Kinetics of long-chain branching in emulsion polymerization: 2. Vinyl acetate polymerization

Hidetaka Tobita
Department of Materials Science and Engineering, Fukui University, Fukui, Japan 910
(Received 30 August 1993; revised 12 October 1993)

The loci of polymerization in emulsion polymerization are the polymer particles, with diameters usually in the submicrometre range. The effect of such compartmentalization of the reaction system on the molecular weight distribution development in non-linear polymerization is investigated by application of newly developed simulation models for emulsion polymerizations that include chain transfer to polymer and terminal double bond polymerization. Kinetic parameters and experimental data for vinyl acetate polymerization reported by Friis *et al.* (1974, 1975) are used. It was found that the effect of compartmentalization must be accounted for in vinyl acetate emulsion polymerizations, and that the kinetics of long-chain branching in this reaction system needs careful reinvestigation using an appropriate reaction model and analytical techniques with higher precision.

(Keywords: molecular weight distribution; chain transfer to polymer; poly(vinyl acetate))

INTRODUCTION

In Part 1 of this series[1], the fact that the loci of polymerization in emulsion polymerization are very small polymer particles must be accounted for when the branching frequency is high enough for non-linear polymerizations. It is important to examine if such a compartmentalization effect is important in a real system or not. In this paper, the effect of compartmentalization on the kinetics of vinyl acetate emulsion polymerization is investigated by application of the kinetic parameters and experimental data reported by Friis *et al.*[2,3].

In order to investigate the effect of compartmentalization, two types of model are required: one assumes no system boundary effects and the other accounts for such effects. As a model without a system boundary, the method of moments has been applied widely for vinyl acetate polymerizations[2-8]; however, this method clearly overestimates the weight-average chain length when branching frequency is high in emulsion polymerization[1] and in a homogeneous polymerization in a continuous stirred tank reactor[9,10], therefore it cannot be used for the present purpose. In order to obtain an exact solution for the model that does not consider the effect of compartmentalization, the branching density distribution method (BDD method) is extended to include both chain transfer to polymer (CTP) and terminal double bond polymerization (TDBP) as was done for polymerization in homogeneous media[10,11]. Then the calculated results based on the BDD method are compared with a direct simulation method in which all polymer molecules in each polymer particle selected randomly are simulated, as in Part 1 of this series[1].

MODEL DEVELOPMENT

Elementary reactions

In vinyl acetate polymerization, long-chain branches are formed by CTP and TDBP[2-8,12-14]. Important elementary reactions in vinyl acetate emulsion polymerization are as follows: initiation, propagation (rate constant, k_p), chain transfer reactions to monomer (k_{fm}) and to small molecules (k_{fT}), CTP (k_{fp}), TDBP (k_b^*), and bimolecular termination (k_t). Short-chain branches may also be formed via backbiting[15]; however, this reaction does not change the molecular weight distribution (except that a small fraction of reactive sites for chain transfer to polymer is consumed); therefore, backbiting is not included in the present analysis.

The chain termination in vinyl acetate polymerization is quite often transfer-dominated even for polymerization in homogeneous media[5-7]. This is more likely the case in emulsion polymerizations[2,3], since the time interval in which initiator radicals decomposed in the water phase enter a polymer particle is quite often more than every 100 s while primary polymer molecules can be formed via chain transfer to monomer and to polymer within 1 s when monomer droplets exist, as shown in the following simple calculation:

$$\bar{t}_{life} = \frac{1\Big/\left(C_m + C_{fp}\dfrac{x_c}{1-x_c}\right)}{k_p[M]_p} = \frac{(1)\Big/\left[(2.32\times10^{-4}) + (3.98\times10^{-4})\dfrac{(0.2)}{(1-0.2)}\right]}{(2850)(9)} = 0.118 \text{ (seconds)} \quad (1)$$

where C_m is the monomer transfer constant that is given by k_{fm}/k_p, C_{fp} is the polymer transfer constant defined by k_{fp}/k_p, x_c is the weight fraction of polymer in the polymer particles that is kept constant as long as monomer droplets exist, and $[M]_p$ is the monomer concentration

0032-3861/94/14/3032-07

in the polymer particles (mol l^{-1}). All kinetic parameters are taken from the literature[2] at 50°C in emulsion polymerization and are used throughout the present paper.

Branching density distribution (BDD) method

The BDD method for emulsion polymerization that involves CTP was developed in Part 1 of this series[1]. Extension of the BDD method to account for the TDBP in homogeneous reaction media was shown in earlier papers[10,11]. Here, we will discuss only essential equations and necessary modifications for emulsion polymerizations that include TDBP.

In the present analysis, the effect of the particle nucleation mechanism, which is still controversial[16], is neglected, and all polymer particles are assumed to be formed at conversion, $x=0$. An important difference in the kinetics of emulsion polymerization from 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 monomer droplets exist. Therefore, an emulsion polymerization may be modelled effectively as a semibatch reactor with a two-stage process as shown in *Figure 1*: the additional monomer is supplied continuously in order to maintain the monomer concentration constant as long as monomer droplets exist, and the monomer addition is stopped after that. This type of model building appears to be plausible; however, once the reaction system is modelled as a semibatch reactor as shown in *Figure 1*, the information that the size of this reaction system, namely the diameter of polymer particles, is $<1\ \mu$m, is lost.

The BDD method provides an excellent way to sample polymer molecules from an infinite number of polymer molecules, and can provide an exact solution if the effect of the system boundary is negligible (i.e. the simple model shown in *Figure 1* is valid).

In order to establish various probabilities necessary for the BDD method, let us first consider the mole fraction of the unreacted terminal double bonds within the monomeric units bound in the primary polymer molecules formed at $x=\theta$, $F_b^*(\theta,\psi)$ where ψ is the conversion at present time. The balance equation for the number of unreacted terminal double bonds during the conversion interval, ψ to $\psi+\Delta\psi$ is given by:

$$n_\theta\{F_b^*(\theta,\psi)-F_b^*(\theta,\psi+\Delta\psi)\}=k_b^* n_\theta F_b^*(\theta,\psi)[R^\cdot]_\psi \Delta t \quad (2)$$

where n_θ is the total number of monomeric units bound in the polymer chains formed at $x=\theta$, $[R^\cdot]_\psi$ is the total radical concentration at $x=\psi$, and Δt is the infinitesimal time change.

For an emulsion polymerization, it is straightforward to derive fundamental equations for $F_b^*(\theta,\psi)$ based on equation (2):

$$\frac{\partial F_b^*(\theta,\psi)}{\partial\psi}=\begin{cases}-\left(\dfrac{KF_b^*(\theta,\psi)}{[(1-x_c)/x_c]\psi}\right) & (\psi<x_c)\\ -\left(\dfrac{KF_b^*(\theta,\psi)}{1-\psi}\right) & (x_c<\psi)\end{cases} \quad (3)$$

where $K=k_b^*/k_p$, and x_c is the conversion at which monomer droplets disappear. Since the terminal double bonds are formed only via chain transfer to monomer in the present reaction scheme:

$$F_b^*(\theta,\theta)=C_m \quad (4)$$

When K is considered constant, equation (3) can be solved to give:

$$F_b^*(\theta,\psi)=\begin{cases}C_m\left(\dfrac{\theta}{\psi}\right)^{Kx_c/(1-x_c)} & (\theta<\psi<x_c)\\ C_m\left(\dfrac{\theta}{x_c}\right)^{Kx_c/(1-x_c)}\left(\dfrac{1-\psi}{1-x_c}\right)^K & (\theta<x_c<\psi)\\ C_m\left(\dfrac{1-\psi}{1-\theta}\right)^K & (x_c<\theta<\psi)\end{cases} \quad (5)$$

On the other hand, Friis *et al.*[2,3] postulated a diffusion-controlled TDBP after the depletion of monomer droplets, and proposed the following empirical equation for K:

$$K=\begin{cases}a_0 & (x<x_c)\\ a_0+a_1x+a_2x^2+a_3x^3 & (x>x_c)\end{cases} \quad (6)$$

where $a_0=0.566$, $a_1=-0.0595$, $a_2=-0.168$ and $a_3=-0.356$ at 50°C. When equation (6) is used, the following equation must be used instead of equation (5) when

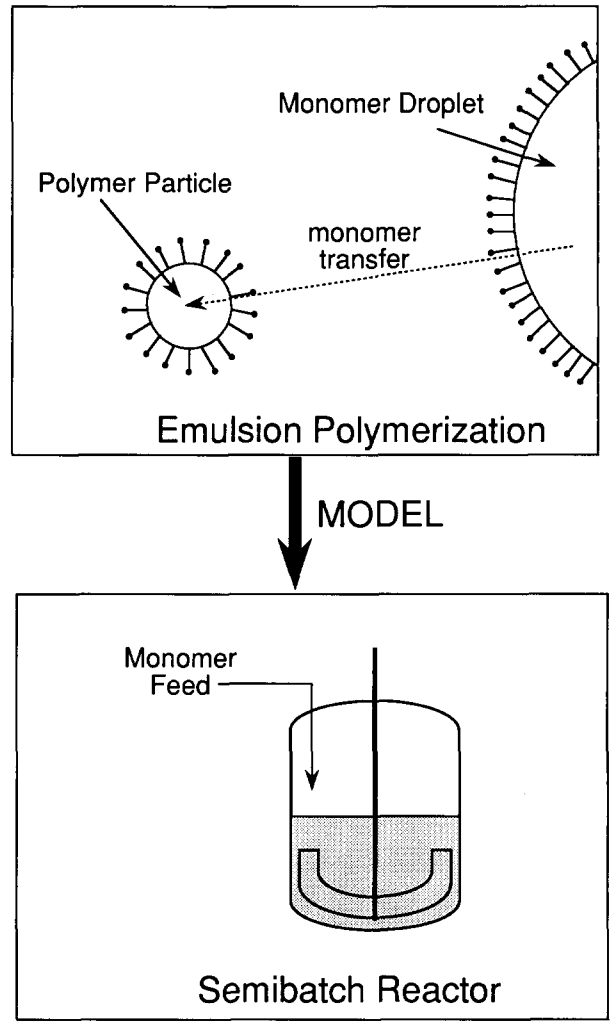

Figure 1 Simplified representation of emulsion polymerization and a possible modelling policy using a semibatch reactor

$\psi > x_c$:

$$F_b^*(\theta,\psi)=\begin{cases} C_m\left(\dfrac{\theta}{x_c}\right)^{Kx_c/(1-x_c)}\exp[g(x_c,\psi)] \\ \quad\times\left(\dfrac{1-\psi}{1-x_c}\right)^{(a_0+a_1+a_2+a_3)} & (\theta<x_c<\psi) \\ C_m\exp[g(\theta,\psi)]\left(\dfrac{1-\psi}{1-\theta}\right)^{(a_0+a_1+a_2+a_3)} & (x_c<\theta<\psi) \end{cases} \quad (7)$$

where $g(\theta,\psi)$ is given by:

$$g(\theta,\psi)=\frac{a_3}{3}(\psi^2-\theta^3)+\frac{a_3+a_2}{2}(\psi^2-\theta^2)+(a_3+a_2+a_1)(\psi-\theta) \quad (8)$$

Equation (5) or (7) gives information on the probability of possessing an unreacted terminal double bond, and can be used to develop important probabilities shown below.

Now, let us select a primary polymer molecule randomly from the reaction mixture on a weight basis at conversion, $x=\psi$. Assume that the conversion of its birth time is $x=\theta$ $(0<\theta<\psi)$. The chain length of this primary polymer molecule follows the weight–chain length distribution given by[17]:

$$W(r,\theta)=[\tau(\theta)+C_p(\theta)]^2 r\exp\{-[\tau(\theta)+C_p(\theta)]r\} \quad (9)$$

where r is the chain length, $\tau(\theta)=(R_{fm}(\theta)+R_{fT}(\theta))/R_p(\theta)$, R_{fm} is the rate of chain transfer to monomer, R_{fT} is the rate of chain transfer to small molecule, R_p is the propagation rate, $C_p(\theta)=R_{fp}(\theta)/R_p(\theta)$, and R_{fp} is the rate of chain transfer to polymer. Note that initiation and termination reactions are ignored in terms of the molecular weight distribution.

Let us consider the probability that the primary polymer molecule formed at $x=\theta$ is connected with another primary polymer molecule formed in the conversion interval, θ to ψ $(\theta<\psi)$, via terminal double bond polymerization, $P_{b,a}^*(\theta,\psi)$. This type of TDBP is schematically shown in *Figure 2*. This probability, $P_{b,a}^*(\theta,\psi)$ is given by:

$$P_{b,a}^*(\theta,\psi)=P_b^*(\theta)\left\{1-\frac{F_b^*(\theta,\psi)}{C_m}\right\} \quad (10)$$

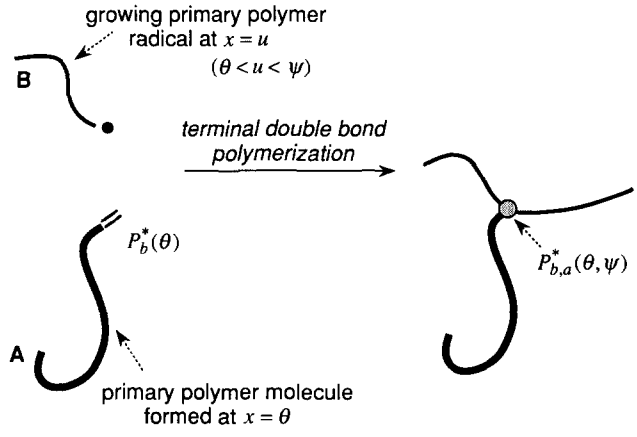

Figure 2 Schematic drawing of the process of TDBP in which a tri-branching point is formed by consuming the terminal double bond located at the end of the primary polymer molecule **A** at $x=u$ after the formation of **A** $(\theta<u<\psi)$

where $P_b^*(\theta)$ is the probability that a primary polymer molecule formed at $x=\theta$ selected randomly possesses a terminal double bond at the time of its formation, and is given by:

$$P_b^*(\theta)=\frac{R_{fm}(\theta)}{R_I(\theta)+R_{fm}(\theta)+R_{fT}(\theta)+R_{fp}(\theta)} \quad (11a)$$

where R_I is the initiation rate.

Since $R_I \ll R_{fm}+R_{fT}+R_{fp}$, equation (11a) is approximated by:

$$P_b^*(\theta)=\frac{R_{fm}(\theta)}{R_{fm}(\theta)+R_{fT}(\theta)+R_{fp}(\theta)} \quad (11b)$$

By application of equation (5) or (7) and equation (11), $P_{b,a}^*(\theta,\psi)$ can be calculated from equation (10).

Once the probability that a primary polymer molecule formed at $x=\theta$ is connected with a primary polymer molecule formed at $x>\theta$ via TDBP is determined, we must next determine the birth time of the connected primary polymer molecule. The conditional probability that a primary polymer molecule formed at $x=\theta$ is connected with the primary polymer molecule formed in the conversion interval, θ to u $(\theta<u<\psi)$, given that the terminal double bond has already reacted at $x=\psi$, is given by:

$$CP_a^*(u|\theta)=\frac{1-F_b^*(\theta,u)/C_m}{1-F_b^*(\theta,\psi)/C_m} \quad (12)$$

When the birth conversion of the connected primary polymer molecule is determined as $x=u$, the chain length distribution follows the weight–chain length distribution, $W(r,u)$ that is given by equation (9). Equations (9)–(12) can be used iteratively until no further primary polymer molecules are connected. Note that primary polymer chains formed later $(x>\theta)$ are connected in this process.

The above probabilities, however, do not give all the possible connections. The primary polymer molecule selected randomly, namely, the primary polymer molecule formed at $x=\theta$, may be connected to other primary polymer molecules formed earlier $(x<\theta)$ during its formation at $x=\theta$ as shown in *Figure 3*. The instantaneously formed branching density via TDBP, $B_i^*(\theta)$ is given by:

$$B_i^*(\theta)=\frac{R_b^*(\theta)}{R_p(\theta)} \quad (13)$$

where R_b^* is the rate of TDBP.

If the chain length r has already been determined from equation (9), the number of instantaneous branch points can be determined using $B_i^*(\theta)$. The probability that a primary polymer molecule with chain length r and instantaneous branching density $B_i^*(\theta)$ possesses m branch points follows the binomial distribution:

$$p^*(m)=\binom{r}{m}(B_i^*(\theta))^m[1-B_i^*(\theta)]^{r-m} \quad (14)$$

Next, we are to determine the birth conversion of the primary polymer molecules thus connected. Let us consider the conditional probability that the primary polymer molecule formed at $x=\theta$ is connected to the primary polymer molecule formed in the conversion interval, 0 to z $(0<z<\theta)$ via TDBP shown in *Figure 3*, $CP_i^*(z|\theta)$. The reaction rate at which the terminal double bonds on the primary polymer molecules whose birth conversions are $x=0$ to z react with a particular primary polymer radical is proportional to the mole fraction of

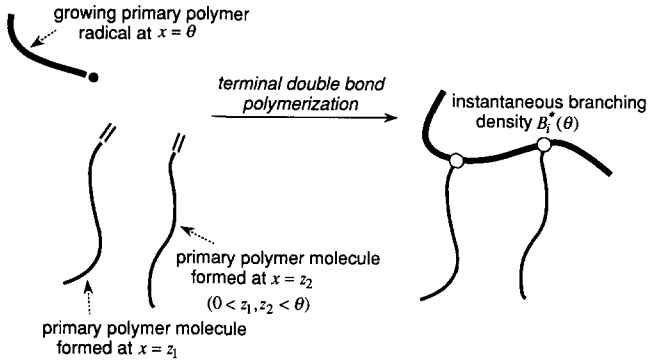

Figure 3 Schematic drawing of the process of TDBP in which a growing primary polymer radical at $x=\theta$ reacts with the terminal double bonds on primary polymer molecules formed prior to $x=\theta$

the unreacted terminal double bonds; therefore, $CP_i^*(z|\theta)$ is given by:

$$CP_i^*(z|\theta)=\frac{\int_0^z F_b^*(z,\theta)\,dz}{\int_0^\theta F_b^*(z,\theta)\,dz} \tag{15}$$

The chain length of the connected primary polymer molecule via the TDBP shown in *Figure 3* follows the number–chain length distribution, since the chain end is selected randomly.

$$N(r,z)=\{\tau(z)+C_P(z)\}\exp\{-[\tau(z)+C_P(z)]r\} \tag{16}$$

By application of equations (13)–(16), primary polymer molecules formed prior to θ can be simulated.

By combining the treatment for the CTP developed in Part 1 of this series[1], simulation of the emulsion polymerization of vinyl acetate has now become possible. More detailed information on each probability can be found elsewhere[10,11].

Direct simulation method

In emulsion polymerization, the reaction system is compartmentalized, and the total number of molecules involved in each reaction locus, i.e. the polymer particle, is not infinite; therefore, models that assume an infinite system size such as the BDD method would be approximate. The total number of monomeric units in a polymer particle during polymerization is less than 3×10^6 if the diameter of the final polymer particle is 0.1 μm[1]. On the other hand, taking advantage of the fact that the system size is finite, it is possible to make a direct simulation as shown earlier for emulsion polymerization that involves CTP[1].

The simulation algorithm is shown in *Figure 4*. The particle nucleation mechanism, which is neglected in the present paper, would play an important role at least in the initial stages of polymerization. However, in order to simplify the discussion, it is assumed that all primary polymer molecules follow equation (16) as a function of their birth time, and the effect of the particle size distribution is neglected. In vinyl acetate emulsion polymerization, the molecular weight distribution of the primary polymer molecules is considered to be transfer-dominated. Assuming no externally added chain transfer agent exists, the primary polymer molecule is formed via either chain transfer to monomer or chain transfer to polymer. The probability that this primary polymer is formed by CTP is given by:

$$P_b(x)=\frac{C_P(x)}{C_m+C_P(x)} \tag{17}$$

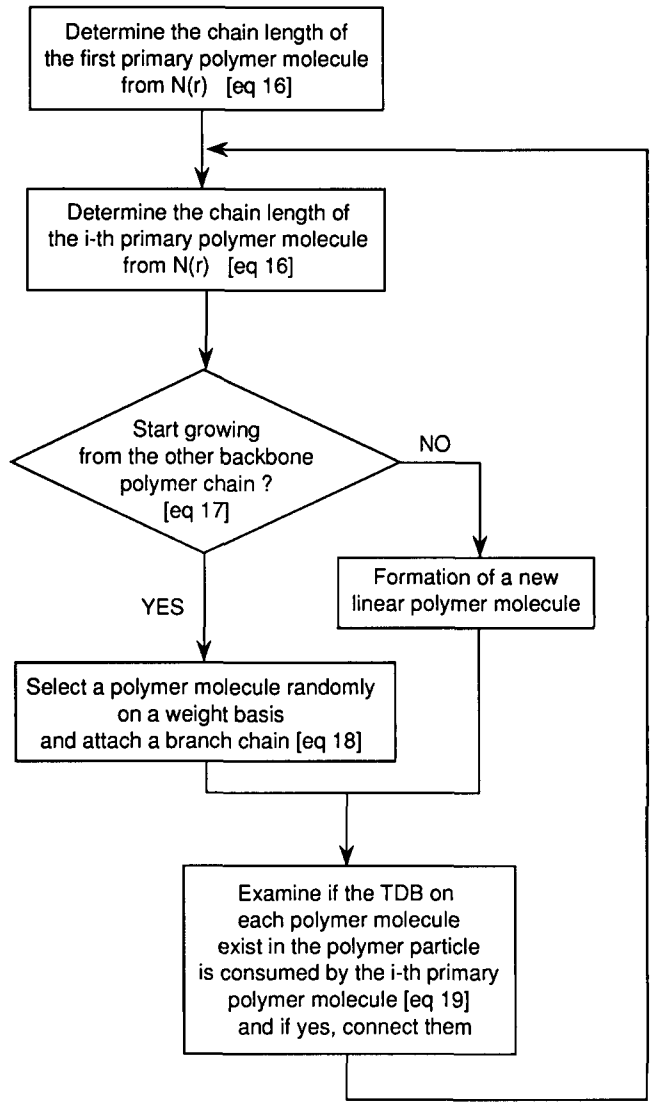

Figure 4 Simulation algorithm of a direct simulation method for emulsion polymerization with CTP and TDBP

If the primary polymer molecule is formed via CTP, the next primary polymer molecule starts growing from another polymer molecule. The connected polymer is selected on a weight basis. In a polymer particle that consists of N polymer molecules (not of primary polymer molecules), the probability that the jth polymer molecule with degree of polymerization r_j is selected is given by:

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

Next, we have to consider the chain connection via TDBP. When no externally added chain transfer agent exists and the effect of both initiation and termination can be neglected in terms of the chain length distribution of the primary polymer molecules, it would be reasonable to consider that every polymer molecule (not primary polymer molecule) possesses one terminal double bond. At the time when the total number of monomer molecules in the polymer particle is n_m, the probability that a particular polymer molecule that has already been formed in the polymer particle is *not* connected via TDBP with the primary polymer molecule whose chain length is r is given by:

$$p_{\text{noTDBP}}=(1-K/n_m)^r \tag{19}$$

Equation (19) is examined for all polymer molecules in the polymer particle every time that a primary polymer molecule is formed. In the present simulation, the total number of monomer molecules n_m was calculated using the value when one half of the primary polymer molecule is formed, namely, the n_m value at the time when the total number of monomeric units in polymer molecules is $r/2+\sum_{j=1}^{N} r_j$ was used.

RESULTS AND DISCUSSION

The experimental data and kinetic parameters reported by Friis *et al.*[2,3] for vinyl acetate emulsion polymerization at 50°C are used in the present discussion, namely, $x_c=0.2$, $C_m=2.32\times10^{-4}$, $C_{fp}=3.98\times10^{-4}$ and $K=0.566-0.0595x-0.168x^2-0.356x^3$. The value of C_{fp} is larger than that of C_m since both tertiary hydrogen in the polymer backbone and the acetoxy methyl hydrogen can be abstracted in chain transfer to polymer while chain transfer to monomer occurs solely at the acetoxy methyl group[14].

Comparison with the method of moments

In this section, assuming no system boundary effects, the applicability of the method of moments[2,3] is examined. *Figure 5* shows the calculated and experimental average chain length development. In the BDD method, 5000 polymer molecules (not primary polymer molecules) are simulated. In the conversion interval $x<0.2$ during which monomer droplets exist, the method of moments clearly overestimates the weight-average chain length, which indicates that the effect of polyradicals must be accounted for when the effects of the system boundary are not considered. One may argue that the average number of radicals per polymer particle is quite often less than 0.1 in vinyl acetate emulsion polymerization and it is expected that virtually no polymer particles that contain more than one polymer radical exist. This argument would be true in the real world; however, the information on the average number of radicals per polymer particle is not accounted for in the models that do not consider the compartmentalization effects.

Owing to the discrepancy in the region with monomer droplets, the calculated weight-average chain lengths based on the method of moments are higher than those from the BDD method in the whole reaction period. The experimental data for the weight-average chain lengths (P_W) are lower than those predicted in the BDD method at low conversion, and higher at high conversions.

Figure 6 shows calculated molecular weight distribution (*MWD*) development using the BDD method, and *Figure 7* shows comparison with experimental data by Friis *et al.*[3]. At $x=0.38$, the agreement is satisfactory; however, at $x=0.79$, the distribution shape is somewhat different.

Direct simulation method

Figure 8 shows the calculated weight-average chain length development as a function of the number of monomeric units bound in polymer molecules per polymer particle (n) when monomer droplets exist based on the simulation of 100 polymer particles. It takes a very long time for the calculated weight-average chain length to reach the steady state, and the steady state cannot be attained within a reasonable time-scale. (Note that the monomer droplets disappear at $x=0.2$ in the present reaction system.) If particle agglomeration occurs in the nucleation period as postulated in the coagulative nucleation theory[18], it is expected that this would delay the *MWD* development in terms of n since premature polymer particles are combined; however, this would occur only at the beginning of the reaction when the weight-average chain length increases rapidly, so the overall picture would not change. *Figure 8* clearly shows that the effect of compartmentalization must be accounted for in vinyl acetate emulsion polymerization.

Figure 9 shows the comparison of the calculated weight–chain length distribution between the direct simulation method when the total number of monomeric units bound in polymer chains is as large as $n=1.508\times10^6$ and the BDD method that gives the steady state value. A small but clear deviation still exists, especially at large chain length tails. Incidentally, the direct simulation method is conducted on a number basis; therefore, the weight–chain length distribution profile shows fluctuations at a larger chain length tail. (The total number of

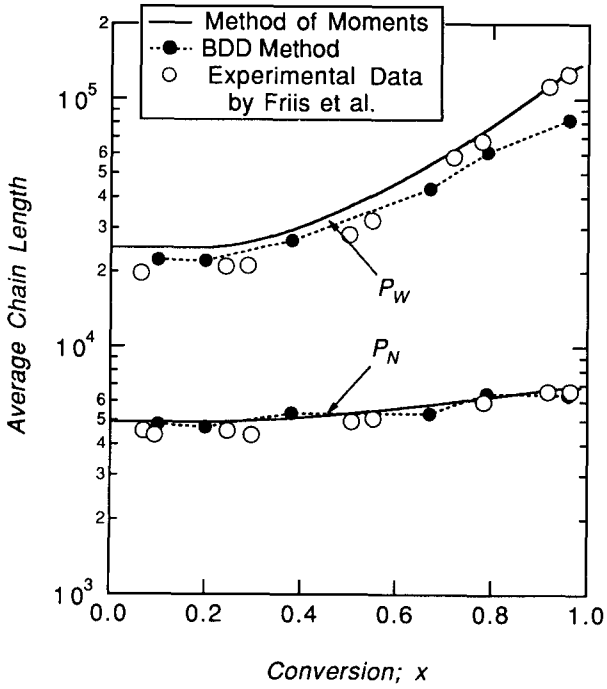

Figure 5 Average chain length development in vinyl acetate emulsion polymerization

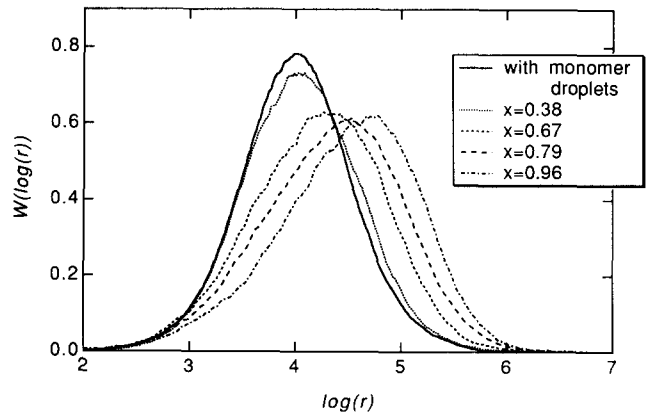

Figure 6 Calculated weight–chain length distribution development using the BDD method

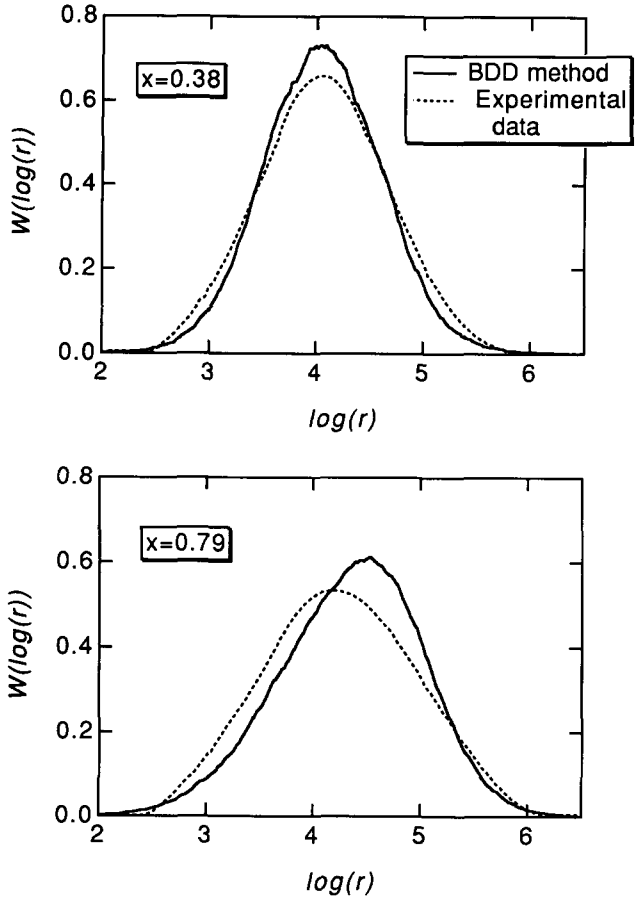

Figure 7 Weight–chain length distribution calculated from the BDD method and the experimental results by Friis *et al.*[3]

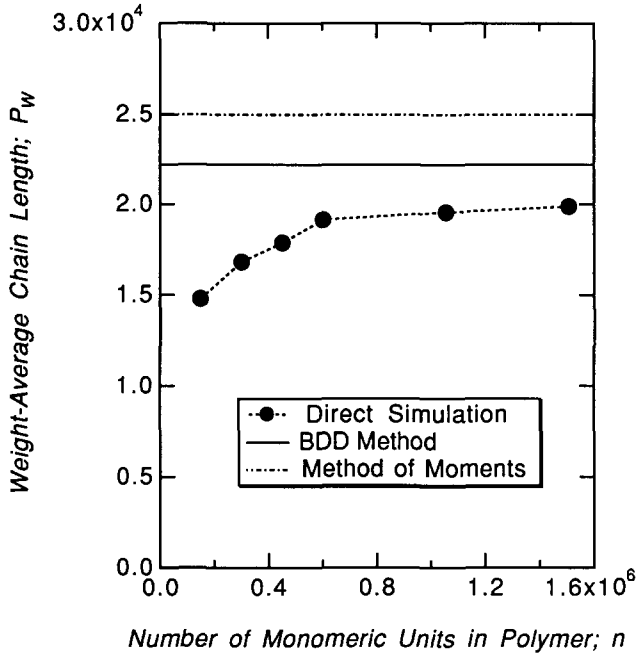

Figure 8 Calculated weight-average chain length development as a function of the total number of monomeric units bound in polymer chains in a polymer particle, n

simulated polymer molecules in *Figure 9* is 3×10^4 in the direct simulation method while 1×10^4 polymer molecules are simulated in the BDD method in which the simulation is conducted on a weight basis.)

It is known that the molecular weights are insensitive to the number of polymer particles and their sizes in an

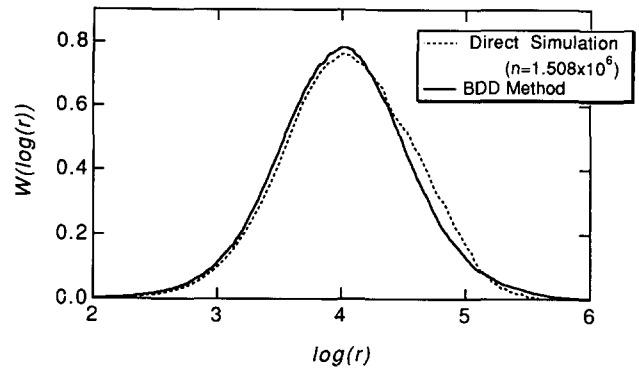

Figure 9 Calculated weight–chain length distribution using the BDD method and the direct simulation method

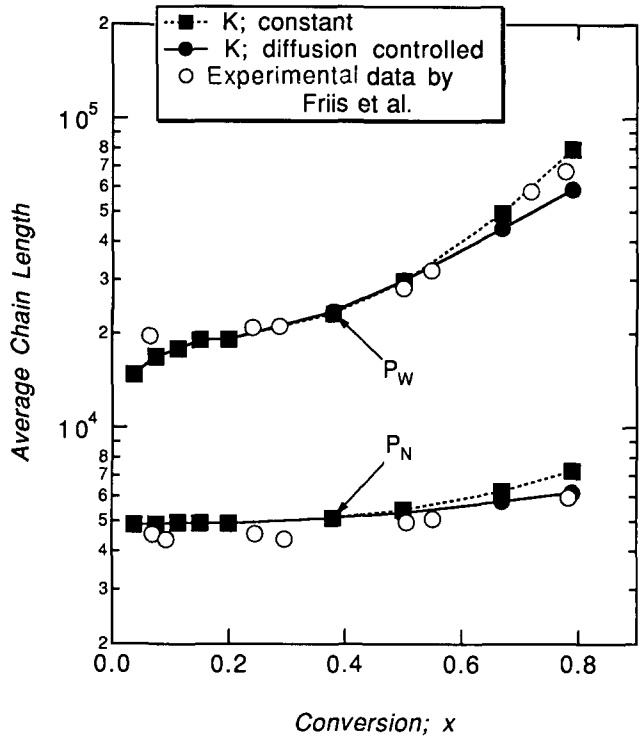

Figure 10 Weight-average chain length development calculated from the direct simulation method and the experimental results by Friis *et al.*[3]

emulsion polymerization of vinyl acetate with a wide range of polymerization conditions[2,3,19]. Assuming the total number of monomeric units per polymer particle at 100% conversion to be 4×10^6, the direct simulation is conducted for a wide conversion range. *Figure 10* shows the comparison of the calculated average chain lengths from the simulation of 100 polymer particles with experimental data. If the kinetic parameters estimated by Friis *et al.*[2,3] are employed, the calculated weight-average chain length is clearly smaller than the experimental data at high conversions as shown in *Figure 5*; therefore, another simulation that does not assume the diffusion-controlled TDBP (K is assumed to be constant) was also conducted. Concerning the weight-average chain length, the calculated results with constant K agree satisfactorily with the experimental data; however, the calculated number-average chain lengths are clearly larger than the experimental results at high conversions.

In solution polymerization of vinyl acetate in a batch reactor[5,6,11] and in a continuous stirred tank reactor (CSTR)[10], diffusion-controlled TDBP need not be

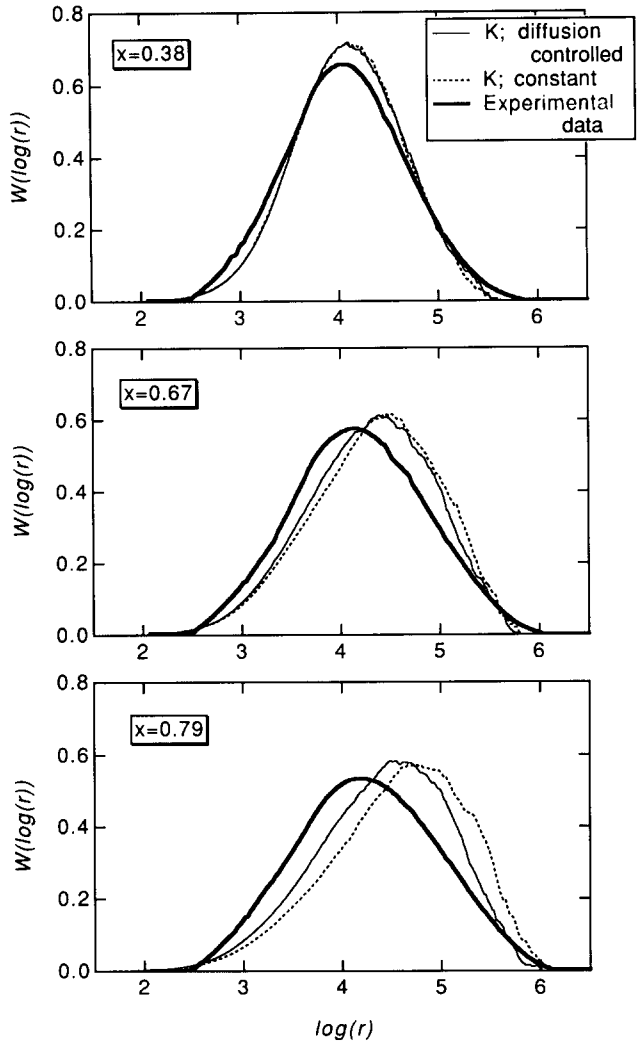

Figure 11 Comparison of the weight–chain length distribution

assumed. However, because no solvent is used in emulsion polymerization and polymer molecules with much higher molecular weights are formed in emulsion polymerization, it may be possible to postulate that the TDBP in emulsion polymerization is diffusion-controlled. However, it seems impossible to resolve this problem only from *Figure 10*.

Figure 11 shows the comparison of the weight–chain length distribution. Even when diffusion-controlled TDBP is assumed, the shape of the distribution is still different from the experimental results. At least two points must be pointed out concerning the discrepancy of the chain length distribution.

First, if diffusion-controlled TDBP is operative, the rate constant for TDBP, k_b^* should be chain-length dependent as well as conversion-dependent. The conversion dependence of k_b^* proposed by Friis *et al.*[2] was the number-average rate constant for the TDBP that was estimated from the number-average chain length development; therefore, the use of the present kinetic parameter will not be appropriate for the calculation of the *MWD* development. If the rate of increase in molecular weight via TDBP for larger polymer molecules is slower than that for smaller polymer molecules due to the chain-length dependent TDBP, the skewed distribution shape may be modified and the distribution shape may approach the experimental results that are rather symmetrical in shape. In the direct simulation method, it is straightforward to account for the chain-length dependence; however, more detailed experimental information such as the number of branch points formed via TDBP as a function of the size of the polymer molecule would be required in order to establish the functional form of the chain-length dependence.

Another problem worth mentioning here is that the *MWD* was determined using gel-permeation chromatography (g.p.c.) in the experiments of Friis *et al.* The molecular weights determined from g.p.c. clearly underestimate the molecular weights of the branched polymers. Furthermore, the determined average chain lengths are sensitive to the low-molecular-weight tail for the number-average and to the high-molecular-weight tail for the weight-average. Careful reinvestigation of the experimental data would be necessary in order to determine the kinetic parameters with higher precision.

CONCLUSIONS

New simulation models for emulsion polymerization of vinyl acetate were proposed. It was found that the method of moments conventionally applied clearly overestimates the weight-average chain lengths. The effect of compartmentalization must be considered in this reaction system, and a realistic model must account for the fact that each reaction locus in emulsion polymerization is very small.

The direct simulation method is very promising to clarify the complicated phenomena involved in non-linear emulsion polymerizations. With more detailed and reliable data on vinyl acetate emulsion polymerization, it would be possible to determine all important kinetic parameters by application of the direct simulation method.

REFERENCES

1 Tobita, H. *Polymer* 1994, **35**, 3023
2 Friis, N., Goosney, D., Write, J. D. and Hamielec, A. E. *J. Appl. Polym. Sci.* 1974, **18**, 1247
3 Friis, N. and Hamielec, A. E. *J. Appl. Polym. Sci.* 1975, **19**, 97
4 Nagasubramanian, K. and Graessley, W. W. *Chem. Eng. Sci.* 1970, **25**, 1559
5 Nagasubramanian, K. and Graessley, W. W. *Chem. Eng. Sci.* 1970, **25**, 1549
6 Chatterjee, A., Kabra, K. and Graessley, W. W. *J. Appl. Polym. Sci.* 1977, **21**, 1751
7 Chatterjee, A., Park, W. S. and Graessley, W. W. *Chem. Eng. Sci.* 1977, **32**, 167
8 Taylor, T. W. and Reichert, K. H. *J. Appl. Polym. Sci.* 1985, **30**, 227
9 Tobita, H. *Polym. React. Eng.* 1993, **1**, 379
10 Tobita, H. *J. Polym. Sci., Polym. Phys. Edn* in press
11 Tobita, H. *J. Polym. Sci., Polym. Phys. Edn* in press
12 Stein, D. J. *Makromol. Chem.* 1964, **76**, 169
13 Nozakura, S., Morishima, Y. and Murahashi, S. *J. Polym. Sci., Polym. Chem. Edn* 1972, **10**, 2781
14 Nozakura, S., Morishima, Y. and Murahashi, S. *J. Polym. Sci., Polym. Chem. Edn* 1972, **10**, 2853
15 Odian, G. 'Principles of Polymerization', John Wiley, New York, 1991, p. 258
16 El-Aasser, M. S. In: 'Scientific Methods for the Study of Polymer Colloids and Their Applications', (Eds F. Candau and R. H. Ottewill), Kluwer Academic, Dordrecht, The Netherlands, 1990, p. 1
17 Hamielec, A. E. and Tobita, H. In: 'Ullmann's Encyclopedia of Industrial Chemistry', Vol. A21, VCH Publishers, Weinheim, Germany, 1992, p. 305
18 Feeney, P. J., Napper, D. H. and Gilbert, R. G. *Macromolecules* 1984, **17**, 2520
19 Nomura, M., Harada, M. Nakagawara, K., Eguchi, W. and Nagata, S. *J. Chem. Eng., Japan* 1971, **4**, 48