

Entry and Exit Rate Coefficients in Emulsion Polymerization of Styrene

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SYNOPSIS

The rate coefficient for entry of radicals into the polymer particles and the radical exit rate coefficient were estimated in seeded emulsion polymerization of styrene. The dependence of both coefficients on the particle size was used in an attempt to discriminate between the models proposed for these coefficients. The results obtained were found to be consistent with a model in which the entry of radicals into the polymer particles occurs by the propagational mechanism and the radicals desorb from the polymer particles by diffusion. A comparison between the estimated values of the coefficients and those calculated theoretically using the equations derived from the corresponding mechanisms was performed.

INTRODUCTION

An important characteristic of emulsion polymerization is that, unlike other polymerization processes, polymerization rate and molecular weight can be increased at the same time. This is due to the compartmentalization of the system that reduces the probability of mutual termination of the propagating radicals. The behavior of this compartmentalized system depends on the rate of exchange of species between the elements of the system. For most emulsion systems the rate of polymerization is controlled by the rate of entry and exit of free radicals to and from latex particles, not by the rate of monomer transfer to the polymerization sites. Considerable effort has been devoted to investigate these processes. Thus, the entry of radicals into the polymer particles has been treated as a collisional process¹ as well as a diffusional process² and a colloidal process.³ More recently, a new mechanism involving the propagation of the free radicals in the aqueous phase as the rate-determining step for entry has been postulated by Morrison et al.⁴

Nomura et al.^{5,6} and Asua et al.⁷ have proposed different exit rate coefficients. The main difference

between these models is that Nomura et al.^{5,6} considered that if a previously desorbed single-unit monomeric radical entered a polymer particle containing one radical, instantaneous termination would occur, whereas Asua et al.⁷ took into account the possibility of redesorption. This resulted in large differences between the predicted desorption rate coefficients under conditions in which extensive desorption of radicals occurs, i.e., highly water-soluble monomers. The model proposed by Asua et al.⁷ was able to explain the experimental results obtained by Adams et al.,⁸ whereas Nomura's model^{5,6} failed to fit these results.

The determination of the values of both the entry rate coefficient and the exit rate coefficient is a primary goal for the discrimination between these models and, consequently, for elucidation of the mechanisms involved in emulsion polymerization. In addition, accurate values of the parameters are required for the use of predictive mathematical models of industrial emulsion polymerization processes. Recently, Asua et al.⁹ presented a critical review of the approaches for parameter estimation in emulsion polymerization systems, analyzing both the type of data used in each approach and the corresponding data analysis method. These authors concluded that the time dependence of the conversion during the approach to steady-state values of the average number of radicals per particle, \bar{n} ,¹⁰ is

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more sensitive to the values of the parameters than both steady-state measurements¹¹ and particle size distribution analysis.¹² In addition, Asua et al.⁹ reported some weaknesses of the methods of data analysis used previously¹⁰⁻¹³ and proposed a new method for parameter estimation in emulsion polymerization systems. The method is based on an algorithm for parameter estimation in ordinary differential equations and uses the evolution of the monomer conversion in chemically initiated seeded emulsion polymerizations. By using simulated data for a "zero-one" system, the authors⁹ analyzed the effect of both random and systematic errors, concluding that the random errors did not affect the values of the estimated parameters, whereas systematic errors greatly affected the accuracy of the estimated parameters. In addition, it was found that a minimum number of experiments carried out under a minimum range of variation of experimental conditions were required to estimate the parameters accurately.

In this article, the approach proposed by Asua et al.⁹ was used to estimate the entry and exit rate coefficients in the emulsion polymerization of styrene using data of the time evolution of the conversion during the approach to steady-state values of \bar{n} reported in the literature.^{10,14} The dependence of these coefficients on the particle size was used in an attempt to discriminate between the models proposed for the entry and exit rate coefficients.

EXPERIMENTAL DATA USED FOR THE ESTIMATION OF THE KINETIC PARAMETERS

Two sets of data on seeded emulsion polymerization of styrene were used in the present study. The first consisted of experiments carried out with a latex of an unswollen diameter of 94 nm and a particle concentration of 4.9×10^{13} particles/cm³ of water.¹⁰ Experiments were conducted at 50°C in interval II. The concentration of initiator (K₂S₂O₈) was varied from 1.6×10^{-8} to 8.33×10^{-5} mol/cm³. The second set included experiments carried out in intervals II and III at 50°C using a 154-nm-diameter seed latex.¹⁴ The concentration of polymer particles was varied from 0.98×10^{13} to 2.04×10^{13} particles/cm³ of water and the initiator (K₂S₂O₈) concentration varied between 0.21×10^{-7} and 5.01×10^{-7} mol/cm³. Unfortunately, there are no unprocessed conversion-time data available for these sets of experiments.¹⁵ Nevertheless, conversion-vs.-time data can be generated using the values of the pseudo-first-

order rate coefficients for both entry of free radicals into the latex particles (ρ) and exit of free radicals from the latex particles (k) given for each of the experiments in Refs. 10 and 14. For the experiments considered $\bar{n} < 0.5$, i.e., these were zero-one systems, and thus conversion-vs.-time data could be generated by considering the typical recipe given in Ref. 10 and integrating the following equations:

$$\frac{dx}{dt} = \frac{k_p [M]_p N_1}{M_0 N_A} \quad (1)$$

$$\frac{dN_1}{dt} = \rho(N_T - 2N_1) - kN_1 \quad (2)$$

where x is the fractional conversion, k_p the propagation rate constant, $[M]_p$ the concentration of monomer in the polymer particles, M_0 the amount of monomer initially charged into the reactor, N_A Avogadro's number, N_1 the number of polymer particles containing one radical, and N_T the total number of polymer particles. Experiments for which values of either ρ or k were not reported were not taken into consideration. In addition, only experiments carried out in interval II were considered. Therefore, experiments 15–21, 23, 24, 26, and 27 in Ref. 10 and experiments 61–63, 67, 68, 71, 74, 78, 79, and 84 in Ref. 14 were used. The concentration of monomer in the polymer particles was taken to be 5.8×10^{-3} for set 1 and 5.5×10^{-3} mol/cm³ for set 2 and the propagation rate constant used was $k_p = 2.58 \times 10^5$ cm³/mol s. These were the values used in Refs. 10 and 14 to calculate the reported values of ρ and k . Figures 1 and 2 present the data obtained for these experiments described previously.

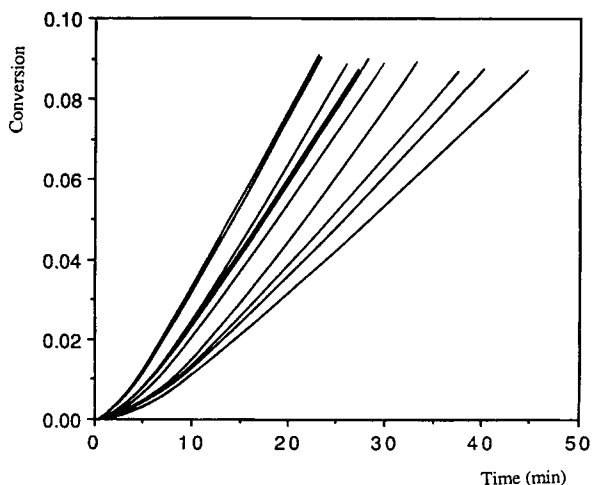


Figure 1 Data obtained for experiments in set 1.

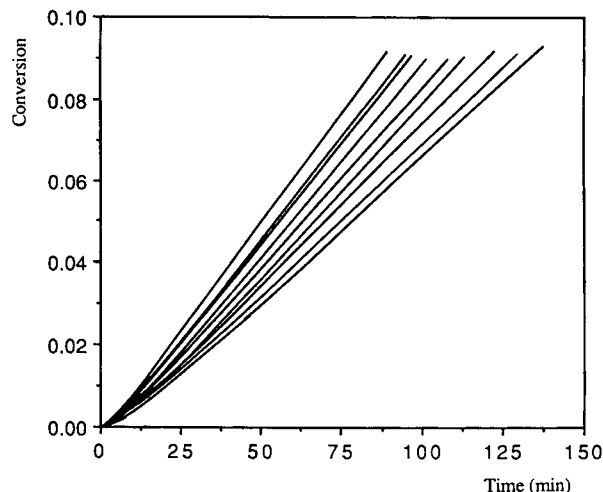


Figure 2 Data obtained for experiments in set 2.

ESTIMATION OF THE PARAMETERS

For styrene, the contribution of the aqueous phase polymerization to the overall conversion is negligible, and hence the monomer material balance for a zero-one system is

$$\frac{dx}{dt} = \frac{k_p[M]_p N_1}{M_0 N_A} \quad (3)$$

For a zero-one system the population balance for N_1 is

$$\frac{dN_1}{dt} = k_a[R]_w(N_T - 2N_1) - k_d N_1 \quad (4)$$

where k_a is the entry rate coefficient, k_d the desorption rate coefficient, and $[R]_w$ the concentration of free radicals in the aqueous phase that can be calculated by means of the material balance for radicals in the aqueous phase:

$$\frac{d[R]_w}{dt} = 0 = 2k_I[I]N_A + k_d N_1 - k_a[R]_w N_T - 2k_{tw}[R]_w^2 N_A \quad (5)$$

where k_I is the rate coefficient for the generation of free radicals from initiator decomposition and k_{tw} the termination rate constant in the aqueous phase. It has been demonstrated that the pseudo-steady-state assumption can be safely used⁹ in Eq. (5). For a chemically initiated system, the initial conditions for Eqs. (3)–(5) are

$$t = 0 \quad x = 0 \quad [R]_w = 0 \quad N_1 = 0 \quad (6)$$

Asua et al.⁹ discussed the advantages of using the model given by Eqs. (3)–(5) instead of those represented by Eqs. (1) and (2), concluding that the main advantage of the present model is that it uses more fundamental parameters that are independent of experimental conditions, such as concentration of polymer particles and concentration of initiator. Consequently, the parameters of the model can be readily used in mechanistic studies, and the model is useful for predictive work. Asua et al.⁹ demonstrated that all of the parameters of the model, except k_{tw} , which is correlated with k_a , can be accurately estimated when enough experimental data are available.

Some of the parameters of the model, namely, k_a and k_d , depend on the monomer swollen polymer particle diameter. Table I presents the dependence of the entry rate coefficient on the particle size predicted for the different models proposed in the literature. The following expression has been proposed for the desorption coefficient⁷:

$$k_d = k_{fm}[M]_p \frac{K_0}{\beta K_0 + k_p[M]_p} \quad (7)$$

where k_{fm} is the chain transfer rate coefficient, β the probability that a desorbed single-unit monomeric radical reacts in the aqueous phase by either propagation or termination, and K_0 is the rate of exit of a monomeric radical from the polymer particle. Assuming a diffusion mechanism and no additional resistance in the interphase, Nomura⁶ derived the following equation for K_0 :

$$K_0 = \frac{12(D_w/m_d)}{1 + 2(D_w/m_d D_p)} \frac{1}{dp^2} \quad (8)$$

where D_w and D_p are the diffusion coefficients of a monomeric radical in the aqueous phase and the polymer particles, respectively; m_d the partition coefficient of such a radical between polymer particles and aqueous phase, and dp the diameter of the monomer swollen polymer particle.

Table I Dependences of Entry Rate Coefficient on Particle Size Predicted by Different Models

Model	Dependence
Collisional (Ref. 1)	dp^2
Diffusional (Ref. 2)	dp
Colloidal (Ref. 3)	$(dp + de)^2/dp \quad de \approx dp$
Propagational (Ref. 4)	Almost no dependence ^a

^a For a constant number of particles.

Table II Values of Estimated Parameters Using Both Sets of Experiments Separately

	Set 1		Set 2	
	1	2	1	2
Two parameters				
k_a (cm ³ /mol s)		6.55×10^8		7.42×10^8
k_d (s ⁻¹)		7.18×10^{-4}		5.42×10^{-4}
$\sum e^2$		6.014×10^{-5}		9.59×10^{-6}
Three parameters				
k_a (cm ³ /mol s)	4.58×10^8	1.25×10^9	5.27×10^8	1.25×10^9
k_d (s ⁻¹)	8.07×10^{-4}	1.39×10^{-3}	5.12×10^{-4}	8.35×10^{-4}
k_t (s ⁻¹)	2.25×10^{-6}	7.66×10^{-7}	2.25×10^{-6}	9.24×10^{-7}
$\sum e^2$	5.46×10^{-5}	1.01×10^{-4}	9.21×10^{-6}	1.09×10^{-5}

^a Column 1 initial guess: $k_a = 1 \times 10^9$; $k_d = 5 \times 10^{-4}$; $k_t = 1 \times 10^{-6}$. Column 2 initial guess: $k_a = 2 \times 10^{10}$; $k_d = 1 \times 10^{-3}$; $k_t = 5 \times 10^{-7}$.

The parameter estimation approach gives a single value of each estimated parameter for the whole range of experimental conditions in which the data used for the estimation are obtained. Because the two sets of experiments were carried out using different seed sizes, they were analyzed separately using the algorithm proposed by Asua et al.⁹ Table II presents the results obtained taking two rate coefficients (k_a and k_d) and three rate coefficients (k_a , k_d , and k_t) as estimable parameters. The estimation was performed using the values of k_p and $[M]_p$ employed in the generation of data, namely, $k_p = 2.58 \times 10^5$ cm³/mol s, $[M]_p = 5.8 \times 10^{-3}$ mol/cm³ for set 1 and $[M]_p = 5.5 \times 10^{-3}$ mol/cm³ for set 2. In addition, the termination rate constant in the aqueous phase was $k_{tw} = 7 \times 10^{10}$ cm³/mol s,¹⁴ and when

two parameters were estimated, k_t was taken to be equal to 1.3×10^{-6} s⁻¹.¹⁴ When only two adjustable parameters were used, the estimated values of k_a and k_d were found to be independent of the initial guess. However, when three adjustable parameters were considered, the values of k_a , k_d , and k_t depended on the initial guess, as shown in Table II. In addition, the values of the average residual sum of squares per point ($\sum e^2$) show that the fitting of the data was not significantly improved by increasing the number of estimated parameters from 2 to 3 and large confidence intervals were determined when three-parameter estimation was used. This means that the experiments do not contain enough information to estimate more than two parameters. Figures 3 and 4 present a comparison between experi-

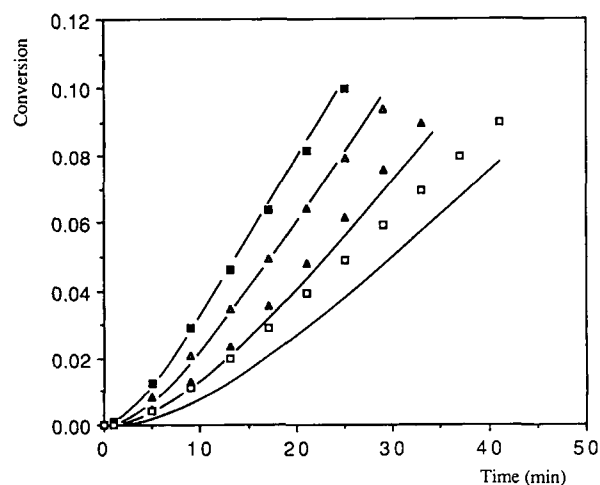


Figure 3 Comparison between experimental results and model predictions (solid lines) for some experiments from set 1: (■) experiment 16; (△) experiment 20; (▲) experiment 24; (□) experiment 26.

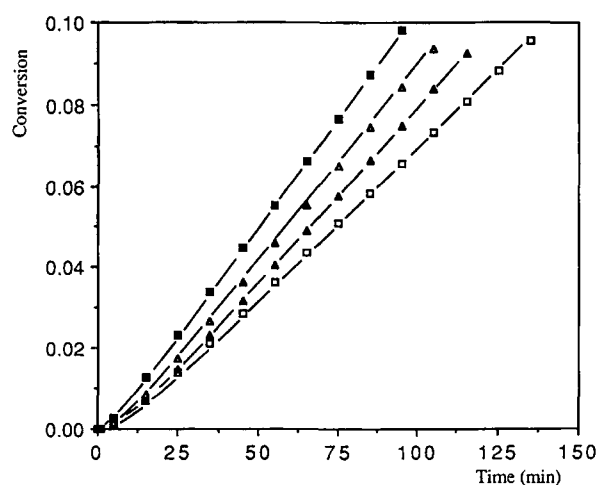


Figure 4 Comparison between experimental results and model predictions (solid lines) for some experiments from set 2: (■) experiment 79; (△) experiment 71; (▲) experiment 74; (□) experiment 67.

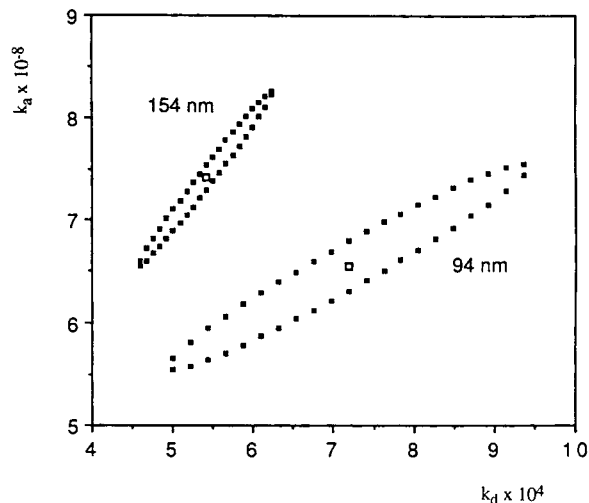


Figure 5 The 95% confidence regions for k_a and k_d obtained using experiments in set 1 (seed particle diameter, 94 nm) and set 2 (seed particle diameter, 154 nm).

mental results and model predictions obtained using Eqs. (3)–(6) and the parameters given in Table II for the two-parameter estimation. It can be seen that good fitting was obtained for intermediate and large concentrations of initiator. The lack of fit at low initiator concentrations is due to thermal initiation, which is not included in Eqs. (3)–(6). Figure 5 presents the 95% confidence regions for the parameters estimated from both sets of experiments using a two-parameter estimation. It can be seen that k_a increased and k_d decreased when the size of the swollen seed particles increased from 140 to 218 nm. However, it should be pointed out that the individual confidence intervals, estimated as the projection of the confidence regions onto the corresponding axis, for both sets of experiments intersected one another. From Figure 5, it can be estimated that k_a presented a 0.65 power dependence on the polymer particle diameter, whereas a -1.47 power dependence on dp was found for k_d . These dependences do not coincide with those given for k_a in Table I and for k_d by Eqs. (7) and (8). However, de la Cal et al.¹⁶ have demonstrated that significant errors in the estimated values of k_a and k_d , and hence in their dependence with respect to the particle size, can be introduced by neglecting the variation of the particle size during polymerization.

In order to take into account the variation of the parameters during the polymerization, the entry rate coefficient and the rate coefficient for radical desorption were written as follows:

$$k_a = k_a^* dp^{\alpha_1} \quad (9)$$

$$k_d = \frac{k_d^*}{dp^{\alpha_2}} \quad (10)$$

where α_1 can take the values 0, 1, or 2 depending on the model chosen from Table I and $0 \leq \alpha_2 \leq 2$. The limits of α_2 were calculated from Eqs. (7) and (8):

$$\beta K_0 \ll k_p[M]_p \quad k_d \div \frac{1}{dp^2} \quad (11)$$

$$\beta K_0 \gg k_p[M]_p \quad k_d \text{ is independent of } dp \quad (12)$$

For sparingly water-soluble monomers such as styrene $\beta K_0 < k_p[M]_p$, and therefore, a value of α_2 close to 2 is expected.

Equations (9) and (10) were substituted into Eqs. (3)–(5) and the parameter estimation algorithm employed to estimate k_a^* and k_d^* for given values of α_1 and α_2 . The results are presented in Table III together with the corresponding average residual sum of squares. The values of the entry rate coefficient k_a and desorption rate coefficient k_d calculated for a polymer particle of 200 nm using Eqs. (9) and (10) are also included in Table III. Note that although wide changes in α_1 and α_2 were used, only small variations on both k_a and k_d were obtained. The results presented in Table III did not allow the unambiguous determination of α_1 and α_2 because several pairs of α_1 and α_2 gave an equivalent fitting of the data. This means that the data, because of the relatively small range of variation of the particle size, did not contain enough information for the estimation of unique values for α_1 and α_2 . Therefore, a complete discrimination between models in Table I is not possible. Nevertheless, the results shown in Table III allowed the rejection of several models presented in Table I. In Figure 6, the α_1 – α_2 space has been divided into two regions according to the averaged residual sum of squares per point obtained for each α_1 – α_2 pair. The excluded region represents the pairs of values α_1 – α_2 that gave large values of $\sum e^2$. The boundary between the two regions is a non-well-defined zone that depends on the degree of exigency of the test used for model discrimination. Figure 6 shows that the collisional model¹ ($\alpha_1 = 2$), the diffusional model² ($\alpha_1 = 1$), and the colloidal model³ ($\alpha_1 = 1$) are incompatible with the assumption that desorption of radicals occurs through a diffusion mechanism with no additional resistance in the interphase because a value of α_2 close to 2 is expected from Eqs. (7) and (8) for styrene. On the other hand, the propagational model⁴ for k_a (α_1 close to zero) and Eqs. (7) and (8) for k_d ($1.5 < \alpha_2 < 2$) are the only combination of models that cannot be

Table III Values of Parameters Using Different Particle Size Dependences

α_1	α_2	k_a^*	k_a (200 nm) (cm ³ /mol s)	k_d^*	k_d (200 nm) (s ⁻¹)	Σe^2
1.00	0.0	5.10×10^{13}	1.02×10^9	8.96×10^{-4}	8.96×10^{-4}	3.01×10^{-5}
0.25	1.0	1.05×10^{10}	7.02×10^8	1.11×10^{-8}	5.55×10^{-4}	3.07×10^{-5}
0.00	1.5	7.67×10^8	7.67×10^8	5.61×10^{-11}	6.27×10^{-4}	3.15×10^{-5}
0.00	0.0	5.11×10^8	5.11×10^8	3.33×10^{-4}	3.33×10^{-4}	3.15×10^{-5}
0.50	1.0	2.13×10^{11}	9.52×10^8	1.65×10^{-8}	8.25×10^{-4}	3.29×10^{-5}
0.25	1.5	1.18×10^{10}	7.89×10^8	5.69×10^{-11}	6.36×10^{-4}	3.55×10^{-5}
0.00	2.0	7.71×10^8	7.71×10^8	2.41×10^{-13}	6.02×10^{-4}	3.82×10^{-5}
0.50	1.5	2.29×10^{11}	1.02×10^9	7.70×10^{-11}	8.61×10^{-4}	4.11×10^{-5}
2.00	0.0	5.48×10^{18}	2.19×10^9	1.96×10^{-3}	1.96×10^{-3}	4.56×10^{-5}
0.25	2.0	1.17×10^{10}	7.82×10^8	2.35×10^{-13}	5.87×10^{-4}	4.58×10^{-5}
0.50	2.0	2.18×10^{11}	9.74×10^8	3.02×10^{-13}	7.55×10^{-4}	5.50×10^{-5}
1.00	1.5	6.82×10^{13}	1.36×10^9	1.00×10^{-10}	1.12×10^{-3}	5.86×10^{-5}
1.00	2.0	6.31×10^{13}	1.26×10^9	3.75×10^{-13}	9.37×10^{-4}	7.99×10^{-5}
2.00	2.0	1.05×10^{19}	4.20×10^9	1.07×10^{-12}	2.67×10^{-3}	1.43×10^{-4}

discarded using the results presented in Figure 6. However, it should be pointed out that this result is based on a limited amount of data using a rather small range of particle sizes.

It is interesting to compare the values of k_a and k_d in Table III with the predictions of Eqs. (7) and (8) for k_d and the propagational model⁴ for k_a . The value of the radical desorption rate coefficient calculated from Eqs. (7) and (8) and the values of the parameters given in Table IV is $k_d = 8.6 \times 10^{-4} \text{ s}^{-1}$. This value, considering the uncertainty associated with D_w , is in good agreement with the values of k_d in Table III.

To our knowledge, the propagational model⁴ has not been formulated in such a way that an equation for k_a has been proposed. The Appendix shows that

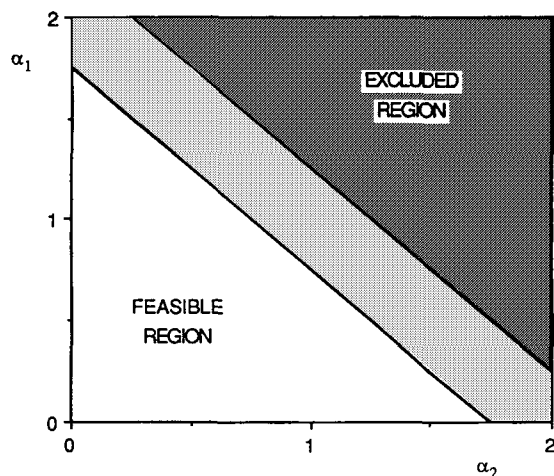
the following approximate equation for the entry rate coefficient can be derived:

$$k_a = k_p [M]_w \frac{\sigma_0 \sigma^{z-2}}{1 + \sigma_0 [(1 - \sigma^{z-1}) / (1 - \sigma)]} \frac{N_A}{N_T} \quad (13)$$

where $[M]_w$ is the concentration of monomer in the aqueous phase, z the critical degree of polymerization of oligomers in the aqueous phase, σ_0 the probability that an initiator radical undergoes a propagation reaction in the aqueous phase, and σ the probability that a growing oligomer propagates in the aqueous phase given approximately by

$$\sigma = \frac{k_p [M]_w}{k_p [M]_w + k_{tw} [R]_w} \quad (14)$$

Note that according to the propagational model,⁴ k_a depends on $[R]_w$ and hence on experimental conditions such as the concentration of initiator and

**Figure 6** Feasible region for α_1 and α_2 .**Table IV** Values of Parameters Used to Calculate k_d

$k_p = 2.58 \times 10^5 \text{ cm}^3/\text{mol s}$
$[M]_p = 5.65 \times 10^{-3} \text{ mol}/\text{cm}^3$
$m_d = 1800^a$
$\beta = 0.30^b$
$k_{fm} = 2.7 \text{ cm}^3/\text{mol s}^a$
$D_w = 5 \times 10^{-6} \text{ cm}^2/\text{s}$
$dp = 200 \text{ nm}$

^a Ref. 17.^b Ref. 7.

Table V Values of Entry Rate Coefficients Calculated Using Equations (5), (13) and (14) for Different Values of the Critical Degree of Polymerization z

z	k_a (cm ³ /mol s)
4	1.6×10^9
5	1.0×10^9
6	6.6×10^8

the concentration of the number of latex particles. For experiment 15 in Ref. 10, which used an initiator concentration of 1.3×10^{-6} mol/cm³ and a concentration of number of particles of 4.9×10^{13} particles/cm³, assuming that $\sigma_0 = 1$, the values of the entry rate coefficients calculated by means of Eqs. (13) and (14) for different values of z are given in Table V. Comparison of these values with those in Table III gives a critical degree of polymerization of about 5–6, which is a reasonable value for a styrene oligomer stabilized by a hydrophilic end group.

CONCLUSIONS

The approach proposed by Asua et al.⁹ was used to estimate both the entry rate coefficient and the exit rate coefficient in emulsion polymerization of styrene using data of the time evolution of the conversion during the approach to the steady-state values of \bar{n} reported in the literature.^{10,14} These data included experiments in which the concentration of polymer particles as well as the initiator concentration were varied. Two different seed particle sizes were used. Parameter estimation was carried out taking into account the variation of the particle size during polymerization. Good fitting of experimental results was achieved. The dependence of k_a and k_d on the particle size was used in an attempt to discriminate between the models proposed in the literature for the entry and exit rate coefficients. It was found that the collisional model, the diffusional model, and the colloidal model were incompatible with the assumption that desorption of radicals occurred through a diffusion mechanism with no additional resistance in the interphase. The results obtained were consistent with a model in which the entry of radicals into the polymer particles occurred by the propagational mechanism and the radicals desorbed from the polymer particles by diffusion. In addition, the values of k_a and k_d calculated using the

equations derived from these mechanisms agreed with those estimated in this work from experimental data.

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NOMENCLATURE

d_e	Precursor diameter (cm)
d_p	Diameter of the monomer swollen polymer particle (cm)
D_p, D_w	Diffusion coefficients of a monomeric radical in the polymer particles and the aqueous phase, respectively (cm ² /s)
$[I]$	Concentration of initiator (mol/cm ³)
$[IM_z]$	Concentration of oligomers of length z in the aqueous phase (mol/cm ³)
k	Pseudo-first-order exit rate coefficient (s ⁻¹)
k_a^*, k_d^*	Parameters defined by Eqs. (9) and (10), respectively
k_a	Entry rate coefficient (cm ³ /mol s)
k_d	Desorption rate coefficient (s ⁻¹)
k_{fm}	Chain transfer rate coefficient (cm ³ /mol s)
k_I	Rate coefficient for initiator decomposition (s ⁻¹)
k_p	Propagation rate constant (cm ³ mol ⁻¹ s ⁻¹)
k_{tw}	Termination rate constant in the aqueous phase (cm ³ mol ⁻¹ s ⁻¹)
K_0	Rate of exit of a monomeric radical from a polymer particle (s ⁻¹)
m_d	Partition coefficient of the monomer between polymer particles and aqueous phase
$[M]_p, [M]_w$	Concentration of the monomer in the polymer particles and aqueous phase, respectively (mol/cm ³)
M_0	Amount of monomer initially charged into the reactor (mol/cm ³ of water)
\bar{n}	Average number of radicals per particle
N_A	Avogadro's number

N_l	Number of polymer particles containing one radical per cubic centimeter of water
N_T	Total number of latex particles per cubic centimeter of water
$[R]_w$	Concentration of free radicals in the aqueous phase (mol/cm ³)
x	Conversion
z	Critical degree of polymerization of oligomers in the aqueous phase

Greek Symbols

α_1, α_2	Parameters defined by Eqs. (9) and (10)
β	Probability that a desorbed single-unit monomeric radical reacts in the aqueous phase by either propagation or termination
ρ	Pseudo-first-order entry rate coefficient (s ⁻¹)
σ	Probability that a growing oligomer propagates in the aqueous phase
σ_0	Probability that an initiator radical undergoes a propagation reaction in the aqueous phase

REFERENCES

- J. L. Gardon, *J. Polym. Sci. Part A-1*, **6**, 643 (1968).
- J. Ugelstad and F. K. Hansen, *Rubber Chem. Tech.*, **49**(3), 536 (1976).
- P. J. Feeney, D. H. Napper, and R. G. Gilbert, *Macromolecules*, **17**, 2520 (1984).
- B. R. Morrison, I. A. Maxwell, R. G. Gilbert, and D. H. Napper, II Intern. Symp. on Copolymerization and Copolymers in Dispersed Media, Lyon, 1989.
- M. Nomura, M. Harada, K. Nakagawara, W. Eguchi, and S. Nagata, *J. Chem. Eng. Jpn.*, **4**(2), 160 (1971).
- M. Nomura in *Emulsion Polymerization*, I. Piirma, Ed., Academic Press, New York, 1982.
- J. M. Asua, E. D. Sudol, and M. S. El-Aasser, *J. Polym. Sci., Polym. Chem. Ed.*, **27**, 3903 (1989).
- M. E. Adams, D. H. Napper, R. G. Gilbert, and D. F. Sangster, *J. Chem. Soc., Faraday Trans. 1*, **82**, 1979 (1986).
- J. M. Asua, M. E. Adams, and E. D. Sudol, *J. Appl. Polym. Sci.*, **39**, 1183 (1990).
- B. S. Hawkett, D. H. Napper, and R. G. Gilbert, *J. Chem. Soc., Faraday Trans. 1*, **76**, 1323 (1980).
- M. Nomura, *Makromol. Chem. Suppl.*, **10/11**, 25 (1985).
- G. Lichti, B. S. Hawkett, R. G. Gilbert, D. H. Napper, and D. F. Sangster, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 925 (1981).
- R. G. Gilbert and D. H. Napper, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.*, **c23**(1), 127 (1983).
- I. A. Penboss, R. G. Gilbert, and D. H. Napper, *J. Chem. Soc., Faraday Trans. 1*, **82**, 2247 (1986).
- R. G. Gilbert, private communication.
- J. C. de la Cal, M. E. Adams, and J. M. Asua, *Makromol. Chem. Makromol. Symp.*, **35/36**, 23 (1990).
- J. Forcada and J. M. Asua, *J. Polym. Sci., Polym. Chem. Ed.*, **28**, 987 (1990).

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APPENDIX

The propagational model⁴ for entry of free radicals into the polymer particles assumes that free radicals polymerize in the aqueous phase until the oligomers reach a critical degree of polymerization z . Then the oligomer will enter into the polymer particle. Therefore, the rate of growth to the critical degree of polymerization is the rate-determining step for entry of free radicals into particles. The rate of entry of free radicals per particle is

$$\rho = k_p [IM_{z-1}^*] [M]_w \frac{N_A}{N_T} \quad (\text{I.1})$$

where $[IM_{z-1}^*]$ is the concentration of oligomers of length $z - 1$.

Assuming pseudo-steady-state conditions for the radicals in the aqueous phase the following equation can be written:

$$\begin{aligned} [IM_{z-1}^*] &= \sigma [IM_{z-2}^*] = \sigma^2 [IM_{z-3}^*] = \dots \\ &= \sigma^{z-2} [IM_1^*] \end{aligned} \quad (\text{I.2})$$

where σ is the probability that a growing oligomer propagates in the aqueous phase. An approximate expression for σ is given by Eq. (10).

The concentration of oligomers of length 1 is

$$[IM_1^*] = \sigma_0 [I^*] \quad (\text{I.3})$$

where σ_0 is the probability that an initiator radical undergoes a propagation reaction in the aqueous phase.

The total concentration of radicals in the aqueous phase is

$$\begin{aligned}
 [R]_w &= [I^*] + \sigma_0[IM_1^*] + \sigma_0\sigma[IM_2^*] \\
 &\quad + \cdots + \sigma_0\sigma^{z-2}[IM_{z-1}^*] \\
 &= [I^*] \left(1 + \sigma_0 \frac{1 - \sigma^{z-1}}{1 - \sigma} \right) \quad (I.4)
 \end{aligned}$$

Combining Eqs. (I.1)–(I.4), the following equation for the rate of entry of radicals per particle was obtained:

$$\rho = k_p[M]_w \frac{N_A}{N_T} \frac{\sigma_0\sigma^{z-2}}{1 + \sigma_0[(1 - \sigma^{z-1})/(1 - \sigma)]} [R]_w \quad (I.5)$$

According to the model used in the present work, the rate of entry is given by

$$\rho = k_a[R]_w \quad (I.6)$$

Combining Eqs. (I.5) and (I.6), the following equation for k_a was derived:

$$k_a = k_p[M]_w \frac{N_A}{N_T} \frac{\sigma_0\sigma^{z-2}}{1 + \sigma_0[(1 - \sigma^{z-1})/(1 - \sigma)]} \quad (I.7)$$