Molecular Weight Distribution in Free-Radical Cross-Linking Copolymerization

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ABSTRACT: A new theory to predict the molecular weight distribution in free-radical copolymerization of vinyl and divinyl monomers is proposed. This theory is based on the cross-linking density distribution of the primary polymer molecules proposed earlier. The cross-linking density distribution is a very important feature of polymer networks synthesized in a kinetically controlled system; it provides information on how each chain is connected to other chains, and, therefore, a full molecular weight distribution and detailed structural information can be known by application of the Monte Carlo simulation. The present theory accounts for the history of the generated network structure and can be applied to various polymerization systems as well as for various reactor types. The present simulation is a direct solution for the chemically controlled network formation, and, therefore, it provides a testing method for the applicability of earlier theories of network formation.

Introduction

The prediction of the molecular weight distribution (MWD) in three-dimensional polymers may not be a novel topic; however, it continues to be an attractive research field combining at the same time fundamental and applied topics of great interest. On the basis of the pioneering work of Flory and Stockmayer,[1-4] various statistical models have been developed for polymeric network formation.[5-13] Although these models provide information on the various average molecular weights, a full MWD cannot be calculated except for very simple reaction systems, such as the step-growth polymerization of A_3 monomer without the substitution effect and the crosslinking of polymer chains having a very simple MWD. At present, experimentally we may only measure average molecular weights of cross-linked polymers; however, the MWD would provide more insight into the complex phenomena of network formation. Recently, the method of moments was applied to vinyl/divinyl copolymerization, and a set of differential equations to calculate any order of moment was proposed.[14-16] Since any order of moment of MWD is given, in principle, it would be possible to know the full distribution function. The approximation using the Laguerre polynomials was proposed earlier[17-20] for these kinds of calculations; however, this may not be practically possible since the series does not converge fast depending on the breadth and the shape of distribution functions.[21]

Free-radical polymerization is kinetically controlled, so that the history of the generated network structure must be properly accounted for. By considering the history of the primary polymer molecules, the cross-linking density distribution was recently proposed.[15,16,22-26] The existence of the cross-linking density distribution is a very important feature of polymer networks synthesized in kinetically controlled systems, indicating that the polymer networks are heterogeneous at least on a microscopic scale, and, therefore, this concept is very important to consider the network structure of polymeric gels. From the cross-linking density distribution, it is also possible to know how each primary polymer molecule is connected to other primary polymer molecules. Since the MWD is the result of the connection of all primary polymer molecules, it would be possible to calculate the MWD based on the cross-linking density distribution. In this paper, a new theory to predict the molecular weight distribution in free-radical copolymerization of vinyl and divinyl monomers based on the cross-linking density distribution is proposed, and the Monte Carlo method is used to simulate the combination of each primary polymer molecule.

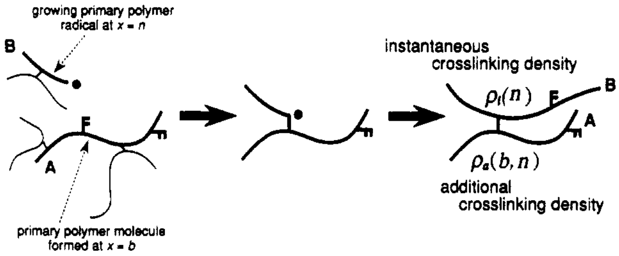

Figure 1. Schematic drawing of the process of cross-linking. At $x = n$, the cross-linking density of the primary polymer molecules which were formed at $x = b$ is given by eq 1.

Theoretical Section

Network Structure Development. In order to describe the cross-linked structure development, the structural change of a primary polymer molecule is considered. The process of cross-linking reaction is schematically shown in Figure 1. As proposed earlier,[15,16,22-27] the cross-linking points are divided into two types, namely, the instantaneous and additional cross-linking points. The cross-linking points that are formed during the formation of the primary polymer molecule are defined as the instantaneous cross-linking points, and those formed after the primary polymer molecule is born are defined as the additional cross-linking points as shown in Figure 1. The mathematical importance of the difference between the instantaneous and additional cross-linking density is that the instantaneous cross-linking density is solely a function of its birth time, while the additional cross-linking density is a function of both its birth time and the present time. Since a cross-linking point is defined as a unit which bears a tribranching point, the cross-linking density is given by the sum of these two types of cross-linking densities. Therefore, at the total monomer conversion $x = n$, the total number of cross-linking points on a given primary polymer molecule that was formed at $x = b$ is given by the sum of the cross-linking points that are formed during the formation of the primary polymer molecule (instantaneous cross-linking density, $\rho_i(b)$) and the additional cross-linking points that are added in the conversion interval b to n

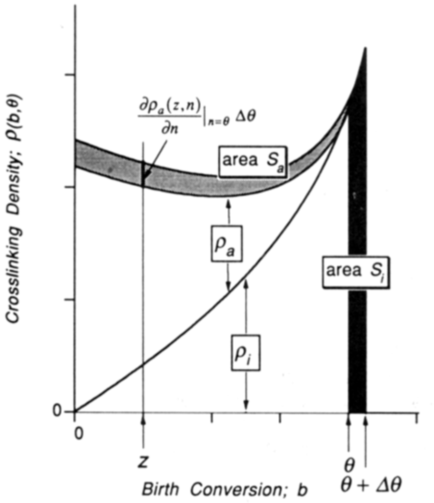

Figure 2. Schematic drawing of the cross-linking density distribution at $x = \theta$. When the polymerization proceeds from $x = \theta$ to $\theta + \Delta\theta$, the increase in the additional cross-linking points is given by the area S_a, while that in the instantaneous cross-linking points is given by S_i.

(additional cross-linking density, $\rho_a(b,n)$).

$$\rho(b,n) = \rho_i(b) + \rho_a(b,n) \tag{1}$$

Fundamental equations of each type of cross-linking density can be derived from simple balance equations.[16,22,25] For batch cross-linking copolymerization, they are given by

$$\frac{\partial\rho_a(b,n)}{\partial n} = \left(\frac{k_p{}^{*0}(n)}{k_p(n)}\right)\left\{\frac{F_2(b) - \rho_a(b,n) - \rho_c(b,n)}{1-n}\right\} \tag{2}$$

$$\rho_i(b) = \left(\frac{k_p{}^{*0}(b)}{k_p(b)}\right)\left(\frac{b}{1-b}\right)\{\bar{F}_2(b) - \bar{\rho}_a(b) - \bar{\rho}_c(b)\} \tag{3}$$

where $k_p{}^{*0}$ and k_p are the pseudokinetic rate constants[15,16,22-26,28] for cross-linking and propagation reactions, respectively. F_2 is the instantaneous mole fraction of divinyl monomer bound in the polymer chains, and ρ_c is the cyclization density which is the mole fraction of pendant double bonds wasted by cyclization reactions. All superscript bars in eq 3 are used to designate the accumulated values at a given conversion. Therefore, the right-hand side of eq 2 is the ratio between the cross-linking reaction rate of the primary polymer molecules formed at $x = b$ and the propagation rate of the reaction system at $x = n$. On the other hand, the right-hand side of eq 3 shows the ratio of the total cross-linking reaction rate in the system to the propagation rate at $x = b$.

By application of the above equations, it is possible to calculate the cross-linking density distribution of the primary polymer molecules. The cross-linking density distribution is a very important concept to describe the network structure development. More discussion on the cross-linking density distribution can be found elsewhere.[16,22-26,29]

Molecular Constitution of Cross-Linked Polymers. When a primary polymer molecule is formed at $x = \theta$, this primary polymer molecule may possess cross-linking points based on the probability given by the instantaneous cross-linking density, $\rho_i(\theta)$. These instantaneous cross-linking points must be connected to primary polymer molecules that were formed prior to $x = \theta$, namely, in the conversion interval 0 to θ.

Figure 2 shows a schematic drawing of an example of the cross-linking density distribution at $x = \theta$. When the polymerization proceeds from $x = \theta$ to $\theta + \Delta\theta$, the total number of the instantaneous cross-linking points formed within this conversion interval is given by the area S_i. Since every instantaneous cross-linking point needs to have its own partner, namely, the additional cross-linking point, the relationship, $S_i = S_a$ must be satisfied. From the present consideration, it is obvious that the instantaneous cross-linking points formed at $x = \theta$ are connected to the primary polymer molecules formed at $x = z$ $(0 < z < \theta)$ based on the magnitude, $\partial\rho_a(z,n)/\partial n|_{n=\theta}$. The probability that the primary polymer molecule formed at $x = \theta$ is connected via its instantaneous cross-linking points to the primary polymer molecules formed in the conversion interval $x = z$ to $z + \Delta z$, $P_i(z|\theta)\Delta z$, is given by

$$P_i(z|\theta)\Delta z = \frac{\left.\dfrac{\partial\rho_a(z,n)}{\partial n}\right|_{n=\theta}\Delta z}{\displaystyle\int_0^\theta \left.\frac{\partial\rho_a(z,n)}{\partial n}\right|_{n=\theta} \mathrm{d}z} = \frac{\{F_2(z) - \rho_a(z,\theta) - \rho_c(z,\theta)\}\Delta z}{\int_0^\theta \{F_2(z) - \rho_a(z,\theta) - \rho_c(z,\theta)\}\,\mathrm{d}z} \tag{4}$$

Equation 4 shows the probability is given by the mole fraction of live pendant double bonds located on the primary polymer molecule, which is a direct result from the assumption that the reactivity of all pendant double bonds is the same at a given time.

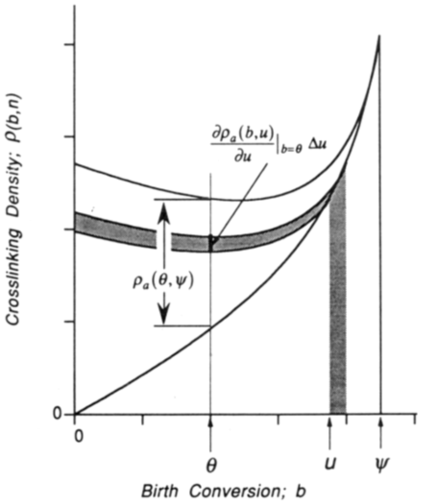

Figure 3. Schematic drawing of the cross-linking density distribution at $x = \psi$. The increase in the additional cross-linking points on the primary polymer molecule formed at $b = \theta$ in the conversion interval u to $u + \Delta u$ is given by $\partial\rho_a(b,u)/\partial u|_{b=\theta}\Delta u$.

Next, let us consider the connection of the primary polymer molecules through the additional cross-linking points. In a primary polymer molecule that was formed at $x = \theta$, it would possess additional cross-linking points at the present conversion, $x = \psi$, based on the probability given by the additional cross-linking density, $\rho_a(\theta,\psi)$. These additional cross-linking points must be connected to primary polymer molecules that were formed after $x = \theta$, namely, in the conversion interval θ to ψ. From Figure 3, one would notice that the probability that a primary polymer molecule formed at $x = \theta$ is connected to the primary polymer molecules formed at $x = u$ $(\theta < u < \psi)$ is based on the rate of increase in the additional cross-linking density at $x = u$ for the primary polymer molecule formed at $x = \theta$, namely, $\partial\rho_a(b,u)/\partial u|_{b=\theta}$. Therefore, the probability that the primary polymer molecule formed at $x = \theta$ is connected via its additional cross-linking points to the primary polymer molecules formed in the conversion interval $x = u$ to $u + \Delta u$, $P_a(u|\theta)\Delta u$, is given by

$$P_a(u|\theta)\Delta u = \frac{\left.\dfrac{\partial\rho_a(b,u)}{\partial u}\right|_{b=\theta}\Delta u}{\displaystyle\int_\theta^\psi \left.\dfrac{\partial\rho_a(b,u)}{\partial u}\right|_{b=\theta}\mathrm{d}u} =$$

$$\frac{\left(\dfrac{k_p{}^{*0}(u)}{k_p(u)}\right)\left\{\dfrac{F_2(\theta) - \rho_a(\theta,u) - \rho_c(\theta,u)}{1-u}\right\}\Delta u}{\displaystyle\int_\theta^\psi\left[\left(\dfrac{k_p{}^{*0}(u)}{k_p(u)}\right)\left\{\dfrac{F_2(\theta) - \rho_a(\theta,u) - \rho_c(\theta,u)}{1-u}\right\}\right]\mathrm{d}u} \quad (5)$$

By application of eqs 4 and 5, it is possible to know how each primary polymer molecule formed at $x = \theta$ is connected with primary polymer molecules formed at $x = z$ $(0 < z < \theta)$ and $x = u$ $(\theta < u < \psi)$. At present, the deterministic solution for the MWD under constraints given by eqs 4 and 5 is not given. However, at least it is possible to make a computer simulation using the Monte Carlo method.

Simulation Algorithm. A computer simulation can be conducted with the following algorithm: (1) Select a primary polymer molecule randomly from the conversion interval 0 to ψ, namely, determine the birth time of the primary polymer molecule of the zeroth generation. (2) Determine the chain length of the given primary polymer molecule by application of the MWD of the primary polymer molecules formed at the given time. (3) On the basis of the cross-linking density and the chain length of the primary polymer molecule, determine the number of both instantaneous and additional cross-linking points. (4) On the basis of eqs 4 and 5, determine how each cross-linking point is connected to other primary polymer molecules with different birth time. At this stage, the birth time and the chain length of the connected primary polymer molecules (next generation) are determined. Steps 3 and 4 are reiterated until no chains are connected.

The weight–chain length distribution of the primary polymer molecules is given by

$$W(r) = (\tau + \beta)\left\{\tau + \frac{\beta}{2}(\tau + \beta)(r - 1)\right\}r\exp\{-(\tau + \beta)r\} \quad (6)$$

where $\tau = [R_f(x) + R_{td}(x)]/R_p(x)$, $\beta = R_{tc}(x)/R_p(x)$, r is the chain length, $R_p(x)$ is the polymerization rate, $R_f(x)$ is the rate of chain transfer to monomer and small molecules, $R_{td}(x)$ is the rate of termination by disproportionation, and $R_{tc}(x)$ is the rate of termination by combination.

For the Monte Carlo simulation, the cumulative weight–chain length distribution would be easier to apply. Since $\tau, \beta \ll 1$ in free-radical polymerization, the cumulative weight–chain length distribution, which is the weight fraction of primary polymer molecules with chain length less than r, is given by

$$\mathrm{CW}(r) = 1 - \left\{1 + (\tau + \beta)\left(1 + \frac{\beta}{2}r\right)r\right\}\exp\{-(\tau + \beta)r\} \quad (7)$$

The probability that a primary polymer molecule with chain length r and the instantaneous cross-linking density ρ_i possesses m instantaneous cross-linking points, $p_i(m)$ is given by the following binomial distribution:

$$p_i(m) = \binom{r}{m}\rho_i{}^m(1 - \rho_i)^{r-m} \quad (8)$$

The number of additional cross-linking points can also be calculated from the binomial distribution.

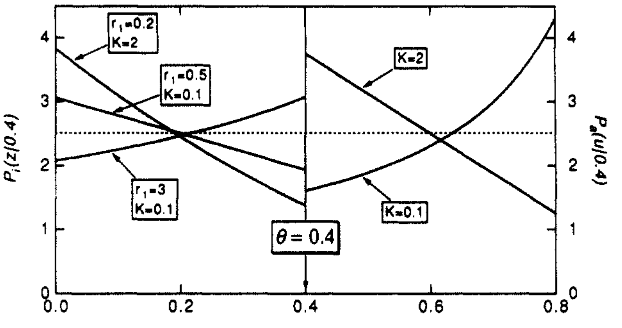

Figure 4. Probability density distributions showing how the primary polymer molecules formed at $b = 0.4$ are connected to other chains with different birth conversions, when the present conversion is $\psi = 0.8$. The dotted line corresponds to Flory's simplifying assumptions shown in the text.

With eqs 1–8 and random numbers, one can make a Monte Carlo simulation for the molecular constitution of network polymers.

Simulation. The main purpose of the present simulation is to know the effect of cross-linking density distribution on the molecular constitution, more specifically, on the MWD development in the pregelation period. (Consideration of the postgelation period will be reported in the near future.) In order to simplify the simulation, we are to make the following assumptions: (1) There are no cyclizations. (2) The mole fraction of divinyl monomer is much smaller than unity and the ratio of the rate constants, $k_p{}^{*0}/k_p$ is kept constant until the point of gelation. (3) The MWD of the primary polymer molecules does not change up to the gel point. These assumptions may not be realistic; especially, the effect of cyclization would be important for many systems; however, the effect of the cross-linking density distribution on the MWD can be investigated effectively with these simplifying assumptions. With assumptions (1) and (2), the mole fraction of live pendant double bonds is approximated by

$$F_2(b) - \rho_a(b,n) \approx \frac{f_{20}}{r_1}(1 - b)^{(1-r_1)/r_1}\left(\frac{1 - n}{1 - b}\right)^K \quad (9)$$

where $K = k_p{}^{*0}/k_p$, r_1 is the reactivity ratio, and f_{20} is the initial mole fraction of divinyl monomer. Note that when $f_{20} \ll 1$, r_2 does not have a significant effect on the copolymer composition.

In this case, $P_i(z|\theta)$ and $P_a(u|\theta)$ are given by

$$P_i(z|\theta) = \left(\frac{1 - Kr_1}{r_1}\right)\left\{\frac{(1 - z)^{(1-r_1-Kr_1)/r_1}}{1 - (1 - \theta)^{(1-Kr_1)/r_1}}\right\} \quad (10)$$

$$P_a(u|\theta) = \frac{K(1 - u)^{K-1}}{(1 - \theta)^K - (1 - \psi)^K} \quad (11)$$

Figure 4 shows the distribution function for $\theta = 0.4$ at the present conversion $\psi = 0.8$; namely, Figure 4 shows the probability density functions indicating how the primary polymer molecules formed at conversion 0.4 are connected to other primary polymer molecules formed at different conversions through the instantaneous cross-linking points (the left axis) and through the additional cross-linking points (the right axis). The dotted line corresponds to Flory's simplifying assumptions for vinyl/divinyl copolymerization; namely, (1) the reactivities of all types of double bonds are equal, (2) all double bonds react independently, and (3) there are no cyclization reactions in finite molecules. Under these assumptions,

Table I
Calculation Conditions Investigated[a]

	C1	C2	C3
τ	0.005	0.005	0.001
r_1, r_2	0.5, 2.0	0.5, 2.0	3.0, 0.333
K	1.0	0.1	0.1

[a] Initial mole fraction of divinyl monomer, $f_{20} = 0.01$, and $\beta = 0$ for all conditions. The reactivity ratio, r_2, was used only for the calculations of the cross-linking density distribution.

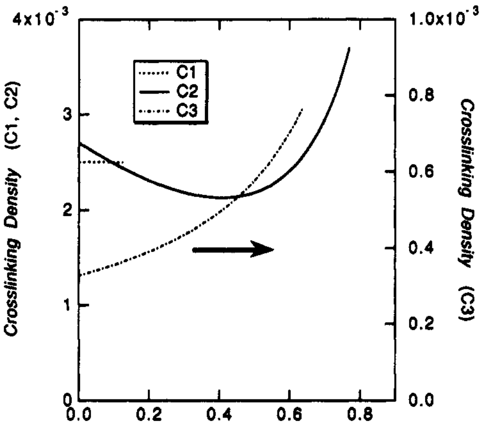

Figure 5. Cross-linking density distribution at the gel point. The conversion at the gel point, x_c, for each condition is summarized in Table II.

the connections between primary polymer chains are completely at random, and any primary polymer molecule can be connected with equal probability. However, in general, the probability of forming a bonding between primary polymer molecules is different depending on the birth time of both primary polymer molecules in a kinetically controlled system. The probability density function shown in Figure 4 changes with the reactivity ratios, the reactivity of the pendant double bonds, and the cyclization reactions.

The cumulative distribution function which is convenient for the Monte Carlo simulation is given as follows. The probability that the primary polymer molecule formed at $x = \theta$ is connected via its instantaneous cross-linking points to the primary polymer molecules formed in the conversion interval $x = 0$ to z $(0 < z < \theta)$, $\mathrm{CP_i}(z|\theta)$, is given by

$$\mathrm{CP_i}(z|\theta) = \frac{1 - (1 - z)^{(1-Kr_1)/r_1}}{1 - (1 - \theta)^{(1-Kr_1)/r_1}} \tag{12}$$

On the other hand, the probability that the primary polymer molecule formed at $x = \theta$ is connected via its additional cross-linking points to the primary polymer molecules formed in the conversion interval $x = \theta$ to u $(\theta < u < \psi)$, $\mathrm{CP_a}(u|\theta)$, is given by

$$\mathrm{CP_a}(u|\theta) = \frac{(1 - \theta)^K - (1 - u)^K}{(1 - \theta)^K - (1 - \psi)^K} \tag{13}$$

Results and Discussion

Three conditions, shown in Table I, were investigated in the computer simulations. The calculated cross-linking density distribution at the gel point for these conditions is shown in Figure 5. C1 corresponds to Flory's simplifying assumptions, and a homogeneous network is formed under these conditions.[16,23,26] The network structure for C2 and C3 at the gel point is shown to be heterogeneous.

Molecular Weight Distribution Development. The weight-average chain length was calculated from the simulation of 1000 polymer molecules. Simulation of 1000 polymer molecules was found to be satisfactory both for the average chain lengths and the MWD for the polycondensation of A_3 type monomer.[30] The calculated results are shown in Figure 6. Comparison was made with the method of moments[14-16,22-24] and the Flory–Stockmayer model.[1-4] In the Flory–Stockmayer model, the weight-average chain lengths were calculated using the following equation.

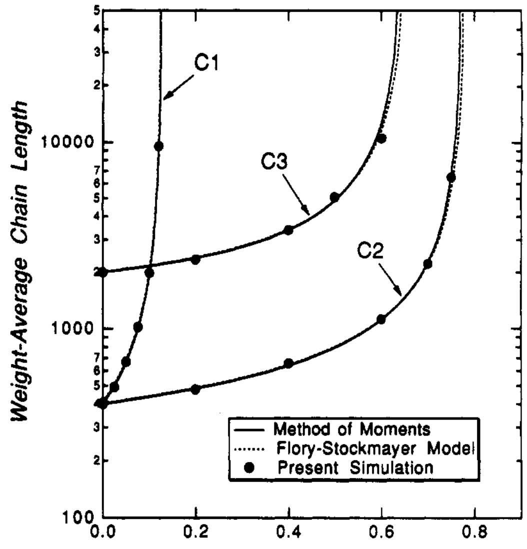

Figure 6. Calculated weight-average chain-length development.

$$\bar{P}_w = \frac{\bar{P}_{wp}}{1 - \bar{\rho}\bar{P}_{wp}} \tag{14}$$

where $\bar{P}_{wp}$ is the accumulated weight-average chain length of the primary polymer molecule and $\bar{\rho}$ is the average cross-linking density.

As shown in earlier papers,[16,24] the method of moments and the Flory–Stockmayer model agree satisfactorily for many polymerization conditions. The applicability of these models under the present calculation conditions is now confirmed by the present simulation. The present results show that the cross-linking density distribution has a minor effect on the MWD, although it does have a significant effect on the network structure.

There are two important assumptions in deriving the moment equations in the method of moments. (1) Every polymer radical possesses only one radical center, and the effect of polyradicals[31] was neglected. (2) The mole fraction of live pendant double bonds is independent of chain length and is given by the average mole fraction of live pendant double bonds. It is worth noting here that the presence of polyradicals does not give serious problems in the present simulation. When bimolecular termination by combination does not occur, the MWD is the same for primary polymer molecules with and without radical centers, so that the existence of polyradicals never changes the whole MWD. On the other hand, when bimolecular termination by combination does occur, the chain length of a primary polymer molecule is different depending on the existence of a radical center. However, from the point of view of the primary polymer molecules, the weight fraction of primary polymer molecules with radical centers is negligibly small compared with the total amount of polymers produced, even though large polymer molecules with many cross-linking points tend to possess radical centers. Therefore, it is expected that the existence of

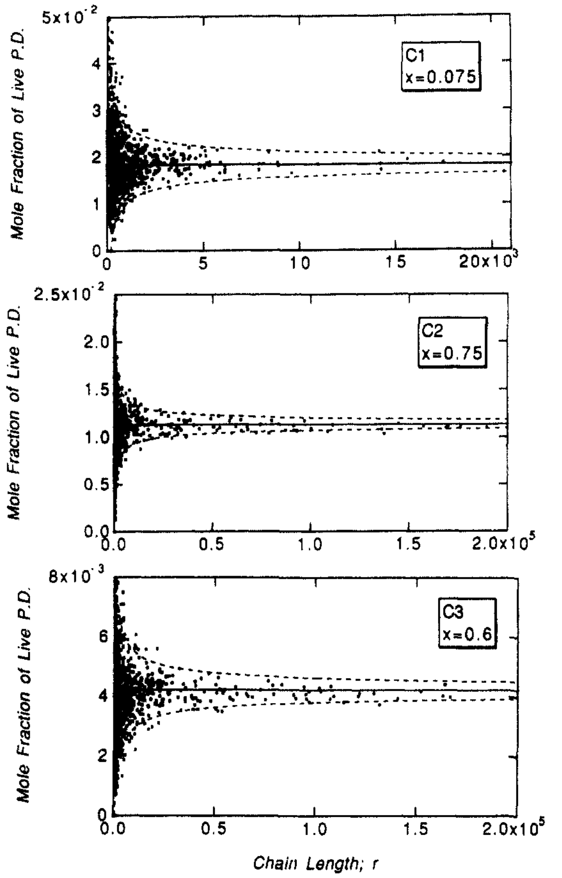

Figure 7. Calculated mole fraction of live pendant double bonds as a function of chain length.

polyradicals can never give a serious effect in the present simulation. Concerning the second assumption employed in the method of moments, it is possible to make a direct test using the present simulation; namely, the number of live pendant double bonds is simulated for each primary polymer molecule and the average over a whole cross-linked polymer molecule can be calculated. Figure 7 shows the calculated mole fraction of live pendant double bonds, and it does show the independence of chain length. If the probability that a randomly selected monomeric unit on the polymer molecule possesses a live pendant double bond is the same for all monomeric units, the distribution is binomial. Assuming the binomial distribution, the average cross-linking density and the region of ±2 (standard deviation) are also shown in Figure 7. These funnel shapes agree satisfactorily with the simulated results, and the independence of chain length is confirmed.

One of the remarkable features of the present method is that it is possible to calculate the whole MWD profile. Figure 8 shows the calculated MWD development based on the simulation of 1000 polymer molecules. The distribution profile is fairly rough; however, an important feature of the change in MWD can be seen. The shape of the low molecular weight tails is essentially the same irrespective of the extent of reaction, while high molecular weight tails are increased significantly as the reaction proceeds.

It is worth noting here that it took less than 3 h to obtain a whole distribution profile using a personal computer (Macintosh IIci), even though the total number of simulated monomeric units reaches more than 10 million in some calculations. This method is quite powerful, and the distribution profile can be improved by increasing the number of simulated polymer molecules easily.

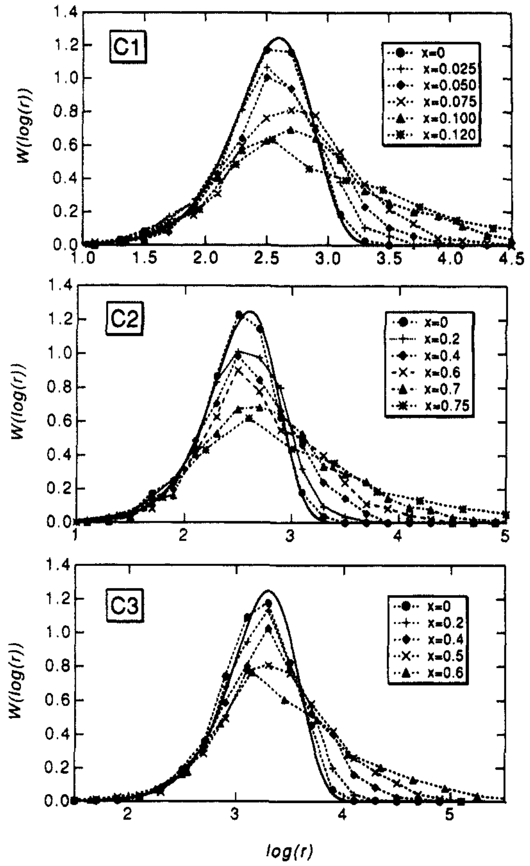

Figure 8. Weight–chain length distribution development during cross-linking copolymerization. Solid curves are the distributions at $x = 0$, i.e., the weight–chain length distribution of the primary polymer molecules.

Gel Point. The onset of gelation was determined in the following manner: (1) The polymer molecule with more than 100 generations is considered a gel molecule. (2) Determine the weight fraction of the gel molecule by simulating 100 polymer molecules, and iterate this calculation five times. (3) From the results in item (2), the 95% confidence intervals of the weight fraction of gel molecule are calculated, and when the confidence interval fails to include zero, the gel point is determined. This criterion for the onset of gelation worked well for the polycondensation reactions of an A_3 type monomer.[30] In order to shorten the calculation time, a polymer molecule that possesses more than 100 primary polymer molecules in one generation when the generation is larger than 50 was also considered a gel molecule in addition to the criterion shown in (1). Figure 9 shows the calculated weight fraction of gel with their 95% confidence intervals. From these figures the gel point for each polymerization condition was determined as shown in Table II. Table II shows the gel point calculated from other methods also. A significant deviation from other methods was not observed even though the variance of the cross-linking density distribution is fairly large in conditions C2 and C3.

Flory's theory[4,32] shows that the cross-linking density of the gel molecule at the gel point is twice as large as the average cross-linking density. This was tested by the present simulation using polymer molecules that reach 100 generations. The number of trials was too small for this purpose (only 2–5 gel molecules are tested), and, therefore, statistically valid values were not obtained; however, Flory's theory seems to be roughly verified as shown in Table III. More detailed analysis on the postgelation period will be reported in the near future.

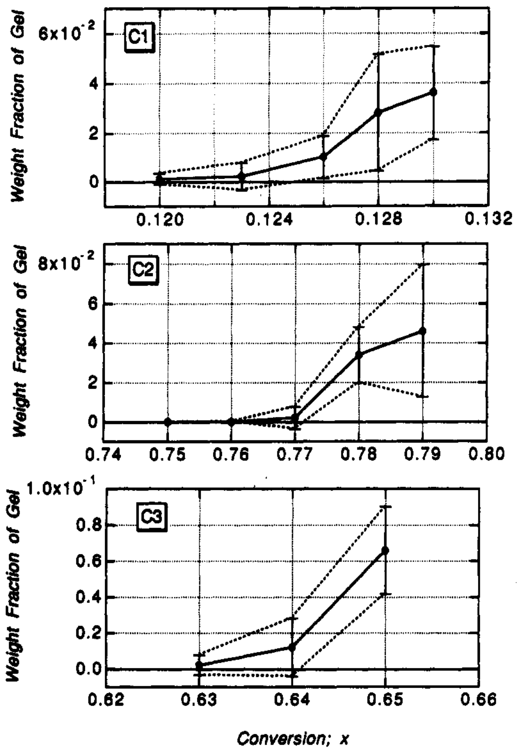

Figure 9. Calculated weight fraction of gel at the vicinity of the gel point with the 95% confidence intervals.

Table II
Calculated Gel Point, x_c

	C1	C2	C3
method of moments	0.126	0.772	0.645
Flory/Stockmayer model	0.126	0.780	0.655
present simulation	0.125	0.772	0.641

Table III
Cross-Linking Density within Gel Fraction at the Gel Point, $\bar{\rho}_{gel}|_{x=x_c}$

	C1 (x = 0.126)	C2 (x = 0.78)	C3 (x = 0.64)
$\bar{\rho}_{gel}$	5.06×10^{-3}	5.08×10^{-3}	1.01×10^{-3}
2ρ	5.00×10^{-3}	5.00×10^{-3}	9.48×10^{-4}

The present theory is quite general and can be used for various complex reaction systems including cross-linking, branching, and degradation reactions. The application to the polymerizations that include chain transfer to polymer in a batch reactor[33] and a continuous stirred tank reactor[30] can be found elsewhere.

Conclusions

A new simulation method to predict the network formation in free-radical copolymerization of vinyl and divinyl monomers is proposed. This method is based on the cross-linking density distribution of the primary polymer molecule, which is a very important feature of the network formation in a kinetically controlled system. The present simulation confirmed that the method of moments and the Flory–Stockmayer theory are good approximations for the prediction of the MWD in the pregelation period. In terms of the MWD a significant effect of the cross-linking density distribution was not observed. The present theory accounts for the history of the generated molecular structure and can be applied to various polymerization systems as well as for various reactor types.

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