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Network Formation in Emulsion Cross-Linking Copolymerization

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ABSTRACT: A new Monte Carlo simulation model for the kinetics of emulsion copolymerization of vinyl and divinyl monomers is proposed. The polymer particles formed in emulsion polymerizations usually consist of less than 10^8 monomeric units; therefore, the kinetic behavior of all polymer molecules in each polymer particle can be simulated easily using the Monte Carlo method. It was found that the molecular weight distribution development in emulsion cross-linking copolymerization is completely different from that in homogeneous polymerizations. A drastic change in molecular weights at the gel point that is characteristic of homogeneous polymerizations is not a requisite for the microgel formation. It is expected that there are cases in which the gel point cannot be determined experimentally, and a new definition for gel may be required for emulsion polymers.

Introduction

More than 40 years ago it was already recognized that a microgel formed in emulsion polymerization possesses only supermolecular size and weight; it usually consists of about 10^6 monomeric units.[1] For example, let us assume the diameter of polymer particle $d_p = 0.1$ μm, the density of polymer $\rho_p = 1$ g/cm^3, and the molecular weight of monomeric unit $M = 100$. In this case, the total number of monomeric units in a polymer particle is calculated to be 3×10^6. Therefore, if all monomeric units are bound into a microgel and the number-average chain length of the primary polymer molecules is 1000, a microgel consists of only 3000 primary polymer molecules, and such a small number of molecules can be handled well in computers these days. This simple example illustrates that a computer simulation using the Monte Carlo method is a promising technique to analyze the kinetics of emulsion cross-linking copolymerization.

The Monte Carlo method has been applied widely to simulate polymeric network formation in homogeneous media.[2–11] Except a sampling technique proposed recently,[10,11] they use a finite reaction system to represent an infinite reaction system approximately; i.e., a very small part is cut out from the reaction mixture and the kinetic behavior of all molecules involved in it is simulated. This is clearly an approximation for homogeneous polymerization; however, this is the case for emulsion polymerization, and the effect of system boundary that is entrenched as a polymer particle must be properly accounted for. The only modification would be to account for the transfer of monomer and radicals between phases correctly. The monomer transfer from monomer droplets to polymer particles during interval II endows the cross-linked polymers formed in emulsion polymerization with unique features; i.e., the cross-linking density is high even from very early stages of polymerization, and polymer networks tend to be highly heterogeneous.[12]

In this paper, a new Monte Carlo simulation model for emulsion cross-linking copolymerization is proposed, various detailed information such as the full molecular weight distribution profile (MWD) and the distributions of cross-linked units and cycles is calculated, and differences from network formation in homogeneous media are discussed.

Model Development

Various levels of simulation models can be used in the Monte Carlo method. However, here we are to propose one of the simplest methods; namely, we are to generate primary polymer molecules based on the chain length distribution of the primary polymer molecules and then connect these chains every time a new primary polymer molecule is formed using an appropriate probability assuming the mass action law is valid.

Chain Length and Composition of the Primary Polymer Molecule. The MWD formed in emulsion polymerization is complicated even in a linear polymerization and shows a different tendency from that formed in homogeneous media. Quite often chain transfer to small molecules (monomer, chain-transfer agent, etc.) tends to become a dominant chain stoppage mechanism due to a long time interval of radical entry with a very fast bimolecular termination rate in small polymer particles.[13,14] In order to simplify our discussion, we are to assume that chain stoppage is transfer-dominated. This is not a requisite for the present Monte Carlo simulation. For example, a new Monte Carlo simulation method recently proposed for emulsion polymerization[15] can be incorporated with the present simulation directly. However, in order to focus our attention on the statistical property changes due to cross-linkages formed, we used a very simple MWD for primary polymer molecules even though virtually any MWD can be applied for the present simulation method.

In the present simulation, all polymer molecules in each polymer particle are simulated. The instantaneous number fraction distribution of the primary polymer molecules when chain transfer to small molecules is the dominant mode of chain stoppage is given by the following most probable distribution:[13,14,16]

$$N(r) = \tau \exp(-\tau r) \qquad (1)$$

where r is the chain length (degree of polymerization), $\tau = R_f/R_p$, R_f is the rate of chain transfer to small molecules, and R_p is the propagation rate.

In statistical copolymerization, the chain length of a primary copolymer chain is finite; therefore, the compositions of the primary polymer molecules formed instantaneously cannot be identical. On the basis of the terminal model for copolymerization, the copolymer composition of each primary polymer molecule can be determined from the Stockmayer bivariate distribution of chain length and composition.[17,18] The Stockmayer bivariate distribution

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$W(r,y)$ consists of the product of weight-based chain length distribution $W(r)$ and composition distribution Comp($y|r$) that is given by the conditional probability distribution given the chain length r.

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

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

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

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

where $F_{2,\mathrm{mean}}$ is the instantaneous mole fraction of divinyl monomer bound in polymer molecules, F_2 is that in a particular primary polymer molecule, and r_1 and r_2 are the reactivity ratios.

The loci of polymerization in the usual emulsion polymerization are the polymer particles; therefore, the concentrations used in eqs 1 and 2 must be those in the polymer particles. In order to simplify the present theoretical analysis, we are to assume that the comonomer composition in the polymer particles is the same as monomer droplets. In this case, the copolymer composition drift during polymerization is the same as that for homogeneous batch copolymerization and is given by[19]

$$\frac{\mathrm{d}f_2}{\mathrm{d}x} = \frac{f_2 - F_{2,\mathrm{mean}}}{1 - x} \tag{3a}$$

or its integrated form[20-23]

$$x = 1 - \left(\frac{f_1}{f_1^{\,0}}\right)^{\alpha} \left(\frac{f_2}{f_2^{\,0}}\right)^{\beta} \left(\frac{f_1^{\,0} - \delta}{f_1 - \delta}\right)^{\gamma} \tag{3b}$$

where x is the total monomer conversion, $\alpha = r_2/(1 - r_2)$, $\beta = r_1/(1 - r_1)$, $\gamma = (1 - r_1 r_2)/\{(1 - r_1)(1 - r_2)\}$, $\delta = (1 - r_2)/(2 - r_1 - r_2)$, f_2 is the mole fraction of unreacted divinyl monomer in the reaction mixture, and $f_2^{\,0}$ is the initial value of f_2.

By application of eqs 1–3, the chain length and the composition of each primary polymer molecule can be determined by use of the Monte Carlo method.

Kinetics of Cross-Linking. In the present simulation, we assume the mass action law is valid for the cross-linking reactions, and the structure and chain length dependence of the reactivity of the pendant double bonds and polymer radicals was neglected. The space dimensionality was therefore not included in the present simulation; however, since Monte Carlo simulations make it possible to observe the structure of each cross-linked polymer molecule directly and to determine the spatial distribution of the cross-linked polymer chains as shown earlier,[24] the present simulation results would provide a reasonable start point to clarify the spatial correlation problems.

When a new primary polymer molecule with chain length r is formed, the probability that a given pendant double bond is not incorporated into this primary polymer molecule is given by

$$P_{\mathrm{noCL}} = \left(1 - \frac{K}{n_{\mathrm{m}} + K(n_{\mathrm{pd}} - 1)}\right)^{r} \tag{4a}$$

where n_{m} is the total number of monomer molecules in the given polymer particle, n_{pd} is the total number of pendant double bonds in that polymer particle, $K = k_{\mathrm{p}}^{*0}/k_{\mathrm{p}}$ shows the reactivity of pendant double bonds, k_{p}^{*0} is the rate constant for the cross-linking reaction, and k_{p} is the propagation rate constant. When the initial mole fraction of divinyl monomer $f_2^{\,0}$ is much smaller than unity, eq 4a can be approximated by

$$P_{\mathrm{noCL}} = (1 - K/n_{\mathrm{m}})^{r} \tag{4b}$$

Equation 4 is examined for all pendant double bonds in the polymer particle every time a new primary polymer molecule is formed. In the present calculations, the n_{m} value at the time when half of the new primary polymer molecule is formed, i.e., n_{m} value at the time when the total number of monomeric units in the polymer molecules is $r/2 + \sum_{j=1}^{N} r_j$, was used, where N is the total number of polymer molecules in the polymer particle.

For a number of monomers with linear polymerization, it is known that the volume fraction of polymer in the polymer particle is kept constant with the existence of monomer droplets. It is worth noting here that this may be a good approximation even for many emulsion cross-linking copolymerization systems as shown both theoretically[12] and experimentally.[25] In the present simulation, the polymer/monomer ratio within the polymer particles until the depletion of monomer droplets is assumed to be constant even though the ratio may be determined theoretically if the average cross-linking density is known.[12,25]

Kinetics of Cyclization. In the present simulation, the spatial correlation is neglected, and the mass action law is assumed to be valid even for cyclization reactions. This assumption is, in fact, the same as the Flory/Stockmayer theory;[26] however, there is a clear difference from polymerization in homogeneous media in the obtained results on cyclization. In homogeneous polymerization, the weight fraction of one sol polymer molecule is always zero, while the weight fraction of a gel molecule possesses a nonzero value. Therefore, if the mass action law is valid and spatial correlation is neglected, the probability of ring formation within a sol polymer molecule is zero since the concentration of the functional group on its own polymer molecule is zero, while it is possible for a gel molecule to form rings. This is the so-called "ring-free" model. However, in the case of emulsion polymerization, the system size is finite; therefore, each polymer molecule possesses a nonzero weight fraction, which shows cyclization is possible for all polymer molecules even under the ring-free model.

In the present analysis, we divide cyclization reactions conveniently into two types: primary and secondary cyclization.[27-29] 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. In terms of the elastic properties of polymeric networks, it would be reasonable to consider that the secondary cycles which are expected to form larger rings than the primary cycles are more important.

Microgels possess only supermolecular size; therefore, it would be very difficult to define by their size, and they are quite often soluble at least when the human eye is used as a reference standard. Funke et al.[30] proposed microgels as intramolecularly cross-linked macromolecules. The existence of cycles, or intramolecular cross-links, may be one of the common features of a gel molecule (even though at present there is no clear definition of the term "gel" even for gels in macroscale[31]). In this regard, secondary cycles may be a notable feature of microgels.

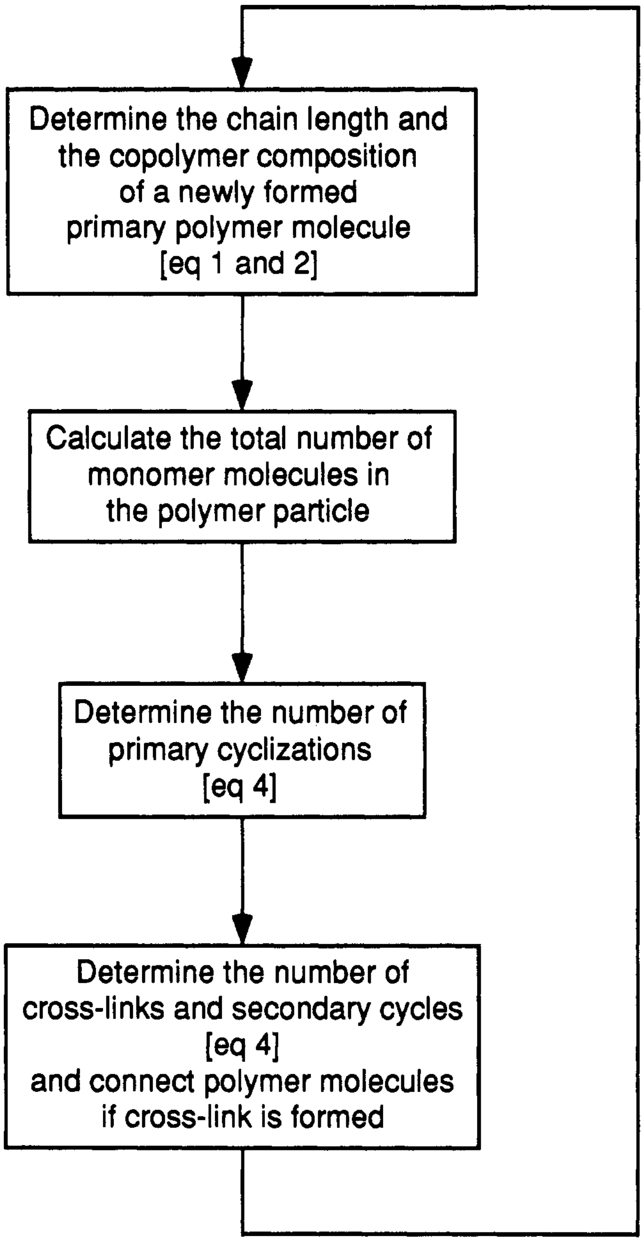

Figure 1. Simulation algorithm.

In the present simulation, the probability given by eq 4 is used for all pendant double bonds, and if the cross-link formed is within the primary polymer molecule, it is regarded as the primary cycle. On the other hand, if the cross-link formed is within the same polymer molecule but with different primary polymer molecules, it is regarded as the secondary cycle.

Simulation. In the present simulation, all primary polymer molecules including the very first primary polymer molecule formed in a polymer particle are assumed to follow the MWD given by eq 1, and the particle nucleation mechanism, which is still controversial,[32] is not considered. The simulation algorithm is quite simple and is shown in Figure 1. The simulation algorithm is fundamentally the same as the usual Monte Carlo simulations in finite systems except that the number of unreacted monomers, i.e., the system size, must be calculated at each step.

Table 1. Calculation Conditions Investigated

	C1	C2	C3	C4
f_2^0	3×10^{-3}	3.4×10^{-4}	7×10^{-6}	2×10^{-2}
r_1, r_2	0.5, 2.0	0.5, 2.0	0.1, 10.0	3.0, 0.333
$k_p{*}^0/k_p$	1.0	1.0	4.0	0.1
τ	1×10^{-3}	1×10^{-3}	1×10^{-3}	1×10^{-3}
x_c[a]	0.4	0.4	0.4	0.2

[a] Weight fraction of polymer in the polymer particles with the existence of monomer droplets, which is equal to the total monomer conversion at which monomer droplets disappear.

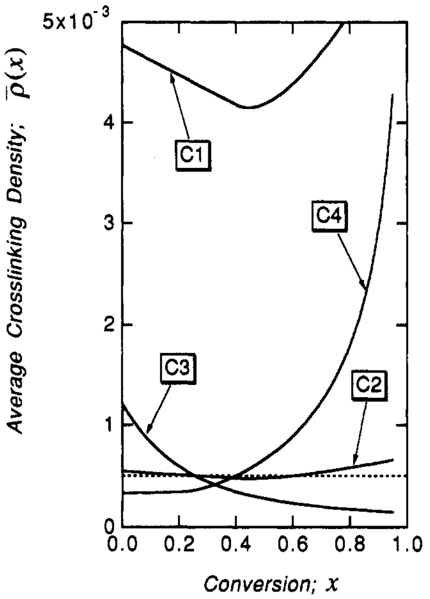

Figure 2. Calculated average cross-linking density development. The broken line shows the cross-linking density at the gel point for an equilibrium homogeneous polymerization, $(\bar{\rho}_{gp})_{equil}$.

Results and Discussion

Four conditions shown in Table 1 are investigated in the computer simulations. The primary chain length drift during polymerization was not included in order to focus our attention on the effect of cross-links on the whole molecular weight distribution. Note that the reactivity ratios shown in Table 1 are defined with respect to the monomeric unit, not the double bond. The conditions C1 and C2 correspond to Flory's simplifying assumptions for vinyl/divinyl copolymerization.[10,26] Under these conditions, the expected cross-linking density is the same for all primary polymer molecules in homogeneous polymerization[28,29] although a completely heterogeneous network is formed in emulsion polymerization.[12] Roughly, C3 shows the case in which the reactivity of the double bonds in the divinyl monomer is higher than that in the monovinyl monomer, while in C4 the reactivity of the double bonds in the divinyl monomer is lower.

The calculated average cross-linking density development[12] is shown in Figure 2, assuming all consumption of pendant double bonds results in cross-linking. The broken line shows the necessary cross-linking density level at the gel point when a homogeneous polymerization in an equilibrium state is assumed;[26] namely

$$(\bar{\rho}_{gp})_{equil} = 1/\bar{P}_{wp} \tag{5}$$

where $\bar{P}_{wp}$ is the weight-average chain length of the primary polymer molecules.

Since free-radical polymerization is kinetically controlled, this level $(\bar{\rho}_{gp})_{equil}$ does not possess any clear physical meaning; however, in light of the fact that the determined gel point in homogeneous polymerization does not change much due to a nonequilibrium effect as shown earlier,[10] it would be possible to clarify the feature of emulsion polymerization using $(\bar{\rho}_{gp})_{equil}$ as a reference standard. Note that, in the context of equilibrium theories, gelation must occur for all calculation conditions investigated since the average cross-linking density is larger than $(\bar{\rho}_{gp})_{equil}$ at least for a certain period of time.

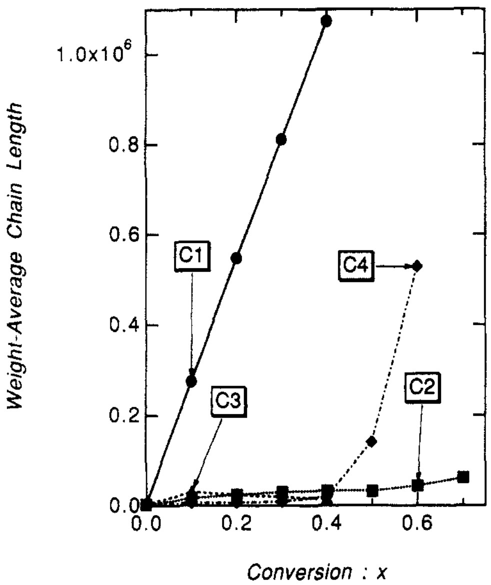

Figure 3. Weight-average chain length development.

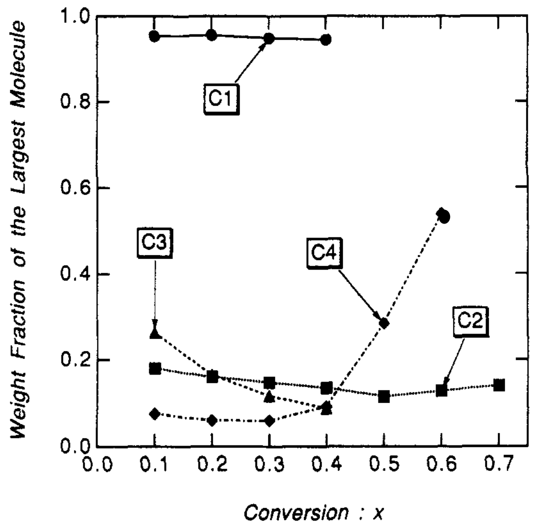

Figure 4. Weight fraction of the largest polymer molecule in a polymer particle.

The average cross-linking density of C1 is much higher than $(\bar{\rho}_{gp})_{equil}$ all through the polymerization, while the average cross-linking density in C2 is almost the same as the cross-linking density that would be required for gelation to occur in homogeneous polymerization, $(\bar{\rho}_{gp})_{equil}$. The condition C1 may be a typical example for microgel preparation in which the average cross-linking density is much higher than the required gel formation although the average cross-linking density development trajectory may be different depending on the comonomers used and reaction conditions. Under condition C3, the cross-linking density level is higher than $(\bar{\rho}_{gp})_{equil}$ in the earlier stages of polymerization but lower in the later stages. At least under condition C3, equilibrium theories like Flory's cannot be applied for the onset of gelation; if they are applied, gelation occurs at a very early stage of polymerization and the formed gel must disappear at the later stage of polymerization since the average cross-linking density is smaller than the required level for the gel formation. In C4 the average cross-linking density increases as polymerization proceeds and crosses the $(\bar{\rho}_{gp})_{equil}$ level on the way.

Note that in homogeneous polymerization the average cross-linking density, fundamentally, increases with reaction time, while in emulsion polymerization the cross-linking density is fairly high even from a very early stage of polymerization.[12] This difference especially in the earlier stages of polymerization can be explained qualitatively based on the difference in the pendant double bond concentration in the reaction system. In homogeneous polymerization, the polymer concentration, i.e., the pendant double bond concentration, in the earlier stages of polymerization is very low, resulting in low cross-linking reaction rates. On the other hand, the polymer concentration in the polymer particles is fairly high even from the start of polymerization in emulsion polymerization, resulting in a higher probability of cross-link formation in emulsion polymerization.

In order to obtain statistically valid results, at least 10^4 polymer molecules were generated. The number of simulated polymer particles was about 50 at low conversions and 11–30 particles at high conversions. The total number of monomeric units bound into polymer chains per polymer particle at 100% conversion was assumed to be 3×10^6, which is approximately 0.1 μm in diameter.

Figure 3 shows the calculated weight-average chain length development. Under condition C1, the weight-average chain length increases linearly; a drastic change in the weight-average chain length, which is characteristic of homogeneous cross-linking polymerization, cannot be observed, and the gel point could not be determined experimentally. However, since the weight-average chain length is very large, the polymer particles formed under condition C1 may be considered microgels. Under conditions C2 and C3, a drastic change in molecular weights was not observed. On the other hand, a sharp change in the weight-average chain length was observed in C4 at conversion $x \approx 0.4$, even though the change is less drastic compared with homogeneous polymerizations. The kinetic behavior in C4 is basically similar to a homogeneous polymerization.

Figure 4 shows the weight fraction of the largest polymer molecule in a polymer particle (averaged for all polymer particles simulated). Under condition C1, approximately 95% of polymer in weight belongs to the maximum cluster, which may be considered the weight fraction of the gel. Under condition C4, the weight fraction of the largest polymer molecule increases sharply again at $x \approx 0.4$. By consideration of the size of the largest polymer molecule, it would be reasonable to think that microgels are formed under conditions C1 and C4. On the other hand, both the weight-average chain length and the maximum cluster size are relatively small in C2 and C3.

Figures 5–8 show the calculated chain length distribution. In the present simulation, all polymer molecules in each polymer particle are simulated; therefore, the obtained results are fundamentally the chain length distribution on the number basis. That is why the obtained distributions on the weight basis show fluctuations especially for larger polymer molecules as shown in Figures 6 and 7. However, in terms of the physical properties of polymers, the weight fraction distribution would give more meaningful features of the system. The weight-based chain length distribution shown in the logarithmic scale is fundamentally equivalent to the elution curve in the GPC.

In C1, the gel polymer molecule just keeps on growing as polymerization proceeds, and the MWD of "sol" fraction is essentially the same during the course of polymerization. In C2, there is a high molecular weight peak on the weight basis, and this peak grows larger with polymerization. In fact, a small margin exists between two peaks at $x = 0.7$, which is a feature similar to that of C1 where clearly microgels are formed. In terms of the shape of the MWD, it is very difficult to determine if microgels are formed in

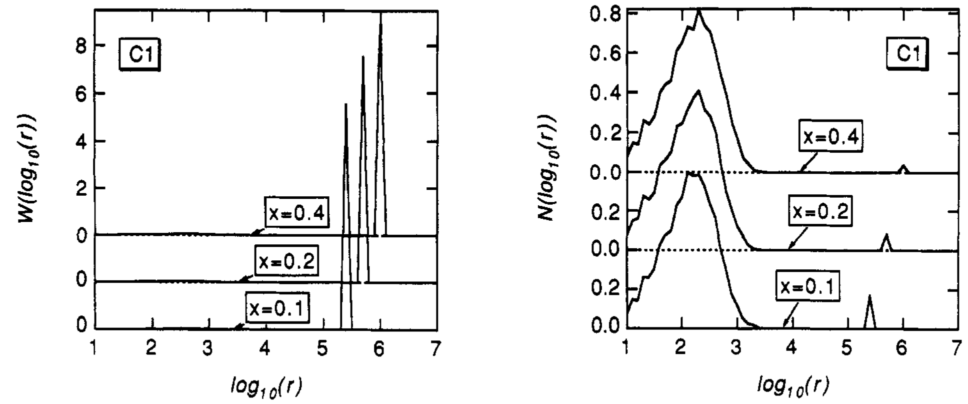

Figure 5. Calculated number-(*N*(log *r*)) and weight-based chain length distribution (*W*(log *r*)) development under condition C1.

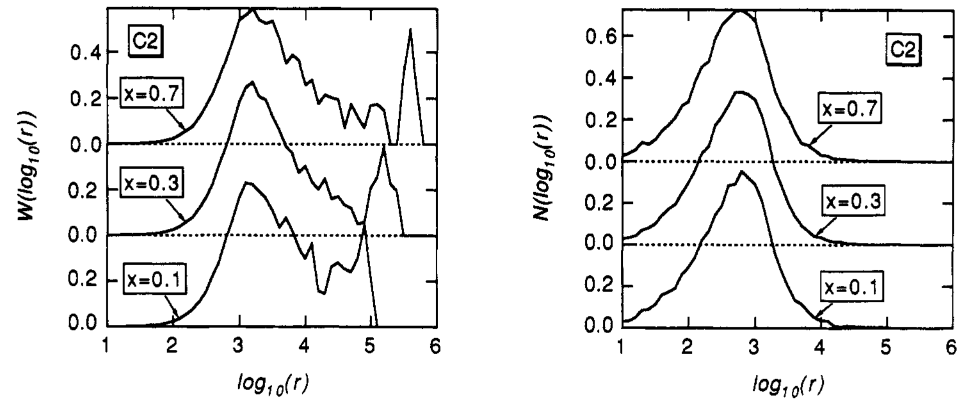

Figure 6. Calculated number-(*N*(log *r*)) and weight-based chain length distribution (*W*(log *r*)) development under condition C2.

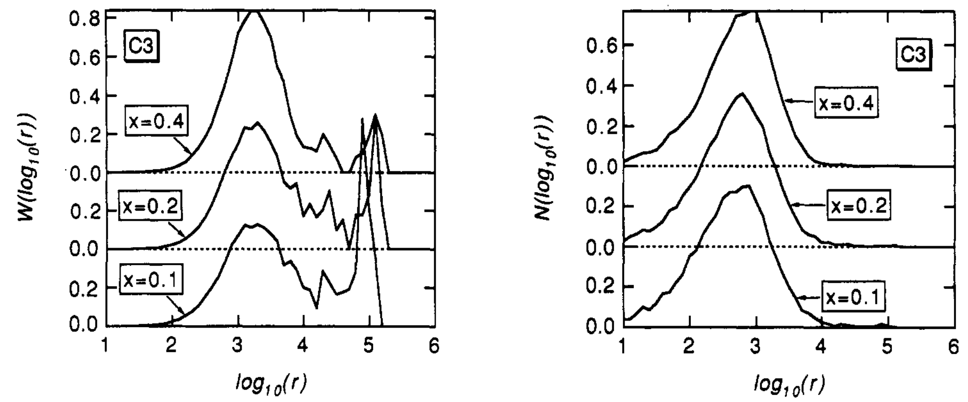

Figure 7. Calculated number-(*N*(log *r*)) and weight-based chain length distribution (*W*(log *r*)) development under condition C3.

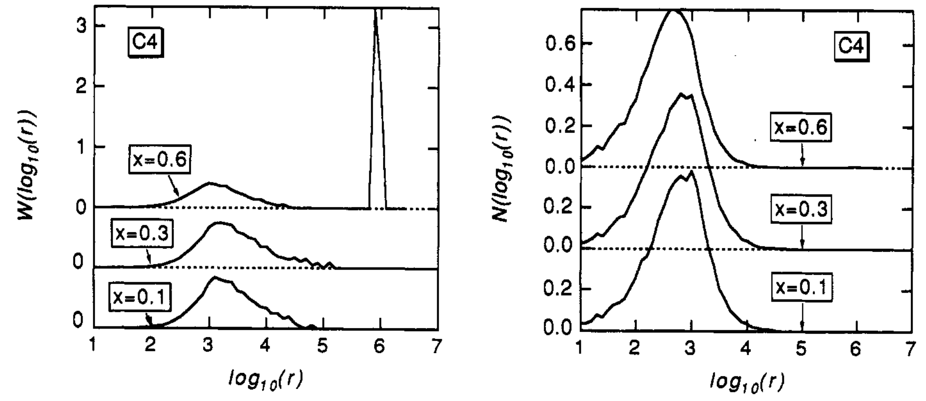

Figure 8. Calculated number-(*N*(log *r*)) and weight-based chain length distribution (*W*(log *r*)) development under condition C4.

C2. Under condition C3, again a higher molecular weight peak on the weight basis is observed; however, this time the peak does not grow larger even though it proceeds slightly to higher molecular weights. In C4, a clear microgel peak is observed at $x = 0.6$.

When a Monte Carlo simulation in finite systems is used as an approximation for an infinite reaction system, the gel point is often determined by plotting the change in the weight-average chain length without the largest polymer molecule. However, in emulsion polymerization this type

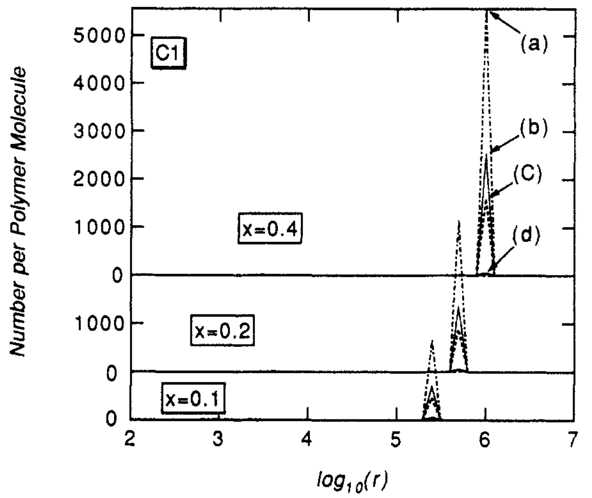

Figure 9. Consumption of pendant double bonds under condition C1. (a) Total number of divinyl monomer units bound per polymer molecule. (b) Total number of pendant double bonds consumed ($=N_x + N_{c1} + N_{c2}$). (c) Total number of pendant double bonds consumed by cyclization ($=N_{c1} + N_{c2}$). (d) Total number of pendant double bonds consumed by primary cyclization ($=N_{c1}$).

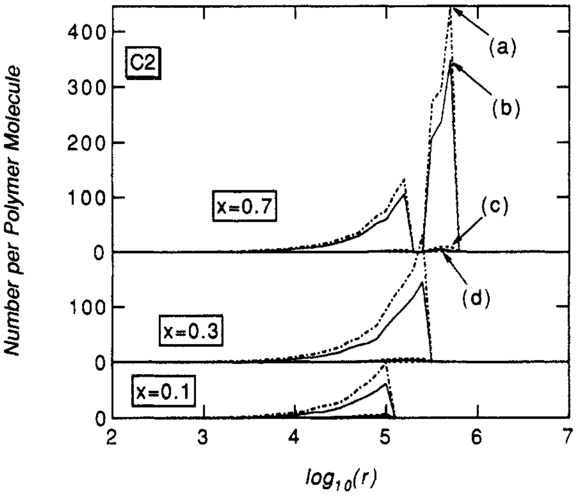

Figure 10. Consumption of pendant double bonds under condition C2.

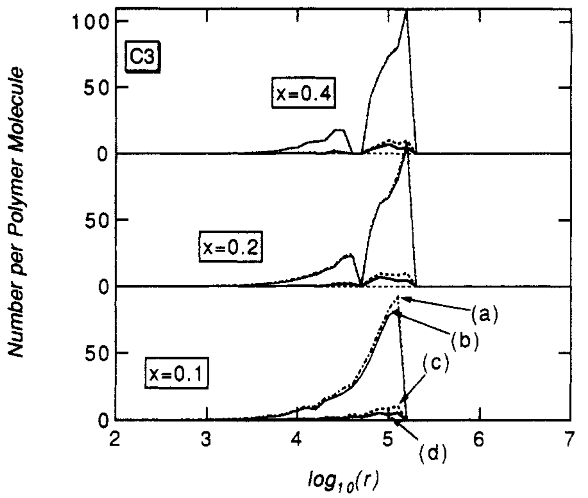

Figure 11. Consumption of pendant double bonds under condition C3.

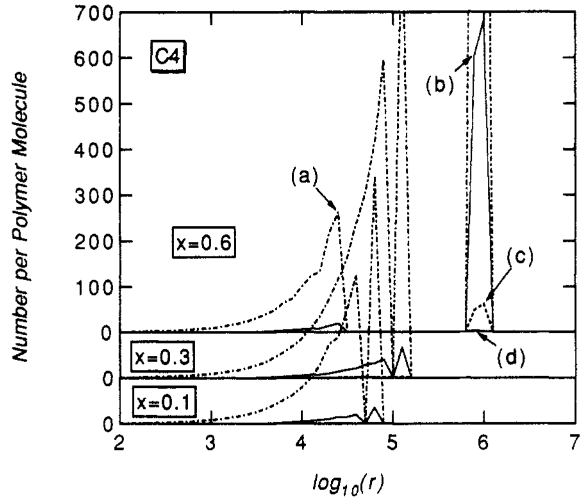

Figure 12. Consumption of pendant double bonds under condition C4.

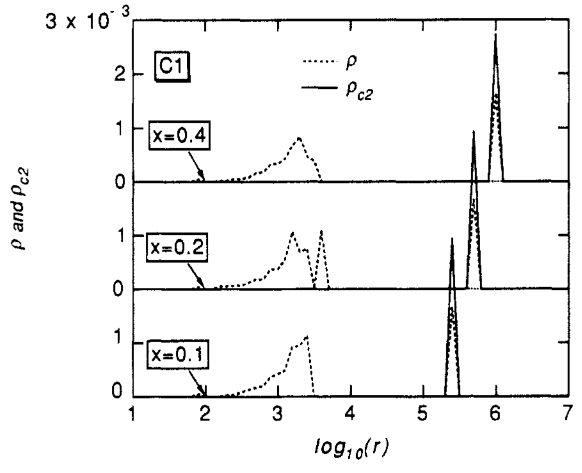

Figure 13. Cross-linking density (ρ) and secondary cyclization density (ρ_{c2}) as a function of chain length under condition C1.

of plot does not give any useful information for the onset of gelation.

Next, we are to investigate the structure of the higher molecular weight peak. Figures 9–12 show how pendant double bonds are used as a function of chain length. The lowest line shows the number of primary cycles per polymer molecule (N_{c1}), and the second lowest line shows the sum of the number of primary (N_{c1}) and secondary cycles (N_{c2}), so the amount in between shows the number of secondary cycles (N_{c2}). The next line (second highest line) shows the total number of pendant double bonds consumed, namely, the sum of the number of cross-links (N_x), N_{c2}, and N_{c1} per polymer molecule. The highest line is the total number of divinyl monomer units bound into one polymer molecule.

In all cases, the number of the primary cycles is very small. In C1, many secondary cycles are formed for the higher molecular weight peak, and they can be considered intramolecularly cross-linked macromolecules. However, in C2 and C3, small numbers of secondary cycles are formed and the number does not increase much with polymerization; they possess a cross-linked structure with many intermolecular cross-links but almost no intramolecular cross-links. According to Funke et al.'s definition,[30] they are not microgels. In C4, a significant number of secondary cycles are formed for the higher molecular weight peak at $x = 0.6$. This peak may be considered microgels.

Figures 13–16 show the cross-linking density (ρ) and the secondary cyclization density (ρ_{c2}) as a function of chain length. Essentially, only very large polymer molecules formed under conditions C1 and C4 that may be considered microgels possess a nonzero secondary cyclization density that is comparable with the cross-linking density. In C3, the secondary cyclization density decreases

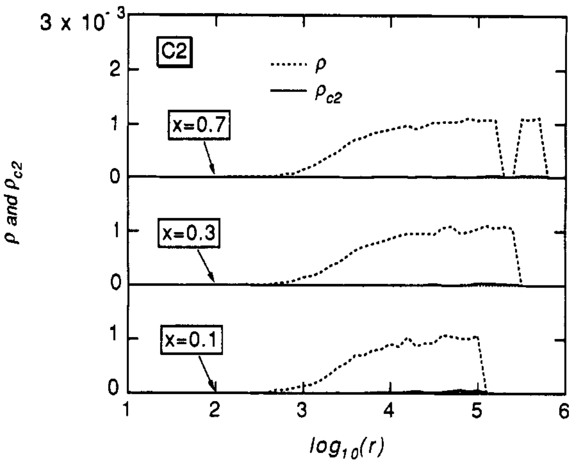

Figure 14. Cross-linking density (ρ) and secondary cyclization density (ρ_{c2}) as a function of chain length under condition C2.

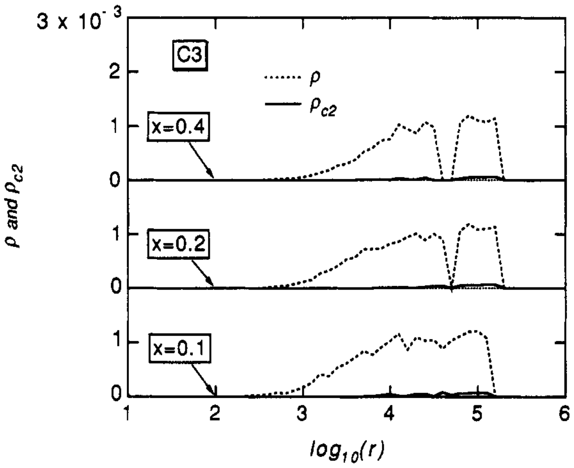

Figure 15. Cross-linking density (ρ) and secondary cyclization density (ρ_{c2}) as a function of chain length under condition C3.

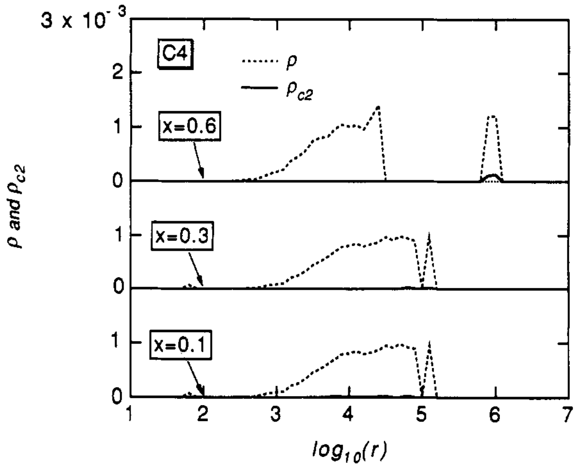

Figure 16. Cross-linking density (ρ) and secondary cyclization density (ρ_{c2}) as a function of chain length under condition C4.

as polymerization proceeds, which is a clear difference from the behavior in C4. The secondary cyclization and the relative size of the largest polymer molecule, i.e., the weight fraction of the largest polymer molecule in the polymer particle, would be the key factors to define microgels.

Incidentally, the conditions C2–C4 show the feature that the cross-linking density approaches a certain value asymptotically as the chain length increases, which is a common feature of nonlinear polymerization irrespective of the reactor type used at least when the mass action law is valid.[10b,33-37] In C1, this feature is difficult to find, since the polymer molecules possess properties similar to those formed at well beyond the gel point and they lack polymer molecules between two molecular weight peaks.

Application of the present direct simulation method to the polymerization with long-chain branching due to chain transfer to polymer and terminal double bond polymerization in emulsion polymerization can be found elsewhere.[38]

Conclusions

A new Monte Carlo simulation model for the kinetics of emulsion cross-linking copolymerization is proposed. In emulsion polymerization, the number of monomeric units involved in each polymer particle is limited; therefore, a simulation in a finite system using the Monte Carlo method is very promising to elucidate the complicated phenomena of emulsion cross-linking copolymerization. In the Monte Carlo simulation, since one can observe each polymer molecular directly, very detailed information can be obtained easily.

The kinetics of emulsion cross-linking copolymerization is completely different from that in homogeneous polymerizations. A sharp change in the weight-average molecular weight may not be observed even when microgels are formed. There may be cases where very large polymer molecules that contain many intermolecular cross-links without the formation of intramolecular cross-links are formed. In this regard, the microgels may be conveniently defined as intramolecularly cross-linked macromolecules with sufficiently high molecular weights.

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