

Free-Radical Transport from Latex Particles

R. N. MEAD and G.W. POEHLEIN, *School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332*

Synopsis

A rate constant for the diffusion of monomer radicals from latex particles is derived using the transport equations describing the generation, diffusion, and reaction of monomer radicals within the particles. Calculations for styrene emulsion polymerization show that this "desorption constant" accounts for nonuniform distribution of monomer radicals within the particle while some previously published theories do not. The difference in the desorption constant calculated with the model derived in this work and the "uniform concentration" models could be an order of magnitude when diffusivity of monomer radicals in the particles is small. The monomer radical transport theory is extended to emulsion copolymerization. Desorption rate constants accounting for nonuniform distribution of monomer radicals are derived for emulsion copolymerization.

INTRODUCTION

The transport of free radicals to and from monomer-swollen latex particles are important phenomena in emulsion polymerization reactions. The original recursion equation of Smith and Ewart¹ for the number of particles, N_n , containing n free radicals includes terms for absorption and desorption of free radicals and for the termination of free radicals within the particles. The steady-state form of the Smith-Ewart recursion equation is reproduced below:

$$\begin{aligned} \frac{\rho_A N_{n-1}}{N_p} + (n+1)k_d N_{n+1} + (n+1)(n+2) \frac{k_t N_{n+2}}{v_p} \\ = \frac{\rho_A N_n}{N_p} + nk_d N_n + n(n-1) \frac{k_t N_n}{v_p} \end{aligned} \quad (1)$$

The volume of the monomer-swollen latex particle is v_p , k_t is the termination rate constant within the particle, and k_d is the desorption rate constant. The phenomenon of radical transport out of latex particles, incorrectly called "desorption," is the subject of this article.

Polymerizing radical oligomers of any significant molecular weight are not expected to transfer from the particles to the aqueous phase. Such molecules would normally be strongly hydrophobic and perhaps entangled with polymer molecules in the particles. Radical desorption is generally believed to follow a transfer reaction in which a small mobile free radical is formed. Such a radical could reinitiate polymerization by reacting with monomer or diffuse to the surface of the particle and cross the interface into the aqueous phase. Mathematical modeling of this phenomenon involves the classic concepts of diffusion with simultaneous chemical reaction.

Published theories for the desorption rate coefficient are based on several questionable assumptions. These theories are reviewed in this article and alternate models are presented. The theories presented in this article only include consideration for desorption of radicals formed by transfer reactions with monomer. Extension to include reactions with added chain transfer agent (CTA) would, however, be straightforward.

REACTIONS AND MASS TRANSFER FUNDAMENTALS

The chemical reactions that take place in an emulsion polymerization system that could influence radical desorption include chain transfer, reinitiation of polymerization, and termination. These reactions and related rate expressions are summarized below:

Reaction	Mechanism	Rate
Transfer to monomer	$P^* + M \rightarrow P-H + M_m^*$	$k_{fm}[P^*]_p[M]_p$
Transfer to CTA	$P^* + T \rightarrow P-X + T^*$	$k_{TT}[P^*]_p[T]_p$
Reinitiation	$M_m^* + M \rightarrow P^*$ $T^* + M \rightarrow P^*$	$k'_p[M_m^*]_p[M]_p$ $k'_T[T^*]_p[M]_p$
Termination	$P^* + P^* \rightarrow \text{dead poly}$	$k_t[P^*]_p^2$
Propagation	$P^* + M \rightarrow P^*$	$k_p[P^*]_p[M]_p$

The long-chain free radical is P^* and M_m^* is the monomer M free radical. The rate constants for chain transfer to monomer and chain transfer agent, T are k_{fm} and k_{TT} , respectively. The rate constants for reinitiation of oligomer radicals from M_m^* and T^* radicals are k'_p and k'_T , respectively. The net rate of monomer radical formation, R_A , is the rate of chain transfer to monomer minus the rate of reinitiation of oligomer radicals by monomer radicals.

$$R_A = k_{fm}[P^*]_p[M]_p - k'_p[M_m^*]_p[M]_p \quad (2)$$

Ugelstad and Hansen² observed that k'_p may not be equal to the rate constant for the propagation of oligomer radicals, k_p .

Termination reactions involving monomer radicals or radicals formed from CTA are not considered important in determining their respective concentration profiles because the probability for reinitiation is normally much greater. The parallel between transfer with monomer and CTA is apparent, but, as mentioned earlier, the effect of added CTA will not be treated in this article.

The process of monomer free radical transport from latex particles can result in concentration gradients within the particle and in the aqueous phase as shown in Figure 1. For this example $[P^*]_p$ is assumed to be constant with respect to radial position in the particle. C_p is the position-dependent concentration of monomer free radicals within the particle. The monomer free radical concentration at the particle side of the particle-water interface is C_{ps} and the concentration at the water side of the interface is C_{ws} . Ugelstad and

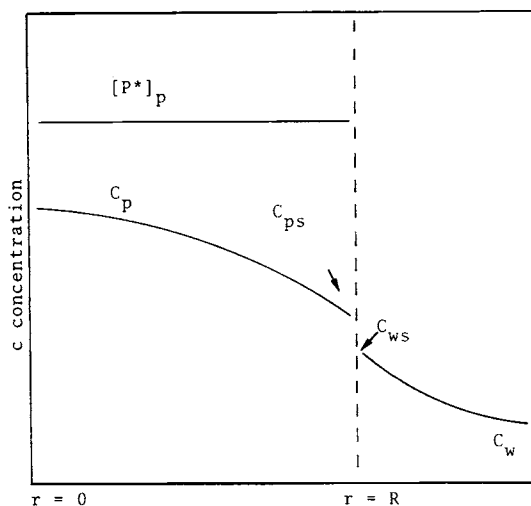


Fig. 1. Concentration profiles of monomer radicals.

Hansen² assumed C_{ws} can be related linearly to C_{ps} as in

$$C_{ws} = C_{ps}/a \quad (3)$$

The term a is the partition coefficient for monomer free radicals between the aqueous and particle phases.

Models for concentration profiles and transport rates in nonconvective systems are obtained by shell balances. Equation (4) is the fundamental steady-state differential equation for transport with chemical reaction of any species in a symmetrical spherical system:

$$\frac{d}{dr}(r^2N) = r^2R_A \quad (4)$$

The radial distance from the center of the sphere is r , N is the diffusive flux in moles per unit area-time normal to the radial direction, and R_A is the net rate of reaction of the diffusing species in moles per unit volume-time. In the absence of bulk flow of the diffusing species the flux is given by Fick's first law:

$$N = -D_{ij} dC/dr \quad (5)$$

The diffusivity of species i in medium j is D_{ij} . The total mass transfer rate across any spherical surface of radius r is given by

$$Q = -4\pi^2D_{ij}(dC/dr) \quad (6)$$

Ugelstad and co-workers²⁻⁴ and Nomura et al.⁵⁻⁷ derived expressions for Q_w , the mass transfer rate on the water side of the particle-aqueous phase

interface. The following boundary conditions were used:

$$r = R, \quad C_w = C_{ws} \quad (\text{i})$$

$$r \rightarrow \infty, \quad C_w = C_{wi} = 0 \quad (\text{ii})$$

Ugelstad and Hansen² assumed chain transfer and reinitiation reactions are negligible in the aqueous phase; thus $R_A = 0$ when eq. (4) is applied to the diffusion of radicals in the aqueous phase. Equations (2)–(4) and (6) were used with boundary conditions (i) and (ii) to derive

$$Q_w = 4\pi RD_w(C_{ws} - C_{wi}) \quad (7)$$

The mass transfer rate on the water side of the interface, Q_w , is expressed in units of moles per unit time. D_w is the diffusivity of the monomer radical in the aqueous phase. The derivation of an expression for the mass transfer rate on the particle side of the interface, Q_p , is more difficult because monomer free radicals will be produced by chain transfer and consumed by reinitiation within the particle. Ugelstad and Hansen² presented an expression for Q_p which is given by

$$Q_p = -4\pi RD_p(C_{ps} - C_p^*) \quad (8)$$

The diffusivity of monomer radicals in the particle is D_p . C_p^* was defined as "the mean radical concentration in the middle of the particle." Ugelstad and Hansen stated that "this is the same as the mean concentration of radicals in the particle, because the radical is formed at a random point in the particle and has a mean diffusion path $L = R$ " (p. 603). The appropriate boundary conditions for steady-state monomer free radical transport from latex particles are presented below:

$$r = 0, \quad dC_p/dr = 0 \quad (\text{iii})$$

$$r = R, \quad C_p = C_{ps} \quad (\text{iv})$$

If boundary conditions (iii) and (iv) are used with eq. (3) when R_A is nonzero, the expression for Q_p is not the same as that derived by Ugelstad and Hansen.²

The derivation of Ugelstad and Hansen's expression for Q_p is unclear; however, if eq. (8) is accepted as a valid expression for Q_p , the derivation of the desorption rate constant can be repeated. Q_p and Q_w are equated at steady state and eq. (2) can be used with the result of this equality to obtain the following relation for C_{ws} :

$$C_{ws} = \frac{C_p^*}{a + (D_w/D_p)} \quad (9)$$

The steady-state mass transfer rate of monomer free radicals from the particle is Q :

$$Q = \frac{4\pi R \langle C_p \rangle D_w}{(a + D_w/D_p)} \quad (10)$$

The mean concentration of monomer free radicals in the particle, $\langle C_p \rangle$, is equal to $\bar{n}_m/v_p N_A$. The average number of monomer radicals per particle is \bar{n}_m and v_p is the volume of the monomer-swollen particle. The monomer free radical desorption constant k_{dm} is given by eq. (11) in units of s^{-1} .

$$k_{dm} = \frac{Q}{\langle C_p \rangle v_p} = \frac{12D_w}{(a + D_w/D_p)d_p^2} \quad (11)$$

The diameter of the monomer-swollen particle is d_p . The desorption coefficient used in emulsion polymerization models is normally applied to the average of the total number of radicals per particle, \bar{n} . Ugelstad and Hansen² derived an expression for k_d as in

$$k_d = \frac{k_{fm}}{k'_p} k_{dm} \quad (12)$$

Ugelstad and Hansen² obtained an expression for k_d by combining eqs. (11) and (12):

$$k_d = \frac{k_{fm}}{k'_p} \left[\frac{12D_w}{(a + D_w/D_p)d_p^2} \right] \quad (13)$$

The particle-size-independent desorption rate constant is k'_d :

$$k'_d = k_d v_p^{2/3} = \frac{k_{fm}}{k'_p} \left[\frac{12(\pi/6)^{2/3} D_w}{a + D_w/D_p} \right] \quad (14)$$

Nomura et al.⁵⁻⁷ derived a similar expression for k'_d independently of Ugelstad and Hansen² by using both deterministic and stochastic approaches:

$$k'_d = \frac{k_{fm}}{k'_p} k_0 \left(\frac{(\pi/6)^{2/3} d_p^2 k_p [M]_p}{K_0 \bar{n} + k_p [M]_p} \right) \quad (15)$$

where

$$K_0 = \frac{12D_w}{d_p^2(a + 2D_w/D_p)}$$

EXTENSION OF MONOMER RADICAL TRANSPORT THEORY

Neither Ugelstad et al. or Nomura et al. considered the case where the monomer free radical concentration could vary significantly within the particle. It is, however, possible that the monomer free radical concentration profile would vary significantly with particle radius. This could occur for two reasons: (1) very low diffusivity of monomer free radicals in the particle or (2) a nonuniform generation of free radicals within the particle. These phenomena are considered separately in the following two sections.

Diffusion-Limited Transport from Particles

If the oligomer free radicals and monomer molecules are assumed to be distributed uniformly in the particle, the monomer free radicals will be produced at a constant rate everywhere within the particle. The monomer free radical concentration, however, may not be constant with respect to radial position in the particle if the diffusivity of the monomer free radical is low.

Possible monomer free radical concentration profiles are shown in Figure 2. If the diffusivity of the monomer radical is high the profile should be flat as in curve (a), even for the case of nonuniform oligomer free radical distribution. However, at higher conversion the viscosity of the monomer-polymer mixture will be much greater than the viscosity at low to medium conversion. Increased viscosity may cause the diffusivity of the monomer free radical, D_p , to decrease significantly. At high conversion the monomer free radical concentration profile may look like curve (b). The following section includes the derivation of a desorption rate constant based on the assumption that oligomer free radicals are distributed uniformly in the particles. The derivation differs from the previous models because reinitiation of monomer radicals to form oligomer chains is coupled with diffusion considerations.

The assumptions used in the derivation are: (1) a steady-state monomer free radical concentration profile is established; (2) the oligomer free radicals are distributed uniformly throughout the particle; (3) monomer free radicals may reinitiate oligomer chains by adding a monomer molecule; and (4) the concentration of monomer free radicals at the particle surface is in equilibrium with the concentration of monomer free radicals on the water side of the particle-water interface as described by eq. (3). The monomer free radical concentration in the aqueous phase at infinite distance from the particles is very small and may be set to zero.

Chern⁸ developed a steady-state balance on monomer free radicals about a differential element of the particle. The rate of diffusion of monomer free radicals into the element minus the rate of diffusion of monomer free radicals out of the element was set equal to the net rate of generation of monomer free radicals within the element:

$$\begin{aligned} & \left[-4\pi r^2 D_p \frac{dC_p}{dr} \right]_r - \left[-4\pi (r + \Delta r)^2 D_p \frac{dC_p}{dr} \right]_{r+\Delta r} \\ & = 4\pi r^2 \Delta r (k'_p C_p - k_{fm} [P^*]_p) [M]_p \end{aligned} \quad (16)$$

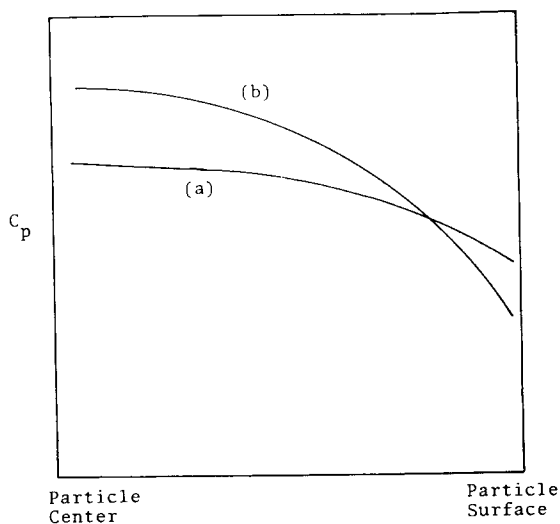


Fig. 2. Possible monomer radical concentration profiles: (a) large D_p ; (b) small D_p .

Chern assumed D_p remained constant within the particle and obtained a nonhomogeneous ordinary differential equation, which is a form of eq. (4):

$$D_p \frac{d^2 C_p}{dr^2} + \frac{2D_p}{r} \frac{dC_p}{dr} - k'_p [M]_p C_p = -k_{fm} [M]_p [P^*]_p \quad (17)$$

The following boundary conditions apply:

$$\text{at } r = 0, \quad dC_p/dr = 0 \quad (v)$$

$$\text{at } r = R, \quad 4\pi R D_w C_{ps}/a = \frac{4}{3}\pi R^3 (k_{fm} \langle [P^*]_p \rangle - k'_p \langle C_p \rangle) [M]_p \quad (vi)$$

The volume-average concentration $\langle C_p \rangle$ is defined in

$$\langle C_p \rangle = \frac{4\pi \int_0^R C_p r^2 dr}{\frac{4}{3}\pi R^3} \quad (18)$$

Chern did not assume the oligomer radical concentration $[P^*]_p$ was uniform throughout the particle, so he could not obtain an analytical solution for eq. (17). In this work the oligomer free radicals are assumed to have a uniform distribution throughout the particle in order to obtain an analytical solution to eq. (17).

The analytical solution to eq. (17) subject to boundary conditions (v) and (vi) was obtained and is given by

$$C_p = \frac{k_{fm}[P^*]_p}{k'_p} \left[1 - \frac{2D_w \sinh(\phi r')}{\{ak'_p[M]_p R^2 X/3 + 2D_w \sinh(\phi)\} r'} \right] \quad (19)$$

where

$$\phi = R \left[\frac{k'_p[M]_p}{D_p} \right]^{1/2}$$

$$r' = r/R, \quad X = 6 \left[\frac{\cosh(\phi)}{\phi} - \frac{\sinh(\phi)}{\phi^2} \right]$$

The volume-average concentration is given in

$$\langle C_p \rangle = \frac{k_{fm}[P^*]_p}{k'_p} \left[1 - \frac{D_w X}{\{ak'_p[M]_p X R^2/3 + 2D_w \sinh(\phi)\}} \right] \quad (20)$$

The oligomer radical concentration $[P^*]_p$ is given by

$$[P^*]_p = \frac{\bar{n}}{N_A v_p} \left(1 - \frac{k_{fm}}{k_p} \right) \quad (21)$$

Figure 3 is a plot of C_p vs. dimensionless radius for ST emulsion polymerization at 60°C. The parameters used in the calculation are listed in Table I. The value of \bar{n} used in the calculation of $[P^*]_p$ was 0.5; thus $[P^*]_p$ was assumed to be constant. Lee⁹ used the data of Goffloo and Kosfeld¹⁰ to estimate D_p as $2.0E - 6$ for ST-saturated polystyrene particles. The concentration profile for a D_p of $2.0E - 6$ relatively constant while the profiles for D_p equal to $20E - 8$ and $2.0E - 11$ show an increased concentration in the bulk of the particle with a larger concentration gradient near the particle surface. The concentration profiles in Figure 3 indicate that the surface concentration, C_{ps} , decreases with decreasing D_p . This phenomenon is consistent with the second boundary condition of eq. (17):

b.c. vi: at $r = R$,

$$4\pi R D_w C_{ps} / a = \frac{4}{3} \pi R^3 (k_{fm} \langle [P^*]_p \rangle - k'_p \langle C_p \rangle) [M]_p$$

If $[P^*]_p$ is constant, $\langle C_p \rangle$ will increase when D_p decreases and the net rate of production of monomer free radicals (rhs b.c. vi) will decrease. The decrease in net production is balanced by a reduction in C_{ps} and Q . The decreasing values of C_{ps} with decreasing D_p are also consistent with Ugelstad and Hansen's theory. The flux at the surface, Q , defined by eq. (6), must be equal to the flux defined by eq. (10). These criteria have been verified numerically for the ST emulsion polymerization example.

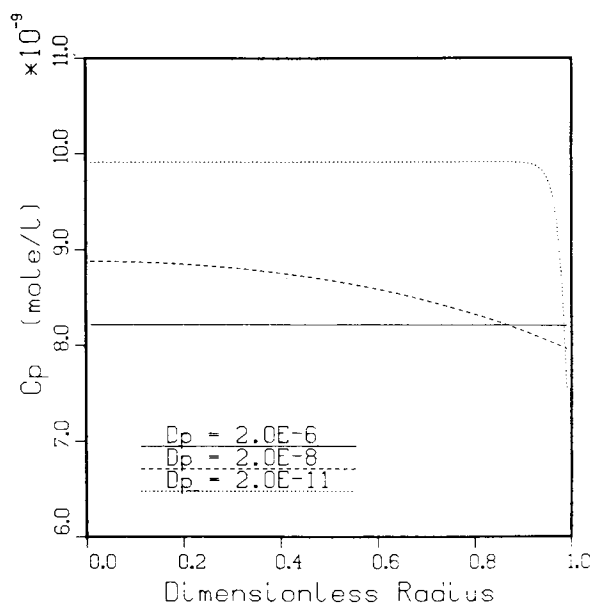


Fig. 3. Calculated monomer radical concentration profiles for styrene emulsion polymerization. D_p : (—) $2.0E-6$; (---) $2.0E-8$; (...) $2.0E-11$.

Desorption Rate Constant

The flux of monomer free radicals at the particle surface, Q_p , is given by eq. (6), which is reproduced here:

$$Q_p = -4\pi R^2 D_p \left. \frac{dC_p}{dr} \right|_{r=R} \quad (6')$$

The monomer free radical desorption constant, k_{dm} , is defined by

$$k_{dm} = Q / \langle C_p \rangle v_p \quad (22)$$

The expression for k'_d is given by

$$k'_d = k_d v_p^{2/3} = (k_{jm}/k'_p) k_{dm} v_p^{2/3} \quad (23)$$

TABLE I
Parameters for Styrene Emulsion Polymerization Simulation

Parameter	Source	
T	60°C	—
k_{jm}	$8.8E-3$ L/mol s	Odian ¹³
k'_p	176 L/mol s	Lee ⁹
D_w	$2.0E-5$ cm ² /s	Wilke and Chang ¹⁴
a	1300	Lee ⁹
D_p	Varied cm ² /s	

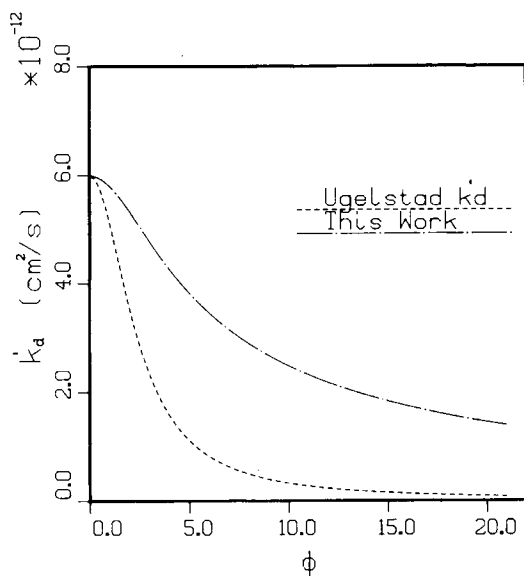


Fig. 4. Calculated k'_d vs. ϕ for styrene emulsion polymerization: (---) Ugelstad k'_d ; (-·-) this work.

Equation (6), the expression for $\langle C_p \rangle$ [eq. (20)], the expression for k_{dm} [eq. (22)], and the expression for k'_d [eq. (23)] are combined to derive an expression for k'_d :

$$k'_d = \frac{k_{fm}}{k'_p} 12(\pi/6)^{2/3} D_w \left/ \left\{ \alpha + \frac{D_w \{ \sinh(\phi)(1 + 3/\phi^2) - 3 \cosh(\phi)/\phi \}}{k'_p [M]_p R^2 [\cosh(\phi)/\phi - \sinh(\phi)/\phi^2]} \right\} \right. \quad (24)$$

Ugelstad and Hansen's expression for k'_d differs in form from eq. (24) because of the assumption of uniform monomer free radical concentration. Equation (24) and Ugelstad and Hansen's equation for k'_d should give the same values for k'_d in the limiting case where D_p is relatively large and the concentration is uniform. This case corresponds to a small value of ϕ in eq. (24). Equations (14) and (24) were used to calculate k'_d for ST emulsion polymerization using the parameter values in Table I. Figure 4 is a plot of k'_d vs. ϕ . The values of k'_d calculated using Ugelstad and Hansen's equation and eq. (24) both converge as ϕ approaches zero and D_p becomes relatively large. As D_p decreases Ugelstad and Hansen's equation for k'_d predicts a much smaller desorption constant than eq. (24). Ugelstad and Hansen's model cannot account for an increasing nonuniform distribution of monomer free radicals in the particle as D_p decreases.

EMULSION COPOLYMERIZATION

During emulsion copolymerization there are two monomer radical species A_m^* and B_m^* which may be generated and diffuse from the particle at different

TABLE II
Chain Transfer and Reinitiation Reactions for Copolymerization.

Chain transfer	Rate
$A^* + A \rightarrow \text{Dead Poly} + A_m^*$	$k_{AA}[A^*]_p[A]_p$
$A^* + B \rightarrow \text{Dead Poly} + B_m^*$	$k_{AB}[A^*]_p[B]_p$
$B^* + A \rightarrow \text{Dead Poly} + A_m^*$	$k_{BA}[B^*]_p[A]_p$
$B^* + B \rightarrow \text{Dead Poly} + B_m^*$	$k_{BB}[B^*]_p[B]_p$
Reinitiation	Rate
$A_m^* + A \rightarrow A^*$	$k'_{pAA}[A_m^*]_p[A]_p$
$A_m^* + B \rightarrow B^*$	$k'_{pAB}[A_m^*]_p[B]_p$
$B_m^* + A \rightarrow A^*$	$k'_{pBA}[B_m^*]_p[A]_p$
$B_m^* + B \rightarrow B^*$	$k'_{pBB}[B_m^*]_p[B]_p$

rates. The chain transfer and reinitiation reactions for monomers A and B are shown in Table II. The rate constants for propagation of monomer free radicals, k'_{pij} , may not be equal to the rate constants for the propagation of oligomer radicals.

Nomura et al.^{11,12} developed a kinetic model for batch emulsion copolymerization. These authors used a stochastic approach to derive rate constants for the desorption of A_m^* and B_m^* radicals formed by chain transfer within the particles. Their work indicated that the two monomer radical species may desorb at different rates depending on the monomer concentration ratios within the particles and the rates of chain transfer to both monomers. The rate constants for the desorption of A_m^* and B_m^* radicals are k_{dA} and k_{dB} :

$$k_{dA} = \frac{K_{0A}(k_{AA} + Lk_{BA})[A]_p}{K_{0A}\bar{n} + k'_{pAA}[A]_p + k'_{pAB}[B]_p} \quad (25a)$$

$$k_{dB} = \frac{K_{0B}(k_{AB}/L + k_{BB})[B]_p}{K_{0B}\bar{n} + k'_{pBB}[B]_p + k'_{pBA}[A]_p} \quad (25b)$$

where

$$K_{0A} = \frac{12D_{wA}}{d_p^2 \left[a_A + (D_{wA}/D_{pA}) \right]}, \quad K_{0B} = \frac{12D_{wB}}{d_p^2 \left[a_B + (D_{wB}/D_{pB}) \right]}$$

The mass transfer constants for the diffusion of monomer i radicals from the particles are K_{0i} . The diffusivities of monomer i radicals in the aqueous and particle phases are D_{wi} and D_{pi} , respectively. The term a_i is a partition coefficient for monomer i radicals between the particles and aqueous phase. The relations for the mass transfer coefficients were derived based on an

approach similar to the derivation of Ugelstad and Hansen's eq. (8). Nomura et al. combined the expressions for k_{dA} and k_{dB} in a mean desorption constant \bar{k}'_d :

$$\bar{k}'_d = v_p^{2/3} \left(\frac{k_{dA} + Lk_{dB}}{1 + L} \right) \quad (26)$$

Nomura et al. did not derive their mass transfer coefficient from a diffusion-reaction differential equation with the form of eq. (17). The following section contains the derivation of desorption rate constants for emulsion copolymerization which are based on differential equations describing the diffusion and reaction of A_m^* and B_m^* radicals within the particle.

MONOMER RADICAL CONCENTRATION PROFILES FOR COPOLYMERIZATION

A steady-state balance on A_m^* radicals about a small incremental volume of the particle yields the diffusion-reaction differential equation for A_m^* radicals with boundary conditions at $r = 0$ and $r = R$:

$$\begin{aligned} D_{pA} \frac{d^2 C_{Ap}}{dr^2} + \frac{2D_{pA}}{r} \frac{dC_{Ap}}{dr} - \{k'_{pAA}[A]_p + k'_{pAB}[B]_p\} C_{Ap} \\ = - \{k_{AA}[A^*]_p + k_{BA}[B^*]_p\} [A]_p \end{aligned} \quad (27)$$

$$\text{b.c. 1:} \quad r = 0, \quad dC_{Ap}/dr = 0$$

$$\text{b.c. 2:} \quad r = R, \quad \frac{4\pi D_{wA} R C_{Aps}}{a_A}$$

$$\begin{aligned} = \frac{4}{3}\pi R^3 \{ (k_{AA}[A^*]_p + k_{BA}[B^*]_p) [A]_p \\ - (k_{pAA}[A]_p + k_{pAB}[B]_p) \langle C_{Ap} \rangle \} \end{aligned}$$

The variable concentration of A_m^* radicals in the particle is C_{Ap} , C_{Aps} is the concentration of A_m^* radicals at the particle side of the particle-water interface, and $\langle C_{Ap} \rangle$ is the volume-average of C_{Ap} in the particle. The solution to eq. (27) subject to the boundary conditions is presented in eq. (28):

$$C_{Ap} = \bigcap_A \left(1 - \frac{2D_{wA} \sinh(\phi_A r')}{\{a_A R^2/3(k_{pAA}[A]_p + k_{pAB}[B]_p) X_A + 2D_{wA} \sinh(\phi_A)\} r'} \right) \quad (28)$$

where

$$\begin{aligned} \bigcap_A &= \frac{(k_{AA}[A^*]_p + k_{BA}[B^*]_p)[A]_p}{k_{pAA}[A]_p + k_{pAB}[B]_p} \\ \phi_A &= R \left[\frac{k_{pAA}[A]_p + k_{pAB}[B]_p}{D_p} \right]^{1/2} \\ r' &= rR; \quad X_A = 6 \left[\frac{\cosh(\phi_A)}{\phi_A} - \frac{\sinh(\phi_A)}{\phi_A^2} \right] \end{aligned}$$

Equation (28) reduces to the form of Equation (19) for homopolymerization of monomer A if the limit $[B]_p \rightarrow 0$ is taken as shown below:

$$C_{Ap} = \frac{k_{AA}[A^*]_p}{k_{pAA}} \left[1 - \frac{2D_{wA} \sinh(\phi_A r')}{\{a_A(R^2/3)k_{pAA}[A]_p X_A + 2D_{wA} \sinh(\phi_A)\} r'} \right] \quad (29)$$

The volume-average concentration $\langle C_{Ap} \rangle$ is expressed by

$$\langle C_{Ap} \rangle = \bigcap_A \left[1 - \frac{D_{wA} X_A}{a_A(R^2/3)(k_{pAA}[A]_p + k_{pAB}[B]_p) X_A + 2D_{wA} \sinh(\phi_A)} \right] \quad (30)$$

The flux of A_m^* radicals from the particle surface to the aqueous phase is Q_{As} :

$$Q_{As} = \frac{4\pi R D_{wA} C_{Aps}}{a_A} \quad (31)$$

The desorption rate constant for A_m^* radicals, k_{dmA} , is expressed by

$$k_{dmA} = \frac{Q_{AS}}{\langle C_{Ap} \rangle v_p} \quad (32)$$

The desorption rate constant k_{dA} is given by

$$k_{dA} = \frac{(k_{AA} + Lk_{BA})[A]_p}{k_{pAA}[A]_p + k_{pAB}[B]_p} k_{dmA} \quad (33)$$

The desorption rate constant defined by $k'_{dA} = k_{dA} v_p^{2/3}$ has the following form:

$$k'_{dA} = U_A \left(12(\pi/6)^{2/3} D_{wA} \left/ \left\{ a_A + \frac{D_{wA} \{ \sinh(\phi_A)(1 + 3/\phi^2) - 3 \cosh(\phi_A)/\phi_A \}}{R^2(k_{pAA}[A]_p + k_{pAB}[B]_p) X_A/6} \right\} \right) \right) \quad (34)$$

where

$$U_A = \frac{(k_{AA} + Lk_{BA})[A]_p}{k_{pAA}[A]_p + k_{pAB}[B]_p}$$

A relation for the concentration of B_m^* radicals in the particle was derived using the treatment applied to monomer A free radicals. The concentration of B_m^* radicals in particle, C_{Bp} , is expressed by

$$C_{Bp} = \bigcap_B \left[1 - \frac{2D_{wB} \sinh(\phi_B r')}{\{a_B(R^2/3)(k_{pBA}[A]_p + k_{pBB}[B]_p)X_B + 2D_{wB} \sinh(\phi_B)\} r'} \right] \quad (35)$$

where

$$\bigcap_B = \frac{(k_{AB}[A^*]_p + k_{BB}[B^*]_p)[B]_p}{k_{pBA}[A]_p + k_{pBB}[B]_p}$$

$$\phi_B = R \left(\frac{k_{pBA}[A]_p + k_{pBB}[B]_p}{D_{pB}} \right)^{1/2}, \quad X_B = 6 \left[\frac{\cosh(\phi_B)}{\phi_B} - \frac{\sinh(\phi_B)}{\phi_B^2} \right]$$

The volume-average concentration of B_m^* radicals, $\langle C_{Bp} \rangle$, is given by

$$\langle C_{Bp} \rangle = \bigcap_B \left[1 - \frac{D_{wB} X_B}{a_B(R^2/3)(k_{pBA}[A]_p + k_{pBB}[B]_p)X_B + 2D_{wB} \sinh(\phi_B)} \right] \quad (36)$$

The desorption rate constant k'_{dB} is expressed by

$$k'_{dB} = U_B \left(12(\pi/6)^{2/3} D_{wB} \left\{ a_B + \frac{D_{wB} \{ \sinh(\phi_B)(1 + 3/\phi^2) - 3 \cosh(\phi_B)/\phi_B \}}{R^2(k_{pBA}[A]_p + k_{pBB}[B]_p)X_B/6} \right\} \right) \quad (37)$$

where

$$U_B = \frac{(k_{AB}/L + k_{BB})[B]_p}{k_{pBA}[A]_p + k_{pBB}[B]_p}$$

To date there is no method to determine the cross chain transfer constants k_{AB} and k_{BA} independently. These constants are required for the numerical comparison of eq. (34) and (37) with Nomura's equations (25a) and (25b).

NONUNIFORM MONOMER RADICAL GENERATION

Chern⁸ considered the case where the oligomer free radicals are nonuniformly distributed in the particle. Chern assumed the nonpropagating end of the growing polymer chain is anchored to the surface of the particle by the hydrophilic initiator end group and that the growing free radical end is free to propagate in any direction within the particle. Chern used Monte Carlo simulations to show that the propagating free radical is more likely to reside close to the surface of the particle. The nonuniform oligomer free radical distribution was used to determine a nonuniform monomer free radical distribution and derive a desorption rate constant for monomer free radicals. Chern's theory was supported by experiments with styrene polymerization in polybutadiene seed particles.

Chern developed an expression for $[P^*]_p$ as a function radical position in the particle:

$$[P^*]_p = \frac{1.439\bar{n}}{N_A v_p} \left(1 - \frac{k_{fm}}{k_p} \right) \exp \left[-k \left(1 - \frac{r}{R} \right) \right] \quad (38)$$

The parameter k was determined from Monte Carlo simulations of the growth of a long-chain free radical in the latex particle. Chern calculated $[M_m^*]_p$ as a function of radial position by a simultaneous numerical solution of eq. (38) and the differential equation for diffusion and reaction of the monomer free radical [eq. (17)]. Monomer free radical concentration profiles calculated by Chern for ST emulsion polymerization are presented in Figure 5. The param-

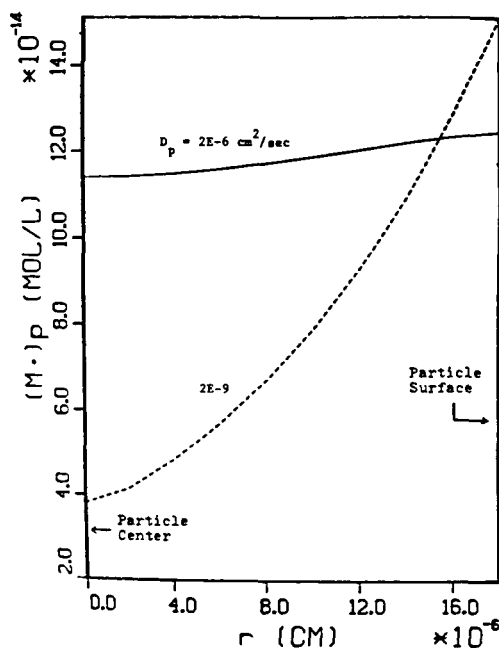


Fig. 5. Monomer radical concentration profiles from Ref. 8.

TABLE III
Calculated Desorption Rate Constants for Styrene Emulsion Polymerization^a Chern⁸

D_p (cm ² /s)	k'_d (cm ² /s)		
	Chern ⁸	Ugelstad, ² Nomura ⁶	This work
2.0×10^{-6}	2.3×10^{-13}	6.0×10^{-13}	6.0×10^{-13}
2.0×10^{-9}	2.6×10^{-13}	6.9×10^{-14}	3.7×10^{-13}

^a $T = 60^\circ\text{C}$, $k_{fm} = 8.8 \times 10^{-3}$ L/mol s, $k'_p = 1760$ L/mol s $D_w = 2.0 \times 10^{-5}$ cm²/s, $a = 1300$, $R = 5.0 \times 10^{-6}$ -cm.

ters used in the calculation are included in Table III. Chern's model predicts that the oligomer free radical is more likely to reside close to the particle surface; hence the rate of production and concentration of monomer free radicals are greater near the surface.

Chern used eq. (38) to develop an expression for k'_d which is shown below:

$$k'_d = \frac{k_{fm}}{k'_p} \frac{(4\pi/3)^{2/3} D_w}{a [1/k' - 1/k'^2 + 2/k'^3 - 2 \exp(-k')/k'^3]} \quad (39)$$

Chern used the parameters in Table III to calculate k'_d for ST emulsion polymerization with his model, Ugelstad's eq. (14) and Nomura's eq. (15). The results summarized in Table III indicate that Chern's model predicts the k'_d will not be a strong function of D_p . A decrease in D_p reduces monomer radical diffusion but causes a higher oligomer concentration near the surface. Hence the monomer radicals that are formed need not diffuse very far to reach the particle surface. All three models predict similar k'_d values when D_p is large (2.0×10^{-6}). The Ugelstad-Nomura model, however, predicts a more significant reduction in k'_d when D_p decreases to 2.0×10^{-9} .

CONCLUSIONS

Three models of transport of monomer free radicals from latex particles have been presented. The models of Ugelstad et al. and Nomura et al. were derived assuming uniform distributions of monomer free radicals and long chain free radicals within the particle. A model has been developed in this work that accounts for nonuniform distribution of monomer free radicals within the particle. Numerical comparison of Ugelstad's model and the model derived in this work has shown that the deviation between Ugelstad's k'_d and the k'_d based on the solution to the diffusion-reaction equation increases with decreasing D_p . The model developed by Chern accounts for nonuniform distributions of monomer free radicals and long chain free radicals. Numerical integration is required for the calculation of k'_d with Chern's model.

APPENDIX: NOMENCLATURE

a_i	partition coefficient for monomer i radicals
C_p	concentration of monomer radicals in particle (mol/L)
C_{ps}	concentration of monomer radicals at particle side of particle-aqueous interface (mol/L)

C_w	concentration of monomer radicals in aqueous phase (mol/L)
C_{wi}	concentration of monomer radicals at infinite distance from particle (mol/L)
C_{ws}	concentration of monomer free radicals at water side of particle-aqueous interface (mol/L)
d_p	diameter of monomer-swollen particle (cm)
D_{pi}	diffusivity of monomer i radical in particle (cm^2/s)
D_{wi}	diffusivity of monomer i radical in aqueous phase (cm^2/s)
k	term defined by Chern in eq. (38)
k'	term defined by Chern in eq. (39)
k_d	desorption rate constant (s^{-1})
k'_d	particle diameter independent desorption rate constant (cm^2/s)
k_{dA}, k_{dB}	desorption rate constants for copolymerization of monomers A and B, respectively (s^{-1})
k'_{dA}, k'_{dB}	particle diameter independent desorption rate constants for monomers A and B (cm^2/s)
k_{dm}	desorption rate constant for monomer radicals (s^{-1})
k_{dmA}, k_{dmB}	desorption rate constants for monomer A and B radicals, respectively (s^{-1})
k_{jm}	rate constant for chain transfer to monomer (L/mol s)
k_{ij}	rate constant for chain transfer from radical i to monomer j during copolymerization (L/mol s)
K_{0i}	mass transfer coefficient for monomer radical i (s^{-1})
k_p	rate constant for propagation (L/mol s)
k'_p	rate constant for reinitiation of oligomer radicals from monomer radicals (L/mol s)
k_{pij}	propagation rate constant for copolymerization (L/mol s)
k'_{pij}	rate constant for reinitiation of oligomer radicals for copolymerization (L/mol s)
k_t	rate constant for termination within particles (L/mol s)
k'_t	rate constant for reinitiation of oligomer radicals from CTA radicals (L/mol s)
k_{TT}	rate constant for chain transfer to CTA (L/mol s)
L	ratio of B^* radicals to A^* radicals in particle
M	monomer molecule
M_m^*	monomer free radical
\bar{n}	average number of radicals per particle
N	flux of diffusing species ($\text{mol}/\text{cm}^2 \text{ s}$)
N_A	Avogadro's number
N_p	number of particles per liter aqueous phase
P^*	long chain free radical
Q	mass transfer rate of monomer radicals from particle surface (mol s)
Q_{is}	mass transfer rate of monomer i radicals from particle surface during copolymerization (mol/s)
Q_p	mass transfer rate of monomer radicals at particle side of particle-aqueous interface (mol/s)
Q_w	mass transfer rate of monomer radicals at water side of particle-aqueous interface (mol/s)
r	radial position within monomer-swollen particle (cm)
R	radius of monomer-swollen particle (cm)
r'	dimensionless radius from eq. (19)
R_A	net rate of reaction of diffusing species (mol/L s)
T	chain transfer agent molecule
U_A	dimensionless term from eq. (34)
U_B	dimensionless term from eq. (37)
v_p	Volume of monomer-swollen polymer particle (cm^3)
X	dimensionless term from eq. (19)
X_A	dimensionless term from eq. (28)
X_B	dimensionless term from eq. (35)

Greek Letters

ρ_A	net rate of absorption of radicals by particles (mol/L H_2O s)
ϕ	dimensionless term defined in eq. (19)

\int_A	dimensionless term defined in eq. (28)
ϕ_A	dimensionless term defined in eq. (28)
\int_B	dimensionless term defined in eq. (35)
ϕ_B	dimensionless term defined in eq. (35)

This article is based upon work supported by the National Science Foundation under Grant No. CBT-8717926. The S. C. Johnson Co., Hercules, Inc., Unocal, and the Plastics Institute of America.

References

1. W. V. Smith and R. H. Ewart, *J. Chem. Phys.*, **16**, 592 (1948).
2. J. Ugelstad and F. K. Hansen, *Rubber Chem. Technol.*, **49**, 536 (1976).
3. J. Ugelstad, P. C. Mork, and J. O. Aasen, *J. Polym. Sci.*, A-1, **5**, 2281 (1967).
4. J. Ugelstad and P. C. Mork, *Brit. Polym. J.*, **2**, 31 (1970).
5. M. Nomura, M. Harada, K. Nakagowara, W. Eguchi, and S. Nagata, *J. Chem. Eng. Jpn.*, **4**, 160 (1970).
6. M. Nomura, M. Harada, W. Eguchi, and S. Nagata, *J. Appl. Polym. Sci.*, **15**, 675 (1971).
7. M. Nomura, H. Kojima, M. Harada, W. Eguchi, and S. Nagata, in *Emulsion Polymerization*, I. Piirma and J. C. Gardon, Eds., ACS Symposium Series **24**, Am. Chem. Soc., Washington, DC, 1976, p. 102.
8. C. S. Chern, Ph.D. dissertation, School of Chemical Engineering, Georgia Institute of Technology, Atlanta, 1987.
9. H. C. Lee, Ph.D. dissertation, School of Chemical Engineering, Georgia Institute of Technology, Atlanta 1985.
10. K. Goffloo and R. Kosfeld, *Angew. Makromol. Chem.*, **37**, 105 (1974).
11. M. Nomura, K. Yamamoto, I. Horie, and K. Fujita, *J. Appl. Polym. Sci.*, **27**, 2483 (1982).
12. M. Nomura, M. Kubo, and K. Fujita, *J. Appl. Polym. Sci.*, **28**, 2767 (1983).
13. G. Odian, *Principles of Polymerization*, ed., Wiley, New York, 1981.
14. C. R. Wilke and P. Chang, *AIChE J.*, **1**(2), 264 (1955).

Received January 29, 1988

Accepted August 8, 1988