Kinetics of long-chain branching in emulsion polymerization: 1. Chain transfer to polymer

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New simulation models to predict the molecular weight distribution in emulsion polymerization that includes chain transfer to polymer are proposed. When the frequency of branching is not very large, the kinetics of emulsion polymerization can be modelled effectively as a large number of semibatch reactors as long as monomer droplets exist and of batch reactors after the disappearance of monomer droplets. In such cases, a simulation method based on the branching density distribution proposed earlier for non-linear polymerizations in homogeneous media shows its versatility to describe the kinetics of non-linear emulsion polymerization. However, the calculated results based on a direct simulation model that simulates all polymer molecules in each polymer particle clearly show that the fact that each polymer particle consists of a limited number of polymer molecules must be accounted for as the branching density increases. In general, such compartmentalization effects are important when one considers the molecular weight distribution development of non-linear polymer chains that are formed in emulsion polymerization.

(Keywords: molecular weight distribution; non-linear polymerization; branching density distribution)

INTRODUCTION

The kinetics of non-linear polymerizations in emulsion systems has received very little attention from researchers in spite of its growing importance in commercial products. This is partly due to lack of an appropriate theoretical model to describe non-linear free-radical polymerizations. Free-radical polymerizations are clearly kinetically controlled; therefore, the history of the generated non-linear structure must be properly accounted for. On the basis of the assumptions that the rate of transfer to polymer is proportional to its degree of polymerization, and that no more than one radical centre per polymer radical is permissible, the method of moments has been applied to calculate average molecular weight development in free-radical polymerization with long-chain branching[1–10], and it is also applied to emulsion polymerization[11,12].

Recently, a new theory for the non-linear polymerizations that include branching[13–16] and crosslinking[17–19] has been proposed. This theory is based on the branching and crosslinking density distribution formed in a non-equilibrium system, and a very effective simulation algorithm using the Monte Carlo method was developed. This type of simulation method for polymerization with long-chain branching, which is called the branching density distribution method (BDD method) in this paper, can give exact solutions for the statistical properties of non-linear polymer molecules. For polymerizations in homogeneous media, it was shown that the method of moments can be considered a good approximation until the point of gelation in a batch reactor at least for the second or lower moments[14,15,17,18]; however, it breaks down for a continuous stirred tank reactor at high conversions mainly due to the significant effects of polyradicals and radical outflow that are not considered in the conventional method of moments[13,16]. This new simulation model gives excellent agreement with the experimental data for vinyl acetate polymerization in a continuous stirred tank reactor (CSTR) that could not be explained based on the method of moments[16].

For polymerization in homogeneous media, the number of monomeric units involved is effectively infinite; therefore, it is impossible to simulate all polymer molecules produced. The BDD method gives an excellent way to sample polymer molecules on a weight basis from an infinite number of polymer molecules, and simulation of only about a few thousand polymer molecules usually gives satisfactory representation of the statistical property changes of polymer population such as the molecular weight distribution (*MWD*). Quite often this simulation model can be handled on a personal computer.

On the other hand, in emulsion polymerization the number of loci of polymerization, namely the polymer particles, is effectively infinite (typically, 10^{16} to 10^{18} particles per litre emulsion), while the number of molecules in each polymer particle is finite. For example, let us assume the diameter of polymer particle $d_p = 0.1\ \mu$m, the density of polymer $\rho_p = 1\ \mathrm{g\,cm^{-3}}$, 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 the number-average chain length is 1000, a polymer particle consists of only 3000 polymers, which cannot be considered infinite. This simple example implies the necessity of models that

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account for the compartmentalization effects in emulsion polymerization.

In this paper, first, the BDD method is extended to emulsion polymerization assuming that an infinitely large number of monomer units are involved in the reaction, and the applicability of the method of moments[11,12] is examined. Then, a direct simulation model that simulates all polymer molecules in each polymer particle is developed, and the effect of the compartmentalization on the *MWD* is investigated.

BRANCHING DENSITY DISTRIBUTION (BDD) METHOD

Aside from chain transfer to polymer, the following general elementary reactions in free-radical polymerization are considered: initiation, propagation (rate constant, k_p), chain transfer reactions to monomer (k_{fm}) and to small molecules (k_{fT}), and bimolecular termination (k_t). The process of chain transfer to polymer is shown schematically in *Figure 1*. A tri-branching point is formed by chain transfer to polymer. It is assumed that the rate of transfer to a polymer molecule is proportional to its number of reactive sites, and that no more than one branch point per monomeric unit is permissible. Shielding of interior segments from radical attack is therefore not included in this paper.

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 the dominant chain stoppage mechanism due to a long time interval of radical entry with a very fast bimolecular termination rate in small polymer particles[20,21]. In order to simplify the discussion, we are to assume that chain stoppage is transfer-dominated, and that the *MWD* is independent of initiation and termination rate, although this assumption can be eliminated easily in the BDD method as well as in the direct simulation method shown later. When the *MWD* is transfer-dominated, the instantaneous *MWD* formed in linear polymerization reduces to the most probable distribution even in emulsion polymerization[20,21].

An important difference in the kinetics of emulsion polymerization and polymerization in homogeneous media 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. For a number of monomers with linear polymerization, it is known that the volume fraction of polymer in the polymer particles is kept constant with the existence of monomer droplets, and it is worth noting here that this is a good approximation even for emulsion crosslinking copolymerization[22,23]. 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 $x=0$, although it is straightforward to develop a model which accounts for the nucleation period of the polymer particles if only the nucleation mechanism is made clear. If the effect of system boundary that is entrenched as a polymer particle is neglected and the number of monomeric units involved in the polymerization is assumed to be infinite, the reaction system can be modelled effectively as a large number of semibatch reactors in which additional monomer is added to maintain the monomer concentration constant as long as monomer droplets exist and monomer addition is stopped after the depletion of monomer droplets. First, we are to consider this two-stage process.

In the BDD method, branched polymer molecules are generated as a combination of the primary polymer molecules. The primary polymer molecule is a linear polymer molecule that would exist if all branch points connected to it were severed. In free-radical polymerization, the lifetime of a growing primary polymer radical is usually much smaller than the time required for high conversion of monomer to polymer; therefore, it would be reasonable to consider that each primary polymer molecule is formed instantaneously. In order to determine the molecular constitution of the branched polymer molecule in the BDD method, it is necessary to determine (1) the expected branching density as a function of the birth time of the primary polymer molecule, (2) the instantaneous *MWD* of the primary polymer molecules, and (3) the connection probability among primary polymer molecules, which can be determined from the branching density distribution change. With these conditions, the molecular constitution of branched structure is determined uniquely. Unfortunately, however, the deterministic solution under these constraints has not been derived and a simulation model using the Monte Carlo method was proposed. These three properties will be mentioned briefly, and a simulation algorithm will be shown. More detailed accounts for this method can be found elsewhere[13-16].

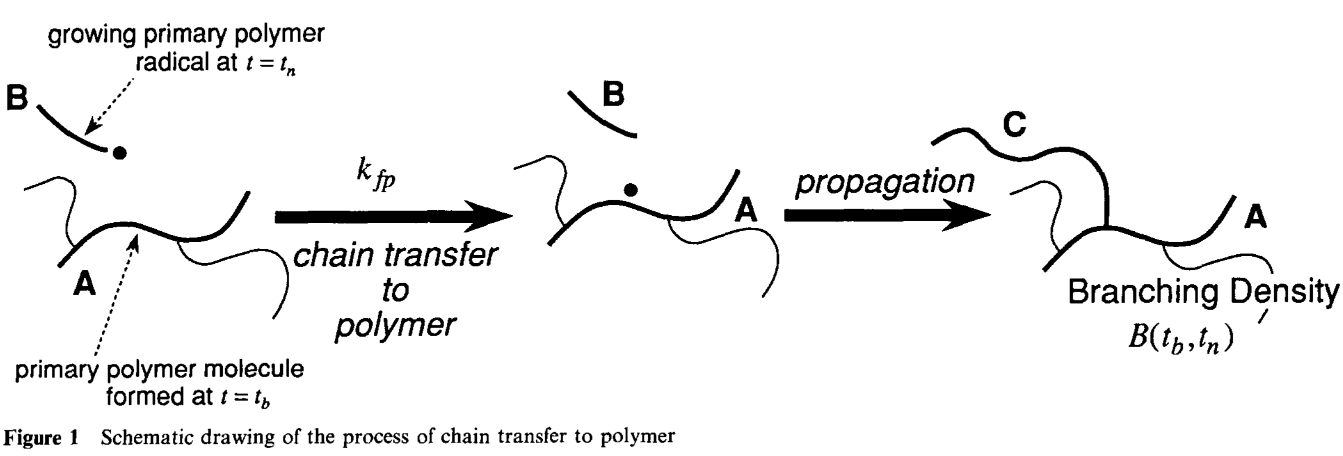

Figure 1 Schematic drawing of the process of chain transfer to polymer

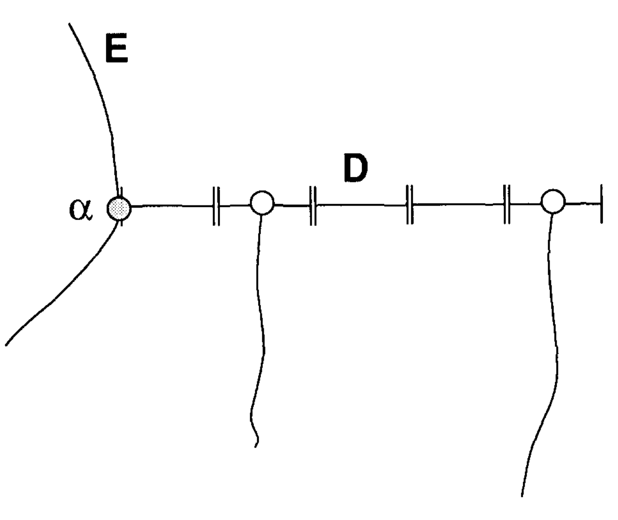

Figure 2 Schematic example of a branched polymer molecule

First, let us consider the branching density distribution of the primary polymer molecule as a function of birth time. The branching density of a primary polymer molecule is defined as the fraction of units which bear a tri-branching point:

$$B = \frac{\text{number of branched units in the primary polymer molecule}}{\text{total number of monomeric units bound in the primary polymer molecule}} \qquad (1)$$

The branching density of the primary polymer molecule **D** shown in *Figure 2* is 2/5, and the branch point α is considered to be a branch unit that belongs to the primary polymer molecule **E**.

In the branching reaction shown in *Figure 1*, the primary polymer molecule **A** was formed at time t_b. At time t_n ($t_n > t_b$), the primary polymer radical **B** attacks the primary polymer molecule **A**, and an active centre is transferred to the primary polymer molecule **A**. At the same time, a long-chain branch **C** is formed via propagation on **A**. Therefore, the branching density on the primary molecule **A**, $B(t_b, t_n)$ is a function of both its birth time and the present time. Here, $B(t_b, t_n)$ is the branching density experienced in the time interval, t_b to t_n. Based on the present model, it is possible to estimate the branching density of each primary polymer molecule depending on its birth time, thus the branching density distribution can be calculated. Free-radical polymerization is kinetically controlled, so each primary polymer molecule experiences a different history, and the primary polymer molecules that are subject to branching reaction for longer times are expected to have a larger number of branch points; therefore, the branched structure may become heterogeneous depending on the residence time distribution of the primary polymer molecules.

Since we are to consider a batch emulsion polymerization, let us use conversion, x, as an independent variable instead of time. At conversion $x=n$, the average branching density of the primary polymer molecules that were formed at conversion $x=b$ is given by[24]:

$$\frac{\partial B(b,n)}{\partial n} = C_{fp}\frac{1-B(b,n)}{[\mathrm{M}]_p V_p/([\mathrm{M}]_0 V_0)} \qquad (2)$$

where C_{fp} is the polymer transfer constant defined by k_{fp}/k_p, $[\mathrm{M}]_p$ is the monomer concentration in the polymer particle, V_p is the total volume of polymer particles, and $[\mathrm{M}]_0 V_0$ gives the total number of moles of monomer in the reaction system at $t=0$. The right-hand side of equation (2) shows the ratio between the branching reaction rate of the primary polymer molecules formed at $x=b$ and the propagation rate of the whole reaction system at $x=n$; therefore the physical meaning of equation (2) is obvious.

Practically, $B(b,n) \ll 1$ and equation (2) can be solved to give[24]:

$$B(b,n) = \begin{cases} C_{fp}\dfrac{x_c}{1-x_c}\ln\left(\dfrac{n}{b}\right) & (b<n<x_c) \quad (3) \\[2ex] C_{fp}\dfrac{x_c}{1-x_c}\ln\left(\dfrac{x_c}{b}\right) + C_{fp}\ln\left(\dfrac{1-x_c}{1-n}\right) & (b<x_c<n) \quad (4) \\[2ex] C_{fp}\ln\left(\dfrac{1-b}{1-n}\right) & (x_c<b<n) \quad (5) \end{cases}$$

Note that the weight fraction of polymer in the polymer particle as long as monomer droplets exist (x_c) is identical to the monomer conversion at which monomer droplets disappear.

When $b \to 0$, the relationship $B(b,n) \ll 1$ does not hold; therefore, the following equation must be used instead of equations (3) and (4), which can be derived from equation (2):

$$B(b,n) = \begin{cases} 1-\left(\dfrac{b}{n}\right)^{C_{fp}x_c/(1-x_c)} & (b \approx 0 \text{ and } b<n<x_c) \quad (3a) \\[2ex] 1-\left(\dfrac{b}{x_c}\right)^{C_{fp}x_c/(1-x_c)} + C_{fp}\ln\left(\dfrac{1-x_c}{1-n}\right) & (b \approx 0 \text{ and } b<x_c<n) \quad (4a) \end{cases}$$

Incidentally, the average branching density is given by[24]:

$$\bar{B}(n) = \begin{cases} C_{fp}\left(\dfrac{x_c}{1-x_c}\right) & (n<x_c) \quad (6) \\[2ex] C_{fp}\left\{\dfrac{1}{n}\ln\left(\dfrac{1-x_c}{1-n}\right) - \dfrac{n-x_c}{n} + \left(\dfrac{x_c}{1-x_c}\right)\left(\dfrac{x_c}{n}\right)\right\} & (n>x_c) \quad (7) \end{cases}$$

Figures 3a and *b* show the average branching density development and the branching density distribution change, respectively. Comparison was made with homogeneous polymerization. As discussed earlier[24], the residence time distribution and the degree of mixing have a significant effect on the branched structure. The primary polymer molecules formed at an earlier stage of polymerization tend to possess higher branching density than those formed in a later stage, and this tendency is much larger in emulsion polymerization. *Figure 4* shows the weight fraction of the primary polymer molecules with branching density smaller than B, $W_{cum}(B)$ at $x=0.5$. The variance of the branching density distribution as well as the average branching density is much larger in emulsion polymerization. As a matter of fact, the functional form of $W_{cum}(B)$ is the same as that for a homogeneous continuous stirred tank reactor (HCSTR)[24].

The BDD is an important concept to the understanding of the branched structure of the formed polymer

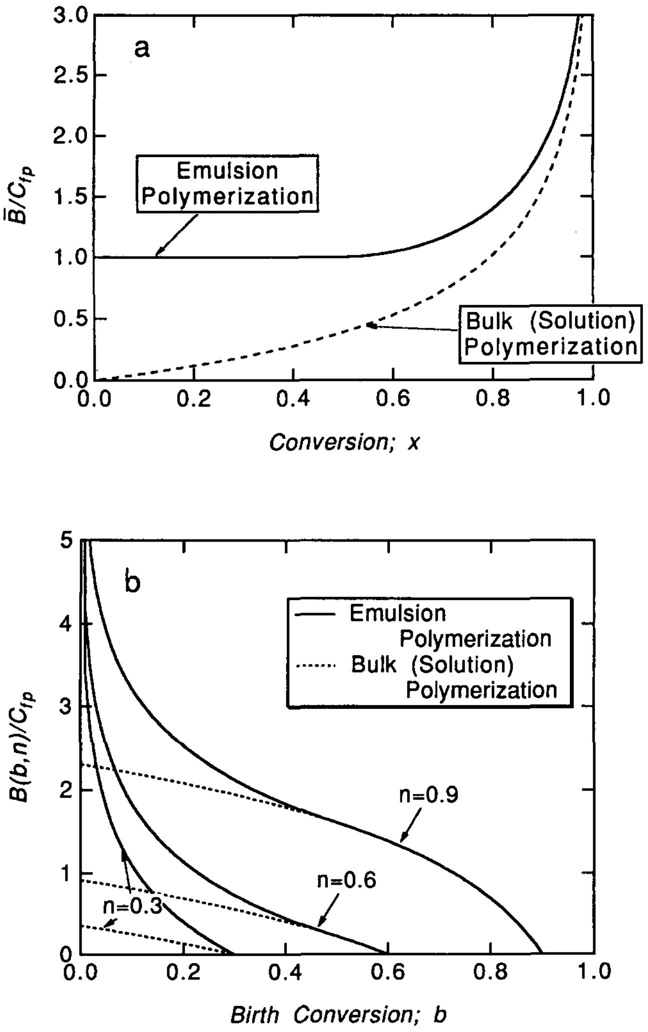

Figure 3 Average branching density (a) and branching density distribution (b) development. The conversion at which monomer droplets disappear in emulsion polymerization is assumed to be $x_c = 0.5$

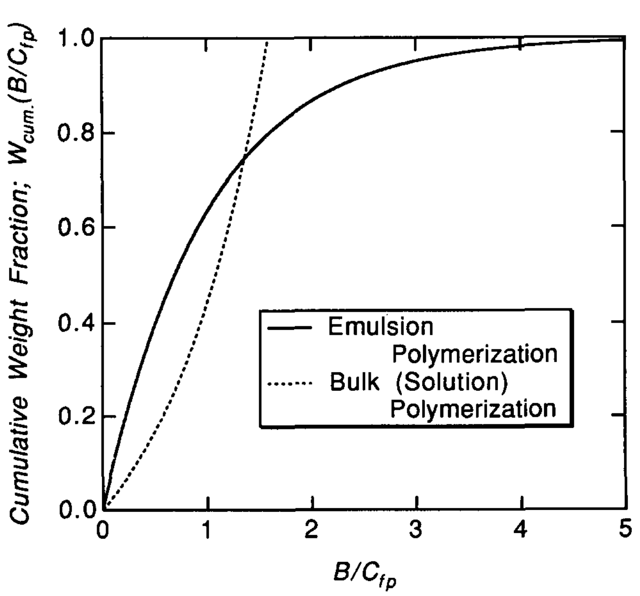

Figure 4 Cumulative weight fraction of the primary polymer molecules whose branching density is less than B at conversion $x = 0.5$ with $x_c = 0.5$ for emulsion polymerization

molecules. Assuming the reaction system size is large enough, the BDD provides information on how each chain is connected to other chains; therefore, a full *MWD* and detailed structural information can be derived. This BDD method gives an exact solution for the assumed reaction mechanisms, so it can be used to examine whether conventional approaches are valid or not.

Since the model development for free-radical polymerization with chain transfer to polymer in batch polymerization[14,15] and in an HCSTR[13,16] was shown earlier, only essential equations are listed below.

First, we are to select a primary polymer molecule randomly on a weight basis from the reaction mixture at $x = \psi$. To do this, determine the birth conversion of this primary polymer molecule, θ randomly from $0 < \theta < \psi$, and determine the chain length of this primary polymer molecule. When the birth conversion is fixed, the chain length of this primary polymer molecule can be determined from the following weight–chain length distribution[25]:

$$W(r,\theta) = (\tau(\theta) + C_P(\theta))^2 r \exp\{-(\tau(\theta) + C_P(\theta))r\} \qquad (8)$$

where $\tau(\theta) = R_f(\theta)/R_p(\theta)$, $C_P(\theta) = R_{fp}(\theta)/R_p(\theta)$, R_f is the rate of chain transfer to monomer and small molecules, R_p is the propagation rate, and R_{fp} is the rate of chain transfer to polymer. Note that we assume that the chain length distribution of the primary polymer molecules is transfer-dominated.

The branching density of the primary polymer molecule formed at $x = \theta$ is given by equations (3)–(5). The number of branching points m on this primary polymer molecule (chain length, r) can be determined from the following binomial distribution:

$$p(m) = \binom{r}{m}(B(\theta,\psi))^m (1 - B(\theta,\psi))^{r-m} \qquad (9)$$

The conditional probability that a primary polymer molecule formed at $x = \theta$ is connected to the primary polymer molecule formed in the conversion interval, θ to u ($\theta < u < \psi$), given that the branch chain is connected, $CP_a(u|\theta)$ is given by[14]:

$$CP_a(u|\theta) = \frac{B(\theta,u)}{B(\theta,\psi)} \qquad (10)$$

The chain length of the chains thus connected follows the number–chain length distribution, $N(r,u)$, since the chain ends are selected randomly.

$$N(r,u) = \{\tau(\theta) + C_P(\theta)\} \exp\{-[\tau(\theta) + C_P(\theta)]r\} \qquad (11)$$

By reiterating the above processes, the connection of primary polymer molecules to those formed later can be determined.

Next, let us consider the probability that the primary polymer molecule formed at $x = \theta$ started growing from a radical centre on another primary polymer molecule and is connected to the primary polymer molecule formed previously (backbone polymer chain). This probability is given by[14]:

$$P_b(\theta) = \frac{C_P(\theta)}{\tau(\theta) + C_P(\theta)} \qquad (12)$$

The conditional probability that the primary polymer molecule formed at $x = \theta$ started growing from the primary polymer molecule formed in the conversion interval, 0 to z ($0<z<\theta$), is simply given by:

$$CP_i(z|\theta)=\frac{z}{\theta} \tag{13}$$

The chain length of the primary polymer molecule thus connected follows the weight–chain length distribution of the primary polymer molecules, $W(r, z)$ given by equation (8), since any monomeric unit in the primary polymer molecule can be selected. Reiteration of equations (12), (13) and (8) gives the connection of the primary polymer molecules to those formed prior to θ.

APPLICABILITY OF THE METHOD OF MOMENTS

As mentioned earlier, the BDD method provides an excellent way to sample branched polymer molecules on a weight basis from an infinite number of polymer molecules, and can give an exact solution for the postulated reaction mechanisms. In this section, comparison is made with the method of moments that has been widely applied to non-linear polymerizations[1–12]. One of the problems with the conventional method of moments is the monoradical assumption, that is, each polymer radical is assumed to possess only one radical centre. This assumption may not be valid for polymerizations in which very large polymer molecules are formed since larger polymer molecules have a better chance of being attacked by polymer radicals. The method of moments has proved to be a good approximation for batch polymerizations[14,15,17,18]; however, it overestimates the weight-average chain length for an HCSTR[13,16].

Assuming that τ is constant, the number-average chain length is simply given by:

$$P_{\mathrm{N}}=\frac{1}{\tau} \tag{14}$$

Equation (14) results from the fact that the chain transfer reaction to polymer does not change the total number of polymer molecules, and the method of moments need not be used. On the other hand, based on the method of moments, the weight-average chain length is given by[10–12]:

$$P_{\mathrm{W}}=\begin{cases} \dfrac{2}{\tau-C_{\mathrm{fp}}x_{\mathrm{c}}/(1-x_{\mathrm{c}})} & (x<x_{\mathrm{c}}) \quad (15) \\[2ex] \dfrac{1}{(C_{\mathrm{fp}}+\tau)x}\left\{2x-1+\left(\dfrac{\tau+(C_{\mathrm{fp}}-\tau)x}{\tau+(C_{\mathrm{fp}}-\tau)x_{\mathrm{c}}}\right)^{2C_{\mathrm{fp}}/(C_{\mathrm{fp}}-\tau)}\right. \\ \qquad \left.\times\left(1-2x_{\mathrm{c}}+\dfrac{2x_{\mathrm{c}}(C_{\mathrm{fp}}+\tau)}{\tau-C_{\mathrm{fp}}x_{\mathrm{c}}/(1-x_{\mathrm{c}})}\right)\right\} & (x>x_{\mathrm{c}} \text{ and } \tau\neq C_{\mathrm{fp}}) \quad (16) \\[2ex] \dfrac{1}{2C_{\mathrm{fp}}x}\left\{2x-1+\exp[2(x-x_{\mathrm{c}})]\right. \\ \qquad \left.\times\left(1-2x_{\mathrm{c}}+\dfrac{4C_{\mathrm{fp}}x_{\mathrm{c}}}{\tau-C_{\mathrm{fp}}x_{\mathrm{c}}/(1-x_{\mathrm{c}})}\right)\right\} & (x>x_{\mathrm{c}} \text{ and } \tau=C_{\mathrm{fp}}) \quad (17) \end{cases}$$

Equation (15) shows that the weight-average chain length goes to infinity when $\tau=C_{\mathrm{fp}}x_{\mathrm{c}}/(1-x_{\mathrm{c}})$. A similar situation happens also in an HCSTR in the context of the method of moments. However, as proven earlier, in the present reaction mechanisms that do not include an interlinking reaction such as bimolecular termination by combination, gelation never occurs[14]. This can be explained qualitatively using a branched molecule schematically shown in *Figure 5a*. Within a branched polymer molecule, the oldest primary polymer molecule that was formed earliest is taken to be the zeroth generation for convenience, and is designated as P_0. The primary polymer molecule P_1 is formed after P_0 is formed; therefore, the expected branching density is smaller than that for P_0 (see *Figure 3b* for the BDD profile). Similarly, the expected branching density of P_2 is even smaller than P_1. The branching density decreases as the generation proceeds and approaches zero as shown in *Figure 3b*; therefore, an infinitely large polymer molecule can never be formed with this reaction mechanism. On the other hand, if the bimolecular termination by combination is involved, P_1 shown in *Figure 5b* is formed after P_0 was formed; however, if another chain end is also connected to the primary polymer molecule, P_2 is formed earlier than P_1, so the expected branching density of P_2 is larger than that of P_1. By reiterating these processes, an infinitely large molecule might be formed. It is worth noting here, however, that it may be very difficult for two polymer radicals of sufficiently large size to coexist in emulsion polymerization owing to a very small size of polymer particles. If the bimolecular termination is fast enough, a gel molecule cannot be formed even when bimolecular termination involves combination in emulsion polymerization.

As shown in *Figure 5*, the present reaction mechanisms cannot form an infinitely large polymer molecule, while equation (15) predicts gelation. This fact clearly shows that the method of moments cannot be applied to emulsion polymerization, at least when $\tau\leqslant C_{\mathrm{fp}}x_{\mathrm{c}}/(1-x_{\mathrm{c}})$.

Figure 6 shows the calculated weight-average chain length formed with the existence of monomer droplets. Note that the *MWD* is kept constant as long as monomer droplets exist if the effect of system boundary (compartmentalization) is neglected. The method of moments predicts gelation when $\tau=C_{\mathrm{fp}}x_{\mathrm{c}}/(1-x_{\mathrm{c}})$, while the BDD method predicts finite weight-average chain lengths for all region. The BDD method was used to simulate three sets of 5000 polymer molecules. Usually, for homogeneous polymerizations, a simulation of 1000 polymer molecules is enough for the calculation of the weight-average chain length and a simulation of 5000 polymer molecules gives satisfactory representation of the whole *MWD* profile[13–18]. However, the variance of the calculated weight-average chain lengths is much larger in the emulsion polymerizations. The range of standard deviation is shown in the figure. Except for the case $\tau=C_{\mathrm{fp}}x_{\mathrm{c}}/(1-x_{\mathrm{c}})$, the range is within the size of the circular symbols; however, the variance becomes larger as C_{fp} value increases. It is true that all simulated polymer molecules possess finite chain lengths; however, very large polymer molecules with chain lengths in the order of approximately 10^8 are occasionally produced when C_{fp} is large. This is the reason for the large variance. This is understandable when one realizes that the branching density of the primary polymer molecules formed at $x=0$ is unity as shown in equation (3a), which is not realizable, but the present model requires this condition. This type of situation also happens for the primary polymer molecules in an HCSTR with infinitely long residence time.

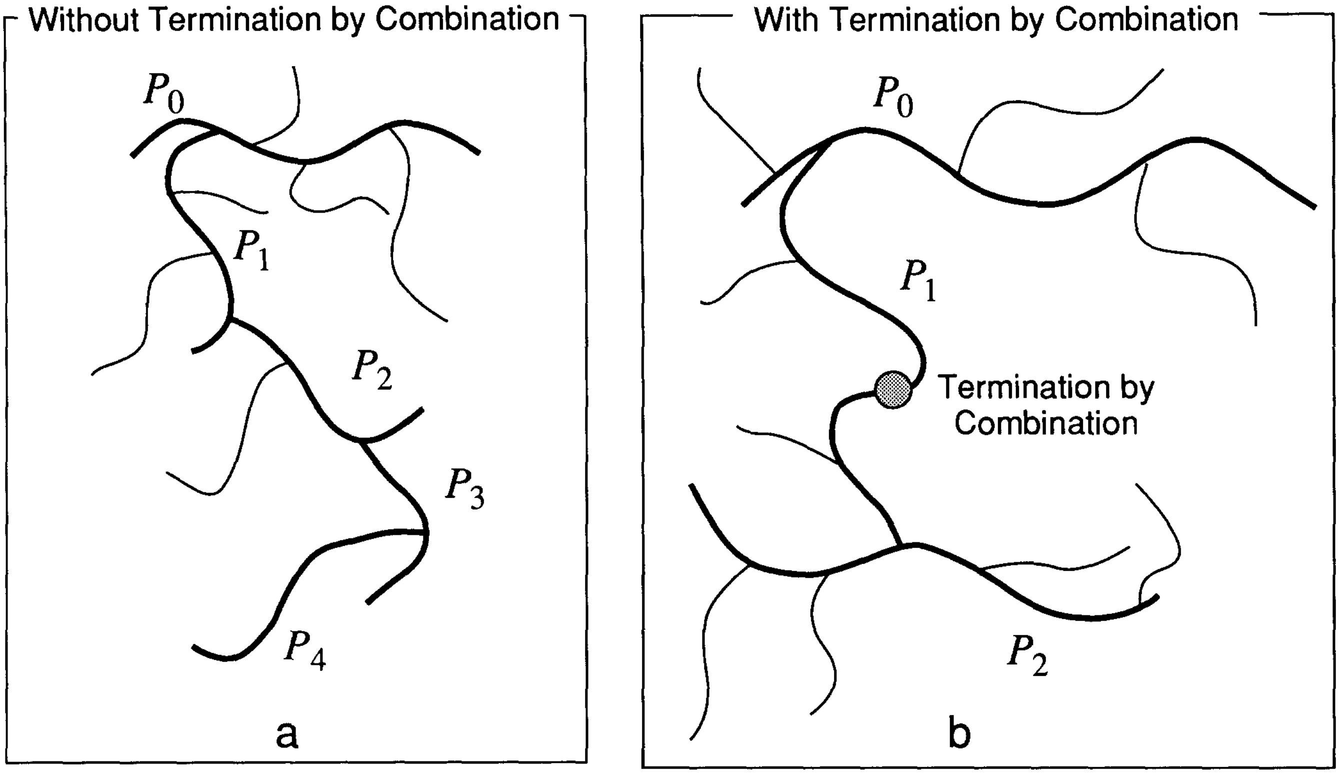

Figure 5 Schematic drawing of the branched polymer molecule (a) formed without bimolecular termination by combination, and (b) formed with bimolecular termination by combination

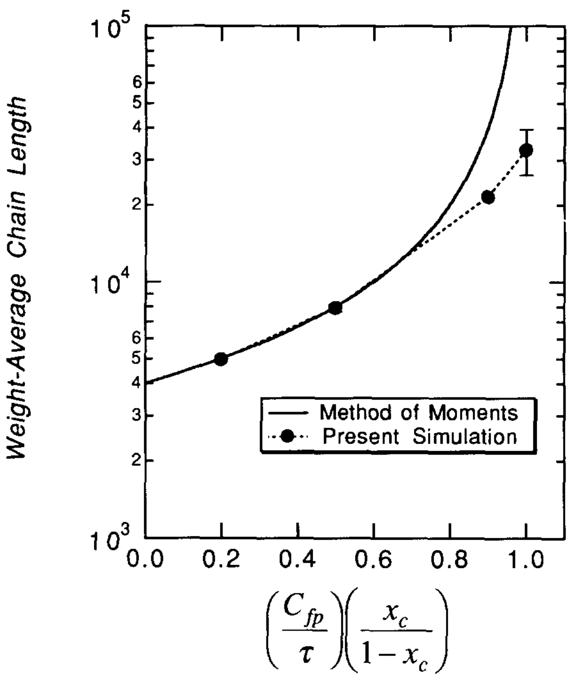

Figure 6 Calculated weight-average chain length with the existence of monomer droplets with $x_c = 0.5$ and $\tau = 5 \times 10^{-4}$. The solid curve is calculated from the method of moments[11,12]

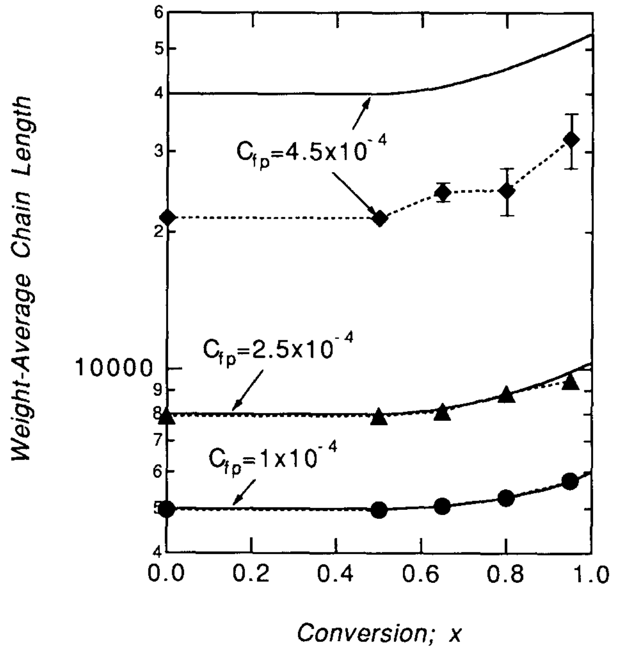

Figure 7 Calculated weight-average chain length development during emulsion polymerization with $x_c = 0.5$ and $\tau = 5 \times 10^{-4}$. The solid curve is calculated from the method of moments[11,12]

Figure 7 shows the calculated weight-average chain length development as a function of conversion. When C_{fp} is much smaller than τ, the method of moments can be considered a good approximation; however, deviation becomes larger as C_{fp} increases. *Figure 8* shows the calculated weight–chain length distribution with the existence of monomer droplets.

The error involved in the conventional method of moments is considered to be caused by the effect of polyradicals. One may argue that it is very difficult to imagine the existence of polyradicals in emulsion polymerization since the average number of radicals per polymer particle is quite often less than 0.5. However, it is worth noting here that the effect of a very small reaction system, which

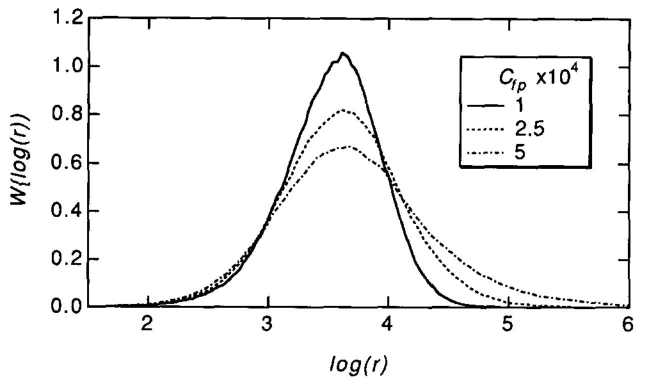

Figure 8 Calculated weight–chain length distribution with the existence of monomer droplets ($x_c = 0.5$ and $\tau = 5 \times 10^{-4}$)

endows emulsion polymerization with its unique features, is not considered in the present model calculations; therefore, the present results show that the effect of polyradicals becomes significant as C_{fp} increases in a reaction system with infinite system size.

As shown in the Introduction, the total number of monomeric units in a polymer particle with diameter 0.1 μm is about 3×10^6, while several simulated polymer molecules are as large as 10^8 when C_{fp} is large. This fact clearly shows that the limitation of molecular weights due to a very small reaction locus must be accounted for in non-linear emulsion polymerization, which is the topic of the next section.

DIRECT SIMULATION METHOD

In the case of polymerization in homogeneous media, the number of reaction systems is unity while the number of monomeric units involved in the reaction is effectively infinite. On the other hand, in emulsion polymerization since the monomer units are compartmentalized into very small polymer particles, the number of monomeric units in each reaction locus is finite as discussed earlier. The BDD method is a powerful method when the reaction system involves an infinite number of molecules; however, it is not exact for emulsion polymerization. When the system size is infinite, it is impossible to conduct a direct simulation of all polymer molecules produced; however, this can be easily done for emulsion polymerization. In the direct simulation method proposed in this paper, polymer particles are sampled randomly, and all polymer molecules in each polymer particle are simulated.

In this paper, we perform simulation prior to the depletion of the monomer droplets, although the extension to the periods after the depletion of monomer droplets is straightforward. The simulation algorithm is quite simple, and is shown in *Figure 9*. In the present simulation all primary polymer molecules including even the first primary polymer molecule produced in a polymer particle are assumed to follow the *MWD* given by equation (11). When a primary polymer molecule is generated, the probability that this primary polymer molecule has started growing from the other primary polymer molecule is given by P_b (see equation (12)). This probability is constant as long as monomer droplets exist. If the primary polymer molecule is connected to another polymer, the backbone polymer is selected randomly on a weight basis within this polymer particle, namely, in a polymer particle that consists of N polymer molecules

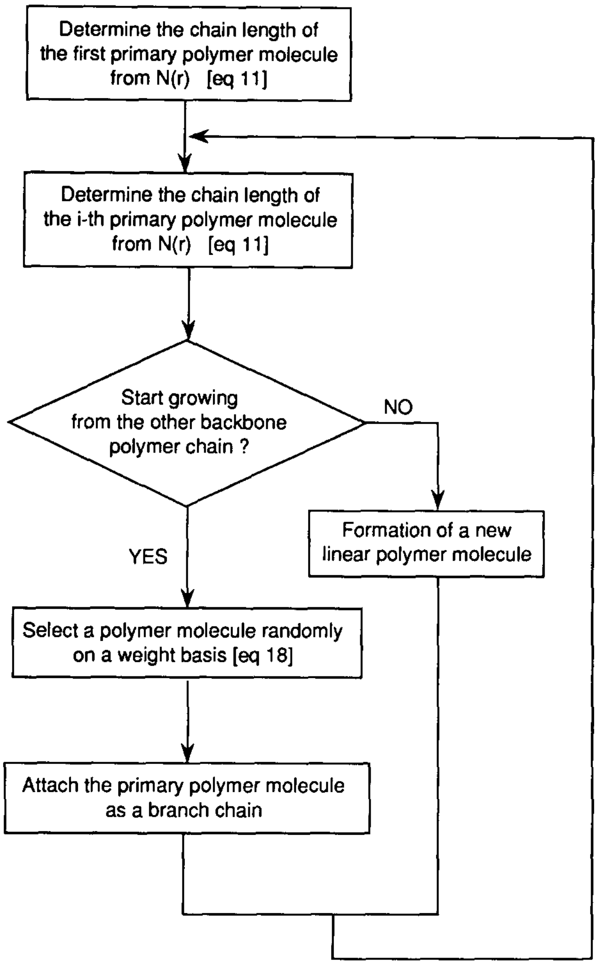

Figure 9 Simulation algorithm for a direct simulation of emulsion polymerization with chain transfer to polymer

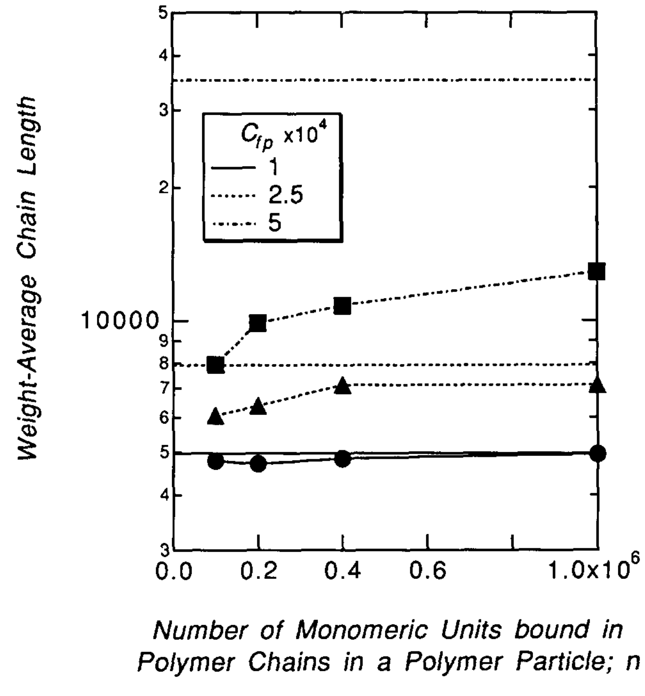

Figure 10 Calculated weight-average chain length development with $x_c = 0.5$ and $\tau = 5 \times 10^{-4}$. The lines without symbols are calculated from the BDD method, and symbols are calculated from the direct simulation method

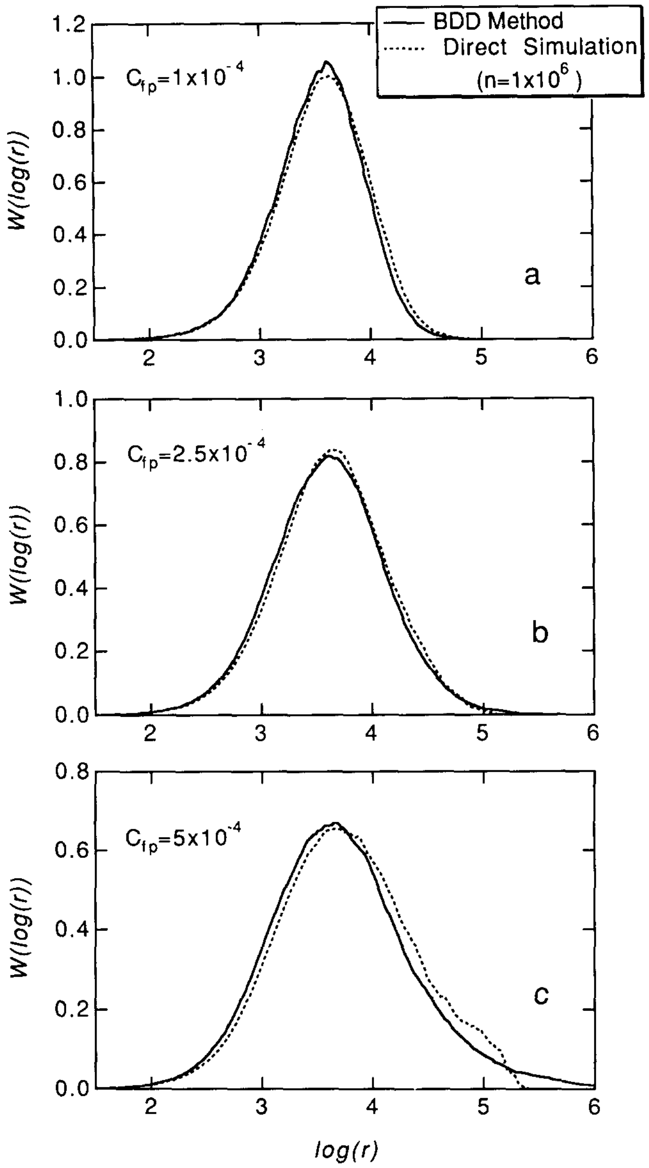

Figure 11 Comparison of the calculated weight–chain length distribution. In the direct simulation method, the total number of monomeric units bound into polymer chains $n = 1 \times 10^6$; $x_c = 0.5$ and $\tau = 5 \times 10^{-4}$ for both methods

(not of primary polymer molecules), the probability that the *j*th polymer molecule with chain length r_j is selected, p_j, is given by:

$$p_j = \frac{r_j}{\sum_{j=1}^{N} r_j} \tag{18}$$

This simulation algorithm can be handled well on a personal computer as long as the number of simulated monomeric units is less than 10^8, which covers most emulsion polymerizations.

Figure 10 shows the calculated weight-average chain length development based on the simulation of 100 polymer particles as a function of the total number of monomeric units bound in the polymer chains in a polymer particle, *n*. When C_{fp} is small, the weight-average chain length reaches the steady state rapidly; however, it takes a very long time to reach the steady state when C_{fp} is large. In particular, when $C_{fp} = 5 \times 10^{-4}$ it seems impossible to reach the steady state within a reasonable time-scale. This result clearly indicates that the effect of compartmentalization is very important in emulsion polymerization with high branching densities.

Figure 11 shows the comparison of the calculated *MWD* between the BDD method and the direct simulation method when the total number of monomeric units bound in the polymer chains in a polymer particle, *n* $= 1 \times 10^6$. A small but clear deviation is observed. *Figure 11c* clearly illustrates the origin of the present problem. When $n = 1 \times 10^6$, the maximum chain length of the polymer molecule allowed to exist in a polymer particle is $r_{max} = 1 \times 10^6$. However, the *MWD* at steady state that was calculated from the BDD method shows that the existence of polymer molecules with chain lengths larger than $r = 1 \times 10^6$ is required, which is clearly impossible for the small polymer particle with $n = 1 \times 10^6$.

Incidentally, the direct simulation method gives the *MWD* on the number basis, so a larger number of polymer molecules is required to be simulated in order to obtain the *MWD* on the weight basis with satisfactory precision. In *Figure 12*, approximately 5×10^4 polymer molecules are simulated in the direct simulation method, while only 1.5×10^4 polymer molecules are generated in the BDD method.

CONCLUSIONS

The method of moments conventionally applied is shown to be a good approximation even for emulsion polymerization that includes chain transfer to polymer as long as the branching density is small; however, it clearly overestimates the weight-average chain lengths for highly branched systems. The BDD method is a powerful method to simulate the kinetics of non-linear polymerizations as long as the effect of the system boundary is not important even for an emulsion polymerization. When the branching density is large in emulsion polymerization, however, the effect of compartmentalization must be accounted for, and a direct simulation of all polymer molecules in each polymer particle is recommended.

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