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# Behavior of free radical transfer between aqueous phase and latex particles in emulsion polymerization

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**Abstract**

The free radical transfer between aqueous phase and latex particles was investigated in the seeded emulsion polymerization using potassium persulfate (KPS) as an initiator. The effects of seed particle size, initiator concentration and polymerization temperature on the radical entry into and/or exit from the particles were emphatically examined. The results suggest that the aqueous-phase radical entry into the particles should be a competitive process, i.e. the competition between radical diffusion from the bulk aqueous phase to the interface of particles and its reactions in the aqueous phase determines whether it may be adsorbed into the particles or not. This implies that the reactions and properties of radicals in the aqueous phase play an essential role in particle nucleation in the emulsion polymerization.

*Keywords:* Emulsion polymerization; Radical entry and exit; Particle nucleation

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## 1. Introduction

Emulsion polymerization has received a great deal of attention due to its widespread applications for recent several decades [1–3]. However, because of its complexity and heterogeneity, the particle nucleation has been ambiguous though at least three kinds of mechanisms, namely, micellar [4,5], homogeneous [6–8] and precursor nucleation (or homogeneous-coagulation nucleation) [9], have been proposed so far. One of the above-mentioned mechanisms, dependent on the solubility of monomer in water, has been selected to describe the behavior of particle nucleation involved in the specific emulsion polymerization, but there has been little strong experimental evidence that enables to completely support or refute one of the proposed ones [10]. Actually, particle nucleation in an emulsion polymerization is tightly related with a number of difficult processes such as radical diffusion, adsorption and desorption as well as its various reactions in diverse phases. Therefore, to well understand the behavior of radical entry into and exit from the species (e.g. particles, micelles) and to efficiently evaluate the profound experimental data such as the size and its distribution of particles initially formed seem to be more helpful to clearly elucidate the behavior of particle nucleation in an emulsion system. This is because they presumably induce us to recognize the phenomenon of particle nucleation for the case of emulsion polymerization. To date, some arguments of radical entry into particles, e.g. diffusion [11], collision [12], colloid [13,14] and propagation controlled entry processes [15], have been proposed. Napper and Gilbert's group [16] reported that particle size distribution at the end of nucleation period in the emulsion polymerization occurred skewed. They thought that either the acceleration of particle nucleation or the coagulation of primary particles appeared at the entire nucleation stage. Brooks [17] found no apparent change in the rate coefficient of radical entry into the particles even though emulsifier concentration initially charged was sharply decreased in the seeded styrene emulsion polymerization without the existence of monomer droplets. It was evident that radical movement through the water/particle interface should not be a rate-determined step for its transport between aqueous phase and the particles. It also reflected that the radicals entering the particles should be of suitable properties. Nevertheless, it was reported that there was no obvious change in the rate coefficient of radical entry into latex particles using an irradiation initiation with varying ionic or irradiation strength [18].

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In this paper, the rate coefficients of radical entry into and exit from particles were measured by means of the seeded emulsion polymerization. The effects of the sizes of seed latex, initiator concentration and polymerization temperature on the adsorption and desorption rate coefficients were emphatically investigated. In addition, a novel argument of radical entry was proposed, and then a series of equations for the determination of entry rate coefficient were developed, and finally simulated numerically in order to demonstrate its validity.

## 2. Experimental part

### 2.1. Materials

Styrene (St) was distilled under a reduced-pressure nitrogen atmosphere after washed with a dilute NaOH solution and then deionized water. Potassium persulfate (KPS) was purified via recrystallization before use. Sodium lauryl sulfate (SLS) with extra pure grade was adopted as an emulsifier without any treatment, and other reagents used were of high quality.

### 2.2. Preparation of seed particles

Seed polystyrene (PS) particles were prepared using emulsion polymerization with a small addition of SLS at 70 °C. A typical recipe was St/SLS/$H_2O$/KPS = 10.0/0.2/150/0.35 (wt/wt). The reactants except initiator solution were charged into the reactor and then deoxygenated by bubbling highly pure nitrogen for 30 min under stirred condition. The polymerization began after rapidly injecting initiator solution, and generally ended at the conversion over 98%. The obtained seed latexes were purified via the process of centrifugation, decantation and redispersion. Seed particle size and its distribution were determined by means of transmission electron microscopy (TEM).

### 2.3. Seeded emulsion polymerization

Seeded emulsion polymerization was carried out at 50 °C in the same apparatus as that used in the seed preparation. One of typical recipes was consisted of the ratio of monomer to polymer 0.1 wt/wt, KPS $5.0 \times 10^{-4}$ mol/l-water and SLS 0.05 g/l-water. Seed PS latex particles were first swollen under a moderate stirring for 8 h with a small amount of SLS added in order to avoid the coagulation of latex particles. The initiator solution was injected to induce the seeded emulsion polymerization after the mixture was raised to desired temperature. The samples were periodically withdrawn in order to gravimetrically determine the conversions during the course of polymerization. The particle size and its distribution were measured using dynamic light scattering (DLS), and observed by TEM to distinguish whether secondary nucleation occurred.

### 2.4. Evaluation of rate coefficients of radical entry and exit

The rate coefficients of free radical entry and exit are estimated by the following equations, as previously reported [19], where made is the assumption that each particle contains at most one radical anytime. Here, the instantaneous population balance equations are written as

$$\frac{dN_0(t)}{dt} = -\rho(N_0(t) - N_1(t)) + kN_1(t) \tag{1}$$

$$\frac{dN_1(t)}{dt} = \rho(N_0(t) - N_1(t)) - kN_1(t) \tag{2}$$

where $\rho$, $k$ are the rate coefficients of radical entry into and exit from the particles, respectively. $N_0(t)$, $N_1(t)$ indicate the numbers of polymer particles containing no and one radical at $t$ time, respectively. To apply Laplace transform to Eqs. (1) and (2), and hence the general solution is given as follows

$$N_1(t) = \frac{\rho}{2\rho + k} + \left[\frac{\rho - (2\rho + k)N_1(t = t_0)}{(2\rho + k)}\right] \times \exp[-(2\rho + k)t] \tag{3}$$

where $N_1(t = t_0)$ is the number of particles containing one radical at $t = t_0$. Supposing that no monomer droplet appears at the initial stage of seeded emulsion system, the conversion will be logarithmically proportional to the reaction time, namely, $\ln(1 - \chi(t)) - \ln(1 - \chi(t = 0)) = at + b$. Therefore, the rate coefficients of radical entry and exit are given as

$$\rho = -\frac{a^2}{bA}\left[1 - \frac{A}{b}N_1(t = t_0)\right] \tag{4}$$

$$k = \left[\frac{A}{b} - 2\right]\rho = -\frac{a^2}{bA}\left[\frac{A}{b} - 2\right]\left[1 - \frac{A}{b}N_1(t = t_0)\right] \tag{5}$$

where $A = k_p[M]_p/(N_A v_p)$, $k_p$ is the propagation rate constant, $[M]_p$ expresses the monomer concentration inside the particle, $v_p$ is the volume of one particle and $N_1(t = 0) = 0$ in our case.

## 3. Results and discussion

### 3.1. Seeded emulsion polymerization

In order to evaluate the rate coefficients of radical entry into and exit from the particles using the mode of seeded emulsion polymerization, it seems necessary to avoid the appearance of secondary nucleation there. The latex particles produced after seeded emulsion polymerizations were observed via TEM. The typical TEM views of the particles before and after seeded polymerization are shown in Fig. 1. It was found that no new particles were formed under the present experimental conditions. Therefore, it was regarded that the polymerization solely occurred inside the particles, if neglecting the consumption of monomer in the aqueous phase. A series of the conversion-time profiles obtained in the seeded emulsion polymerization with different initiator concentrations are shown in Fig. 2. The conversions gradually increased with the increase in reaction time during the initial stage of polymerizations. Since the polymerization runs were carried out in the absence of monomer droplets, the dependence of the conversion upon the reaction time was dealt with as Eqs. (4) and (5), the rate coefficients of radical entry into and exit from the particles were thus determined.

### 3.2. Effect of seed particle size

Fig. 3 shows the effect of seed particle size on the rate coefficients of radical absorption and desorption in the seeded emulsion polymerizations where a series of monodispersed seed particles of different sizes were adopted. The entry rate coefficient was proportional to the 0.45 power of the size of particles. It was obvious that the power order in the present case was not in accordance with the value of 2.0 for the case of collision-controlled entry and 0.8 for diffusion entry [12]. Thus, the argument of collision-controlled radical entry into particles was denied. The above conclusive announcement was strongly supported by the fact that the rate coefficient of radical entry was not linearly proportional to the number of seed particles [13,14]. However, from the result it seems insufficient to ignore the contribution of radical diffusion in the aqueous phase on the radical entry into the particles in the emulsion polymerization.

Fig. 3 also shows the dependence of the rate coefficient ($k$) of radical exit from the particles upon the radius of particles. The desorption rate coefficient was proportional to the $-1.7$ power of seed particle size. The power level was quite consistent with that given by Gilbert [20]. Furthermore, the value of $k$ for the case of the presence of monomer droplets was of the same order of magnitude as that for the case of the absence of ones. This influences that the exit rate of free radical from the particles was hardly affected by the monomer concentration inside the particles to a certain extent. Nomura [21] discussed the influences of diffusion inside the particle and in the aqueous phase on the rate of radical desorption. He pointed out that the diffusion of an exit radical inside the particle became more important only at high conversion, but at usual circumstance, its diffusion in the aqueous phase should be dominant. However, our result implies that the rate-determining step(s) for free radical desorption in the present polymerization system really occur in the aqueous phase and/or o/w interface, not inside the viscous monomer-swollen particles.

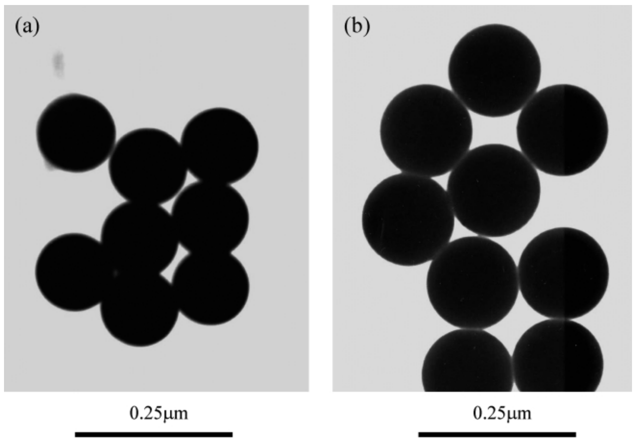

Fig. 1. Typical TEM views of seed particles (a) and the particles after seeded emulsion polymerization (b).

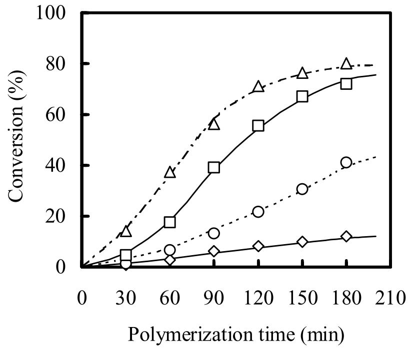

Fig. 2. The typical conversion vs. time profiles in the seeded emulsion polymerization. $[M_0] = 0.1$ g/l-water; $N_p = 3.0 \times 10^{14}$ particles/l-water; $T = 50$ °C; $[I_0] = 5.0 \times 10^{-5}$ (◇); $1.0 \times 10^{-4}$ (○); $3.0 \times 10^{-4}$ (□); $3.0 \times 10^{-3}$ (△) mol/l-water.

### 3.3. Effect of polymerization temperature

The effect of polymerization temperature on the rate coefficient of radical adsorption is represented in Fig. 4. The apparent activation energy for the radical entry into the particles was estimated to be approximately 74.9 kJ/mol in the present case. The value suggested that free radical entry into the particles should not be determined by a single

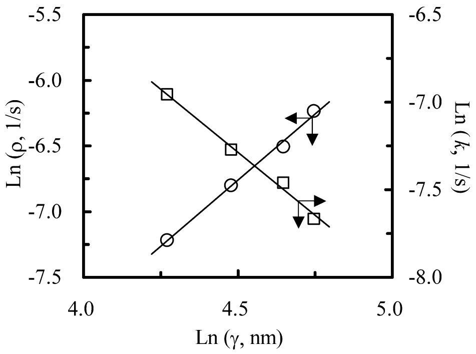

Fig. 3. Dependence of rate coefficients of radical entry into and exit from the particles on the radius of seed particles. $[I_0] = 3.0 \times 10^{-4}$ mol/l-water; $N_p = 3.0 \times 10^{14}$ particles/l-water; $T = 50$ °C.

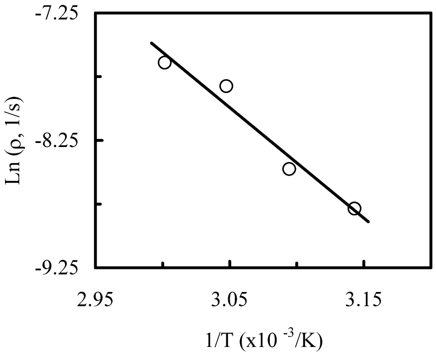

Fig. 4. Effect of the temperature on the rate coefficient of radical entry into the particles. $[M_0] = 0.1$ g/l-water; $[I_0] = 10^{-4}$ mol/l-water; $N_p = 3.0 \times 10^{13}$ particles/l-water.

propagation process [22]. As well known, the adsorption of aqueous-phase radicals into the particles presumably undergoes three procedures, namely, the diffusion of adsorbed radicals from the bulk of aqueous phase to the interface of particle/water; then its transfer through the interface layer with the dense coverage of surfactant molecules if available; finally its mobility inside the particles in which polymerization is initiated. According to the above descriptions, diffusion process seems necessary for the radicals to cross towards the particle/water interface and really plays a certain role in radical entry into the particles in an emulsion system. As for the emulsion system in the presence of a highly water-soluble initiator, primary radicals originated from the decomposition of initiator and/or even the radicals added several monomer units are of strongly hydrophilic. Such hydrophilic radicals have to modify their characters via various reactions in the aqueous phase in order to fulfill the required properties for the entry. Oligomeric radicals containing hydrophilic and hydrophobic segments are more appropriate to transport between aqueous phase and the monomer-swollen particles. Here, the oligomeric radicals bearing the above-said properties are termed as *surfactant-like* ones. Thermodynamically speaking, such radicals enable to smoothly transfer from the aqueous phase to the particles though some effects including steric hindrance probably exist. Thus, with respect to the whole process of radical entry, the first step should be for primary radicals to propagate in the aqueous phase to establish so-called surfactant-like nature with accompanying their reactions in the aqueous phase, the second for surfactant-like radicals to diffuse through the bulk of aqueous phase and the interface of water/particle, and the third to enter the particles. Of course, the above procedures have not been clearly discriminated yet because of their complexities. However, it is obvious that the diffusion of surfactant-like oligomeric radicals from the aqueous phase to the particles for their entry into particles should be simultaneously coexisted with their reactions in at least two phases, especially in the aqueous phase.

### *3.4. Effect of initiator concentration initially charged*

Fig. 5 shows the effect of initiator concentration initially charged on the rate coefficient of radical entry into the particles. The rate coefficient was monotonically increased as the initiator concentration was raised. In the higher initiator concentration, the constant tendency of the entry rate coefficient was observed. If the efficiency of radical entry could be defined as the entry rate divided by the production rate of radicals in the aqueous phase, the entry efficiency was reduced as the initiator concentration initially charged was increased. This means that the decomposition of initiator in the aqueous phase was not a rate-determining step for the entry event. The decrease in the radical entry efficiency is probably caused by various reactions in the aqueous phase when the radicals are developing their thermodynamic properties and diffusing towards the water/particle interfaces.

### *3.5. A novel argument of radical entry into latex particles*

Based on the results described above, proposed was the novel argument of radical entry into the particles involved in the emulsion system using a conventional water-soluble initiator, as expressed as follows

$$\begin{aligned} &R_i^* \xrightarrow{k_\rho} P \text{ (entry)}, \\ &R_i^* + M \xrightarrow{k_p} R_{i+1}^* \text{ (propagation)} \quad (z \le i \le s) \end{aligned} \tag{6}$$

where the radicals with the chain length from $z$ (shortest) to $s$ (longest) are assumed as surfactant-like ones that satisfy the necessary properties for the entry. The levels of $z$ and $s$ depend mainly upon the physiochemical characters of initiator and monomer used. Eq. (6) takes into account: (1) that only oligomeric radicals with reasonable thermodynamic nature enable to complete their entry into the particles due to the minimum of various interferences, and (2) that the competition between the aqueous reactions, mainly propagation, and diffusion of so-called surfactant-like radicals determines whether they enter the particles or

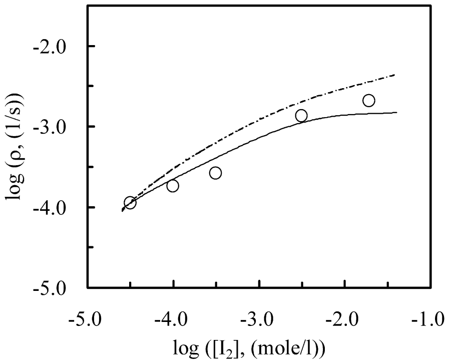

Fig. 5. Effect of initiator concentration on the rate coefficient of radical entry into the particles in the emulsion polymerization. $[M_0] = 0.1$ g/l-water; $N_p = 3.0 \times 10^{14}$ particles/l-water; $T = 50$ °C.

not. The above scheme reflects that the combination of thermodynamic and kinetic behavior of oligomeric radicals contributes on the radical entry into the particles in the emulsion polymerization.

To verify the entry concept, a mathematical model will be derived out. At first, let us define the average rate coefficient of radical entry into the particles as [15]

$$\rho = k_\rho (N_\mathrm{A}/N_\mathrm{p}) \sum_{i=z}^{s} [R_i^*] \qquad (7)$$

where $[R_i^*]$ is the concentration of radical with chain length $i$, $N_\mathrm{p}$ and $N_\mathrm{A}$ are the number of particles and Avogadro's number, respectively. $k_\rho$ is the rate constant of Eq. (7). In combination with the population balance equations of radicals in the aqueous phase, a series of model equations are established as follows

$$\rho = k_\rho (N_\mathrm{A}/N_\mathrm{p}) \alpha_1^{z-2} \left\{ \frac{\alpha_2 - \alpha_2^{s-z+2}}{1-\alpha_2} \right\} [\mathrm{M}^*] \qquad (8)$$

where

$$\alpha_1 = \frac{k_\mathrm{p}[\mathrm{M}]_\mathrm{w}}{k_\mathrm{p}[\mathrm{M}]_\mathrm{w} + 2k_\mathrm{t}[R^*]} \qquad (8a)$$

$$\alpha_2 = \left( \frac{1}{\alpha_1} + \frac{k_\rho}{k_\mathrm{p}[\mathrm{M}]_\mathrm{w}} \right)^{-1} \qquad (8b)$$

$$[R^*] = \Bigg\{ \left( \frac{1-\alpha_1^{z-1}}{1-\alpha_1} \right) + \alpha_1^{z-2} \left( \frac{\alpha_2 - \alpha_2^{s-z+2}}{1-\alpha_2} \right) + \alpha_1^{z-2}\alpha_2^{s-z+1} \left( \frac{\alpha_1 - \alpha_1^{n-s+1}}{1-\alpha_1} \right) \Bigg] \Bigg\} [\mathrm{M}^*] \qquad (8c)$$

$$[\mathrm{M}^*] = \frac{2k_\mathrm{d}[\mathrm{I}_2]}{k_\mathrm{p}[\mathrm{M}]_\mathrm{w} + 2k_\mathrm{t}[R^*]} \qquad (8d)$$

$n$ is the critical chain length of oligomeric radicals precipitated out in the aqueous phase, $[\mathrm{I}_2]$ and $[\mathrm{M}]_\mathrm{w}$ are the concentrations of initiator and monomer in the aqueous phase, respectively, $k_\mathrm{d}$ is the decomposition rate constant of initiator, $k_\mathrm{p}$ and $k_\mathrm{t}$ are the rate constants of propagation and termination, respectively.

The established equations were numerically simulated using the values of parameters as shown in Table 1 to evaluate the rate coefficient of radical entry. A comparison between the model simulated and the experimental data has also been shown in Fig. 5. The solid line was given by the present model and the dotted line was by Maxwell's one that was based on the propagation-controlled entry of radicals [15]. Apparently, a significant agreement was clearly observed. Fig. 6 shows another comparison between the observed and simulated data. The solid line indicated the predicted values and the open points were experimental data given by Maxwell [15]. It was clear that the predicted results had a good agreement with the observed values. As to a sparingly water-insoluble styrene monomer, the propagation rate in the aqueous phase is much smaller due to very low monomer concentration in the aqueous phase, and the range of chain length of oligomeric radicals entering the particles seems relatively narrow. In that case, the lifetime of oligomeric radicals in the aqueous phase may be short, and even near to that of the diffusion of the radicals absorbed into the particles. The propagation and diffusion of the radicals in the aqueous phase really compete each other during the course of radical entry. Nevertheless, it was worth noting that the difference of entry rate coefficient between in Fig. 5 and in Fig. 6 was probably caused by different experimental conditions, specially the number and size of seed particle used.

The present concept of radical adsorption probably induces a novel argument for particle nucleation in a conventional emulsion polymerization. The water-soluble initiator used in an emulsion system initially decomposes and hence generates almost highly hydrophilic primary radicals. The primary radicals have to propagate in order to gain proper hydrophobicity in the aqueous phase. How many monomeric units should be added depends mainly upon the characteristic of monomer itself. The produced oligomeric radicals that have an appropriate range of chain length diffuse from aqueous phase and then enter monomer-swollen micelles from which mature particles are easily formed due to rapid polymerization. On the other hand, some oligomeric radicals that exceed the

Table 1
The parameters used in the model simulations

| Parameter (unit) | Value | | Reference |
|---|---|---|---|
| | Maxwell's data | Present data | |
| $k_\mathrm{p}$ (dm$^3$/mol/s) | 258 | 258 | [20] |
| $k_\mathrm{tw}$ (dm$^3$/mol/s) | $3.7 \times 10^9$ | $3.7 \times 10^9$ | [15] |
| $k_\mathrm{d}$ (1/s) | $10^{-6}$ | $10^{-6}$ | [23] |
| $k_\rho$ (1/s) | 39.7 | 3.4 | This work |
| $[\mathrm{M}]_\mathrm{w}$ (mol/dm$^3$) | $4.31 \times 10^{-3}$ | $3.37 \times 10^{-3\mathrm{a}}$ | [24] |
| $z$ | 2 | 2 | [15] |
| $s$ | 3 | 3 | This work |

[a] $[\mathrm{M}]_\mathrm{w} = ([\mathrm{M}]_\mathrm{p}/[\mathrm{M}]_\mathrm{psat})^{0.6}[\mathrm{M}]_\mathrm{wsat}$ [15].

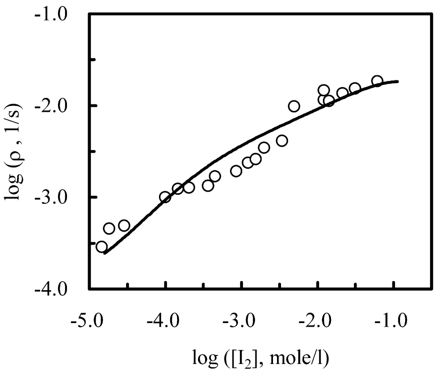

Fig. 6. A comparison between the observed (points) and predicted (line) rate coefficients of radical entry into the particles. Experimental data from Maxwell et al. [15].

critical chain length are impossible to adsorb into monomer-swollen micelles due to steric hindrance and the lack of thermodynamic nature, but it seems possible for those radicals to become the particles only if continuously propagating until precipitation with accompanying the adsorption of surfactant molecules in the aqueous phase. Which of the two routes described above has not been significantly discriminated yet, but it is reasonably thought that particle nucleation may be related with the reactions and nature of oligomeric radicals just in the aqueous phase.

## 4. Conclusions

The rate coefficients of radical entry into and exit from the particles were determined using seeded emulsion polymerization under the condition of the existence of no monomer droplets. The effects of the seed particle size, initiator concentration and the temperature on the entry and exit rate coefficients were examined. The results suggested that radical entry exhibited the competitive process between the diffusion and various reactions of oligomeric radicals in the aqueous phase. Based on the consideration of competitive radical entry, the model equation of radical entry into the particle in the emulsion polymerization was established, and its validity was then demonstrated by comparing the simulated results with experimental data. In addition, it was found that the rate-determining step for the radical exit from the particles was in the aqueous phase, not inside the particles.

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