

Desorption of Free Radicals in Semibatch Emulsion Polymerization of Methyl Acrylate

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SYNOPSIS

Desorption of free radicals from particles can cause an emulsion polymerization system to deviate from Smith–Ewart case II kinetics. A mechanistic model has been developed to predict the effect of desorption of radicals from particles on the kinetics of semibatch emulsion polymerization of methyl acrylate under the monomer-starved condition. Experimental data available in the literature are used to assess the proposed kinetic model. The model predicts the experimental data reasonably well for a wide range of monomer feed rates. The rate of polymerization increases with an increase in the rate of monomer addition. The kinetic data are also useful in evaluating the desorption rate constant (K'_d) for methyl acrylate. The best fitted value of K'_d at 50°C is 4×10^{-12} cm²/s, which is in good agreement with the theoretical values predicted by desorption theory. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Semibatch emulsion polymerization is a widely used process for commercial production of polymeric materials such as coatings, adhesives, elastomers, and specialty products. Emulsion polymerization involves the dispersion of a hydrophobic monomer in the continuous aqueous phase with the aid of an oil-in-water surfactant. The polymerization is carried out in the segregated polymer particles with a water-soluble initiator. The latex product is a colloidal dispersion of particles (50–1000 nm in diameter) stabilized by surfactant molecules.

The reaction mechanisms of emulsion polymerization is very complicated due to the compartmentalization of free radicals in a large number of tiny monomer-swollen particles dispersed in water. The macroradical in a particle can (i) grow in chain length via the propagation reaction, (ii) transfer its radical activity to a neighboring monomer molecule or other small molecules such as chain transfer agent, or (iii) terminate with the incoming radical. If event (ii) is significant, desorption of radicals from particles may have an important influence on the reaction kinetics. The desorption mechanism in-

volves the transfer of the activity of a macroradical to monomer or other small molecules, followed by diffusion of the mobile monomeric radical to the particle surface. The relatively water-soluble species may cross the interface into water. Finally, the exit process is completed by diffusion of the monomeric radical to the bulk aqueous phase.

The desorbed radical may be reabsorbed into another particle or terminated with an oligomeric radical in the aqueous phase. In general, the desorption process will result in a decrease in the concentration of radicals in the particles and hence cause the rate of polymerization to decrease. Numerous examples of deviation from Smith–Ewart case II kinetics due to desorption of radicals out of the particles have been documented in the literature.^{1–7} Transport of radicals out of the particles is generally believed to play an important role in emulsion polymerization of monomers such as vinyl acetate and vinyl chloride, which have relatively high water solubility and monomer chain transfer constants.

Gerrens⁸ studied semibatch emulsion polymerization of a relatively water-soluble monomer, methyl acrylate. In one series of his experiments, all of the water, surfactant, and initiator and 17.1% of the total monomer were charged to the reactor. Nucleation of primary particles took place at 50°C over 30 min. The remaining monomer was then

added to the reactor at a prescribed feed rate. Polymerization temperature was kept at 50°C throughout the reaction. Based on Smith–Ewart case II kinetics^{9–11} (average number of radicals per particle, $\bar{n} = 0.5$), the experimental data were used to calculate the propagation rate constant (K_p). The parameter K_p was estimated to be $4.72 \times 10^5 \text{ cm}^3/\text{mol}\cdot\text{s}$ at 50°C, which was lower than the literature value ($1.5 \times 10^6 \text{ cm}^3/\text{mol}\cdot\text{s}$).¹² If the value of K_p reported in the literature is correct, then \bar{n} must have been less than 0.5. Considering the relatively high water solubility of monomeric radicals (assumed to be similar to that of methyl acrylate monomer, ca. 5.3%)¹³ and chain transfer to monomer constant (ca. $3.6 \times 10^{-6} K_p$ to $3.25 \times 10^{-5} K_p$ at 60°C),¹⁴ the effect of desorption of radicals from particles on the reaction kinetics may not be neglected. Thus, the controversy may be attributed to the desorption process.

Recently, the author has developed a mechanistic model based on diffusion-limited reaction mechanisms to predict the changes in the termination rate constant in the particle phase (K_{tp}) and the propagation rate constant (K_p) with the viscosity of the monomer-swollen particles [i.e., modeling events (i) and (iii) described above] in semibatch emulsion polymerization of styrene.¹⁵ Transport of radicals out of the particles was assumed to be insignificant because the water solubility of styryl radicals and chain transfer to styrene constant were relatively low.

It was concluded that the polymerization system approached Smith–Ewart case II kinetics when the concentration of styrene in the particles was close to the saturation value. On the other hand, the system under the monomer-starved condition was governed by diffusion-controlled reaction mechanisms. The model developed in Ref. 15 will be used in this work to evaluate the impact of diffusion-controlled reaction mechanisms on the kinetics of methyl acrylate polymerization.

The objective of this work was to develop a mechanistic model to study the kinetics of emulsion polymerization of a more water-soluble monomer, methyl acrylate, operated in a semibatch mode. Experimental data taken from the literature⁸ will be used to verify the proposed kinetic model. Another major thrust of this investigation is to use the experimental data to evaluate the desorption rate constant for methyl acrylate.

MODEL DEVELOPMENT

The rate of polymerization (R_p) carried out in a semibatch reactor can be written as

$$R_p = K_p[M]_p(\bar{n}N_p/N_a). \quad (1)$$

Note that the reported values of R_p were normalized by dividing by the final latex volume, 2000 cm³ (units of R_p : mol/cm³·s).⁸ Here, N_p is the number of particles per cubic centimeters of latex and N_a is Avogadro's number. The term $[M]_p$ is the concentration of monomer in the particles. The saturated concentration of methyl acrylate in the particles is about $9.6 \times 10^{-3} \text{ mol/cm}^3$, representing 13% monomer conversion.⁸ The value of $[M]_p$ can be calculated by the following equations¹⁶:

$$[M]_p = \frac{[F_m \rho_m(t - t_{\text{imc}}) + W_{\text{imc}}](1 - X_t)/MW_m}{[F_m \rho_m(t - t_{\text{imc}}) + W_{\text{imc}}]X_t/\rho_p + [F_m \rho_m(t - t_{\text{imc}}) + W_{\text{imc}}](1 - X_t)/\rho_m} \quad (2)$$

$$X_t = \frac{W_m X}{F_m \rho_m(t - t_{\text{imc}}) + W_{\text{imc}}} \quad (3)$$

where X is the overall monomer conversion, defined as the ratio of the amount of monomer converted to the total amount of monomer in the recipe. The X -vs.- t (reaction time) data for various values of monomer addition rate (R_a) are available in Gerners's paper.⁸ The term X_t is defined as the ratio of the amount of monomer converted to the amount of monomer added up to that time; F_m is the monomer feed rate with the units of cubic centimeters per second; ρ_m and ρ_p are the densities of the monomer and polymer, respectively; and MW_m is the molecular weight of monomer. The time t_{imc} is for the initial monomer charge to polymerize. The weight W_{imc} is that of initial monomer charge and W_m is the total weight of monomer shown in the recipe.

The parameter N_p for the finished batch was determined to be $1.16 \times 10^{15} \text{ cm}^{-3}$ from the light-scattering technique.⁸ Secondary nucleation of primary particles or coagulation of particles is assumed to be insignificant during the monomer addition period; that is, the total number of reaction loci (N_p) available for polymerization is a constant throughout the reaction.

With the assumption that termination in the aqueous phase is not important, O'Toole's approach¹⁷ was used to calculate \bar{n} at pseudo-steady state:

$$\bar{n} = a/4[I_m(a)/I_{m-1}(a)] \quad (4)$$

where $a = (8\alpha')^{1/2}$ and I_m and I_{m-1} are the Bessel functions of the first kind of order m and $m - 1$, respectively. The kinetic parameters $\alpha' = \rho_i V_p / K_{tp} N_p$ and $m = K_0 a_p / K_{tp}$ are the dimensionless groups re-

lated to the generation of radicals in water and desorption of radicals from particles, respectively. The term ρ_i is the rate of production of radicals in the aqueous phase, V_p is the volume of a monomer-swollen particle, K_0 is the rate constant for desorption of radicals from particles, and a_p is the surface area of a monomer-swollen particle.

In order to calculate \bar{n} and ultimately R_p , the only task left is to determine the three parameters $\alpha' = \rho_i V_p / K_{tp} N_p$, $m = K_0 a_p / K_{tp}$, and K_p . The parameters α' and K_p can be calculated according to Chern¹⁵ and only a set of relevant equations is given below:

$$\rho_i = 2fK_{dec}[I]_w \quad (5)$$

$$V_p = W_m(\% \text{ monomer added})/$$

$$N_p V_t [\rho_m(1 - \Phi_p) + \rho_p \Phi_p] \quad (6)$$

$$\Phi_p = 1 - ([M]_p MW_m / \rho_m) \quad (7)$$

$$K_{tp} = K_{tp0} \exp[B_t(1/V_{f0} - 1/V_f)] \quad (8)$$

$$V_f = V_{fm}(1 - \Phi_p) + V_{fp}\Phi_p \quad (9)$$

$$V_{fm} = 0.025 + 0.001(T - T_{gm}) \quad (10)$$

$$V_{fp} = 0.025 + 4.8 \times 10^{-4}(T - T_{gp}) \quad (11)$$

$$K_p/K_{p0} = D_m/D_{m0}$$

$$= \exp[B_p(1/(V_{f0})_m - 1/V_f)]$$

$$\text{when } V_f < (V_{f0})_m \quad (12)$$

$$K_p = K_{p0} \quad \text{when } V_f > (V_{f0})_m \quad (13)$$

where f is the initiator efficiency factor, K_{dec} is the initiator decomposition rate constant, $[I]_w$ is the concentration of initiator in the aqueous phase, V_t is the total volume of the finished batch and Φ_p is the volume fraction of polymer in the particles, K_{tp0} is the termination rate constant at the reference fractional free volume $(V_{f0})_m$, V_f is the fractional free volume of the monomer-swollen particles, B_t is an adjustable parameter which is a measure of the degree of diffusion control, V_{fp} and V_{fm} are the fractional free volumes contributed by polymer and monomer, respectively, and T is the polymerization temperature. Equations (10) and (11) used to calculate V_{fp} and V_{fm} for ethyl acrylate and propyl acrylate in Ref. 18 are assumed to be applicable to methyl acrylate polymerization. The terms K_{p0} and D_{m0} are the propagation rate constant and diffusion coefficient of monomer at zero conversion, respectively, D_m is the diffusion coefficient of monomer in the particles, B_p is an adjustable parameter, and $(V_{f0})_m$ is the critical fractional free volume at which the propagation rate constant starts to decline.

At this point, it is only necessary to assign values to the dimensionless group for desorption ($m = K_0 a_p / K_{tp}$) and other miscellaneous parameters in order to carry out the computer simulation. The specific desorption rate constant K_0 (in centimeters per second) is related to other desorption rate constants K_d (per second) and K'_d (square centimeters per second), often found in the literature, by the following equations¹⁹:

$$K_d = K_0 a_p / V_p = K'_d / [(\pi/6)^{2/3} d_p^2] \quad (14)$$

$$K'_d = K_{fm} / K_p [12(\pi/6)^{2/3} D_w / (\alpha' + D_w / D_{mr})] \quad (15)$$

where K_{fm} is the monomer chain transfer constant, K'_p is the reinitiation rate constant for monomeric radicals, D_w and D_{mr} are the diffusion coefficients of the monomeric radicals in the water and particle phases, respectively, and α' is a partition coefficient for monomeric radicals between the particle phase and the aqueous phase. Please note that K'_d is independent of the particle size. Thus, it will be used as an adjustable parameter in the following computer simulations since d_p will increase during the monomer addition period.

RESULTS AND DISCUSSION

Gerrens⁸ used the monomer feed process to study the kinetics of semibatch emulsion polymerization of methyl acrylate at 50°C. In his work, the rate of monomer addition ranged from 3.69×10^{-7} to 3.32×10^{-6} mol/cm³-s. The \bar{n} -vs.- X data for $R_a = 1.11 \times 10^{-6}$ mol/cm³-s are selected to evaluate K'_d , and the data are shown as discrete points in Figure 1. As shown in the plot, \bar{n} increases with an increase in conversion (X) and it is less than 0.5 throughout the reaction. The \bar{n} data are obtained from the measured R_p and the calculated K_p according to Eq. (1). The simulation results indicate that the propagation reaction is not diffusion limited and K_p remains constant (1.5×10^6 cm³/mol-s) throughout this work. The parameters necessary for calculations are obtained from the literature or estimated from the reaction conditions and are compiled in Table I.

The only remaining parameter that needs to be specified before computer modeling can be carried out is m or K'_d . For the run with $R_a = 1.11 \times 10^{-6}$ mol/cm³-s, the model predictions with various values of K'_d are shown in Figure 1. As expected, a high value of K'_d yields a high value of m and this will lower \bar{n} . The curve with $K'_d = 4 \times 10^{-12}$ cm²/s gives the best fit for the experimental data. The calculated

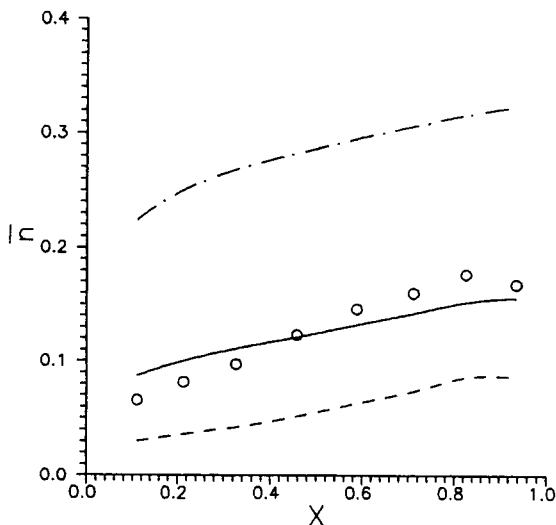


Figure 1 Average number of free radicals per particle as function of conversion: $R_a = 1.11 \times 10^{-6}$ mol/cm³-s, $Y = 0$, (○) experimental data, (----) $K'_d = 4 \times 10^{-11}$, (—) $K'_d = 4 \times 10^{-12}$, (- · -) $K'_d = 4 \times 10^{-13}$ cm²/s.

d_p , K_{tp} , and $[M]_p$ profiles as a function of X are shown in Figures 2–4, respectively. During the monomer addition, d_p increases with an increase in X , whereas both $[M]_p$ and K_{tp} decrease with an increase in X . For the run with $R_a = 1.11 \times 10^{-6}$ mol/cm³-s, K_{tp} decreases from 1.8×10^9 to 9.1×10^7 cm³/mol-s. The gel effect is not very significant because the reaction temperature is way above the glass transition temperature of polymethyl acrylate. Thus, desorption of monomeric radicals out of the particles predominates in the reaction kinetics and leads to values of \bar{n} lower than 0.5.

The proposed model with $K'_d = 4 \times 10^{-12}$ cm²/s

Table I Kinetic Parameters for Semibatch Emulsion Polymerization of Methyl Acrylate

Parameter	Numerical Value	Reference
MW _m	86 g/mol	
ρ_m	0.955 g/cm ³	14
ρ_p^a	1.1 g/cm ³	18
f	1	
K_{tp0}^b	7.41×10^9 cm ³ /mol-s	14
B_t	0.6	20
B_p	0.38	20
V_{f0}^a	0.1613	18
$(V_{f0})_m$	0.047	20
T_{gp}	6°C	
T_{gm}	-106°C	20

^a Estimated from polyethyl acrylate data.

^b Estimated from data at 60°C.

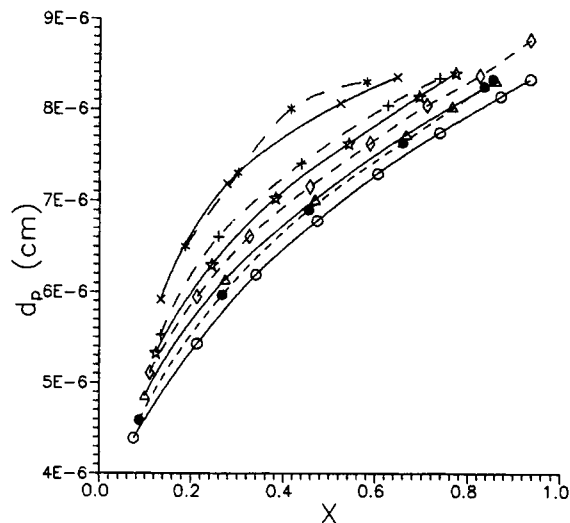


Figure 2 Particle size as function of conversion: (○) $R_a = 3.69 \times 10^{-7}$, (●) $R_a = 5.58 \times 10^{-7}$, (△) $R_a = 8.32 \times 10^{-7}$, (◇) $R_a = 1.11 \times 10^{-6}$, (☆) $R_a = 1.39 \times 10^{-6}$, (+) $R_a = 1.66 \times 10^{-6}$, (×) $R_a = 2.22 \times 10^{-6}$, (*) $R_a = 3.32 \times 10^{-6}$ mol/cm³-s.

predicts the \bar{n} -vs.- X data reasonably well for the entire range of R_a , as shown in Table II. Again, \bar{n} increases with an increase in X . The experimental data also display a general trend that at a fixed conversion \bar{n} increases with an increase in R_a , and the reason for this observation is unclear at this time. Closely examining the experimental data and predicted values of \bar{n} in Table II indicates that the model does

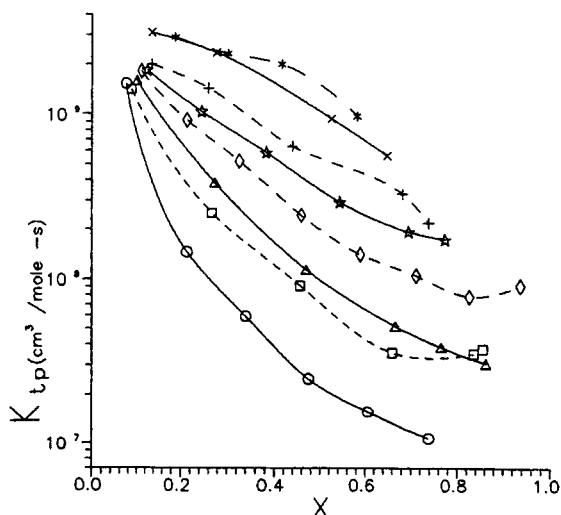


Figure 3 Termination rate constant in particle as function of conversion: (○) $R_a = 3.69 \times 10^{-7}$, (□) $R_a = 5.58 \times 10^{-7}$, (△) $R_a = 8.32 \times 10^{-7}$, (◇) $R_a = 1.11 \times 10^{-6}$, (☆) $R_a = 1.39 \times 10^{-6}$, (+) $R_a = 1.66 \times 10^{-6}$, (×) $R_a = 2.22 \times 10^{-6}$, (*) $R_a = 3.32 \times 10^{-6}$ mol/cm³-s.

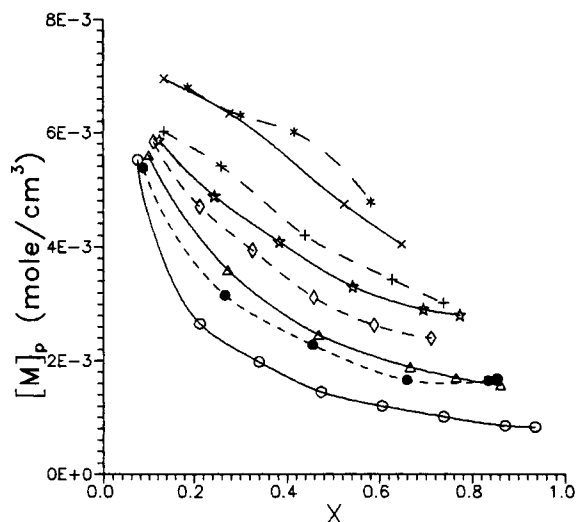


Figure 4 Concentration of monomer in particle as function of conversion: (O) $R_a = 3.69 \times 10^{-7}$, (●) $R_a = 5.58 \times 10^{-7}$, (Δ) $R_a = 8.32 \times 10^{-7}$, (\diamond) $R_a = 1.11 \times 10^{-6}$, (\star) $R_a = 1.39 \times 10^{-7}$, (+) $R_a = 1.66 \times 10^{-6}$, (\times) $R_a = 2.22 \times 10^{-6}$, (*) $R_a = 3.32 \times 10^{-6}$ mol/cm³-s.

not work very well when R_a is very small ($R_a \leq 5.58 \times 10^{-7}$ mol/cm³-s) or extremely large ($R_a = 3.32 \times 10^{-6}$ mol/cm³-s).

The calculated d_p , K_{tp} , and $[M]_p$ as a function of X for various values of R_a are also included in Figures 2–4. Figure 2 shows that at a fixed conversion d_p increases with an increase in R_a . This observation can be explained by the fact that the greater the R_a , the more the unreacted monomer present in the particles and hence the larger the monomer-swollen particles, as shown by the $[M]_p$ -vs.- X curves in Figure 4. In addition, the $[M]_p$ -vs.- X curves show that all of the Gerrens experiments were carried out under the monomer-starved condition (i.e., $[M]_p < 9.6 \times 10^{-3}$ mol/cm³). It is shown in Figure 3 that at a fixed conversion the termination reaction becomes less affected by diffusion-controlled mechanisms when R_a is increased (see the $[M]_p$ -vs.- X curves in Fig. 4). Nevertheless, the simulation results suggest that even large changes in K_{tp} do not show any significant effect on the rate of polymerization when desorption of radicals from particles is the dominant event ($\bar{n} < 0.5$).

In an attempt to understand why the proposed model exhibits limited success at extremely low values of R_a , the run with $R_a = 3.69 \times 10^{-7}$ mol/cm³-s is chosen for further study. Figure 5 shows the effect of aqueous phase termination [$Y = 2N_aK_{tw}K_{tp}/K_c^2V_pN_p$; ranged from 0 to 1×10^4] on the reaction kinetics. The parameter Y is the dimensionless group related to the termination reac-

tion in the aqueous phase. The term K_{tw} is the termination rate constant in the aqueous phase and K_c is the rate constant for capture of radicals by particles. In this series of computer simulations, \bar{n} is calculated according to Ugelstad and co-workers^{1,3} [also see Eqs. (3)–(7) in Ref. 15]. A reduction in \bar{n} is expected as a result of the termination reaction in water. The kinetic model with the assumption of $Y = 0$ predicts a higher value of \bar{n} than the experimental data. To increase Y from zero to 1×10^4 shows a significant effect on the \bar{n} -vs.- X profile. Indeed, the simulation results show that \bar{n} decreases with an increase in Y . However, the derivative $d\bar{n}/dX$ behaves very differently as Y is increased from zero to 1×10^4 . It even changes in sign as Y is increased from zero to 1×10^4 , and this transition occurs roughly at a value of Y between 1 and 100. It is quite clear that changing Y alone does not improve the model predictions to any extent.

Generally, the termination reaction in the aqueous phase was assumed to be insignificant in the literature, although the work of Lichti et al.²¹ and Gilbert and Napper²² showed that termination of radicals in water could be important. Lee and Poehlein²³ indicated that the effect of Y on \bar{n} was not significant if $m < 1$ and $\alpha' < 0.01$. For the run with $R_a = 3.69 \times 10^{-7}$ mol/cm³-s, the values of α' and m during the monomer addition period are listed in Table III. The simulation results shown in Figure 5 in combination with the computed values of α' and m suggest that the termination reaction in the aqueous phase cannot be ruled out from semibatch emulsion polymerization of methyl acrylate. The aqueous phase termination would become significant for the conditions of fast rates of initiation, low concentrations of particles, and large particles. Future research on the reaction mechanisms of termination of radicals in water for emulsion polymerization of methyl acrylate is required.

The author also examines the effect of gel effect [through the parameter B_t in Eq. (8)] on the reaction kinetics because K_{tp} is expected to increase with a decrease in B_t . The increased rate of termination in the particles will cause a reduction in \bar{n} . The calculated K_{tp} -vs.- X curves for different values of B_t are illustrated in Figure 6. When $B_t = 0$, the termination reaction is chemical reaction controlled and hence K_{tp} remains unchanged throughout the reaction. The termination reaction then gradually shifts from chemical reaction limited to diffusion controlled as B_t is increased from 0 to 0.6. The calculated \bar{n} -vs.- X curves along with the experimental data are presented in Figure 7. The simulation results show that the proposed model does predict a

Table II \bar{n} -vs.- X Data and Model Predictions^a

$R_a = 3.69 \times 10^{-7} \text{ mol/cm}^3\text{-s}$								
X	0.0745	0.213	0.340	0.475	0.606	0.738	0.872	0.936
\bar{n}	0.0231 (0.0756)	0.0480 (0.0958)	0.0645 (0.115)	0.0882 (0.145)	0.107 (0.177)	0.126 (0.214)	0.149 (0.259)	0.154 (0.273)
$R_a = 5.58 \times 10^{-7} \text{ mol/cm}^3\text{-s}$								
X	0.0872	0.267	0.457	0.660	0.835	0.855		
\bar{n}	0.0359 (0.0791)	0.0612 (0.103)	0.0845 (0.124)	0.116 (0.154)	0.117 (0.169)	0.114 (0.168)		
$R_a = 8.32 \times 10^{-7} \text{ mol/cm}^3\text{-s}$								
X	0.0993	0.273	0.470	0.667	0.765	0.862		
\bar{n}	0.0515 (0.0832)	0.0800 (0.104)	0.117 (0.124)	0.153 (0.147)	0.169 (0.161)	0.183 (0.175)		
$R_a = 1.11 \times 10^{-6} \text{ mol/cm}^3\text{-s}$								
X	0.110	0.213	0.326	0.459	0.589	0.711	0.826	0.936
\bar{n}	0.0658 (0.0871)	0.0816 (0.100)	0.0973 (0.111)	0.123 (0.121)	0.146 (0.132)	0.160 (0.142)	0.177 (0.152)	0.168 (0.156)
$R_a = 1.39 \times 10^{-6} \text{ mol/cm}^3\text{-s}$								
X	0.124	0.244	0.383	0.543	0.695	0.773		
\bar{n}	0.0817 (0.0904)	0.0980 (0.105)	0.117 (0.117)	0.145 (0.128)	0.165 (0.138)	0.171 (0.143)		
$R_a = 1.66 \times 10^{-6} \text{ mol/cm}^3\text{-s}$								
X	0.135	0.259	0.440	0.628	0.738			
\bar{n}	0.0956 (0.0935)	0.106 (0.110)	0.137 (0.122)	0.168 (0.134)	0.191 (0.140)			
$R_a = 2.22 \times 10^{-6} \text{ mol/cm}^3\text{-s}$								
X	0.135	0.277	0.525	0.649				
\bar{n}	0.110 (0.0993)	0.121 (0.118)	0.162 (0.131)	0.190 (0.136)				
$R_a = 3.32 \times 10^{-6} \text{ mol/cm}^3\text{-s}$								
X	0.188	0.301	0.417	0.582				
\bar{n}	0.169 (0.108)	0.182 (0.121)	0.191 (0.130)	0.240 (0.135)				

^a Model predictions shown by numbers in parentheses.

lower value of \bar{n} when B_t is decreased from 0.6 to zero. However, the model again fails to move the curve in parallel with the curve with $B_t = 0.6$. Therefore, the extent of diffusion control for the termination reaction taking place in the particle phase cannot be a decisive variable in determining the kinetic behavior of semibatch emulsion polymerization of methyl acrylate.

Finally, Eq. (15) is used to calculate the theoretical value of K'_d for semibatch emulsion polymerization of methyl acrylate at 50°C. This K'_d value can be compared with the value ($4 \times 10^{-12} \text{ cm}^2/\text{s}$) obtained from the fitting process discussed above. The value of a' for monomeric radicals is estimated to be 1.56×10^2 ($\sim [M]_p/[M]_w$, where $[M]_p = 9.6 \times 10^{-3} \text{ mol/cm}^3$ and $[M]_w$ is determined from the water sol-

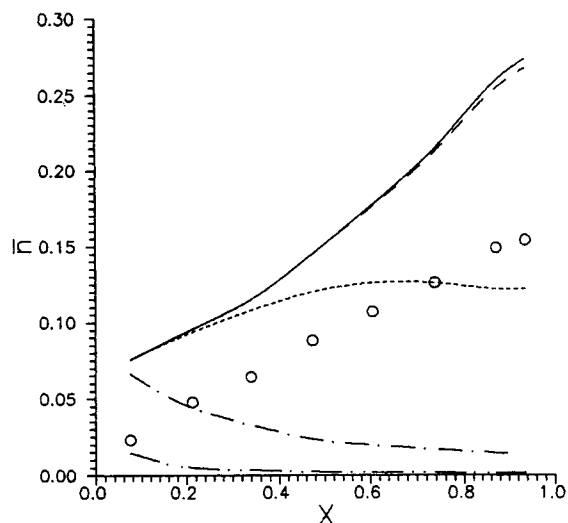


Figure 5 Average number of free radicals per particle as function of conversion: $R_a = 3.69 \times 10^{-7}$ mol/cm³-s, $K'_d = 4 \times 10^{-12}$ cm²/s, (O) experimental data, (—) $Y = 0$, (---) $Y = 10^{-2}$, (.....) $Y = 1$, (- · -) $Y = 10^2$, (- · · -) $Y = 10^4$.

ubility of monomer). The parameter D_w for methyl acrylate is assumed to be equal to that for styrene because the size of methyl acrylate monomer radicals is comparable to that of styrene monomer radicals. The term D_w for styrene at 60°C is about 2×10^{-5} cm²/s.²³ If the temperature dependence of D_w follows the hydrodynamical theory or Eyring rate theory (i.e., $D_w \sim T$),²⁴ then D_w for methyl acrylate is estimated to be about 1.94×10^{-5} cm²/s at 50°C. The ratio of D_w/D_{mr} is set at 10 based on the work of Lee and Poehlein.²³ Because of the lack of knowledge, the values of K'_p are usually set equal to K_p . With this assumption, the theoretical values of K'_d predicted by Eq. (15) are listed in Table IV. The fitted value of K'_d obtained in the present study is within the range of the theoretical values, and it is closer to the one with $K_{fm}/K'_p = 3.6 \times 10^{-6}$. Thus,

Table III Calculated Values of α' and m for Experiment with $R_a = 3.69 \times 10^{-7}$ mol/cm³-s

X	α'	m
0.0745	7.52×10^{-5}	5.57×10^{-3}
0.213	1.49×10^{-3}	7.20×10^{-2}
0.340	5.41×10^{-3}	2.02×10^{-1}
0.475	1.70×10^{-2}	5.28×10^{-1}
0.606	3.40×10^{-2}	9.10×10^{-1}
0.738	5.90×10^{-2}	1.41×10^0
0.872	9.80×10^{-2}	2.11×10^0
0.936	1.11×10^{-1}	2.29×10^0

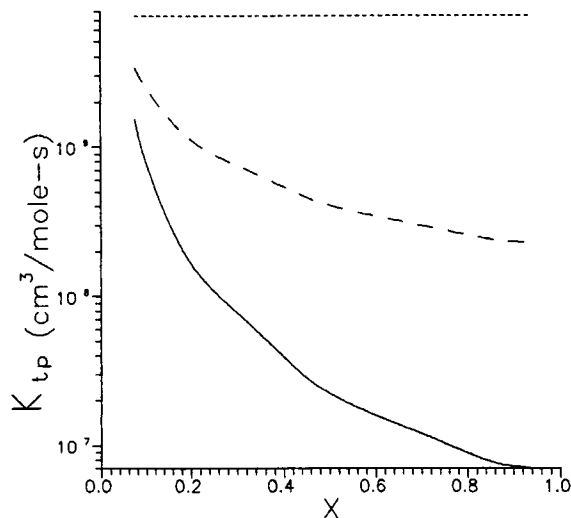


Figure 6 Termination rate constant in particle as function of conversion: $R_a = 3.69 \times 10^{-7}$ mol/cm³-s, $K'_d = 4 \times 10^{-12}$ cm²/s, (—) $B_t = 0.6$, (---) $B_t = 0.3$, (.....) $B_t = 0$.

the validity of the proposed model in predicting the kinetics of semibatch emulsion polymerization of methyl acrylate is reconfirmed. Furthermore, the ratio of K_{fm}/K'_p for methyl acrylate is estimated to be 4.4×10^{-6} at 50°C.

CONCLUSIONS

Transport of free radicals out of the particles plays an important role in the reaction kinetics of semi-

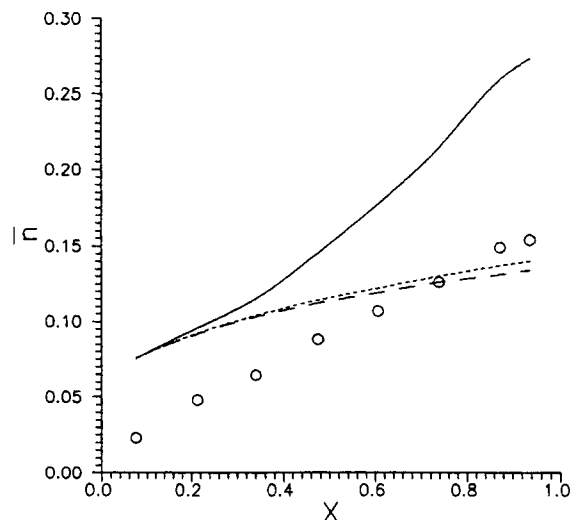


Figure 7 Average number of free radicals per particle as function of conversion: $R_a = 3.69 \times 10^{-7}$ mol/cm³-s, $K'_d = 4 \times 10^{-12}$ cm²/s, (O) experimental data, (—) $B_t = 0.6$, (---) $B_t = 0.3$, (.....) $B_t = 0$.

Table IV Theoretical Values of K'_d Predicted by Eq. (15)

K_{fm}/K'_p ^a	K'_d (cm ² /s)
3.60×10^{-6}	3.3×10^{-12}
1.81×10^{-5}	1.7×10^{-11}
3.25×10^{-5}	3.0×10^{-11}

^a From Ref. 14.

batch emulsion polymerization of methyl acrylate. Such a desorption process can cause the reaction system to deviate from Smith-Ewart case II kinetics. A mechanistic model has been developed to predict the \bar{n} -vs.- X data for emulsion polymerization of methyl acrylate in a semibatch reactor operated at 50°C. Agreement between the model predictions and experimental data for various rates of monomer addition is good. The kinetic data show a trend that the rate of polymerization increases with an increase in the rate of monomer addition. The simulation results also suggest that the effect of diffusion-controlled termination reaction on the reaction kinetics is not significant when \bar{n} is lower than 0.5. The experimental data can be used to evaluate the desorption rate constant K'_d for methyl acrylate. The best fitted value of K'_d at 50°C is 4×10^{-12} cm²/s, and it is in good agreement with the theoretical values of K'_d predicted by desorption theory. In addition, the ratio of K_{fm}/K'_p for methyl acrylate is estimated to be 4.4×10^{-6} at 50°C.

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