Molecular Weight Distribution in Free-Radical Polymerization with Chain-Length-Dependent Bimolecular Termination. 2. Emulsion Polymerization

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ABSTRACT: The loci of polymerization in usual emulsion polymerizations are the polymer particles whose diameters are in the submicrometer range; therefore, each polymer particle can be considered a segregated microreactor that contains a small number of macroradicals. It is straightforward to extend the microreactor method proposed in Part 1 of this series[1] to emulsion polymerizations by taking account of the transfer processes of oligomeric radicals between phases, and as a consequence, the formation process of each polymer molecule is simulated directly. The molecular weight distribution can be significantly different from those predicted using a single constant bimolecular termination rate coefficient. The average termination rate coefficient is smaller for larger polymer particles or for longer time intervals between radical entry. Monte Carlo simulations promise to provide greater insight into the complex molecular processes that occur during emulsion polymerizations.

Introduction

Emulsion polymerizations involve complex molecular processes including mass transfer and phase equilibria, and a wide variety of processes that occur simultaneously must be properly accounted for. After the particle nucleation period, which is still controversial, however, the overall picture of the kinetics of emulsion polymerization is relatively well understood. If one accepts such standard kinetic schemes, the difficulties involved in the theoretical studies mainly reside in the complication due to various types of synchronized kinetic events.

The theoretical description of the molecular weight distribution (MWD) in linear emulsion polymerization has been proposed on the basis of the kinetic population balance equations[2−5] and Markovian statistics.[6−8] These approaches have clarified that the MWD formed in emulsion polymerization can be fundamentally different from homogeneous polymerizations. However, due to the complexities involved in the heterogeneous nature of the polymerization system in which entry and desorption of oligomeric radicals are involved, the application of these methods to real systems is not straightforward. Publications containing the full MWDs that are formed under chain-length-dependent bimolecular termination in emulsion polymerization are virtually nonexistent except when pseudobulk kinetics is valid[9] in which a large number of radicals are involved in each polymer particle and unique characteristics of emulsion kinetics are lost.

On the other hand, the Monte Carlo method is a versatile technique that can handle complicated phenomena in a straightforward manner, provided each kinetic process, or the transition probabilities, can be defined explicitly. Especially, when one realizes that the polymer particles produced in emulsion polymerizations are in the submicrometer range and they contain only 10^5−10^8 monomeric units, it is rather straightforward to simulate the formation processes of all polymer molecules in each polymer particle by application of the Monte Carlo method with a well-designed algorithm. In emulsion polymerization, the microreactors used in Part 1 of the present series[1] are not imaginary reactors but possess clear physical meaning as polymer particles. Recently, we proposed a new Monte Carlo simulation method for emulsion polymerizations[10,11] which utilizes the competition technique to reduce the amount of calculations required to simulate the formation of polymer molecules in each polymer particle. Further advantages of using Monte Carlo methods in emulsion polymerization include that more complex molecular processes such as branching[10,12] and cross-linking[13] can be accounted for quite easily. In this paper, the effect of the chain-length-dependent bimolecular termination on the MWD formed in emulsion polymerization is investigated by application of the Monte Carlo simulation method.

Theoretical Section

Simulation Method. We employ the competition technique[1,10,11] to simulate the formation process of each polymer molecule. Figure 1 shows the case where two polymer radicals exist in a polymer particle. The chain lengths shown in the figure, r_{f1}, r_{f2}, r_{12}, and r_e, are imaginary chain lengths for each event to occur. Part 1 of this series[1] should be referred to for a more detailed discussion of each event. The only difference from the microreactor method in the bulk system is that one must account for the transfer processes of radicals. An important feature of radical transfer in emulsion polymerization is that the radicals with extremely short chain lengths can be transferred between phases. Therefore, if the chain transfer to monomer is the real event as illustrated in Figure 1, one has to examine whether this transfer radical exists from the polymer particle or not. The full simulation algorithm can be found elsewhere.[10,11] Modification is necessary only for the bimolecular termination reactions as discussed in Part 1 of the present series.

For emulsion polymerization, especially with an extremely small polymer particle size, one needs to use the probability of bimolecular termination for a pair of radicals r_i and r_j, $\xi(r_i,r_j)$, as follows (see Appendix):

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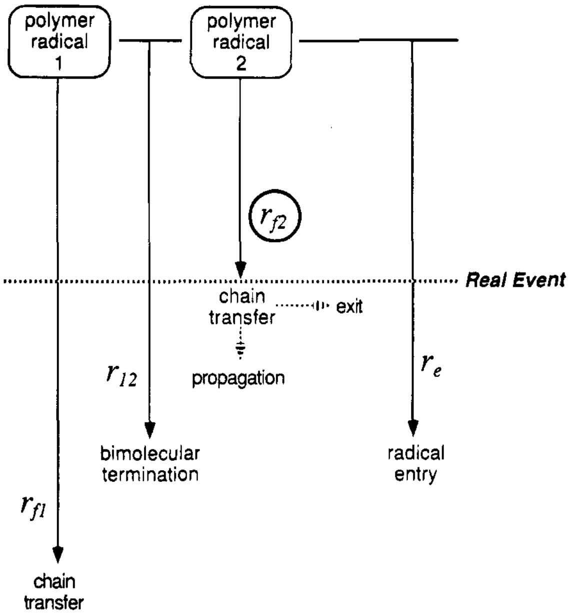

Figure 1. Schematic drawing of the simulation method for emulsion polymerization based on the competition technique.

$$\xi(r_i,r_j) = \frac{k_t(r_i,r_j)}{k_p[M]vN_A + k_t(r_i,r_j)} \qquad (1)$$

where $k_t(r_i,r_j)$ is the bimolecular termination rate coefficient, r_i and r_j are the chain lengths of the ith and jth radicals in the polymer particle, k_p is the propagation rate constant, [M] is the monomer concentration in the polymer particle, v is the volume of the polymer particle, and N_A is Avogadro's number. Modification from eq 8 in ref 1 is required, because $k_t(r_i,r_j)$ may not be small enough compared with $k_p[M]vN_A$. Note that $v \propto (d_p)^3$, where d_p is the diameter of a polymer particle, so $\xi(r_i,r_j)$ decreases significantly with increasing the particle diameter, and $k_t(r_i,r_j)$ becomes much smaller than $k_p[M]vN_A$.

Radical Desorption. An important feature of emulsion polymerization is that the oligomeric radical may diffuse out of the polymer particle. The probability of desorption for the ith radical with chain length r_i is given by

$$P_{des}(r_i) = \frac{K_0(r_i)}{k_p[M] + k_{fm}[M] + k_{fT}[T] + K_0(r_i) + \sum_{j\neq i}\frac{k_t(r_i,r_j)}{vN_A}} \qquad (2)$$

where $K_0(r_i)$ is the desorption rate coefficient for the oligomeric radical with chain length r_i, and the rate constants k_{fm} and k_{fT} are for chain transfer to monomer and to chain transfer agent T, respectively.

The overall desorption rate ϱ_{des} that can be determined from the polymerization experiments is given by

$$\varrho_{des} = \sum_{r=1}^{\infty} K_0(r)N_R(r)\bar{n}N_T = k_f\bar{n}N_T \qquad (3)$$

where $N_R(r)$ is the number-based chain length distribution of radicals in polymer particles, $\bar{n}$ is the average number of radicals in a polymer particle, N_T is the number of polymer particles, and k_f is the overall desorption rate coefficient. Therefore, in order to determine k_f on the basis of $K_0(r)$, knowledge of the chain length distribution of radicals $N_R(r)$ is required. A further problem is that the functional form for $K_0(r)$ has not been established yet, even though $K_0(r) \cong 0$ except for oligomeric chains, especially for hydrophobic monomers.

On the other hand, assuming only oligomeric radicals with very small chain lengths ($r = 1, 2, \cdots$) can exit from the polymer particles, Nomura et al. proposed the relationship between k_f and $K_0(r)$ as follows:[14,15]

$$K_0(r) = k_f/(sC_f) \quad (r \leq s)$$
$$= 0 \quad (r > s) \qquad (4)$$

where s is the largest chain length that can exit from the polymer particle, and $C_f = (k_{fm}[M] + k_{fT}[T])/(k_p[M])$. Equation 4 can be considered a good approximation at least when chain transfer is a major mode of chain stoppage and s is small enough. Good agreement with experimental data for various types of monomer with a wide variety of experimental conditions has been reported by employing $s = 1$.

In this paper, we assume only radicals with chain length unity can be transferred between phases ($s = 1$) and use eq 4 for the desorption rate coefficient, although it is not a requisite for the present simulation method.

Results and Discussion

As in Part 1 of this series,[1] we use the functional form for the bimolecular termination rate coefficient developed by Russell et al.[9,16] The parameters used are shown in Table 1 of ref 1 (C1), which are intended to be germane to styrene polymerization at 50 °C and polymer weight fraction $w_p = 0.76$. In styrene polymerization, the termination mode is considered by combination. However, in order to examine the effect of the termination mode, we use both types of termination modes. As a matter of fact, important features of the MWD formed in emulsion polymerization are contrasted well with homogeneous polymerization when bimolecular termination is assumed to be fully by disproportionation.[11] The average time interval between radical entry is $\bar{t}_e = 50$ s, and it is assumed that reabsorption of the desorbed radicals from polymer particles is included in $\bar{t}_e$. The Monte Carlo simulations were conducted to produce 2×10^4 polymer molecules at each condition.

Termination Independent of Chain Length. In order to highlight the importance of the chain-length-dependent bimolecular termination, let us first examine the MWD formed with a single constant termination rate coefficient before analyzing the chain-length-dependent termination. For bulk polymerization, it was determined that the average termination rate coefficient is $\bar{k}_{t,bulk} = 8994$ L·mol^{-1}·s^{-1}.[16] First, we use this value assuming a single constant bimolecular termination coefficient. Figure 2 shows the instantaneous chain length distribution formed in polymer particles with the diameter of polymer particles $d_p = 0.02$ μm. In such small polymer particles, when a radical enters a polymer particle that possesses a macroradical in it, the bimolecular termination reaction rate is very fast and the newly entered radical is terminated before it grows to a sufficient chain length. Therefore, a peak at a small chain length is formed in the number fraction distribution if the bimolecular termination mode is disproportionation. However, the weight fraction of such a peak

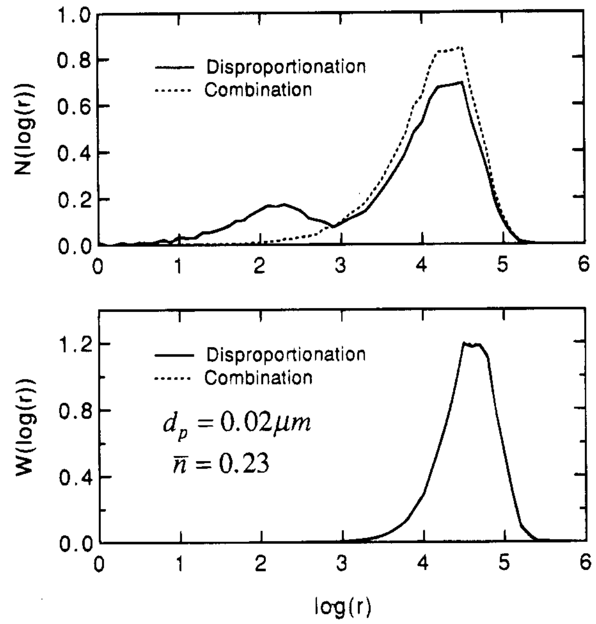

Figure 2. Instantaneous number-based ($N(\log(r))$) and weight-based ($W(\log(r))$) chain length distribution formed with a single constant bimolecular termination rate coefficient that is equal to $\bar{k}_{\mathrm{t,bulk}}$. The particle diameter is $d_p = 0.02$ μm and the average number of radicals per polymer particle under the present calculation condition is $\bar{n} = 0.23$.

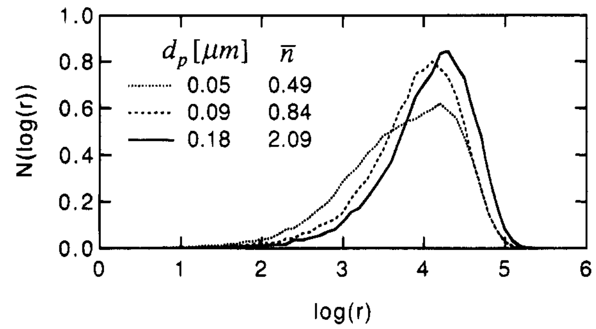

Figure 3. Effect of particle size on the instantaneous number fraction distribution of polymers using a constant bimolecular termination rate coefficient that is equal to $\bar{k}_{\mathrm{t,bulk}}$. The bimolecular terminations are assumed to be fully by disproportionation.

is so small that it cannot be observed if the MWD is plotted on a weight basis; i.e., the effect of the termination mode on the MWD cannot be detected if one obtains $W(\log(r))$ by size exclusion chromatography (SEC).

Figure 3 shows the effect of the particle size on the number fraction distribution of polymers. The termination mode is assumed to be by disproportionation. When the particle size is increased and the average number of radicals per polymer particle $\bar{n}$ becomes larger, the peak at the smaller chain lengths moves toward larger chain lengths, and two peaks merge to form a single peak. The MWD formed under conditions with $\bar{n}$ larger than 2 is very close to the most probable distribution as reported earlier,[11] and the reaction system can be represented well by pseudobulk kinetics.

Termination Dependent on Chain Length. The number-average bimolecular termination rate coefficient for bulk polymerization is given by

$$\bar{k}_{\mathrm{t,bulk}} = \sum_{l=1}^{\infty}\sum_{m=1}^{\infty} k_t(l,m) N_R(l) N_R(m) \qquad (5)$$

where l and m are chain lengths of radicals.

On the other hand, in emulsion polymerization not all combinations of radicals are physically possible. For example, the polymer radicals that exist solely in a polymer particle cannot cause bimolecular termination. Therefore, it would be reasonable to define the average termination rate coefficient only for polymer particles that contain more than one radical. The number-average bimolecular termination rate coefficient for polymer particles that contain n radicals ($\bar{k}_{\mathrm{t,n}}$) could be defined by

$$\bar{k}_{\mathrm{t,n}} = \sum_{l=1}^{\infty}\sum_{m=1}^{\infty} k_t(l,m) N_{\mathrm{R,n}}(l) N_{\mathrm{R,n}}(m) \qquad (n \geq 2) \quad (6)$$

where $N_{\mathrm{R,n}}(l)$ is the number-based chain length distribution of radicals within polymer particles that consist of n radicals.

The fact that pseudobulk kinetics is approximately valid for $\bar{n} \geq 2$ may imply that the chain length distribution of radicals does not change much with the number of radicals per particle, n. Therefore, $\bar{k}_{\mathrm{t,n}}$ may not change much with n ($n \geq 2$). If $\bar{k}_{\mathrm{t,n}}$ is constant irrespective of n ($n \geq 2$), the number-average bimolecular termination coefficient for polymer particles that contain more than one radical could be determined from the Smith–Ewart equation.[17] Assuming a stationary state with known rates of radical entry and exit, Stockmayer[18] and O'Toole[19] solved the Smith–Ewart equation to obtain the average number of polymer particles, $\bar{n}$, and the number fraction distribution of n as follows:

$$\bar{n} = \left(\frac{a}{4}\right)\frac{I_m(a)}{I_{m-1}(a)} \qquad (7)$$

$$P(n) = \frac{a^n (2^{\{(m-1-3n)/2\}}) I_{m-1+n}(a/2^{1/2})}{n! I_{m-1}(a)} \qquad (8)$$

where I denotes the modified Bessel function of the first kind, $a = (8\alpha)^{0.5}$, $\alpha = 2vN_A/(\bar{k}_t\bar{t}_e)$, and $m = 2k_f vN_A/\bar{k}_t$. Strictly, the dependence of k_f on n must also be considered. However, in light of the small k_f value for the present reaction system, such a dependence could be neglected except for very small polymer particles in which the desorption of radicals is significant.

In eqs 7 and 8, $\bar{k}_t$ is the number-average bimolecular termination coefficient for polymer particles that contain more than one radical only when $\bar{k}_{\mathrm{t,n}}$ is constant irrespective of n ($n \geq 2$). Otherwise, the physical meaning of $\bar{k}_t$ is rather obscure. On the other hand, the average number of radicals per polymer particle can be determined experimentally on the basis of the polymerization rate and the number of polymer particles. If eq 7 is used, one can calculate $\bar{k}_t$ anyway. In the present paper, we use the average bimolecular termination rate coefficient $\bar{k}_t$ that gives the same average number of radicals per polymer particle, $\bar{n}$, that is obtained in the present simulation.

Figure 4 shows the comparison of the number fraction distribution of the number of radicals. The points show the simulation results, while the solid curves are calculated from eq 8 by using $\bar{k}_t$ values that are determined from eq 7, i.e., the $\bar{k}_t$ value that gives the same $\bar{n}$ as the simulation results when eq 7 is used. Excellent agreement is shown in Figure 4 irrespective of the particle diameter. Obviously, more rigorous discussion is required concerning the definition of $\bar{k}_t$;

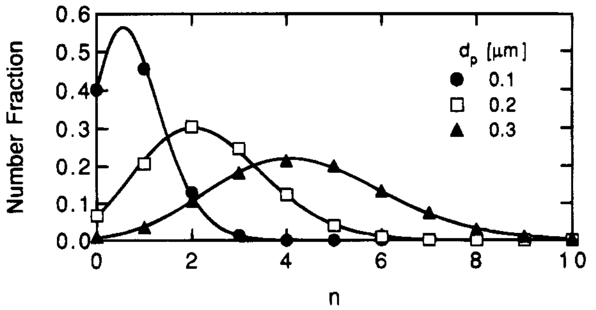

Figure 4. Distribution of the number of radicals per polymer particle, n. The solid curves are calculated from the O'Toole equation (eq 8).

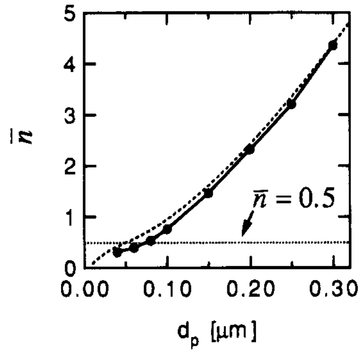

Figure 5. Effect of particle size on the average number of radicals in a polymer particle, $\bar{n}$. The broken curve is calculated from eq 7 by using a constant bimolecular termination rate coefficient, $\bar{k}_{t,bulk}$ = 8994 L·mol^{-1}·s^{-1}.

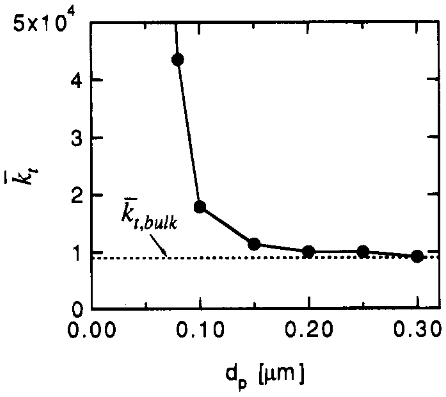

Figure 6. Effect of particle size on the average bimolecular termination rate coefficient, $\bar{k}_t$.

however, the $\bar{k}_t$ values so determined are quite useful to estimate the distribution of the number of radicals at least for the present functional form of $k_t(l,m)$. The excellent agreement shown here may imply that $\bar{k}_{t,n}$ does not change much with n.

Figure 5 shows the effect of the particle size on $\bar{n}$. The circles show the simulated results that consider the chain length dependence of the bimolecular termination rate coefficient, while the broken curve is calculated from eq 7 by using the average termination rate coefficient for bulk polymerization $\bar{k}_{t,bulk}$. Clear deviation from $\bar{k}_{t,bulk}$ is observed except when polymer particle size is large and pseudobulk kinetics is valid. The discrepancy shown here means that the number-average bimolecular termination rate coefficient determined in bulk systems cannot be used to estimate the average number of radicals in emulsion systems.

Figure 6 shows the effect of particle size on the $\bar{k}_t$ values. When the particle size is very small, the termination reactions are mostly caused between a macroradical in the polymer particle and the incoming oligomeric radical. Because the termination rate coefficient for short chains is much larger than that for longer chains, the average termination rate coefficient is very large. Note that $k_t(1,10^3) \approx k_t(1,10^5) = 3.37 \times 10^7$ in the present calculation conditions. As the particle size increases, $\bar{k}_t$ approaches that for a bulk system and pseudobulk kinetics becomes valid.

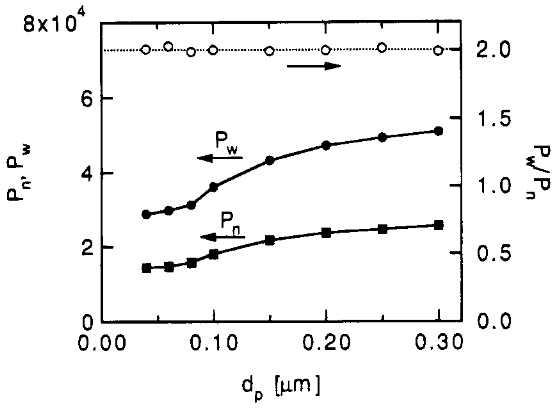

Figure 7. Effect of particle size on the number-average (P_n) and weight-average (P_w) chain lengths. The bimolecular terminations are assumed fully by combination.

Figure 7 shows the simulated number- (P_n) and weight-average (P_w) chain lengths as a function of particle size assuming the bimolecular terminations are fully by combination. Average chain lengths increase with the particle size due to the decrease in bimolecular termination rate. The polydispersity index (P_w/P_n) is almost constant irrespective of the particle diameter. When the particle size is small, the termination rate is very fast and the incoming oligomeric radical is terminated by a macroradical that has existed in the polymer particle. The radical entry time interval is considered random and thus follows the most probable distribution. Therefore, the distribution of macroradicals would follow the most probable distribution. Since the chain length distribution is essentially unchanged due to the coupling of oligomeric radicals, the formed distribution of dead polymer chains follows the most probable distribution whose polydispersity index is $P_w/P_n = 2$. When the bimolecular termination reaction rate is extremely fast in a very small polymer particle, the chain-length-dependent bimolecular termination does not play a role, and $P_w/P_n = 2$ is obtained even when a single constant k_t is used[4,5,11,20] as long as k_t is large enough and the termination mode is combination.

On the other hand, for larger particles pseudobulk kinetics is valid. When the bimolecular terminations are dominated by interactions between radicals with short and long chain lengths, the formed MWDs tend to become the most probable distribution if the termination mode is combination as discussed in Part 1 of this series.[1] Under the present calculation conditions, the approach to the most probable distribution is enhanced by the domination of the chain transfer to monomer for larger polymer particles.

Figure 8 shows the average chain lengths formed when the termination mode is fully by disproportionation. Note that the change of the termination mode does not change the weight-average chain length (P_w) significantly, while the number-average chain length (P_n) becomes smaller compared with Figure 7, especially for smaller polymer particles. As a consequence, the

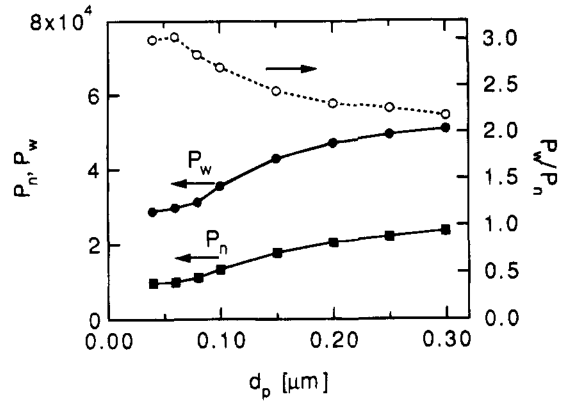

Figure 8. Effect of particle size on the number-average (P_n) and weight-average (P_w) chain lengths. The bimolecular terminations are assumed fully by disproportionation.

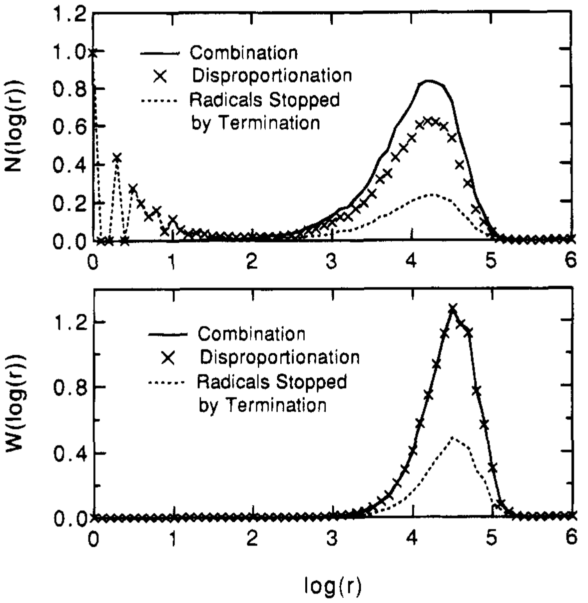

Figure 9. Instantaneous number- and weight-based chain length distribution formed in polymer particles with $d_p = 0.1$ μm.

polydispersity index is much larger than 2 for smaller polymer particles. The polydispersity index takes a maximum around $d_p = 0.6$ μm. Such behavior is also obtained when one uses a constant bimolecular termination rate coefficient.[5,11] As the particle size becomes larger, the polydispersity index approaches 2 mainly because a larger number of polymer chains are formed by chain transfer to monomer rather than bimolecular termination.

Figure 9 shows the MWD formed in polymer particles with $d_p = 0.1$ μm. The oligomeric peaks appear in the number fraction distribution similarly with the bulk polymerization that involves chain-length-dependent bimolecular termination (see Figures 8 and 10 of ref 1) if the termination mode is disproportionation. Since the weight fraction of the oligomeric peaks is very small, such peaks are not observed in the weight fraction distribution.

Figure 10a shows the comparison of the number fraction distribution assuming bimolecular terminations are fully by disproportionation. The circles are obtained using a constant termination rate coefficient that is equal to $\bar{k}_t$. Note that $\bar{k}_t$ may be obtained experimentally by measuring the polymerization rate; however, one cannot use $\bar{k}_t$ to estimate the MWD, especially when the termination mode is disproportionation. The difference from the prediction with a single constant $\bar{k}_t$ occurs because k_t for oligomeric radicals is much larger than $\bar{k}_t$; thus the interactions between short and long radicals are underestimated if $\bar{k}_t$ is used. This is clearly shown in the MWD of radicals stopped via bimolecular termination (Figure 10b); i.e., the oligomeric peaks and high molecular weight peak are formed due to such pairing. On the other hand, however, the difference in the radical pairs for bimolecular termination is obscured in the dead polymer distribution if the bimolecular termination mode is shifted to combination as shown in Figure 11.

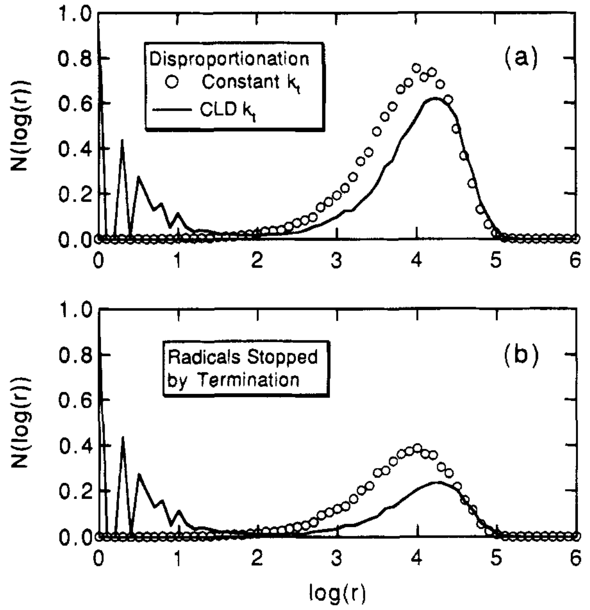

Figure 10. Number fraction distribution formed in polymer particles with $d_p = 0.1$ μm assuming bimolecular terminations are fully by disproportionation (a) and that of radicals stopped by bimolecular termination reactions (b). The circles are obtained based on a single constant termination rate coefficient that is equal to $\bar{k}_t$, while the chain-length-dependent termination rate coefficient is used for the solid curve.

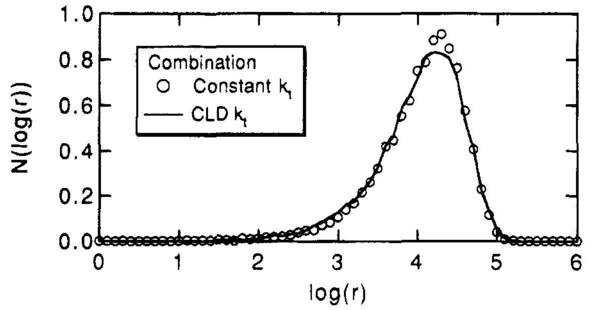

Figure 11. Number fraction distribution formed in polymer particles with $d_p = 0.1$ μm assuming bimolecular terminations are by combination. The circles are obtained by using a single constant termination rate coefficient that is equal to $\bar{k}_t$.

Figure 12 shows the effect of the particle size on the MWD. The termination mode is disproportionation in which the effect of chain length dependence is pronounced. As the particle size increases, the size of the oligomeric peaks becomes smaller mainly due to the domination of chain transfer to monomer in forming polymer chains. Compare with the MWDs shown in Figures 2 and 3 in which a single constant bimolecular termination rate coefficient is used. The shift of the smaller chain length peak to larger chain lengths that is observed in Figures 2 and 3 does not occur in Figure

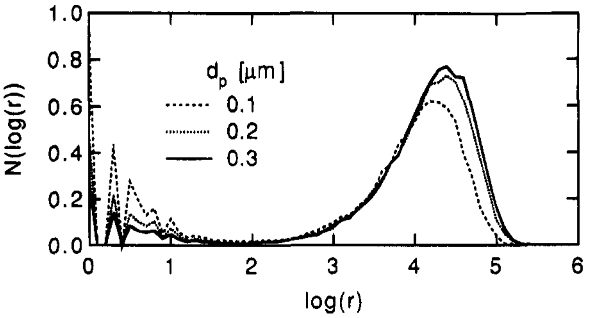

Figure 12. Effect of particle size on the instantaneous number fraction distribution where bimolecular terminations are by disproportionation.

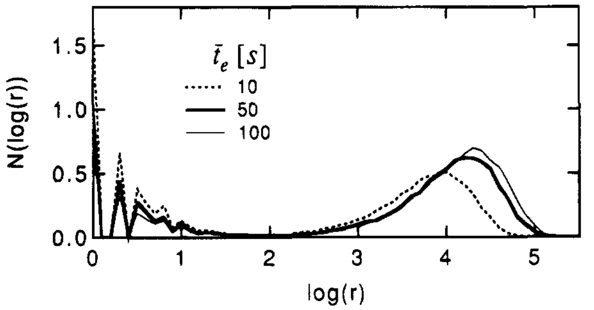

Figure 13. Effect of the average time interval between radical entry $\bar{t}_e$ on the instantaneous number fraction distribution where bimolecular terminations are by disproportionation.

12. The difference in the effect of particle size on the MWD with or without chain-length-dependent kinetics is quite impressive.

Figure 13 shows the effect of the time interval between radical entry $\bar{t}_e$ on the MWD. The increase in $\bar{t}_e$ possesses a similar effect as the increase of the particle diameter, and $\bar{k}_t$ becomes smaller as $\bar{t}_e$ increases.

In the present paper, we have calculated only the instantaneous properties. However, the fact that the number of monomeric units involved in each polymer particle is rather small is a great advantage for one to make computer simulations, and the time evolution can be followed in a straightforward manner.[10] Due to a higher polymer concentration in the polymer particles even from very early stages of polymerization as well as the fact that a larger number of terminal double bonds tend to be formed by chain transfer to monomer in emulsion polymerization, the effect of long-chain branching may not be neglected including monomers whose branching reactions are not significant in homogeneous polymerizations.[10,12] It is straightforward to simulate the formation process of each polymer molecule in each polymer particle in the Monte Carlo simulations even for reaction systems that involve branching and cross-linking during polymerization.[10,12,13] We believe that the Monte Carlo simulation will become a standard tool to analyze the kinetics of emulsion polymerization.

Conclusions

A new computer simulation technique for emulsion polymerization that involves chain-length-dependent bimolecular termination is proposed. The molecular weight distribution can be significantly different from those predicted using a single constant bimolecular termination rate coefficient. Especially when bimolecular termination includes disproportionation, oligomeric molecules that are large in number but small in weight may be formed. The average termination rate coefficient changes with the reaction conditions employed, and it is smaller for larger polymer particles or for longer time intervals between radical entry. In principle, neither idealizations nor approximations are required in the Monte Carlo technique, and the Monte Carlo analyses are suitable especially for emulsion polymerizations due to the finiteness of the reaction system entrenched as polymer particle.

Acknowledgment. I acknowledge Professor R. G. Gilbert, University of Sydney for useful comments.

Appendix

In the present context of the competition technique, when a pair of radicals with chain lengths r_i and r_j are selected from the radicals in the polymer particle, the probability that this radical pair causes bimolecular termination is given by

$$\xi(r_i,r_j) = \frac{k_t(r_i,r_j) + k_t(r_j,r_i)}{2(k_p[M] + k_{fm}[M] + k_{fT}[T])vN_A + \sum_{m\neq i} k_t(r_i,r_m) + \sum_{m\neq j} k_t(r_j,r_m)} \tag{A1}$$

When $k_p[M]vN_A$ is much larger than any other term in the denominator, eq A1 reduces to

$$\xi(r_i,r_j) = \frac{k_t(r_i,r_j)}{k_p[M]vN_A} \tag{A2}$$

Equation A2 is usually valid when the particle volume v is not very small. This is particularly true for the cases where pseudobulk kinetics is valid, and equation A2 was used in the analysis for bulk polymerization.[1]

On the other hand, when the particle volume is very small and the magnitude of $k_p[M]vN_A$ is comparable to other terms, eq A1 needs to be applied. However, in usual emulsion polymerizations with a very small particle size, more than two radicals cannot coexist in a polymer particle. Therefore, eq A1 reduces to eq 1 in the text. (Note that $k_p[M] \gg k_{fm}[M] + k_{fT}[T]$ in usual free-radical polymerizations.) Equation 1 is a good approximation for many cases even when there exist more than two radicals, because (1) $k_t(r_i,r_j)$ becomes very large only when r_i is extremely small, so the termination terms for other radical pairs are much smaller than the propagation term, and (2) when the particle contains more than two radicals, the relationship $k_p[M]vN_A \gg k_t(r_i,r_j)$ quite often holds.

Incidentally, when the bimolecular termination rate coefficient is independent of chain length, eq A1 reduces to

$$\xi_{ij} = \frac{k_t}{(k_p[M] + k_{fm}[M] + k_{fT}[T])vN_A + k_t(n-1)} \tag{A3}$$

which was used in the earlier investigations.[10,11]

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