

Exit process and re-entry rate in emulsion polymerization

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(Received 7 July 1995; revised 14 September 1995)

The re-entry rate in emulsion polymerization is reformulated by taking into account both the enter and exit processes together. The role that the free radicals play in these rate processes is used directly in the formulation. Based on the formulation, expressions are derived for the re-entry and exit rate coefficients, the average number of free radicals in a polymer particle, and the total free radical concentration in the aqueous phase. The model results require only the basic parameters that are determined in independent experiments and do not involve parameter fitting. The results are applicable to the zero-one system in which there is only one or no free radical in the particle that prevails in interval II of the polymerization. A criterion is developed for determining the applicability of the zero-one system. Particle size dependence of the exit rate coefficient is also given. The model results are compared with literature data and are shown to predict certain exit rate behaviour that has been inexplicable hitherto. Copyright © 1996 Elsevier Science Ltd.

(Keywords: exit; re-entry; emulsion polymerization)

INTRODUCTION

In emulsion polymerization, the interior of the polymer latex particle is the major locus of polymerization. The free radicals generated in the aqueous phase are captured into the particles, leading to the growth by propagation therein. The rate of entry of free radicals into the particles and the rate of desorption from the particles, therefore, play a key role in emulsion polymerization¹.

Many theories have been advanced regarding the mechanism of entry and its rate-controlling step. These include diffusion-control theory^{2,3}, surfactant displacement theory⁴, colloidal behaviour theory³ and a theory based on free radicals of critical size⁵.

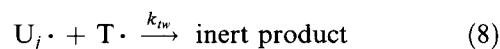
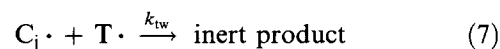
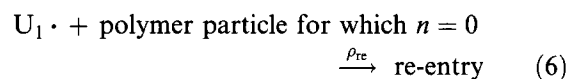
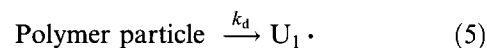
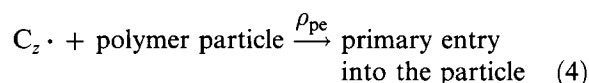
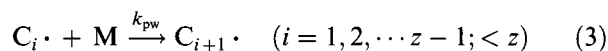
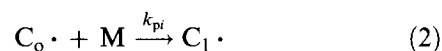
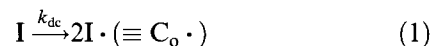
The free radicals that enter the particles can also exit from the particles. Nomura and Harada⁶, and Asua and De La Cal⁷ advanced theories for this exit behaviour. While these two theories are similar in that only a single unit monomeric radical can re-enter or desorb and the exit process is governed by mass transfer (diffusion), they differ with regard to the manner in which the exited single-unit monomeric radical re-enters the particles and re-desorbs⁷.

Casey *et al.*⁸ and Morrison *et al.*⁹ took into account both the entry and exit processes in their formulation. Unlike the formulation here, however, they took the approach of extracting information on the exit and entry rates of free radicals from balance equations with the aid of pseudo-steady state approximation. On the other hand, the approach here is to formulate the exit and entry rates directly from the rate processes involving free radical exit, entry and re-entry. As a result, size dependence of the rates and the non-linear nature of the role of free radicals emerge.

In this paper, both the entry and the exit processes are considered together for the purpose of obtaining the exit rate coefficient, re-entry rate coefficient, total concentration of free radicals in the aqueous phase and the average number of free radicals in a particle.

ENTRY AND EXIT PROCESSES

The events and reactions in the aqueous phase can be represented as follows:



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Here, I is the initiator, M is the monomer, $C_o \cdot$ is the charged (surface-active) single primary free radical formed from the initiator, and $C_i \cdot$ is the charged oligomeric free radical, including i th monomer. $U_1 \cdot$ is the single-unit monomeric radical desorbed from the polymer particle, and $T \cdot$ is the sum of all the radicals in the aqueous phase. A few assumptions are made in writing the above events and reactions. One assumption is that the oligomer free radical should reach a critical size z ($C_z \cdot$ in equation (4)) for it to enter a polymer particle⁵. Another assumption is that only a single unit monomeric radical ($U_1 \cdot$ in equations (5) and (6)) can exit from a polymer particle⁷.

It is seen from equation (6) that only a monomeric free radical can re-enter the particle. The monomeric free radical can also propagate in the aqueous phase, eventually leading to the inert product (equation (9)). Thus, the uncharged (surface-inactive) monomeric free radical that desorbs can either re-enter the polymer particle that does not contain any free radical by diffusion, or propagate in the aqueous phase. The rate constant for cross-termination is usually one or two orders of magnitude larger than that for homotermination¹⁰. But for simplicity in equations (7) and (8) they are not distinguished and taken as k_{tw} .

Reiterating, only the surface-active oligomer of a certain size can enter the latex particle, which means that a surface-inactive oligomer of the same size cannot. The source or the origin of this surface-inactive oligomer is the single unit monomeric radical in the particle that is formed by chain transfer, which becomes surface-inactive in the process. This surface-inactive monomeric radical can desorb and then add monomers in the aqueous phase. But the oligomer thus formed cannot enter the particle because of the lack of surface activity and thus eventually ends up as an inert product by termination in the aqueous phase. The surface-inactive monomeric radical that desorbs from the particle can also re-enter the particle by diffusion but the probability of such a radical entering a particle with no radical (N_0) is much larger than the probability of it entering a particle that already contains a radical (N_1). The free radical concentration difference between particle and aqueous phase and thus the driving force for diffusion is much larger for N_0 for N_1 . Therefore, only the re-entry into a particle with no radical is accounted for. The case of allowing re-entry into a particle with a radical already present is given in the Appendix.

The essence of the model presented above lies in the different treatment for charged and uncharged free radicals. The distinction here is on the basis of surface-active (charged) and surface-inactive (uncharged) nature of the radical. Charged free radicals denoted by $C \cdot$ either enter the polymer particle upon reaching the critical size by surface activity or terminate by reaction with other radicals in the aqueous phase, yielding inert products. Uncharged free radicals denoted by $U \cdot$ are initiated by monomeric uncharged free radical that desorbs from the polymer particle. Upon desorbing, it either re-enters a polymer particle that does not contain any free radical by diffusion or propagates in the

aqueous phase, eventually leading to termination with reaction with other free radicals.

The difference between our theory and that of Asua *et al.*⁷ is that their theory is mainly for the exit mechanism whereas ours combines the theory of Maxwell *et al.*⁵ for the entry mechanism and that of Asua *et al.*⁷ for the exit mechanism. As a consequence, an *a priori* model results that does not require curve-fitting. The result that emerges when the two theories are combined provides new insights into the overall behaviour such as an explanation for the behaviour that was inexplicable hitherto.

EXIT RATE AND RE-ENTRY RATE FOR ZERO-ONE SYSTEM

Consider a zero-one system in which there is only one or no radical in the polymer particles. A monomeric free radical formed by chain transfer in such a particle can propagate, desorb or terminate. The rates for these events are:

$$\text{Propagation: } r_p = k_p[M]_p \left(\frac{1}{N_A} \right) / V_p \quad (10)$$

$$\text{Desorption: } r_d = K_o \left(\frac{1}{N_A} \right) / V_p \quad (11)$$

$$\text{Termination: } r_t = \rho_{pe} \left(\frac{N_1}{N_A} \right) \quad (12)$$

where k_p is the propagation rate constant in the polymer particle, $[M]_p$ is the monomer concentration in the particle, N_1 is the number of polymer particles per unit volume that contain one free radical, V_p is the volume of the particle, and K_o is a parameter given⁶ by

$$K_o = \frac{12D_w}{m_d d_p^2} \left(1 + \frac{6D_w}{m_d D_p} \right)^{-1} \quad (13)$$

where D_w and D_p , respectively, are the diffusivity in the aqueous phase and that in the polymer particle, m_d is the equilibrium constant for the radical concentration at the interface, and d_p is the particle diameter. The quantity m_d is usually expressed in terms of the ratio of the monomer concentration in the polymer particle to that in the aqueous phase.

The probability P_{ex} that the monomeric free radical formed by the chain transfer desorbs from a particle can be expressed in terms of the three events given by equations (10), (11) and (12) as follows:

$$P_{ex} = \frac{K_o}{k_p[M]_p + K_o + \rho_{pe}N_1V_p} \quad (14)$$

In general, $\rho_{pe}N_1V_p$ is much less than either $k_p[M]_p$ or K_o . Therefore, the above expression can be approximated as follows:

$$P_{ex} = \frac{K_o}{k_p[M]_p + K_o} \quad (15)$$

The exit rate is the sum of the desorption rate after chain transfer reaction and that of free monomeric radical that re-entered the particle, i.e.

$$k_d \bar{n} N_c = k_{ct}[M]_p P_{ex} N_1 + k_d P_{re} P_{ex} N_1 \quad (16)$$

where k_{ct} is the chain transfer rate constant, k_d is the exit

rate coefficient, P_{re} is the probability of the free monomeric radical in the aqueous phase entering the polymer particle. Rearranging equation (16) for k_d yields

$$k_d = \frac{k_{ct}[M]_p P_{ex}}{1 - P_{re} P_{ex}} = k_{ct}[M]_p \frac{K_o}{(1 - P_{re})K_o + k_p[M]_p} \quad (17)$$

where equation (15) has been used for P_{ex} .

Equation (17) is the same as the relationship derived by Asua *et al.*⁷. However, P_{re} in the equation requires further elaboration than that given by Asua *et al.*⁷. Consider the events and reactions involving the uncharged monomeric radical in the aqueous phases. These are:

$$\text{Propagation rate: } k_{pw}[M]_w[U_1 \cdot]_w \quad (18)$$

$$\text{Termination rate: } k_{tw}[T \cdot][U_1 \cdot]_w \quad (19)$$

$$\text{Adsorption rate: } k_a[U_1 \cdot]_w N_o \quad (20)$$

where $[M]_w$ is the monomer concentration in the aqueous phase, $[U_1 \cdot]$ is the concentration of the uncharged monomeric radical in the aqueous phase, N_o is the number of polymer particles per unit volume that do not contain any radical, and the mass transfer coefficient k_a is that given⁷ by

$$k_a = 2\pi D_w d_p \left(1 + \frac{6D_w}{m_d D_p}\right)^{-1} \quad (21)$$

Here $[T \cdot]$ is the concentration of all the radicals in the aqueous phase and is given by

$$[T \cdot] = \sum_{i=0}^{z-1} C_i \cdot + \cdot U_1 \cdot + U \cdot \quad (22)$$

Note that $U \cdot$ denotes all the uncharged free radicals excluding $U_1 \cdot$. As discussed earlier, only the uncharged monomeric radical $U_1 \cdot$ in the aqueous phase can re-enter the polymer particles that are devoid of free radicals as shown in equation (20).

The probability of re-entry follows from equations (18), (19) and (20):

$$P_{re} = \frac{k_a N_o}{k_{pw}[M]_w + k_{tw}[T \cdot] + k_a N_o} \quad (23)$$

where k_{tw} and k_{pw} are usually replaced by k_t and k_p , respectively. Now that the expression for P_{re} has been obtained, the re-entry rate can be written as follows:

Re-entry rate = (exit rate) (re-entry probability of $U_1 \cdot$)

which yields

$$r_{re} = \rho_{re} \left(\frac{N_c}{N_A}\right) = k_d \bar{n} \left(\frac{N_c}{N_A}\right) P_{re} \quad (24)$$

where N_c is the total number of polymer particles per unit volume in aqueous phase. In equation (21), k_a is proportional to the diffusivity of uncharged radicals and inversely proportional to $1 + 6D_w/m_d D_p$. Here, the equilibrium constant of the radicals at the interface, m_d , represents the water solubility. In general, $6D_w/m_d D_p$ is much smaller than unity for monomeric radicals as well as the oligomeric radicals. Since m_d is larger for the oligomeric radicals compared to the monomeric radicals, the value of $6D_w/m_d D_p$ for

the oligomeric radicals is smaller than that for the monomeric radicals, making $1 + 6D_w/m_d D_p$ for the oligomeric radicals even closer to unity. Therefore, k_a is largely determined by the diffusivity of the uncharged radicals. The diffusivity of the uncharged oligomeric radicals in the aqueous phase is smaller than that of the monomeric radical. Hence, only the monomeric radicals are considered here.

The re-entry rate coefficient follows directly from equation (24):

$$\rho_{re} = k_d \bar{n} P_{re} \quad (25)$$

where P_{re} is given by equation (23).

The exit rate obtained here is in the same form as that obtained by Asua *et al.*⁷. However, the content is different because of the expression for the re-entry probability. The re-entry probability that was obtained by considering the entry and the exit together is given by equation (23). The re-entry rate coefficient then follows directly from the equation.

AVERAGE NUMBER OF FREE RADICALS IN PARTICLES AND TOTAL RADICAL CONCENTRATION

For the zero-one system being considered, the total number of polymer particles is simply the sum of N_o and N_1 :

$$N_c = N_1 + N_o \quad (26)$$

It is known that polymerization does take place even when there is no initiator present. This polymerization is due to the thermal effect and is reproducible¹¹. The uncharged free radicals of styrene monomer that are thermally induced can re-enter the polymer particles. This thermal effect should be relatively small when the initiator concentration is relatively low but becomes negligible at high initiator concentrations. A mass balance on N_1 including the thermal effect yields

$$\frac{dN_1}{dt} = (\rho_{re} + \rho_{pe})N_o - k_d N_1 - \rho_{pe} N_1 + \tau N_o \quad (27)$$

where τ is the parameter for the thermal emulsion polymerization effect, i.e. thermal rate coefficient. The coefficient τ is determined by the average number of free radicals in a polymer particle when there is no initiator present, and ρ_{re} is given later (equation (34)).

Assuming the pseudo-stationary state and using equation (26) yields

$$N_1 = \frac{\rho_{pe} + \rho_{re} + \tau}{2\rho_{pe} + k_d + \rho_{re} + \tau} N_c \quad (28)$$

This shows that $N_1 = N_c/2$ when ρ_{pe} is much larger than k_d and ρ_{re} . Using equation (25) in equation (28) yields

$$N_1 = \frac{\{a^2 + 4k_d P_{re}(\rho_{pe} + \tau)\}^{1/2} - a}{2k_d P_{re}} N_c \quad (29)$$

where

$$a \equiv 2\rho_{pe} + k_d(1 - P_{re}) + \tau 2\rho_{pe} + k_d(1 - P_{re}) + \tau \quad (30)$$

Note that equation (30) is an implicit function of N_1 since P_{re} is a function of N_1 . When the thermal effect is negligible, $\tau = 0$.

The concentration of all the radicals in the aqueous phase can be found from the following mass balance:

$$\frac{d}{dt}[\text{T}\cdot] = 2k_{dc}[\text{I}] - k_{tw}[\text{T}\cdot]^2 - \rho_{pe}N_o/N_A - \rho_{re}N_o/N_A + k_dN_1/N_A \quad (31)$$

where ρ_{pe} is the primary entry rate coefficient. Making the pseudo-stationary state assumption, equation (31) becomes, when solved for $[\text{T}\cdot]$

$$[\text{T}\cdot] = (b/k_{tw})^{1/2} \quad (32)$$

where

$$b \equiv 2k_{dc}[\text{I}] - \rho_{pe}N_c/N_A + k_d(1 - P_{re})N_1/N_A \quad (33)$$

Therefore, the primary entry rate coefficient is that given by Maxwell *et al.*⁵, i.e.

$$\rho_{pe} = 2k_{dc}[\text{I}] \left(\frac{N_A}{N_c} \right) \frac{k_{pi}[\text{M}]_w}{k_{pi}[\text{M}]_w + k_{tw}[\text{T}\cdot]} \left(\frac{k_{pw}[\text{M}]_w}{k_{pw}[\text{M}]_w + k_{tw}[\text{T}\cdot]} \right)^{z-1} \quad (34)$$

Maxwell *et al.*⁵ do not take into account the effect of $[\text{U}_1\cdot]$ and $[\text{U}\cdot]$ on $[\text{T}\cdot]$. However, $[\text{T}\cdot]$ is dependent on $[\text{U}_1\cdot]$ and $[\text{U}\cdot]$ as given in equation (22). The effect should be prominent when $[\text{I}]$ is relatively small and k_{dc} is small at low temperatures. The total concentration of free radicals in the aqueous phase affects the primary entry, exit and re-entry of free radical through ρ_{pe} and P_{re} that contain $[\text{T}\cdot]$, leading to the non-linear expressions for the rates.

The solutions for N_1 and $[\text{T}\cdot]$ require numerical solutions of equations (17), (29) and (32) that are coupled. The starting values for the numerical solutions may be taken as follows:

$$[\text{T}\cdot] = (2k_{dc}[\text{I}]/k_t)^{1/2} \quad (35)$$

$$N_1 = N_c/2 \quad (36)$$

POLYMER PARTICLE DIAMETER AND A CRITERION

The results obtained so far are for a zero-one system for which the polymer particle size is small. When the particle size is sufficiently small, a radical within a particle would react and terminate instantaneously with a radical that enters the particle. Therefore, all the polymer particles would have either one or zero radical within the particles. Let us estimate the particle diameter for which the one-zero system holds. Let us consider the case where the propagation rate within the particle is of the same order of magnitude as the termination rate.

The propagation rate is given by equation (10). The termination rate is given by

$$r_t = k_t \left(\frac{2}{N_A V_p} \right) \left(\frac{1}{N_A V_p} \right) \quad (37)$$

By setting the propagation rate equal to the termination rate, one can arrive at the following expression for the

polymer particle diameter:

$$d_p = \left(\frac{12k_t}{\pi k_p [\text{M}]_p N_A} \right)^{1/3} \quad (38)$$

Let us calculate the diameter for polystyrene. For the styrene system⁷, $k_t = 7.0 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_p = 1.25 \times 10^5 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $[\text{M}]_p = 4.8 \times 10^{-3} \text{ mol cm}^{-3}$, $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$. These numbers, when substituted into equation (38), yield a diameter of $9.04 \times 10^{-6} \text{ cm}$ or about 90 nm. For the condition where $r_t \gg r_p$, say $r_t = 100r_p$, the diameter becomes about 10 nm. It is seen that the range of the diameter for instantaneous termination is 10 to 90 nm.

Consider now the probability that a radical can enter a polymer particle that contains an existing radical ($n = 1$). The probability P_m is

$$P_m = \frac{\rho_{pe} N_1 V_p}{k_p [\text{M}]_p + K_o + \rho_{pe} N_1 V_p} \quad (39)$$

which can be approximated as follows:

$$P_m \approx \frac{\rho_{pe} N_c V_p}{k_p [\text{M}]_p + K_o} \quad (40)$$

Suppose that one wants to obtain the particle diameter for which the probability of the entry is 0.0001. Using P_m of 0.0001 in equation (40) and solving the equation for d_p yields

$$d_p = \left(\frac{0.0012 k_p [\text{M}]_p}{\pi \rho_{pe} N_c} \right)^{1/3} \quad (41)$$

where $k_p [\text{M}]_p$ is set equal to K_o since they are of the same order of magnitude. Combining equations (34) and (41) yields

$$d_p = \left(\frac{0.0006 k_p [\text{M}]_p}{\pi k_{dc} [\text{I}] \sigma N_A} \right)^{1/3} \quad (42)$$

where σ is defined as follows:

$$\rho \equiv \frac{k_{pi} [\text{M}]_w}{k_{pi} [\text{M}]_w + k_{tw} [\text{T}\cdot]} \left(\frac{k_{pw} [\text{M}]_w}{k_{pw} [\text{M}]_w + k_{tw} [\text{T}\cdot]} \right)^{z-1} \quad (43)$$

The particles with a diameter less than that given by equation (42) have a probability of less than 0.01% that a free radical would enter particles that already have one radical. Therefore, within that probability, the system can be considered a one-zero system.

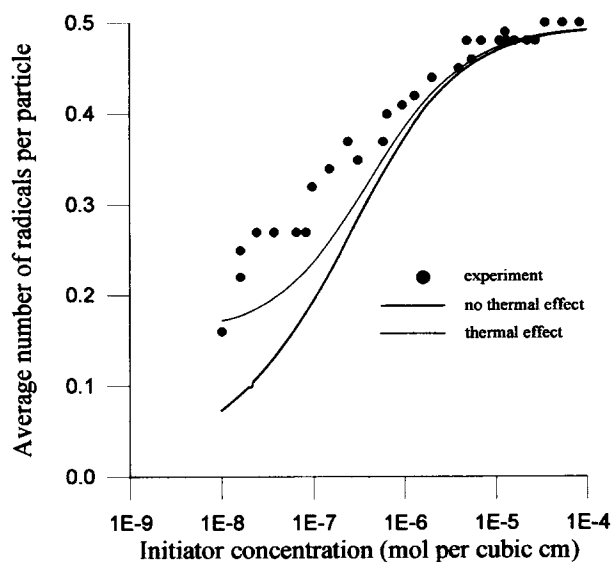
Let us calculate the diameter for the styrene emulsion system. On using $k_{dc} = 4.8 \times 10^5 \text{ s}^{-1}$, $[\text{I}] = 1.0 \times 10^{-5} \text{ mol cm}^{-3}$, $\sigma = 1$ (underestimating the diameter) it is about 700 nm. Both equation (38) and equation (42) can be used as a criterion for determining the diameter below which the zero-one system is valid. But the diameter of a polymer particle calculated by equation (38) is less than that calculated by equation (42). Therefore, equation (38) is to be used as the more conservative criterion for determining the diameter below which the zero-one system is valid.

DISCUSSION AND APPLICATION TO LITERATURE DATA

The strength of the results obtained so far lies in the ability to describe the radical exit and entry processes

Table 1 Basic parameters at 50°C

	k_{dc} (s^{-1})	k_t ($cm^3 mol^{-1} s^{-1}$)	k_p ($cm^3 mol^{-1} s^{-1}$)	k_{ct} (s^{-1})	$[M]_p$ ($mol cm^{-3}$)	$[M]_w$ ($mol cm^{-3}$)	D_w ($cm^2 s^{-1}$)	d_p (cm)	N_c (cm^{-3})
Rate constant	1.3×10^{-6}	7.0×10^{10}	2.58×10^5	14	5.8×10^{-3}	4.5×10^{-6}	4.0×10^{-6}	6.2×10^{-6}	4.9×10^{13}
Reference	3	3	10,11	11	7,11	$[M]_p/[M]_w = 1300$	11	11	11

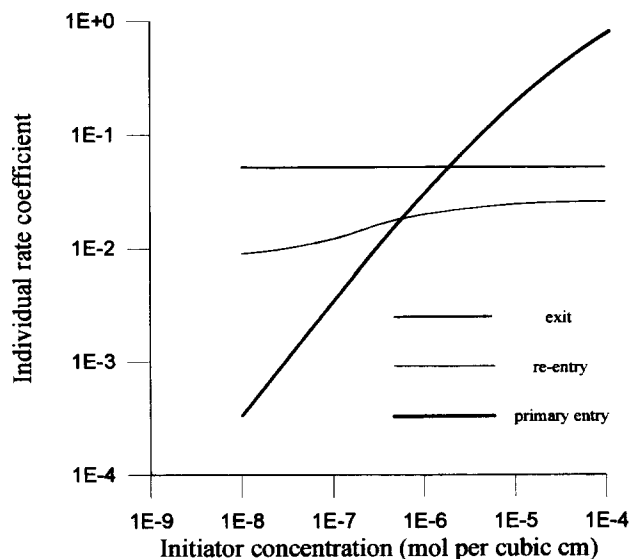
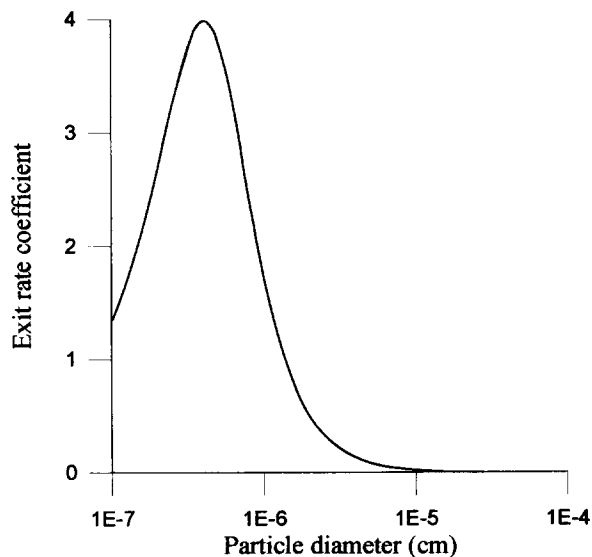
**Figure 1** Average number of radicals per particle (experimental values are from ref. 11)

without having to resort to fitting parameters, i.e. *a priori* model.

Shown in *Figure 1* is a comparison between experiment (filled circles) and our model predictions for the average number of free radicals in a polymer particle as a function of initiator concentration. The basic parameters used in the prediction are summarized in *Table 1*. The solid line in *Figure 1* represents the prediction when no thermal effect is included, this is $\tau = 0$ and the dotted line is for the prediction when the thermal effect is included. The average number of free radicals in a polymer particle is 0.16 in the experiment¹¹ without the initiator according to the calculated value of τ , which is 1.6×10^{-3} . As discussed earlier, the thermal effect is relatively significant only at low initiator concentrations and therefore τ can be negligible at high concentrations. It is seen from the figure that the average number of free radicals in a polymer particle \bar{n} converges to 0.5 as the initiator concentration increases.

The experimental value of \bar{n} is that at steady state, i.e. an average over the particle diameter range that changes with time. In the theory (model), the value used is that at the start of the experiment, i.e. one that corresponds to the initial particle diameter. In reality, the diameter increases and the value of k_d decreases as polymerization progresses, which should result in an increase of \bar{n} . Therefore, the theoretical values in the figure are in general smaller than the experimental ones.

Dependence of primary entry rate coefficient, exit rate coefficient and re-entry rate coefficient on initiator concentration is shown in *Figure 2*. The basic parameters given in *Table 1* are also used to show the trends. Strictly speaking, the exit rate coefficient is not independent of the initiator concentration. However,

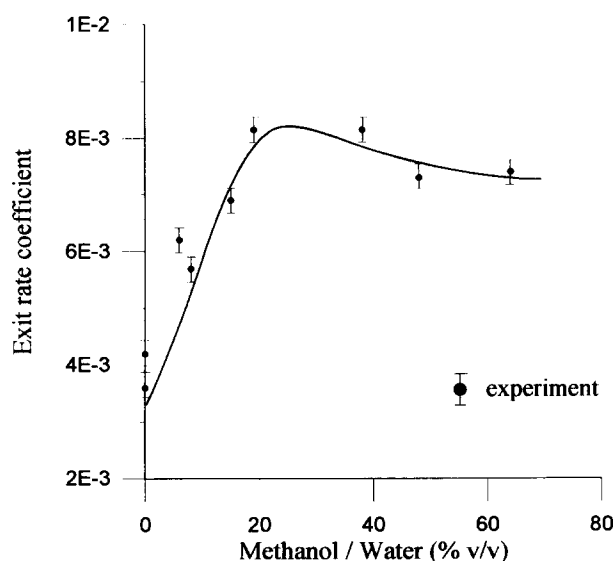
**Figure 2** Dependence of individual rate coefficient on initiator concentration**Figure 3** Exit rate coefficient as a function of particle diameter

$(1 - P_{re})K_o \ll k_p[M]_p$ for the system being considered. Thus, the exit rate coefficient k_d can be approximated as $k_{ct}K_o/k_p$. Therefore, the predicted value of k_d shown in *Figure 2* becomes approximately independent of the initiator concentration. It is seen that at low concentrations, the primary entry rate is lower than the re-entry rate whereas the trend is reversed as the concentration increases.

Dependence of the exit rate coefficient on the average number of free radicals is significant when the particle diameter is small and the initiator concentration is large.

Table 2 Basic parameters at 30°C

	k_{dc} (s ⁻¹)	k_t (cm ³ mol ⁻¹ s ⁻¹)	k_p (cm ³ mol ⁻¹ s ⁻¹)	k_{ct} (s ⁻¹)	$[M]_p$ (mol cm ⁻³)	$[M]_w$ (mol cm ⁻³)	D_w (cm ² s ⁻¹)	d_p (cm)	N_c (no. cm ⁻³)
Rate constant	4.8×10^{-8}	7.0×10^{10}	1.25×10^5	1.5	4.8×10^{-3}	3.0×10^{-6}	5.4×10^{-6}	1.2×10^{-6}	1.0×10^{10}
Reference	5	5	4,13	4,11,13	13	$[M]_p/[M]_w = 1600$	13	13	

**Figure 4** Exit rate coefficient as affected by monomer solubility in the aqueous phase

Shown in *Figure 3* is the dependence of the exit rate coefficient on the particle diameter. The basic parameters used are those in *Table 1*. It is seen that the exit rate is large for particle diameters larger than 5 nm but is small and almost constant for particles larger than, say, 100 nm. When the particle diameter is very small, K_o becomes very large as shown in equation (13) and P_{ex} approaches unity (see equation (15)). Therefore, k_d is determined by P_{re} as indicated in equation (17). Since P_{re} is approximately proportional to the diameter (d_p), k_d first increases with increasing diameter. This is the physical effect of the monomeric radical encountering the particle. However, as the diameter gets larger, i.e. the effect of the encounter is negligible, k_d becomes inversely proportional to d_p^2 and thus it decreases with increasing d_p . The dominant physical effect is that the monomeric radical transfers into the particle. Note that k_d is for the next exit rate, i.e. the difference between P_{re} and P_{ex} . Depending on which of the two dominates, the value of k_d either becomes proportional to d_p (controlling diffusion of monomeric radical) or inversely proportional to d_p^2 (controlling mass transfer of monomeric radical).

The average number of free radicals in a particle is determined by the exit rate coefficient k_d when the particle diameter is small since the primary entry rate is independent of the particle diameter. This fact, together with the large exit rate when the particle diameter is small, means that by the time the small nuclei formed in the interval I reach a certain size that is still small and the number of small particles becomes constant, i.e. interval II, the system becomes a zero-one system. That is, the models developed here are applicable to interval II.

Experiments on the dependence of the exit rate coefficient k_d have been reported by Adams *et al.*¹² for monomer solubility in the aqueous phase, and corresponding analyses were carried out by Adams *et al.*¹² and Asua *et al.*¹³. Shown in *Figure 4* is a comparison between the experiments and our model predictions. The basic parameters used are those in *Table 2*.

The experimental results reproduced in the figure show a maximum, which could not previously be explained. Our model, however, does predict the maximum. The origin of this behaviour is the re-entry rate or the dependence of k on the total free radical concentration. This behaviour is similar to that in *Figure 3*. The difference is that a higher methanol concentration corresponds to a smaller particle diameter and a lower concentration corresponds to a larger diameter. Our model results, as shown in the figure, indicate that the maximum does not exist when the number of particles is relatively small.

SUMMARY

The re-entry rate in emulsion polymerization has been reformulated by taking into account both the entry and the exit rate together. In the process, the entry and the exit rate coefficients are more rigorously expressed. The reformulation allows one to model the entry and exit processes only with basic parameters determined in independent experiments without having to resort to adjusting various parameters to fit the data. It also enables the prediction of peculiar exit rate behaviour that was inexplicable hitherto, and explains precisely how the average number of free radicals in a particle converges to 0.5 as the initiator concentration is increased. The formulation given here gives additional information on the particle size dependence of the exit rate. It also reveals the non-linear nature of the rates involving free radicals, which are usually taken as linear processes.

A criterion has been derived for determining the applicability of the zero-one system to emulsion polymerization. Our model results are applicable to interval II of the polymerization, for which the system is zero or one in terms of the number of free radicals in a polymer particle. Finally, the thermal rate coefficient has to be determined in an independent experiment and should be included in the model when the initiator concentration is low.

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APPENDIX

If the monomeric free radical induced by the exit from the particle might re-enter a particle without free radical as well as a particle with one free radical, then the balance on

the number of particles with one free radical yields:

$$\frac{dN_1}{dt} = (\rho'_{re} + \rho_{pe})N_0 - k_d N_1 - (\rho'_{re} + \rho_{pe})N_1 + \rho N_0 \quad (A1)$$

Assuming that instantaneous termination occurs when the free radical enters the particle with one free radical, the pseudo-steady state version of equation (A1) is

$$N_1 = \frac{\rho_{pe} + \rho'_{re} + \tau}{2\rho_{pe} + k_d + 2\rho'_{re} + \tau} N_c \quad (A2)$$

where the re-entry rate coefficient ρ'_{re} in equation (A1) or equation (A2) is different from ρ_{re} in equation (28). The re-entry rate coefficient ρ'_{re} now takes into account the fact that the monomeric free radical that desorbs may re-enter all the particles. Thus the probability P'_{re} here is different from that in the text. The probability that the monomeric free radical induced by the desorption from the particles re-enters all the particles is

$$P'_{re} = \frac{k_a N_c}{k_{pw}[M]_w + k_{tw}[T \cdot] + k_a N_c} \quad (A3)$$

Therefore, the re-entry rate coefficient, ρ'_{re} is given as follows:

$$\rho'_{re} = k_d \bar{n} P'_{re} \quad (A4)$$