquad (\alpha\neq 1/3, 2/3) \qquad (17)$$

As shown in *Figure 5*, (ρ_{cp}/F_2) is approximately constant over a sufficient range of chain lengths except for oligomeric chain lengths, and therefore, as a first approximation, $\rho_{\mathrm{cp}}(b)$ is given by:

$$\rho_{\mathrm{cp}}(b)=k_{\mathrm{cp}}F_2(b) \qquad (18)$$

The overall primary cyclization density at time t_n is therefore given by:

$$\bar{\rho}_{\mathrm{cp}}(n)=k_{\mathrm{cp}}\bar{F}_2(n) \qquad (19)$$

Quite often, the reactivity of divinyl monomer is higher than that of monovinyl monomer (since one divinyl monomer possesses two double bonds in a monomeric unit), so that the primary cyclization density may be a

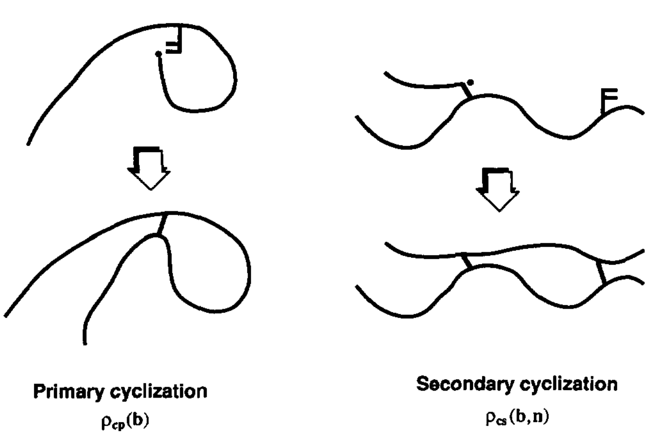
Primary cyclization
$\rho_{\mathrm{cp}}(b)$
Secondary cyclization
$\rho_{\mathrm{cs}}(b,n)$

Figure 4 Classification of cyclization processes

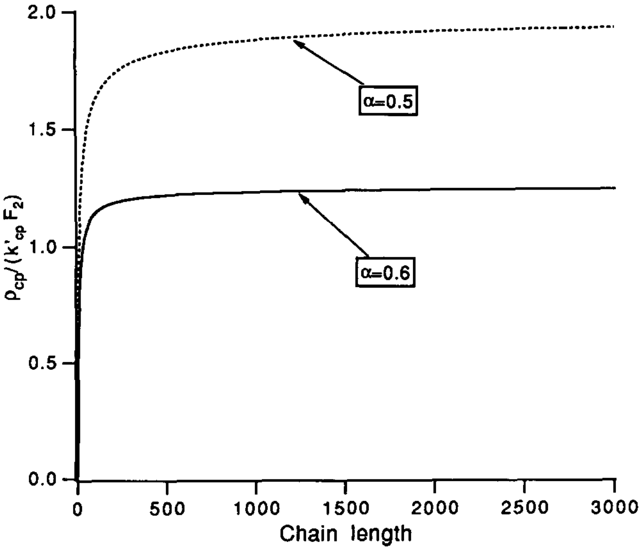

Figure 5 Effect of chain length of the primary polymer molecule on the primary cyclization

maximum in the initial stages of polymerization. The applicability of equation (18) at zero monomer conversion is shown elsewhere[32,33,38].

Secondary cyclization. Although secondary cyclization is also determined by chain conformational statistics like primary cyclization, at present it seems a formidable task to describe the conformation of all chains in a networked polymer system. Instead of doing this, it may be convenient to consider the average number of secondary cycles per crosslink, $\eta(b,n)$, since it is necessary to have crosslinkage in order for secondary cyclization to occur (*Figure 6*). The secondary cyclization of additional type, $\rho_{\mathrm{cs,a}}(b,n)$, and that of instantaneous type, $\rho_{\mathrm{cs,i}}(b)$, are given by:

$$\frac{\partial \rho_{\mathrm{cs,a}}(b,n)}{\partial n} = \eta(b,n)\frac{\partial \rho_{\mathrm{a}}(b,n)}{\partial n} \tag{20}$$

$$\rho_{\mathrm{cs,i}}(b) = \int_0^b \frac{\partial \rho_{\mathrm{cs,a}}(y,b)}{\partial b}\,\mathrm{d}y \tag{21}$$

At time t_n, the secondary cyclization density for the primary polymer molecules formed at time t_b is given by the sum of these two types of secondary cyclization density.

$$\rho_{\mathrm{cs}}(b,n) = \rho_{\mathrm{cs,i}}(b) + \rho_{\mathrm{cs,a}}(b,n) \tag{22}$$

Since primary cycles are quite often formed by small numbers of monomeric units, they may be considered ineffective in adding to elastic properties of gel molecules. However, it may be reasonable to consider that not only the crosslinkages but also the secondary cyclizations are elastically effective, since they are formed between primary polymer molecules. Let us call the sum of crosslinking density, $\rho(b,n)$, and secondary cyclization density, $\rho_{\mathrm{cs}}(b,n)$, the 'elastic crosslinking density', $\rho_{\mathrm{el}}(b,n)$:

$$\rho_{\mathrm{el}}(b,n) = \rho(b,n) + \rho_{\mathrm{cs}}(b,n) \tag{23}$$

$$\rho_{\mathrm{el,a}}(b,n) = \rho_{\mathrm{a}}(b,n) + \rho_{\mathrm{cs,a}}(b,n) \tag{24}$$

$$\rho_{\mathrm{el,i}}(b) = \rho_{\mathrm{i}}(b) + \rho_{\mathrm{cs,i}}(b) \tag{25}$$

The elastic crosslinking density $\rho_{\mathrm{el}}(b,n)$ does not necessarily equal the elastically effective crosslinking density[11], since we do not consider the chain entanglement which may be effective in terms of the elasticity, and the dangling chains which are not effective. In terms of the number of units, the elastic crosslinking density $\rho_{\mathrm{el}}^{\mathrm{f}}(b,n)$ is given by:

$$\rho_{\mathrm{el}}^{\mathrm{f}}(b,n) = \frac{\rho_{\mathrm{el}}(b,n)}{1 + \rho_{\mathrm{el,i}}(b)} \tag{26}$$

From equations (6), (8), (18), (20) and (21) the fundamental equations for the elastic crosslinking density of additional and instantaneous types are given by:

$$\frac{\partial \rho_{\mathrm{el,a}}(b,n)}{\partial n} = [1+\eta(b,n)]\frac{k_{\mathrm{p}}^{*0}(n)[(1-k_{\mathrm{cp}})F_2(b) - \rho_{\mathrm{el,a}}(b,n)]}{k_{\mathrm{p}}(n)[\mathrm{M}]_n V(n)} \tag{27}$$

$$\rho_{\mathrm{el,i}}(b) = \int_0^b \frac{\partial \rho_{\mathrm{el,a}}(y,b)}{\partial b}\,\mathrm{d}y = \int_0^b [1+\eta(b,n)]\frac{\partial \rho_{\mathrm{a}}(y,b)}{\partial b}\,\mathrm{d}y \tag{28}$$

In a real system $\eta(b,n)$ should be a very complicated function of the mole fraction of pendant double bonds on the chain, chain length of the primary molecule, molecular conformation, etc. As the simplest approximation, we will assume η to be constant. This approximation may be too simple to describe the complicated phenomenon of cyclization reactions, however, this simple model has given satisfactory predictions for the pendant double bond conversion change as will be shown in the following section. This kind of simple model for secondary cyclization may be acceptable at this stage of the development of the kinetic model for network formation.

With this approximation, equations (27) and (28) reduce to:

$$\frac{\partial \rho_{\mathrm{el,a}}(b,n)}{\partial n} = \left[\frac{k_{\mathrm{p,e}}^{*0}(n)}{k_p(n)}\right]\frac{[(1-k_{\mathrm{cp}})F_2(b) - \rho_{\mathrm{el,a}}(b,n)]}{[\mathrm{M}]_n V(n)} \tag{27a}$$

$$\rho_{\mathrm{el,i}}(b) = \left[\frac{k_{\mathrm{p,e}}^{*0}(b)}{k_{\mathrm{p}}(b)}\right]\frac{b}{[\mathrm{M}]_b V(b)} \times [(1-k_{\mathrm{cp}})\bar{F}_2(b) - \bar{\rho}_{\mathrm{el,a}}(b)] \tag{28a}$$

where $k_{\mathrm{p,e}}^{*0} = (1+\eta)k_{\mathrm{p}}^{*0}$

APPLICATION

Based on the present model for network formation, the accumulated mole fraction of the pendant double bonds which are consumed by crosslinking and secondary cyclization, $\bar{\rho}_{\mathrm{el,a}}$, in a batch crosslinking copolymerization is given by:

$$\frac{\mathrm{d}(x\bar{\rho}_{\mathrm{el,a}})}{\mathrm{d}x} = \left(\frac{k_{\mathrm{p,e}}^{*0}}{k_{\mathrm{p}}}\right)\left\{\frac{[(1-k_{\mathrm{cp}})\bar{F}_2 - \bar{\rho}_{\mathrm{el,a}}]x}{(1-x)}\right\} \tag{29}$$

where x is the total monomer conversion.

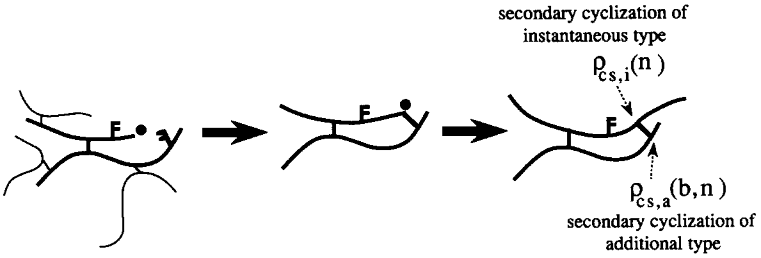

Figure 6 Schematic drawing of the secondary cyclization process

The pendant double bond conversion, x_{pd}, is given by:

$$x_{pd} = \frac{(\bar{\rho}_{cp} + \bar{\rho}_{cl,a})}{\bar{F}_2} = k_{cp} + \frac{\bar{\rho}_{cl,a}}{\bar{F}_2} \qquad (30)$$

Figures 7–9 show comparisons between calculated and experimental results. In the figures f_{20} represents the initial mole fraction of divinyl monomer. An application to the copolymerization of acrylamide and *N,N'*-methylene-bis-acrylamide is shown elsewhere[38]. In all cases, the calculated and experimental results agree reasonably well. The estimated parameters for methyl methacrylate/ethylene glycol dimethacrylate agree with the tendencies discussed previously[32,33,35,41,42]. In order to separate the effect of secondary cyclization from $k^{*0}_{p,e}$, more information concerning the size of polymer molecules such as the onset of gelation, weight-average chain length within sol fractions, etc., is necessary. In this paper this topic is not discussed in detail. However, general tendencies of the estimated parameters in *Figure 7* may be interpreted through the effect of secondary cyclizations. With increasing initial mole fraction of divinyl monomer, f_{20}, the network structure becomes tighter resulting in the enhancement of the tendency toward secondary cyclizations. This will cause an increase

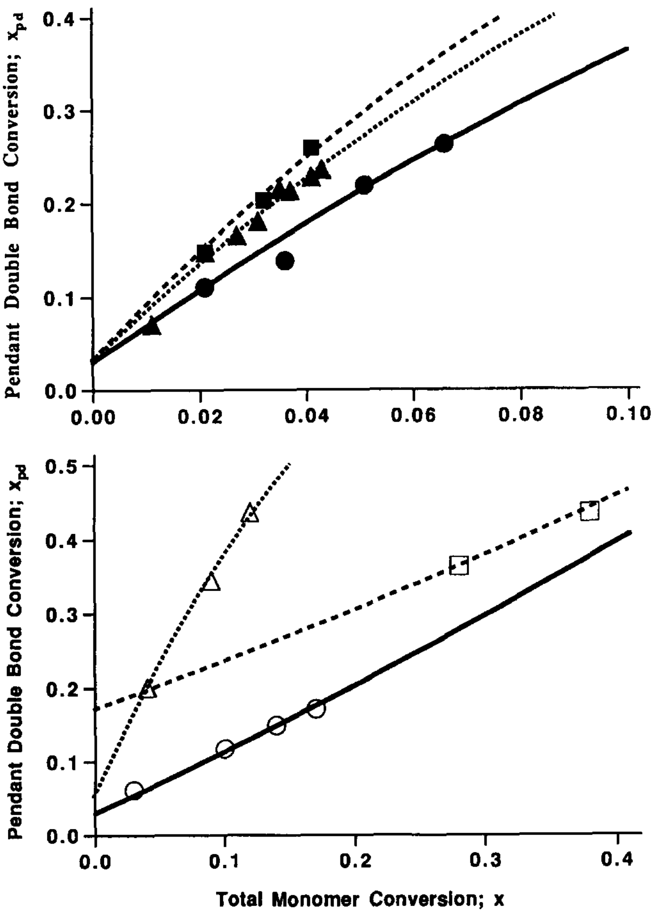

Figure 7 Pendant double bond conversion *versus* total monomer conversion for the copolymerization of methyl methacrylate and ethylene glycol dimethacrylate. The symbols indicate experimental data taken from references 41 and 42. Curves are calculated results using equations (29) and (30). The reactivity ratios used[41–43] for the calculations are $r_1 = 0.5$ and $r_2 = 2.0$. The reaction conditions and estimated parameters are shown below:

Symbol	f_{20}	Polymerization condition	$k^{*0}_{p,e}/k_p$	k_{cp}
●	0.0057	Bulk	8.3	0.03
▲	0.0114	Bulk	11.2	0.03
■	0.017	Bulk	12.7	0.03
○	0.0114	Bulk with CTA	1.7	0.03
△	0.0114	50 vol% in toluene	8.3	0.05
□	0.0114	25 vol% in toluene	1.5	0.17

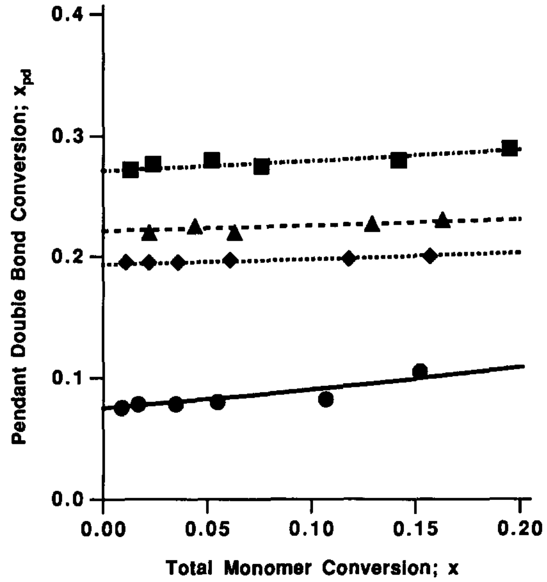

Figure 8 Pendant double bond conversion *versus* total monomer conversion for the copolymerization of styrene and ethylene glycol dimethacrylate (15 vol% in toluene). The symbols indicate experimental data taken from reference 44. Lines are calculated results using equations (29) and (30). The parameters used are shown below:

Symbol	f_{20}	r_1	r_2	$k^{*0}_{p,e}/k_p$	k_{cp}
●	0.01	0.27	1.0	0.3	0.075
◆	0.02	0.27	1.0	0.1	0.192
▲	0.03	0.29	1.0	0.1	0.22
■	0.04	0.29	1.0	0.1	0.27

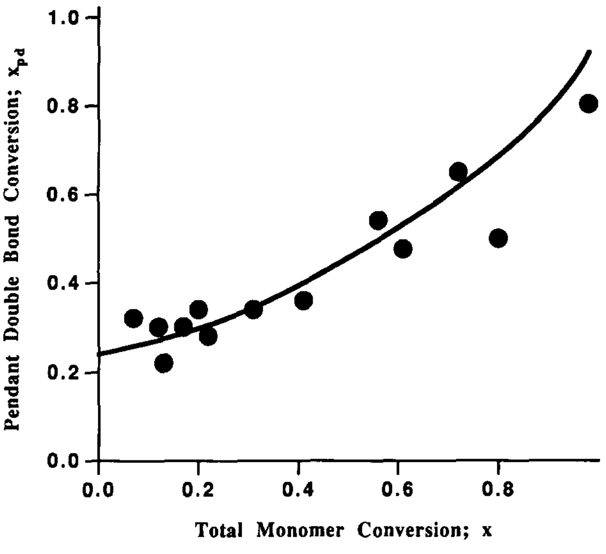

Figure 9 Pendant double bond conversion *versus* total monomer conversion for the copolymerization of styrene and *p*-divinylbenzene with $f_{20} = 0.065$. (●) Experimental data are taken from reference 45. The curve is the calculated results using equations (29) and (30). The reactivity ratios used for the calculations are $r_1 = 0.075$ and $r_2 = 2.44$ (see ref. 45); $k^{*0}_{p,e}/k_p = 0.6$ and $k_{cp} = 0.24$

in $k^{*0}_{p,e}$. When the primary polymer chain length is made shorter, the probability that a growing primary polymer molecule can find two or more pendant double bonds decreases, and therefore, the effect of secondary cyclization decreases resulting in a looser network structure. This may be one of the reasons why $k^{*0}_{p,e}/k_p$ decreases significantly due to the addition of the chain transfer agent (CTA). There may be problems in the experimental data for styrene/ethylene glycol dimethacrylate as discussed previously[32,33,38] so we will not discuss this system further.

Figures 10–12 show some of the calculated crosslinking density distributions using equations (26), (27a) and (28a) with the estimated parameters $k^{*0}_{p,e}/k_p$ and k_{cp}. In the figures, x_b is the monomer conversion at which the given primary polymer molecule is formed, and x_n is the monomer conversion at the present time t_n. For example, in *Figure 10a* at monomer conversion $x_n = 0.8$, the crosslinking density of a primary polymer molecule that has just formed at conversion $x_b = 0.8$ is much smaller than that of a primary polymer molecule that was formed at conversion $x_b = 0.2$. If the crosslinking density $\rho^f_{el}(x_b, x_n)$ possesses a constant value at a given x_n, the polymer network would be perfectly homogeneous, however, if the variance of the crosslinking density distribution is large, the polymer network may be considered inhomogeneous. In all cases except for *Figure 10b*, the variance of the crosslinking density distribution is large, and therefore, it may be reasonable to expect that the polymer networks are inhomogeneous at least on a microscopic scale. By comparing *Figures 10a* and *10b* one can see that the use of CTA reduces the heterogeneity of the polymer network. As was discussed earlier, polymer networks are homogeneous under Flory's simplifying conditions, and therefore, this CTA effect would be understood as reducing the physical effects of the reactivity of pendant double bonds and the effect of secondary cyclization by the formation of shorter primary chains. Qualitatively, this CTA effect agrees with a Monte-Carlo simulation result using a lattice model[25].

If one admits that the polymer networks synthesized by a batch crosslinking copolymerization are quite often heterogeneous, the next question is; how can one synthesize a homogeneous polymer network? In the next section, semi-batch policies to produce homogeneous networks by application of the present kinetic models are formulated.

CONTROL OF CROSSLINKED NETWORK STRUCTURE

A semi-batch operation to produce homogeneous networks

By application of the present kinetic model, it is possible to formulate a semi-batch policy to control the network structure by manipulating polymerization conditions. One of the simplest methods would be to control the monomer composition in the reaction system by feeding in additional monomer. Since a gel molecule is an infinitely large molecule, the limitation of mass, heat and energy transfer would cause problems. Polymerization in a dispersed media such as emulsion and suspension polymerization may be a promising method to overcome these problems. (A kinetic model for emulsion crosslinking copolymerization will be published soon.)

It is sometimes argued that the compositional drift during copolymerization is the cause for the formation of inhomogeneous network structure[46,47]. However, it has already been proven that the 'natural' compositional drift is necessary for the formation of perfectly homogeneous polymer networks[32,33,38] (a significant compositional drift can be seen under Flory's simplifying conditions for a batch copolymerization of vinyl and divinyl monomer even though a perfectly homogeneous

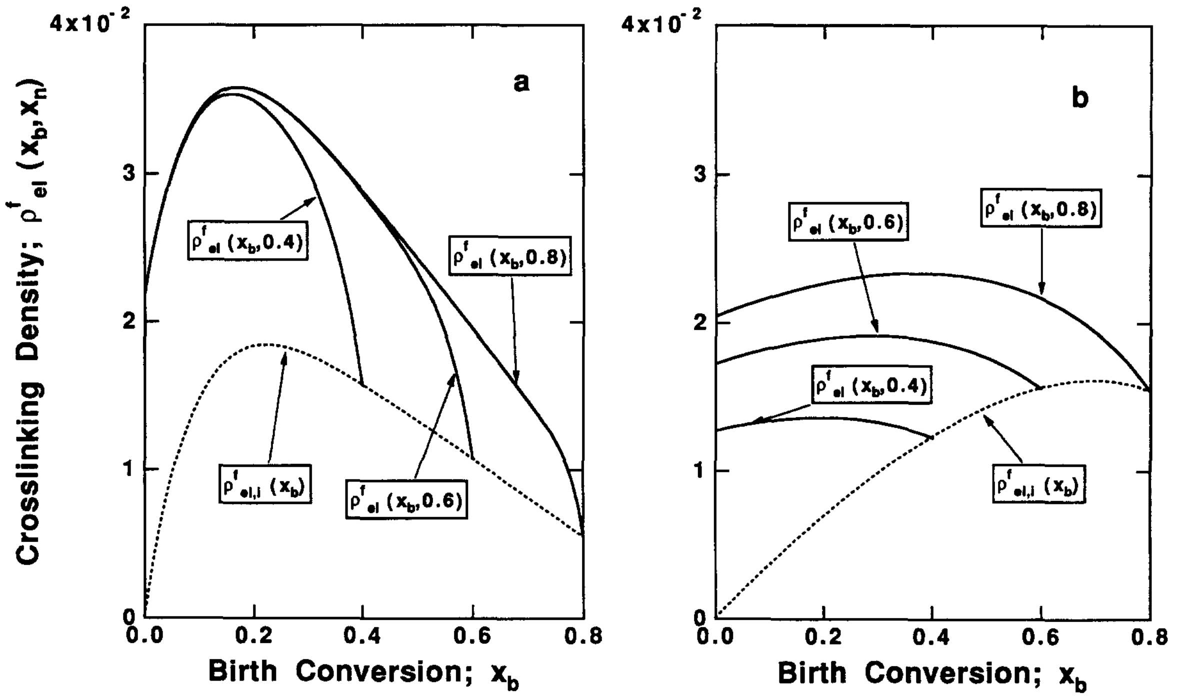

Figure 10 Calculated crosslinking density distribution change during batch copolymerization of methyl methacrylate/ethylene glycol dimethacrylate with the initial mole fraction of divinyl monomer $f_{20} = 0.0114$: (a) bulk polymerization, $k^{*0}_{p,e}/k_p = 11.2$ and $k_{cp} = 0.03$; (b) bulk polymerization with CTA, $k^{*0}_{p,e}/k_p = 1.7$ and $k_{cp} = 0.03$

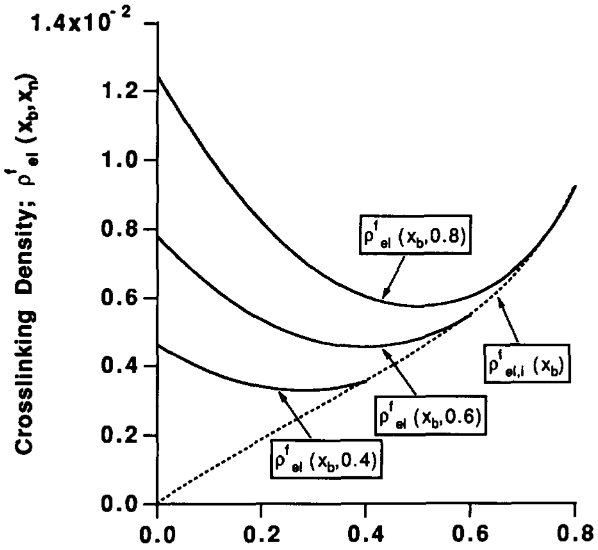

Figure 11 Calculated crosslinking density distribution change during batch copolymerization of styrene/ethylene glycol dimethacrylate (15 vol% in toluene) with $f_{20} = 0.01$; $k^{*0}_{p,e}/k_p = 0.3$ and $k_{cp} = 0.075$

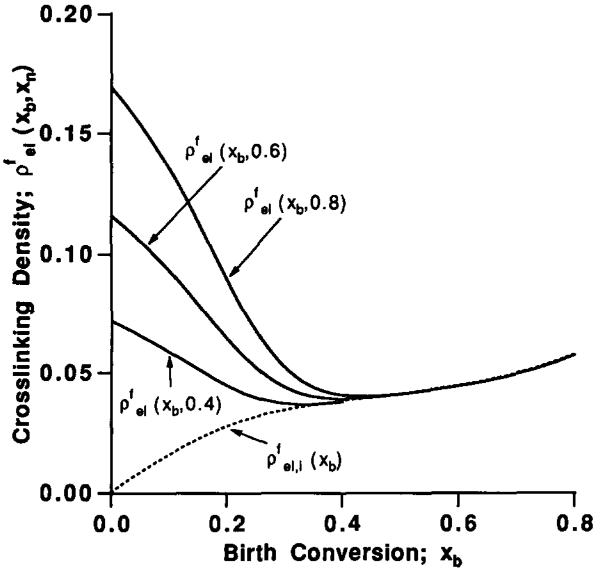

Figure 12 Calculated crosslinking density distribution change during batch copolymerization of styrene/*p*-divinylbenzene with $f_{20} = 0.065$; $k^{*0}_{p,e}/k_p = 0.6$ and $k_{cp} = 0.24$

network is formed), and therefore, the criterion for homogeneous polymer networks by controlling the monomer feed composition to keep a uniform copolymer composition is, in general, invalid.

In order to produce polymer networks with uniform crosslinking density, $\rho^f_{el}(b,n)$ must be independent of t_b at a given t_n, namely:

$$\frac{\partial \rho^f_{el}(b,n)}{\partial b} = 0 \qquad (31)$$

Equations (27a), (28a) and (31) must be solved simultaneously to know the necessary conditions to produce homogeneous polymer networks. Various monomer feed policies can be applied in order to satisfy the above equation. We propose the following simple policy: add parts of both monomers to the reactor at $t = 0$, and use a time-varying monomer feed for both monomers to maintain the total number of moles of monomers, $[M]V = n_0$, constant throughout the semi-batch period. (One of the merits of this policy may be that if the change of the total polymer radical concentration and that of the pseudo-kinetic rate constant for propagation reaction k_p during semi-batch copolymerization is negligible, one can use a constant monomer feed rate with time varying comonomer composition.)

We now assume that the change in the parameter $k^{*0}_{p,e}/k_p$ during semi-batch polymerization is negligible. This condition may be satisfied when the mole fraction of divinyl monomer is much smaller than unity. In this case, using equations (27a) and (28a), one obtains:

$$\rho_{el,a}(Y,Z) = (1-k_{cp})F_2(Y) \times \left\{1-\exp\left[-\left(\frac{k^{*0}_{p,e}}{k_p}\right)(Z-Y)\right]\right\} \qquad (32)$$

$$\rho_{el,i}(Y) = \left(\frac{k^{*0}_{p,e}}{k_p}\right)(1-k_{cp}) \times \int_0^Y F_2(y)\exp\left[-\left(\frac{k^{*0}_{p,e}}{k_p}\right)(Y-y)\right]\mathrm{d}y \qquad (33)$$

where $Y = b/n_0$ and $Z = n/n_0$, and therefore Y shows the magnitude of the total weight of polymer produced at t_b and Z shows that at t_n.

Let us first consider a simple example, with the initial mole fraction of divinyl monomer $f_{20} = 0.01$, the reactivity ratios $r_1 = 0.5$ and $r_2 = 2.0$, the parameter for the crosslinking reaction $k^{*0}_{p,e}/k_p = 2.0$, and the parameter for primary cyclization $k_{cp} = 0.2$. The crosslinking density distribution for batch copolymerization for this condition is shown in *Figure 13*, and it shows the polymer network synthesized is heterogeneous. *Figure 14* shows the necessary conditions to produce polymer networks with uniform crosslinking density at $Z = 2.0$. In the figure, the comonomer composition in the monomer feed, $f_{2,\mathrm{feed}}$, the mole fraction of divinyl monomer in the reaction system f_2, and the instantaneous mole fraction of divinyl monomer in the polymer chains, F_2, are shown. (Note that the monomer feed rate may also change during

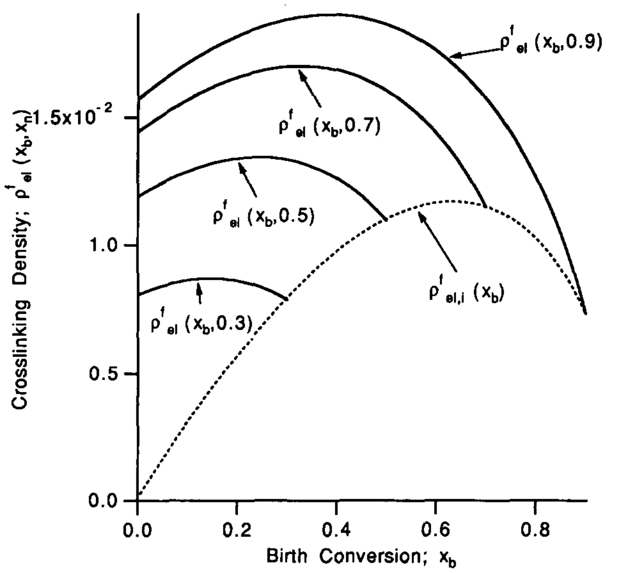

Figure 13 Calculated crosslinking density distribution change during batch copolymerization; $f_{20} = 0.01$, $r_1 = 0.5$, $r_2 = 2.0$, $k^{*0}_{p,e}/k_p = 2.0$ and $k_{cp} = 0.2$

the semi-batch copolymerization if the overall monomer consumption rate changes.) The crosslinking density distribution change during semi-batch polymerization is shown in *Figure 15*. The crosslinking densities of all primary polymer molecules are the same at $Z = 2.0$. Another example in which a homogeneous polymer network is formed at $Z = 5$ is shown in *Figures 16* and *17*. *Figures 18* and *19* show the calculated results for styrene/ethylene glycol dimethacrylate with $f_{20} = 0.01$ by application of the estimated parameters.

In practice, however, time varying monomer composition feed may be difficult to operate. As shown in *Figures 16* and *18*, a constant comonomer composition feed period is long when the Z value at which a homogeneous polymer network is formed is large. *Figure 20* shows the calculated crosslinking density distribution with a constant monomer feed composition and with a combination of three different monomer feed

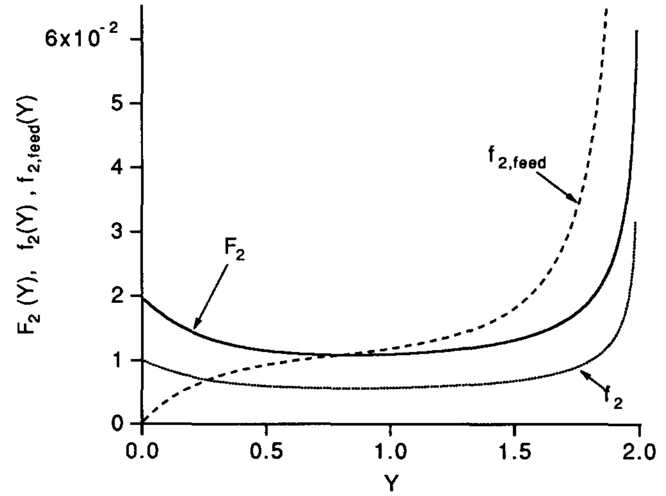

Figure 14 Semi-batch operation conditions to produce homogeneous polymer networks at $Z = 2$ when the total number of moles of monomers in the reaction system n_0 is kept constant. $f_{2,\mathrm{feed}}(Y)$ is the mole fraction of divinyl monomer in the monomer feed. Under these conditions, the mole fraction of divinyl monomer in the reaction system, $f_2(Y)$, and that of divinyl monomer bound in the polymer chains, $F_2(Y)$, change as shown; $f_{20} = 0.01$, $r_1 = 0.5$, $r_2 = 2.0$, $k_{\mathrm{p,e}}^{*0}/k_{\mathrm{p}} = 2.0$ and $k_{\mathrm{cp}} = 0.2$

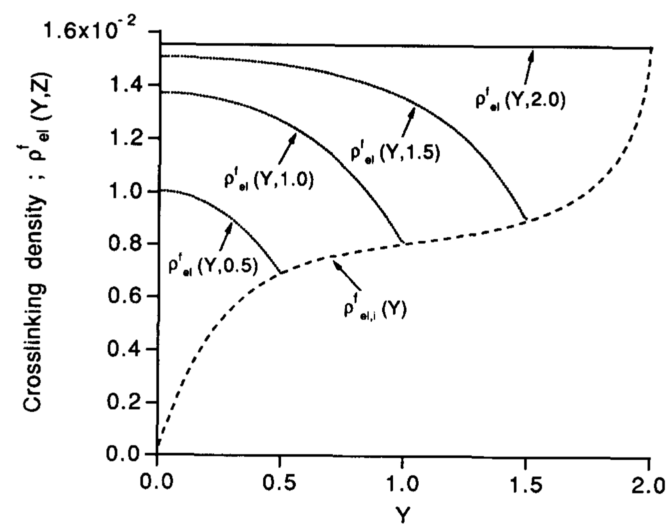

Figure 15 Crosslinking density distribution change during semi-batch crosslinking copolymerization. A homogeneous network is formed at $Z = 2$; $f_{20} = 0.01$, $r_1 = 0.5$, $r_2 = 2.0$, $k_{\mathrm{p,e}}^{*0}/k_{\mathrm{p}} = 2.0$ and $k_{\mathrm{cp}} = 0.2$

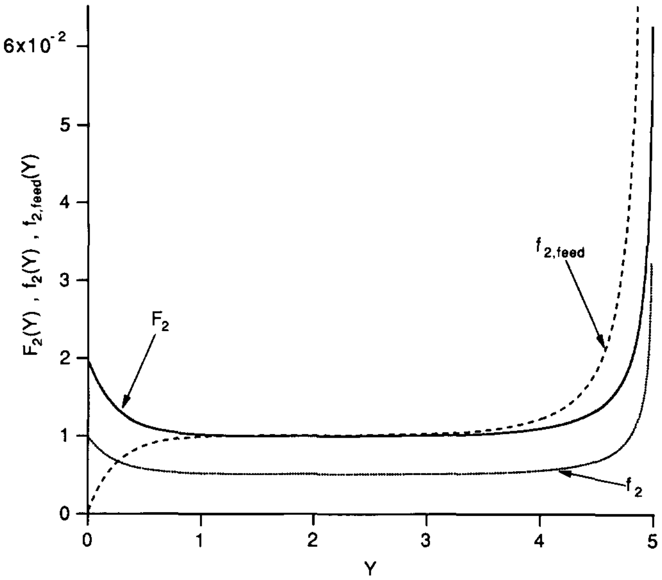

Figure 16 Semi-batch operation conditions to produce homogeneous polymer networks at $Z = 5$; $f_{20} = 0.01, r_1 = 0.5, r_2 = 2.0, k_{\mathrm{p,e}}^{*0}/k_{\mathrm{p}} = 2.0$ and $k_{\mathrm{cp}} = 0.2$

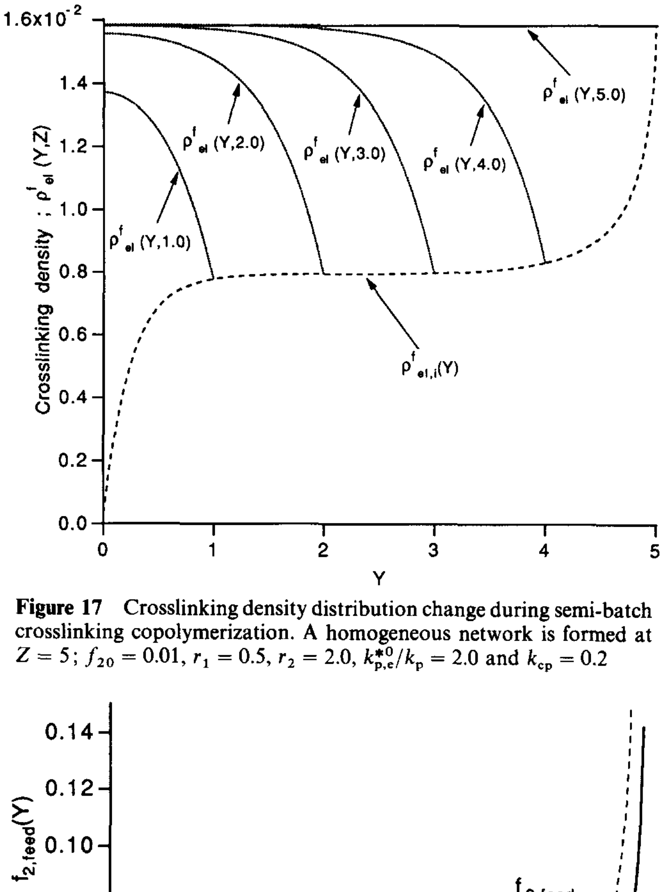

Figure 17 Crosslinking density distribution change during semi-batch crosslinking copolymerization. A homogeneous network is formed at $Z = 5$; $f_{20} = 0.01$, $r_1 = 0.5$, $r_2 = 2.0$, $k_{\mathrm{p,e}}^{*0}/k_{\mathrm{p}} = 2.0$ and $k_{\mathrm{cp}} = 0.2$

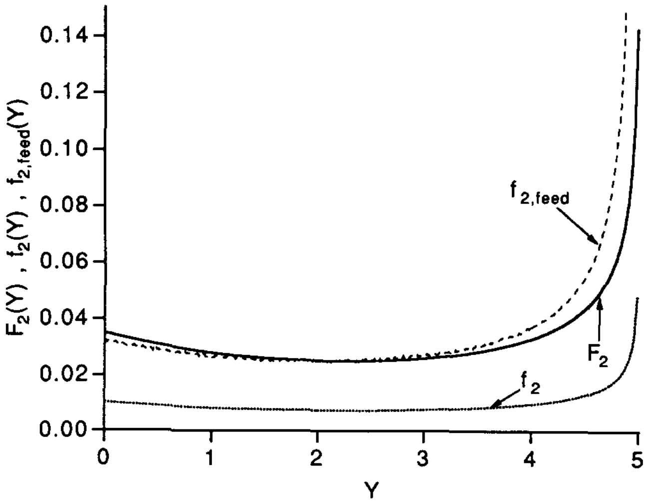

Figure 18 Semi-batch operation conditions to produce homogeneous polymer networks at $Z = 5$ for the copolymerization of styrene and ethylene glycol dimethacrylate with $f_{20} = 0.01$

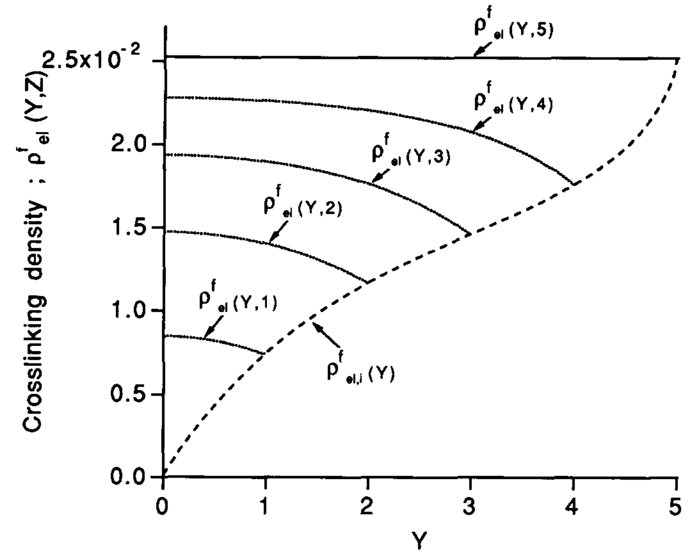

Figure 19 Crosslinking density distribution change during semi-batch crosslinking copolymerization of styrene and ethylene glycol dimethacrylate with $f_{20} = 0.01$. A homogeneous network is formed at $Z = 5$

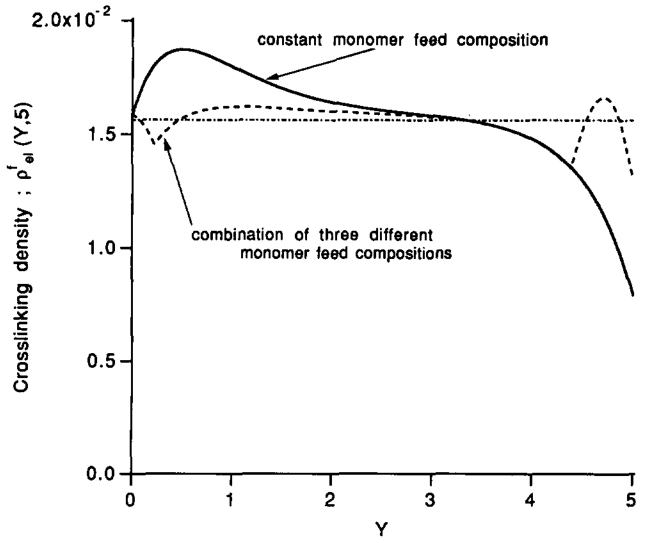

Figure 20 Calculated crosslinking density distribution with a constant monomer feed composition ($f_{2,\text{feed}} = 0.01$) and with a combination of three different monomer feed compositions ($f_{2,\text{feed}} = 0$ during $Y < 0.24$, $f_{2,\text{feed}} = 0.01$ during $0.24 < Y < 4.4$ and $f_{2,\text{feed}} = 0.03$ during $4.4 < Y < 5.0$); $f_{20} = 0.01$, $r_1 = 0.5$, $r_2 = 2.0$, $k^{*0}_{p,e}/k_p = 2.0$ and $k_{cp} = 0.2$

compositions. A combination of the different monomer feed compositions may give a satisfactory result to produce homogeneous polymer networks.

Figure 21 shows the calculated condition to produce homogeneous networks for the copolymerization of methyl methacrylate/ethylene glycol dimethacrylate with $f_{20} = 0.0114$ using the estimated parameters. In this case the necessary monomer feed composition is negative in the early stage of polymerization, and therefore the present monomer feed policy cannot be applied strictly. However, as shown in *Figure 22*, a combination of three different monomer feed compositions may significantly reduce the heterogeneity of the polymer networks.

CONCLUSIONS

A kinetic model which describes the network structure development during free-radical crosslinking copolymerization is proposed. The present model, which accounts for crosslinking and cyclization reactions during crosslinking copolymerization as well as for the history of the generated network structure, was successfully applied to various copolymerization systems to describe the change of pendant double bond conversion during batch crosslinking copolymerization. The model calculations suggest that the polymer networks synthesized by free-radical crosslinking copolymerization in batch reactors are, quite often, inhomogeneous at least on a microscopic scale. The present model can be used to find semi-batch policies to control the network structure. Semi-batch monomer feed policies were used to illustrate the synthesis of homogeneous polymer networks.

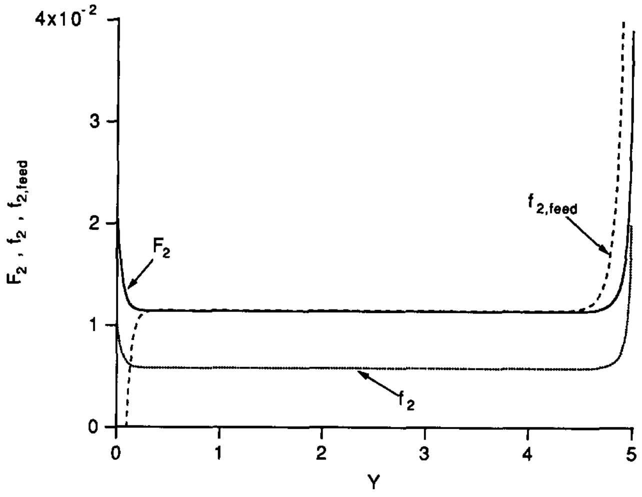

Figure 21 Semi-batch operation conditions to produce homogeneous polymer networks at $Z = 5$ for the copolymerization of methyl methacrylate and ethylene glycol dimethacrylate with $f_{20} = 0.0114$. The mole fraction of divinyl monomer in the additional monomer feed, $f_{2,\text{feed}}$, is negative during $Y < 0.1$

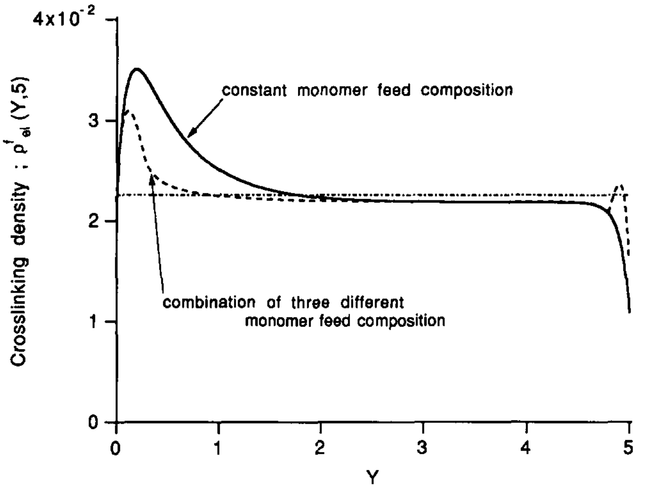

Figure 22 Calculated crosslinking density distribution for the copolymerization of methyl methacrylate and ethylene glycol dimethacrylate with $f_{20} = 0.0114$ with a constant monomer feed composition ($f_{2,\text{feed}} = 0.0114$) and with a combination of three different monomer feed compositions ($f_{2,\text{feed}} = 0$ during $Y < 0.3$, $f_{2,\text{feed}} = 0.0114$ during $0.3 < Y < 4.8$ and $f_{2,\text{feed}} = 0.04$ during $4.8 < Y < 5.0$)

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