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Cross-Linking Kinetics in Emulsion Copolymerization[†]

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ABSTRACT: A kinetic model for network structure development during emulsion cross-linking copolymerization of vinyl and divinyl monomers is proposed. By application of the same kinetic parameters as those for bulk polymerizations, it was found that (1) the cross-linking density is much higher in emulsion polymerizations especially at the initial stage of polymerization and (2) polymer networks tend to be highly heterogeneous. Homogeneous networks cannot be formed even under Flory's simplifying assumptions for vinyl/divinyl copolymerization in emulsion polymerizations. Due to the elastic contribution of the free energy change, the monomer concentration in the polymer particles is lower than with linear polymerizations as long as the monomer droplets exist. A lower monomer concentration results in an enhanced tendency toward cross-linking and may decrease the rate of polymerization per polymer particle if the decrease in the bimolecular termination reaction rate is not significant.

Introduction

Recently, polymeric networks have become a very attractive research area combining at the same time fundamental and applied topics of great interest. Polymeric gels synthesized via free-radical cross-linking copolymerization have found various commercial applications such as ion-exchange resins, packing for gel permeation chromatography (GPC), optical disks, superabsorbent polymers, microgels for paints, contact lenses, and various medical applications, not to mention diene rubber products. Especially, synthesis of network polymers with a controlled structure may permit one to produce a whole range of useful new polymer products. Polymerization in dispersed media such as with emulsion polymerization is a very important production technology for cross-linked polymers. At present, the network structure within these microspheres is not well understood, and a precise control of the cross-linked network structure seems to be a formidable task except controlling the overall cross-linking density by changing the amount of cross-linking agent empirically. This is partly attributed to the lack of an appropriate theoretical model to describe the kinetics of network formation in free-radical emulsion copolymerization.

On the basis of the pioneering work of Flory and Stockmayer,[1-3] various statistical models have been developed for network formation.[4-12] These statistical models give a full description of the system, provided the cross-linking density of the primary polymer molecules is the same regardless of their birth time. However, since free-radical polymerization is kinetically controlled, each primary polymer molecule experiences a different history of cross-linking and cyclization. This characteristic reaction scheme may result in the formation of a cross-linking density distribution among primary polymer molecules. Recently, a new kinetic theory for free-radical copolymerization with long-chain branching and cross-linking has been proposed.[13-18] This kinetic theory accounts for the history of the generated network structure as well as for all of the important elementary reactions in free-radical copolymerization. This theory proves the existence and permits the calculation of the cross-linking density distribution, although most statistical models inevitably employ the assumption that the cross-linking density is the same for all chains.

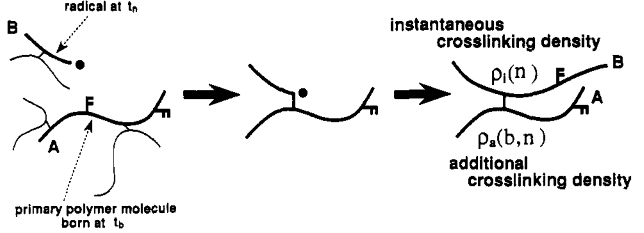

Figure 1. Schematic drawing of the process of cross-linking. At $t = t_n$, the cross-linking density of the primary polymer molecules which were born at $t = t_b$ is given by eq 1.

In this paper, some important features of emulsion cross-linking copolymerization, especially the differences for polymerizations in homogeneous media such as bulk and solution polymerization, are made clear by using a kinetic model for network formation.

Model Development

Process of Cross-Linking. The primary polymer molecule[4,19] is used to observe the history of the generated network structure. The primary polymer molecule is a rather imaginary molecule which would exist if all cross-links connected to it were severed, thus the primary polymer molecule is a linear polymer. In the cross-linking reaction shown in Figure 1, the primary polymer molecule A was born at time t_b when the accumulated number of moles of monomer bound in polymer chains is b. At time t_n when the accumulated number of moles of monomer bound in polymer chains is n ($n > b$), the primary polymer molecule B adds to a pendant double bond on the primary polymer molecule A, which results in a cross-linkage between two primary polymer molecules. (The magnitude of b and n indicates the amount of polymer produced in the polymer particles.) In this case from the point of view of primary polymer molecule B, this cross-linkage is formed during its growth, so that let us call the density of this type of cross-linking point the "instantaneous cross-linking density", $\rho_i(n)$, which is solely a function of its birth time. On the other hand, from the point of view of the primary polymer molecule A, the identical cross-linkage is formed but after it was born, so that let us call this type of cross-linking density the "additional cross-linking density",

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$\rho_a(b,n)$, which is a function of both its birth time and present time. Here, $\rho_a(b,n)$ is the additional cross-linking density experienced in the time interval t_b to t_n. Since a cross-linking point is defined as a unit which bears a tri-branching point, at time t_n, the cross-linking density of the primary polymer molecules which were born at time t_b is given by the sum of these two types of cross-linking densities.

$$\rho(b,n) = \rho_{\mathrm{i}}(b) + \rho_{\mathrm{a}}(b,n) \qquad (1)$$

Each type of cross-linking density is given by[15,18,20]

$$\frac{\partial \rho_{\mathrm{a}}(b,n)}{\partial n} = \frac{k_{\mathrm{p}}^{*0}(n)\,\{F_2(b) - \rho_{\mathrm{a}}(b,n) - \rho_{\mathrm{c}}(b,n)\}}{k_{\mathrm{p}}(n)\,[\mathrm{M}]_n V(n)} \qquad (2)$$

$$\rho_{\mathrm{i}}(b) = \int_0^b \frac{\partial \rho_{\mathrm{a}}(y,b)}{\partial b}\,\mathrm{d}y = \frac{k_{\mathrm{p}}^{*0}(b)\,b}{k_{\mathrm{p}}(b)\,[\mathrm{M}]_b V(b)}\{\bar{F}_2(b) - \bar{\rho}_{\mathrm{a}}(b) - \bar{\rho}_{\mathrm{c}}(b)\} \qquad (3)$$

where $F_2(b)$ is the instantaneous mole fraction of divinyl monomer bound in the polymer chains born at $t = t_b$, $\rho_c(b,n)$ is the mole fraction of pendant double bonds wasted by cyclization reactions for the primary polymer molecules which were born at $t = t_b$, and all superscript bars in eq 3 are used to designate the accumulated values. [M] and V are the monomer concentration and volume at the site of polymerization (i.e., in the polymer particles for emulsion polymerization), respectively. The kinetic rate constant, k_p, is the pseudo-kinetic rate constant for a propagation reaction[13-18,21,22] and is given by

$$k_{\mathrm{p}} = (k_{11}f_1 + k_{12}f_2)\phi_1^{\bullet} + (k_{21}f_1 + k_{22}f_2)\phi_2^{\bullet} + (k_{31}f_1 + k_{32}f_2)\phi_3^{\bullet} \qquad (4)$$

where k_{ij} is the propagation rate constant in which the radical of type i reacts with the double bond of type j, f_i is the mole fraction of monomer of type i, and $\phi_i^{\bullet}$ is the mole fraction of polymer radical of type i. Here, the subscript 1 is used to designate monovinyl monomer, 2 is used for divinyl monomer, and 3 is used for pendant double bonds. On the other hand, k_{p}^{*0} shows the reactivity of pendant double bonds for cross-linking reactions and is given by

$$k_{\mathrm{p}}^{*0} = k_{\mathrm{p}13}^{*}\phi_1^{\bullet} + k_{\mathrm{p}23}^{*}\phi_2^{\bullet} + k_{\mathrm{p}33}^{*}\phi_3^{\bullet} \qquad (5)$$

where $k_{\mathrm{p}i3}^{*}$ is the kinetic rate constant for a cross-linking reaction in which a radical of type i reacts with the pendant double bonds.

The cross-linking density used in eqs 1–3 is defined with respect to a monomeric unit, namely

$$\rho = \frac{(\text{no. of cross-linked units})}{(\text{total no. of monomeric units bound in the polymer chain})} \qquad (6)$$

On the other hand, from the point of view of the elastic properties of polymer networks, the cross-linking density defined as the fraction of units which are cross-linked may be important, namely

$$\rho^{\mathrm{f}} = \frac{(\text{no. of cross-linked units})}{(\text{total no. of units bound in the polymer chain})} \qquad (7)$$

The relationship between these two definitions of cross-linking density is given by[16-18,20]

$$\rho^{\mathrm{f}}(b,n) = \frac{\rho(b,n)}{1 + \rho_i(b)} \qquad (8)$$

When the cross-linking density is much smaller than unity, there is virtually no difference between these two definitions of cross-linking density, however, if a high mole fraction of divinyl monomer is used, say, more than 5 mol %, eq 8 must be used.

By application of eqs 1–3 and 8, it is possible to calculate the cross-linking density distribution as a function of the birth time of the primary polymer molecule. Calculated results for bulk and solution polymerizations can be found elsewhere.[14-18,20,23] The existence of the cross-linking density distribution is a very important feature of polymer networks synthesized by kinetically controlled systems, indicating that the polymer networks are heterogeneous at least on a microscopic scale. The cross-linking density derived here does not necessarily show the spatial distribution of cross-links; however, if the variance of this distribution is large, it would be reasonable to consider the polymer network is heterogeneous.

Process of Cyclization. Cyclization reactions are important in a free-radical cross-linking copolymerization.[24] In our formalism, it is convenient to divide the cyclization reactions into two groups, namely, primary and secondary cyclization.[16,18,20] With primary cyclization the cycle forms within one primary polymer molecule, while with secondary cyclization it is formed between two or more primary polymer molecules. The mathematical importance of the difference between primary and secondary cyclization is that primary cyclization is solely a function of its birth time, while secondary cyclization is a function of both its birth time and the present time. One of the important features of cyclization reactions is that they are controlled not by the conventional rate law using average concentrations of functional groups but by conformational statistics of the sequence of bonds. At present, however, it seems a formidable task to describe the conformation of all chains in network polymer systems, and very simple models for cyclization reactions have been proposed.[16,18,20]

For primary cyclization, the following assumptions were employed: (1) the conformation of each primary polymer molecule follows the Gaussian distribution with an appropriate scaling law for its size disregarding the correlation due to already existing cross-links and cycles, and (2) the chain length of the primary polymer molecule is sufficiently large. On the basis of these assumptions, the primary cyclization density of the primary polymer molecules which were born at $t = t_b$ is given by [16,18,20]

$$\rho_{\mathrm{cp}}(b) = k_{\mathrm{cp}}F_2(b) \qquad (9)$$

where k_{cp} is a rate constant for the primary cyclization reactions.

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

$$\rho_{\mathrm{el}}(b,n) = \rho(b,n) + \rho_{\mathrm{cs}}(b,n) \tag{10}$$

$$\rho_{\mathrm{el,a}}(b,n) = \rho_{\mathrm{a}}(b,n) + \rho_{\mathrm{cs,a}}(b,n) \tag{11}$$

$$\rho_{\mathrm{el,i}}(b) = \rho_{\mathrm{i}}(b) + \rho_{\mathrm{cs,i}}(b) \tag{12}$$

The elastic cross-linking density, $\rho_{\mathrm{el}}(b,n)$, is not necessarily equal to the elastically effective cross-linking density,[4] since we do not consider the chain entanglement which may be effective in terms of the elasticity and the dangling chains which are not effective. In terms of the number of units, the elastic cross-linking density, $\rho_{\mathrm{el}}^{\mathrm{f}}(b,n)$, is given by

$$\rho_{\mathrm{el}}^{\mathrm{f}}(b,n) = \frac{\rho_{\mathrm{el}}(b,n)}{1 + \rho_{\mathrm{el,i}}(b)} \tag{13}$$

Although secondary cyclization is also determined by chain conformational statistics like primary cyclization reactions, at present a theoretical treatment of the long-range correlations necessary for the secondary cyclization reactions has not been established. Instead of doing this, an approximate method to use the average number of secondary cycles per cross-link $\eta(b,n)$ was proposed.[16,18,20] The use of $\eta(b,n)$ is reasonable since it is necessary to have a cross-linkage on the primary polymer molecule in order for the secondary cyclizations to be formed. The next question is, however, how to derive the functional form of $\eta(b,n)$. In a real system, $\eta(b,n)$ should be a very complicated function of the mole fraction of pendant double bonds on the chain, chain length of the primary polymer molecule, molecular conformation, etc. Some simple and perhaps effective approximations were proposed.[16,18] As the simplest approximation, let us assume η to be constant in the theoretical analysis of the present paper. This approximation is clearly too simple to describe the complicated phenomenon of cyclization reactions; however, this simple model has given satisfactory predictions for the pendant double bond conversion change during bulk and solution polymerizations as shown in earlier papers.[20,23] This kind of simple model for secondary cyclization may be acceptable at this stage of the development of the kinetic model for network formation at least to illustrate the fundamental picture of network structure development. With this approximation, the elastic cross-linking density of the additional type, $\rho_{\mathrm{el,a}}$, and that of the instantaneous type, $\rho_{\mathrm{el,i}}$, are given by the equations

$$\frac{\partial \rho_{\mathrm{el,a}}(b,n)}{\partial n} = \left(\frac{k_{\mathrm{p,e}}^{*0}(n)}{k_{\mathrm{p}}(n)}\right) \frac{\{(1-k_{\mathrm{cp}})F_2(b) - \rho_{\mathrm{el,a}}(b,n)\}}{[\mathrm{M}]_n V(n)} \tag{14}$$

$$\rho_{\mathrm{el,i}}(b) = \left(\frac{k_{\mathrm{p,e}}^{*0}(b)}{k_{\mathrm{p}}(b)}\right)\left(\frac{b}{[\mathrm{M}]_b V(b)}\right)\{(1-k_{\mathrm{cp}})\bar{F}_2(b) - \bar{\rho}_{\mathrm{el,a}}(b)\} \tag{15}$$

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

The accumulated elastic cross-linking density, $\bar{\rho}_{\mathrm{el}}$, is given by

$$\frac{\mathrm{d}(n\bar{\rho}_{\mathrm{el}}(n))}{\mathrm{d}n} = 2\left(\frac{k_{\mathrm{p,e}}^{*0}(n)}{k_{\mathrm{p}}(n)}\right)\left(\frac{n}{[\mathrm{M}]_n V(n)}\right)\left\{(1-k_{\mathrm{cp}})\bar{F}_2(n) - \frac{\bar{\rho}_{\mathrm{el}}(n)}{2}\right\} \tag{16}$$

Emulsion Cross-Linking Copolymerization. An important difference in the kinetics of emulsion polymerizations and bulk systems is that monomer is supplied into the polymer particles, which are the loci of polymerization, from the monomer droplets to replace that which has reacted as long as the monomer droplets exist. In addition to the theoretical model described in the previous section, one needs to know the monomer concentration in the polymer particles.

In emulsion polymerization, each polymer particle experiences a different history. However, in order to simplify the discussion, let us assume that all polymer particles are produced instantaneously at $t = 0$, although it is straightforward to develop a model which accounts for the nucleation period of the polymer particles. The following results may also be interpreted as the history of the polymer particles that were born at $t = 0$. The nucleation mechanism, which is still controversial,[25] may play a role in the development of network formation at the initial stage of polymerization; however, it is not essential in this paper.

Until the end of interval II, the monomer concentration in the polymer particle, $[\mathrm{M}]_{\mathrm{p}}$, and the total volume of polymer particles, V, are given by

$$[\mathrm{M}]_{\mathrm{p}} = (1 - \phi_{\mathrm{P}})d_{\mathrm{M}}/\bar{M}_{\mathrm{M}} \qquad (x < x_{\mathrm{c}}) \tag{17}$$

$$V = n_0 x \bar{M}_{\mathrm{P}}/\phi_{\mathrm{P}} d_{\mathrm{P}} \qquad (x < x_{\mathrm{c}}) \tag{18}$$

where d_{M} and d_{P} are the densities of the monomer and polymer, respectively, $\bar{M}_{\mathrm{M}}$ and $\bar{M}_{\mathrm{P}}$ are the average molecular weights of the monomeric unit of the monomer mixture and polymer in the polymer particles, ϕ_{P} is the volume fraction of polymer in the polymer particle, n_0 is the total number of moles of monomer initially present, x is the total monomer conversion, and x_{c} is the total monomer conversion at which interval II ends.

From this point on only batch polymerizations are to be considered, and the total monomer conversion is taken to be the independent variable. The birth conversion, θ, which is the total monomer conversion at which the given primary polymer molecule was born, is used instead of using b, and the present conversion, Ψ, which represents the total monomer conversion at the present time, is used instead of n. By substituting eqs 17 and 18 into eqs 14 and 15, at $x = \Psi$ the cross-linking density of the primary polymer molecules which were born at $x = \theta$ is given by

$$\frac{\partial \rho_{\mathrm{el,a}}(\theta,\Psi)}{\partial \Psi} = \left(\frac{k_{\mathrm{p,e}}^{*0}(\Psi)}{k_{\mathrm{p}}(\Psi)}\right)\left(\frac{(1-k_{\mathrm{cp}})F_2(\theta) - \rho_{\mathrm{el,a}}(\theta,\Psi)}{\Psi}\right) \times \left(\frac{\phi_{\mathrm{P}}}{1-\phi_{\mathrm{P}}}\right)\left(\frac{d_{\mathrm{P}}}{d_{\mathrm{M}}}\right)\left(\frac{\bar{M}_{\mathrm{M}}}{\bar{M}_{\mathrm{P}}}\right) \qquad (\text{for } \Psi < x_{\mathrm{c}}) \tag{19a}$$

$$= \left(\frac{k_{\mathrm{p,e}}^{*0}(\Psi)}{k_{\mathrm{p}}(\Psi)}\right)\left(\frac{(1-k_{\mathrm{cp}})F_2(\theta) - \rho_{\mathrm{el,a}}(\theta,\Psi)}{1-\Psi}\right) \qquad (\text{for } \Psi > x_{\mathrm{c}}) \tag{19b}$$

$$\rho_{\mathrm{el,i}}(\theta) = \left(\frac{k_{\mathrm{p,e}}^{*0}(\theta)}{k_{\mathrm{p}}(\theta)}\right)\{(1-k_{\mathrm{cp}})\bar{F}_2(\theta) - \bar{\rho}_{\mathrm{el,a}}(\theta)\} \times \left(\frac{\phi_{\mathrm{P}}}{1-\phi_{\mathrm{P}}}\right)\left(\frac{d_{\mathrm{P}}}{d_{\mathrm{M}}}\right)\left(\frac{\bar{M}_{\mathrm{M}}}{\bar{M}_{\mathrm{P}}}\right) \qquad (\theta < x_{\mathrm{c}}) \tag{20a}$$

$$= \left(\frac{k_{\mathrm{p,e}}^{*0}(\theta)}{k_{\mathrm{p}}(\theta)}\right)\{(1-k_{\mathrm{cp}})\bar{F}_2(\theta) - \bar{\rho}_{\mathrm{el,a}}(\theta)\}\left(\frac{\theta}{1-\theta}\right) \qquad (\theta > x_{\mathrm{c}}) \tag{20b}$$

The accumulated cross-linking density, $\bar{\rho}_{\mathrm{el}}$, is given by substituting eqs 17 and 18 into eq 16.

$$\frac{\mathrm{d}(x\bar{\rho}_{\mathrm{el}}(x))}{\mathrm{d}x} = 2\left(\frac{k^{*0}_{\mathrm{p,e}}(x)}{k_{\mathrm{p}}(x)}\right)\left(\frac{\phi_{\mathrm{P}}}{1-\phi_{\mathrm{P}}}\right)\left(\frac{d_{\mathrm{P}}}{d_{\mathrm{M}}}\right)\left(\frac{\bar{M}_{\mathrm{M}}}{\bar{M}_{\mathrm{P}}}\right) \times \left\{(1-k_{\mathrm{cp}})\bar{F}_2(x) - \frac{\bar{\rho}_{\mathrm{el}}(x)}{2}\right\} \quad (x < x_{\mathrm{c}}) \tag{21a}$$

$$= 2\left(\frac{k^{*0}_{\mathrm{p,e}}(x)}{k_{\mathrm{p}}(x)}\right)\left(\frac{x}{1-x}\right)\left\{(1-k_{\mathrm{cp}})\bar{F}_2(x) - \frac{\bar{\rho}_{\mathrm{el}}(x)}{2}\right\} \quad (x > x_{\mathrm{c}}) \tag{21b}$$

(Note that $[\mathrm{M}]_{\mathrm{P}}V$ is simply given by $n_0(1 - x)$ in interval III ($x > x_{\mathrm{c}}$).)

For a number of monomers with linear polymerization, it has been observed experimentally that the mass fraction of monomer in polymer particles remains approximately constant until the end of interval II. First, let us examine the important features of emulsion cross-linking copolymerization assuming the volume fraction of polymer in the polymer particle, ϕ_{P}, is constant as long as monomer droplets exist. As proven in earlier papers,[16,18] a completely homogeneous network is formed under Flory's simplifying assumptions[4] for vinyl/divinyl copolymerization in bulk and solution systems; 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. Let us first examine these conditions, namely[16]

$$\frac{k^{*0}_{\mathrm{p,e}}(x)}{k_{\mathrm{p}}(x)} = \frac{k^{*0}_{\mathrm{p}}(x)}{k_{\mathrm{p}}(x)} = \frac{1}{1 + f_2(x)} \approx 1 \quad \text{when } f_2 \ll 1 \tag{22a}$$

$$k_{\mathrm{cp}} = 0 \tag{22b}$$

$$r_1 = 0.5 \text{ and } r_2 = 2.0 \tag{22c}$$

where f_2 is the mole fraction of divinyl monomer in the monomer mixture in the polymer particles, and r_1 and r_2 are the reactivity ratios.

Figure 2 shows the calculated cross-linking density distribution change during bulk and emulsion copolymerization under Flory's simplifying assumptions. Although the cross-linking density of the primary polymer molecules is the same for all chains at any stage of polymerization in bulk polymerizations, this is not true in emulsion polymerizations. Especially, the cross-linking density of the polymer chains formed in earlier stages of polymerization are very high, and the variance of cross-linking density distribution is fairly significant in emulsion polymerization. The bending at $x = 0.4$ occurs because the conversion at which interval II ends; x_{c} is assumed to be 0.4 in these calculations. Again, it is worth noting here that homogeneous networks cannot be formed even under Flory's simplifying assumptions in emulsion cross-linking copolymerization.

Figure 3 shows the average cross-linking density development during bulk and emulsion copolymerization under Flory's simplifying assumptions. Again, it is assumed that x_{c} is 0.4 and that the volume fraction of polymer is constant until the end of interval II. The difference in the average cross-linking density between these two systems is significant. In bulk polymerization the average cross-linking density increases with time, while in emulsion polymerization the cross-linking density is fairly high even from the start of polymerization. This difference in behavior in the earlier stages of polymerization can be explained qualitatively based on the difference in polymer concentration in the reaction system. In bulk polymerization, the polymer 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, which are the loci of polymerization, is fairly high even from the start of polymerization, resulting in high cross-linking reaction rates in emulsion systems. The average cross-linking densities for bulk and emulsion systems converge at high conversions simply because the total amount of divinyl monomer is the same for both systems.

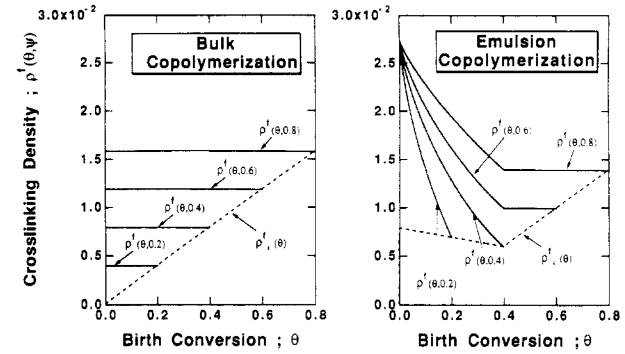

Figure 2. Calculated cross-linking density distribution change during bulk and emulsion copolymerization under Flory's simplifying assumptions. Initial mole fraction of divinyl monomer, $f_{20} = 0.01$; the reactivity ratios, $r_1 = 0.5$, $r_2 = 2.0$; the reactivity of pendant double bonds, $k^{*0}_{\mathrm{p}}/k_{\mathrm{p}} = 1.0$; $\bar{M}_{\mathrm{M}}/\bar{M}_{\mathrm{P}} = d_{\mathrm{P}}/d_{\mathrm{M}} = 1.0$; for emulsion copolymerization the conversion at which interval II ends, $x_{\mathrm{c}} = 0.4$; the monomer composition in the polymer particles is assumed to be the same as that in the monomer droplets.

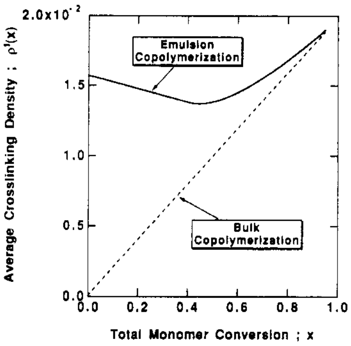

Figure 3. Calculated average cross-linking density development during bulk and emulsion copolymerization under Flory's simplifying assumptions. Calculation conditions are the same as those of Figure 2.

Figure 4 shows the calculated cross-linking density distribution change during bulk and emulsion copolymerization when the parameter for cross-linking reactions (including secondary cyclizations) $k^{*0}_{\mathrm{p,e}}/k_{\mathrm{p}} = 5.0$. It is reported that $k^{*0}_{\mathrm{p,e}}/k_{\mathrm{p}}$ is quite often larger than unity in bulk copolymerizations due to a significant occurrence of secondary cyclizations although $k^{*0}_{\mathrm{p}}/k_{\mathrm{p}}$ is usually lower than unity.[20,23,26] It is expected that the effect of the primary cyclization is small for polymerization without solvent,[18,21,26,30] and $k_{\mathrm{cp}} = 0$ is assumed in the calculations. Again the variance of cross-linking density distribution is much larger in emulsion polymerization. Figure 5 shows the average cross-linking density development during bulk and emulsion copolymerization when $k^{*0}_{\mathrm{p,e}}/k_{\mathrm{p}} = 5.0$. From Figure 5, it may be reasonable to speculate that there may

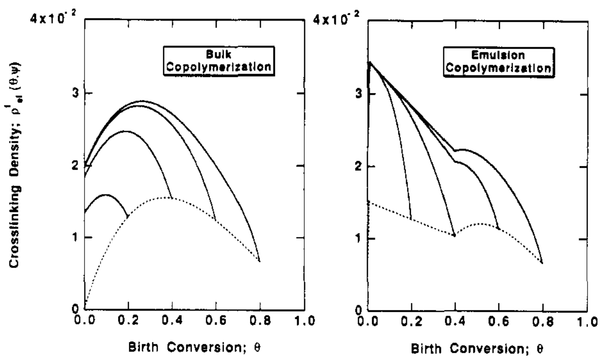

Figure 4. Calculated cross-linking density distribution change during bulk and emulsion copolymerization for $k^{*0}_{p,e}/k_p$ = 5.0. Calculation conditions are the same as those of Figure 2 except that $k^{*0}_{p,e}/k_p$ = 5.0.

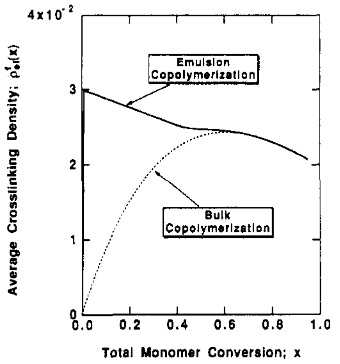

Figure 5. Calculated average cross-linking density development during bulk and emulsion copolymerization for $k^{*0}_{p,e}/k_p$ = 5.0. Calculation conditions are the same as that of Figure 2 except that $k^{*0}_{p,e}/k_p$ = 5.0.

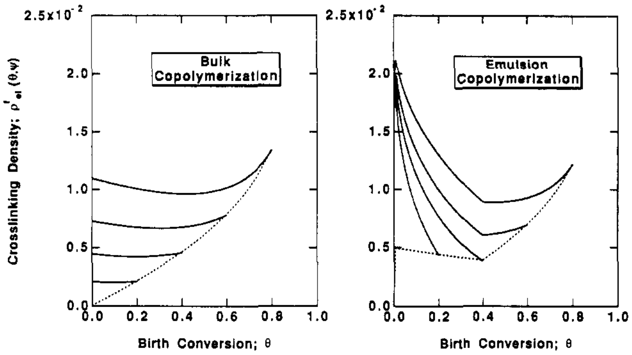

Figure 6. Calculated cross-linking density distribution change during bulk and emulsion copolymerization for $k^{*0}_{p,e}/k_p$ = 0.5. Calculation conditions are the same as those of Figure 2 except that $k^{*0}_{p,e}/k_p$ = 0.5.

be cases where the cross-linking density is highest at the initial stage of polymerization and it gradually decreases. This kind of phenomenon is recently reported for the emulsion copolymerization of styrene and divinylbenzene,[27] and the present calculation results would give a theoretical background for such observations.

Figure 6 shows the calculated cross-linking density distribution change during bulk and emulsion copolymerization when the parameter for cross-linking reactions (including secondary cyclizations) $k^{*0}_{p,e}/k_p$ = 0.5. The decrease in the cross-linking density of the primary polymer molecule during interval II is fairly significant, and the variance of the cross-linking density distribution is much larger in emulsion polymerization. Figure 7 shows the average cross-linking density development during bulk

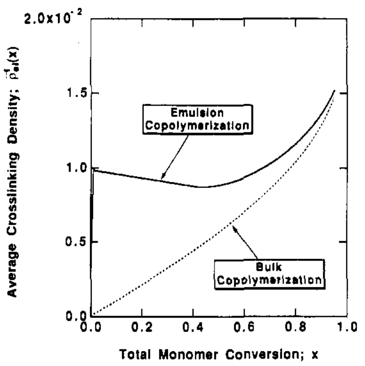

Figure 7. Calculated average cross-linking density development during bulk and emulsion copolymerization for $k^{*0}_{p,e}/k_p$ = 0.5. Calculation conditions are the same as that of Figure 2 except that $k^{*0}_{p,e}/k_p$ = 0.5.

and emulsion copolymerization when $k^{*0}_{p,e}/k_p$ = 0.5. As an average, the cross-linking density change during emulsion copolymerization, especially in interval II, is relatively small, although the polymer network is predicted to be highly heterogeneous as shown in Figure 6. It is worth noting here that the fact that the average cross-linking density does not change during polymerization does not mean that the polymer network is homogeneously cross-linked. It would be interesting to compare the difference of the elastic properties between homogeneous and heterogeneous networks.

Monomer Concentration in the Polymer Particles. In the above discussions, the monomer concentration in the polymer particles is assumed to be constant as long as the monomer droplets exist. However, it may change due to the cross-linked network structure. Taking into account the elastic free energy change due to the cross-linked network structure as well as free energy contributions of mixing and interfacial tension, it is possible to derive the equation which describes the equilibrium monomer concentration in the polymer particles[28,29]

$$\Delta\mu = RT\{\ln(1-\phi_P) + \phi_P + \chi_1{\phi_P}^2\} +$$

(mixing)

$$\frac{2\bar{M}_M\gamma}{rd_M} +$$

(interfacial tension)

$$RT\left(\frac{d_P}{d_M}\right)\left({\phi_P}^{1/3} - \frac{\phi_P}{2}\right)\bar{\rho}_{eff} = 0 \qquad (23)$$

(elasticity)

where χ_1 is the interaction parameter for the particular monomer–polymer pair, γ is the interfacial tension, r is the radius of the polymer particle, and $\bar{\rho}_{eff}$ is the elastically effective cross-linking density.

If the chain entanglement effect is negligible, the elastically effective cross-linking density, $\bar{\rho}_{eff}$, is given by[4]

$$\bar{\rho}_{eff} = \bar{\rho}^{f}_{el,gel} - \frac{2}{\bar{P}^{gel}_N} \qquad (24)$$

where $\bar{\rho}^{f}_{el,gel}$ and $\bar{P}^{gel}_N$ are the elastic cross-linking density and the number-average chain length of the primary polymer molecules which belong to the gel fraction.

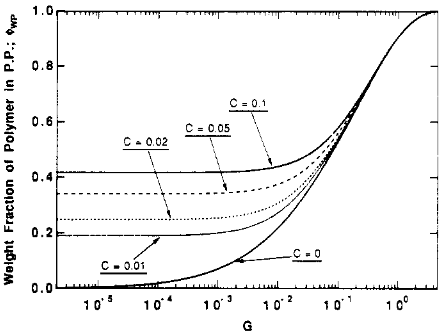

Figure 8. Effect of interfacial tension, G, and that of the cross-linking density, C, on the weight fraction of polymer in the polymer particles, ϕ_{WP}. The interaction parameter $\chi_1 = 0.4$, and the ratio of densities $d_M/d_P = 0.8$.

If $\bar{P}_N^{gel}$ is large enough and $\bar{\rho}^f_{el,sol} \ll \bar{\rho}^f_{el,gel}$, the elastically effective cross-linking density, ρ_{eff}, is approximated by

$$\bar{\rho}_{eff} \approx \bar{\rho}^f_{el} \quad \left(\text{when } \frac{2}{\bar{P}_N^{gel}} \ll \bar{\rho}^f_{el} \text{ and } \bar{\rho}^f_{el,sol} \ll \bar{\rho}^f_{el,gel}\right) \tag{25}$$

By application of eq 25 and the ratio between the radius r_0 of the unswollen polymer particle to the radius r of the swollen polymer particle, $(r_0/r) = \phi_P^{1/3}$, eq 23 can be written as

$$G = -\phi_P^{5/3}\left\{\chi_1 + \frac{1}{\phi_P} + \frac{\ln(1-\phi_P)}{\phi_P^2}\right\} - C\left(1 - \frac{\phi_P^{2/3}}{2}\right) \tag{26}$$

where

$$G \equiv \frac{2\bar{M}_M\gamma}{RTr_0d_M} \tag{27}$$

$$C \equiv \left(\frac{d_P}{d_M}\right)\bar{\rho}^f_{el} \tag{28}$$

The fact that the mass fraction of monomer in polymer particles remains approximately constant until the end of interval II for a number of monomers with linear polymerization shows that the free energy contribution of interfacial tension, G, can be approximated as a constant during polymerization for the calculation of ϕ_P. (Note that the change in r_0^3 does not change ϕ_P significantly.) Figure 8 shows the effect of the interfacial tension, G, and that of the cross-linking density, C, on the equilibrium weight fraction of polymer in the polymer particles with the existence of monomer droplets assuming $\chi_1 = 0.4$. When the interfacial tension is high or the diameter of the polymer particles is small, the effect of the cross-linking density on the polymer (or monomer) concentration in the polymer particles is small. On the other hand, for a smaller interfacial tension or a larger particle diameter, a little increase in cross-linking density may change the polymer (or monomer) concentration significantly. Values of G typically range from 10^{-3} to 10^{-1}, which is a transitional region where the effect of cross-linking density may or may not be significant.

Figure 9 shows the change of the average cross-linking density and that of the weight fraction of monomer in the polymer particles during emulsion copolymerization. The solid curves account for the change in monomer concentration in the polymer particles during interval II assuming a constant G, while for the broken curves it is assumed that the monomer concentration is constant; namely, in the latter case the effect of cross-links on the change of monomer concentration in the polymer particles is neglected and the monomer concentration is assumed to be the same as that for a linear polymerization. By comparing these curves, it can be found that the monomer concentration becomes lower due to the cross-linked network structure. The decrease in the monomer concentration enhances the probability of the cross-linking reactions, and a tighter network structure causes a further decrease in the monomer concentration.

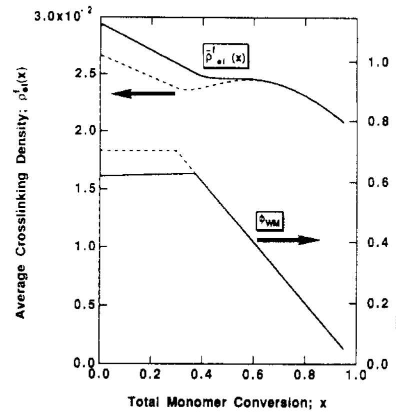

Figure 9. Change of the average cross-linking density and that of the weight fraction of monomer in the polymer particles. The solid curves account for the change in the monomer weight fraction in the polymer particles until the end of interval II assuming a constant G, while the effect of the cross-linked network structure development on the monomer weight fraction is neglected in the broken curves. Calculation conditions: $f_{20} = 0.01$, $r_1 = 0.5$, $r_2 = 2.0$, $k^{*0}_{p,e}/k_p = 5.0$, $d_M/d_P = 0.8$, $\bar{M}_M/\bar{M}_P = 1.0$, $\chi_1 = 0.4$, and the weight fraction of monomer in the polymer particles for linear polymers, ϕ_{WM_0}, is assumed to be 0.3.

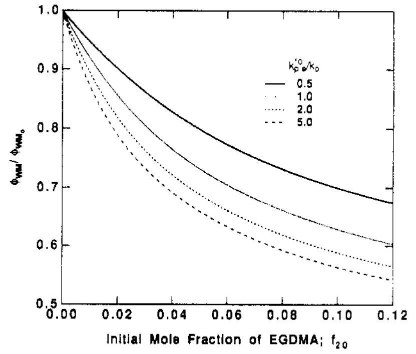

Figure 10. Effect of the initial mole fraction of EGDMA on the monomer weight fraction in the polymer particles for styrene/EGDMA copolymerization. The weight fraction of monomer in the polymer particles for linear polymers, ϕ_{WM_0}, is assumed to be 0.57. $r_1 = 0.26$, $r_2 = 0.92$, $d_M/d_P = 0.865$, $\chi_1 = 0.4$, and $\bar{M}_M/\bar{M}_P = 1.0$.

Since the change of the monomer concentration in the polymer particles during interval II is usually small (see, for example, Figure 9), it is possible to roughly estimate the effect of the addition of a divinyl monomer on the monomer concentration in the polymer particles. Let us take the minimum monomer concentration that is observed at an earlier stage of polymerization as a measure in order to know the effect of the initial mole fraction of a divinyl monomer, f_{20}. The calculated monomer concentration relative to that without cross-links, ϕ_{WM}/ϕ_{WM_0}, for the emulsion copolymerization of styrene and ethylene glycol dimethacrylate (EGDMA) is shown in Figure 10. In the calculation, the reactivity ratios, $r_1 = 0.26$ and $r_2 = 0.92$, were used. These reactivity ratios were estimated from the linear copolymerization of styrene and methyl methacrylate (MMA) ($r_{st} = 0.52$, $r_{MMA} = 0.46$).[31] The reactivity ratios, $r_1 = 0.26$ and $r_2 = 0.92$, were shown to be applicable to the copolymerization of styrene and EGDMA at least when the initial mole fraction of EGDMA, f_{20}, is small.[20,32] (The compositional difference of the monomer mixture between the polymer particles and the monomer droplets is neglected in the present calculations.) As shown in Figure 10, the monomer concentration gradually decreases as f_{20} increases. For the emulsion copolymerization of styrene and EGDMA, it was recently reported that both the equilibrium monomer absorption and the rate of polymerization per particle becomes about half that for the un-cross-linked system when $f_{20} = 0.116$.[33] Roughly, Figure 10 verifies the observation of $\phi_{WM}/\phi_{WM_0} \approx 0.5$ for $f_{20} = 0.116$, and if the decrease in the bimolecular termination reaction rate due to the gel effect is not significant, it is reasonable to expect that the rate of polymerization per particle also becomes half. A more quantitative comparison with experimental data will be shown in a future publication.

Discussion

Various important features can be made clear by application of the present kinetic model for emulsion cross-linking copolymerization. However, there are many problems to be solved before quantitative predictions for real polymerization systems are possible. Basically, in the present model all polymer chains and both monomers are assumed to be distributed homogeneously within the polymer particles. However, since the initially formed polymer latex possesses a fairly tight structure as proven in this paper, buildup at the surface area of the polymer latex particles rather than homogeneous growth may occur for highly cross-linked systems. Furthermore, a distribution both of monomers[29] and of radicals[34] within the polymer particles may occur in some cases. However, the basic concept of the present model could be applicable even for such systems if the formation mechanism of such distributions can be made clear.

The parameter $k_{p,e}^{*0}/k_p$ plays a central role in the formation of network structure. Aside from the intrinsic reactivity of the pendant double bonds, the reactivity of the pendant double bonds for cross-linking reactions may be affected by steric hindrance[35] and the excluded-volume effect.[36] In this paper, comparisons between bulk and emulsion copolymerization were made using the same value of $k_{p,e}^{*0}/k_p$. However, the value of $k_{p,e}^{*0}/k_p$ may differ significantly between bulk and emulsion copolymerization. In the case of bulk copolymerization, initiator radicals are generated inside the polymer–monomer mixture including gel molecules, and smaller polymer radicals with a high mobility exist much more in number than larger ones, and, therefore, both steric hindrance and the excluded-volume effect may have little effect on the overall cross-linking reaction rate. On the other hand, initiator radicals are generated in the water phase in emulsion polymerization. The cross-linkages are essentially formed between large primary polymer chains in emulsion systems, and, therefore, both steric hindrance and the excluded-volume effect may be much larger in emulsion polymerization. Larger primary polymer chain lengths in emulsion systems may enhance these effects, and it may make $k_{p,e}^{*0}/k_p$ smaller, although longer chains may increase secondary cycles due to the increase in the probability of finding two or more pendant double bonds.

Concerning the calculations of monomer concentrations in polymer particles, two points must be mentioned. One concerns the parameter $k_{p,e}^{*0}/k_p$ used in Figure 10. In general, both the kinetics and the network structure change significantly as the initial mole fraction of a divinyl monomer, f_{20}, increases. Therefore, it may not be appropriate to follow the curve with a constant $k_{p,e}^{*0}/k_p$. Another point worth mentioning concerns the applicability of eq 26. The equation would not be applicable for highly cross-linked polymer networks. The reason for this is at least 2-fold, namely, the assumption of Gaussian chains and the effect of chain entanglement. In order for the conformation of the chains to be Gaussian, at least 50 carbon atoms between cross-linking points would be necessary. Furthermore, the chain entanglement seems to play a central role in elasticity[37] except for fairly loosely cross-linked networks. Therefore, the monomer concentration in the polymer particles may be lower than the present estimation as f_{20} increases.

The cross-linking density is fairly high even from very early stages of polymerization in emulsion systems as shown in the present model calculations. Although the instantaneous nucleation of polymer particles is assumed in the present calculations, if the calculation results for the monomer concentration in the polymer particles can be extended to that in the particle nucleation period, the polymerization rate per particle becomes smaller than with linear polymerizations in interval I as well as interval II. On the basis of the Smith–Ewart theory,[38] it is possible to show that a slower volumetric growth rate per particle in the nucleation period contributes to a larger number of polymer particles.[33] Since it was shown experimentally that significantly more and smaller polymer particles are produced in emulsion polymerizations that contain divinyl monomers,[33,39] it may be reasonable to consider the decrease in the monomer concentration in the polymer particles occurs even in interval I.

The present kinetic model can be used to find semi-batch policies to control the network structure.[20] In cross-linked polymer systems, the limitation of mass, heat, and momentum transfer within the polymer networks causes problems. In this respect, polymerization in an emulsion system is promising. There are still many problems to be solved to clarify the complicated phenomena of emulsion cross-linking copolymerization. It is hoped, however, that this kind of kinetic approach will give a great insight into improving the quality of cross-linked polymers.

Conclusions

In this paper, a kinetic model for network structure development during emulsion copolymerization of vinyl and divinyl monomers is proposed. By application of the same kinetic parameters as those for bulk polymerizations, it was found that (1) the cross-linking density is much higher in emulsion polymerizations especially at the initial stage of polymerization and (2) polymer networks tend to be highly heterogeneous. Even for the cases where the change in the average cross-linking density during emulsion polymerization is small, the synthesized polymer networks may be highly heterogeneous. In emulsion polymerizations homogeneous networks cannot be formed even under Flory's simplifying assumptions, although perfectly homogeneous networks are formed under these reaction conditions in bulk polymerizations.

Due to the elastic contribution of free energy change, the monomer concentration in the polymer particles becomes lower than with linear polymerizations even from very early stages of polymerization, which results in an enhanced tendency toward cross-linking and may decrease the rate of polymerization per polymer particle. Since it is known that a much larger number of polymer particles is produced in emulsion polymerizations that contain divinyl monomers, it may be reasonable to consider that a significant decrease in the monomer concentration in the polymer particles as shown in the present model calculations occurs also in the particle nucleation period.

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