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Entry of Free Radicals into Latex Particles in Emulsion Polymerization

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ABSTRACT: A model, together with a comparison with previously published experimental data, is presented for initiator efficiency in seeded styrene emulsion polymerization systems in the absence of secondary particle formation. The data had shown that a number of previous models are inapplicable, viz., those assuming that the rate-determining step for free-radical entry into a particle is either diffusional capture, surfactant displacement, or colloidal entry. The data support the supposition that the rate-determining step for free-radical capture by latex particles is aqueous-phase propagation to a critical degree of polymerization, whereupon capture (irreversible adsorption) of the resulting oligomeric free radical by a particle is essentially instantaneous. Mutual aqueous-phase termination of smaller species also occurs. When account is taken of the fact that the rate coefficients for (a) the first aqueous-phase propagation step and (b) aqueous-phase termination are both in the diffusion limit, this model is in qualitative and quantitative accord with the experimental dependences of the entry rate coefficient on the concentrations of initiator, of surfactant, of aqueous-phase monomer, and of latex particles as well as on particle size and on ionic strength. For styrene emulsion polymerization initiated by persulfate, the critical oligomer size for entry was found to be dimeric.

Introduction

In emulsion polymerizations, the thermal decomposition of water-soluble initiators (e.g., peroxydisulfate anions) generates primary free radicals in the aqueous phase; however, the major locus of polymerization is the interior of the polymer latex particles.[1] This implies that the free-radical activity generated in the aqueous phase is transferred to the latex particles, allowing propagation to ensue therein. Although it is often assumed to the contrary, it is now well established that radical capture efficiencies in these systems can be very low.[2-5] Given that it is incorrect to assume 100% capture efficiency, a reliable model for the entry mechanism is required. Despite its fundamental as well as technical importance, this process of free-radical capture by latex particles is, at present, poorly understood.

The poor understanding of entry mechanisms derives partly from a lack of accurate experimental entry rate coefficient data. This in turn stems mainly from the difficulty involved in circumventing the numerous experimental and theoretical complications encountered in measuring entry rate coefficients. The experimental complications include ensuring a constant known latex particle concentration and size (this is overcome by doing seeded interval II experiments[2]) and obtaining accurate rate data. The theoretical complications include ensuring that the model used to interpret experimental results encompasses all the kinetic features thought to be important. Fortunately, data now exist[2-5] that purport to determine entry rate coefficients (ρ) unambiguously.

In the absence of any critical comparison of theory with experiment, many models for the prediction of ρ have survived. These models are based on a variety of non-equivalent physical or chemical assumptions, and these theories normally cannot predict accurate entry rate coefficients because of innate shortcomings, which are discussed in detail in this paper.

The first microscopic event that must occur for the entry of a free radical into a latex particle is the creation of free radicals from aqueous-phase initiator decomposition. It has long been recognized[6] that, on thermodynamic grounds, most primary free radicals formed from initiator decomposition (e.g., sulfate anion free radicals, $SO_4^{\bullet -}$) would be unlikely to transfer spontaneously from the polar aqueous environment to the organic phase. Priest[6] was perhaps the first to suggest that addition of monomer units to the primary free radicals would be required to effect this transfer.

The major aim of this paper is to show that aqueous-phase free radicals enter latex particles when they attain a particular size and that it is the rate of growth of aqueous-phase free radicals to this size that is rate-determining for entry of radical species into latex particles.[7,8] In the sections that follow, existing theories are reviewed, and a model based upon those ideas propounded above is presented. The predictions of this theory are then compared with reliable experimental values of ρ, and the implications of these comparisons discussed.

Review of Existing Theories of Entry

Diffusion Control. It has been suggested[9-12] that the rate-controlling step for entry is the diffusion of the free radical to the particle surface. The kinetics can then be quantified in terms of the following events:[8]

$$\text{initiator decomposition} \qquad \text{initiator} \xrightarrow{k_i} 2R^\bullet \tag{1}$$

$$\text{aqueous-phase termination} \qquad 2R^\bullet \xrightarrow{k_t} \text{termination} \tag{2}$$

$$\text{entry} \qquad R^\bullet + \text{particle} \xrightarrow{k_e} \text{entry} \tag{3}$$

where $R^\bullet$ denotes a radical that is capable of undergoing entry, it presumably being either surface-active or insoluble. The second-order entry rate coefficient is given by the Stokes–Einstein/Smoluchowski expression:

$$k_e(\text{diffusion}) = (2k_BT/3\eta)(r_s/r_0) \tag{4}$$

where k_B is Boltzmann's constant, T the temperature, η the viscosity of the medium, r_s the swollen radius of the particle, and r_0 the radius of the entering species. One then has[10]

$$\rho = (k_e^2/2k_t)[\{N^2 + (2k_tk_d[I]/k_e^2)\}^{1/2} - N] \tag{5}$$

where N is the latex particle concentration.

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Even if the diffusion of R• to the particle surface is considered to be rate-controlling in this system, this formulation still has some disadvantages. These are that this model artificially divides the processes of propagation and bimolecular termination in the aqueous phase such that (1) termination of species smaller than R• is not considered explicitly and (2) the nature and size of R• are not considered, in which case r_0 is unknown. As a result eq 5 does not accurately reflect those aqueous-phase kinetics that define the entry rate coefficient.

Equation 5 can yield accord with experimental results for ρ if one takes k_e to have the value of ca. 10^6 dm^3 mol^{-1} s^{-1} and k_t to be ca. 10^7 dm^3 mol^{-1} s^{-1}.[10] Moreover, this treatment does not yield any means of calculating k_e from first principles nor indeed give any hint as to the rate-determining step(s) for entry.

Surfactant Displacement. Yeliseeva[13] suggested that displacement of surfactant from the particle surface is the rate-determining step for entry (the foregoing mechanism is readily expanded[4] to include desorption of a surfactant molecule and the subsequent surface adsorption and desorption of the free radical R•). This mechanism implies that ρ should depend on the surface coverage of the latex particle by surfactant. However, a styrene emulsion polymerization[4] wherein the surface coverage was varied from 25 to 100% showed no significant change in the value of ρ. This qualitatively refutes the supposed mechanism.

Colloidal Entry. It has been suggested[10] that the entering species is a large oligomer, whose entry rate coefficient is governed by colloidal (DLVO[14] type) considerations. If this is the sole rate-determining step, then k_e can be obtained from DLVO theory (or appropriate extensions thereof that yield more accurate solutions of the Poisson–Boltzmann equation).[4] This would predict that k_e should depend on the surface charge density and size of the entering species, a mechanism that can be discounted for at least three reasons. (1) As stated, no change in ρ is observed with large changes in the surfactant coverage[4] (i.e., with surface charge density), thereby refuting the mechanism qualitatively. (2) It is found[4] that changing the ionic strength (while keeping all other factors constant) has no effect on ρ in a typical styrene system. Since the coagulation rate should be altered under such circumstances, this would appear to refute the postulate qualitatively; however, the nature of the repulsive barrier in such a heterocoagulation process is uncertain. (3) Using the aqueous-phase kinetics presented later in this paper, it is simple to show that, in the presence of sufficient seed particles, aqueous-phase free radicals should never grow to a size that allows colloidal species to develop.

A New Theory for Entry: Control by Aqueous-Phase Growth

The foundations of the model that will be proposed here bear some similarities to those previously set forth in the HUFT model for free-radical events involved in the homogeneous nucleation model for latex particle formation, due to *H*ansen and *U*gelstad[11] and to *F*itch and *T*sai.[12] In the HUFT treatment, the aqueous-phase kinetics of free radicals deriving from initiator decomposition are fully developed, and it is considered that the formation of latex particles (or their precursors) occurs at a certain critical degree of polymerization of the free-radical oligomers in the aqueous phase. Similarly, we consider the aqueous-phase kinetics of all free-radical species fully. We assume, however, that irreversible free-radical capture by seed latex particles is negligible if the aqueous-phase free radical is below a critical degree of polymerization z and, conversely, that irreversible free-radical capture by seed latex particles is instantaneous for oligomeric free radicals of degree of polymerization z. It will transpire that "instantaneous" in this context merely requires that the frequency of irreversible entry events is high compared with the frequency of aqueous-phase propagation or termination events. We are thus postulating that the growth of the aqueous-phase free radicals to a particular degree of polymerization is the rate-determining step for free-radical capture by latex particles. This concept is different from those generally thought[13] to be rate-determining for free-radical capture by latex particles, it normally being assumed that free-radical capture is controlled by diffusion of the aqueous-phase free radicals to the latex particle surface. In the present model, this diffusive step is supposed to be so fast as not to be rate-determining. The quantification of this new theory for free-radical capture by latex particles is now given.

As in the preceding discussion, we consider the following kinetic events that involve free radicals in the aqueous phase: initiator decomposition, propagation, bimolecular termination, and entry of free radicals into latex particles. Since we are proposing that growth of free radicals to a critical size for entry is the rate-determining step for entry, we assume, for simplicity, that all entering free radicals are of the same size (a distribution of entering sizes of oligomeric free radicals is trivially included in the model).

In the ensuing development, for notational simplicity we shall not explicitly treat that (usually small) component of entry due to "background" thermal production of free radicals.[2,5] What we denote here as ρ is in actuality the component of entry deriving solely from added initiator: that which we have denoted elsewhere[2] as ρ_I. The experimental values of ρ with which we compare the theory have all had the thermal component removed.

Reaction Scheme for Entry. The following reaction scheme (which is basically an expansion of reactions 1–3) is proposed for the aqueous-phase kinetics of an emulsion polymerization initiated by an ionic initiator (more details are given in Appendices A and B). We take this initiator to be peroxydisulfate anion (hereafter persulfate), although the expressions we derive are quite general.

initiator decomposition $$S_2O_8^{2-} \xrightarrow{k_d} 2SO_4^{\bullet -} \qquad (6)$$

initial propagation step $$SO_4^{\bullet -} + M \xrightarrow{k_{pi}} M_1^{\bullet} \qquad (7)$$

subsequent propagation $$M_i^{\bullet} + M \xrightarrow{k_p} M_{i+1}^{\bullet} \qquad (8)$$

termination $$M_i^{\bullet} + T^{\bullet} \xrightarrow{k_t} \text{inert products}, \ i < z \qquad (9)$$

entry $$M_z^{\bullet} + \text{latex particle} \xrightarrow{\rho} \text{entry} \qquad (10)$$

Here M is a monomer unit, $M_1^{\bullet}$ a monomeric radical with a sulfate end group, $M_i^{\bullet}$ an oligomeric radical containing i monomer units and a sulfate end group, z the number of monomer units a primary free radical (e.g., $SO_4^{\bullet -}$) must add before it enters a latex particle, and $M_z^{\bullet}$ thus the entering group. T• is any aqueous-phase free radical, k_d the first-order initiator decomposition rate coefficient, k_{pi} the propagation rate coefficient of a sulfate radical, and k_p the aqueous-phase propagation rate coefficient of the polymeric radical. It is important to note for later use that z is small: typically in the range 2–5. The entry event implied by reaction 10 is supposed to be irreversible adsorption of the free-radical species into a region of the latex particle where the monomer concentration is sufficiently high that rapid propagation takes place (it will be seen later that *reversible* adsorption can occur on a much shorter time scale).

The rate equations derived from reactions 6–10 are (Appendices A and B)

$$\mathrm{d}[\mathrm{SO_4}^{\bullet -}]/\mathrm{d}t = 2k_\mathrm{d}[\mathrm{S_2O_8}^{2-}] - k_\mathrm{pi}[\mathrm{M_{aq}}][\mathrm{SO_4}^{\bullet -}] \quad (11)$$

$$\mathrm{d}[\mathrm{M_1}^\bullet]/\mathrm{d}t = k_\mathrm{pi}[\mathrm{M_{aq}}][\mathrm{SO_4}^{\bullet -}] - k_\mathrm{p}[\mathrm{M_{aq}}][\mathrm{M_1}^\bullet] - 2k_\mathrm{t}[\mathrm{M_1}^\bullet][\mathrm{T}^\bullet] \quad (12)$$

$$\mathrm{d}[\mathrm{M}_i^\bullet]/\mathrm{d}t = k_\mathrm{p}[\mathrm{M_{aq}}][\mathrm{M}_{i-1}] - k_\mathrm{p}[\mathrm{M_{aq}}][\mathrm{M}_i^\bullet] - 2k_\mathrm{t}[\mathrm{M}_i^\bullet][\mathrm{T}^\bullet], \quad i = 2, ..., z - 1 \quad (13)$$

$$\mathrm{d}[\mathrm{M}_z^\bullet]/\mathrm{d}t = k_\mathrm{p}[\mathrm{M_{aq}}][\mathrm{M}_{z-1}^\bullet] - \rho N_\mathrm{c}/N_\mathrm{A} \quad (14)$$

where $[\mathrm{T}^\bullet]$ is the total concentration of free radicals in the aqueous phase, $[\mathrm{M_{aq}}]$ the monomer concentration in the aqueous phase, N_c the latex particle number density, and N_A the Avogadro constant. Note that in eqs 12 and 13, the termination rate contains a factor of 2; this is the IUPAC notation[16] used when the species $\mathrm{M}_i^\bullet$ and $\mathrm{T}^\bullet$ are the same. We justify the use of this notation here as some of the terminating species are oligomeric free radicals of the same size, and to include an extra termination term in the kinetic equations to account for termination between unlike species would be unnecessarily unwieldy. The k_t in eqs 12–14 is therefore to be interpreted as an appropriate "average" termination rate coefficient.

The total radical concentration in the aqueous phase is given by

$$[\mathrm{T}^\bullet] = [\mathrm{SO_4}^{\bullet -}] + \sum_{i=1}^{z-1} [\mathrm{M}_i^\bullet] \quad (15)$$

Because of the large values of the individual rate coefficients, the steady-state approximation is accurate for eqs 11–14 on the time scale of conversion of significant amounts of monomer to polymer. Moreover, it will be shown in the next section that the rate coefficient for the first aqueous-phase propagation step, k_pi, is orders of magnitude greater than that for subsequent steps, and hence eqs 11 and 12 can be replaced by the single result $\mathrm{d}[\mathrm{M_1}^\bullet]/\mathrm{d}t = 2k_\mathrm{d}[\mathrm{S_2O_8}^{2-}] - k_\mathrm{p}[\mathrm{M_{aq}}][\mathrm{M_1}^\bullet] - 2k_\mathrm{t}[\mathrm{M_1}^\bullet][\mathrm{T}^\bullet]$: i.e., eq 11 is not rate-determining. Equations 11–15 then reduce to

$$[\mathrm{M_1}^\bullet] = 2k_\mathrm{d}[\mathrm{S_2O_8}^{2-}]/(k_\mathrm{p}[\mathrm{M_{aq}}] + 2k_\mathrm{t}[\mathrm{T}^\bullet]) \quad (16)$$

$$[\mathrm{M}_i^\bullet] = k_\mathrm{p}[\mathrm{M_{aq}}][\mathrm{M}_{i-1}^\bullet]/(k_\mathrm{p}[\mathrm{M_{aq}}] + 2k_\mathrm{t}[\mathrm{T}^\bullet]), \quad i = 2, ..., z - 1 \quad (17)$$

$$\rho = (N_\mathrm{A}/N_\mathrm{c})k_\mathrm{p}[\mathrm{M_{aq}}][\mathrm{M}_{z-1}^\bullet] \quad (18)$$

$$[\mathrm{T}^\bullet] = \sum_{i=1}^{z-1} [\mathrm{M}_i^\bullet] \quad (19)$$

Entry rate coefficients can then be calculated by solving eqs 16–19 numerically (as is done for the calculations in this paper): for example, by starting with initial condition $[\mathrm{T}^\bullet] = 0$ and iterating until the calculated ρ remains unchanged from one iteration to the next. Alternatively,[11] one may use the result that $[\mathrm{T}^\bullet] = \{(2k_\mathrm{d}[\mathrm{S_2O_8}^{2-}] - k_\mathrm{p}[\mathrm{M_{aq}}][\mathrm{M}_{z-1}^\bullet])/2k_\mathrm{t}\}^{1-z}$ and then assume (as is reasonable for all except highly water soluble monomers) and $2k_\mathrm{d}[\mathrm{S_2O_8}^{2-}] \gg k_\mathrm{p}[\mathrm{M_{aq}}][\mathrm{M}_{z-1}^\bullet]$. Equations 16–19 then reduce to the analytic expression, well-known in the somewhat different context of HUFT theory:[11]

$$\rho = (2k_\mathrm{d}[\mathrm{S_2O_8}^{2-}]N_\mathrm{A}/N_\mathrm{c})[(2k_\mathrm{t}[\mathrm{T}^\bullet]/k_\mathrm{p}[\mathrm{M_{aq}}]) + 1]^{1-z} \quad (20)$$

where the total radical concentration is given approximately by

$$[\mathrm{T}^\bullet] = (k_\mathrm{d}[\mathrm{S_2O_8}^{2-}]/k_\mathrm{t})^{1/2} \quad (21)$$

Equations 20 and 21 are found to be inaccurate by at worst 10% compared to the exact solution of eqs 16–19 for a wide range of conditions.

Values of Rate Coefficients

A result that is crucial to the application of the entry model of this paper is that the rate coefficients for both the first aqueous-phase propagation step (k_pi) and the aqueous-phase termination between (small) oligomers, k_t, are very large: close to the diffusion limit. These conclusions are reached as follows.

Values of k_t for the aqueous phase have been experimentally established for several systems. For small acrylonitrile oligomeric radicals[17] in the aqueous phase at 50 °C, $k_\mathrm{t} = 7 \times 10^9$ dm^3 mol^{-1} s^{-1}. For 2-methylacrylic acid radicals[18] at 16 °C, $k_\mathrm{t} = 1.2 \times 10^9$ dm^3 mol^{-1} s^{-1}. These values are what one expects for a diffusion-controlled process for species of this size. For styryl-type radicals, termination rate coefficients have been measured in a variety of solvents using pulse radiolysis at 25 °C.[19] These also are in the diffusion limit for such termination processes, with values of 10^9–10^{10} dm^3 mol^{-1} s^{-1}. Such a high value of k_t in the aqueous phase is some 2 orders of magnitude greater than typical "zero-conversion" values obtained in the bulk (which are of order 10^7–10^8 dm^3 mol^{-1} s^{-1}). Nevertheless, we adopt a diffusion-controlled k_t value for the species of interest here (which are of small degree of polymerization: say $d_\mathrm{P} = 2$–5) for the following reason. In the bulk system, species of $d_\mathrm{P} = 2$–5 are in vanishingly small concentrations because they propagate to larger chains very rapidly. The zero-conversion k_t values in bulk/solution studies are indeed for chains sufficiently large that termination is controlled by segmental diffusion, *rather than center-of-mass diffusion*. In bulk/solution polymerizations, events involving this degree of polymerization, which might be of order 50, are detectable kinetically because the total population with $d_\mathrm{P} \leqslant 50$ is sufficiently high that there is a significant overall rate of termination between such species at low conversion, whereas the total rate of termination between species of $d_\mathrm{P} \simeq 2$–5 is completely negligible in bulk. Such is not the case for the aqueous-phase events of interest here, since *only* low-d_P species are involved. For such low-d_P species, segmental diffusion cannot occur, and hence the only rate-determining step in their mutual termination is likely to be center-of-mass diffusion. This will have a rate coefficient of the order of 10^{10} dm^3 mol^{-1} s^{-1} for species of this size.

Another essential aspect of the present model is that the value of the initial propagation step, k_pi, is also taken to be diffusion-controlled (or at least sufficiently fast so as not to be rate-determining). There is experimental evidence[20,21] for a very fast propagation rate coefficient (ca. 10^9 dm^3 mol^{-1} s^{-1}) between $\mathrm{SO_4}^{\bullet -}$ and an aqueous-phase monomeric species. For styrene this has been measured[20] at 2×10^9 dm^3 mol^{-1} s^{-1}. That this value should be so much greater than that for the propagation of a *macro*radical with a monomer (which is ca. 10^2–10^3 dm^3 mol^{-1} s^{-1}) can be rationalized as follows. The low value for propagation with a macroradical can be ascribed at least in part to the presence of a large "chemical" activation barrier: typically 30 kJ mol^{-1}. This is typical for the enthalpy difference between reactants (an *unchanged* free radical and a closed-shell monomer molecule at infinite separation) and the transition state formed from these two entities. It is clear on simple electrostatic grounds that there will be strong attractive forces between a *charged* free radical and a closed-shell molecule, and thus this enthalpy difference is likely to be much less than that for a system with a charged free radical (e.g., propagation between a macroradical and a monomer). This will result in a large increase in the propagation rate coefficient, as supposed above. There is also likely to be a contribution to the slow macroradical propagation rate coefficient from "steric" (entropic) effects: the presence of a long chain reduces the rate at which a monomer can achieve the correct orientation relative to the macroradical to cross the activation barrier; this effect will be absent if the radical is small. Thus even for an uncharged small free radical, one would expect a moderately large k_{pi}.

In our simplified description of eqs 6–10, it was assumed that all k_p are the same for $d_P > 1$, while k_p for $d_P = 1$ was many orders of magnitude greater. This cannot be an exact description of what really occurs: one may expect, for example, k_p to only have the large-d_P value for, say, $d_P > 5$, while the $d_P = 2–5$ values of k_p (which we denote k_{p2}, k_{p3}, etc.) would be intermediate between those for k_{pi} and the large-d_P value. Now, there is some evidence,[20] at least for the polymerization of acrylic acid at 16 °C, that the propagation rate coefficient is unchanging for radicals of $d_P > 1$ and, furthermore, that the value of k_p for $d_P > 1$ is that of the macroradical for this monomer. This evidence, however, does not necessarily hold for the relatively low solubility monomers considered in this study. The difficulties created by these considerations are studied more fully in the sensitivity analysis given in a later section.

The effect of solvent on the value of k_p for styrene has been shown to negligible.[22] The effect of a polar solvent, significantly, had little effect on the value of k_p for this monomer. Unfortunately, the value of k_p for styrene in water has not been measured. Therefore, in the absence of other data we will assume that the long-chain k_p is the same in water and organic solvents.

The values of other rate parameters will be discussed in the context of data fitting in the next section.

Results and Discussion

First, it should be remarked that the model is qualitatively consistent with all the general observations regarding the variation of ρ values with various experimental factors. (1) If the aqueous-phase growth of primary free radicals is rate-determining, it follows that neither adsorption onto nor penetration into the particle is rate-determining; this is consistent with the observation[4] that changing the surface characteristics in a styrene system, such as surface charge density, has no effect on ρ (within experimental uncertainties). (2) It is observed[4] that varying the ionic strength of a particular seeded emulsion polymerization system by a factor of 10 does not affect the measured entry rate coefficients. This is in accord with our model because k_d is not significantly affected by the ionic strength of the system (Appendix A). The addition of an indifferent electrolyte should have no other significant effect on the aqueous-phase events that determine entry.

The model can now be tested quantitatively against a range of experimental data. Entry rate coefficients have been measured[2] for emulsion polymerizations of styrene[2-5] and are available over a wide range of experimental conditions, including varying particle sizes, latex particle concentrations, initiator concentrations, ionic strength, surfactant coverage on latex particles and monomer concentrations in the aqueous phase. The details of experimental techniques and data reduction methods have been given elsewhere[2-5] (see also Appendix B).

Table I
Values of Rate Parameters Used To Calculate Styrene Entry Rate Coefficients

k_d/s^{-1} [a]	1×10^{-6}
$k_p/(dm^3\ mol^{-1}\ s^{-1})$	258[b]
$k_t/(dm^3\ mol^{-1}\ s^{-1})$[c]	3.7×10^9
$[M_{aq,sat}]/(mol\ dm^{-3})$	4.3×10^{-3}

[a] Reference 32. [b] Reference 2. [c] Based on refs 17 and 19.

Table II
Experimental Conditions of Measured Entry Rate Coefficients for Styrene and Fitted *z* Values (z_{fit})

N_c/dm^{-3}	r_s/nm	$[S_2O_8^{2-}]/(mol\ dm^{-3})$	z_{fit}	ref	figure
4.9×10^{16}	79	$10^{-5}–10^{-2}$	2–3	5	1
1.0×10^{17}	62	$(0–13) \times 10^{-4}$	2–3	5	3
2.6×10^{17}	44	$(0–9) \times 10^{-4}$	2–3	5	4
$(0.7–3) \times 10^{16}$	56	$10^{-5}–10^{-2}$	3	3	2
5.0×10^{16}	76	5×10^{-4}	2	23	5

To carry out this test, z was treated as an adjustable parameter and optimized to fit experimental data. Values of z were restricted to be integers. We do not consider a distribution of the sizes of the entering free radicals; as stated, such as distribution could be readily taken into account, but this is undesirable as it would introduce more than one adjustable parameter into the model.

The values of the rate coefficients and aqueous-phase monomer concentration used to fit the data are presented in Table I. There are some uncertainties about the value of k_d (Appendix A) mainly arising from possible effects of surfactant, monomer, pH, and impurities on the thermal decomposition rate of persulfate in water. It was found that for the styrene system a k_d of 1×10^{-6} dm^3 mol^{-1} s^{-1} at 50 °C gave good agreement with the data. Better fits could be obtained if k_d were to be used as a free parameter, although in the system studied it should not deviate too far from the value in a pure system, $k_d = (1.7 \pm 0.9) \times 10^{-6}$ dm^3 mol^{-1} s^{-1} at 50 °C (Appendix A).

It must be noted that the entry rate coefficients used in this paper are subject to significant experimental uncertainty.[2] The only uncertainties considered are of a random type, and these are taken to be approximately ±30–50%.

Sodium dodecyl sulfate (SDS) was the surfactant used in all the styrene experiments considered here. All the experiments were carried out at 50 °C.

The experimental conditions and z values that best fit experiments are presented in Table II. Discussion of these results now follows.

Emulsion Polymerization of Styrene

Initiator Concentration. Figures 1, 3, and 4 show variations of the measured entry rate coefficients over a wide range of persulfate concentration. In all cases a z of 2–3 gives an excellent fit to the data, reproducing both the values of the entry rate coefficients and their trend with increasing initiator concentration.

Latex Particle Number Density. Figure 2 shows the experimental variation of ρ with N_c at a constant persulfate concentration and swollen radius of $r_s = 56$ nm.[5] Figure 2 indicates that $z = 3$ furnishes a good fit, within experimental error, to the variation of ρ with N_c.

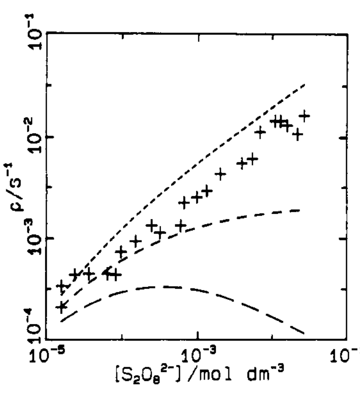

Figure 1. Experimental (points) and calculated (lines) values for the variation of the entry rate coefficient, ρ, with initiator concentration, $[S_2O_8^{2-}]$, for styrene at 50 °C. (- - -) Calculated values with $z = 2$; (— — —) $z = 3$; (——— ———) $z = 4$. Experimental data from Hawkett et al.[5] $N_c = 5 \times 10^{16}$ dm^{-3}, $r_s = 79$ nm.

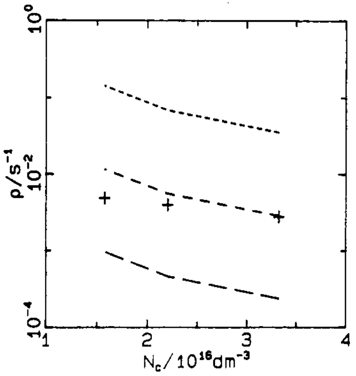

Figure 2. Experimental and calculated values for the variation of the entry rate coefficient, ρ, with latex particle concentration, N_c, for styrene at 50 °C. (- - -) Calculated values with $z = 2$; (— — —) $z = 3$; (——— ———) $z = 4$. Experimental data from Whang et al.[3] $r_s = 56$ nm.

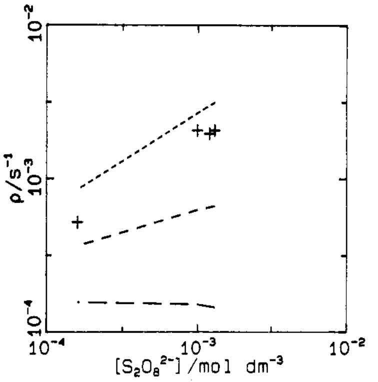

Figure 3. Experimental and calculated values for the variation of the entry rate coefficient, ρ, with initiator concentration, $[S_2O_8^{2-}]$, for styrene at 50 °C. (- - -) Calculated values with $z = 2$; (— — —) $z = 3$; (——— ———) $z = 4$. Experimental data from Hawkett et al.[5] $N_c = 1 \times 10^{17}$ dm^{-3}, $r_s = 62$ nm.

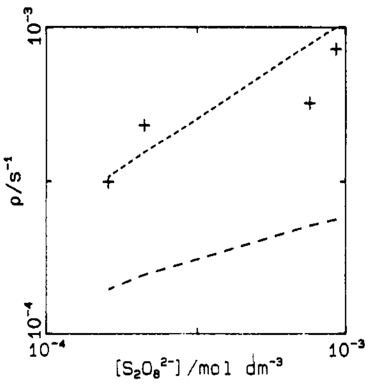

Figure 4. Experimental and calculated values for the variation of the entry rate coefficient, ρ, with initiator concentration, $[S_2O_8^{2-}]$, for styrene at 50 °C. (- - -) Calculated values with $z = 2$; (— — —) $z = 3$. Experimental data from Hawkett et al.[5] $N_c = 3 \times 10^{16}$ dm^{-3}, $r_s = 44$ nm.

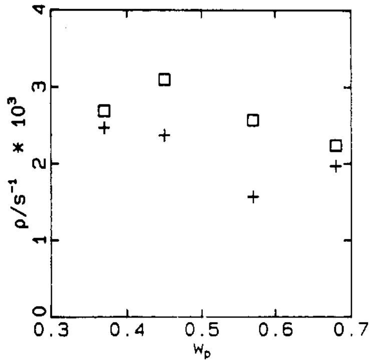

Figure 5. Experimental (+) and calculated (□) values for the variation of the entry rate coefficient, ρ, with weight fraction of polymer, w_p, for styrene at 50 °C. Experimental data from Leslie et al.[23] $N_c \approx 5 \times 10^{16}$ dm^{-3}, $r_s = 76$ nm.

Particle Size. The variation of ρ with latex particle size has been measured[5] at varying N_c. This actually provides a more rigorous test for the model, as there are two varying experimental parameters, particle size and particle concentration. Figure 1 ($r_s = 79$ nm) and Figure 4 ($r_s = 44$ nm) show the variation of ρ with persulfate concentration at two different particle sizes and particle concentrations. However, in each of these plots a z values of 2–3 accurately fits the data, and more importantly the slope of the experimental points of both sets of data corresponds to the theoretically calculated slope using $z = 2$. This is in accord with our model which predicts that, all other things being equal, there should be no effect of latex particle size on the entry rate coefficient.

Surfactant Concentration. The surfactant concentration could conceivably affect k_d (Appendix A). However, in the conditions under which ρ was measured[5] in styrene emulsion polymerizations, the surfactant (SDS) concentrations were all similar. The total surfactant concentration in the experiments of Figures 1, 3, and 4 were all 1.5×10^{-2} mol dm^{-3}. As these experiments all had similar total surface area of polymer, we expect that all had similar surfactant concentration in the aqueous phase. Therefore, we use the same k_d for the model calculations on these experiments. The model predicts that surfactant concentration will not affect ρ (other than through any effect on k_d) as seen experimentally.[4] A value of $z = 2$ produces a good fit to the data.

Aqueous-Phase Monomer Concentration. Finally, Figure 5 shows the variation[23] of ρ with weight fraction polymer in the particle phase (w_p). For the following reason this is a particularly stringent test of the model. The model implies that ρ should show a strong dependence on $[M_{aq}]$. This latter quantity can be varied by changing w_p during interval III of an emulsion polymerization, without changing any other quantities in the system; theory and experiment are then compared. In this comparison, it is necessary to determine $[M_{aq}]$ as a function of w_p experimentally, since partitioning is likely to be nonideal. This was done by adding monomer to a latex particle seed and, after equilibrium, extracting a sample of the water phase by dialysis (employing ordinary dialysis tubing). Determination of the monomer concentration in the aqueous phase was carried out by GC analysis. The results are

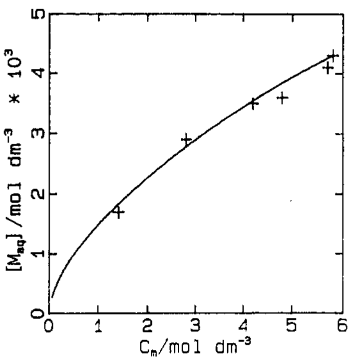

Figure 6. Points: experimental values for the variation of styrene concentration in water with styrene concentration in the latex particles with unswollen radius of 56 nm at 50 °C. The line is the fit to the data represented by eq 22.

displayed in Figure 6. At 50 °C it was found that

$$[\mathrm{M_{aq}}]/[\mathrm{M_{aq,sat}}] \simeq (C_\mathrm{m}/C_\mathrm{m,sat})^{0.6} \qquad (22)$$

where C_m is the concentration of monomer in the particle phase, $C_\mathrm{m,sat}$ the saturation concentration of monomer in the particle phase, and $[\mathrm{M_{aq,sat}}]$ the saturation concentration of monomer in the aqueous phase. Assuming ideal mixing, the concentration of monomer in the particles can be related to w_p by

$$w_\mathrm{p} = \{1/C_\mathrm{m}M - 1/d_\mathrm{m}\}/\{1/d_\mathrm{p} + (1/C_\mathrm{m}M) - 1/d_\mathrm{m}\} \qquad (23)$$

Here, M is the molecular weight of the monomer, and d_m and d_p are the densities of the monomer and polymer, respectively. Using the experimental $[\mathrm{M_{aq}}]$, observed and calculated results for ρ are in good agreement. The maximum in the calculated values (Figure 5) arises from small variations in N_c that were used in the experiment.

Sensitivity Analysis

The degree of polymerization of an entering free radical, z, was treated as the adjustable parameter when fitting the entry model to experiment. The predicted value of ρ is very sensitive to the value taken for z: ρ can change by an order of magnitude as z changes from 2 to 3. Now, it can be seen that no single value of z can provide a proper fit to all the data for styrene: for example, for the results of Figure 2, $z = 2$ is optimal, whereas those of Figure 3 are better fitted by $z = 3$. Is this a weakening of the case for the correctness of the model? We think not and ascribe this (comparatively minor) discrepancy to the following causes.

First, as previously stated, the value of k_p was considered to be unchanging for $d_\mathrm{P} > 1$, but this may be an oversimplification of the real situation. Equations 16–19 can readily be extended to include multiple values of k_p, albeit at the expense of introducing more adjustable parameters (since there are currently no data available on k_p for styrene at such low d_P, although such data can be obtained in principle). Although we have decides against this (for obvious reasons), it is important to understand what effect it would have on the fitting. Since $k_\mathrm{pi} > k_\mathrm{p2} > k_\mathrm{p3} > ... > k_\mathrm{p}$, the inclusion of k_p2, k_p3, etc. would obviously increase the value of z that would fit the data. This is because shorter free radicals could now propagate more rapidly and thus be less likely to undergo termination. Hence one sees that the value of z obtained without taking the d_P dependence of k_p into account is a *lower bound* to the true value. Moreover, one sees that if one can obtain a fit to all data with $z = 2$ or 3 without the addition of the further parameters implied by separate values for k_p2, k_p3, etc., then clearly one would be likely to obtain a single value of z that could fit the data if these adjustable parameters were introduced.

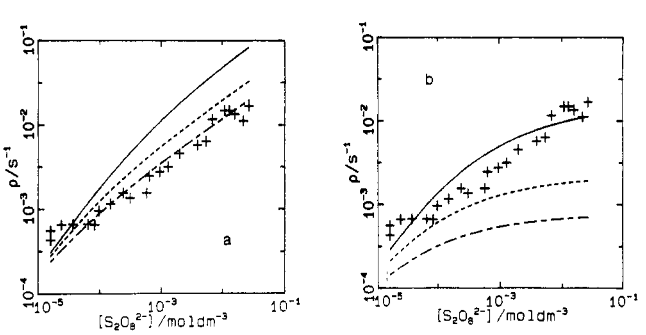

Figure 7. Experimental and calculated values for the variation of the entry rate coefficient, ρ, with initiator concentration, $[\mathrm{S_2O_8}^{2-}]$, for styrene at 50 °C: (a) predictions with $z = 2$; (b) predictions with $z = 3$. (—), (- - -), and (– – –): $k_\mathrm{t} = 5 \times 10^8$, 3.5 × 10^9, and 1 × 10^{10} dm^3 mol^{-1} s^{-1}, respectively. Experimental data from Hawkett et al.[5]

Second, the possible error involved in the measurement of entry rate coefficients has not been considered. As already stated the random error in the entry rate coefficients has been estimated at ±30–50%. This does not include possible systematic errors, which are difficult to eliminate because of the complexity of the experimental techniques, and subsequent data analysis, utilized to obtain entry rate coefficients. It may be that the differences between a fit $z = 2$ and $z = 3$ can be attributed to these possible errors.

Having considered the sensitivity of the data fit to the value of z, we now examine the sensitivity to the values of the other variables, namely, k_t and k_d. The values of k_d and, to a lesser extent, k_t are known only to within certain wide limits (Appendix A); therefore it is important to consider whether the fitted values of z vary widely if the values of these two rate coefficients are changed within their uncertainty.

The sensitivity of the fit of the model to experiment, namely, the variation of ρ values with initiator concentration, was first tested by varying the value of k_t within its uncertainty. In Figure 7 the values of k_t used to calculate the theoretical ρ values are 5 × 10^8, 3.5 × 10^9, and 1.0 × 10^{10} dm^3 mol^{-1} s^{-1}. These values represent, respectively, an anomalously low value, the value suggested by experiments, and the diffusion-limited value. The experimental data[5] comprise the largest variation of ρ values with initiator concentration available. It is apparent that even by varying k_t over nearly in an order of magnitude the same range of z values (2–3) produce fits of similar quality. We therefore conclude that, while sensitive to larger changes in k_t, the fits obtained in this paper are valid when considering the likely smaller error in the actual value of k_t.

The second parameter whose value was tested for sensitivity of fit was k_d. As discussed in Appendix A, we have adopted the value of $k_\mathrm{d} = (1.7 \pm 0.9) \times 10^{-6}$ s^{-1}. For this sensitivity analysis, we have chosen three values of k_d near this range, 1 × 10^{-6}, 2 × 10^{-6}, and 3 × 10^{-6} s^{-1}, and tested the fit with the same experimental data used above.[5] These fits are shown in Figure 8. In each case reasonable fitting is obtained, confirming the validity of the fitting procedures utilized in this paper.

Before we draw conclusions from this sensitivity analysis, it must be pointed out that the slopes of all the theoretically calculated lines using $z = 2$ are similar to those found experimentally. Variations of k_t and k_d within reasonable limits change only the absolute value of the calculated

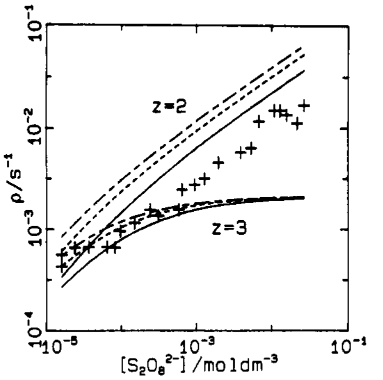

Figure 8. Experimental and calculated values for the variation of the entry rate coefficient, ρ, with initiator concentration, $[S_2O_8^{2-}]$, for styrene at 50 °C: upper lines, predictions with $z = 2$; lower lines, predictions with $z = 3$. (—), (- - -), and (— — —): $k_d = 1 \times 10^{-6}$, 2×10^{-6}, and 3×10^{-6} dm^3 mol^{-1} s^{-1}, respectively. Experimental data from Hawkett et al.[5]

entry rate coefficients. We can then conclude that the uncertainties considered in the values of k_t and k_d do not significantly affect the quantitative fits that are found in this work.

Rationalization of the Values of *z*

The rate of encounter of any aqueous-phase free-radical species (from $SO_4^{\bullet-}$ to $M_zSO_4^-$) with a latex particle is likely to be diffusion-controlled. If all such encounters actually resulted in entry (i.e., irreversible adsorption into a monomer-rich region and subsequent propagation), then it is easily shown that ρ would just reflect the decomposition rate of persulfate (eq 28): that is, most such encounters (particularly those involving small soluble species such as $SO_4^{\bullet-}$) do not result in entry. Hence most encounters by soluble species must never penetrate the interior of the particle and/or must be followed by very rapid *desorption* after the entity encounters the particle surface.

It might be expected that the minimum requirement for a primary free radical generated in the aqueous phase to enter a monomer-swollen latex particle would be for the radical to add sufficient monomer molecules in the aqueous phase to render the resultant oligomeric species surface-active and hence less likely to desorb. Surface activity in this context refers to the ability of the oligomeric species to adsorb strongly onto the surface of a polymer latex particle. We are thus led to consider the thermodynamics of adsorption of the various aqueous-phase free-radical species: the free energy of adsorption, through the equilibrium constant $K = \exp(-\Delta G°/RT)$, will give the ratio of the rate coefficients of adsorption and desorption (since these processes, to a first approximation, are the reverse of each other). The more the equilibrium favors adsorption over desorption, the more likely it is that true entry will occur.

Such adsorption can be considered in thermodynamic terms to be analogous to the association of amphipathic molecules such as occurs in crossed mica plate experiments where the plates are coated with hydrocarbon or in adsorption at the oil/water interface in micellization. The hydrophobic driving forces that result in adsorption would also be expected to be similar to those operative in the dimerization of hydrocarbon species in water. Data from such experiments permit an approximate estimate to be made of the hydrophobic free energy of adsorption of oligomeric chains onto the surfaces of the latex particles. Whether this hydrophobic free energy is sufficient to impart adequate surface activity to the oligomeric species containing the polar residue of the primary free radical species must then be established. The procedure will be first illustrated for styrene and then extended to encompass other monomers.

Israelachvili and Pashley,[24] using crossed mica plates, established empirically that the hydrophobic free energy of dimerization of small solute molecules in water is given by

$$\Delta G^{\text{hyd}}/(\text{kJ mol}^{-1}) \simeq -20\ (\sigma/\text{nm}) \qquad (24)$$

where σ is the diameter of the solute molecule. For a monomeric styryl unit, σ = 0.6 nm, so $\Delta G^{\text{hyd}} \simeq -12$ kJ mol^{-1} per styryl unit. The foregoing value can be cross-checked by two different methods. First, critical micelle concentration studies[25] imply that the removal of each CH_2 residue from an aqueous environment to the interior of a micelle is accompanied by a change in ΔG of ca. −3 kJ mol^{-1}. Note that this value is in good agreement with the value (−3.0 kJ mol^{-1}) predicted by the empirical relationship of Israelachvili and Pashley since $\sigma \simeq 0.15$ nm (the C–C bond length) in this case; further a value of $\Delta G^{\text{hyd}} \simeq -3.3$ kJ mol^{-1} has been found for the removal of each CH_2 from an aqueous environment to an oil/water interface.[26] When these values are coupled with a value of $\Delta G^{\text{hyd}} \simeq -8$ kJ mol^{-1} for the dimerization of benzene in water,[27] a value of $\Delta G \simeq -14$ kJ mol^{-1} is calculated for the hydrophobic free energy accompanying the dimerization of a styryl monomeric unit in water. This result is in reasonable agreement with that (−12 kJ mol^{-1}) predicted by the empirical relationship of Israelachvili and Pashley. The second cross-check comes from the approximate value for ΔG^{hyd} that can be obtained from the saturation solubility ($[M_{\text{aq,sat}}]$) of the monomer in the aqueous phase:

$$\Delta G^{\text{hyd}} \simeq RT \ln\,[M_{\text{aq,sat}}] \qquad (25)$$

For styrene[28] at 50 °C, $[M_{\text{aq,sat}}] = 4.3 \times 10^{-3}$ mol dm^{-3} so that $\Delta G^{\text{hyd}} \simeq -15$ kJ mol^{-1}. The three methods for calculating ΔG^{hyd} all give values lying in the range −(12–15) kJ mol^{-1}. A mean value of −14 kJ mol^{-1} will be adopted in what follows.

The question then arises as to whether the hydrophobic free energy of adsorption is sufficient to impart surface activity to the polar residue of the primary free radical species, such as a sulfate radical anion. This matter can be resolved by considering at what chain length the species $C_nH_{2n+1}SO_4^-$ just becomes surface-active. Micellization of this species definitely occurs for $n = 8$ but the species with $n = 6$ displays little, if any, surface activity.[26] This suggests a minimum value of $n = 6$ or 7 is necessary to impart useful surface activity, corresponding to a $\Delta G^{\text{hyd}} \simeq -(22–25)$ kJ mol^{-1} if allowance is made for the presence of the terminal CH_3 for which[29] $\Delta G^{\text{hyd}} \simeq -7$ kJ mol^{-1}. An absolute value of $|\Delta G^{\text{hyd}}|$ of 23 kJ mol^{-1} will be adopted as the minimum value of the hydrophobic free energy required to impart surface activity. The foregoing calculations of the surface activity of n-alkyl surfactants are likely to be applicable over a temperature range of 25–60 °C. Over this interval, the critical micelle concentrations of typical n-alkyl surfactants change only marginally (e.g., by 10%), although more significant changes are evident over wider temperature ranges.[30] This weak dependence upon temperature is confirmed by the temperature insensitivity reported for the free energy of transfer of CH_2 groups from the aqueous phase to the air/water interface (a change of only 4% is reported over the temperature range 25–60 °C).[25]

Table III
Calculated Values of z for Surface Activity ($z_{\mathrm{min,surf}}$; Eq 26) and Insolubility ($z_{\mathrm{min,insol}}$; Eq 27) of Oligomers of Various Monomers with Persulfate Initiator at 50 °C

monomer	$[\mathrm{M_{aq,sat}}]/(\mathrm{mol\ dm^{-3}})$	ref	$z_{\mathrm{min,surf}}$	$z_{\mathrm{min,insol}}$
styrene	4.3×10^{-3}	28	2	4
butyl acrylate	6.2×10^{-3}	37	2	4
butyl methacrylate	2.5×10^{-3}	38	2	4
butadiene	1.5×10^{-2}	13	2–3	5–6
methyl methacrylate	0.15	39	4–5	10–11
vinyl chloride	0.11	13	4–5	10–11
vinyl acetate	0.3	13	7–8	15–18

The preceding criterion for establishing whether or not an oligomer is surface-active suggests that tail addition of $\mathrm{SO_4}^{\bullet-}$ to one styrene monomer produces a species that displays little surface activity ($|\Delta G^{\mathrm{hyd}}| \simeq 14$ kJ mol^{-1}) whereas the addition of a second monomer unit ($|\Delta G^{\mathrm{hyd}}| \simeq 28$ kJ mol^{-1}) should produce a species with good surface-active properties. A minimum value of $z = 2$ for entry is thus predicted for styrene on thermodynamic grounds, in fair agreement with the experimental results for entry. Of course, values of z greater than 2 correspond to species with even greater surface activity, all capable of entry events. The fact (pointed out at the beginning of this section) that our fitted value of z is in fact a lower bound to the true value should also be borne in mind in this context.

There is a limit, however, to the value of z that can be achieved before the oligomeric species becomes essentially insoluble in water. A crude estimate of this maximum value can be obtained by considering the n-alkyl chain length for which, say, 50 °C corresponds to the Krafft temperature. For the n-alkyl sulfates in water, a value of $n \simeq 17$ is found experimentally[26] so that $\Delta G^{\mathrm{hyd}} \simeq -55$ kJ mol^{-1}; i.e., when $|\Delta G^{\mathrm{hyd}}| > 55$ kJ mol^{-1}, insolubility of the oligomeric species will ensue. For styrene, the latter inequality will be obeyed when only 4 or 5 monomer units have been added. Thus, for $\mathrm{SO_4}^{\bullet-}$ primary free radicals, surface activity would be expected for $z = 2$ and insolubility at $z = 4$ or 5.

The foregoing concepts can be generalized to sulfate anion free radical adducts of other monomers. The minimum value of z necessary for surface activity of the oligomeric species ($z_{\mathrm{min,surf}}$) can be calculated from

$$z_{\mathrm{min,surf}} = 1 + \mathrm{int}\,(-23\ \mathrm{kJ\ mol^{-1}}/\{RT \ln\,[\mathrm{M_{aq,sat}}]\}) \qquad (26)$$

Here the integer function (int) rounds off the quantity in brackets to the lower integer value, and the concentration $[\mathrm{M_{aq,sat}}]$ is in mol dm^{-3}. The value of z required for incipient insolubility ($z_{\mathrm{min,insol}}$) is given by

$$z_{\mathrm{min,insol}} = 1 + \mathrm{int}\,(-55\ \mathrm{kJ\ mol^{-1}}/\{RT \ln\,[\mathrm{M_{aq,sat}}]\}) \qquad (27)$$

Some typical values for $z_{\mathrm{min,surf}}$ and $z_{\mathrm{min,insol}}$ are presented in Table III. It is apparent that, for many monomers studied in emulsion polymerization, the addition of very few monomeric units leads to surface activity of the oligomeric species. Furthermore, in view of the good agreement between the values that can be calculated by this theory and those values found by fitting experimental results with the entry model, it seems likely that once the species become surface-active they will enter the latex particles via irreversible adsorption onto the surface of the particles.

It is most important to note that the values of z, which are the critical degree of polymerization for *entry*, are not necessarily the same as those (usually denoted j_{crit}) for *nucleation*: the kinetics of particle nucleation involve a number of kinetic events in addition to those considered here for entry alone. Thus our maximum and minimum values of z for MMA (spanning the range $4 \leqslant 11$) are considerably less than the $j_{\mathrm{crit}} \simeq 50$ reported by Fitch et al.[31] for homogeneous nucleation in a surfactant-free system. Fitch and co-workers attempted to measure the critical degree of polymerization required for nucleation using 90° light scattering. The magnitude of the scattering intensity depends inter alia upon the number density of particles and their sizes. Whether or not a given scattering intensity at 90° can be detected depends critically upon the sensitivity of the photomultiplier detector; below a certain threshold intensity, the scattering cannot be distinguished from inherent noise. It is not known whether the value of j_{crit} reported by Fitch et al. is that due to nucleation or if it is an artifact arising from the threshold intensity of the photomultiplier. The first observed particles with $j_{\mathrm{crit}} \simeq 50$ would only be of radius about 3 nm, which must be close to the particle size detection limit for angular light scattering, at least at the particle concentrations studied. Even if the value of $j_{\mathrm{crit}} \simeq 50$ were correct, the critical degree of polymerization for nucleation need not be the same as that for entry, the latter being expected to be smaller than the former as the mechanistic events are likely to be somewhat different.

The chemical nature (i.e., charge and size) of the polar residue arising from the primary free radical would be expected to exert some influence on the minimum value of z needed to impart surface activity. Adsorption studies[27] at the oil/water interface suggest that the presence of charge may well reduce the effective surface activity of an oligomer due to the Coulombic repulsion between it and a charged interface. This effect is likely to be small at the ionic strengths used in emulsion polymerization studies, and so the effect of the chemical nature of the polar residue is likely to be small. The variation of z with temperature can be approximately calculated by considering the variation of $[\mathrm{M_{aq,sat}}]$ with temperature and applying eq 26.

We conclude this section by noting that the implication of the ΔG values discussed here is that they actually give the ratios of the adsorption to desorption rate coefficients. By considering the time scales of adsorption, desorption, and aqueous-phase kinetic events, it is shown in Appendix B that even oligomers with a value of z such that entry can occur in fact adsorb and desorb *many times before true entry occurs*. That is, although we have thus far ignored the possibility that the free radical, after it has "entered", could actually desorb again, in fact this event is quite likely. The more complete analysis of Appendix B shows that, for free radicals of our critical degree of polymerization, the desorbed free radical undergoes reentry into another particle with negligible probability of either aqueous-phase termination or propagation, so that the net result is the same as the simpler analysis presented above. Indeed, as stated, simple diffusion theory shows that *all* oligomeric free radicals of d_{P} less than or equal to z will "collide" with a latex particle at a very high rate. The important point about the ΔG for the oligomers that undergo "instantaneous" entry is that their large ΔG means that they are much less likely to desorb subsequent to this collision than is a smaller soluble oligomer and thus much more likely to enter a monomer-rich region of the particle and undergo propagation therein, whereupon subsequent desorption will not take place. Nevertheless, there is the important conceptual point that (as embodied by the probability P_{e} of Appendix B) even a z-mer meets the surface of a latex particle typically 100 times *and desorbs back into the aqueous phase* before it undergoes entry (i.e., irreversible

Table IV
Values of Rate Parameters and Monomer Properties at Various Temperatures

	styrene			MMA
	25 °C	50 °C	80 °C	50 °C
z^a	2	2	2	4
$[M_{aq,sat}]/(\text{mol dm}^{-3})^b$	2.7×10^{-4}	4.2×10^{-4}	7.0×10^{-4}	1.5×10^{-1}
$k_p/(\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})^c$	110	258	646	580
$k_t/(\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})^d$	3.7×10^9	3.7×10^9	3.7×10^9	3.7×10^9
$k_d/\text{s}^{-1\,e}$	2.0×10^{-8}	1.0×10^{-6}	9.2×10^{-5}	1.0×10^{-6}

[a] z calculated from eq 26. [b] $[M_{aq,sat}]$ for styrene and MMA from refs 28 and 39, respectively. [c] k_p for styrene and MMA from refs 40 and 39, respectively. [d] Based on refs 17 and 19. [e] Reference 32.

desorption caused by propagation); however, a z-mer is much more likely to have such a fate instead of undergoing termination or propagation during its sojourn in the aqueous phase. Shorter non-surface-active species, on the other hand, are much more likely to undergo termination or propagation during the time they are in the aqueous phase, rather than irreversible desorption, because their residence time at the surface of any particle is very low. The different fates of these species are determined by the relative rates of adsorption and desorption, which in turn are dictated by the thermodynamics encapsulated in the ΔG values discussed above.

Model Calculations

Given the value of the entry rate coefficient ρ, one can immediately deduce the capture efficiency, which is the relative probability of a free radical formed from initial decomposition undergoing eventual true entry compared to it undergoing aqueous-phase termination. In what follows we present model calculations of the variation of capture efficiencies with some experimental observables, including initiator concentration, monomer concentration in the aqueous phase, and temperature.

If, for a particular particle concentration, all free radicals arising from initiator decomposition enter the latex particles, then the entry rate coefficient (ρ_{max}) is given by

$$\rho_{max} = 2k_d[S_2O_8^{2-}]N_A/N_c \tag{28}$$

The percentage capture efficiency is then given by

$$f = \rho_{calc}/\rho_{max} \times 100 \tag{29}$$

Here, ρ_{calc} is the entry rate coefficient calculated by the entry model.

For the purposes of these model calculations we will calculate capture efficiencies for those two monomers that may be considered to constitute "model" systems for emulsion polymerization, the sparingly water soluble styrene and the relatively water soluble methyl methacrylate (MMA). The values of the rate parameters and monomer properties used in these calculations are given in Table IV. Note that the parameters used for these calculations for styrene are those obtained from the fit to the data discussed above, and thus the theoretical values of f are completely equivalent to the experimental values of ρ; the values of f reported for MMA are predictions, since there are currently no reliable data for ρ for this monomer.

Figure 9 shows the variation of capture efficiencies with initiator concentration at various temperatures for styrene emulsion polymerizations. At all temperatures, capture efficiency decreases with increasing $[S_2O_8^{2-}]$. Furthermore, capture efficiency is enhanced at lower temperatures. Figure 10 is the equivalent plot for MMA at 50 °C. Because of the high concentration of monomer in the aqueous phase, there are very high (ca. 100%) capture efficiencies in this system at low $[S_2O_8^{2-}]$, decreasing somewhat at higher $[S_2O_8^{2-}]$.

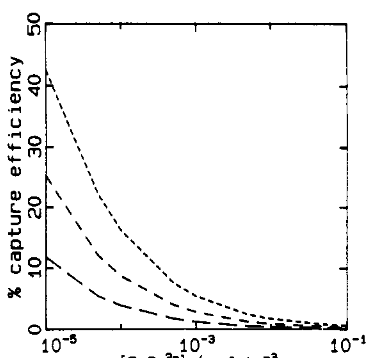

Figure 9. Calculated values for the variation of capture efficiency with initiator concentration, $[S_2O_8^{2-}]$, for styrene: (- - -) 25 °C; (– – –) 50 °C; (— — —) 80 °C.

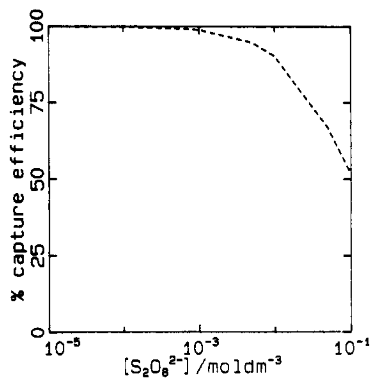

Figure 10. Calculated values for the variation of capture efficiency with initiator concentration, $[S_2O_8^{2-}]$, for methyl methacrylate at 50 °C.

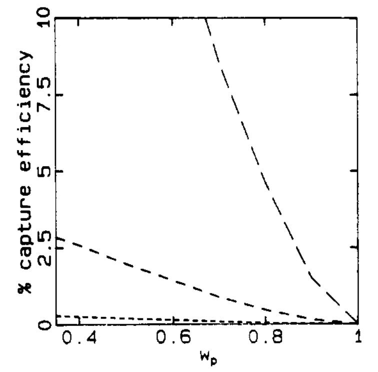

Figure 11. Calculated values for the variation of capture efficiency with weight fraction of polymer, w_p for styrene: (— — —) 25 °C; (– – –) 50 °C; (- - -) 80 °C.

During interval III of an emulsion polymerization, the monomer concentration in the aqueous phase decreases. The relationship between the aqueous-phase monomer concentration and weight fraction polymer in interval III is given in eq 23. Figure 11 depicts the calculated variation of capture efficiency in a styrene emulsion polymerization during interval III at three different temperatures. At all temperatures there is a significant decrease in the capture efficiency at higher weight fraction of polymer.

Conclusion and Outlook

In this paper we have presented a model for those features that are rate-determining in the mechanism of free-radical entry into latex particles in emulsion polymerization. The primary free radical formed from initiator decomposition must grow to a particular degree of polymerization before irreversible entry into a particle can occur; other possible fates for this and other aqueous-phase free radicals are aqueous-phase termination and propagation. Estimates of the free energy of adsorption as a function of oligomer size show that there exists a critical degree of propagation, where the adsorbed free radical is much less likely to desorb back into the aqueous phase compared to a smaller oligomer. All aqueous-phase free radicals encounter the surface of a latex particle at an extremely rapid rate and undergo subsequent desorption; however, thermodynamic considerations show that for oligomers of this critical degree of polymerization, the desorption rate is much slower than that for smaller entities. An adsorbed free radical of this critical length is therefore likely to undergo propagation inside the latex (rather than aqueous-phase propagation or termination) and hence to start a growing macroradical: i.e., entry will have occurred (even though this free radical may have encountered a particle and then desorbed again many times before irreversible entry actually occurs). The rate of formation of free radicals capable of permanent entry is governed by aqueous-phase events, viz., the rate of propagation in the aqueous phase, which competes with the rate of aqueous-phase termination. Two important aspects of the development presented here are that aqueous-phase termination and the first aqueous-phase propagation step for these small oligomers are extremely rapid compared to what occurs for larger macroradicals: they are essentially diffusion-controlled.

Given this, entry rate coefficients could in principle be calculated a priori by calculating z from the thermodynamic treatment presented here and then utilizing this value in the entry model. Unfortunately, the entry rate coefficient is very sensitive to the value of z: changing z from 2 to 3 can change ρ by a factor of 10. Moreover, comparing the model presented here with experiment is complicated by the restriction that we have made of confining the number of propagation rate coefficients to two (a diffusion-controlled first propagation step, and thereafter the long-chain k_p) rather than allowing for a spread of k_p values as one may have in actuality. While this limits the model if one wished to make a completely a priori prediction, it is apparent that fitting of a single datum can then enable one to predict entry rates for that monomer under essentially any conditions.

Proof of the model's general applicability to monomers with a range of z values is necessary, however, before complete confidence can be expressed in this approach. Also, there are conceivable cases where the theory developed in this paper would be inapplicable. For example, if a physical barrier to entry existed, e.g., a thick layer of polymeric surfactant on the latex particles or the latex particles were extremely "dry" (very low monomer concentration), then the rate-determining step for entry of free radicals may become slow diffusion into the latex particle.

The values of z found by fitting the entry model to experiment suggest that oligomeric radicals in the aqueous phase do not grow to a size bigger than that which imparts surface activity. Even if the rate-determining step is not, as we have endeavored to show, the rate of growth of the aqueous-phase oligomers to a particular degree of polymerization, then the actual size at which species enter the latex particles can only be smaller, not bigger, than those fitted in this paper. That is, were another mechanism rate-controlling, then this mechanism would have to predict slower entry than our model, as the aqueous-phase free-radical chemistry would still occur. Thus, this model predicts a maximum value of z. This suggests that those entry mechanisms that rely on the existence of large insoluble entering species, e.g., the colloidal entry mechanism, must be incorrect (at least for the systems considered in this paper). Furthermore, considering that we fit a $z = 2$ for the styrene emulsion polymerization system and given that all our rate coefficients used to calculate capture efficiencies are correct, it seems unlikely that smaller species would be capable of irreversible entry into latex particles, since they are too soluble.

Therefore we conclude that the rate-determining step for entry is neither diffusion to the particle surface, nor colloidal coalescence, nor surfactant displacement; rather it seems to be the growth of primary free radicals to an oligomeric free radical of a size that is likely, on thermodynamic and diffusional grounds, to enter irreversibly. This result suggests that many factors, such as latex particle size and concentration, surfactant concentration, and electrolyte concentration, do not affect the *initiator efficiency*, provided sufficient particles exist to prevent new nucleation, a conclusion that is supported by experiment.[4] There is, in effect, only a certain population of radicals that can enter latex particles, and the size of this population is not at all determined by the latex particles, but only by the aqueous-phase kinetics.

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Appendix A. Aqueous Decomposition of Persulfate

The evaluation of ρ from eqs 16–20 requires a knowledge of k_d. It is shown here that one can ignore other effects that at first sight could also influence the rate of production of free radicals in the aqueous phase.

In pure aqueous systems the initial step of the thermal decomposition of persulfate is understood to be the following reaction:[32]

$$S_2O_8^{2-} \xrightarrow{k_d} 2SO_4^{\bullet -} \qquad (A1)$$

At pH = 7 and at 50 °C the persulfate decomposition rate coefficient has been measured as $k_d = (1.7 \pm 0.9) \times 10^{-6}$ $dm^3\ mol^{-1}\ s^{-1}$. This value is the mean and maximum deviation of those values listed in Sarkar et al.[33]

Effect of pH on k_d. Below a pH of 3, persulfate decomposes by a different mechanism[34] and does not produce free radicals. However, the experimental data analyzed in this paper came from emulsion polymerization systems where the pH ≫ 3. Therefore the alternative mechanisms are not considered.

There is some evidence[32] in the literature that the value of k_d may vary with pH over the range pH = 3–14, although this is still subject to some debate. However, the effect of these supposed changes in k_d on the calculated ρ values may be insignificant when one considers the possible errors in the measured[2] values of ρ. For simplicity, we assume no effect of pH on k_d in a series of experiments with one monomer.

Effect of Ionic Strength on k_d. The value of k_d has been shown[33] not to be affected by ionic strength over the pH range 3–7.

Effect of Surfactant on k_d. In a study[34] of the effect of the surfactants sodium dodecyl sulfate and sodium hexadecyl sulfate on the decomposition rate of persulfate in water at 50 °C, k_d was found to be approximately twice the normal value upon the addition of 5×10^{-4} mol dm^{-3} surfactant. However, the effect of surfactant (an impurities) on k_d in emulsion polymerizations is difficult to quantify because of the complexities of the systems. Within one series of experiments, e.g., styrene with the same surfactant and similar surfactant concentrations, it is expected that k_d would be unchanging within experimental error.

Effect of Monomer on Persulfate Decomposition. Sarkar and co-workers[33,35] considered various possible reaction schemes for persulfate decomposition. They concluded, but did not conclusively proved, that there may be a monomer-catalyzed persulfate decomposition mechanism. However, for ethyl acrylate,[35] a monomer of relatively low solubility, reaction A1 dominates the chemistry of persulfate decomposition. Therefore, for the low-solubility monomers considered in this study, the possibility of monomer-catalyzed pathways for persulfate decomposition is not considered explicitly. However, it is noted that the value of k_d may be affected by the particular monomer being polymerized.

The value of k_d may be affected by surfactant, monomer, pH, and any impurities in the system. For these reasons we cannot dogmatically assign a single value for k_d that will apply in every system. However, under similar conditions the value of k_d for a particular emulsion polymerization system should be relatively constant and not too dissimilar from that value measured in pure systems.

Appendix B. Entry of Free Radicals into Latex Particles

The major assumption made in this paper is that an aqueous-phase free radical will irreversibly enter a latex particle only when it adds a critical number (z) of monomer units. Here, we implicitly assume that entry is so rapid that a free-radical species capable of entry will not partake in any more aqueous-phase kinetics although it is highly likely to encounter, and desorb from, a latex particle many times. The relative rates of adsorption, desorption, termination, and propagation are such that, once the critical degree of propagation has been reached, the oligomer can have no other fate but to undergo propagation in a particle during an adsorption event. This constitutes a true entry event. Justification of this assumption can be made if we compare the frequencies (i.e., reciprocal of the lifetimes) of three of the possible aqueous-phase kinetic events that a free radical capable of entering can undertake.

(*1*) *Bimolecular Termination*: From the diffusion-limited value of k_t, the frequency of termination is $k_t[T^\bullet] = 10^{-1}$–10^{2} s^{-1}.

(*2*) *Propagation*: Typically $k_p = 10^2$–10^3 dm^3 mol^{-1} s^{-1} and $[M_{aq}] = 10^{-3}$–10^{-1} mol dm^{-3} and hence the frequency of propagation is $k_p[M_{aq}] = 10^{-1}$–10^{2} s^{-1}.

(*3*) *Entry into a Latex Particle*: Entry is effected when the entering free radical can polymerize within the interior of the latex particle (i.e., the regime where monomer concentration is close to the average value of the latex particle phase). Considering that an entering species is probably surface-active, it is possible that this species, upon collision with a latex particle, may either propagate into the interior of the particle or desorb into the aqueous phase. The effect of just one propagation step is probably sufficient to cause the species to be relatively insoluble, such that desorption could be ignored. Therefore the rate coefficient for entry (in the sense that propagation to a macroradical will ensue) is the product of the rate coefficient for collisions of the oligomeric radicals and latex particles (k_e) with the probability of entry of a surface-active free radical at the particle surface (P_e). The collision rate coefficient is probably in the diffusion limit and can be approximately calculated by eq 4. P_e is the ratio of the rate of true entry (i.e., subsequent propagation) to the total rates of all possible fates of this adsorbed free radical, i.e., propagation, desorption, and termination:

$$P_e = k_pC_m/(k_pC_m + k_{de} + k_t[I^\bullet]) \qquad \text{(B1)}$$

Here, $[I^\bullet]$ is the interfacial free-radical concentration and k_{de} is the desorption rate coefficient of a surface-active oligomer from the latex particle surface. This may be approximated by

$$k_{de} = 1/\tau \qquad \text{(B2)}$$

Here, τ is the time scale of desorption of a surfactant molecule from an SDS micelle at 50 °C. Typical values[36] of τ are 10^{-4}–10^{-6} s (these values are consistent with the estimates of the free energy of adsorption given in this paper, which, through the equilibrium constant $K = \exp(-\Delta G^\circ/RT)$, gives the relative rates of adsorption and desorption). Considering that the interfacial free-radical concentration is probably similar to the aqueous-phase free-radical concentration and that k_{de} is much greater than both k_pC_m and $k_t[T^\bullet]$, eq B1 reduces to

$$P_e = k_pC_m/k_{de} \qquad \text{(B3)}$$

Using typical values of $C_{m,sat} = 5.8$ mol dm^{-3}, $k_p = 258$ dm^3 mol^{-1} s^{-1}, and $k_{de} = 10^5$ s^{-1} at 50 °C in eq B3, we find $P_e \simeq 10^{-2}$: that is, *even a free radical of the critical degree of polymerization for entry is much more likely to undergo desorption rather than true entry during a given encounter with a latex particle.* Now, typical latex particle concentrations are $N_c/N_A = 10^{-6}$–10^{-8} mol dm^{-3}. Assuming a diffusion-controlled value for k_e, using eq 4 and typical values of $r_s = 100$ nm and $r_0 = 0.6$ nm gives then that the frequency of irreversible entry of the oligomers with the latex particles is $k_eP_eN_c/N_A = 10^2$–10^4 s^{-1}. The frequency of irreversible entry is therefore significantly higher than that of both termination and propagation in the aqueous phase. Therefore, the assumption that a species of degree of polymerization z, assumed capable of entering into a particle, will enter "instantaneously" seems valid. Thus the kinetics of reaction 10 may be written as

$$\mathrm{d}[M_z^\bullet]/\mathrm{d}t = k_p[M_{aq}][M_{z-1}^\bullet] - (N_c/N_A)\rho \qquad \text{(B4)}$$

and hence the entry rate coefficient is given by

$$\rho = k_p[M_{aq}][M_{z-1}^\bullet](N_A/N_c) \qquad \text{(B5)}$$

A final point is that considerations of time scale given in this Appendix suggest that it is quite likely that a free radical that *desorbs* (exists) from a latex particle is highly likely to undergo reentry into another particle, rather than (hetero)termination with an aqueous-phase free radical that would have otherwise itself have undergone entry. In the language we have used elsewhere,[2-5] this suggests that the "fate parameter" α is likely to have a value closer to +1 than −1. If this were to be the case, then this would affect the values of ρ that were deduced from experiment, since those values reported for styrene[2-5] were obtained assuming that $-1 \leqslant \alpha \leqslant 0$. To examine the effect of a different value of α, we recalculated values of ρ from the experimental data using $\alpha = +1$. It was found that the change in values of ρ so obtained differed by no more than 20% from those found with $-1 \leqslant \alpha \leqslant 0$. This variation, although systematic, is less than the experimental scatter of the values of ρ orginally reported. It is therefore apparent that reinterpretation of the data with a different value of α would have no qualitative, and insignificant quantitative, effect on our conclusions.

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