Macromolecules **2003,** *36,* 3921−3931

Entry in Emulsion Polymerization: Effects of Initiator and Particle Surface Charge

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Received September 27, 2002; Revised Manuscript Received March 8, 2003

ABSTRACT: The rate coefficient for radical entry into latex particles in emulsion polymerizations is measured for styrene systems in which the entering species are anionic (from persulfate) and cationic (from 2,2′-azobis(2-methylpropionamidine) dihydrochloride, or V-50). These entry rate coefficients ρ are obtained by measuring rates in seeded emulsion polymerizations where the seeds have either cationic or anionic groups on the surface; "zero-one" conditions are employed, because these offer the advantage that particle size is sufficiently small ($\approx$70 nm diameter) that intraparticle termination is not rate-determining. Data comprise steady-state rates with chemical initiator, combined with loss rates obtained using γ-radiolysis initiation and following the relaxation behavior after removal from the radiation source. Values for ρ as a function of initiator concentration can be meaningfully compared for different initiators through the dependence of initiator efficiency f_{entry} on primary radical generation rate (radical flux). For the anionic latex, this dependence is seen to differ depending on the nature of the initiator used. This may be explained by the entry model [Maxwell, I. A.; Morrison, B. R.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1991**, *24*, 1629] wherein the rate-determining steps in entry are assumed to be only aqueous-phase propagation and termination to form surface-active z-meric oligomeric radicals; entry is solely by z-mers, for which actual entry into the particle is so fast as not to be rate-determining. The cationic latex shows a high rate of spontaneous initiation, which can be explained in terms of amidino radical chemistry; this can be reduced by heat treatment. Accurate f_{entry} values are obtained using the heat-treated cationically stabilized latex for seeded studies. The f_{entry} data are also consistent with the model for both cationic and anionic species entering the cationic latex. Values of z so inferred ($\approx$2 for persulfate, $\approx$1 for amidinium) can be understood in terms of the hydrophobic free energy of these species. The results refute alternative models in the literature that suppose entry is controlled by double-layer (colloidal) interactions, surfactant displacement, or diffusion control.

Introduction

In emulsion polymerization, radicals are almost always generated in the water phase. A radical generated in the water phase can have several fates: aqueous-phase propagation, entering a preexisting latex particle ("entry"), aqueous-phase termination, or particle formation by one of several possible mechanisms. Because of aqueous-phase termination, the rate at which radicals enter latex particles can be significantly lower than the rate of radical generation from initiator. (Indeed, this has often been found in emulsion polymerizations of styrene.[1−4]) A number of theories have been put forward to explain the entry process. The "diffusion control" model[5−7] assumes that diffusion of aqueous-phase radicals to the particle surface is the rate-controlling step for entry. Another theory supposes that displacement of surfactant from the particle surface is the rate-determining step.[8] It has also been suggested that entry can be thought of as a colloidal interaction between a latex particle and an oligomeric aqueous-phase radical.[9] However, the most widely accepted entry model is the "control by aqueous-phase growth" model of Maxwell et al.[10] This theory postulates that free radicals generated in the aqueous phase propagate until they reach a critical degree of polymerization z, at which point they become surface-active and their only fate is irreversible entry into a latex particle; the rate of entry of a z-mer into a particle is assumed to be so fast as not to be rate-determining. An efficiency of less than 100% arises if there is significant aqueous-phase termination of the propagating radicals.

The entry model of Maxwell et al. was deduced from and/or supported by data on the influence of particle surface characteristics (charge, size) on the entry rate coefficient[4,11] and was successfully fitted to the best available experimental data: for the seeded emulsion polymerization of styrene using potassium persulfate as initiator.[1,2,12] Treating the integer z as the sole independent variable, Maxwell et al. concluded that accord between model and experiment (for this particular system) is given when the value of z is 2−3. As will be discussed later in this paper, they formulated a justification for a value of z in this range based on thermodynamic considerations of the entering species.

In the decade since Maxwell et al. published their theory, several experimental investigations have been carried out in this area. It is noted that data interpretation in such studies is least ambiguous if particle *formation* and particle *growth* can be clearly separated, which is best done in a seeded system (polymerization within preexisting particles) in the absence of new particle formation. One approach has been characterization of the oligomeric species generated in the aqueous phase during an emulsion polymerization in order

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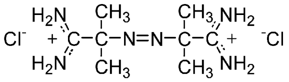
10.1021/ma025695y CCC: $25.00

to gain insights into events related to entry. Poehlein and co-workers employed a range of spectroscopic techniques for characterizing oligomers formed in seeded and unseeded emulsion polymerizations.[13−15] Thomson et al.[16] used MALDI−TOF mass spectrometry to deduce the nature of oligomers from ab initio (unseeded) surfactant-free emulsion polymerizations of methyl methacrylate. They estimated the average degree of polymerization to be in the range 6−9 for oligomers in these systems, consistent with the predictions of Maxwell et al.[10] from thermodynamics. Marestin et al.[17] synthesized a seed latex incorporating amino-TEMPO (4-amino-2,2,6,6-tetramethyl-1-piperidinyloxy, free radical) as spin trap, bound to the particle surface and capable of capturing entrant oligomers upon adsorption onto a particle. This seed latex was used in emulsion polymerizations of MMA, and analysis of oligomers recovered from spin-trapping indicated that $z \approx 5$. In addition, these workers were able to measure the rate of entry in MMA polymerizations by following the decay of the TEMPO EPR signal over time. Marestin et al.[17] also compared kinetic data from their spin-trap/ESR experiments for MMA with KPS and V-50 as initiators, finding that these two initiators gave similar values for the entry rate coefficient under the conditions used. As expanded later in the present paper, when differences in particle concentrations and initiator decomposition rates between these experiments are taken into account, similarity in the value of the entry rate coefficient may not necessarily be indicative of an identical mechanism for entry. Colombié et al.[18] obtained entry rate data using reaction calorimetry. These results showed that varying the relative amounts of anionic and nonionic surfactant used in seeded emulsion polymerizations of styrene had no significant effect on the value of the entry rate coefficient. In a study of an ab initio (unseeded) system, Leemans et al.[19] investigated the kinetic effects of using amphiphilic block polyelectrolytes as electrosteric stabilizers in MMA emulsion polymerizations. Here it was found that the molecular weight of the polyelectrolyte block as well as the nature of the charge may have significant effects on the polymerization rate. However, in the absence of knowledge of the actual rates of particle entry and exit in their ab initio (unseeded) systems, it seems difficult to unambiguously attribute the observed rate disparity to an entry effect, while the possibility of differences in the rates of initiator decomposition and particle formation might further complicate the interpretation of these results. Penboss et al.[20] studied entry in the seeded emulsion polymerization of styrene using three different initiators, namely, the anionic and cationic initiators intended for the present study as well as the Fe^{2+}/H_2O_2 redox initiator system (which generates neutral radicals). These workers reported minimal effect of changing initiator type on the value of the entry rate coefficient. However, these results were obtained using an earlier kinetic scheme for emulsion polymerization; moreover, the raw data span a relatively narrow range of initiator and particle concentrations and cannot be unambiguously reprocessed to yield a value of z. Coen et al.[11] and Vorwerg and Gilbert[21] investigated the kinetic effects of using electrosteric stabilizer in seeded styrene emulsion polymerizations. Data obtained suggest that the rate coefficient for entry is reduced in the presence of extensive electrosteric stabilizer.

Scheme 1. Chemical Structure of 2,2′-Azobis(2-methylpropionamidine) dihydrochloride, or V-50



The aim of this study is to extend the range of quantitative kinetic data on entry and to assess whether the current mechanistic understanding of entry provides satisfactory explanation of such data. In this paper we also work with a styrene seeded system. Two different initiators are employed: potassium persulfate (KPS) and 2,2′-azobis(2-methylpropionamidine) dihydrochloride (V-50), a cationic azo-initiator (Scheme 1). Similarly, two different latex types will be used—one anionically stabilized (with negatively charged groups adsorbed or anchored to the particle surface) and the other cationically stabilized. Well-established methods[22] will be used to extract entry rate data from systems with the four different combinations of initiators and latex types. The objective is to furnish accurate kinetic data for entry covering a wide range of experimental conditions and thereby to provide insights into which factors are most crucial in defining the entry process. Importantly, the data sought here are also such that they are capable of refuting the fundamental postulate of the entry model of Maxwell et al.: if there is a significant effect of radical and/or particle charge on the entry rate coefficient, then this model will be seen to be incorrect.

Background Considerations

The "Control by Aqueous-Phase Growth" Model for Entry. The following briefly summarizes the model for entry proposed by Maxwell et al.[10] The entry process is described by

$$\text{initiator} \xrightarrow{fk_{\mathrm{d}}} 2\mathrm{I}^{\bullet} \tag{1}$$

$$\mathrm{I}^{\bullet} + \mathrm{M} \xrightarrow{k_{\mathrm{pI,w}}} \mathrm{IM}^{\bullet} \tag{2}$$

$$\mathrm{IM}_i^{\bullet} + \mathrm{M} \xrightarrow{k_{\mathrm{p,w}}} I\mathrm{M}_{i+1}^{\bullet} \tag{3}$$

$$\mathrm{IM}_i^{\bullet} + \mathrm{T}^{\bullet} \xrightarrow{k_{\mathrm{t,w}}} \text{inert products}, \quad i < z \tag{4}$$

$$\mathrm{IM}_z^{\bullet} \xrightarrow{\rho_{\mathrm{init}}} \text{entry} \tag{5}$$

wherein $\mathrm{I}^{\bullet}$ is a primary free radical produced by initiation (illustrated here by thermal decomposition of initiator with overall rate coefficient fk_{d}), M is a monomer molecule, $\mathrm{IM}_i^{\bullet}$ is an aqueous-phase radical derived from initiator and containing i monomer units, $\mathrm{T}^{\bullet}$ is any aqueous-phase free radical species, $\mathrm{IM}_z^{\bullet}$ is a surface-active radical bound to undergo entry, and ρ_{init} is the pseudo-first-order rate coefficient for entry of radicals derived from initiator. It is important to note that eq 5 does not imply that every encounter between a surface-active ($\mathrm{IM}_z^{\bullet}$) radical and a particle results in a successful "entry" event. In fact, the above model allows for an $\mathrm{IM}_z^{\bullet}$ species to adsorb and desorb many times before undergoing true, irreversible "entry", defined here as propagation of an adsorbed radical into the particle interior; i.e., the model does not assume that "entry" and "adsorption" are equivalent (although they may be). All the present model assumes is that essentially all $IM_z^\bullet$ species "enter" rather than undergoing any other *chemical* fate.

In what follows it is assumed (based on experimental evidence[23−25]) that the initial propagation step, eq 2, is so fast that it is not rate-determining. The essence of the model is that there is no barrier to entry for a z-meric radical (i.e., $IM_z^\bullet$), and thus the actual entry step is, or is close to being, diffusion-controlled. Therefore, ρ_{init} is simply the rate of formation of the entering species, $IM_z^\bullet$: z is the signature parameter of the model, for a radical enters as soon as it adds this number of monomer units, but no sooner. Of course, this is an oversimplification of reality, for example in that some radicals must propagate beyond length z before undergoing entry. In effect, z is some sort of average chain length for entry. However, the assumption of a single length of entering species is adopted as a useful working approximation which also brings physical understanding.

A value for ρ_{init} may be obtained from numerical solution of the full set of rate equations pertaining to the above reaction scheme. Maxwell et al. also developed an analytical approximation for the value of ρ_{init}:

$$\rho_{\text{init}} \approx \frac{2fk_{\text{d}}[\text{I}]N_{\text{A}}}{N_{\text{c}}}\left\{\frac{2\sqrt{fk_{\text{d}}[\text{I}]k_{\text{t,w}}}}{k_{\text{p,w}}[\text{M}]_{\text{w}}}+1\right\}^{1-z} \tag{6}$$

Here [I] = initiator concentration, N_{A} = Avogadro's constant, N_{c} = number concentration of latex particles, and $[\text{M}]_{\text{w}}$ = water-phase monomer concentration. Values of ρ_{init} obtained using both the numerical method and the analytic approximation of eq 6 show good agreement when parameter values pertaining to styrene systems are used.

The model of Maxwell et al. specifies that entry (eq 5) is one of only two mechanisms for aqueous-phase radical loss, the other being bimolecular termination (eq 4). The rate of entry is thus determined by the probability that an initiator-derived radical will propagate to length z without undergoing termination. In the case where $z = 1$, an entering species is formed after just the initial propagation step and there is no possibility of aqueous-phase termination, and thus $\rho_{\text{init}} \propto [\text{I}]$. For $z \geq 2$, radicals reside longer in the aqueous phase, increasing the probability of termination before an entering species is formed and thus increasing the likelihood that entry efficiency will be <1. The greater the degree of polymerization required for entry, the higher the probability of termination.

Any value of ρ_{init} may be related to $\rho_{100\%}$, the value corresponding to entry of all radicals, by an "entry efficiency" factor f_{entry} (not to be confused with the symbol f denoting initiator efficiency):

$$f_{\text{entry}} \approx \frac{\rho_{\text{init}}}{\rho_{100\%}} = \rho_{\text{init}}\frac{N_{\text{c}}}{2fk_{\text{d}}[\text{I}]N_{\text{A}}} \tag{7}$$

This equation may be used to obtain f_{entry} from experimental values of ρ_{init}. Comparison of eqs 6 and 7 gives the following for the entry model of Maxwell et al.:

$$f_{\text{entry}} \approx \left\{\frac{2\sqrt{fk_{\text{d}}[\text{I}]k_{\text{t,w}}}}{k_{\text{p,w}}[\text{M}]_{\text{w}}}+1\right\}^{1-z} \tag{8}$$

Importantly, eq 8 specifies that the entry efficiency is independent of the latex particle concentration, N_{c}. This is based on the assumption that, for a radical of length z, entry occurs far more rapidly than any other aqueous-phase process—an assumption that is justified by comparison of the reaction frequency for entry with those for aqueous-phase propagation and termination. Indeed, it may be shown that at typical particle concentrations for emulsion polymerization (i.e., N_{c} of the order of 10^{15}−10^{17} L^{-1}) the frequency of entry is several orders of magnitude higher than that of either propagation or termination. Therefore, f_{entry} will be insensitive to changes in particle concentration under typical conditions (as are used in the present work). Only at considerably lower than "typical" particle concentrations, i.e., $N_{\text{c}} \sim 10^{13}$ L^{-1}, would the entry efficiency be expected to show any significant dependence on N_{c}. A more detailed discussion than that given here may be found in the original work of Maxwell et al.[10]

Comparing Entry Data from Different Systems. In this study it will be of interest to compare entry data from different systems. An important consideration here is the sensitivity of ρ_{init} to N_{c}. Since ρ_{init} is the entry rate per particle, it follows that, for two systems with the same total flux of entering radicals, ρ_{init} must decrease as N_{c} is increased, as in eq 6. Therefore, a valid comparison of ρ_{init} values from different systems must take into account any difference in N_{c}. This is achieved by comparing values of f_{entry} rather than ρ_{init}, as the entry efficiency is independent of the particle concentration (eq 8). A further factor is that the entry rate and efficiency are governed by the aqueous-phase radical flux, which is dependent not only on [I] but also on fk_{d} (see eqs 6−8). This means that, for systems with different initiators, meaningful comparison of entry rate data is only possible if the difference in fk_{d} is taken into account. This may be achieved by comparing data at equal values of initiator radical flux, $2fk_{\text{d}}[\text{I}]$, as opposed to equal initiator concentration. All experimental data will be presented in this new and more mechanistically discerning way in this paper. A *caveat* is that k_{d} may vary, for example, because of radical-induced initiator decomposition.[26]

Measurement of Entry Rate Coefficients. In practice, the only kinetic data that can be readily and accurately measured comprise $\text{d}x/\text{d}t$, the overall rate of conversion of monomer into polymer (x = fractional conversion), given by

$$\frac{\text{d}x}{\text{d}t} = \frac{k_{\text{p}}[\text{M}]_{\text{p}}N_{\text{c}}}{n_{\text{M}}^{0}N_{\text{A}}}\bar{n} \tag{9}$$

where k_{p} = intraparticle propagation rate coefficient, $[\text{M}]_{\text{p}}$ = monomer concentration in the particle phase, n_{M}^0 = initial concentration of monomer, and $\bar{n}$ = average number of radicals per latex particle. The value of $\bar{n}$ is determined by all processes that introduce and remove radicals to and from latex particles. This includes entry of radicals from the aqueous phase, radical exit from a particle, and bimolecular termination inside a particle. If the particle diameter is sufficiently small (e.g., <100 nm for styrene or <30 nm for butyl acrylate[27] at 50 °C, the actual value depending on monomer concentration and other quantities), the rate of termination between two radicals in the same particle is so rapid that this reaction is not rate-determining: these are so-called "zero-one" conditions. For zero-one systems, $\bar{n}$ is determined only by the rate coefficients of radical entry and exit, and accurate data for $\bar{n}$ may therefore be used to infer these. The value of $\bar{n}$ is obtained from the observed polymerization rate via eq 9 (using accurate values of $[\mathrm{M}]_\mathrm{p}$ and N_c) and is best obtained in a seeded emulsion polymerization in the absence of secondary nucleation. For most monomers, including styrene, it has been established[22,28,29] that all radicals which have exited will reenter a particle. The rate equation for these "limit 2a" kinetics is given by

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = \rho(1 - 2\bar{n}) - 2k\bar{n}^2 \tag{10}$$

where k is the exit rate coefficient. The rate coefficient for entry may then be inferred from a system in which $\bar{n}$ varies significantly with time by matching this time evolution to the solution of eq 10. Alternatively, if k is known, one can use the steady-state form of eq 10:

$$\rho = 2k\frac{\bar{n}_\mathrm{SS}{}^2}{1 - 2\,\bar{n}_\mathrm{SS}} \tag{11}$$

where $\bar{n}_\mathrm{SS}$ is the steady-state value of $\bar{n}$.

A value for k may be obtained from careful interpretation of the rate data obtained early in the polymerization, before a steady state is attained.[1] However, this method is susceptible to error because of retardation by oxygen.[30] An alternative technique involves the use of γ-radiation as an intermittent source of initiating radicals,[31] by exposing the emulsion system to γ-radiation until a steady-state "in-source" polymerization rate is established. Initiation is then halted by removal from the γ-source. The rate of polymerization slows from the in-source rate to a lower out-of-source rate. By fitting an integrated form of eq 10 to this "γ-relaxation" rate data, a value for k may be calculated,[22,32] free of any retardation effects. While the use of γ-radiolysis in this experimental fashion may be traced back at least 40 years,[33] these pioneering efforts were oblivious of the complexities of emulsion polymerization kinetics, and thus the data were not analyzed to obtain entry or exit rate coefficients.

The out-of-source polymerization rate in the γ-relaxation experiments is usually nonzero[31] (note that this is a genuine phenomenon—even if given more time to relax, the system will not reach a zero rate). The origin of this so-called "spontaneous polymerization" is not fully understood for most emulsion systems,[34] in which it is often more significant than in the equivalent bulk systems. The value of ρ which is obtained, along with k, from fitting of γ-relaxation data (see above) will be denoted ρ_spont. This is the component of entry from "spontaneously generated" radicals. An important kinetic implication here is that the value of ρ obtained (using eq 11) from chemically initiated experiments clearly must incorporate the contribution ρ_spont in addition to entry of radicals derived from initiator, the quantity of primary interest here:

$$\rho = \rho_\mathrm{init} + \rho_\mathrm{spont} \tag{12}$$

An alternative way of determining ρ_spont is to measure the value of $\bar{n}_\mathrm{SS}$ for a seeded emulsion polymerization in the absence of any added initiator and then calculate ρ_spont from eq 11 using the value for k established from γ-relaxation. Both these methods for determining ρ_spont will be used in this work.

Table 1. Seed Latex Preparation and Characteristics

ingredient	seed latex AN01	seed latex CAT02
water (Milli-Q)/g	600	600
styrene/g	92.0	90.0
surfactant/g	11.8 (Aerosol MA-80)	4.57 (DTAB)
$\mathrm{NaHCO_3}$/g	1.25	
polystyrene/g	0.920	0.910
initiator/g	1.30 (KPS)	0.288 (V-50)
temperature (°C)	90	90
reaction time (h)	24	4
number-average unswollen particle diameter/nm	**seed latex AN01**	**seed latex CAT02**
TEM (polydispersity[a])	64 (1.02)	63 (1.06)
CHDF	57	54
PCS[b]	63	70
value used for kinetic analysis	64	63

[a] Ratio of weight-average to number-average particle diameter. [b] PCS average = [(8th moment)/(6th moment)]$^{1/2}$.

It is emphasized that values of ρ_init and f_entry determined in this way from experimental data and using eqs 9−12 and 7, respectively, are measured values and totally independent of the entry model of Maxwell et al. described by eqs 1−6.

Experimental Section

Synthesis of Seed Latexes. Two electrostatically stabilized latexes were prepared for use in seeded experiments; details of these latexes are given in Table 1.

Styrene (Huntsman, stabilized with 4-methoxyphenol inhibitor) was first passed through a column of basic alumina and then distilled under reduced pressure (first and last 10% discarded), before being stored at 0 °C for no longer than 2 weeks before use. Aerosol MA-80 (sodium di(1,3-dimethylbutyl)sulfosuccinate, 80% solution in 2-propanol and water, Cytec), dodecyltrimethylammonium bromide (DTAB, Aldrich), sodium hydrogen carbonate, and potassium persulfate (KPS) (both BDH AnalaR grade) were used without further purification in the seed synthesis. 2,2′-Azobis(2-methylpropionamidine) dihydrochloride (V-50, Aldrich) was recrystallized from water/acetone (50% w/w) prior to use.

For synthesis of seed latexes a 1 L glass reactor was charged with water, surfactant, and buffer, and the solution was heated to 90 °C. A small amount (30 $\mathrm{cm^3}$) of water was retained to dissolve initiator. A trace amount of bulk polystyrene was dissolved in styrene monomer immediately prior to use (a technique thought to improve the efficiency of radical capture in the early stages of polymerization,[35−37] thereby serving to lower the polydispersity of the latex particle size distribution). The polymer/monomer solution was added to the reactor and emulsified by stirring at 450 rpm, and finally initiator was added. The reaction was left to proceed for the specified time with final conversion (gravimetry) of ≈100%.

Seed latexes were dialyzed against distilled water (changed daily) for 8 days, over which time conductivity measurements were seen to converge to a constant value. The dialyzed latexes were filtered through glass wool to remove any traces of coagulum. Particle size distributions were measured by transmission electron microscopy (TEM) and average size by both capillary hydrodynamic fractionation (CHDF) and photon correlation spectroscopy (PCS) for comparison; results are presented in Table 1. These three methods are in relatively good agreement. As TEM is considered the most accurate method of these three for particle sizing, the sizes obtained using TEM were adopted as the values for all kinetic data analysis.

Kinetic Experiments. All kinetic experiments were seeded emulsion polymerizations of styrene commencing in interval II (in the presence of monomer droplets), so that $[\mathrm{M}]_\mathrm{p}$ remains essentially constant. The details of the composition of typical

Table 2. Details of Seeded Emulsion Polymerizations

N_c/L^{-1}	7.5×10^{16}	1.6×10^{17}	N_c/L^{-1}	1.0×10^{17}
seed (AN01) polymer/g	0.60	1.20	seed (CAT02) polymer/g	0.75
styrene/g	2.00	4.00	styrene/g	3.00
AMA-80/g	0.040	0.080	DTAB/g	0.090
KPS or V-50/g	0.00005−0.02		KPS or V-50/g	0.00005−0.02

Table 3. Results of Static Swelling Measurements, Spontaneous Polymerization, and γ-Relaxation Experiments for All Seed Latexes at 50 °C

seed latex	$[\mathrm{M}]_p^{\mathrm{sat}}$/M	$\bar{n}_{\mathrm{SS}}$ spontaneous polymerization	dose rate/Gy h^{-1}	$k/10^{-2}$ s^{-1}	$k_{\mathrm{theor}}/10^{-2}$ s^{-1}	$\rho_{\mathrm{spont}}{}^{a}/10^{-4}$ s^{-1}
AN01	5.4	0.06	188	1.2 ± 0.2	1.4	1.1 ± 0.2
CAT02	6.1	0.30	165	1.0 ± 0.6	1.4	40 ± 20
CATH03	5.7	0.04	158	0.9 ± 0.1	1.4	0.25 ± 0.04

[a] From steady-state spontaneous polymerization.

polymerizations are given in Table 2. For kinetic runs, KPS was recrystallized from water and V-50 from water/acetone (50% w/w). The rate of polymerization was measured by automated dilatometry, with final conversions verified by gravimetry. A water-jacketed 60 cm^3 dilatometer vessel was charged with seed polymer, styrene, surfactant, and water (Milli-Q) and stirred overnight to swell seed latex particles with monomer. The reaction mixture was then overheated to 60 °C and degassed under reduced pressure in order to prevent the formation of any bubbles inside the vessel during the course of a kinetic run (which would make it impossible to measure rate data accurately by dilatometry). For experiments using V-50 particular care was required to ensure that degassing was adequate, as the evolution of N_2 from the decomposition of this initiator increases the chance of bubble formation. After sufficient thermal equilibration time at 50 °C the reaction mixture was stirred vigorously to ensure monomer emulsification. Finally, initiator was added (or, in the case of γ-radiolysis experiments, the system was exposed to the γ-source). At the end of the polymerization a small amount of hydroquinone was added to quench the reaction. Latexes were inspected by TEM and experiments used for kinetic analysis only if no secondary nucleation occurred.

Measurement of $[\mathrm{M}]_p^{\mathrm{sat}}$. It was necessary to measure the saturated-particle monomer concentration, $[\mathrm{M}]_p^{\mathrm{sat}}$, for each latex individually, as this quantity is affected by particle size and surface characteristics. This was done using the "static swelling" method (details of which have been given elsewhere[22,38,39]). In each case the value of $[\mathrm{M}]_p^{\mathrm{sat}}$ was determined at 50 °C (the temperature used in kinetic experiments). The results for all seed latexes are presented in Table 3.

Results and Discussion

Spontaneous Polymerization. Also presented in Table 3 are the values of $\bar{n}_{\mathrm{SS}}$ observed in emulsion polymerizations carried out with no added initiator, i.e., where the only source of initiation was "spontaneously generated" radicals. The rate of spontaneous polymerization for the anionically stabilized latex AN01 was typical of values reported for styrene emulsion polymerization. However, an unusually high (and reproducible) rate was observed for the cationic latex CAT02, giving a value of $\bar{n}_{\mathrm{SS}}$ approximately 5 times larger than that for the anionic latex. Mechanistically this high value for $\bar{n}_{\mathrm{SS}}$ may be explained by either a higher entry spontaneous rate coefficient (ρ_{spont}) or a lower exit rate coefficient (k) in the cationic latex, or a combination of both these effects. γ-Relaxation experiments (presented in Table 3 and discussed in detail later) revealed that k for CAT02 was comparable to that of the anionic latex, indicating that the rate enhancement for spontaneous polymerization was an entry-related phenomenon. As this is a spectacular effect—$\bar{n}_{\mathrm{SS}} \approx 0.3$ for a zero-one system without use of any initiator!—it is worth discussing.

One possible explanation for this high spontaneous entry rate is generation of radicals from a reaction involving residual amine and peroxide species from the seed latex. Various amine products are known to form as products of V-50 radical recombination reactions.[40] Possible processes are

$$\mathrm{IM}_i^{\bullet} + \mathrm{O}_2 \xrightarrow{k_{\mathrm{O}_2}} \mathrm{IM}_i\mathrm{OO}^{\bullet} \tag{13}$$

$$\mathrm{IM}_i\mathrm{OO}^{\bullet} + \mathrm{M} \xrightarrow{k_{\mathrm{p,O}^{\bullet}}} \mathrm{IM}_i\mathrm{OOM}^{\bullet} \tag{14}$$

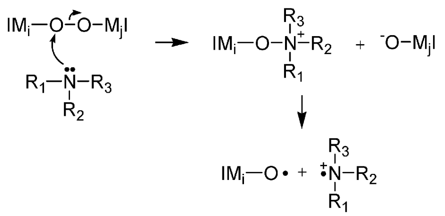
$$\mathrm{IM}_i\mathrm{OO}^{\bullet} + \mathrm{T}^{\bullet} \xrightarrow{k_{\mathrm{t,O}^{\bullet}}} \mathrm{IM}_i\mathrm{OOT}\ \text{(combination)} \tag{15}$$

$$\mathrm{IM}_i\mathrm{OO}^{\bullet} + \mathrm{T}^{\bullet} \xrightarrow{k_{\mathrm{t,O}^{\bullet}}} \mathrm{IM}_i\mathrm{OOH} + \mathrm{T}\ \text{(disproportionation)} \tag{16}$$

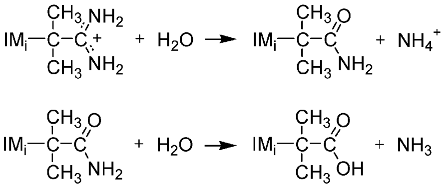
Peroxide species may be formed by the incorporation of oxygen into polymer chains. Oxygen is a very effective radical scavenger, reacting rapidly with carbon-centered radicals according to eq 13, with $k_{\mathrm{O}_2} > 10^9$ M^{-1} s^{-1}, to yield a relatively stable peroxyl radical.[41,42] Peroxyl radical addition to monomer (eq 14) is much slower, with $k_{\mathrm{p,O}^{\bullet}} = 41$ M^{-1} s^{-1} for styrene;[43] nevertheless, successful copolymerization of oxygen and styrene has been reported under certain exceptional conditions.[44,45] However, given that $k_{\mathrm{t,O}^{\bullet}}$ in eqs 15 and 16 is likely to be 10^9−10^{10} M^{-1} s^{-1} for emulsion polymerization, peroxyl radicals are far more likely to undergo termination than copolymerization. Thus, the presence of oxygen enhances the overall rate of radical loss and is responsible for appreciable periods of inhibition and/or retardation commonly seen in the early stages of polymerization.[30] Equations 13−16 show that any oxygen present at the commencement of polymerization will eventually be incorporated into a polymer chain giving a peroxide functionality. The potential for radicals to be formed from thermal homolysis of polymeric peroxides is recognized;[46] however it appears that this is only likely to occur significantly at temperatures in excess of 100 °C.[47,48] Importantly, the presence of various amines has been seen to significantly accelerate peroxide reactions.[47,49]

It is of interest to consider the potential for polymeric peroxide formation in the emulsion polymerization systems used in the present work. The solubility of oxygen in water is approximately 1 mM.[50] While no comparable value was found for the solubility of oxygen in styrene, it may be expected to be similar to that reported for toluene: 9 mM.[51] Since no effort was made

Scheme 2. Amine-Induced Decomposition of Polymeric Peroxide



Scheme 3. Hydrolysis of Polymer Amidinium Functionality



to deoxygenate either water or monomer in the synthesis of seed latexes, it is reasonable to estimate that the overall concentration of oxygen at the commencement of polymerization is $\sim 10^{-3}$ M. In light of the discussion above, this may be expected to yield approximately 10^{-3} M of peroxide functionalities during the polymerization. These peroxide groups would most likely be located mainly in small oligomeric species in the aqueous phase given that any radical that reacts with oxygen to form a peroxyl radical is far more likely to undergo termination than to propagate further to form an entering species, and termination of two non-surface-active radical species will give non-surface-active products. A large proportion of the peroxide-containing oligomers may be expected to be removed from the seed latex during dialysis; however, dialysis is unlikely to remove all traces of oligomer. Therefore, it is not unreasonable to expect the presence of some polymeric peroxides in the seed latexes.

Thermal decomposition of any such polymeric peroxides is expected to have little effect on the kinetic experiments, since these were at 50 °C (although it has been established[34] that these can be a major source of spontaneously generated radicals at this temperature in the emulsion polymerization of chlorobutadiene). It is conceivable, however, that an induced decomposition process might provide a significant source of initiating radicals. Induced decomposition of peroxides by residual amine species present in the aqueous phase of the cationic latex CAT02 thus provides one possible explanation for the unusually high rate of spontaneous polymerization observed for this latex. It is proposed here that radicals are formed via a redox mechanism similar to that described for other amine/peroxide redox couples,[46] as shown in Scheme 2.

The much lower rate of spontaneous polymerization seen in the case of the anionic latex AN01 is consistent with the proposed mechanism in that the synthesis of latex AN01 did not involve any reagents with amine functionality (although polymeric peroxides will still form).

Latex CAT02 was deemed unsuitable for kinetic experiments as entry of spontaneously generated radicals would dominate all entry events even in the presence of added chemical initiator, thereby introducing unacceptable uncertainty to any values of ρ_{init} obtained. However, it was found that extended heat treatment of the latex had a profound effect on the rate of spontaneous polymerization. Latex CAT02 was deoxygenated by sparging with argon and was then heated to 90 °C for 4 days. The value of $\bar{n}_{\text{SS}}$ for spontaneous polymerization of the heat-treated latex (labeled CATH03) was reduced to less than 20% that of the original latex, as shown in Table 3, making latex CATH03 suitable for kinetic experiments to accurately measure ρ_{init}.

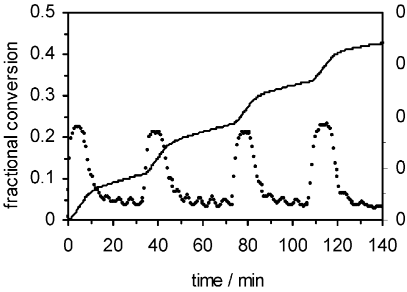


Figure 1. Conversion (line) and $\bar{n}$ (circles) as functions of time for a γ-relaxation run at 50 °C using cationic latex CATH03 and γ-radiolysis dose rate of 158 Gy h^{-1}. Values of k and ρ_{spont} were obtained from data fitting of the γ-relaxation regions 7−34, 42−74, 82−108, and 117−145 min.

The effect of heat treatment may be interpreted in terms of the mechanism proposed above for spontaneous polymerization in latex CAT02. It is suggested that heating to 90 °C results in accelerated decomposition of polymeric peroxides via the reaction in Scheme 2 and as well the simple thermal decomposition process is likely to be more significant at this higher temperature. Four days is sufficient time to cause extensive decay of the polymeric peroxides postulated to be present.

It is important also to consider other possible effects of heat treatment on the latex. In particular, it is recognized that the amidinium functionality of V-50 derived species is susceptible to hydrolysis under such conditions, as shown in Scheme 3. V-50 chain end groups anchored at the latex particle surface provide stabilizing cationic surface charge. Thus, hydrolysis of the amidinium functionality at these sites will result in a lowering of the particle surface charge. However, also contributing to the surface charge is cationic DTAB surfactant added to the seed latex for kinetic experiments. This surfactant is present at the particle surface in considerable excess of the V-50 end groups (approximately 10−20 times by molar ratio), and thus it is unlikely that even extensive hydrolysis of V-50 end groups during the heat treatment would have any significant effect on the overall surface charge of the cationic latex during a seeded experiment.

γ-Relaxation Experiments. γ-Relaxation experiments were carried out for all three seed latexes, AN01, CAT02, and CATH03. Typical data (time dependence of conversion and $\bar{n}$) from such an experiment are shown in Figure 1. Conditions used and kinetic data obtained are given in Table 3. The data were analyzed as outlined above to obtain k and ρ_{spont}. Multiple γ exposures and relaxations were conducted, and the results presented here are average values, along with uncertainties estimated from the scatter in experimental data.

Table 3 also shows the theoretical value for the exit rate coefficient, k_{theor}, calculated with the standard model as follows.[22,52] Radical exit from a particle involves transfer to monomer followed by desorption of the monomeric radical, M$^{\bullet}$, into the aqueous phase.

Alternatively, M$^\bullet$ may undergo propagation before desorption can occur, in which case an exit event is not completed. One then has

$$k_{\text{theor}} = \frac{k_{\text{tr}} k_{\text{dM}}}{k_{\text{p}}^{1}} = \frac{3D_{\text{w}}}{r_{\text{s}}^{2}} \frac{[\text{M}]_{\text{w}}}{[\text{M}]_{\text{p}}} \frac{k_{\text{tr}}}{k_{\text{p}}^{1}} \tag{17}$$

Here D_{w} is monomeric diffusion coefficient in water, k_{tr} the rate coefficient for transfer to monomer, k_{p}^{1} the rate coefficient for propagation of a monomeric radical, and r_{s} the radius of the swollen latex particle. The rate coefficient for desorption of M$^\bullet$ is assumed to be the same as that of a monomer molecule, k_{dM}. The following literature values for styrene at 50 °C were used in calculations: $D_{\text{w}} = 1.5 \times 10^{-9}$ m^2 s^{-1},[53] $[\text{M}]_{\text{w}}^{\text{sat}} = 4.3 \times 10^{-3}$ M,[54] $k_{\text{tr}} = 9.3 \times 10^{-3}$ M^{-1} s^{-1},[55] and $k_{\text{p}}^{1} = 4k_{\text{p}} = 1.0 \times 10^{3}$ M^{-1} s^{-1}.[22]

The results in Table 3 provide good support for the exit model described. The observed similarity in experimental k values obtained for the three seed latexes is as predicted given that all three latexes are of very similar particle size.

The values of $\bar{n}_{\text{SS}}$ and ρ_{spont} presented in Table 3 are those obtained from kinetic runs in the absence of any added initiator (as described earlier). Importantly, these values of $\bar{n}_{\text{SS}}$ and ρ_{spont} agree closely with those obtained from γ-relaxation (not shown). The values of ρ_{spont} yielded by the former method are those adopted for use in eq 12 in all kinetic analysis. This is for two reasons: (1) the steady-state spontaneous polymerizations afford greater precision, and (2) experiments wherein the system is never exposed to γ-radiation should more faithfully reproduce the contribution from spontaneous polymerization present in chemical runs.

Also evident in Table 3 is the considerably larger value of ρ_{spont} obtained for latex CAT02 compared to the other two latexes. This is thought to be due to an additional source of initiating radicals present only in CAT02, as discussed above.

The uncertainties associated with the values of k and ρ_{spont} for latex CAT02 are somewhat greater than for the other two latexes. This is because the γ-relaxation method relies on accurate fitting of rate data obtained during the period where the rate of polymerization decays from its in-source steady-state value to a lower out-of-source value (typically this takes up to 30 min). In the case of latex CAT02 the high out-of-source (“spontaneous”) rate meant that the second-order loss process tends to be masked (see eq 10).[56]

It is also worth noting that at low initiator concentrations ρ_{spont} may constitute up to 20% of the total entry rate coefficient (see values in the following subsection). Taking accurate account of spontaneous entry is thus critical to obtaining accurate entry rate data under such conditions.

Chemically Initiated Experiments. Polymerization rate data from kinetic experiments with added chemical initiator, exemplified in Figure 2, were analyzed using eqs 7 and 9−12. This involved using data presented in Table 3 as well as the following literature values appropriate to styrene emulsion polymerization at 50 °C: $fk_{\text{d}}(\text{KPS}) = 1.0 \times 10^{-6}$ s^{-1},[57] $fk_{\text{d}}(\text{V-50}) = 4.8 \times 10^{-6}$ s^{-1},[40,58] $k_{\text{p}}(\text{styrene}) = 2.6 \times 10^{2}$ M^{-1} s^{-1}.[59] Note in Figure 2 that $\bar{n}$ is seen to increase above 0.5 after the system has entered interval III (60 min into the polymerization). It is well understood that this observed departure from “zero-one” conditions is a consequence of slower termination.[22] To ensure that the zero-one kinetic treatment used here was valid, data analysis was restricted to interval II of polymerization (in the case of Figure 2 only the first 23 min of polymerization) when the termination rate is sufficiently high (in these experiments) that zero-one conditions prevail.

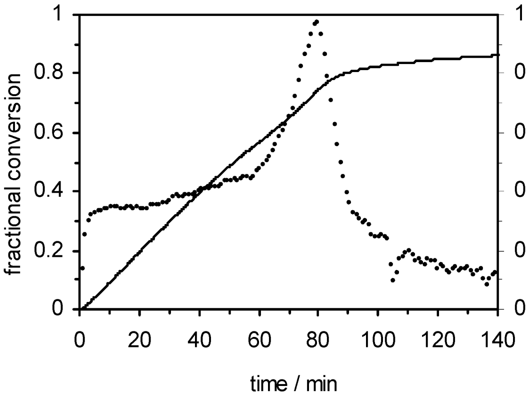


Figure 2. Conversion (line) and $\bar{n}$ (circles) as functions of time for a chemically initiated run at 50 °C using anionic seed latex AN01 and [KPS] = 1.5 mM. The value of $\bar{n}_{\text{SS}}$ is taken from the region 6−23 min.

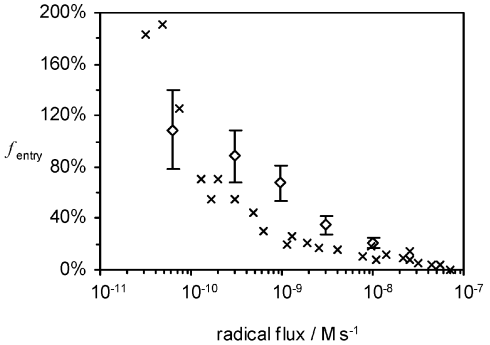


Figure 3. f_{entry} obtained for polymerization system KPS/AN01 (diamonds) at 50 °C, presented together with data reprocessed from refs 31 and 1 (crosses) as a function of radical flux.

Four polymerization systems were examined: the four pairings possible from use of either KPS (anionic) or V-50 (cationic) as initiator and either AN01 (anionic) or CATH03 (cationic) as latex. The following labels specify the pairings: KPS/AN01, V-50/CATH03, KPS/CATH03, V-50/AN01. Detailed numerical results for each of these systems are available as Supporting Information; in what follows results will only be graphically presented.

KPS/AN01. Entry data were obtained using an anionically stabilized latex with KPS as (anionic) initiator to provide a comparison with previous results[1−4] and to establish a benchmark for subsequent experiments. Comparison is made with earlier extensive data obtained by Hawkett et al.[1] for the same type of system, reanalyzed by fitting to eq 10 (second-order loss, which is a better model for such data than the first-order loss assumed in the pioneering paper of Hawkett et al.). For this purpose, the value of k was obtained by reanalyzing the γ-relaxation data obtained by Lansdowne et al.[31]on the same latex.

Figure 3 gives values of f_{entry} for the system KPS/AN01 presented along with estimated experimental uncertainties arising mainly from the values for ρ_{spont} and k. These data show acceptable agreement with the reprocessed data of Hawkett et al. One has the expected

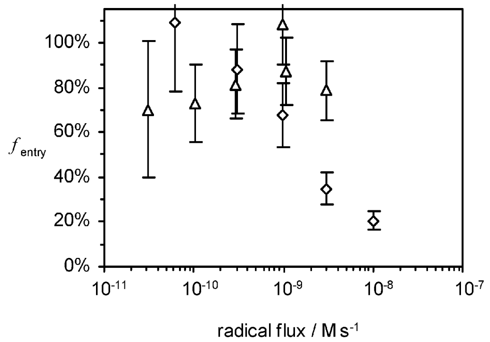


Figure 4. f_{entry} as a function of radical flux for polymerization systems KPS/AN01 (diamonds) and V-50/CATH03 (triangles) at 50 °C.

trend of decreasing entry efficiency with increasing radical flux, although in most cases the efficiencies obtained in the present work are somewhat higher than those previously published. Also of note are f_{entry} values apparently greater than 100% for radical flux less than 1×10^{-11} M s^{-1} (or [KPS] $< 5 \times 10^{-5}$ M) in both sets of data. This is not to suggest that the flux of initiating radicals is being supplemented by some unknown radical source but is more likely the result of uncertainty in one or more of the values used to calculate f_{entry} in eq 7, possibly the initiator decomposition rate coefficient, fk_{d}, a quantity which is sensitive to the precise experimental conditions.[57] It is also possible that ρ_{spont} may vary with radical flux and thus that an incorrect value of ρ_{spont}—to which ρ_{init} is highly sensitive at low radical flux—has been used.

V-50/CATH03. f_{entry} data obtained for this system are presented in Figure 4 and reveal a high entry efficiency that shows no consistent variation with changing radical flux (an approximately constant f_{entry} means an entry rate coefficient that shows a linear increase with initiator concentration, as implicit in eq 7). Experiments were attempted at higher initiator concentration, but the high rate of evolution of nitrogen gas from V-50 decomposition under such conditions resulted in bubble formation early in the polymerization, making accurate dilatometric measurement of the polymerization rate impossible.

Comparing the f_{entry} data from system V-50/CATH03 with those from KPS/AN01 in Figure 4 shows the effect of changing from a polymerization system where both entering species and particle surface are anionically charged to one in which both are cationically charged. It is clear that the trend with increasing initiator radical flux is not the same in both cases. This may be the result of an inherent difference in entry in anionic vs cationic systems, although it seems unlikely that this difference is related to any charge interaction, given that entry in both these systems involves the interaction of entering species and latex particles of like charge. The difference may be more specifically related to changing either the initiator type or the latex type. To more explicitly determine the nature of this entry effect, and indeed the existence of any significant charge effect, we next consider the results of the two systems which combine oppositely charged initiators and latex particles.

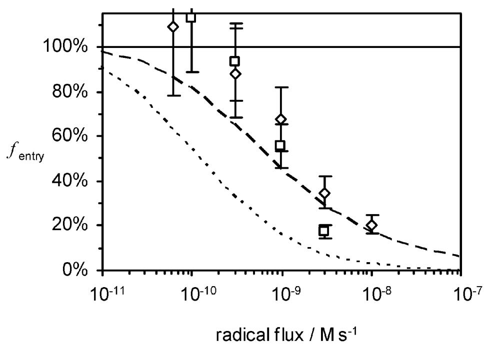


Figure 5. Comparison of f_{entry} as a function of radical flux for entry of anionic initiator into anionic and cationic latex. Points: experimental; KPS/AN01 (diamonds) and KPS/CATH03 (squares). Lines: modeled values calculated using Maxwell et al.; $z = 1$ (—), $z = 2$ (— — —), and $z = 3$ (- - -); parameter values in text.

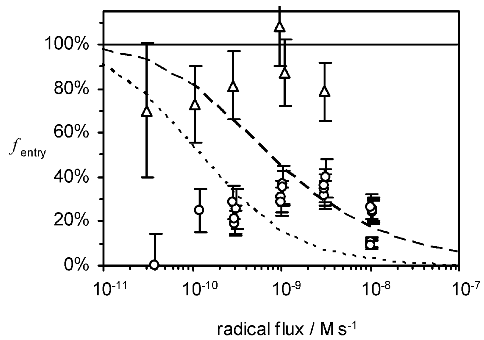


Figure 6. f_{entry} as a function of radical flux for entry of cationic initiator into cationic and anionic particles. Points: experimental; V-50/CATH03 (triangles) and V-50/AN01 (circles). Lines: modeled values calculated using Maxwell et al.; $z = 1$ (—), $z = 2$ (— — —), and $z = 3$ (- - -); parameter values in text.

KPS/CATH03. f_{entry} data obtained for this system, incorporating anionic initiator and cationic latex particles, are presented in Figure 5. The trend seen for this system is very similar to that seen in the other KPS system (KPS/AN01), with f_{entry} decreasing as the initiator concentration is increased. As before, apparent values of f_{entry} in excess of 100% were obtained; in this case a value of 318% lies well outside the limits of any reasonable experimental uncertainty. These data (with the highest result omitted in the interests of scale) are presented along with those from KPS/AN01 in Figure 5. These two data sets are very close, suggesting that the common element between these two systems, the initiator type (KPS), is of central importance in defining the nature of the entry process: changing the nature of the particle surface charge has little or no effect on entry, completely consistent with the entry model of Maxwell et al. Equally, it seems that there is little effect from any charge−charge interaction between entering species and particle surface, since changing from like to unlike charges has no clear impact on the values of f_{entry} obtained. These findings are fully consistent with the entry model of Maxwell et al.,[10] but they are difficult to reconcile with suggestions that the entry rate is controlled by diffusion to the particle surface,[5−7] by surfactant displacement,[8] or by colloidal interactions.[9]

V-50/AN01. The final system to be considered is that in which V-50 was used as initiator in combination with the anionic latex AN01. The entry efficiency data obtained here are shown in Figure 6. Experiments carried out with V-50 concentration in excess of 10^{-3} M resulted in rapid coagulation of the seed latex (as the electrostatic repulsion between like-charged particles is diminished by the high concentration of ions in the aqueous phase) and provided no usable rate data. Also, the rate of entry observed in experiments with V-50 concentration 4×10^{-6} M was approximately the same as that in the absence of any added initiator, and therefore no experiments were undertaken at lower initiator concentration than this.

Entry efficiencies for this system are low and, as for the other V-50-initiated system V-50/CATH03, are relatively invariant with initiator concentration, generally falling in the range 0.2−0.4. These somewhat unusual results prompted more exhaustive experimental investigations to ensure that these low efficiencies were indeed reproducible, as was indeed found to be the case. Also, in an attempt to elicit more information about entry in this system, experiments were carried out at two different particle concentrations. Notably, changing the particle concentration appears to have no significant effect on f_{entry} (as indeed is predicted by the model—a point discussed earlier in the text).

The results from the systems discussed above suggest that, of the variables considered in this study, initiator type may be of most importance in defining the entry process. Figure 6 compares results from V-50/AN01 (cationic entry into anionic latex) with those from V-50/CATH03 (cationic entry into cationic latex). Unlike the results seen for the KPS systems, there is clearly a discrepancy between entry data obtained from the two V-50 systems. Changing from cationically to anionically stabilized latex particles results in a consistent and general decrease in entry efficiency. Possible reasons for this will shortly be discussed.

As well as the obvious difference between these two data sets, a similarity is also noted: in both cases f_{entry} is relatively invariant with changing initiator concentration. This observation will be seen to be significant in the light of the modeling results presented below.

Modeling Entry. The experimental data for all four polymerization systems above are now interpreted in terms of the entry model of Maxwell et al.[10] It is important to note that this entry model is applied only to entry of radicals derived from (chemical) initiator and is not used to model the processes of exit or reentry: radicals which reenter after exiting, which arise from transfer within a latex particle, are chemically quite distinct from those derived directly from aqueous-phase initiator.

Equation 8 was used to calculate values for f_{entry} under the same conditions used in experiments. Parameter values were as stated above, along with $k_{\mathrm{t,w}} = 1.75 \times 10^{9}$ $\mathrm{M}^{-1}\ \mathrm{s}^{-1}$,[10] letting z range from 1 to 3; results are shown in Figures 5 and 6. Maxwell et al.[10] noted that the model may be improved with a chain-length-dependent $k_{\mathrm{p,w}}$, thus allowing for slightly higher propagation rate coefficients for very short (i.e., 1-meric or 2-meric) radicals. This modification[22] provides some improvement in the fitting of experimental data from KPS-initiated styrene polymerizations, but the fit with chain-length-independent $k_{\mathrm{p,w}}$ was satisfactory for the present work.

Figure 5 shows that the experimental data for both KPS systems are fitted reasonably well by the model with $z \approx 2$. These results are in good agreement with the value of z between 2 and 3 put forward by Maxwell et al. for the corresponding system.

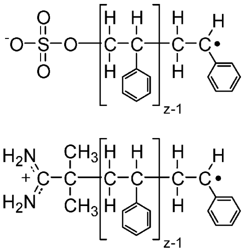
Figure 6 compares model with experiment for both V-50 systems. The interpretation of these results is more ambiguous than for KPS. In the case of the V-50/CATH03 system, the model seems to give the closest fit with $z = 1$. Although the experimental results are generally less than the model prediction of 100%, it is clear that efficiencies are very high and that f_{entry} is relatively invariant with changing radical flux. This is as expected for $z = 1$ where an entering species is formed after only the first (rapid) propagation event, and there is thus no possibility of termination. If the radical takes any longer to become ready to enter, then f_{entry} must decrease as initiator concentration increases, but this is not observed for either V-50 system.

On the basis of the model of Maxwell et al. and results for the KPS systems, one would expect that changing from cationic to anionic latex particles while keeping the same initiator should have no effect on entry rates. However, this is not the case for the V-50/AN01 system. The fact that f_{entry} is relatively invariant with radical flux for this system is certainly in line with a value of $z = 1$, but the much lower entry efficiencies obtained suggest that the entry model of Maxwell et al. does not provide a complete explanation for this system.

Alternative entry mechanisms may be suggested to explain this anomaly. One may be charge−charge interactions between initiator and particles. However, not only do KPS results indicate that no such effect exists, but the V-50 results are qualitatively inconsistent with this suggestion: one would expect higher entry rates for the situation of positive initiator and negative particle surface, but the opposite is observed. A more likely explanation is as follows. The apparent difference in z for KPS ($z = 2$) and V-50 ($z = 1$) suggests that V-50 is inherently more surface-active than KPS. As a result, V-50 may be more susceptible to interaction with the particle surface: a significant proportion of V-50 initiator may be adsorbed onto the particle surface. This would entail different mechanisms for initiation and entry compared to those for initiation strictly in the aqueous phase. One can imagine that more V-50 might be absorbed onto the negatively charged surface and that the resulting surface-phase initiation may have a lower fk_{d} than in the aqueous phase, e.g., a lower f due to the close proximity of radicals on the surface or a lower k_{d} due to the less polar environment. This suggestion is speculative, and further investigations in this regard are underway. What is clear is that some surface activity of V-50 makes it easy to justify that its f_{entry} values are relatively independent of initiator concentration: wherever effective initiation occurs, the resulting radicals very quickly enter latex particles and start polymerizing.

Understanding *z* Values. Maxwell et al. rationalized the value of $z = 2$ for styrene polymerization with KPS as initiator using thermodynamic considerations: an aqueous-phase radical incorporating an initiator end group and two monomer units is sufficiently surface-active to adsorb strongly to (or go inside) a latex particle. These authors considered the driving forces associated with such an adsorption process. First, they estimated the hydrophobic free energy of adsorption ΔG_{hyd} for a styrene molecule by considering its different components. They similarly estimated (from surfactant micellization data) the value of ΔG_{hyd} required to render a polar $\mathrm{SO_4}^{-}$ group surface-active. Comparison of these two values enabled an estimate to be made for the minimum number of styrene units required to yield a surface-active oligomeric KPS−styrene radical. This method was generalized to provide estimates for z for any monomer with KPS as initiator using eq 18 (where

Scheme 4. Structure of Oligomeric Styrene Entering Species Derived from KPS (Top) and V-50 (Bottom)



the integer function "int" reduces to the next lowest integer value):

$$z(\mathrm{KPS}) = 1 + \mathrm{int}\left\{\frac{-23\ \mathrm{kJ\ mol^{-1}}}{RT\ \ln([\mathrm{M}]_\mathrm{w}/\mathrm{mol\ dm^{-3}})}\right\} \quad (18)$$

Equation 18 gives a value of $z = 2$ for styrene.

Entering species derived from KPS and V-50 are shown in Scheme 4. Both entering species include a polar end group, but for V-50 there is a nonpolar $C(CH_3)_2$ component also present. It is suggested that this nonpolar functionality may best be considered as part of the hydrophobic portion of the entering species, along with the z styrene monomeric units incorporated. Assuming that the hydrophilic character of the polar $C(NH_2)_2^+$ group from V-50 is approximately the same as that of SO_4^- (in the absence of any better estimate), then due to the presence of the nonpolar functionality in the V-50 end group, one expects that fewer hydrophobic monomer units are needed to form a surface-active entering species (i.e., z is lower for V-50).

It remains to determine whether this effect is sufficient to justify a difference in z of one monomer unit as has been suggested. An estimate may be made based on the reasoning of Maxwell et al. In calculating the value for ΔG_hyd of 23 kJ mol^{-1} required for KPS, these workers assumed a value of approximately 3 kJ mol^{-1} for ΔG_hyd corresponding to a single CH_2 group. Such a contribution from each of the three carbon atoms in the nonpolar part of the V-50 end group to the total hydrophobic free energy of the oligomer would result in a reduction from the 23 kJ mol^{-1} associated with KPS to approximately 14 kJ mol^{-1} for V-50. Thus, a modification of eq 18 may be formulated to estimate z for any monomer with V-50 as initiator:

$$z(\mathrm{V\text{-}50}) = 1 + \mathrm{int}\left\{\frac{-14\ \mathrm{kJ\ mol^{-1}}}{RT\ \ln([\mathrm{M}]_\mathrm{w}/\mathrm{mol\ dm^{-3}})}\right\} \quad (19)$$

which yields $z = 1$ for styrene and V-50, in accord with deductions from experimental data. In view of this, the only unexplained aspect of all our entry data is that fk_d seems to be lower than expected in the V-50/anionic seed system, as discussed above.

Conclusions

Kinetic data for radical entry in the emulsion polymerization of styrene have been obtained for four different systems, incorporating an anionic and a cationic initiator (persulfate and V-50) into both anionically and cationically charged latexes. Presenting data in the form of f_entry as a function of radical flux permits direct comparison, independent of any effects from differences in the rate of initiation and particle concentration between polymerization systems.

Data for an anionic initiator with anionic latex showed acceptable agreement with previously published data for a similar system.[1] Moreover, changing the nature of the latex particle surface charge had a minimal effect on the entry efficiency, suggesting that charge interactions between the particle surface and entering radicals have little or no impact on the entry process, consistent with the entry model of Maxwell et al.[10] However, changing the initiator charge had a significant effect on the initiator efficiency: the anionic initiator had decreasing entry efficiency with increasing radical flux, whereas the cationic initiator had efficiencies that were relatively invariant with changing radical flux. These results demonstrate the importance of the nature of the initiator (in the sense of the initiating radicals it gives rise to) in defining the mechanism for entry in emulsion polymerization.

Experimental results were also compared with results calculated using the entry model of Maxwell et al. under the same conditions. The model assumes that aqueous-phase chemistry alone determines the rate of entry and gives excellent accord with experiments where KPS was the initiator with $z = 2$; i.e., a primary KPS radical must undergo two propagation events before a species capable of entry is formed, the first being rapid. This value of z is in accord with predictions made by the same authors on the basis of thermodynamic considerations. Where V-50 was used, comparison with model results is somewhat more ambiguous. Entry efficiency for this cationic initiator is high. A value for $z = 1$ (i.e., virtually every radical enters a particle without aqueous-phase termination) appears most likely, although further experiments may be required to verify this. This value for z may be understood using thermodynamic reasoning similar to that given by Maxwell et al. for the peroxide initiator.

The results refute alternative models in the literature[5−9] that entry may be controlled by double-layer (colloidal) interactions, surfactant displacement, or diffusion control.

It was observed that the cationically charged latex had a very high rate of spontaneous initiation, which is rationalized in terms of peroxidic functionalities in combination with amidino radical chemistry.

Acknowledgment. The support of a New Zealand Foundation for Research Science and Technology Bright Future Scholarship is gratefully acknowledged, as is the support of the P.A. Rolfe Scholarship Fund, and also a Shirtcliffe Fellowship. Dr. Chris Ferguson and Dr. Hank De Bruyn are thanked for their guidance in experimental techniques and helpful discussions. Jelica Strauch is thanked for performing the CHDF and PCS experiments. The support of the Australian Institute for Nuclear Science and Technology and the help of David Sangster with γ-radiolysis work are also greatly appreciated. The Key Centre for Polymer Colloids is established and supported under the Australian Research Council's Research Centres Program.

Supporting Information Available: Values of $\bar{n}_\mathrm{SS}$, ρ_init, and f_entry from the four sets of chemically initiated experiments of this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA025695Y