

# Rate Coefficient for Radical Desorption in Emulsion Polymerization

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## Synopsis

Investigators have proposed the rate coefficient for radical desorption from polymer particles to explain the kinetic deviation of the emulsion polymerization of water-soluble monomers such as vinyl acetate and vinyl chloride from the classical Smith and Ewart theory.<sup>6</sup> In this article, the rate coefficient for radical desorption is theoretically derived by a different approach, and its applicability to vinyl acetate and vinyl chloride emulsion polymerization is examined in detail using experimental data available in the literature. The theory developed here predicts the average number of radicals per polymer particle in the emulsion polymerization of vinyl acetate and vinyl chloride.

## INTRODUCTION

The kinetic behavior of emulsion polymerization is greatly affected by radical desorption from polymer particles.<sup>1-5</sup> The deviation of the kinetic behavior of the emulsion polymerization of water-soluble monomers such as vinyl acetate and vinyl chloride from the Smith-Ewart case II kinetic theory<sup>6</sup> is partially due to dominant desorption of radicals from the polymer particles. Although the importance of this physical phenomenon was pointed out by Smith and Ewart in the 1940s, the quantitative understanding was insufficient to explain the kinetic deviation of the emulsion polymerization of vinyl acetate or vinyl chloride from the Smith-Ewart case II kinetic theory.

Recently, Ugelstad et al.<sup>1</sup> proposed a semiempirical rate coefficient for radical desorption in vinyl chloride emulsion polymerization. On the other hand, the present authors<sup>3</sup> have derived a rate coefficient for radical desorption theoretically with a stochastic approach and have successfully applied it to vinyl acetate emulsion polymerization. In this article a theoretical rate coefficient for radical desorption will be derived with a deterministic approach for better understanding of this important physical process, and its applicability will be examined using experimental data available in the literature.

## DEFINITION OF RADICAL DESORPTION

For simplicity, let us consider an emulsion polymerization system where the number of polymer particles is constant, the polymer particles contain, at most, one radical, and instantaneous termination takes place when another radical enters the particle which already contains one radical. These conditions are usually satisfied in the emulsion polymerization of vinyl acetate and vinyl chloride. In this case, the radical desorption process is defined in the following equation for active polymer particles containing a radical:

$$\frac{dN^*}{dt} = -k_f N^* - k_a R_w^* N^* + k_a R_w^* N_0 \quad (1)$$

The first term on the right-hand side of eq. (1) shows the rate of decrease in the number of active polymer particles by radical desorption from the polymer particles containing a radical, and  $k_f$  is the radical desorption coefficient. The second term usually expresses the rate of increase in the number of active polymer particles containing two radicals by radical entry from the water phase if instantaneous termination does not occur. However, if instantaneous termination does occur when another radical enters the particle already containing a radical, this term represents the rate of decrease in the number of active polymer particles containing a radical and, hence, should be negative. The third term indicates the rate of increase in the number of active polymer particles containing a radical by radical entry into the dead polymer particles containing no radical.

Let us consider here the diffusion of radicals. According to the two-film theory developed by Lewis and Whitman<sup>7</sup> for mass transfer across the interface between two phases, the concentration gradients near the phase boundary can be assumed as shown in Figure 1. Considering the concentration gradients and Fick's diffusion law, the rate of radical desorption from a single polymer particle which contains  $n$  radicals is expressed by

$$J_{R^*} = -\frac{d(v_p R_p^*)}{dt} = -\frac{dn}{dt} = k_s a_p (R_p^* - R_{pi}^*) = k_w a_p (R_{wi}^* - R_w^*) \quad (2)$$

where  $k_s$  and  $k_w$  respectively denote the film mass-transfer coefficients for the inner and outer diffusion films adjacent to the interface between the polymer particle and the water phase. The concentrations of the escaping radicals at the interface, which may be low, at equilibrium can be expressed by the following linear relationship:

$$R_{pi}^* = m R_{wi}^* \quad (3)$$

Using eqs. (2) and (3), we have

$$J_{R^*} = \frac{(R_p^* - m R_w^*)}{(1/k_s a_p) + (m/k_w a_p)} = K_s a_p (R_p^* - m R_w^*) \quad (4)$$

$$= \frac{(R_p^*/m - R_w^*)}{(1/m k_s a_p) + (m/k_w a_p)} = K_w a_p (R_p^*/m - R_w^*) \quad (5)$$

where

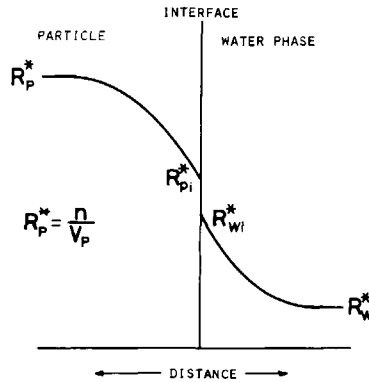


Fig. 1. Schematic diagram of concentration gradients near phase boundary.

$$\frac{1}{K_s} = \frac{1}{k_s} + \frac{m}{k_w} \quad (6)$$

and

$$\frac{1}{K_w} = \frac{1}{mk_s} + \frac{1}{k_w} \quad (7)$$

The overall resistance for mass transfer is the sum of individual ones. From eqs. (6) and (7), we obtain

$$K_s m = K_w \quad (8)$$

Let us consider the mass transfer coefficient in the individual diffusion films. There are a large number of published studies concerning the mass transfer coefficient around a spherical particle. One of these is the following semitheoretical equation proposed by Rantz and Marshall<sup>8</sup>:

$$\text{Sh} = 2 + 0.6\text{Re}^{1/2}\text{Sc}^{1/3} \quad (9)$$

where Sh is the Sherwood number =  $k_w d_p / D_w$ , Re is the Reynolds number =  $d_p u \rho / \mu$ , and Sc is the Schmidt number =  $\mu / \rho D_w$ . Since such small spheres as emulsion polymer particles will move with the eddies of the fluid, there will be no relative velocity between the surface of the polymer particle and the fluid. Therefore, the value of Re can be regarded as zero, and hence Sh = 2. From the value of Sh = 2 we get

$$k_w = \frac{2D_w}{d_p} \quad (10)$$

On the other hand, mass transfer inside the viscous polymer particles occurs by molecular diffusion. According to an analytical solution to the mass transfer problem inside the polymer particle, average mass transfer coefficient between time 0 ~ t,  $\bar{k}_s$ , is given as follows<sup>9</sup>:

$$\bar{k}_s = -\frac{d_p}{6t} \ln \left[ \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -\frac{4n^2 \pi^2 D_p t}{d_p^2} \right) \right] \quad (11)$$

Since this coefficient is too complicated for our present purpose, and since it will be doubtful whether it is possible to apply the above coefficient to the diffusion of radicals inside the polymer particle where only one radical is transporting, we use an approximate mass transfer coefficient derived by the following simple treatment. The average time spent by a radical inside a polymer particle before it escapes out of the polymer particle,  $\bar{t}$ , can be calculated by the Einstein diffusion equation as follows:

$$\bar{t} = \frac{d_p^2}{2D_p} \quad (12)$$

On the other hand, since the radical concentration at the interface will be very low, the rate of radical desorption from a single polymer particle is expressed, according to eq. (2), as follows:

$$J_{R^*} = -\frac{d(v_p R_p^*)}{dt} = k_s a_p R_p^* \quad (13)$$

The average time spent by a radical before it escapes out of the polymer particle,  $\bar{t}$ , will be given as

$$\bar{t} = \frac{(v_p R_p^*)}{J_{R^*}} = \frac{(v_p R_p^*)}{k_s a_p R_p^*} = \frac{d_p}{6k_s} \quad (14)$$

Comparing eq. (12) with eq. (14), we can obtain

$$k_s = \frac{D_p}{3d_p} \quad (15)$$

Inserting eqs. (10) and (15) into eqs. (6) and (7) leads to

$$K_s = \frac{2D_w}{md_p} \left( 1 + \frac{6D_w}{mD_p} \right)^{-1} = \frac{2D_w \delta}{md_p} \quad (16)$$

$$K_w = mK_s = \frac{2D_w \delta}{d_p} \quad (17)$$

where

$$\delta = \left( 1 + \frac{6D_w}{mD_p} \right)^{-1} \quad (18)$$

Although it is doubtful whether it is possible to apply the diffusion theory to a polymer particle where only one radical is transporting, the above theory will be applied as a limiting case to the emulsion polymerization system where polymer particles contain, at most, one radical.

The desorption rate of  $d$ -unit radicals from polymer particles equals the rate of decrease in the number of active polymer particles containing a  $j$ -unit radical. Applying eq. (4), we have

$$-\frac{dN_j^*}{dt} = K_{sj} a_p \left[ \left( \frac{1}{v_p} \right) - m_j R_{wj}^* \right] N_j^* + K_{sj} a_p \left[ \left( \frac{0}{v_p} \right) - m_j R_{wj}^* \right] (N_0 + N_1^* + N_2^* + \dots + N_{j-1}^* + N_{j+1}^* + \dots) \quad (19)$$

The first term on the right-hand side of eq. (19) represents the desorption rate of  $j$ -unit radicals from the polymer particles containing a  $j$ -unit radical. The last term expresses the absorption rate of  $j$ -unit radical from the water phase into the polymer particles. Rewriting eq. (19), we get

$$\frac{dN_j^*}{dt} = -K_{sj} a_p \left( \frac{a_p}{v_p} \right) N_j^* + K_{sj} a_p m_j R_{wj}^* N^* + K_{sj} a_p m_j R_{wj}^* N_0 \quad (20)$$

where

$$N^* = N_1^* + N_2^* + \dots + N_{j-1}^* + N_j^* + N_{j+1}^* + \dots$$

The second term on the right-hand side of eq. (20) usually represents the rate of increase in the number of polymer particles containing two radicals, one of which is a  $j$ -unit radical. However, this term should be changed from positive to negative, because it expresses the rate of radical termination in the polymer particles. That is, it expresses the rate of decrease in the number of active polymer particles containing a radical if instantaneous termination is assumed to occur when another radical enters the polymer particle which already contains one. Thus, using eq. (8), eq. (20) can be rewritten as follows:

$$\frac{dN_j^*}{dt} = -K_{sj} \left( \frac{a_p}{v_p} \right) N_j^* - K_{wj} a_p R_{wj}^* N^* + K_{wj} a_p R_{wj}^* N_0 \quad (21)$$

Summation of eq. (21) with respect to  $N_j^*$  leads to

$$\frac{dN^*}{dt} = \frac{d\sum N_j^*}{dt} = -(\sum K_{sj}N_j^*)\left(\frac{a_p}{v_p}\right) - (\sum K_{wj}R_{wj}^*)a_pN^* + (\sum K_{wj}R_{wj}^*)a_pN_0 \quad (22)$$

Equation (22) defines the radical desorption and absorption in the polymer particles and corresponds to eq. (1). Therefore, comparing the corresponding terms in eqs. (1) and (22), we have

$$k_f = \left(\frac{\sum K_{sj}N_j^*}{N^*}\right)\left(\frac{a_p}{v_p}\right) = \sum K_{0j} \left(\frac{N_j^*}{N^*}\right) \quad K_{0j} = K_{sj} \left(\frac{a_p}{v_p}\right) \quad (23)$$

$$k_a = \left(\frac{\sum K_{wj}R_{wj}^*}{R_w^*}\right)a_p = \sum K_{aj} \left(\frac{R_{wj}^*}{R_w^*}\right) \quad K_{aj} = K_{wj}a_p \quad (24)$$

where

$$R_w^* = R_{w1}^* + R_{w1}^* + R_{w2}^* + \dots + R_{wj-1}^* + R_{wj}^* + R_{wj+1}^* + \dots$$

### QUANTITATIVE EXPRESSION FOR RADICAL DESORPTION AND ABSORPTION COEFFICIENTS

To simplify the subsequent treatments, we make the following five assumptions: (1) Polymer particles contain at most one radical. (2) A radical no longer than  $s$  units can desorb from and enter the polymer particles with the same rate regardless of its chain length. (3) Instantaneous termination occurs when another radical enters the polymer particle which already contains a radical. (4) No distinction is made between radicals with or without an initiator fragment on its end. (5) Water-phase reactions such as termination and propagation can be neglected from the kinetic point of view.

According to assumption (2) given above, we can regard the values of  $K_{0j}$  and  $K_{aj}$  in eqs. (23) and (24) to be constant and equal to  $K_0$  and  $K_a$ , respectively. Moreover, no radical longer than  $s$  units will be found in the water phase. Thus, eqs. (23) and (24) can be rewritten as follows;

$$k_f = K_{0I} \left(\frac{N_I^*}{N^*}\right) + K_0 \left(\frac{N_1^*}{N^*}\right) + K_0 \left(\frac{N_2^*}{N^*}\right) + \dots + K_0 \left(\frac{N_s^*}{N^*}\right) \quad K_{0j} = K_0 \quad (25)$$

$$k_a = K_a \sum_{j=1}^s \left(\frac{R_{wj}^*}{R_w^*}\right) = K_a = K_w a_p \quad (26)$$

where  $K_{0I}$  is the coefficient for initiator radicals and  $K_0$  is the coefficient for the radicals other than initiator radicals. Discrimination between the initiator and other radicals is made because chemical and physical properties are very different between these and, accordingly, the values of  $K_{0I}$  and  $K_0$  may be different.

In order to get the relationship between  $N_j^*$  and  $N^*$ , we balance equations with respect to  $N_I^*$  and  $N_j^*$  which contain an initiator and a  $j$ -unit radical, respectively. Applying a stationary-state hypothesis to these equations, we obtain

$$\frac{dN_I^*}{dt} = K_a I R_{wI}^* N_0 - (k_a R_w^* + k_{mf} M_p + k_i M_p + K_{0I}) N_I^* = 0 \quad (27)$$

$$\frac{dN_1^*}{dt} = K_a R_{w1}^* N_0 + k_i M_p N_1^* + k_{mf} M_p N^* - (k_a R_w^* + k_{mf} M_p + k_p M_p + K_0) N_1^* = 0 \quad (28)$$

$$\frac{dN_j^*}{dt} = K_a R_{wj}^* N_0 + k_p M_p N_{j-1}^* - (k_a R_w^* + k_{mf} M_p + k_p M_p + K_0) N_j^* = 0 \quad (29)$$

$$\frac{dN_s^*}{dt} = K_a R_{ws}^* N_0 + k_p M_p N_{s-1}^* - (k_a R_w^* + k_{mf} M_p + k_p M_p + K_0) N_s^* = 0 \quad (30)$$

$$R_w^* = R_{w1}^* + R_{w1}^* + R_{w2}^* + \cdots + R_{ws-1}^* + R_{ws}^* \quad (31)$$

Further, by balancing with respect to the water phase radicals and applying a stationary-state hypothesis, we have

$$\frac{dR_{wi}^*}{dt} = r_i + K_{0I} N_i^* - K_{aI} R_{wi}^* N_T = 0 \quad (32)$$

$$\frac{dR_{w1}^*}{dt} = K_0 N_1^* - K_a R_{w1}^* N_T = 0 \quad (33)$$

$$\frac{dR_{wj}^*}{dt} = K_0 N_j^* - K_a R_{wj}^* N_T = 0 \quad (34)$$

$$\frac{dR_{ws}^*}{dt} = K_0 N_s^* - K_a R_{ws}^* N_T = 0 \quad (35)$$

Since high-molecular-weight polymers are produced in emulsion polymerization it is assumed that

$$k_a R_w^*, k_{mf} M_p \ll k_p M_p, k_i M_p, K_{0I}, K_0 \quad (36)$$

From eqs. (27) and (32) and the definition that  $N^* = \bar{n} N_T$ , we obtain

$$N_i^* = \frac{r_i(1 - \bar{n})}{K_{0I}\bar{n} + k_i M_p} \quad (37)$$

By similar treatments we have

$$N_1^* = \left( \frac{k_{mf} M_p}{K_0 \bar{n} + k_p M_p} \right) N^* + \left( \frac{k_i M_p}{K_0 \bar{n} + k_p M_p} \right) N_i^* \quad (38)$$

and

$$N_j^* = \left( \frac{k_p M_p}{K_0 \bar{n} + k_p M_p} \right)^{j-1} N_1^* = \left( \frac{k_p M_p}{K_0 \bar{n} + k_p M_p} \right)^j \left[ \left( \frac{k_{mf}}{k_p} \right) N^* + \left( \frac{k_i}{k_p} \right) N_i^* \right] \quad (39)$$

Inserting eq. (39) into eq. (25) we have

$$k_f = K_{0I} \left( \frac{N_i^*}{N^*} \right) + K_0 \left[ \left( \frac{k_{mf}}{k_p} \right) + \left( \frac{k_i}{k_p} \right) \left( \frac{N_i^*}{N^*} \right) \right] \sum_{j=1}^s \left( \frac{k_p M_p}{K_0 \bar{n} + k_p M_p} \right)^j \quad (40)$$

Initiator radicals are so reactive that the number of polymer particles containing an initiator radical,  $N_i^*$ , will be maintained at a low value. Therefore, when the transfer to monomer reaction is dominant, that is, the value of  $k_{mf}/k_p$  is large, it will be reasonable to consider that the term  $N_i^*/N^*$  in eq. (40) can be neglected. Thus, eq. (40) can be simplified as

$$k_f = K_{0z} \left( \frac{k_{mf}}{k_p} \right) = \frac{12D_w \delta z}{m d_p^2} \left( \frac{k_{mf}}{k_p} \right) \quad (41)$$

where

$$z = \sum_{j=1}^s \left( \frac{k_p M_p}{K_0 \bar{n} + k_p M_p} \right)^j \quad (42)$$

According to eq. (42), the value of  $z$  satisfies the following inequality:

$$0 < z < s \quad (43)$$

Equation (41) is the final expression for the rate coefficient for radical desorption from polymer particles. On the other hand, the rate coefficient for radical absorption can be obtained from eqs. (17) and (26) as follows:

$$k_a = 2\pi D_w \delta d_p \quad (44)$$

## DISCUSSION

In the emulsion polymerization of vinyl acetate and vinyl chloride under normal conditions, the polymer particles contain, at most, one radical. For such emulsion polymerization systems, the following steady-state equations hold with reasonable accuracy for the number of active polymer particles,  $N^*$ , and the radical concentration in the water phase,  $R_w^*$ :

$$\frac{dN^*}{dt} = k_a R_w^* N_0 - k_f N^* - k_a R_w^* N^* = 0 \quad (45)$$

$$\frac{dR_w^*}{dt} = r_i + k_f N^* - k_a R_w^* N_T = 0 \quad (46)$$

Inserting eq. (46) into eq. (45) and solving it for  $\bar{n}$ , we have

$$\bar{n} = \frac{N^*}{N_T} = \frac{1}{2} \left[ - \left( \frac{r_i}{k_f N_T} \right) + \sqrt{\left( \frac{r_i}{k_f N_T} \right)^2 + 2 \left( \frac{r_i}{k_f N_T} \right)} \right] \quad (47)$$

For two limiting cases, eq. (47) is simplified as follows:

$$\bar{n} = \begin{cases} \frac{1}{2} & \frac{r_i}{k_f N_T} \rightarrow \infty \\ \left( \frac{r_i}{2k_f N_T} \right)^{1/2} & \frac{r_i}{k_f N_T} < 10^{-2} \end{cases} \quad (48)$$

In Figure 2, theoretical values of  $\bar{n}$  calculated according to eq. (47) are plotted against the value of  $r_i/k_f N_T$ . Experimental data concerning vinyl acetate and vinyl chloride emulsion polymerization are also plotted and compared with the theoretical values (Fig. 2) to demonstrate that (1) eq. (47) is valid and (2) the desorption rate coefficient  $k_f$  can be applied to these emulsion polymerization systems. The numerical values for the constants used in this calculation are shown in Table I where only monomer radical can desorb from the polymer particles, that is,  $s = 1$ . The experimental data for vinyl chloride emulsion polymerization coincide very well with the theoretical values regardless of the uncertainty of the value of the effective initiator decomposition rate constant,  $k_{df}$ . As for the emulsion polymerization of vinyl acetate (Fig. 2), the reported data<sup>5,11</sup> deviate somewhat from the theoretical values, although the experimental data reported by Friis et al.<sup>4</sup> are in good agreement with the theoretical values. The exact reason for this is not clear at present, but one possible cause may be

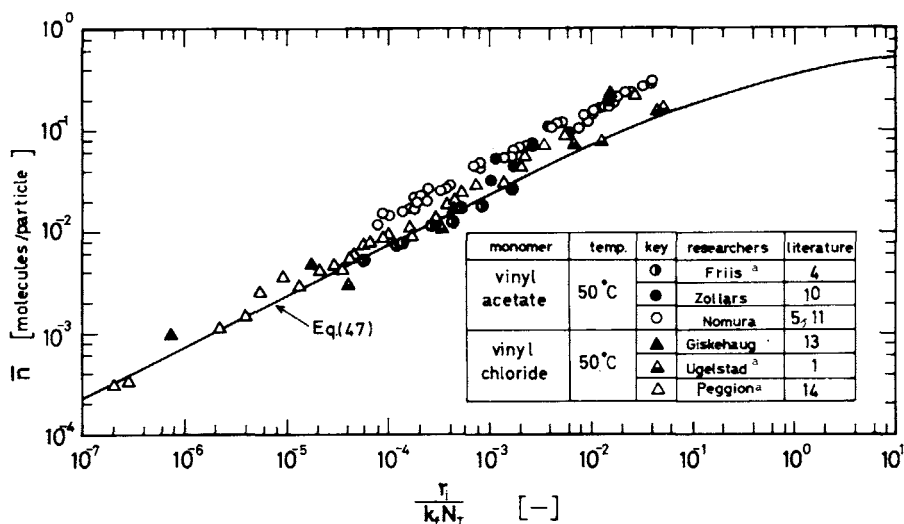


Fig. 2. Comparison between theoretical and experimental values of average number of radicals per particle,  $\bar{n}$ , calculated from conversion-vs.-time curve and the number of polymer particles.

the difference in the rate of radical production, because the experimental data reported by the former groups agree well with the theoretical values if  $5 \times 10^{-6} \text{ sec}^{-1}$  is employed as the value of  $k_{df}$ . Among the three groups cited above, the reaction conditions and the ingredients used were the same, except that Friis et al. used  $\text{NaHPO}_3$  to buffer the water phase; however, the difference of pH may not cause such a large decrease in the rate of radical production.

We refer here to the values of  $\delta$  and  $z$ . In the beginning of the polymerization where monomer droplets exist in the water phase and hence the polymer particles are saturated with monomer, the value of  $\delta$  (Table I) seems to be unity because the decrease in the value of  $D_p$  is not so remarkable. However, in a higher conversion range, the value of  $D_p$  will decrease markedly with the progress of the polymerization due to an increase in the viscosity inside the polymer particles. When the condition  $6D_w/mD_p \gg 1$  is satisfied, namely, the diffusion resistance inside the polymer particle becomes dominant, the rate coefficient for radical desorption,  $k_f$ , is rewritten in the form

$$k_f = \frac{2D_p}{d_p^2} z \left( \frac{k_{mf}}{k_p} \right) \quad (50)$$

TABLE I  
Numerical Values of Constants Used (50°C)

Constant	Unit	Vinyl acetate	Vinyl chloride
$k_p$	l./mole sec	3340	10000
$k_{mf}/k_p$	—	$2 \times 10^{-4}$	$1.2 \times 10^{-3}$
$m$	—	28	35
$D_w$	$\text{cm}^2/\text{sec}$	$1.9 \times 10^{-5}$ <sup>a</sup>	$2.5 \times 10^{-5}$ <sup>a</sup>
$k_{df}$	l./sec	$1.5 \times 10^{-6}$ <sup>b</sup>	$1.5 \times 10^{-6}$ <sup>b</sup>
$[M_p]_c$	moles/l.	8.9	6.2
$z$	—	1.0	1.0
$\delta$	—	1.0	1.0

<sup>a</sup> From Wilke and Chang.<sup>15</sup>

<sup>b</sup> From Morris and Parts.<sup>16</sup>



In such a high monomer conversion range, the value of  $k_f$  decreases with the progress of polymerization, corresponding to the decrease in the value of  $D_p$ . As for the value of  $z$ , on the other hand, the actual value is almost unity because the comparison between the theoretical values and experimental data made assuming the value of  $z = 1$ , gives good agreement (Fig. 2). Further, since the value of  $K_0\bar{n}$  in eq. (42) is usually about an order of magnitude smaller than that of  $k_pM_p$ , the radical which can desorb from the polymer particles seems to be principally a monomer radical.

Let us consider the rate of emulsion polymerization where eqs. (42) and (49) can be applied due to the high number of polymer particles. Combining eqs. (42) and (49), we have

$$r_p \propto \bar{n}N_T \propto N_T^{1/2}I_0^{1/2}d_p \propto N_T^{1/2}I_0^{1/2}v_p^{1/3} \quad (51)$$

After the complete absorption of monomer existing as droplets in the water phase, the following equation holds:

$$N_T v_p = V_p \quad (52)$$

where  $V_p$  is the total volume of polymer particles per unit water volume. Substitution of eq. (52) into eq. (51) leads to

$$r_p \propto N_T^{1/6}I_0^{1/2}V_p^{1/3} \quad (53)$$

Ugelstad et al.<sup>1</sup> reported that when the number of polymer particles is high, the rate of vinyl chloride emulsion polymerization was proportional to the 0.15 power of the number of polymer particles and to the 0.3 power of the total volume of polymer particles,  $V_p$ . The present authors<sup>5,11</sup> reported that eq. (53) predicted the rate of emulsion polymerization of vinyl acetate. van der Hoff<sup>12</sup> also reported that the rate of emulsion polymerization of styrene was proportional to the 0.17 power of the number of polymer particles if the number of polymer particles was very high. These experimental findings also support the validity of the theory developed in this work.

## CONCLUSIONS

The rate coefficient for radical desorption derived in this study can be applied to the emulsion polymerization of vinyl acetate and vinyl chloride for predicting the average number of radicals per particle. In addition, the coefficient involves no unknown parameters which are impossible to estimate theoretically. This is a convenient and unique characteristic as compared with the coefficients proposed by Friis et al.<sup>4</sup> and Ugelstad et al.<sup>1</sup> Finally, we hope that other investigators will examine the applicability of the rate coefficient for radical desorption to emulsion polymerization of other monomers.

## NOMENCLATURE

$a_p$	surface area per polymer particle
$d_p$	diameter of polymer particle
$D_w$	diffusion coefficient of radicals in water
$D_p$	diffusion coefficient of radicals in a polymer particle
$I_0$	initial initiator concentration
$J_{R^*}$	radical flux across the phase boundary
$k_f$	rate coefficient for radical desorption from a polymer particle

$k_a$	rate coefficient for radical absorption by a polymer particle
$k_s$	film mass transfer coefficient defined by eq. (2)
$k_w$	film mass transfer coefficient defined by eq. (2)
$k_{df}$	effective production rate constant for initiator radicals
$K_s$	overall mass transfer coefficient defined by eq. (4)
$K_{sj}$	overall mass transfer coefficient defined by eq. (4) for $j$ -unit radical
$K_w$	overall mass transfer coefficient defined by eq. (4)
$K_{wj}$	overall mass transfer coefficient defined by eq. (4) for $j$ -unit radical
$K_{af}$	mass transfer coefficient defined by eq. (24) for initiator radical
$K_{of}$	mass transfer coefficient defined by eq. (23) for initiator radical
$k_p$	propagation rate constant
$k_i$	rate constant for initiation reaction
$k_{mf}$	rate constant for chain transfer to monomer
$m$	partition coefficient for radical between polymer particle and water phases defined by eq. (3)
$m_j$	partition coefficient for $j$ -units radical between polymer particle and water phases defined by eq. (3)
$M_p$	monomer concentration in polymer particle
$n$	number of radicals per polymer particle
$\bar{n}$	average number of radicals per particle
$N^*$	number of active polymer particles containing a radical
$N_0$	number of dead polymer particles containing no radical
$N_j^*$	number of active polymer particles containing $j$ -unit radical
$N_i^*$	number of active polymer particles containing an initiator radical
$N_T$	total number of polymer particles per unit volume of water
$r_i$	rate of radical production defined by $2k_{df}I_0$
$R_w^*$	radical concentration in water phase
$R_{wj}^*$	concentration of $j$ -unit radicals in water phase
$R_p^*$	radical concentration in polymer particle defined by $n/v_p$
$R_{pj}^*$	concentration of $j$ -unit radicals in polymer particle
$R_{of}^*$	concentration of initiator radical in water phase
$u$	relative velocity between surface of polymer particle and water phase
$v_p$	volume per polymer particle
$V_p$	total volume of polymer particle in unit volume of water
$\rho$	density of polymer particle
$\mu$	viscosity in water phase
$\delta$	ratio of film mass transfer resistance to overall mass transfer resistance $(m/k_w)/(1/K_s)$

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