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Molecular Weight Distribution in Emulsion Polymerization

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ABSTRACT: A new Monte Carlo simulation model for the kinetics of emulsion polymerization is proposed. Normally, for emulsion polymerizations, each polymer particle consists of less than 10^8 monomeric units; therefore, the kinetic behavior of all polymer molecules in each polymer particle can be simulated easily using the Monte Carlo method with a well-designed algorithm. In the Monte Carlo technique, it is straightforward to account for virtually any kinetic event, such as the desorption of oligomeric radicals and chain length dependence of kinetic parameters, and as a consequence very detailed information such as the full distributions of the dead polymer molecular weights and macroradicals among polymer particles can be obtained. When no chain transfer agents are used, chain transfer to monomer tends to become the dominant chain stoppage mechanism due to the long time interval between radical entry, and this may result in active terminal double bonds on polymer chains depending on the monomer transfer mechanism. If active terminal double bonds are formed and polymerize, the present simulations show that the effect of long-chain branching on the molecular weight distribution is significant with the formation of very high molecular weight chains. Monte Carlo simulations provide greater insight into the complex molecular processes which occur during emulsion polymerization.

Introduction

The calculation of the molecular weight distribution (MWD) in emulsion polymerization may not be a novel topic and several solution methods of the population balance equations have already been proposed for linear polymerizations.[1-7] However, due to the complexity of heterogeneous polymerizations in which entry and desorption of oligomeric radicals are involved, the application of these methods to real systems is not straightforward. For example, at present none of them properly account for the chain length dependence of reaction kinetics such as for the desorption of oligomeric radicals and bimolecular termination reactions. Since emulsion polymerization involves various kinds of kinetic events which occur simultaneously, analytical solution techniques are limited to very special cases and numerical solutions can be complicated and time-consuming. Publications containing the full molecular weight distribution, particularly with long-chain branching, for emulsion polymerization are virtually nonexistent.

In emulsion polymerization, the number of monomeric units in each polymer particle is finite, i.e., usually less than 10^8. For example, let us assume the diameter of polymer particle $d_p = 0.1$ μm, the density of polymer $\rho_p = 1$ g/cm^3, and the molecular weight of monomeric unit $M = 100$. In this case, the total number of monomeric units in a polymer particle is calculated to be 3×10^6. Therefore, if the number-average chain length is assumed to be 1000, a polymer particle contains only 3000 polymer molecules, and for such a small number of molecules one can readily calculate the full MWD using Monte Carlo techniques. (In fact, the number-average chain length in most emulsion polymerizations is much larger than 1000, which makes the number of polymer molecules even smaller.) This simple example clearly illustrates that a computer simulation using Monte Carlo methods is potentially a powerful technique for the analysis of the kinetics of emulsion polymerization.

In this paper, a new Monte Carlo simulation model for emulsion polymerization is proposed, and various detailed statistical properties such as the full molecular weight distribution profile and the distribution of radicals among polymer particles are calculated. Also investigated is the extent of long-chain branching in emulsion polymerization by taking advantage of this technique.

Model Development

The loci of polymerization in usual emulsion polymerization are the polymer particles whose diameters are in the submicron range, and one has to consider the transfer of oligomeric radicals to and from polymer particles as well as the polymerization reactions occurring inside the polymer particles. The particle nucleation mechanism, which is still controversial,[8] can affect the MWD in the initial stages of polymerization; however, since most polymer chains are produced after the end of the nucleation period (end of stage 1), we consider polymer chains formed during stages 2 and 3. However, the authors believe that computer simulations using Monte Carlo methods would provide new information on nucleation mechanisms if used for this purpose.

Various levels of model sophistication can be employed in a Monte Carlo simulation. For example, at the most elementary level one can connect each monomeric unit to a radical center one by one with consideration of the effect of particle size distribution on the radical entry frequency at each instant. However, here we use a simpler but more elegant method that can be readily handled even on a personal computer; namely, we generate one linear polymer molecule with a couple of random numbers using appropriate probability density distribution functions. In order to illustrate the present simulation model, we used the following simplifying assumptions, even though none of them are essential to conducting the Monte Carlo simulations. (a) The radical entry frequency is assumed to be the same for all polymer particles. (b) All kinetic constants do not change during polymerization, and the chain length dependence is neglected. On the other hand, the chain length dependence of radical desorption, i.e., the fact that only oligomeric radicals can exit, as well as the reentry of radicals is accounted for in the present simulations.

In order to make a Monte Carlo simulation, the probability functions for various kinetic events must be

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formulated. In the present simulation method, we use the following probabilities: (1) the probability density distribution of the radical entry intervals, (2) the probability of radical desorption for oligomeric radicals, and (3) the probability of chain stoppage for a polymer radical inside the polymer particles by chain transfer and bimolecular termination reactions.

Overall Entry and Desorption of Radicals. Let us consider the case where the number of polymer particles is constant after the nucleation period. The overall rate of radical entry ρ at steady state is given by

$$\rho = \rho_w + \rho_{des} - R_{t,w} \tag{1}$$

where ρ_w is the entry rate of radicals produced in the water phase, ρ_{des} is the rate of radical desorption from polymer particles, and $R_{t,w}$ is the rate of radical termination in the water phase.

For a normal emulsion polymerization, since the average time for a radical to be deactivated by the bimolecular termination in the water phase is much larger than that for entering the polymer particles,[9] it is reasonable to neglect the bimolecular termination reaction in the water phase, and $R_{t,w} = 0$ is assumed in the present model for simplicity.

The overall desorption rate ρ_{des} is given by

$$\rho_{des} = k_f \bar{n} N_T \tag{2}$$

where k_f is the desorption rate coefficient, $\bar{n}$ is the average number of radicals per polymer particle, and N_T is the number of polymer particles.

It is well-known that k_f is inversely proportional to the square of the particle diameter, $(d_p)^2$; namely, $k_f = a/(d_p)^2$ where a is a constant.[10,11] For example, in styrene emulsion polymerization, the value of a has been found to be approximately 2×10^{-5} when d_p is given in micrometers.[12,13]

In order to calculate the overall desorption rate, one has to determine the average number of radicals per polymer particle, $\bar{n}$. Stockmayer[14] and O'Toole[15] obtained exact steady-state solutions to the Smith–Ewart equations[16] and presented their results for $\bar{n}$ in terms of Bessel functions. On the other hand, the value of $\bar{n}$ can be predicted by the following empirical equation within an error less than 4% when bimolecular termination in the water phase is neglected.[17] We used eq 3 in order to make the computer simulation faster.

$$\bar{n} = \frac{1}{2}\left[\left\{\left(a_w + \frac{a_w}{m}\right)^2 + 2\left(a_w + \frac{a_w}{m}\right)\right\}^{1/2} - \left(a_w + \frac{a_w}{m}\right)\right] + \left(\frac{1}{4} + \frac{a_w}{2}\right)^{1/2} - \frac{1}{2} \tag{3}$$

where $a_w = [2(\rho_w/N_T)]/[k_t/(\nu_p N_A)]$, $m = (2k_f)/[k_t/(\nu_p N_A)]$, ν_p is the volume of the swollen polymer particle, k_t is the bimolecular termination constant in the polymer particles, and N_A is Avogadro's number.

By application of eqs 1–3, it is basically possible to determine the overall rate of entry and desorption of radicals. In the present simulation method, however, we are to use the above equations only to determine the radical entry frequency for the polymer particle. The desorption of radicals from the polymer particles is directly simulated in the computer calculations. The average radical entry interval, $\bar{t}$ is given by

$$\bar{t} = \frac{N_T}{\rho} = \frac{1}{\dfrac{\rho_w}{N_T} + k_f \bar{n}} \tag{4}$$

Entry and Desorption of Radicals for a Particular Polymer Particle. Assuming the probability of radical entry is the same for all polymer particles, the probability density distribution of the time interval for entering a radical to a particular polymer particle is given by the following most probable distribution.

$$P_e(t) = \frac{1}{\bar{t}} \exp\left(-\frac{t}{\bar{t}}\right) \tag{5}$$

It is worth noting here that eq 5 is valid not only for the time interval between radical entry but also for the time required for a radical to enter a particle starting from an arbitrary time.

An important feature of radical transfer between polymer particles and the water phase is that only oligomeric radicals can do so. Conventional theoretical approaches usually account for the effect of radical desorption as a first order chain termination as an approximation to describe the MWD. That means that even large polymer radicals can exit from polymer particles, and in addition chain length dependence of the desorption rate coefficient was not accounted for. In the Monte Carlo simulation chain length dependence can be readily accounted for. However, at present the functional form of the chain length dependence is unknown, and therefore we assume that only oligomeric radicals with chain length unity can transfer between the phases, and chain growth in the water phase is neglected. (This assumption is used also for radicals generated in the water phase, although this is not essential for the present simulation model.) In light of the fact that very long polymer chains are usually produced in emulsion polymerization, the effect of chain length of the oligomeric radicals that enter and exit on the MWD would be negligible as long as the chain length of such radicals is small enough.

Now assuming the desorption rate coefficient for the oligomeric radical is K_0, the probability of desorption for an oligomeric radical from the polymer particle is given by

$$P_{des} = \frac{K_0}{k_p[M]_p + k_{fm}[M]_p + k_{fT}[T]_p + k_t \dfrac{n-1}{\nu_p N_A} + K_0} \tag{6}$$

where n is the number of radicals in the polymer particle, and k_p, k_{fm}, and k_{fT} are the rate constants for propagation, chain transfer to monomer, and chain transfer to some small molecule T, respectively.

Note that $K_0 \neq k_f$ since k_f is the average desorption rate coefficient for all radicals in polymer particles. According to Nomura et al.[11,18,19] the relationship between k_f and K_0 is given by

$$k_f \cong K_0\left(C_m + C_{fT}\frac{[T]_p}{[M]_p}\right) \tag{7}$$

where C_m and C_{fT} are the chain transfer constant ratios for monomer and small molecule T, respectively.

Equation 7 can be considered a good approximation, at least when chain transfer is a major mode of chain stoppage, and has shown good agreement with experimental data for various monomer types for a wide range of experimental conditions.[9,17–20] In the calculations shown later, we used the relationship given by eq 7 although it is not essential for the present simulation model.

Dead Polymer Formation in Polymer Particles. When an oligomeric radical with chain length unity does not exit, this radical can propagate until the chain is stopped by chain transfer or bimolecular termination. The probability density that a radical adds r monomer units before it ceases growing by chain transfer is given by the following most probable distribution:

$$P_f(r) = C_f \exp(-C_f r) \tag{8}$$

where $C_f = [k_{fm}[M]_p + k_{fT}[T]_p]/(k_p[M]_p)$. Note the above probability density is valid starting from any moment; namely, a polymer radical of any chain length follows eq 8.

When a dead polymer chain is formed by the chain transfer reaction, it may be necessary to distinguish between chain transfer to monomer and chain transfer agent, T, in order to determine the type of transfer radical (and chain end of the growing macroradical if the transfer radical does not exit). This can be done simply by using the conditional probability for the formation of a dead polymer molecule by chain transfer to the monomer given the polymer chain is formed via a chain transfer reaction.

$$P_{m|f} = \frac{k_{fm}[M]_p}{k_{fm}[M]_p + k_{fT}[T]_p} \tag{9}$$

On the other hand, the probability density that a radical adds r monomer units until it ceases growing by bimolecular termination with a particular radical pair is given by

$$P_t(r) = \xi \exp(-\xi r) \tag{10}$$

where $\xi = [k_{tp}/(\nu_p N_A)]/(k_p[M]_p)$. Note eq 10 must be considered for all possible radical pairs; namely, the probability provided by eq 10 is examined ${}_nC_2 = n(n-1)/2$ times for the polymer particle with n radicals.

In eq 10, the chain length dependence of the bimolecular termination is neglected; however, it is straightforward to account for such effects in a Monte Carlo simulation if the functional form of the chain length dependence is made clear. Termination by combination (k_{tc}) and disproportionation (k_{td}) can be distinguished by simply applying the following conditional probability:

$$P_{c|t} = \frac{k_{tc}}{k_{tc} + k_{td}} \tag{11}$$

Simulation. Using the probabilities given by eqs 5, 6, and 8–11, the kinetic behavior of emulsion polymerization can be simulated. The simulation method is schematically shown in Figure 1. Figure 1 shows the case where two polymer radicals exist in a polymer particle after a certain event occurs. Then one calculates the "imaginary times" when each polymer radical ceases growing due to chain transfer reactions, t_{f1} and t_{f2}, the imaginary time for bimolecular termination, t_{12}, and the imaginary time for radical entry, t_e. At this stage, a kind of competition of events is considered; namely, the shortest imaginary time is chosen as the "real time". In the figure, t_{f2} is chosen for the real time, that means that events given by the imaginary times, t_{f1}, t_{12}, and t_e, never happened. If the radical chain growth is stopped by a chain transfer reaction, one has to examine whether the resulting transfer radical exits from the polymer particle or not. If the chain stoppage mode is bimolecular termination, the other polymer radical must also become a dead polymer chain. The whole simulation algorithm is shown in Figure 2. As mentioned earlier because the particle nucleation mechanisms are uncertain, the present simulation is made only after the formation of all the polymer particles, and the initial size of the polymer particle is assumed given. In the present simulation, the probability of desorption is assumed to be the same irrespective of the chemical structure of the oligomeric radicals (whose chain length is assumed to be unity in the present simulation). The algorithm is complicated due to the various kinetic events

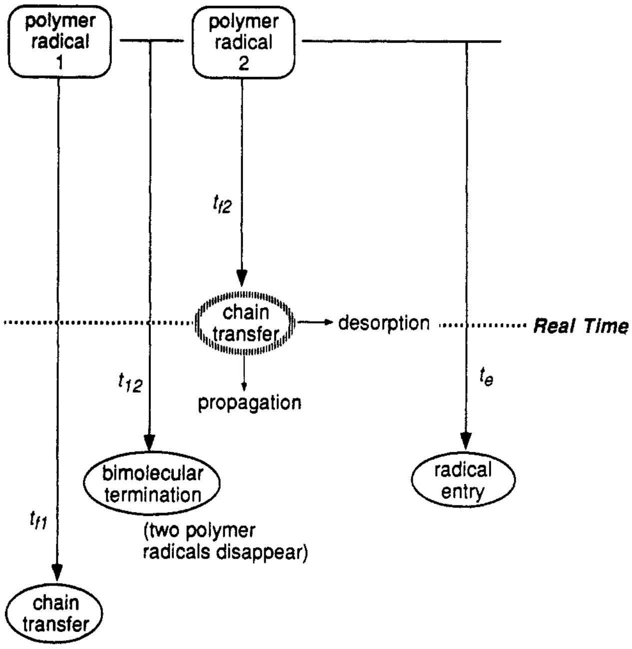

Figure 1. Schematic drawing for the simulation method.

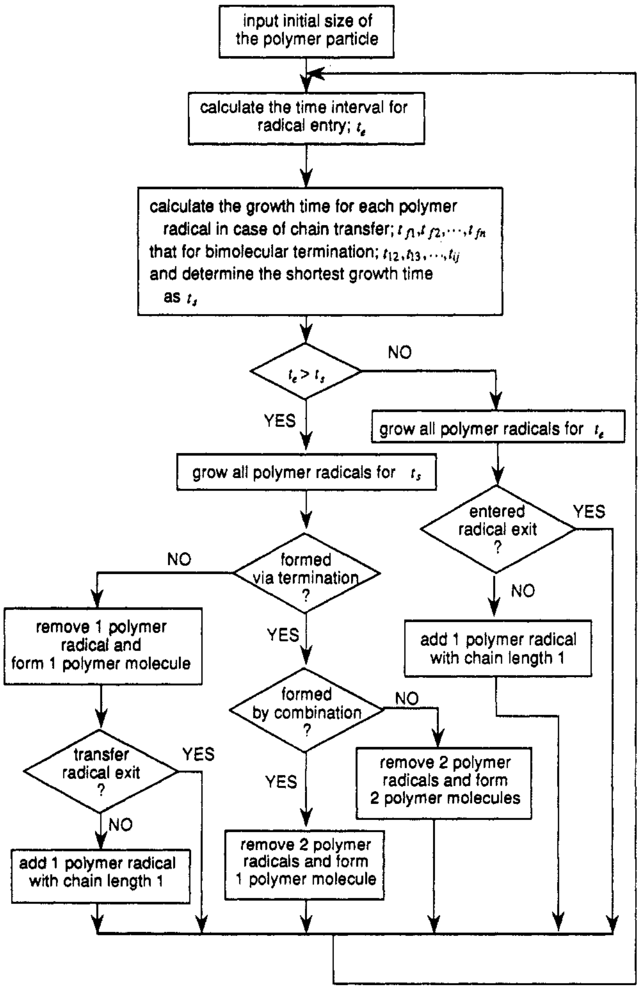

Figure 2. Simulation algorithm for linear emulsion polymerization.

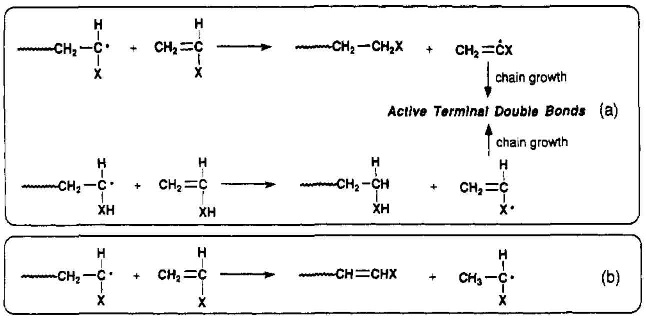

Figure 3. Schematic representation of the chain transfer to monomer.

involved in emulsion polymerization; however, all probabilities used are mathematically quite simple and it is straightforward to include more detailed kinetic events.

Extent of Long-Chain Branching. Before making simulations, we would like to consider the possibility of long-chain branching. There are two types of long-chain branch formation that may occur fortuitously: chain transfer to the polymer and terminal double bond polymerization (TDBP). For emulsion polymerizations, since the polymer concentration in the polymer particles (the loci of polymerization) is higher than for homogeneous polymerizations (in stage 2), the possibility of long-chain branching formed by chain transfer to the polymer is greater for emulsion polymerization. This has been shown earlier.[21,22] However, here we are to focus our attention on the latter type of long-chain branching (TDBP).

As already pointed out,[4,5] quite often chain transfer to small molecules tends to become the dominant chain stoppage mechanism due to the long time interval between radical entry and with an instantaneous bimolecular termination rate in small polymer particles. Even when chain transfer agents are not used, chain transfer to the monomer is inevitable, and chain transfer to the monomer tends to become a dominant chain stoppage mechanism if the radical entry interval is long enough. It is customary to consider that the chain transfer to monomer reaction involves abstraction of hydrogen from the monomer, as shown in Figure 3a. However, transfer of hydrogen from the polymer radical may also occur in some cases (Figure 3b), although the products of reaction (b) are not appreciably more stable than the reactants.[23] If reaction (b) occurs, the produced TDBs are both substituted and, therefore, inactive toward free-radical polymerization. On the other hand, if reaction (a) occurs, the formed TDBs can react to form long-chain branches. Active TDBs are likely produced for monomers with α methyl groups such as methyl methacrylate because the new radicals formed are relatively stable. For many types of monomer, however, it has not been determined which type of chain transfer is dominant. In order to investigate the potential importance of the TDBP in emulsion polymerization, we are to consider the cases where chain transfer to a monomer of type (a) is dominant. The reactivity of such TDBs is affected both chemically and physically and is usually difficult to determine experimentally. Even for vinyl acetate polymerization where chain transfer to monomer is attributed to transfer from the acetoxy methyl group, the reactivity of the TDBs is reported to be $K = k_p^*/k_p = 0.66$ where k_p^* is the rate constant for TDBP,[24] which implies that the physical effects cannot be neglected.

The monomer chain transfer constants are generally small for most monomers, and C_m is usually in the range 10^{-5} to 10^{-4}. Let us roughly examine the effect of TDBP by assuming the monomer transfer constant $C_m = 5 \times 10^{-5}$, the weight fraction of polymer in the polymer particles with the existence of monomer droplets $x_c = 0.5$, and the reactivity of TDB $K = 0.5$. If all polymer chains are formed via chain transfer to the monomer, the number-average chain length of linear polymer chains is $P_N = 1/C_m = 2 \times 10^4$, which gives the upper limit for the number-average chain length of the linear polymer chains for a given monomer. Assuming all polymer chains are linear and each polymer chain possesses one TDB, the probability that a polymer radical reacts with a TDB rather than monomer P_{TDBP} is given by

Table 1. Parameters Used for the Simulation

k_p	210 [$L/mol{\cdot}s$]
$[M]_p$	5.48 [mol/L]
k_{tc}	6.0×10^6 [$L/mol{\cdot}s$]
C_m	6×10^{-5}
x_c	0.43
a	2×10^{-5} [$(\mu m)^2/s$]
ρ_p/ρ_m[a]	1.16
M[b]	104

[a] Density ratio between polymer and monomer. [b] Molecular weight of monomer.

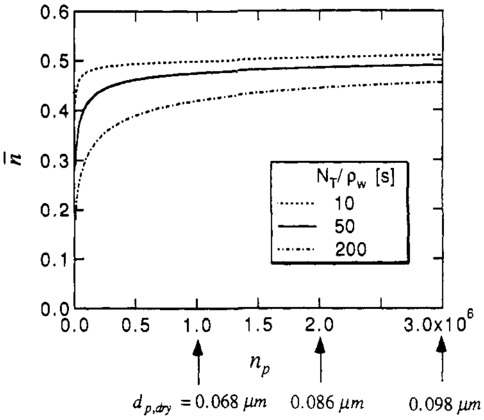

Figure 4. Change in $\bar{n}$ during polymerization using kinetic parameters given in Table 1. The arrows indicate the diameter of the unswollen polymer particles, $d_{p,dry}$.

$$P_{TDBP} = \frac{K\sum_{r=1}^{\infty}[P_r]}{[M]_p} = \frac{Kx_c}{(1-x_c)P_N} = 2.5 \times 10^{-5} \quad (12)$$

Therefore, the probability of forming a TDBP is negligibly small at any moment. However, the probability that a new polymer chain with chain length equal to P_N can be formed without reacting any TDB is given by

$$(1 - P_{TDBP})^{P_N} = (1 - 2.5 \times 10^{-5})^{2\times10^4} = 0.607 \quad (13)$$

Therefore, the possibility of reacting at least one TDB is 39.3%, which cannot be neglected. The above simple example illustrates the potential importance of the TDBP in emulsion polymerization when the dominant chain stoppage mechanism is shifted to chain transfer to the monomer.

In the present Monte Carlo simulation, the TDBP can be included simply by the use of the following probability. At the time when the total number of monomer molecules in the given polymer particle is n_m, the probability that a particular TDB does *not* react when a polymer radical adds r monomeric units is given by

$$P_{noTDBP} = \left(1 - \frac{K}{n_m}\right)^r \quad (14)$$

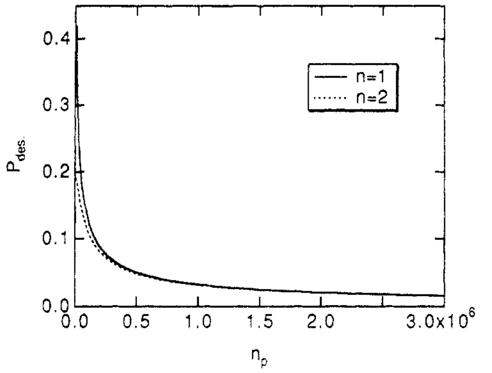

Figure 5. Probability of desorption for oligomeric radicals with $N_T/\rho_w = 50$ (s) for the number of radicals in the polymer particle $n = 1$ and 2.

Equation 14 is examined for all TDBs in the polymer particle every time polymer radicals grow. In the present calculations, the n_m value when half the monomeric units between events are added to all polymer radicals was used. More discussion of the TDBP in emulsion polymerization can be found elsewhere.[25]

Results and Discussion

In order to illustrate the present simulation model, we are to make simulations using the kinetic parameters shown in Table 1 without the use of a chain transfer agent. Bimolecular termination is assumed to be combination alone. All simulations were made after the formation of the polymer particles was complete, and the initial value for the number of monomeric units bound in polymer molecules per polymer particle n_p was 1×10^4. The simulation was conducted for stage 2 during which monomer droplets exist, although it is straightforward to extend the present simulation method to stage 3. For polymerizations without TDBP, 600 polymer particles are simulated until $n_p = 5 \times 10^5$, and 300 polymer particles are simulated after that. For polymerizations with TDBP, approximately 1×10^4 polymer molecules are simulated in order to obtain statistically valid results. In the Monte Carlo simulations, it is straightforward to follow the history of polymerization and to calculate the properties of the accumulated dead polymer. Note that in the analytical approaches, it is common to formulate equations for the instantaneous MWD (that is formed in a very small time interval), and the accumulated MWDs that can be compared with experimental data directly are obtained by integration of the instantaneous MWDs. (The calculation of the instantaneous MWD using the present techniques can be found elsewhere.[26])

In fact, the kinetic parameters shown in Table 1 are for the polymerization of styrene at 50 °C, which is considered a typical example of emulsion polymerization that conforms to $\bar{n} \cong 0.5$. However, as for the monomer chain transfer mechanism, it is speculated that the experimentally observed C_m for styrene may be due in large part to the Diels–Alder dimer transferring a hydrogen to the monomer,[27,28] and a significant amount of active TDBs may not be formed. Therefore, some of the present simulation results that include TDBP should be understood as showing the potential importance of TDBP in general.

Figure 4 shows the change of the average number of radicals per polymer particle during particle growth. In the early stages of polymerization, radical desorption cannot be neglected; however $\bar{n}$ soon approaches 0.5. Figure 5 shows the probability of desorption for an oligomeric radical. The probability of desorption decreases as the polymer particle grows, and it differs significantly depending on the number of radicals in the polymer particle only for the very early stages of polymerization.

Figure 6 shows the distribution of the number of radicals per polymer particle. The upper figures show the instantaneous distribution at a given reaction time while lower figures show the accumulated time fraction until the given values of n_p. These figures show that the fraction of polymer particles with more than one radical is extremely small, and the distribution profile changes as the average time interval for radicals produced in the water phase N_T/ρ_w changes. Note that the results shown in Figures 4–6 are valid irrespective of the occurrence of TDBP and, therefore, should be valid for styrene polymerization.

Figure 7 shows the average chain length development with and without TDBP assuming $K = 0.6$ and 0.3. The effect of TDBP on the weight-average chain length P_W becomes significant as the average radical entry interval

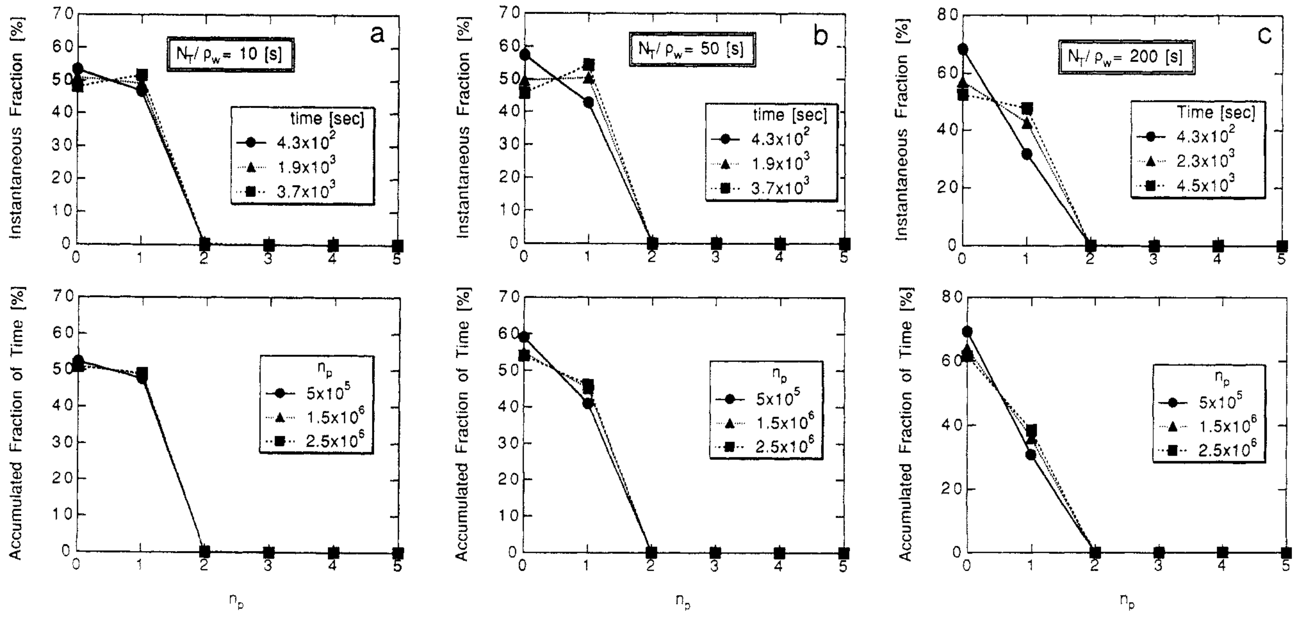

Figure 6. Distribution of the number of radicals per polymer particle.

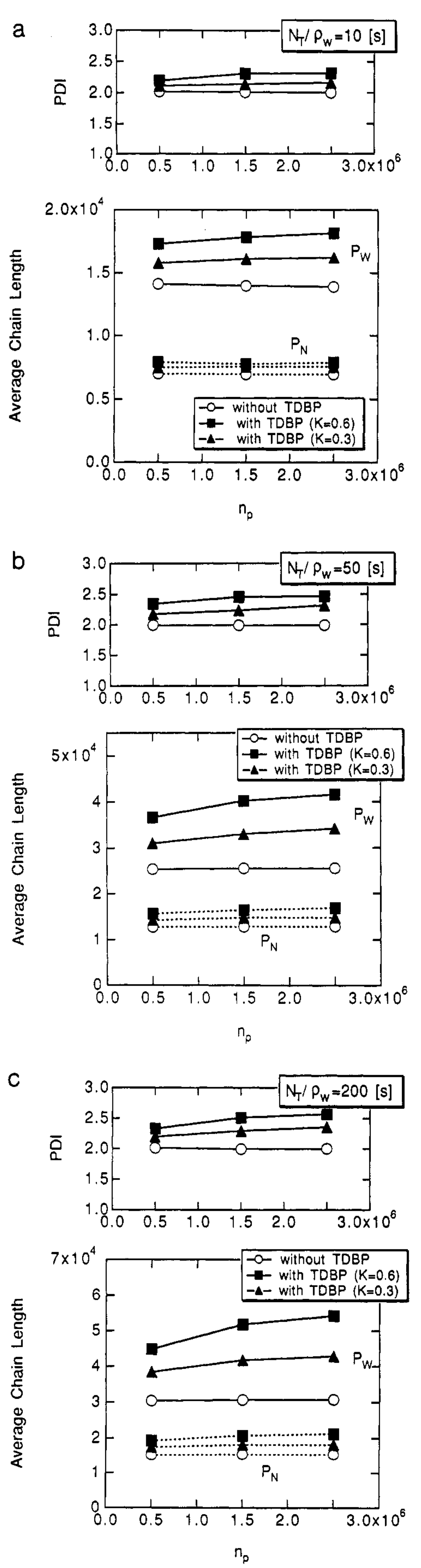

Figure 7. Average chain length development during polymerization.

N_T/ρ_w becomes larger. When no TDBP occurs, the polydispersity index (PDI = P_W/P_N) is very close to 2 and

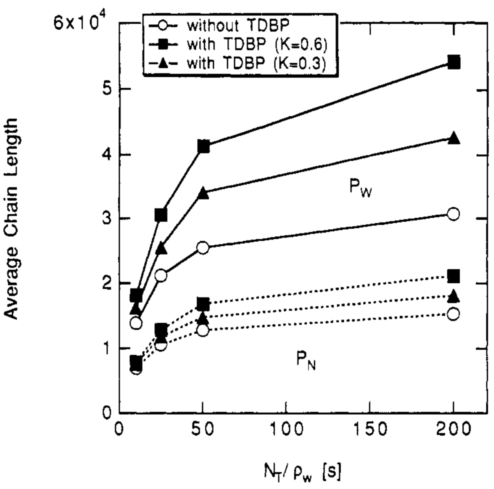

Figure 8. Effect of the entry interval of radicals generated in the water phase on the average chain length at $n_p = 2.5 \times 10^6$.

is pretty much the same during the polymerization even when the radical entry interval (and therefore, the relative importance of chain stoppage by termination and chain transfer) is changed. Note that for polymerizations in which bimolecular termination is considered to be solely combination, the PDI for the instantaneously formed polymers in homogeneous polymerization is 1.5. As shown in Figure 6, the number fraction of polymer particles with more than one radical is extremely small in the present calculation conditions, indicating that a newly entered radical (with chain length unity in the present simulation) terminates almost instantaneously with a longer polymer radical that has been growing in the polymer particle; therefore, the instantaneous MWD of the dead polymer chains is essentially the same as the MWD of the polymer radicals that is given by the most probable distribution (see eqs 8 and 10). As pointed out earlier,[29] the PDI of the instantaneous MWD is always larger for emulsion polymerization when no TDBP occurs, although the PDI for the accumulated polymer may be smaller for emulsion polymerization since the molecular weight produced in emulsion polymerization remains almost constant during stage 2 due to the constant monomer/polymer ratio. The occurrence of the TDBP makes the consideration on the MWD even more complicated when one realizes that for emulsion polymerization long-chain branch formation is enhanced.[21,22] Note that even for reaction systems for which the formation of TDBs due to monomer transfer is negligible in homogeneous polymerization, the TDBP may significantly affect the MWD when emulsion polymerization is employed. When the TDBP does occur, the estimated monomer transfer constants using emulsion polymerization are invalidated if linear chains are assumed to be formed exclusively.

Figure 8 shows the average chain length at $n_p = 2.5 \times 10^6$ as a function of N_T/ρ_w. The main reason for the production of polymers with high molecular weights in emulsion polymerization is that the radicals are separated in each polymer particle and the time interval between radical entry is long. However, it may be reasonable to speculate that terminal double bond polymerization may contribute to polymer chain formation with extremely large molecular weights if active TDBs are produced via chain transfer to the monomer.

Figure 9 shows the weight–chain length distribution development. When TDBP occurs, the high chain length tail increases slightly as reaction proceeds, while the distribution is almost the same during polymerization as long as monomer droplets exist in the absence of TDBP.

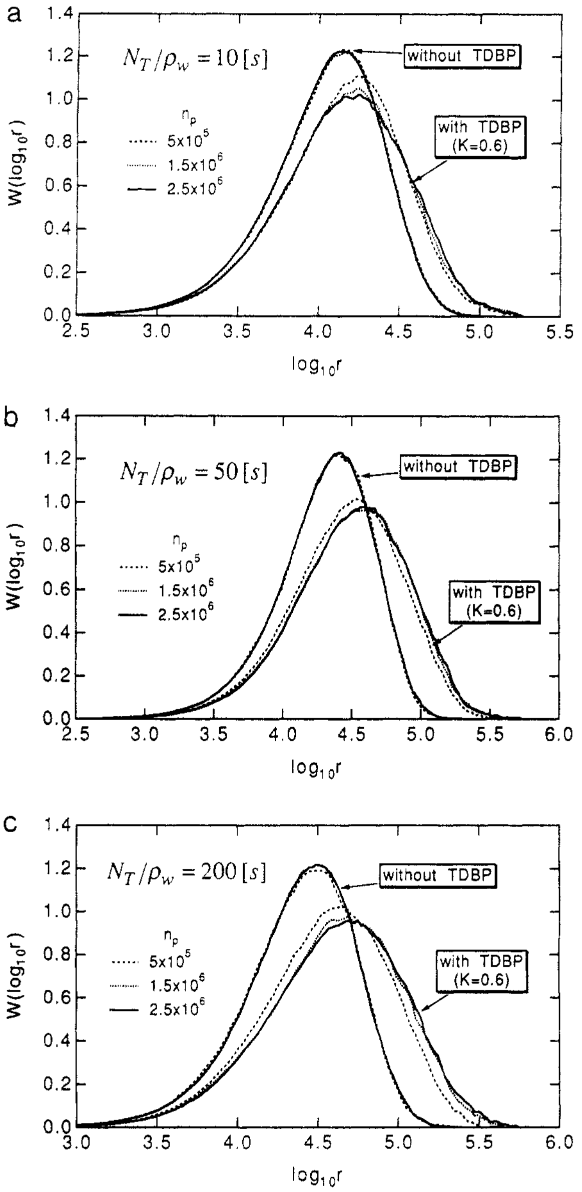

Figure 9. Weight–chain length distribution development with and without terminal double bond polymerization.

Since the present simulation is made on a number basis, the distribution profile plotted on the weight basis shows some small scatter at higher molecular weights.

Figure 10 shows the number and weight fraction distribution of the number of branch points. There are more linear than branched chains on both a number and weight basis; however, the effect of branches on the molecular weights cannot be neglected especially when the primary polymer chain lengths are large, i.e., for larger N_T/ρ_w. Figure 11 shows the number- and weight-average number of branch points per polymer molecule.

Figure 12 shows the average number of unreacted terminal double bonds per polymer molecule. Since the number of polymer molecules with more than one unreacted TDB is very small, Figure 12 shows approximately the number fraction of polymer molecules with unreacted TDB. As N_T/ρ_w increases, the possibility of chain formation via chain transfer to monomer becomes larger, and when N_T/ρ_w = 200 (s) approximately 80% of polymer molecules possess unreacted TDB.

The Monte Carlo method is a very useful technique for the analysis of the kinetics of emulsion polymerization. This is particularly true because the size of each reaction locus is very small, i.e., in a submicron range. Besides the TDBP, the effect of chain transfer to the polymer in emulsion polymerization is more significant than for homogeneous polymerizations due to a higher polymer concentration even at the point of birth of a polymer particle. Application of the direct simulation method to the polymerization with long-chain branching due to chain

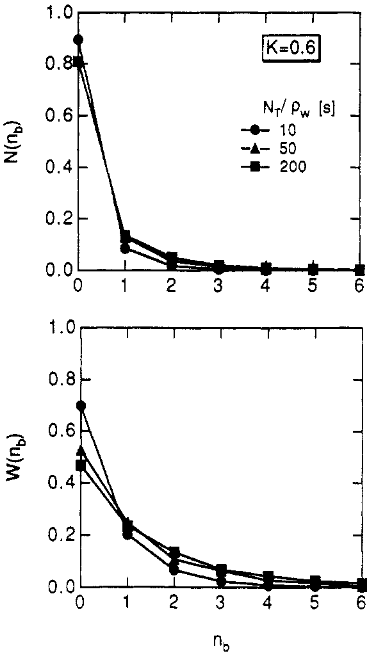

Figure 10. Number ($N(n_b)$) and weight ($W(n_b)$) fraction distribution of the number of branch points (n_b) on a polymer molecule at n_p = 2.5 × 10^6.

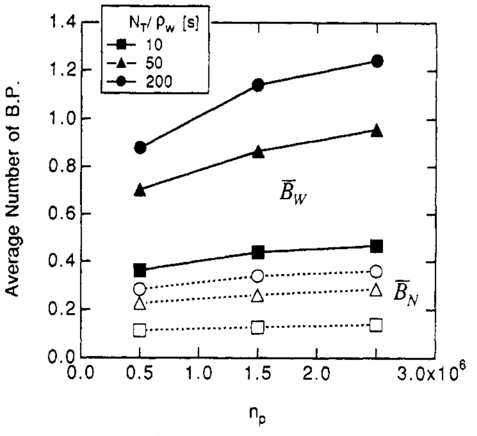

Figure 11. Number- ($\bar{B}_N$) and weight-average ($\bar{B}_W$) number of branch points per polymer molecule for K = 0.6.

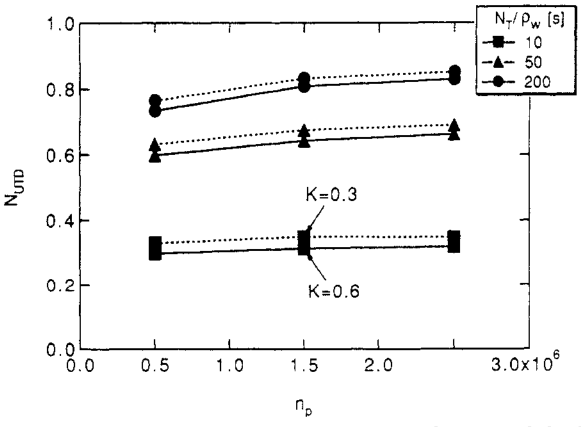

Figure 12. Average number of the unreacted terminal double bonds per polymer molecule (N_{UTD}).

transfer to the polymer[22] and TDBP,[25] and vinyl/divinyl copolymerization[30] in emulsion systems can be found elsewhere.

Conclusions

A new Monte Carlo simulation model for the kinetics of emulsion polymerization has been developed. In emulsion polymerizations, since the number of monomeric units involved in each polymer particle is limited, a simulation in a finite system using the Monte Carlo method is very promising. In the Monte Carlo simulation, it is quite straightforward to include various kinetic events, and very detailed information can be obtained since one can observe each polymer molecule as well as each polymer particle directly.

By application of the present simulation method, it was shown that the TDBP may not be neglected in emulsion polymerization if active TDBs are produced via chain transfer to the monomer. The possibility of TDBP may have to be considered for virtually all emulsion polymerizations when a chain transfer agent is not used, as then the formation of a very high molecular weight polymer due to long-chain branching is quite likely.

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