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Mechanism of Radical Entry in Electrosterically Stabilized Emulsion Polymerization Systems

Stuart C. Thickett and Robert G. Gilbert*

Key Centre for Polymer Colloids, School of Chemistry F11, Sydney University, NSW 2006, Australia

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ABSTRACT: The kinetics and mechanism for the process of radicals entering latex particles from the aqueous phase ("radical entry") in electrosterically stabilized emulsion polymerization particles were studied. Polystyrene particles stabilized with differing lengths of poly(acrylic acid) chains bound to the surface were synthesized using RAFT-controlled radical polymerization techniques to ensure that the hydrophilic block was of low polydispersity; these latexes had been studied previously to examine the exit rate coefficient (k) in such systems via γ-relaxation experiments. Particles stabilized with poly(acrylic acid) chains were shown to have a significantly lower average number of radicals per particle (n) (and hence reaction rate) than that of equivalent systems stabilized with a conventional surfactant when used in seeded chemically initiated dilatometry experiments with styrene. Assuming that these emulsion systems obey second-order loss kinetics (i.e., an exited radical will re-enter another particle to either propagate or terminate, a phenomenon well accepted for styrene emulsion systems), the calculated entry rate coefficient (ρ) was significantly lower than that predicted by the "control by aqueous phase growth" mechanism for radical entry. Excellent agreement with the accepted entry model was found to occur when radical loss was assumed to be a first-order process with respect to $\bar{n}$ (i.e., an exited radical is terminated in the aqueous phase) or if significant amounts of aqueous phase termination is introduced into the evolution equations of initiator-derived oligomers. These results may be explained by rapid transfer of radical activity to a poly(acrylic acid) chain on the surface, forming "midchain radicals" that increase the likelihood of termination events in the poly(acrylic acid) surface layer.

Introduction

For the synthesis of emulsion polymers on an industrial scale,[1] it is common to polymerize the monomer of interest in the presence of a water-soluble comonomer (such as acrylic acid) to generate polymer particles that are (electro)sterically stabilized by polymer chains anchored onto the surface of the particle. It is also common to add block copolymers to an emulsion polymerization recipe as a stabilizing component; such species are adsorbed to the surface of the formed particles. However, despite the technical importance of (electro)steric stabilizers, most basic kinetic studies carried out on such emulsion polymerizations systems have yielded ambiguous mechanistic information; rationalization of mechanisms for various phenomena has only been carried out on systems that are electrostatically stabilized. The first such work where a model electrosterically stabilized emulsion system was used to examine the mechanism of a particular kinetic event (radical exit) was reported only recently;[2] the work presented in this paper is a direct follow-on from those results.

To better control the polymerization rate and the final properties of the latex formed via such methods, there is a need to quantitatively understand the impact that these water-soluble polymer chains (the "hairs" on the surface) have on the kinetics and mechanisms that control the polymerization processes and hence, particle sizes, rates, and molecular weight distributions in these systems. It was shown[3] in ab initio experiments using diblock copolymers as surfactants in emulsion polymerization systems that the reaction rate was extremely sensitive to the combination of charge on the initiating radical as well as the charge on the hydrophilic component of the diblock; this led to the postulate that diffusion of radicals entering the particle from the aqueous phase had become rate-determining. The same work demonstrated that, under some conditions, an increase in the "surfactant" concentration led to a decrease in the polymerization rate, the exact opposite of what was postulated in Smith and Ewart's[4] pioneering work. While no rate coefficients were able to be extracted from this work due to the complications of particle formation, it is evident that electrosteric stabilizers behave rather differently from ionic stabilizers. This was validated in the recent work on radical exit,[2] when the rate of exit was seen to be dependent on the length of the electrosterically stabilizing block.

Seeded dilatometric experiments have become a common method[5] to look at the kinetics of particle growth in the absence of particle formation (no secondary nucleation). If intraparticle termination is so fast as to not be considered rate-determining (i.e., a radical entering a particle already containing a growing polymeric radical results in instantaneous termination, the definition of a "zero−one" system), then the rate coefficients for radical entry into (ρ) and exit from (k) can be determined directly from appropriate rate data. It has been shown experimentally[6] and theoretically[7] that this "zero−one" limit applies for small particles ($<\sim$100 nm diameter) for styrene emulsion polymerizations at 50 °C. One important point regarding this work, however, is that elucidation of rate coefficients via this method requires the "zero−one" approximation to hold, as this allows the data to be processed with essentially no model-based assumptions. This approach has allowed calculation of both rate coefficients in question for ionically stabilized polystyrene particles, with the values showing very good agreement with currently accepted theoretical models for a wide range of systems.[8−11]

The present work involves the quantification of the impact of electrosteric stabilization by comparing entry and exit rate coefficients in such systems with those determined for compa-

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* Corresponding author. E-mail: gilbert@chem.usyd.edu.au. Telephone: +61 2 9351 3366. Fax: +61−2−9351 8651.

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rable ionically stabilized emulsion systems. Only a limited amount of work has been previously conducted on the subject, with the most recent work of Vorwerg and Gilbert[12] providing ambiguous results regarding the entry and exit rate coefficients in such systems. Using a polystyrene seed latex further polymerized in the presence of acrylic acid and styrene to create an electrosterically stabilized latex, it was shown that both ρ and k in these systems were reduced (this included corrections to earlier work by Coen et al.[13]). A significant pH dependence was seen for the extent of secondary nucleation as well as the reduction in ρ and k, with extensive secondary nucleation as well as a large decrease in both rate coefficients seen at neutral pH conditions. Despite the complications of the presence of newly formed particles, this work demonstrated that analyzing the behavior in these systems was a multivariable problem.

The biggest limitation in prior work on the subject was the inability to synthesize a "hairy layer" of known, controllable width on the surface of the particle. Using conventional free radical polymerization to create a hairy layer on the particle surface results in a very broad molecular weight distribution (MWD) of the hydrophilic blocks; this issue is further complicated by the inability to size the hairy layer, despite using attempts using sophisticated techniques such as SANS.[14] This has only recently been overcome by developments in controlled radical polymerization in emulsion from Ferguson et al.,[15] whereby latex particles with a grafted hairy layer of well-defined and narrow molecular weight distribution have been synthesized. Using an amphipathic RAFT (reversible addition fragmentation chain transfer) agent dissolved in water, polymerization of a hydrophilic monomer such as acrylic acid (AA) takes place, with the AA/RAFT molar ratio dictating the average length of hydrophilic block. As these chains are capped with the RAFT endgroup at the conclusion of the reaction, the chains are still active but lie dormant and can be further polymerized with another monomer.[16] Further polymerization of the second, hydrophobic monomer then takes place under starved−feed conditions (to prevent droplet nucleation[15−17]) in the aqueous phase until the diblocks begin to self-assemble; this is the precursor of particle formation. Particles can then be grown further to an appropriate size for kinetic studies, providing an ideal system for this present work, because the length and nature of the stabilizing block is well characterized and relatively monodisperse.[18,19]

This present paper examines the kinetics and mechanism of radical entry for latexes that are electrosterically stabilized by grafted oligo(acrylic acid) chains, using rate data for entry obtained by varying the length of the stabilizing block and the charge on the initiating radical. The most common method of calculating an indirect value of ρ, a procedure which is used in this work, is to use the steady-state rate from seeded kinetic studies that begin in Interval 2 (the presence of monomer droplets at the beginning of the reaction) as well as the value of the exit rate coefficient k (measured directly from γ-relaxation dilatometry experiments[20]). These k values were calculated in recent work that demonstrated a significant dependence on the length of the stabilizing block;[2] a "restricted diffusion" mathematical model gave excellent semiquantitative agreement with experiment. Considering the departure from the "expected" exit kinetics in these systems, it is anticipated that the behavior of ρ will also depart from predicted kinetic models. This will allow, for the first time, elucidation of the entry mechanism in electrosterically stabilized emulsion systems.

Theory

Emulsion Polymerization Rate Equations. The rate in an emulsion polymerization is given by

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{k_\mathrm{p}[M]_\mathrm{p}N_\mathrm{p}}{n_\mathrm{M}{}^0 N_\mathrm{Av}}\bar{n} \qquad (1)$$

where x = fractional conversion, k_p = propagation rate coefficient, $[M]_\mathrm{p}$ = monomer concentration inside the particles, $n_\mathrm{M}{}^0$ = initial monomer concentration per unit volume of aqueous phase, N_p = particle number per unit volume of aqueous phase, N_Av = the Avogadro constant, and $\bar{n}$ = average number of radicals per particle. Equation 1 is used to determine $\bar{n}$ in systems where no secondary nucleation is observed. For styrene at 50 °C, it has been shown that monomeric styryl radicals formed by transfer may exit a particle, then re-enter another particle without re-escaping (known as Limit 2a).[5] This leads to the rate equation

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = \rho(1 - 2\bar{n}) - 2k_\mathrm{cr}\bar{n}^2 \qquad (2)$$

where k_cr is the second-order exit rate coefficient assuming complete re-entry ("cr"), while ρ is the pseudo-first-order rate coefficient for the number of entry events per particle per unit time. The entry rate coefficient is usually considered to be the sum of the initiator-derived entry events as well as the "spontaneous" or thermal entry component, a well-accepted phenomenon in styrene emulsion polymerization systems.[21] Once an independent value of k_cr is found using γ-relaxation experiments, the value of ρ is indirectly calculated from the magnitude of $\bar{n}$ during the steady-state polymerization period (denoted $\bar{n}_\mathrm{ss}$) by rearranging eq 2, namely:

$$\rho = \frac{2k_\mathrm{cr}\bar{n}_\mathrm{ss}{}^2}{1 - 2\bar{n}_\mathrm{ss}} \qquad (3)$$

Subtraction of the thermal or "spontaneous" entry component (also found from γ-relaxation experiments) from the calculated value of ρ yields the entry rate coefficient purely due to initiator-derived radicals, allowing direct comparison with established mechanistic models.

It is pertinent to mention that the "Limit 2a" version of zero−one kinetics to describe emulsion polymerization systems is only one of a variety of different sublimits; one other limit is known as "Limit 1" and considers the radical loss mechanism to be a first-order process. This limit is applicable in cases where exited radicals undergo termination in the aqueous phase without re-entering another particle, or undergo continual re-entry and re-escape.[5] The Limit 1 kinetic equation is given by

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = \rho(1 - 2\bar{n}) - k_\mathrm{ct}\bar{n} \qquad (4)$$

where k_ct is the first-order exit rate coefficient assuming complete termination ("ct").

The advantage of the zero−one kinetic treatment is that the two rate coefficients of interest are deduced in an unambiguous way from experimental data, data which have been shown to contain no more than two independent pieces of information; for example, the shape of the relaxation rate in γ-relaxation experiments can be reproduced within experimental uncertainty by just two parameters, the long-time slope and intercept of $x(t)$. Similarly the entry rate coefficient is found solely from the steady-state slope of $x(t)$. This eliminates incorrect mechanistic inferences from model-based assumptions or parameters that are, to date, immeasurable via experiment.[22,23]

Currently Accepted Entry Model for Electrostatically Stabilized Particles. Many varied mechanistic models to rationalize the entry process have been put forward in the literature over time. The work of Hawkett[6] demonstrated that, for styrene, the entry efficiency (the fraction of radicals that actually enter a particle relative to the number of initiator-derived moieties) was much less than unity, indicating significant aqueous phase termination of growing radicals. Models such as the diffusion control theory (stating that diffusion of the entering oligomer to the particle surface is the rate-determining step[24]) as well as the "surfactant displacement"[25] and "colloidal entry"[26] models used explain the entry mechanism have all been refuted in some manner.[27]

The "control by aqueous phase growth" model proposed by Maxwell et al.[11] (the "Maxwell−Morrison model") has provided excellent agreement with the limited literature on studies involving electrostatically stabilized latex systems[10,11,13,28,29] and to date has not been refuted. Rather than considering the actual entry event as the rate-determining step in the entry process, the crucial step in the model is the addition of a sufficient number (denoted z) of monomer units to an initiator-derived radical so that the oligomer becomes surface active; the entry process at this stage is assumed to be so fast as to be diffusion controlled. Termination of growing oligomers in the aqueous phase can take place, rationalizing the low measured entry efficiencies. The key reactions controlling this model are:

$$\text{initiator} \xrightarrow{fk_\text{d}} 2I^\bullet \tag{5}$$

$$I^\bullet + M \xrightarrow{k_\text{pw}} IM_i^\bullet \tag{6}$$

$$IM_{i-1}^\bullet + M \xrightarrow{k_\text{pw}} IM_{i-1}^\bullet, \qquad i < z \tag{7}$$

$$IM_z^\bullet + T^\bullet \xrightarrow{k_\text{tw}} \text{dead product}, \qquad i < z \tag{8}$$

$$IM_z^\bullet + \text{particle} \xrightarrow{\rho_\text{init}} \text{entry} \tag{9}$$

where $I^\bullet$ is a radical derived from thermal decomposition of the initiator (rate coefficient fk_d), M a monomer unit, $T^\bullet$ any aqueous phase radical, $IM_i^\bullet$ an aqueous-phase oligomer containing i monomer units and $IM_z^\bullet$ a surface-active oligomer. The rate coefficients for propagation, termination, and entry (all in the aqueous phase) are given by k_pw, k_tw, and ρ_init, respectively. Equation 9 does not imply that every encounter between a "z-mer" and a latex particle results in "irreversible" entry (entry is normally considered to have been successful when the oligomer begins to propagate in the interior of a particle), as adsorption and desorption may occur numerous times, but rather that the only chemical fate that a z-mer undergoes will be entry.

The only unknown parameter within this model is the value of z; while the model is an oversimplification of reality (as there will be oligomers that propagate beyond the length z), it helps to provide physical understanding to the kinetics as an "average" degree of polymerization in the aqueous phase. The value of z can be rationalized on thermodynamic grounds: by considering the free energy of adsorption, it can be estimated as to how many monomer units are required to make the initiator-derived radical surface active.[11] It was predicted that $z \approx 2-3$ for the commonly used persulfate-initiating species in styrene emulsion polymerization systems.

The solution of eqs 5−9 in the steady state yields the approximate analytic solution for ρ_init:

$$\rho_\text{init} \approx \frac{2fk_\text{d}[I]N_\text{Av}}{N_\text{p}}\left\{\frac{2\sqrt{fk_\text{d}[I]k_\text{t,w}}}{k_{\text{p},w}[M]_\text{w}} + 1\right\}^{1-z} \tag{10}$$

where $[M]_\text{w}$ is the concentration of monomer in the aqueous phase. The values of parameters used in the Maxwell−Morrison expression are given in Table 3. Equation 10 gives excellent agreement with experimentally measured entry rate coefficients[10,11] for styrene−persulfate systems with a z value of 2, consistent with the thermodynamically predicted value. (It should also be pointed out that the persulfate radical is a unique case: an induced decomposition in water yields hydroxyl radicals that can enter latex particles without the addition of any monomer units.[30] This effect, however, is likely to be small relative to entry events involving sulfate-ended oligomers.)

As the value of ρ_init is dependent on the number of latex particles (N_p), it is important to have a method of comparing the entry behavior across different systems that are likely to have different system parameters. To do this, results presented in this work will be both as ρ and as entry efficiency (f_entry) values (f_entry is the entry rate per particle divided by the entry rate assuming every radical enters a particle); the latter quantity is independent of N_p. The reason for reporting both the entry rate coefficient and initiator efficiency will be apparent later in the paper. Similarly, as different initiators have different fk_d values, the same initiator concentration for different initiators will yield potentially very different radical fluxes. As such, effort was made to ensure approximately the same radical flux was used from experiment to experiment, regardless of initiator type. Comparison with the "Maxwell−Morrison" entry model and mechanistic understanding can hence be gained from this approach without confusion.

Experimental Section

Reagents. Acrylic acid (AA) (Sumika) was purified by vacuum distillation to remove dimeric species and polymerization inhibitors. Styrene (Sigma Aldrich) was purified by passing the monomer through an inhibitor removal column (Sigma Aldrich) twice to remove inhibitor and other extraneous species. Granular NaOH (Sigma Aldrich) and the initiators 4,4′-azobis(4-cyanopentanoic acid) (V-501, Wako Industries), 2,2′-azobis(2-methylpropionamide) dihydrochloride (V50, Wako Industries), 2,2′-azobis[2-methyl-N−(2-hydroxyethyl)propionamide] (VA-086, Wako Industries), and potassium persulfate (KPS, Merck) were used as received. The RAFT agent, 2-{[(butylsulfanyl)carbonothioyl]sulfanyl}propanoic acid (denoted "RAFT V") was received in recrystallized form from Dulux Australia. *tert*-Butyl hydroperoxide (TBHP, 70% aqueous solution, Sigma Aldrich), sodium hydrogencarbonate (Sigma Aldrich), butanone (Sigma Aldrich), and the surfactants AMA-80 (sodium dihexyl sulfosuccinate and a few branched isomers thereof, Cytec Industries) and sodium dodecyl sulfate (SDS, Sigma Aldrich) were used as received. All water used in this work was high-purity deionized water (MilliQ).

Synthesis of Conventional Seed Latex. Sodium hydrogencarbonate (0.85 g, 10 mmol) and AMA-80 (8.48 g, 22 mmol) were added to water (405 g), and the resultant mixture was stirred magnetically to ensure complete dissolution. Deoxygenated styrene (49.8 g, 0.48 mol) was added to the reaction vessel and stirred vigorously to effect emulsification. High-purity nitrogen was bubbled through the emulsion to remove any dissolved oxygen for thirty minutes while the reaction vessel was brought to 90 °C. KPS (0.88 g, 3.2 mmol) dissolved in water (5 mL) was introduced via syringe, and polymerization took place for 5 h. The resultant latex was filtered through glass wool and dialyzed for one week to

Table 1. Particle Size (measured by TEM), Particle Number, and Polydispersity Data for Latexes Used in this Work

latex	diameter (nm)	polydispersity	N_p (L^{-1})
ST0	44.0	1.01	1.13×10^{18}
ST5	23.6	1.03	9.66×10^{18}
ST10	22.9	1.04	9.61×10^{18}
ST20	23.2	1.03	7.2×10^{18}

remove any residual surfactant. This latex (denoted ST0) was used as a benchmark to compare to our electrosterically stabilized particles.

Electrosterically Stabilized Seed Latex Synthesis. The synthesis of electrosterically stabilized seed latexes with hydrophilic stabilizers of controlled length is a complex, multistep process. The full procedure can be found in the previous publication on this subject;[2] a summary of the process is given below.

A series of RAFTV−(styrene)$_x$−(acrylic acid)$_x$ diblocks were synthesized (x = 5, 10, 20) in butanone at 70 °C, with V-501 the initiating species. The molecular weight distribution of the AA block (before addition of the styrene) was checked via electrospray mass spectrometry, with a narrow distribution centered around the target chain length in all cases, as reported for similar syntheses by Ferguson et al.[15]

These diblocks were used as the precursor units in the synthesis of three styrene seed latexes, using a slightly modified approach to that taken by Ferguson et al.[15] The diblocks were dried overnight in a vacuum oven and then dissolved in water in the presence of NaOH to assist dissolution (NaOH was added in equimolar amounts relative to the amount of carboxylic acid units present in the diblock). Again, using V-501 as the initiator, styrene was then added to the reaction mixture under "starved−feed" conditions over 6 h at 80 °C; starved−feed conditions are necessary so that the aqueous phase is never saturated with styrene, thus preventing droplet nucleation. The target in these systems was for latexes of approximately 10% solids. The formed latexes (denoted ST5, ST10, and ST20 in accordance with the number of acrylic acid units on the surface) were then filtered through glass wool to remove any coagulum. Active RAFT endgroups were then oxidized to a nonactive state through the heating of the latex at 80 °C for 24 h in the presence of TBHP (2% w/w), a procedure that was developed and verified in a subsequent publication.[2] Successful modification of the RAFT agent was verified via UV−visible spectrometry; dialysis of the latex was carried out over two weeks with twice-daily changes of water to remove any residual TBHP (itself a transfer agent[31]).

Particle sizes were checked using transmission electron microscopy (TEM, performed at the University of Sydney's Electron Microscope Unit) as well as hydrodynamic chromatography (HDC) using a particle size distribution analyzer (Polymer Labs) and a capillary hydrodynamic fractionator (Matec), results of which are presented in Table 1.

Chemically Initiated Dilatometry. For each seed latex, the following methodology was employed for seeded kinetic studies:

Styrene (5 g, 48 mmol), Milli-Q water (17 g) and seed latex (10 g) were separately degassed under vacuum and then loaded into a jacketed dilatometer vessel. SDS (0.005 g, 3.5 μmol) was added in order to stabilize monomer droplets, the dilatometer vessel sealed with a rubber septum, and the headspace evacuated via syringe at room temperature. Magnetic stirring of the solution took place overnight to allow transfer of monomer to the particle interior, and the mixture was then heated to 50 °C. Stirring was ceased, and the reaction vessel evacuated again to remove dissolved oxygen.

In a separate vessel, an aqueous initiator solution was prepared: the three initiators used here being KPS (negatively charged radical), VA-086 (neutral radical), and V-50 (positive radical). The initiator solution was degassed under vacuum and heated to reaction temperature; 2 mL of the solution was then added to the dilatometry vessel via a syringe. Typical initiator concentrations ranged from 0.1 to 10 mM, with the aim to keep the same radical flux ($2k_d[I]$) between initiators.

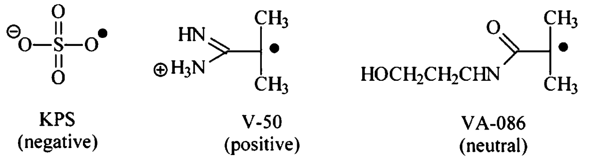

Figure 1. Radicals formed from thermal initiators used in this work.

Upon addition of the initiator solution, a glass capillary (1.51 mm radius) was inserted into the top of the vessel. The capillary was filled with water; stirring then recommenced. Dodecane (1 mL) was added to the top of the water to provide a smooth meniscus and to prevent evaporation. The meniscus height was monitored automatically using a LED "tracker" to provide conversion/time data. The resultant latex was checked for secondary nucleation via HDC to ensure the validity of the kinetic analysis. All kinetic data are provided in the Supporting Information.

Synthesis of Poly(acrylic acid) Oligomers and Chain Transfer Constant Measurement. Using a variation on a recipe described in Doherty's work,[32] acrylic acid (1.13 g, 15.6 mmol) was polymerized in the presence of distilled dodecanethiol (3.64 g, 18 mmol) in distilled toluene (15.3 g) for 24 h at 50 °C. The initiator was recrystallized azobisisobutylonitrile (AIBN, 0.062 g, 0.4 mmol), chosen specifically as it has a low initiator transfer constant.[31] The target molecular weight was approximately 1000 g mol^{-1}, i.e., short chains to model the oligomeric "hairs" on the particle surface. Conversion was measured by gravimetry and was ≈ 100%. Measurement of the molecular weight distribution (MWD) was attempted for the formed oligo(AA) using size exclusion chromatography (performed on a Shimadzu SEC system with 2 × PLGel Mixed B columns, THF eluent with a flow rate of 1 mL min^{-1}, 28 polystyrene standards from 160 to 5×10^6 g mol^{-1} used for calibration).

Measurement of the chain transfer constant ($C_{tr,AA} = k_{tr,AA}/k_p$) of styrene with poly(acrylic acid) as the "chain transfer agent" was achieved by polymerizing bulk styrene in the presence of different amounts of the synthesized oligo(AA); the [pAA]/[styrene] ratios used were 0, 0.01, 0.05, and 0.48. AIBN was used as initiator; 0.01 g was used for every 2 g of styrene. Polymerization took place at 50 °C under continuous magnetic stirring for 1 h; the fractional conversion was low (less than 3% in all experiments), with the samples quenched after 1 h with a 0.05% hydroquinone solution to prevent any subsequent polymerization. The MWD of the formed polystyrene was measured on the same SEC setup described above.

Results and Discussion

Chemically Initiated Dilatometry Experiments. It is well established through prior work that, for electrostatically stabilized styrene emulsion polymerization systems, the critical z value is approximately 2−3 for KPS[10,11] and 1 for V-50.[10] This can be rationalized on the basis of the number of styrene units required to add on to the initiator-derived radical before the oligomer becomes surface active; as the radical from the thermal decomposition of V-50 is not as water-soluble as the persulfate radical due to functional groups in the radical (see Figure 1), it takes less styrene units to impart surface activity. As the value of z is the critical parameter in the Maxwell−Morrison entry model, the z values for the initiators considered in this work for electrostatically stabilized emulsion systems will act as the reference point for comparison to our electrosterically stabilized systems. As no experimental z value has been reported for the VA-086 radical, it was measured via seeded kinetic studies using the ST0 latex. Using the value of the exit coefficient k found from independent γ-relaxation experiments[2] and the $[M]_p$ value found via the "static swelling" method[5,33] (results reported in Table 2), the entry efficiency as a function of radical flux was found for the ST0/VA-086 system (as shown in Figure 2). It can be seen that the f_{entry} values are in excellent agreement with

Table 2. Values of $[M]_p$ Measured by the "Static Swelling" Method as Well as Exit Rate Coefficient and Spontaneous Entry Rate Coefficient Values

latex	$[M]_p$ (M)	k (Limit 2a) (s^{-1})*	k (Limit 1) (s^{-1})^a	ρ_{spont} (s^{-1})^a
ST0	6.09	3.87×10^{-2}	n/a	2.18×10^{-5}
ST5	6.91	1.51×10^{-2}	6.76×10^{-3}	≈ 0
ST10	7.09	5.14×10^{-3}	5.12×10^{-3}	≈ 0
ST20	6.95	4.32×10^{-3}	5.05×10^{-3}	≈ 0

[a] Calculated in the work of Thickett et al, *Macromolecules* 2006, *39*, 2081-2091.

Table 3. Parameter Values Used in the Calculation of the "Maxwell−Morrison" Entry Rate Coefficient Equation

parameter	value
k_p	260 M^{-1} s^{-1}
$k_{t,w}$	1.75 10^9 M^{-1} s^{-1}
fk_d	
KPS	1 10^{-6} s^{-1}
KPS, electrosterically stabilized latexes	4 10^{-6} s^{-1}
VA-086	7.4 10^{-7} s^{-1}
V-50	4.9 10^{-6} s^{-1}
N_p	see Table 1
$[M]_p$	see Table 2

the Maxwell−Morrison entry model assuming $z \approx 3$. Using group contribution values to the free energy of hydration (ΔG^{hyd}) for the VA-086 radical,[34] a good estimate for this species is $\Delta G^{hyd} = -33$ kJ mol^{-1}. An approximate value for ΔG^{hyd} is given by $RT \ln[M]_w$, which is approximately -15 kJ mol^{-1} for styrene at 50 °C. Using the equation[11]

$$z = 1 + \text{int}\left(\frac{-33 \text{ kJ mol}^{-1}}{RT \ln[M]_w}\right) \quad (11)$$

we obtain a theoretical z value of 3, in agreement with experiment. This value is our reference value for the neutral VA-086 initiator.

The first comparison made between a conventional latex and an electrosterically stabilized system was the comparison between the ST0 and ST5 latexes using KPS as initiator. Five different initiator concentrations were used spanning 2 orders of magnitude, with eq 1 used to calculate the steady-state value of $\bar{n}$. As seen in Figure 3, a significant reduction in $\bar{n}$ was seen in the ST5 seeded experiments; while a smaller $\bar{n}$ is predicted by theory for smaller particles,[5] the reduction seen here is substantially lower than the expected "zero−one" value.

Calculation of ρ_{init} and f_{entry} via eq 3 (second-order loss kinetics) for these two latexes yields excellent agreement with the Maxwell−Morrison model for ST0 ($z = 2$, as demonstrated in previous work), but an extremely low, but apparently constant, entry efficiency for the ST5 latex (Figure 4, left panel). A constant entry efficiency suggests $z = 1$; however, the values measured here are orders of magnitude lower than the expected 100% entry of initiator-derived radicals. Moreover, the calculated values of ρ_{init} for the ST5/KPS system are 2 orders of magnitude lower than "normal" values of the entry rate coefficient in typical emulsion polymerization systems ($\rho_{init} = 10^{-7} - 10^{-6}$ s^{-1}; see Figure 4, right panel); rate coefficients this small are smaller than that of an expected thermal or "spontaneous" polymerization entry rate coefficient[21] often seen in conventionally stabilized systems. While no spontaneous polymerization entry rate was observed in the electrosterically stabilized systems in this work, these values of ρ_{init} are extremely small and it is debatable whether they are physically unreasonable. It should be pointed out that other latex/initiator combinations yield even lower values of ρ_{init}, adding weight to the theory that they are not physically reasonable values for this rate coefficient.

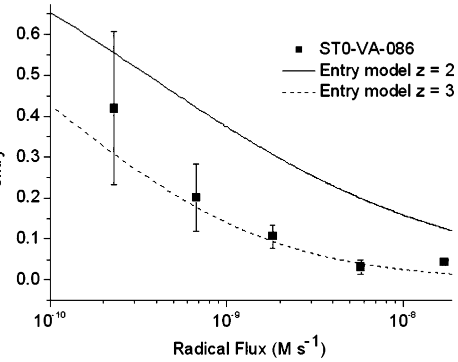

Figure 2. Entry efficiency (f_{entry}) as a function of radical flux for the ST0 latex, VA-086 as initiator; predicted entry efficiency from the Maxwell−Morrison model shown for $z = 2$ (solid line) and $z = 3$ (dashed line).

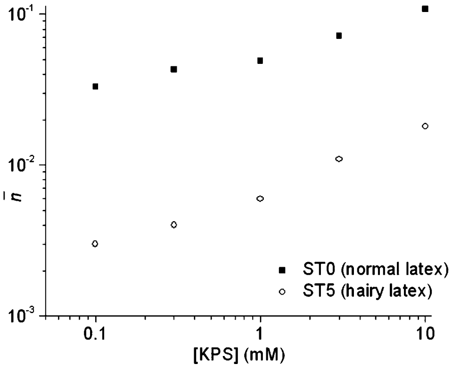

Figure 3. Variation of $\bar{n}$ for the ST0 (black squares) and ST5 (open circles) latexes, initiated with KPS.

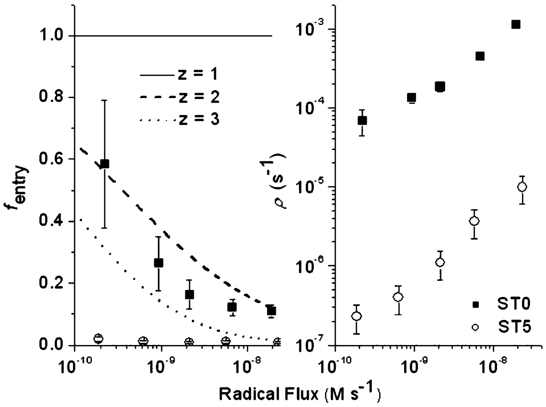

Figure 4. Comparison of f_{entry} (left panel) and ρ (right panel) the ST0 (black squares) and ST5 (open circles) latexes (initiated with KPS), assuming Limit 2a kinetics. Predicted f_{entry} values for $z = 1$ (solid line), $z = 2$ (dashes), and $z = 3$ (dots) are also shown.

These preceding values were obtained assuming Limit 2a kinetics, which is that applicable for styrene emulsion polymerization in electrostatically stabilized particles. However, using first-order loss kinetics (eq 4) to calculate ρ_{init} and f_{entry} values from the experimental $\bar{n}$ for ST5 (using the Limit 1 value of k for this latex) gives both physically reasonable values of ρ_{init} and f_{entry} values that are also in excellent agreement with the Maxwell−Morrison entry model (well approximated with $z = 2-3$; see Figure 5). (It should be noted that a different value of k_d, 4×10^{-6} s^{-1}, was used for KPS in this system, as the presence of acrylic acid accelerates the decomposition of KPS[35] due to its complicated decomposition mechanism). This suggests that the impact that electrosteric stabilization has on the emulsion kinetics is not a reduction in f_{entry}/increase in z (as suggested

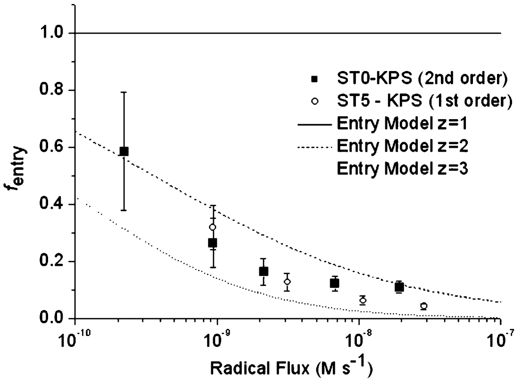

Figure 5. Comparison of f_{entry} for the ST0 (black squares) and ST5 (open circles) latexes (initiated with KPS), assuming Limit 1 kinetics for the ST5 system. Predicted f_{entry} values for $z = 1$ (solid line), $z = 2$ (dashes), and $z = 3$ (dots) are also shown.

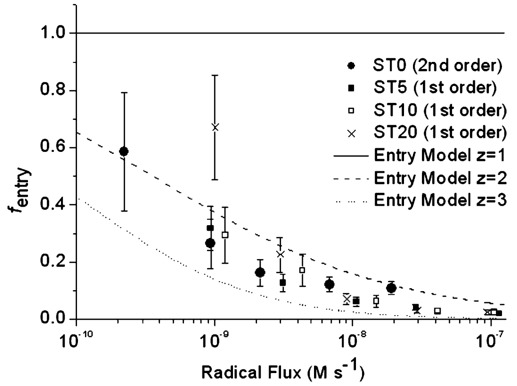

Figure 6. Comparison of f_{entry} for the ST0 (black circles) with the three electrosterically stabilized latexes assuming Limit 1 kinetics: ST5 (black squares), ST10 (open circles), and ST20 (crosses). Systems initiated by KPS. Predicted f_{entry} values for $z = 1$ (solid line), $z = 2$ (dashes), and $z = 3$ (dots) are also shown.

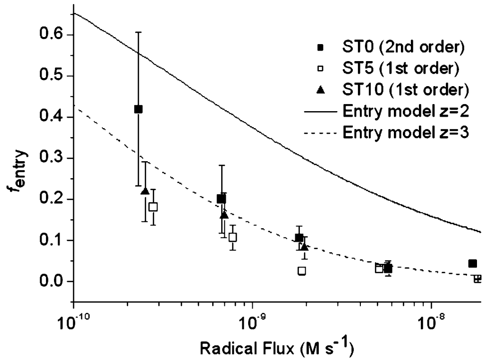

Figure 7. Variation of f_{entry} as a function of stabilizing block length for the ST5 (open squares) and ST10 (black triangles) latexes using VA-086 as initiator, assuming Limit 1 kinetics. Results for the ST0 latex (filled circles, Limit 2a kinetics) shown for comparative purposes. Predicted f_{entry} values for $z = 2$ (solid line) and $z = 3$ (dashes) are also shown.

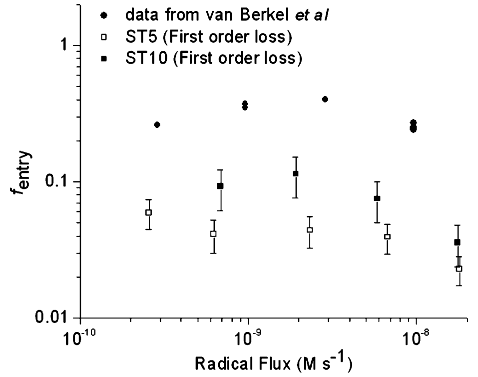

Figure 8. Variation of f_{entry} as a function of stabilizing block length for V-50 initiated systems. ST5 (open circles) and ST10 (black squares) are assumed Limit 1 kinetics; comparison is made to the data of van Berkel et al. (black circles).

previously[13]) but instead arises because the kinetic limit changes from a second-order loss mechanism to a first-order one. This very surprising result will be discussed extensively later in this paper.

Processing all data obtained from the three electrosterically stabilized latexes in question (ST5, ST10, and ST20) assuming first-order loss kinetics, it was found that the value of f_{entry} was independent of the length of the stabilizing unit on the surface of the particle (see Figure 6). This is a different result than that obtained for the radical exit mechanism in the corresponding work on the same system,[2] which saw a monotonic decrease in the exit rate coefficient k as a function of AA chain length. One may conclude that, as the rate of adsorption of an entering oligomer onto a particle surface is so fast (diffusion-controlled) compared to the magnitude of the desorption rate coefficient k_{dM}, the time scale is insufficient for the decreased diffusion coefficient within the "hairy layer" to affect the entry process.

The neutral entering radical generated via decomposition of the VA-086 initiator (expected value of $z = 3$) also demonstrated no difference in entry efficiency in electrosterically stabilized systems (see Figure 7), apart from the necessity of processing the data using Limit 1 kinetics. The positively charged radical from V-50 decomposition ($z = 1$), however, showed a significant reduction in f_{entry} (Figure 8) when compared to an electrostatically stabilized polystyrene system.[10] This may be rationalized as being due to the opposite charges on the poly(acrylic acid) hairs and the entering oligomer; electrostatic attraction between the two may lead to greater residence times of the entering species in the aqueous phase, increasing the likelihood of termination before entry. The major conclusion from this work however is (besides the case where the stabilizing unit and the entering oligomer of opposite charge) that emulsion particles stabilized by poly(acrylic acid) in this manner appear to obey a first-order loss mechanism, with no impediment to the entry process due to the stabilizing blocks on the surface.

It is essential to note that this first-order mechanism in this electrosterically stabilized (polyAA) system results in a much lower rate compared to that in an electrostatically stabilized one which obeys second-order radical loss.

Rationalization of the First-Order Loss Mechanism. It would appear from the experimental results presented in this work that the kinetics in the present pAA electrosterically stabilized emulsion polymerization systems support a first-order loss mechanism. This is on the basis that excellent agreement with the accepted entry model is obtained as well as the calculation of unfeasibly small entry rate coefficients when second-order loss kinetics are assumed.

The postulate that a styrene emulsion polymerization system, electrosterically stabilized or otherwise, obeys first-order loss kinetics is hard to understand. It has been well established both experimentally and theoretically[5,7] that, in these types of electrostatically stabilized systems, styrene emulsion systems obey a second-order loss mechanism. That is, an exited monomeric radical will re-enter another particle and either propagate or terminate (radical loss is second order because termination only occurs if the entered particle contains a free radical, the probability of which is proportional to $\bar{n}$, while the rate of exit from the original particle is also proportional to $\bar{n}$).

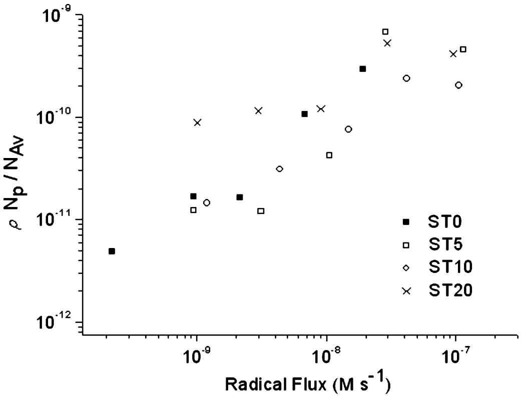

Figure 9. Overall entry rate as a function of radical flux for all latexes calculated by the "slope and intercept method". Points shown are ST0 (filled squares), ST5 (open squares), ST10 (open circles), and ST20 (crosses).

This can be rationalized by considering that the rate of re-entry is orders of magnitude higher than the rate of aqueous-phase termination, namely

$$k_{\mathrm{re}}\frac{N_{\mathrm{p}}}{N_{\mathrm{Av}}} \gg k_{\mathrm{t,aq}}[T^{\bullet}] \tag{12}$$

where k_{re} is the second-order radical re-entry rate coefficient (given by the Smoluchowski equation for diffusion-controlled reactions), N_{p} the particle number, $k_{\mathrm{t,aq}}$ the aqueous-phase termination rate coefficient, and $[T^{\bullet}]$ the total radical concentration in the aqueous phase. Even with the reduced re-entry rate coefficient due to diffusion through a two-phase (water plus polyAA layer) regime,[2] the value of N_{p} in all but the most unusual emulsion systems is so high as to cause the re-entry rate to significantly outweigh the rate of termination. Clearly, considering that it would appear that the electrosterically stabilized systems in question are obeying first-order kinetics, it would seem that some other chemical event is taking place to modify the overall kinetics.

One validation of the postulate that using first-order loss kinetics is appropriate to model the ST5, ST10, and ST20 latexes is the use of the "slope and intercept" method[5] to calculate the overall rate of entry ($\rho N_{\mathrm{p}}/N_{\mathrm{Av}}$) assuming first-order loss and compare this to the value for the electrostatically stabilized ST0 system assuming second-order loss. The "slope and intercept" method calculates ρ from the gradient and y-intercept of the linear fit to the steady-state region of the conversion-time ($x(t)$) curve without the use of an independent k value calculated from separate experiments. While this method is more prone to error than the indirect calculation used in this work due to oxygen inhibition/retardation that may affect the approach to steady state, it makes use of additional data within a single experiment to obtain ρ rather than combining data from two experiments (γ relaxation plus chemical steady state) used elsewhere in this paper. It can be seen (Figure 9) that, when using this approach, the same overall entry rate (within experimental error) is seen across all four latexes in question. (The overall entry rate was the parameter examined due to the fact that the entry rate coefficient is dependent on the particle number which differs from latex to latex.) This would support the supposition that the entry efficiency in electrosterically stabilized latexes stabilized in this manner is as predicted by the Maxwell–Morrison entry model, but the overall reaction process obeys first-order loss kinetics.

One hypothesis to explain the observed behavior seen in the electrosterically stabilized latexes in this work is that transfer of radical activity from exited radicals and/or initiator-derived oligomers) to the poly(acrylic acid) hairs on the surface takes place. It is well established that chain transfer to polymer is a significant reaction in the acrylate family (especially the intramolecular "backbiting" mechanism in *n*-butyl acrylate[36–38]), and any transfer event to a poly(AA) hair on the particle surface would lead to a tertiary radical that would be slow to propagate and thus would eventually terminate, essentially a "radical loss" event. If an exited monomeric radical either undergoes this postulated transfer reaction while exiting a particle, or attempting to re-enter another particle, this would make the radical loss a first-order loss process.

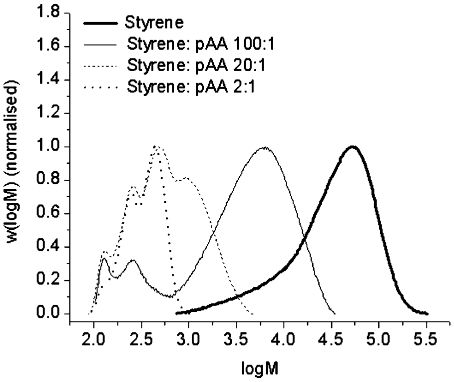

Figure 10. Normalized SEC distributions of styrene polymerized in the presence of different amounts of poly(acrylic acid).

Testing the "First-Order" Hypothesis. While the kinetic data collected in this work suggest that our electrosterically stabilized systems obey first-order loss kinetics (with no effect on the entry rate coefficient when making this assumption), there is no direct evidence to prove that the system is first order or that the reason for this effect is chain transfer to the poly(acrylic acid) hairs on the particle surface. To help validate this postulate, one must perform experiments that have the potential to refute what we believe is happening.

To obtain "proof of concept", that is, to prove that chain transfer to poly(acrylic acid) can take place in a styrene polymerization, samples of styrene were polymerized in bulk in the presence of differing amounts of oligo(acrylic acid), made via the precipitation polymerization procedure of Doherty et al.[32] (see Experimental section) with an aim to measure the chain transfer constant of poly(acrylic acid). Very short poly(acrylic acid) chains were targeted to simulate the length of the stabilizing blocks found on the surface of the latex particles used in this work. The measured $\bar{M}_{\mathrm{w}}$ of the poly(acrylic acid) was far lower than predicted at 400 g mol^{-1} (corresponding to approximately a 3-mer with a dodecyl endgroup); however, universal calibration breaks down at extremely low molecular weights, and as such, the precision in the measured value is questionable.

When this poly(acrylic acid) was used in chain transfer experiments with styrene, a substantial decrease in the average molecular weight of the formed polystyrene was observed (Figure 10), even when very small amounts of poly(AA) are present in the reaction mixture. This would suggest that the poly(AA) is an extremely efficient transfer agent. It is unclear as to why the MWDs of the very low molecular weight polystyrene samples appear multimodal. Experiments when the molecular weight distributions of RAFT–acrylic acid blocks were analyzed by SEC using online UV detection have shown maxima corresponding to specific chain lengths at very low molecular weights. As the molecular weights in question in this work are very low, these peaks may correspond to individual chain

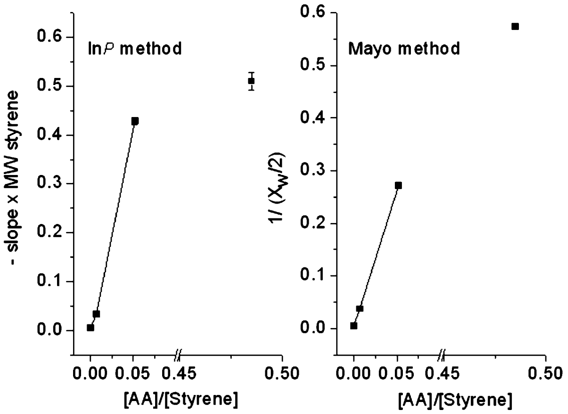

Figure 11. Mayo and ln*P* plot comparison to calculate the value of transfer constant $C_{tr,AA}$ for poly(AA) as a chain transfer agent for styrene polymerizations.

Table 4. Values of *C* for Poly(acrylic acid) as a Chain Transfer Agent in Styrene Polymerizations, Determined via Different Methods

method	*C*
ln *P* method	8.4 ± 0.4
Mayo method	5.1 ± 0.1

resolution. The nature of the observed multimodal distribution may be due to a midchain poly(acrylic acid) radical that has undergone termination by combination with a short initiator-derived styrene oligomer, forming a small branched structure that would appear at low MWs. Whatever the origin of these peaks, it is apparent that the main peak shifts to significantly lower molecular weights upon the addition of small amounts of poly(acrylic acid).

The value of $C_{tr,pAA}$ was calculated via the Mayo method[31] as well as the "ln *P*" approach[39] to examine the consistency between the two approaches. The Mayo and ln *P* plots are shown in Figure 11 (both plots exclude the final point from the linear fit as it would seem the formed polystyrene cannot go to lower molecular weights). The ln *P* method is considered more reliable as it utilizes the slope of the ln *P*(M) plot taken at the maximum of the GPC distribution to take band broadening into account;[40] both approaches yield a very high value of C_{tr} (see Table 4).

The value of $C_{tr,pAA}$ from the ln *P* method (8.4), while large, is not physically unreasonable. For example, the measured value of C_{tr} for dodecanethiol in styrene polymerizations is reported as 16−17 at 50 °C.[31] A primitive estimate of the maximum value of this quantity can be made as follows. Elementary transition-state theory considerations for this type of transfer reaction[41] suggest that a reasonable upper bound for the frequency factor is $\sim 10^7$ M^{-1} s^{-1}. The activation energy is much harder to estimate. A lower bound for the activation energy hydrogen transfer can be guessed by noting that termination in acrylate systems is by disproportionation rather than combination, and thus the rate coefficient for the former process must be less than that of the latter; because the combination reaction has a very low activation energy, $\lesssim 20$ kJ mol^{-1}, it is not unreasonable to take this as a lower bound for the transfer process. These values of the activation energy and frequency factor predict a transfer constant $\sim$ 24 at 50 °C, which is significantly greater than the values given in Table 4. This suggests that the values of the transfer constant inferred from the data, although high, are not physically unreasonable. Thus it would seem that chain transfer to poly(AA) is both probable and extremely efficient; this experiment is therefore consistent with the postulated mechanism. Had the change in MWD not been seen, it would have refuted the hypothesis.

The conclusion that there exists significant midchain radicals that are slow to propagate formed by exposing poly(acrylic acid) is at first surprising because this phenomenon must be widespread in the common use of this monomer in many applications. The first implication is that one expects to see significant branching in acrylic acid polymerization, and indeed, this has been reported in the literature.[42] The reasoning as to why synthesis of styrene−AA blocks is possible in the present system, despite the possibility of transfer to acrylic acid taking place, is that the activity of the RAFT agent is so high that the most likely event (by orders of magnitude) is the transfer of radical activity to a RAFT endgroup, a phenomenon that allows excellent molecular weight control in these systems. Similarly, while the transfer constant to AA may be high, the molar ratio of the two monomers is important in dictating rates and the molecular weight distribution, and so at the relatively low AA concentrations which are commonly used, significant amounts of transfer/termination events are unlikely to occur.

While the results presented do not refute the hypothesis that the kinetics in electrosterically stabilized emulsion systems follow first-order loss kinetics, it still remains unclear as to whether an exited species would predominantly undergo the fate of transfer or termination as opposed to re-entry. The pseudo-first-order rate coefficients for transfer to an acrylic acid unit on the surface ($k_{tr,AA}$[AA]) or termination with a midchain radical (MCR) formed after a transfer event ($k_{tr,w}$[MCR]) are both orders of magnitude lower than the re-entry rate $k_{re}N_p/N_{Av}$ of an exited species. Thus, while the agreement with the Maxwell−Morrison entry model when Limit 1 kinetics are used to process kinetic data is excellent, it is currently hard to justify the use of this kinetic limit on mathematical grounds. However, agreement with a modified version of the "control by aqueous phase growth" entry model can be obtained by incorporating rapid transfer and termination into the evolution equations for initiator-derived oligomers while still using the expected Limit 2a kinetics to account for the fate of an exited monomeric radical. These transfer and termination terms can be easily added to the rate equations that lead eq 10, giving a modified expression for ρ_{init}:

$$\rho_{init} \approx \frac{2fk_d[I]N_{Av}}{N_p}\left\{\frac{2\sqrt{fk_d[I]k_{t,w}} + k_{tr}[AA] + 2k_{tw}[\mathrm{MCR}]}{k_{p,w}[M]_w} + 1\right\}^{1-z} \tag{13}$$

where all terms are as defined previously. These extra terms in the numerator of the power expression in eq 13 have the effect of dramatically reducing the value of ρ_{init} (and hence f_{entry}) due to the larger magnitude of the transfer and termination with MCR terms compared to the term due to aqueous-phase termination of oligomers. Similarly, as these two new terms dominate the equation, the dependence on [*I*] (the initiator concentration) reduces to an approximately linear dependence from the component of eq 13 that is located outside the parentheses. A linear dependence on [*I*] gives an essentially constant entry efficiency, which is observed experimentally when assuming Limit 2a kinetics.

Using the value of $k_{tr,AA}$ calculated from the measurement of the transfer constant (2100 L mol^{-1} s^{-1}), the bulk concentration of AA units (1.4×10^{-2} M for the ST5 latex) and the steady-state concentration of MCR's (1.75×10^{-8} M, calculated from the analytic solution of MCR's as a function of time assuming generation by transfer and loss by termination) and all other values as defined previously, excellent agreement with experi-

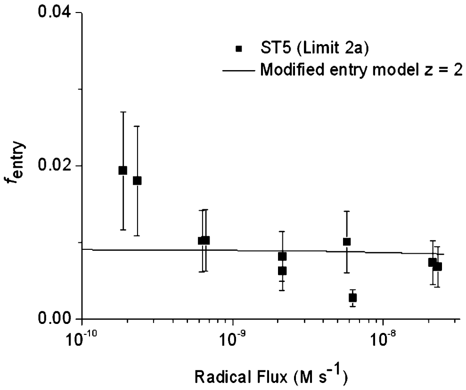

Figure 12. f_{entry} data for ST5/KPS (Limit 2a kinetics, black squares) and comparison with modified "Maxwell−Morrison" entry model with transfer and termination of aqueous-phase oligomers.

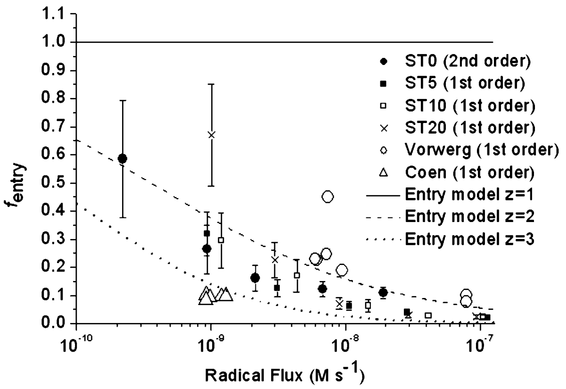

Figure 13. Comparison of f_{entry} data for electrosterically stabilized latexes analyzed in this work with reprocessed data from Vorwerg et al. (large open circles) and Coen et al. (large open triangles).

ment was observed, as seen in Figure 12. This suggests that the obtained entry rate coefficient and efficiency data can be explained in one of two ways, assuming Limit 1 kinetics (termination of exited radicals in the aqueous phase), or extensive transfer and termination of initiator-derived oligomers before entry while assuming Limit 2a kinetics. This approach, however, indicates extremely low entry rate coefficients, which may not be physically reasonable. Further work is planned to attempt to distinguish between the two limits; however, each method demonstrates a significant dependence on the postulated transfer to poly(acrylic acid) event.

Reconsideration of Prior Work. Similar work in the same area conducted by Coen[13] and Vorwerg,[12] albeit with "uncontrolled" poly(acrylic acid) hairs on the particle surface, revealed a reduction in ρ (assuming Limit 2a kinetics) but nowhere near the reduction in $\bar{n}$ as seen in the work presented here. This is due in part to the much lower particle number and larger particle size of the latexes used in that work (meaning that their calculated $\bar{n}$ should be significantly higher); however, it is possible that the data presented in their respective work can be treated assuming first-order loss kinetics. At lower values of N_p, there is only a minor difference between the expected $\bar{n}$ value in electrostatically stabilized systems using Limit 1 and Limit 2a kinetics; reprocessing the old data assuming first-order loss gives reasonable agreement with the data collected in this work (Figure 13). It is possible that, at such high N_p as used in this work ($>10^{18}$ L^{-1}), the effect of the poly(AA) hairs becomes more pronounced in the mathematical treatment of the data; such low $\bar{n}$ values provide a significant difference in the calculation of ρ when different kinetic limits are used.

The work of Vorwerg also showed that secondary nucleation took place in electrosterically stabilized latexes at neutral pH, a phenomenon that was not observed in this work. This is most likely due to the much higher particle number of the latexes used here, as the likelihood of secondary nucleation decreases rapidly with increasing particle number.[43] However, it does seem that electrosteric stabilization with AA can lead to rapid formation of new particles, which may be in part due to aqueous-phase termination of either exited monomeric radicals or initiator-derived oligomers, providing sites that may act as precursor particles. As the surface of particles stabilized in this manner are much more hydrophilic than in a conventional latex system, the driving force for radicals, both oligomers and exited monomeric radicals, to enter a particle (the free energy of hydration) may not be as great and so the likelihood of radicals to stay in the water phase is greater. This would suggest adsorption of entering species onto an electrosterically stabilized latex would follow a different isotherm, which is an area for future research.

Conclusions

Using newly developed techniques to synthesize electrosterically stabilized latexes with known lengths of poly(AA) stabilizing blocks, the kinetics of the polymerization of styrene was studied in order to measure the entry rate coefficient (ρ) in such systems as a function of hair length and initiator type.

With the exit rate coefficient (k) for the three latexes in question (stabilized with acrylic acid blocks comprising 5, 10, and 20 monomer units) measured independently in previously performed γ-relaxation experiments, ρ was measured indirectly from the steady-state rate in chemically initiated dilatometric experiments. Conditions were chosen such that zero−one kinetics were obeyed, allowing unambiguous calculation of the rate coefficient of interest from the experimental data with a minimum of adjustable parameters, given a knowledge of the appropriate limit for the fate of exited radicals.

The "Limit 2a" subdivision of the zero−one approximation has been shown to be appropriate for an *electrostatically* stabilized styrene system of this type; this assumes that an exited monomeric radical re-enters another particle (and subsequently propagates or terminates with another radical). Applying this limit to the present *electrosterically* stabilized system yields a low, constant entry efficiency for the three electrosterically stabilized latexes, with the corresponding entry rate coefficient being extremely small. However, excellent agreement with the "Maxwell−Morrison" model for radical entry was seen for an electrostatically stabilized seed latex. Upon reprocessing the electrosteric experimental data using Limit 1 kinetics, which assumes termination of exited radicals in the aqueous phase, equally good agreement with the Maxwell−Morrison model was obtained. It was also shown that increasing the length on the stabilizing block had no effect on the entry efficiency in these systems, and that for a negatively charged initiator (KPS) and a neutral initiator (VA-086), there was no restriction of entry. A lower than expected entry efficiency was seen when the positively charged V-50 initiator was used; this was attributed to charge interaction with the negatively charged poly(AA) hairs, possibly increasing residence time in the aqueous phase and making termination before entry more probable. Assuming Limit 1 kinetics when reprocessing γ-relaxation data to calculate the exit rate coefficient k does not change the qualitative trend that radical exit is a "restricted diffusion" process that is dependent on the length of the stabilizing unit; it is the subsequent fate of the exited species that dictates the choice of kinetic limit.

It was proposed that the apparent first-order behavior was due to a rapid transfer event whereby radical activity was transferred from either the exited monomeric radical, or an entering *z*-mer, to the poly(acrylic acid) hairs on the particle surface. If the resulting midchain radicals are slow to propagate but quick to terminate with the exiting radicals, this leads to Limit 1 kinetics. This idea was found to be consistent with data obtained when bulk polymerization of styrene is in the presence of short-chain acrylic acid; these data demonstrated a significant shift to lower molecular weights as the concentration of poly(acrylic acid) increased. The experimentally measured entry efficiency data for electrosteric systems, however, can also be explained assuming Limit 2a kinetics but introducing extensive transfer and termination into the evolution equations of initiator-derived oligomers, demonstrating the importance of the role of the acrylic acid stabilizing unit in the kinetics of these systems.

Reprocessing of data from previous work using conventional free radical polymerization techniques to create electrosterically stabilized particles also demonstrated that first-order loss kinetics give excellent agreement for the entry efficiency in comparison to the Maxwell−Morrison entry model. Therefore, the body of evidence presented suggests that the radical entry mechanism in polyAA−electrosterically stabilized systems is no different than that observed in latexes stabilized in a traditional manner; loss of radical activity in the aqueous/surface phase due to midchain radicals on the AA units, however, has significant implications in the overall kinetics of this industrially significant system. The result is a large reduction in the polymerization rate compared to that in a corresponding system stabilized electrostatically. The apparent aqueous/surface-phase termination of either exited radicals or initiator-derived oligomers, both by “traditional” termination or a transfer to poly(acrylic acid) event, is a major kinetic discovery in the field of emulsion polymerization and has an important impact in the modeling and understanding of this important component in many commercial latex syntheses.

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Supporting Information Available: Tables of radical entry efficiency as a function of radical flux for all latexes presented in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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