Kinetics of Network Formation in Free-Radical Cross-Linking Copolymerization

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Received April 1, 1993; Revised Manuscript Received June 16, 1993[•]

ABSTRACT: A new kinetic theory for network formation in free-radical copolymerization of vinyl and divinyl monomers is used to investigate various important property changes in the postgelation period, such as the weight fraction of gel, the molecular weight distribution, the cross-linking density within sol and gel fractions, the partition of the unreacted pendant double bonds between sol and gel, etc. This theory is based on the cross-linking density distribution among primary polymer molecules, and the history of the generated network structure is fully accounted for. It is shown clearly that the deviation from the Flory–Stockmayer theory becomes significant as the variance of the cross-linking density distribution increases. The present simulation model is quite general and can be applied to various complex polymerization systems that involve cross-linking and branching in a kinetically controlled system irrespective of the reactor types used.

Introduction

Some 50 years ago, Flory and Stockmayer proposed a statistical theory for polymeric network formation.[1-4] The Flory–Stockmayer theory was a brilliant development, and various statistical models[5-13] developed since then are still within the realm of the Flory–Stockmayer theory even though the mathematical languages used are slightly different. Since the Flory–Stockmayer theory is based on the most probable chain length distribution given the number of cross-link points and the chain length distribution of the primary polymer molecules, the prediction is expected to deviate for nonequilibrium systems such as for free-radical cross-linking polymerization. However, even when a kinetic approach is used for free-radical cross-linking copolymerization, the obtained results do not deviate much from the Flory–Stockmayer theory in the pregelation period as long as the detailed structural differences among various polymer molecules are ignored and the average properties over a whole system are considered.[14]

A notable paradigm shift was made in the advent of the percolation theory[15-30] that belongs to a non-mean-field theory. The percolation theory has opened new aspects in the computational physics and has developed along with the progress achieved in computer hardware. The space-dimensionality and nonrandomness in the distribution of the cross-link points can be accounted for in this theory. De Gennes wrote in his book[31] that "it took more than 30 years to convince experimentalists that mean-field theory was wrong", and very detailed simulation models are being developed for the kinetics of network formation. However, the "virtual reality" processed in a supercomputer is still far from simulating the real world mainly due to the limitation of the computational ability of the supercomputers. This is understandable when one realizes that 1 mol consists of 6×10^{23} molecules. Therefore, percolation theory has been essentially devoted to describe the behavior near the critical threshold (gel point), where the system-specific features are not important. At present, the mean-field and non-mean-field approaches have both merits and demerits. What is really important at this stage of the development of a realistic model for polymeric network formation would be not to decide which type of model is more appropriate but to refine both types of theories to accommodate various system-specific features.

Recently, by a consideration of the history of each primary polymer molecule formed at different time, the cross-linking density distribution among primary polymer molecules was proposed for free-radical cross-linking copolymerization.[32-35] The cross-linking density distribution is a very important feature in polymeric networks formed in a kinetically controlled system, and it states that polymeric networks are heterogeneous at least on a microscopic scale, which is a clear difference from a network formed in an equilibrium system. Since the cross-linking density distribution provides information on how each chain is connected to other chains, a detailed analysis on the kinetics of network formation becomes possible by application of the Monte Carlo simulation.[36,37] In this method, not only averages but also various distributions, such as the molecular weight distribution, the distribution of cross-linked units, and the distribution of the unreacted pendant double bonds among various polymer molecules can be calculated. This method is basically a percolation on a Bethe lattice; however, it provides an efficient way to sample polymer molecules from an infinite number of polymer molecules in the reaction mixture on a weight basis, and the amount of calculations can be reduced significantly compared with the usual percolation calculations. In this paper, this method is applied to investigate the network formation in free-radical copolymerization of vinyl and divinyl monomers in the postgelation period.

Theoretical Section

Cross-Linking Density Distribution. 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. The cross-link points are divided into two types, namely, the instantaneous and additional cross-links points.[32-38] The cross-link points that are formed during the formation of the primary polymer molecule are defined as the instantaneous cross-link points, while those formed after the primary polymer molecule was born are defined as the additional cross-link points as shown in Figure 1. Since a cross-link 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 density. Therefore, at the total monomer conversion $x = n$, the total number of cross-link points on a given primary polymer molecule that is formed at $x = b$ is given by the sum of the cross-link points that are formed during the formation of the primary polymer molecule (instantaneous cross-linking density, $\rho_i(b)$) and the additional cross-link points that are added in the conversion interval b to n (additional cross-linking density, $\rho_a(b,n)$).

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

Fundamental equations for each type of cross-linking density can be derived from simple balance equations. For a batch cross-

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[•] Abstract published in *Advance ACS Abstracts*, August 15, 1993.

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linking copolymerization, they are given by[33,34]

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

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

where k_p^{*0} and k_p are the pseudokinetic rate constants[32-34,39] for cross-linking and propagation reactions, respectively. F_2 is the mole fraction of divinyl monomer bound in the given primary polymer molecules, 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.

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 understand the network structure development. More discussion on the cross-linking density distribution can be found elsewhere.[32-34]

On the basis of the cross-linking density distribution, it is possible to determine how each primary polymer molecule is connected to other primary polymer molecules with a different birth time (or conversion).[36,37] The additional cross-link points on a primary polymer molecule that is formed at conversion $x = \theta$ must be connected to the primary polymer molecules that are formed after $x = \theta$, namely, in the conversion interval θ to ψ. The probability density that the primary polymer molecule formed at $x = \theta$ is connected via its additional cross-link points to the primary polymer molecules formed at $x = u$ ($\theta < u < \psi$), $P_a(u|\theta)$, is given by[36]

$$P_a(u|\theta) = \frac{\left.\dfrac{\partial \rho_a(b,u)}{\partial u}\right|_{b=\theta}}{\displaystyle\int_\theta^\psi \left.\frac{\partial \rho_a(b,u)}{\partial u}\right|_{b=\theta} du} = \frac{\left(\dfrac{k_p^{*0}(u)}{k_p(u)}\right)\left\{\dfrac{F_2(\theta) - \rho_a(\theta,u) - \rho_c(\theta,u)}{1-u}\right\}}{\displaystyle\int_\theta^\psi \left[\left(\frac{k_p^{*0}(u)}{k_p(u)}\right)\left\{\frac{F_2(\theta) - \rho_a(\theta,u) - \rho_c(\theta,u)}{1-u}\right\}\right] du} \tag{4}$$

On the other hand, the instantaneous cross-link points on a primary polymer molecule that is formed at conversion, $x = \theta$, must be connected to the primary polymer molecules that were formed prior to $x = \theta$, namely, in the conversion interval 0 to θ. The probability density that the primary polymer molecule formed at $x = \theta$ is connected via its instantaneous cross-link points to the primary polymer molecules formed at $x = z$ ($0 < z < \theta$), $P_i(z|\theta)$, is given by[36]

$$P_i(z|\theta) = \frac{\left.\dfrac{\partial \rho_a(z,n)}{\partial n}\right|_{n=\theta}}{\displaystyle\int_0^\theta \left.\frac{\partial \rho_a(z,n)}{\partial n}\right|_{n=\theta} dz} = \frac{\{F_2(z) - \rho_a(z,\theta) - \rho_c(z,\theta)\}}{\displaystyle\int_0^\theta \{F_2(z) - \rho_a(z,\theta) - \rho_c(z,\theta)\}\, dz} \tag{5}$$

By application of eqs 4 and 5, it is possible to determine how each primary polymer molecule formed at $x = \theta$ is connected with other primary polymer molecules formed at $x = z$ ($0 < z < \theta$) and $x = u$ ($\theta < u < \psi$). To date, the deterministic solution that satisfies the constraints given by eqs 2–5 is not given. However, at least it is possible to make a computer simulation using the Monte Carlo method.[36,37]

Simulation Method. First, select a primary polymer molecule randomly on a weight basis from the reaction mixture at $x = \psi$ and determine the birth conversion of the selected primary polymer molecule, θ. When the birth conversion is fixed, the chain length of this primary polymer molecule can be determined from the weight-chain length distribution given by[40]

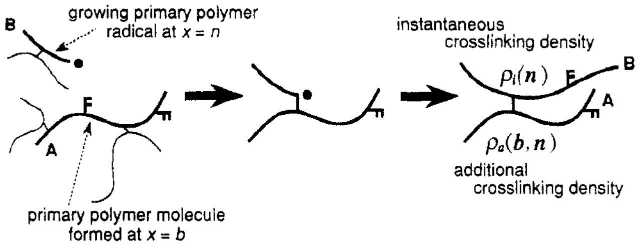

Figure 1. Schematic drawing of the process of cross-linking. At $x = n$, the cross-linking density of the primary polymer molecule which was formed at $x = b$ is given by eq 1.

$$W(r,\theta) = (\tau + \beta)\{\tau + (\beta/2)(\tau + \beta)(r-1)\}r \exp\{-(\tau + \beta)r\} \tag{6}$$

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

Once the chain length of the primary polymer molecule is fixed, the number of cross-link points on this primary polymer molecule can be determined on the basis of the cross-linking density distribution. The additional cross-link points must be formed on the divinyl monomer units in the sequence of the polymer chain; therefore, one has to account for the statistical copolymer composition distribution for copolymer chains in a strict sense especially when the chain length is small. On the basis of the terminal model for copolymerization, this distribution is conveniently given by the Stockmayer bivariate distribution of chain length and composition.[39,41] The Stockmayer bivariate distribution $W(r,y)$ consists of the product of weight-chain length distribution $W(r)$ (see eq 6) and composition distribution $Comp(y|r)$ that is given by the conditional probability distribution given the chain length r.

$$Comp(y|r) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{y^2}{2\sigma^2}\right) \tag{7a}$$

$$y = F_2 - F_{2,\mathrm{mean}} \tag{7b}$$

$$\sigma^2 = \frac{F_{1,\mathrm{mean}} F_{2,\mathrm{mean}} K}{r} \tag{7c}$$

$$K = \{1 + 4F_{1,\mathrm{mean}} F_{2,\mathrm{mean}}(r_1 r_2 - 1)\}^{0.5} \tag{7d}$$

After determination of the number of divinyl monomer units in the given primary polymer molecule (n) based on the compositional distribution for instantaneously formed primary polymer molecules, the number of additional cross-links (m) can be determined from the following binomial distribution:

$$p_a(m) = \binom{n}{m}\left(\frac{\rho_a}{F_2}\right)^m \left(1 - \frac{\rho_a}{F_2}\right)^{n-m} \tag{8}$$

Note that F_2 is the mole fraction of divinyl monomer bound in the given primary polymer molecule that is determined from eq 7; therefore ρ_a must be determined by substituting F_2 so determined into eq 2 when the bivariate distribution must be taken into account.

However, when the chain length of the primary polymer molecule is large enough and the effect of the copolymer composition distribution is virtually negligible, or the monomer sequence in polymer chain is considered random (namely, the product of the reactivity ratios $r_1 r_2$ is equal to unity or the mole fraction of divinyl monomer is much smaller than unity), the probability that a primary polymer with chain length r and the additional cross-linking density ρ_a possesses m additional cross-link points, $p_a(m)$, is given by the following binomial distribution:

$$p_a(m) = \binom{r}{m}\rho_a^{\,m}(1 - \rho_a)^{r-m} \tag{9}$$

In this case, F_2 reduces to the instantaneous mole fraction of divinyl monomer bound in the primary polymer chains; namely, $F_{2,\mathrm{mean}}$ is used to calculate ρ_a in eq 2. In this paper, eq 9 is used in the computer simulations.

Since the reactivity of the pendant double bonds is influenced by the physical effects such as steric hindrance[42] and the excluded volume effect,[43] the number of the instantaneous cross-link points on the given primary polymer molecule cannot be calculated from simple copolymerization equations. However, at least when the cross-linking density is much smaller than unity, the number of instantaneous cross-links points can be determined from the binomial distribution.

$$p_i(m) = \binom{r}{m}\rho_i^{\,m}(1-\rho_i)^{r-m} \tag{10}$$

If the given primary polymer molecule possesses cross-link points, the connectivity to other primary polymer chains through additional and instantaneous cross-link points can be determined using eqs 4 and 5. The chain length of the connected primary polymer molecule can be determined from the weight-chain length distribution given by eq 6. These processes are reiterated until all primary polymer molecules fail to be connected to the next generation. By simulation of a large number of polymer molecules, the statistical properties of cross-linked polymers can be determined effectively. The present simulation method gives a direct solution for the Bethe lattice formed under nonequilibrium conditions; therefore, it can be used to examine the applicability of the earlier theories of network formation to kinetically controlled systems. More details on the simulation method can be found elsewhere.[36,37]

Until the conversion not greater than the gel point, all cross-links are formed intermolecularly since the weight fraction of its own polymer molecule is virtually zero. Therefore, structural information of all polymer molecules can be obtained until the point of gelation including the gel point using the present simulation method. However, in the postgelation period there is a finite probability that the cross-links are formed within a gel molecule since the weight fraction of gel is not zero. Therefore, it is worth noting here that the properties of a whole gel molecule in the postgelation period must be obtained from the difference between the overall property and the property of the sol fraction. A direct simulation of the cross-linked structure of a gel molecule is possible only in a limited domain in which the probability of cycle formation via cross-links is negligibly small.

Results and Discussion

The simulation results for the pregelation period can be found elsewhere.[36,37] In this paper, various property changes during the postgelation period are simulated. The main purpose of the present simulation is to investigate the effect of the cross-linking density distribution on the molecular constitution in the postgelation period. Toward this end, the following simplifying conditions are used to make computer calculations: (1) There is no cyclization reactions within finite polymer molecules. (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 during polymerization. These assumptions may not be realistic; especially, the cyclization would be important for many systems. However, the cyclization within finite polymer molecules is not included in the present simulation on the basis of the following reasons: (a) Even without cyclization reactions, one can investigate the cross-linked polymer networks formed under given cross-linking density distribution, and the effect of the cross-linking density distribution on the molecular consitution can be discussed effectively. (b) Various models for the cyclization reactions have been proposed even in the context of a mean-field theory[33,34,44–51] (the percolation theory includes cyclization reactions by nature). These models or the results obtained from the percolation theory could be incorporated into the present model calculations; however, the obtained results for cyclization reactions are still too premature to elucidate the real cyclizations. Therefore, incorporation of cyclization would just obscure the present aim of simulation. On the other hand, since cyclization reactions are dominated by the molecular conformation of polymer chains, the detailed information that can be obtained from the present simulation could be used to develop a new approach for cyclizations in the future.

Table I. Calculation Conditions Investigated

	C1	C2	C3	C4
f_{20}[a]	0.01	0.01	0.01	1×10^{-3}
r_1, r_2	0.5, 2.0	0.5, 2.0	3.0, 0.333	0.1, 10.0
k_p^{*0}/k_p	1.0	0.1	0.1	4.0
τ[b]	5×10^{-3}	5×10^{-3}	1×10^{-3}	5×10^{-3}
β[b]	0	0	0	0

[a] Initial mole fraction of divinyl monomer. [b] τ and β are not used in the calculation for the chain length distribution between cross-links.

Four conditions shown in Table I are investigated in the computer simulations. The conditions C1–C3 are the same as those used in the previous papers[36,37] for the calculations up to the gel point. The calculated cross-linking density distribution changes are shown in Figure 2. The condition C1 corresponds to Flory's simplifying assumptions for vinyl/divinyl copolymerization,[4] 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. A homogeneous network is formed under these conditions, and the expected cross-linking density is the same for all chains.[33,34,51] The cross-linked structures for C2–C4 are shown to be heterogeneous. C2 is the case where the reactivity of the pendant double bonds is decreased while the reactivities of the monomeric double bonds are the same. Roughly, C3 shows the case in which the reactivity of the double bonds in the divinyl monomer is lower than that in the monovinyl monomer, while in C4 the reactivity of the double bonds in divinyl monomer is higher. A similar type of cross-linking density distribution shown in C4 might also be observed when the pendant double bonds are consumed significantly in the earlier stages of polymerization due to a significant effect of cyclizations.

Weight Fraction of Gel. Since a gel molecule is a polymer molecule with infinite chain length, the polymer molecule that continues to be connected infinitely is a gel molecule. Practically, the polymer molecules with chain length larger than $150\bar{P}_{w,sol}$ (where $\bar{P}_{w,sol}$ is the weight-average chain length within sol fraction) are considered gel molecules in the present calculations. Figure 3 shows the calculated weight fraction of gel as a function of conversion from a set of calculations for 2000 polymer molecules. The comparison was made with Flory's theory[4,52] (eq 11) and the generalized Flory's theory[32,33,53] (eq 12), where $\overline{W}_g$ is the weight fraction of gel and $\overline{W}(r)$ is the weight-chain length distribution of the accumulated primary polymer molecules. All superscript bars indicate the accumulated values up to the present time.

$$\overline{W}_g = 1 - \sum_{r=1}^{\infty} \overline{W}(r)(1-\bar{\rho}\overline{W}_g)^r \tag{11}$$

$$W_g(\theta,\psi) = 1 - \sum_{r=1}^{\infty} W(r,\theta)(1-\rho(\theta,\psi)W_g(\theta,\psi))^r \tag{12a}$$

$$\overline{W}_g(\psi) = \frac{1}{\psi}\int_0^{\psi} W_g(\theta,\psi)\,d\theta \tag{12b}$$

In C1 in which a homogeneous polymer network is formed, these three types of model calculations agree completely. As shown in C2–C4, the generalized Flory's theory does not always generalize Flory's theory for

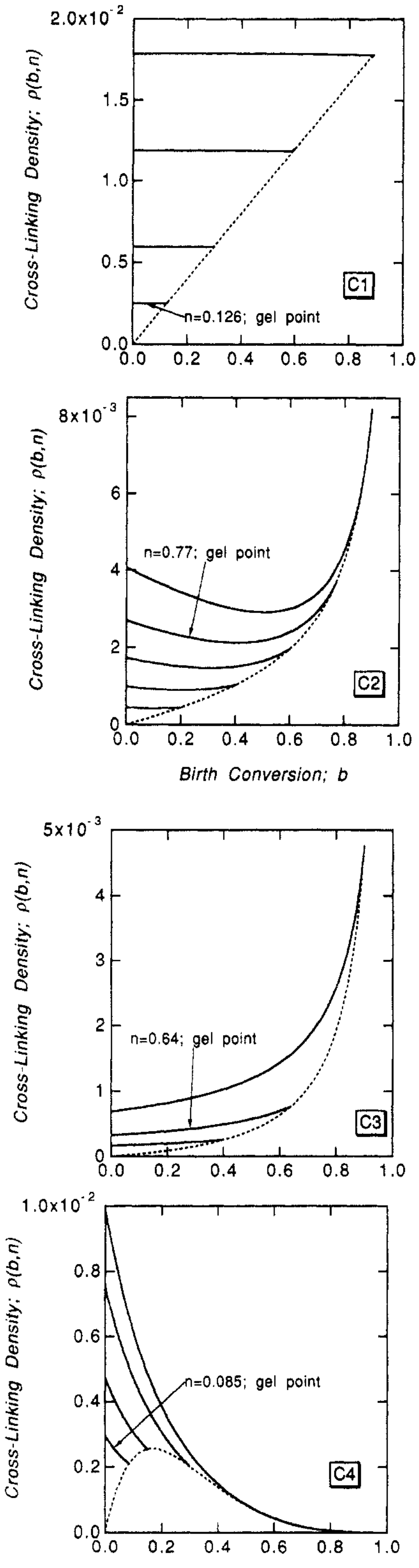

Figure 2. Calculated cross-linking density distribution development under conditions shown in Table I.

kinetically controlled systems. Flory's theory assumes an equilibrium system, and the deviation from Flory's theory is large under conditions C3 and C4 in which the variance of the cross-linking density distribution is large. Especially in C4, Flory's theory predicts that a gel molecule formed at $x = 0.0855$ disappears at $x = 0.800$. The disappearance of a gel molecule could never occur in a free-radical polymerization in which the bondings once formed are not broken, which is correctly accounted for in the present simulation.

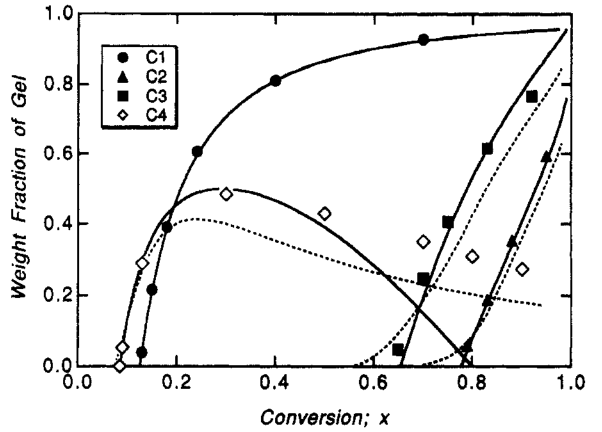

Figure 3. Calculated weight fraction of gel. The solid curves are calculated from Flory's theory, while the broken curves are from the generalized Flory's theory.

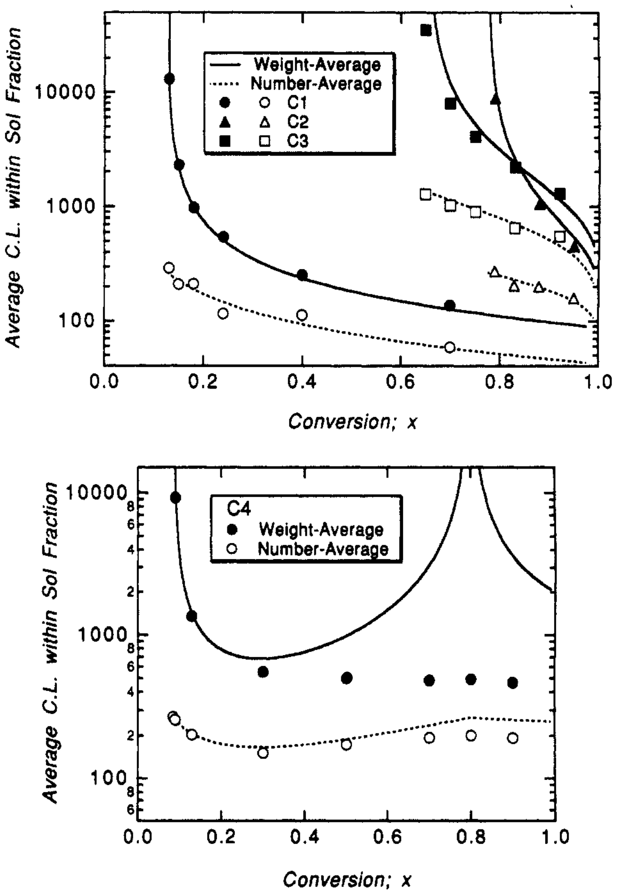

Figure 4. Calculated average chain length development within sol fraction. Curves are calculated from Flory's theory.

Molecular Weight Distribution Development. Figure 4 shows the calculated weight- and number-average chain lengths within sol fraction. The curves are calculated from Flory's theory.[4,52] In C1 the agreement with Flory's theory is satisfactory. This is a direct proof that the statistical theory developed by Flory provides an exact solution for random cross-linking of primary polymer molecules. Somewhat larger scattering in the number-average chain length is attributed to the fact that the present simulation is conducted on the basis of the weight-chain length distribution and not the number basis.[37,54] The scattering can be reduced by conducting the simulation on a number basis or by increasing the number of the simulated polymer molecules. The calculated weight-average chain lengths deviate from Flory's theory significantly in C3 and C4.

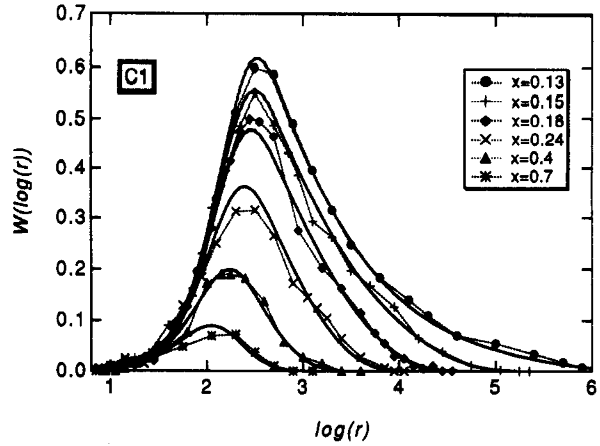

Figure 5. Calculated weight-chain length distribution change in the postgelation period for C1. Solid curves are calculated from eq 14.

One of the remarkable features of the present simulation method is that it is possible to calculate various distributions for heterogeneously cross-linked systems. In the context of the Flory–Stockmayer theory that is based on the most probable size distribution, the molecular weight distribution (MWD) profile can be calculated only when all cross-link points are distributed homogeneously. In order to examine the effect of cross-linking density distribution on the MWD, let us compare the present simulation results with homogeneously cross-linked systems using the average cross-linking density. In the present calculation conditions (C1–C4), the chain length drift during polymerization is not considered, and $\beta = 0$ in the weight-chain length distribution given in eq 6; therefore, the weight-chain length distribution of all primary polymer molecules is simply given by

$$W^0(r) = \frac{r}{(\bar{P}_{\rm np})^2}\exp\left(-\frac{r}{\bar{P}_{\rm np}}\right) \tag{13}$$

where $\bar{P}_{\rm np}$ is the number-average chain length of the primary polymer molecules. When these primary polymer molecules are cross-linked randomly, the weight-chain length distribution of the cross-linked polymers is given by[55,56]

$$W(r) = \frac{r}{(\bar{P}_{\rm np})^2}\exp\left\{-\frac{(\bar{P}_{\rm np}\bar{\rho}+1)r}{\bar{P}_{\rm np}}\right\}\sum_{k=0}^{\infty}\frac{\left(\frac{r}{\bar{P}_{\rm np}}\right)^{3k}(\bar{P}_{\rm np}\bar{\rho})^k}{(k+1)!(2k+1)!} \tag{14}$$

Note that the necessary number of terms in eq 14 increases significantly as the chain length increases.

Comparisons with eq 14 (the solid curves) are shown in Figures 5–8. All simulation results are based on the 2000 simulated polymer molecules; therefore, total number of simulated sol molecules decreases significantly as the weight fraction of gel increases; nevertheless, MWD profiles with satisfactory accuracy can be obtained with these small number of simulated polymer molecules. Since the MWD developments in the pregelation period for C1–C3 are shown earlier,[36,37] the MWD changes during the whole course of polymerization are now given.

No systematic deviations are observed under conditions C1 and C2 as shown in Figures 5 and 6. In C3, except at $x = 0.83$ at which the weight fraction of gel agrees with Flory's theory (see Figure 3), deviation from eq 14 is observed; the higher molecular weight tails for $x = 0.65$–0.75 are slightly smaller than in eq 14 while the area is much larger at $x = 0.92$. In C4, eq 14 may be a reasonable approximation until $x = 0.3$; however, significant deviations are observed for high conversions ($x = 0.5$–0.9). In these high conversions, most polymer molecules produced are linear.

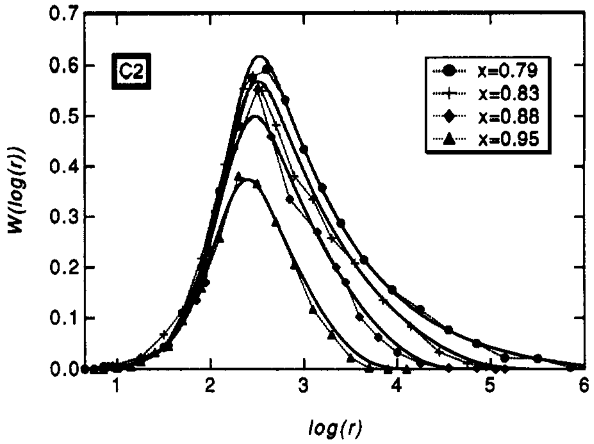

Figure 6. Calculated weight-chain length distribution change in the postgelation period for C2. Solid curves are calculated from eq 14.

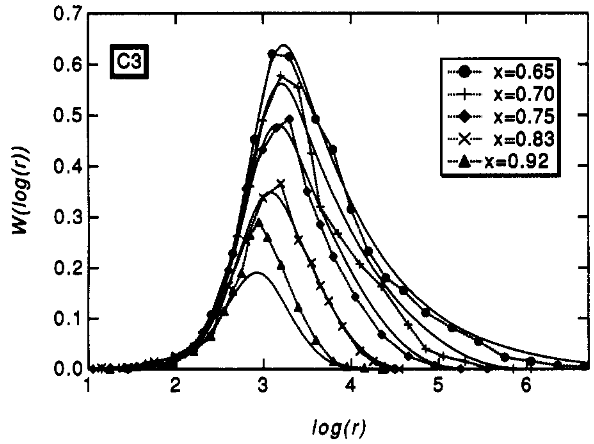

Figure 7. Calculated weight-chain length distribution change in the postgelation period for C3. Solid curves are calculated from eq 14.

Partition of Cross-Link Points between Sol and Gel. In the present simulation method, it is possible to determine the distribution of cross-link points. Figures 9–12 show the calculated average cross-linking density within sol and gel fractions. Complete agreement with Flory's theory is shown for C1; however, clear deviations are observed in C2–C4. In C2, the property changes concerning molecular size distribution agree satisfactorily with the homogeneous system (Flory's theory); however, the partition of cross-link points is clearly different. This fact implies that even when the MWD agrees with a certain theory this fact does not necessarily mean that the theory reflects true structural information.

In the previous paper,[37] the cross-linking densities of very large polymer molecules are shown to approach a certain cross-linking density as the chain length increases in the pregelation period. In fact, this result can be observed for other distribution functions for nonlinear polymerizations such as free-radical polymerization with long-chain branching[54,57,58] and the Stockmayer distribution for nonlinear polycondensation.[2,59] The asymptotic cross-linking density for the maximum cluster $\rho_{\rm M}$ was also estimated, and it was found that $\rho_{\rm M}$ is much larger than the average cross-linking density $\bar{\rho}$.[37] The maximum cluster in the postgelation period is a gel molecule, and the change in the ratio $\rho_{\rm M}/\bar{\rho}$ is also shown in Figures 9–12.

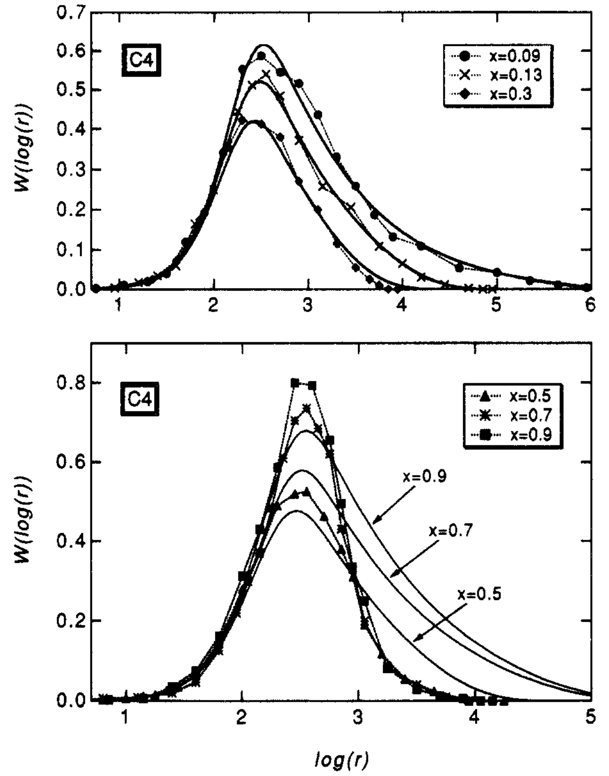

Figure 8. Calculated weight-chain length distribution change in the postgelation period for C4. Solid curves are calculated from eq 14.

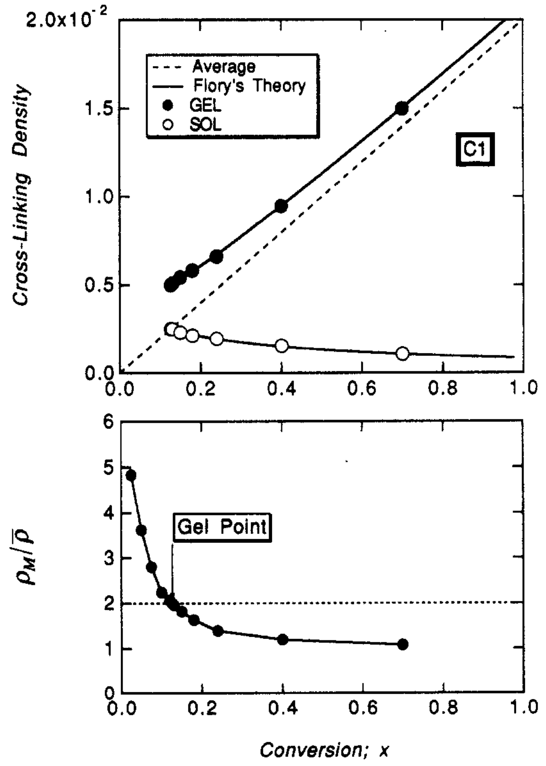

Figure 9. Calculated average cross-linking density within sol and gel fractions and the ratio of the cross-linking density of the largest polymer molecule (ρ_M) to the average cross-linking density ($\bar{\rho}$) under condition C1.

The ratio decreases continuously in C1–C3, while it takes minimum around $x = 0.3$ in C4. Flory's theory[4,52] predicts the ratio is 2 at the gel point; however, a small but statistically valid deviation is observed in C2–C4.[37] (Note that a direct simulation of the whole network structure of a gel molecule is possible only right at the gel point; therefore, the variance is very small at the gel point.)

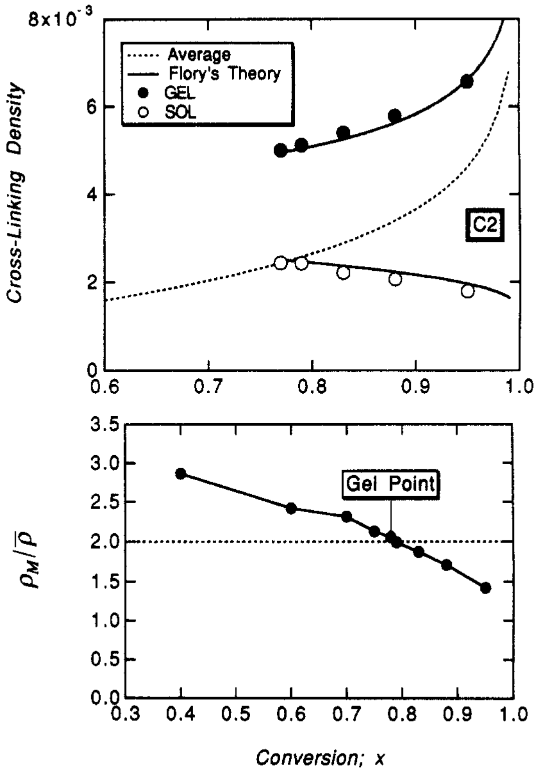

Figure 10. Calculated average cross-linking density within sol and gel fractions and the ratio of the cross-linking density of the largest polymer molecule (ρ_M) to the average cross-linking density ($\bar{\rho}$) under condition C2.

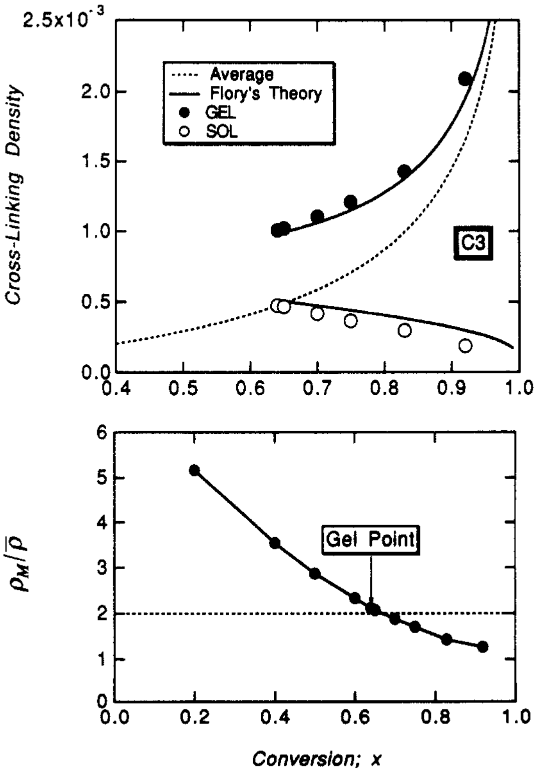

Figure 11. Calculated average cross-linking density within sol and gel fractions and the ratio of the cross-linking density of the largest polymer molecule (ρ_M) to the average cross-linking density ($\bar{\rho}$) under condition C3.

Partition of the Unreacted Pendant Double Bonds. An earlier paper[36] shows that the distribution of the unreacted pendant double bonds can be considered homogeneous as a good approximation; namely, the mole fraction of the unreacted pendant double bonds is independent of chain length in the pregelation period. Figure

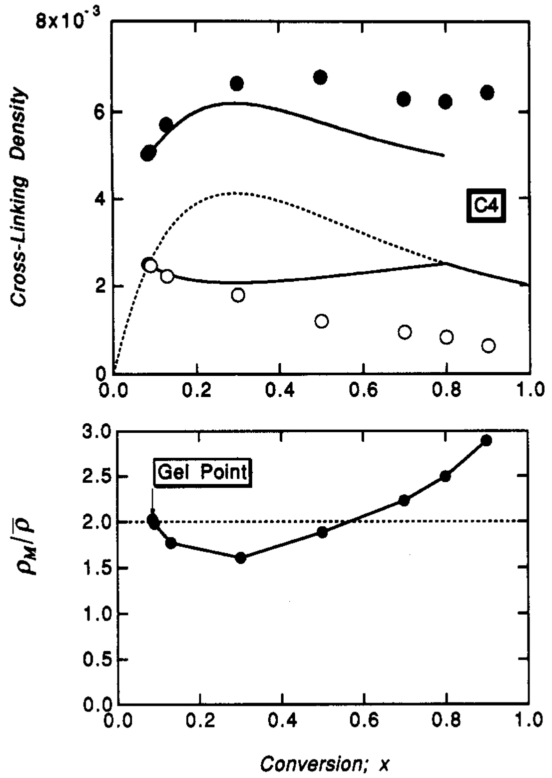

Figure 12. Calculated average cross-linking density within sol and gel fractions and the ratio of the cross-linking density of the largest polymer molecule (ρ_M) to the average cross-linking density ($\bar{\rho}$) under condition C4.

13 shows the mole fraction of the unreacted pendant double bonds of each polymer molecule as a function of chain length at the gel point, x_c. The solid lines indicate the average mole fraction of the unreacted pendant double bonds. Except for C1, small but clear deviation is observed for larger polymer molecules; however, the deviation is still small and the mole fraction of the unreacted pendant double bonds approaches a certain value asymptotically. In the postgelation period, the latter feature is preserved within the sol fraction; however, the average mole fraction of the unreacted pendant double bonds within the sol fraction deviates from the average over a whole system as shown in Figure 14. Except for C1, the partition of the unreacted pendant double bonds within sol and gel fractions is different.

Effect of Chain Length Drift. Up to the present, the MWD of the primary polymer molecules is assumed to be constant during polymerization; however, the chain length of the primary polymer molecule may decrease due to the reduced monomer concentration or increase significantly due to the decrease in the bimolecular termination reaction rate known as the gel effect. Since the mobility of the chains bound in the gel molecule is restricted severely, the bimolecular termination reaction rate is expected to decrease significantly and a significant acceleration in polymerization rate has been observed especially in the postgelation period.[60,61] Except when the chain-transfer reactions dominate the chain length distribution of the primary polymer molecules, the chain length drift is expected to occur especially in the postgelation period. The effect of chain length drift can easily be accounted for in the present simulation method.

In order to examine the effect of chain length drift, the following drift of τ value in eq 6 is used for C3:

$$\tau = 1 \times 10^{-3} \exp\{-10(x - 0.66)\} \quad (x > 0.66) \qquad (15)$$

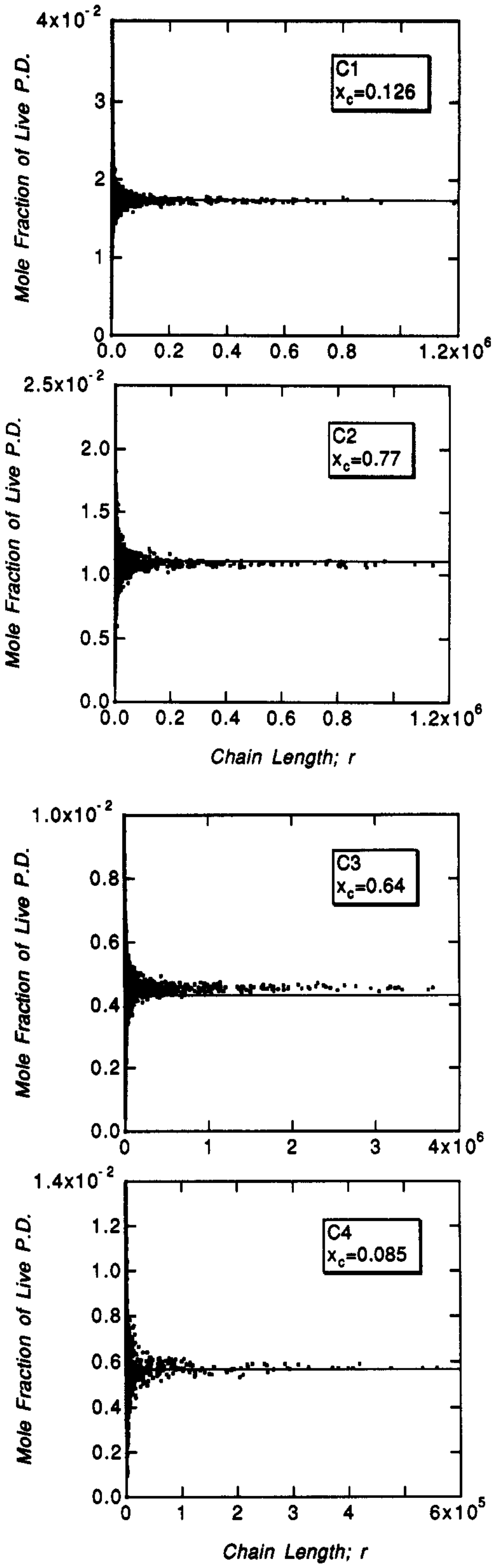

Figure 13. Distribution of the unreacted pendant double bonds at the gel point. The solid line shows the average mole fraction of the unreacted pendant double bonds.

The chain length drift of the primary polymer molecules is assumed to occur in the postgelation period. The weight-average chain length drift of the accumulated primary polymer molecules and that of the instantaneously formed primary polymer molecules are shown in Figure 15. The chain length drift for the accumulated primary polymer molecules is small although instantaneous distribution changes significantly.

Figure 16 shows the calculated weight fraction of gel, and the partition of the unreacted pendant double bonds is shown in Figure 14 (C3d). The chain length drift

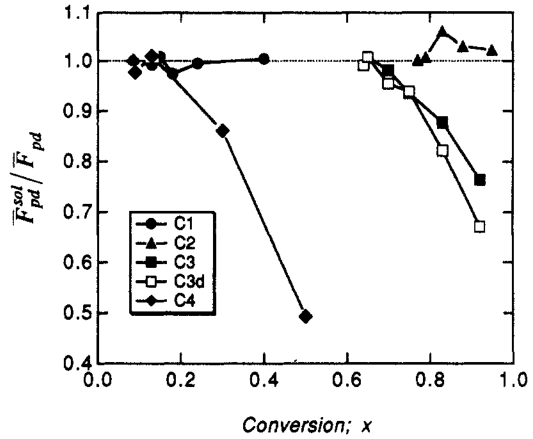

Figure 14. Ratio of the mole fraction of the unreacted pendant double bonds within sol fraction ($\overline{F}^{sol}_{pd}$) to the average mole fraction ($\overline{F}_{pd}$).

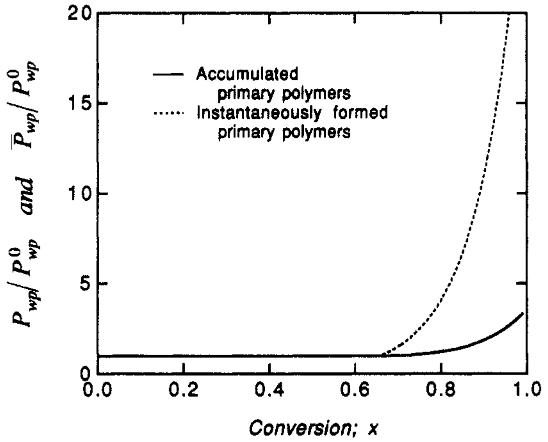

Figure 15. Weight-average chain length drift of the primary polymer molecules during polymerization for C3d in which the chain length drift is given by eq 15.

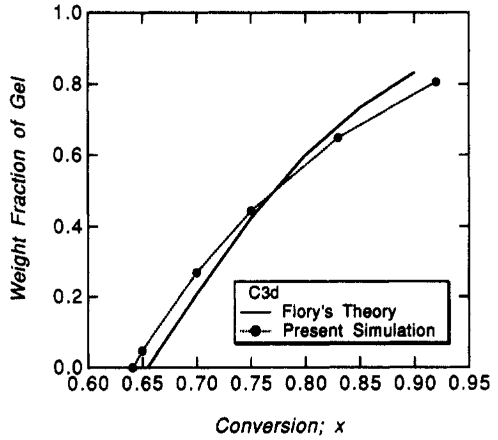

Figure 16. Calculated weight fraction of gel for C3d.

enhances the difference in the connectivity of each primary polymer molecule, and the deviation from Flory's theory becomes more significant. It is worth noting here that Flory's theory is valid as long as all primary polymer molecules are connected randomly; therefore, Flory's theory is still valid for the condition C1 with chain length drift.

Chain Length Distribution between Cross-Links. On the basis of the cross-linking density distribution, it is possible to determine the chain length distribution between cross-links. The cross-linking density that has been used in the present paper is defined with respect to the monomeric unit; however, for the purpose of the detailed investigation on the network structure, the cross-linking density that is defined with respect to units $\rho^f(b,n)$ (in which a divinyl monomer that constitutes a cross-linkage is counted as two units) would be more convenient to use. The relationship between $\rho(b,n)$ and $\rho^f(b,n)$ is given by[14,33,51]

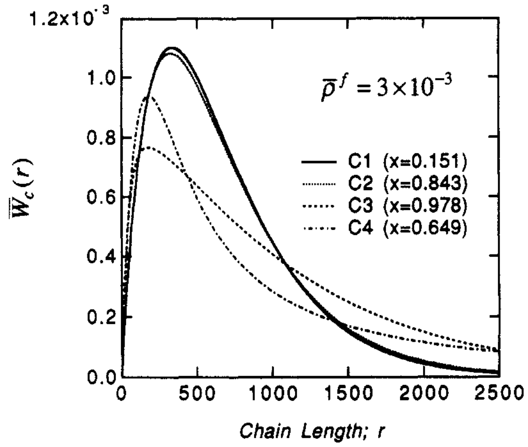

Figure 17. Calculated weight-chain length distribution between cross-links.

$$\rho^f(b,n) = \frac{\rho(b,n)}{1+\rho_i(b)} \qquad (16)$$

Obviously, the difference between ρ and ρ^f is negligible when the cross-linking density is much smaller than unity.

We are to make the following assumptions in order to simplify the calculations: (1) The sequence of units is random; namely, $r_1r_2 = 1$ and the instantaneous cross-link points are distributed randomly within a primary polymer molecule. (2) The chain length of the primary polymer molecules is large enough, and the effects of chain ends are not considered. Under these assumptions, the weight-chain length distribution between cross-links is given by

$$W_c(r,\theta,\psi) = r\{1-\rho^f(\theta,\psi)\}^{r-1}(\rho^f(\theta,\psi))^2 \qquad (17a)$$

$$\overline{W}_c(r,\psi) = \frac{1}{\psi}\int_0^{\psi} W_c(r,\theta,\psi)\, d\theta \qquad (17b)$$

In order to examine the effect of the cross-linking density distribution, the weight-chain length distribution between cross-links for C1–C4 with $\tau \approx 0$ is investigated at the same average cross-linking density level; namely, $\overline{\rho}^f = 3 \times 10^{-3}$. Figure 17 shows the calculated distribution. Since the average cross-linking density is fixed, the conversion levels in each condition are different as shown in the figure. The distribution profile for C2 is quite similar to the homogeneous network at this average cross-linking density level. The distributions for C3 and C4 are completely different from that of a homogeneous network. A more detailed analysis on the network structure of a gel molecule will be reported in the near future.

The present theory is quite general and can be used for various complex polymerization systems that includes cross-linking and branching regardless of the reactor types used. The application to polymerizations with long-chain branching can be found elsewhere.[54,62,63]

Conclusions

A kinetic theory for network formation in free-radical copolymerization of vinyl and divinyl monomers that is based on the cross-linking density distribution is used to investigate various important property changes in the postgelation period such as the weight fraction of gel, the molecular weight distribution development, the cross-linking density within sol and gel fractions, the partition of the unreacted pendant double bonds between sol and gel, etc. It is shown that the Flory–Stockmayer theory may be a good approximation as long as the variance of the cross-linking density distribution is small; however, the deviation is shown to be intolerable when the heterogeneity in the distribution of the cross-link points is significant.

The present theory accounts for the history of the generated molecular structure and can be applied to various complex polymerization systems as well as for various reactor types.

Acknowledgment. The author acknowledges financial support provided by the Iketani Science and Technology Foundation, Tokyo, Japan.

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