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Rate of Entry in Emulsion Polymerization: Free-Radical Entry Controlled by Aqueous Phase Growth

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ABSTRACT: Reaction and diffusion of free radicals within a latex particle are investigated for the entry rate in emulsion polymerization when the entry requires that the oligomeric free radical reach a certain size. Transient expressions obtained for the entry rate show that the events within the particle do play a role in the transients but that they have no role in the steady-state entry rate. The transient behavior is shown to reveal useful information on the critical size of the oligomeric free radical. Initiator and monomer concentrations control the approach to the stationary state. A concise expression is obtained for a condition that has to be satisfied for the usual stationary state assumption.

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 capture rate or the rate of entry of free radicals into the particles, therefore, plays a key role in emulsion polymerization.

There are many theories advanced for the entry regarding the mechanism and its rate-controlling step. Diffusion control theory[1-3] considers the diffusion of the free radicals to the particle surface as the rate-controlling step. Surfactant displacement theory[4,5] suggests that displacement of surfactant from the particle surface is the rate-controlling step and by inference implies that the rate of entry depends on the surface coverage of the particle by the surfactant. Another theory[3,6] is that the entering species is a large oligomer, whose entry rate is governed by colloidal behavior.

A new theory proposed by Maxwell et al.[7] is that, for a free radical to enter a particle, it has to reach a critical size and that the rate-controlling step is the aqueous-phase growth of this free radical to the critical size. Another major premise of the theory is that the oligomeric free radical of the critical size is captured by the latex particle instantaneously and irreversibly regardless of what happens within the particle.

In this paper, the second premise is critically examined. Transient rate of entry is obtained for the case where the events in the particle have no effect on the rate of entry. The transient rate is also obtained for the case where the events do have an effect. The transient behavior is then examined to shed light on the critical size of the oligomeric free radical and to examine the relevance of the second premise.

Process of Radical Entry

In this theory of radical entry controlled by aqueous phase growth,[7] the water-soluble initiator is decomposed thermally and the resulting free radical propagates in the aqueous phase, growing in size. The oligomers thus formed can terminate by reactions with other radicals. The oligomers still remaining can enter the latex particles when they reach a certain size. The kinetics for the sequence of events can be described as follows:

Initiator decomposition

$$I \xrightarrow{k_d} 2M_0^{\bullet} \tag{1}$$

Propagation

$$M_0^{\bullet} + M \xrightarrow{k_{pi}} M_1^{\bullet} \tag{2}$$

$$M_i^{\bullet} + M \xrightarrow{k_p} M_{i+1}^{\bullet} \ (i = 1, 2, ..., z-1) \tag{3}$$

Termination

$$M_i^{\bullet} + T^{\bullet} \xrightarrow{k_t} \text{inert products} \ (i = 0, 1, 2, ..., z-1) \tag{4}$$

Entry

$$M_z^{\bullet} + \text{latex particle} \xrightarrow{\rho} \text{entry} \tag{5}$$

Here, M is the monomer unit, $M_0^{\bullet}$ is the primary free radical (e.g., $SO_4^{\bullet}$), $M_i^{\bullet}$ is an oligomeric radical containing i monomer units and an initiator end group, z is the number of monomer unit is that a primary free radical must add before it can enter a latex particle, $M_z^{\bullet}$ is thus the entering group, $T^{\bullet}$ is any aqueous-phase free radical, and I is the initiator. The rate constant k_d is for the initiator decomposition, k_{pi} is the propagation rate constant for the monomeric radical, k_p is the propagation rate constant, k_t is the termination rate constant, and ρ is the entry rate coefficient.

A key feature of the theory[7] is that the capture of polymeric radicals by seed latex particles is negligible if the size of the aqueous phase free radical is below a critical degree of polymerization z. Conversely, the irreversible free radical capture by seed latex particles is instantaneous for oligomeric free radicals of degree of polymerization z.

The rate equations resulting from reactions 1-5 are

$$\frac{d[M_0^{\bullet}]}{dt} = 2k_d[I] - k_{pi}[M_{aq}][M_0^{\bullet}] \tag{6}$$

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$$\frac{\mathrm{d}[\mathrm{M}_1{}^\bullet]}{\mathrm{d}t} = k_{\mathrm{p}i}[\mathrm{M}_{\mathrm{aq}}][\mathrm{M}_0{}^\bullet] - k_\mathrm{p}[\mathrm{M}_{\mathrm{aq}}][\mathrm{M}_1{}^\bullet] - 2k_\mathrm{t}[\mathrm{M}_1{}^\bullet][\mathrm{T}^\bullet] \tag{7}$$

$$\frac{\mathrm{d}[\mathrm{M}_i{}^\bullet]}{\mathrm{d}t} = k_\mathrm{p}[\mathrm{M}_{\mathrm{aq}}][\mathrm{M}_{i-1}{}^\bullet] - k_\mathrm{p}[\mathrm{M}_{\mathrm{aq}}][\mathrm{M}_i{}^\bullet] - 2k_\mathrm{t}[\mathrm{M}_i{}^\bullet][\mathrm{T}^\bullet] \quad (i = 2, ..., z-1) \tag{8}$$

$$\frac{\mathrm{d}[\mathrm{M}_z{}^\bullet]}{\mathrm{d}t} = k_\mathrm{p}[\mathrm{M}_{\mathrm{aq}}][\mathrm{M}_{z-1}{}^\bullet] - \rho\frac{N_c}{N_\mathrm{A}} \tag{9}$$

where $[\mathrm{M}_{\mathrm{aq}}]$ is the monomer concentration in the aqueous phase, [X] is the concentration of species X therein, N_c is the latex number density, and N_A is Avogadro's number. From the definition of $[\mathrm{T}^\bullet]$, it follows that

$$[\mathrm{T}^\bullet] = \sum_{i=0}^{z-1}[\mathrm{M}_i{}^\bullet] \tag{10}$$

Combining eqs 6–8 and summing over i yield

$$\frac{\mathrm{d}[\mathrm{T}^\bullet]}{\mathrm{d}t} = 2k_\mathrm{d}[\mathrm{I}] - k_\mathrm{p}[\mathrm{M}_{\mathrm{aq}}][\mathrm{M}_{z-1}{}^\bullet] + 2k_\mathrm{t}[\mathrm{M}_0{}^\bullet][\mathrm{T}^\bullet] - 2k_\mathrm{t}[\mathrm{T}^\bullet]^2 \tag{11}$$

The second and third terms in the right-hand side of eq 11 can be considered negligible compared with the other terms. Integrating eq 11 then yields

$$[\mathrm{T}^\bullet] = \left(\frac{k_\mathrm{d}[\mathrm{I}]}{k_\mathrm{t}}\right)^{1/2} \tanh[2(fk_\mathrm{d}k_\mathrm{t}[\mathrm{I}])^{1/2}t] \cong \left(\frac{k_\mathrm{d}[\mathrm{I}]}{k_\mathrm{t}}\right)^{1/2} \tag{12}$$

When the argument of the hyperbolic tangent is large, say larger than 3, the function approaches unity and the expression is given by the last line in eq 12, which is the usual form obtained from the pseudo-steady-state assumption. Integrating eq 6 yields

$$[\mathrm{M}_0{}^\bullet] = \frac{a^2}{b_i}\{1 - \exp(-b_i t)\} \tag{13}$$

where

$$a^2 = 2k_\mathrm{d}[\mathrm{I}] \qquad b_i = k_{\mathrm{p}i}[\mathrm{M}_{\mathrm{aq}}] \tag{14}$$

When eq 7 is used in eq 6 and integrated, the result is

$$[\mathrm{M}_i{}^\bullet] = b_i b^{i-1}\mathrm{e}^{-(b+ac)t}\int_0^t\int_0^{\tau_{i-1}}...\int_0^{\tau_1} \times [\mathrm{M}_0{}^\bullet]\mathrm{e}^{-(b+ac)\tau_0}\,\mathrm{d}\tau_0...\mathrm{d}\tau_{i-2}\,\mathrm{d}\tau_{i-1} \tag{15}$$

where

$$b = k_\mathrm{p}[\mathrm{M}_{\mathrm{aq}}] \tag{16}$$

$$c^2 = 2k_\mathrm{t}$$

The desired concentration $\mathrm{M}_{z-1}{}^\bullet$ follows directly from eq 15 when $z-1$ is substituted for i, yielding

$$[\mathrm{M}_{z-1}{}^\bullet] = b_i b^{z-2}\mathrm{e}^{-(b+ac)t}\int_0^t\int_0^{\tau_{z-2}}...\int_0^{\tau_1} \times [\mathrm{M}_0{}^\bullet]\mathrm{e}^{-(b+ac)\tau}{}_0\,\mathrm{d}\tau_0...\mathrm{d}\tau_{z-3}\,\mathrm{d}\tau_{z-2} \tag{17}$$

Rate of Entry

There are two ways of describing the entry process. If the oligomeric free radicals of critical size are captured into the seed particles irreversibly and instantaneously as proposed by Maxwell et a.,[7] then the rate of entry is simply proportional to the concentration of the oligomeric free radical. In this case, the rate of entry is entirely independent of what happens in the latex particle. Thus the number of free radicals in the particle could keep increasing with time. On the other hand, it is quite plausible that the rate of entry depends on what happens within the latex particle. The rate of entry for both cases will be obtained.

For the first case of irreversible and instantaneous entry, the rate of entry E is given by

$$E = k_\mathrm{e}[\mathrm{M}_z{}^\bullet] \tag{18}$$

where k_e is the rate constant.

The rate of entry is related to the entry rate coefficient ρ by

$$E = \rho(N_c/N_\mathrm{A}) \tag{19}$$

so that ρ is given by

$$\rho = k_\mathrm{e}N_\mathrm{A}[\mathrm{M}_z{}^\bullet]/N_c \tag{20}$$

Use of eqs 18 and 19 in eq 9 yields

$$\frac{\mathrm{d}[\mathrm{M}_z{}^\bullet]}{\mathrm{d}t} = b[\mathrm{M}_{z-1}{}^\bullet] - k_\mathrm{e}[\mathrm{M}_z{}^\bullet] \tag{21}$$

where $\mathrm{M}_{z-1}{}^\bullet$ is given by eq 17. If k_e is constant, then the solution is

$$[\mathrm{M}_z{}^\bullet] = \mathrm{b}\mathrm{e}^{-k_\mathrm{e}t}\int_0^t[\mathrm{M}_{z-1}{}^\bullet](\bar{t})\mathrm{e}^{k_\mathrm{e}\bar{t}}\,\mathrm{d}\bar{t} \tag{22}$$

Thus, from eq 20 the entry rate coefficient is given by

$$\rho = \frac{N_\mathrm{A}bk_\mathrm{e}}{N_c}\mathrm{e}^{-k_\mathrm{e}t}\int_0^t[M_{z-1}{}^\bullet](\bar{t})\mathrm{e}^{k_\mathrm{e}\bar{t}}\,\mathrm{d}\bar{t} \tag{23}$$

For the second case, where the entry rate depends on what happens in the latex particle, the rate of entry E is related to the flux at the particle surface J as follows:

$$E = (3/r_\mathrm{s})N_cJ \tag{24}$$

where r_s is the radius of the latex particle. For the flux, a mass balance for the free radical in a latex particle, which is assumed spherical, is written as follows:

$$\frac{\partial R^\bullet}{\partial t} = \frac{D_\mathrm{p}}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R^\bullet}{\partial r}\right) - kR^\bullet \tag{25}$$

where $R^\bullet$ is the concentration of the free radical in the particle, D_p is its diffusivity, and k is the apparent rate constant for the reactions involving the free radical. The boundary conditions are

$$\partial R^\bullet/\partial r = 0, \quad \text{at } r = 0 \tag{26}$$

$$R^{\bullet} = R^{*}\ (\equiv K[\mathrm{M}_z^{\bullet}]),\quad \text{at } r = r_{\mathrm{s}} \tag{27}$$

The first of the boundary conditinos is due to the symmetry around the center. The second represents an equilibrium between the free-radical concentration in the aqueous phase and that within the particle at r_{s}, which is R^{*}, through the equilibrium constant K. The free radical inside the particle either propagates through reaction with monomer or terminates through reactions with other radicals. Thus the apparent rate constant k is given by

$$k = \bar{k}_{\mathrm{p}}[\mathrm{M_p}] + n(k_{\mathrm{tp}}/v_{\mathrm{p}}) \tag{28}$$

where $[\mathrm{M_p}]$ is the monomer concentration in the particle, n is the number of free radicals in the particle, v_{p} is the particle volume, $\bar{k}_{\mathrm{p}}$ and k_{tp} respectively are the propagation and termination rate constants.

The solution of eq 25, when solved for the gradient, yields the following for the flux:

$$J = 8\pi r_{\mathrm{s}} D_{\mathrm{p}} R^{*} \sum_{i=1}^{\infty} \frac{1 + i^2 h \exp\{-(1 + hi^2)kt\}}{1 + i^2 h} \tag{29}$$

where

$$h = D_{\mathrm{p}}\pi^2/kr_{\mathrm{s}}^{2} \tag{30}$$

The first term in the summation dominates and it is sufficiently accurate to take only the first term, or

$$J \cong 8\pi r_{\mathrm{s}} D_{\mathrm{p}} K[\mathrm{M}_z^{\bullet}]\left[\frac{1 + h\exp\{-(1 + h)kt\}}{1 + h}\right] \tag{31}$$

where eq 27 has been used for R^{*}.

The expression for the rate of entry requires knowledge of $M_z^{\bullet}$. For this purpose, eq 9 is rewritten with the aid of eqs 19 and 24 as follows:

$$\frac{\mathrm{d}[\mathrm{M}_z^{\bullet}]}{\mathrm{d}t} = b[\mathrm{M}_{z-1}^{\bullet}] - \frac{3}{r_{\mathrm{s}}} N_{\mathrm{c}} J \tag{32}$$

This can be solved with eq 31 for J, which contains $\mathrm{M}_z^{\bullet}$, and eq 17 for $\mathrm{M}_{z-1}^{\bullet}$.

Before proceeding to the solution of eq 32 for the flux, examine the significance of parameter h. When the rate of diffusion is small compared with the reaction within the particle, that is, when diffusion controls, the value of h is much smaller than unity, leading to the following for the flux:

$$J = 8\pi r_{\mathrm{s}} \mathrm{D_p} K[\mathrm{M}_z^{\bullet}] \qquad \text{diffusion control} \tag{33}$$

$$\frac{\mathrm{d}[\mathrm{M}_z^{\bullet}]}{\mathrm{d}t} = b[\mathrm{M}_{z-1}^{\bullet}] - \bar{k}_{\mathrm{e}}[\mathrm{M}_z^{\bullet}];\quad \bar{k}_{\mathrm{e}} \equiv 24\pi N_{\mathrm{c}} D_{\mathrm{p}} K \tag{34}$$

Note that eq 34 is the same as eq 21, which is the result for the case of irreversible and instantaneous capture of the radicals by the particle, except for the definition of a rate constant, i.e., k_{e} vs $\bar{k}_{\mathrm{e}}$. Thus, the entry rate coefficient[7] in this case is the same as that given by eq 21 with k_{e} replaced by k_{e}'. Typical values of the physical parameters in h, at least for that system,[7] are such that diffusion is likely to control.

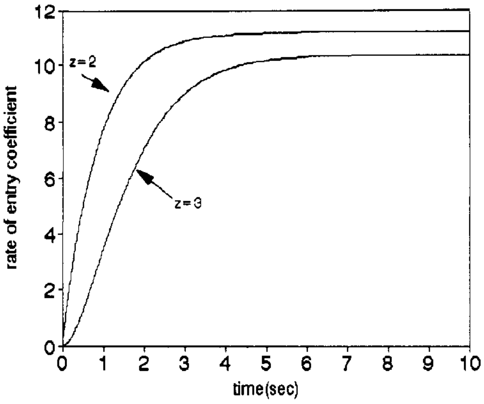

Figure 1. Entry rate coefficient as a function of time. ($N_{\mathrm{c}} = 5.0 \times 10^{10}$ number/L, $[\mathrm{I}] = 1.0 \times 10^{-6}$ mol/L, $[\mathrm{M_{aq}}] = 4.3 \times 10^{-3}$ mol/L, $k_{\mathrm{d}} = 1.0 \times 10^{-6}\ \mathrm{s}^{-1}$, $k_{\mathrm{p}} = 258$ L/(mol s), $k_{\mathrm{p}i} = 2 \times 10^{9}$ L/(mol s), $k_{\mathrm{t}} = 3.7 \times 10^{9}$ L/(mol s), $D_{\mathrm{p}} = 1.0 \times 10^{-7}\ \mathrm{dm}^2$/s, and $K = 1300$).

When the reaction within the particle controls, h is much larger than unity but the expression for J does not simplify. For the general case where both diffusion and reaction contribute, one may make a stationary state assumption for J with respect to the rate of change in the aqueous phase. Then eq 32 can be rewritten as

$$\frac{\mathrm{d}[\mathrm{M}_z^{\bullet}]}{\mathrm{d}t} = b[\mathrm{M}_{z-1}^{\bullet}] - k_{\mathrm{e}}'[\mathrm{M}_z^{\bullet}];\quad k_{\mathrm{e}}' \equiv \frac{24\pi N_{\mathrm{c}} D_{\mathrm{p}} K}{1 + h} \tag{35}$$

Solving eq 35, substituting the result into eq 31 and then into eq 24, and using the definition of eq 20 for the entry rate coefficient yield

$$\rho = 24\pi N_{\mathrm{A}} D_{\mathrm{p}} K b k_{\mathrm{e}}' \left\{\frac{1 + he^{-(1+h)kt}}{1 + h}\right\} \times \mathrm{e}^{-k_{\mathrm{e}}'t} \int_0^t [\mathrm{M}_{z-1}^{\bullet}](\bar{t})\mathrm{e}^{k_{\mathrm{e}}'-t}\,\mathrm{d}\bar{t} \tag{36}$$

Equation 36 is an expression of ρ that does not involve any stationary state assumption.

Transients and Steady-State Rate of Entry

It has been shown that the entry rate coefficient is given by eq 23 when the free radical of critical size is captured irreversibly and instantaneously by the latex particle. The same expression applies with k_{e} replaced by $\bar{k}_{\mathrm{e}}$ when the entry rate coefficient depends on what happens in the latex particle with diffusion controlling the process. Otherwise, the entry rate coefficient is given by eq 36.

The transient behavior of the entry rate coefficient reveals useful information regarding the magnitude of the critical size of oligomeric free radical, z. According to Maxwell et al.,[7] the value of z is about 2 or 3 in the styrene emulsion polymerization. In this light, examine the expression for the entry rate coefficient given by eq 23. If indeed the value of z is 2, the entry rate coefficient should increae rapidly with time initially. However, if the vlaue of z is 3, then the entry rate coefficient should increase gradually with time as shown in Figure 1 (refer to Appendix). Typical values of the parameters for the styrene emulsion polymerization, as detailed in Figure 1, have been used for the entry rate coefficient shown in the figure.

This transient behavior of the entry rate coefficient can be utilized as a spectroscopic method for detecting the magnitude of z. For this purpose, the differential of the entry rate coefficient, $\mathrm{d}\rho/\mathrm{d}t$, is plotted as a function of time in Figure 2. It is seen that the differential decreases monotonically with time when z is 2, whereas it goes through a maximum when z is 3. In fact, there exists a peak for all z greater than 2, and the peak moves to the right side of the time axis (longer time) with increasing z. Therefore, this differential behavior can be utilized to

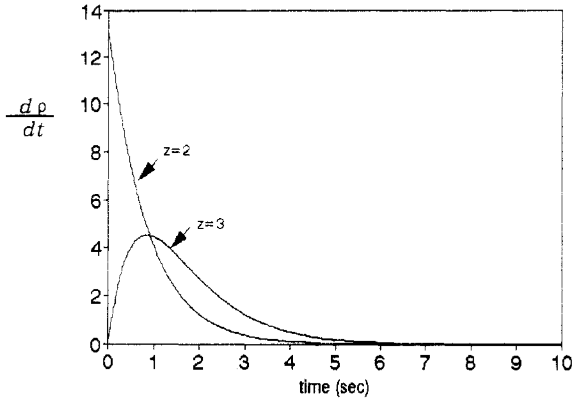

Figure 2. Differential of the entry rate coefficient with respect to time.

determine the critical size. The spectroscopy should definitely tell us whether z is 2 or it is greater.

Another important piece of information one can gain from transients is the conditions under which the usual stationary state (pseudo-steady-state) assumption can be made. Given in the appendix are expressions of ρ for z of 2 and 3. An examination of eqs A1 and A2 in the appendix shows that the approach to steady state is determined by the speed with which the exponentials vanish with time. The value of k_e is very large so that only e^{-b_it} and $e^{-(b+ac)t}$ need to be considered. It is experimentally clear that $b_i > b + ac$ so that the slowest approach to the steady state is controlled by $e^{-(b+ac)t}$. Let β be the percent approach to steady state, say 95% or 99% depending on the choice, which means that 95% or 99% of the steady-state value is reached. Then

$$e^{-(b+ac)t} < 1 - \beta/100$$

or

$$(k_p[M_{aq}] + 2(k_dk_t[I])^{1/2})t > \ln(1 - \beta/100) \qquad (37)$$

If the above condition is satisfied, then the steady state reaches $(100 - \beta)$%. The same holds for the case where the particle phase events affect the entry rate, i.e., eq 36. A condition of the same meaning has recently been put forward for a free-radical polymerization.[8] An important conclusion regarding the stationary-state assumption is that the magnitude of the initiator and monomer concentrations controls the approach to the stationary state. Note in this regard that k_d, k_p, and k_t are constants for a given system.

Steady-state values of the entry rate coefficient are obtainable directly from eqs 23 and 36. It is notable that, regardless of whether or not the rate of entry is dependent on the events within the latex particle, the steady-state value is the same, given by

$$\rho = \left(\frac{N_A}{N_c}\right)\frac{a^2}{(1 + ac/b)^{z-1}} \qquad (38)$$

The conclusion that can be drawn is that only the transient is affected by the events within the latex particle and not the steady-state value of the entry rate coefficient. Another important conclusion is that, if one is interested only in the steady-state behavior, it is not necessary for the theory[7] to state that the capture of the free radical by the latex particle is instantaneous and irreversible, the only essence of the theory being that the free radical must reach a certain size for it to enter the latex particle.

Appendix

When $z = 2$,

$$\rho = \frac{N_Aa^2b}{N_c}\left\{\frac{1 - e^{-k_et}}{b + ac} + \frac{k_e(e^{-(b+ac)t} - e^{-k_et})}{(k_e - b - ac)(b + ac - b_i)} - \frac{k_e(e^{-(b+ac)t} - e^{-k_et})}{(k_e - b - ac)(b + ac)} - \frac{k_e(e^{-b_it} - e^{-k_et})}{(k_e - b_i)(b + ac - b_i)}\right\} \qquad (A1)$$

When $z = 3$,

$$\rho = \frac{N_Aa^2b^2}{N_c}\left[\frac{1 - e^{-k_et}}{(b + ac)^2} + \frac{k_e(e^{-(b+ac)t} - e^{-k_et})}{(k_e - b - ac)(b + ac - b_i)^2} - \frac{k_e(e^{-(b+ac)t} - e^{-k_et})}{(k_e - b - ac)(b + ac)^2} - \frac{k_e(e^{-b_it} - e^{-k_et})}{(k_e - b_i)(b + ac - b_i)} + k_e\left(\frac{1}{b + ac - b_i} - \frac{1}{b + ac}\right)\left\{\frac{te^{-(b+ac)t}}{k_e - b - ac} - \frac{e^{-(b+ac)t} - e^{-k_et}}{(k_e - b - ac)^2}\right\}\right] \qquad (A2)$$

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