# Extended Mechanistic Description of Particle Growth in Electrosterically Stabilized Emulsion Polymerization Systems

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ABSTRACT: Polymeric (steric and electrosteric) stabilizers, based on water-soluble polymers such as poly(acrylic acid) and poly(ethylene oxide), are widely used to make surface coatings by emulsion polymerization and form a “hairy layer” which provides colloidal stability to the latex particles. It is shown by a combination of NMR and rate studies that the growth of these polymer colloids is dominated by a hitherto unsuspected combination of mechanisms: an abstraction reaction in the “hairy layer” which results in a radical on the water-soluble polymer which is slow to propagate but quick to terminate (*Macromolecules* **2006**, *39*, 6495−6504) and can also undergo $\beta$-scission reactions. Termination with radicals which would otherwise lead to particle growth leads to radical loss, i.e., a slower polymerization rate, while $\beta$-scission leads to radicals which can enter the water phase and cause secondary particle formation. Both of these effects are undesirable from a manufacturing point of view, and the newly discovered mechanism could be used to mitigate these undesirable features.

## Introduction

Emulsion polymerization is the method of choice to synthesize large quantities of polymer and latex on an industrial scale.[1] Industrially, the emulsion (latex) particles are sometimes stabilized solely electrostatically, through the addition of an ionic surfactant, but in many industrial applications (surface coatings, paints, adhesives) it is more common for the stabilization system to include a steric stabilizer such as one based on poly(ethylene oxide), or an electrosteric stabilizer formed in situ by addition of a water-soluble comonomer (e.g., acrylic acid, AA) at some stage in the emulsion polymerization process. The water-soluble comonomer preferentially polymerizes in the aqueous phase, leading to grafted hydrophilic chains anchored on the particle surface (a “hairy layer”), giving steric (or electrosteric) stability. In industrial latexes, (electro)steric stabilization is often in addition to that provided by a simple electrostatic stabilizer.

Despite their industrial significance, there is a lack of kinetic studies on (electro)sterically stabilized emulsion systems in such a way as to give unambiguous mechanistic information. Data that enable mechanisms to be obtained unambiguously must include rate studies in “seeded” systems (growth in the absence of secondary particle formation), including the changes in rate as the system is forced to move from one steady state to another by removing the source of free radicals. The electrosteric stabilizer must also be well characterized. However, (electro)sterically stabilized systems are notoriously prone to secondary particle formation during seeded growth (for example, the work of Coen[2] and Vorwerg[3] using poly(acrylic acid) stabilized latexes). Moreover, hairy layers are expected to be quite polydisperse in molecular weight (and probably in composition), and are much smaller than the overall particle size, so that heroic efforts[4] are required to effect even an incomplete characterization.

The situation is quite different for electrostatically stabilized latexes, with the kinetics and mechanisms that govern particle formation and particle growth now thought to be well understood, through complementary experiments and theory.[5] For example, in simple electrostatic systems, the rate coefficients for both radical entry ($\rho$) and radical exit ($k$) into and out of a latex particle have been comprehensively studied; as a result there are generally accepted mechanisms for both entry (“control by aqueous phase growth”[6] to a critical degree of polymerization $z$, with the actual entry of a $z$-mer being so fast as not to be rate-determining) and exit (transfer to monomer[7] followed by desorption into the aqueous phase, as well as considering the fate of an exited radical).[8,9] The magnitude of $\rho$ and $k$ dictate the rate of polymer growth within the particle, but for electrosterically stabilized particles, the only unambiguous studies have been[5] for polystyrene latexes stabilized by polyAA.[2,3,10,11] In the works just cited, it was seen that both $\rho$ and $k$ were significantly reduced relative to the predicted electrostatic models (as well as secondary nucleation occurring under certain conditions, which restricted the range over which reliable data could be obtained), suggesting that the accepted mechanisms for these processes in electrostatically stabilized systems may not apply to (electro)sterically stabilized ones. There appears to have been no successful seeded kinetic studies of particle growth in systems sterically stabilized by poly(ethylene oxide)-based stabilizers in the absence of significant secondary nucleation.

The successful development of “RAFT-in-emulsion” [12] to create monodisperse latexes stabilized by hydrophilic blocks of known length and narrow molecular weight distribution now allows for mechanistic testing for the effect of the width of the hairy layer, particle size, charge, etc. on the entry and exit rate coefficients in these systems.[10,11] However, the results presented previously for the impact of electrosteric stabilization on both radical entry and exit are difficult to rationalize. The systems chosen for study are kinetically “zero-one” ,[5] whereby a radical entering a particle already containing a growing radical results in instantaneous termination, whether this entering radical arises directly from aqueous-phase initiation or by desorption of a radical into the aqueous phase from a growing particle. For styrene systems of this type, desorbed (exited) radicals always reenter another particle, and so the loss of these radicals is kinetically second-order (“limit 2a” kinetics),[5] because the

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desorption rate is proportional to $\bar{n}$, the average number of radicals per particle, and the probability of a particle entered by a desorbed radical containing a growing radical is also equal to $\bar{n}$. The result from the work on radical exit[10] in poly(acrylic acid)-stabilized latexes was in agreement with the prior work in the field using uncontrolled latexes—there was a significant reduction in $k$ compared to the expected value for particles of that size. This was successfully modeled using a "restricted diffusion" model, whereby a dense polymeric layer on the surface reduces the rate at which an exiting (monomeric) radical successfully desorbs; radical loss by desorption was assumed to be second-order. For radical entry,[11] the polymerization rate was up to an order of magnitude lower than that expected for an electrostatically stabilized latex at the same initiator concentration, an extremely significant effect. These extremely low $\bar{n}$ values were explained by assuming that loss of desorbed radicals was *first* order ("limit 1" kinetics),[5] justified by assuming the occurrence of rapid transfer via hydrogen-atom abstraction from a polyAA hair on the surface of the particle once the species exits:[11,13,14] the formation of midchain radicals on the surface which are slow to propagate but quick to terminate. There is thus an apparent inconsistency (first vs second order) in the kinetics assumed for loss of desorbed radicals.

In this paper, new data are presented to resolve this contradiction for these polyAA-stabilized systems. The postulate of rapid transfer of an exiting radical with an acrylic acid unit in the hairy layer on the particle surface, or termination with the resultant midchain radical (MCR), are tested in a series of qualitative and semiquantitative experiments (such as NMR spectroscopy) designed to provide direct experimental evidence for this claim. Evidence is also obtained for a hitherto unsuspected mechanistic event: $\beta$-scission of midchain radicals on the particle surface. Inclusion of all these events in an extended kinetic model resolves the inconsistency in radical-loss kinetics. The inclusion of $\beta$-scission also provides a qualitative justification for the significant amounts of new particle formation seen in such systems, because desorption of radicals following this event provides a site in the aqueous phase that can aid secondary nucleation through further reaction (i.e., termination to form a surface-active species).

The data used to reveal the new mechanisms comprise the following: (a) The first data considered are rate data from seeded growth of electrosterically stabilized particles with well characterized and controllable hairy layers made by RAFT-in-emulsion synthesis, the rate data including both steady-state rates from chemical initiation and the change in rate seen by initiating with $\gamma$ radiolysis and then rapidly removing the polymerizing system from the radiation source ("$\gamma$-radiolysis relaxation"). Data reduction to $\rho$ and $k$ followed standard methodology.[5] (b) Analysis of the products from radical reactions involving the electrosteric stabilizing moieties (or the corresponding compounds in solution experiments) was performed by both NMR and size-exclusion chromatography (SEC); these analyses were performed for one of the commonest types of (electro)steric stabilizers, namely poly(acrylic acid).

The revelation, resulting from the present work of a hitherto unsuspected combination of mechanisms in one of the commonest industrial processes has the potential to yield improved processes and products.

## Experimental Section

**Reagents.** Acrylic acid (AA) (Sumika), toluene (Sigma Aldrich) and dodecanethiol (Sigma Aldrich) were purified by vacuum distillation to remove any 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. Azobisisobutylonitrile (AIBN, Sigma Aldrich) was recrystallized in hexane prior to use. Granular NaOH (Sigma Aldrich) and potassium persulfate (KPS, Merck) were used as received. *tert*-Butyl hydroperoxide (TBHP, 70% aqueous solution, Sigma Aldrich), sodium hydrogen carbonate (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 (Milli-Q). Deuterium oxide $D_2O$ (99.9%) was purchased from Cambridge Isotope Laboratories Inc.

**Synthesis of Acrylic Acid Oligomers.** Oligomers of AA were synthesized using a variation of the precipitation polymerization procedure reported by Doherty et al.[15] AA (1.13 g, 15.6 mmol) was polymerized in the presence of dodecanethiol (3.64 g, 18 mmol) in toluene (15.3 g) for 24 h at 50 °C. The initiator was azobisisobutylonitrile (AIBN, 0.062 g, 0.4 mmol), chosen specifically as it has a low initiator transfer constant.[16] The target molecular weight was approximately 1000, i.e., short chains to model the oligomeric "hairs" on the particle surface. Conversion was measured by gravimetry and was $\approx$100%. The solvent was removed and the polymer washed twice with hexane to remove any impurities. A variation of this above recipe was also performed to synthesize a polyAA sample of much higher molecular weight, with more AA (2 g, 28 mmol) used in the presence of less chain transfer agent (0.22 g dodecanethiol, 1 mmol).

**Bulk Chain-Transfer Experiments.** Experiments to determine the extent of chain transfer of styrene with polyAA as the "chain transfer agent" was achieved by polymerizing bulk styrene in the presence of different amounts of the synthesized oligoAA; the [pAA]:[styrene] ratios used were 0, 0.01, 0.05, and 0.48. An identical experiment was performed using the longer chain polyAA at a [pAA]:[styrene] ratio of 0.1 AIBN was once again the initiator; 0.01 g was used for every 2 g of styrene. Polymerization took place at 323 K 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, as well as any "modifications" to the MWD of the original pAA, was measured using SEC.

**Synthesis of Electrostatically Stabilized Seed Latex.** Sodium hydrogen carbonate (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 30 min 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 1 week to remove any residual surfactant.

**Seeded Dilatometric Experiments: Conventional Latex with Added pAA.** 0.032 g of the synthesized oligoAA was added to 30 g of the conventional styrene seed latex. NaOH was added to ensure complete ionization of all AA groups. This amount of polymer was added to mimic the total weight fraction of AA in the electrosterically stabilized polystyrene latexes synthesized by the RAFT-in-emulsion method (see previous work).[10,11] This seed latex (10 g), along with styrene (5 g, 48 mmol) and Milli-Q water (17 g) were all separately degassed under vacuum and then loaded into a jacketed dilatometer vessel. SDS (0.005 g, 3.5 $\mu$mol) 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 then heated to 323 K. Stirring was stopped and the reaction vessel evacuated again to remove dissolved oxygen.

In a separate vessel, an aqueous solution of KPS was prepared at the desired initiator concentration, degassed under vacuum and heated to reaction temperature; 2 mL of the solution was then added to the dilatometry vessel via a syringe. The range of initiator concentrations used was 0.1−10 mM.

Upon addition of the initiator solution a glass capillary (1.51 mm internal radius) was inserted into the top of the vessel. The capillary was filled with water; stirring was 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 hydrodynamic chromatography (HDC; Polymer Laboratories PSDA).

**Size Exclusion Chromatography.** SEC was performed on a Shimadzu SEC system with a Waters HR1-HR2-HR3-HR4 Styragel column set, THF with 0.1% w/w trifluoroacetic acid as eluent with a flow rate of 1 mL min$^{-1}$. Polystyrene standards from 160 to 5 × $10^6$ were used for calibration; both UV (254 nm) and DRI detection were employed.

***β*-Scission Experiments.** Poly(acrylic acid) synthesized previously (0.011 g) was dissolved in 2 mL of water, with NaOH added to adjust the pH to 7. KPS (0.026 g) was added to the solution and the sample heated at 323 K under stirring for 24 h. Radical flux was quenched with the addition of 0.1 mL of a hydroquinone solution. The molecular weight distribution of the poly(acrylic acid) was measured before and after treatment with KPS via SEC. An identical experiment was performed with poly(ethylene oxide) (Sigma Aldrich) of molecular weight $10^5$.

**Nuclear Magnetic Resonance.** The samples produced for the "chain transfer" experiments originally performed[11] to prove the concept of poly(acrylic acid) acting as a chain transfer agent in the polymerization of styrene were analyzed by NMR. The oligo(acrylic acid) sample before styrene polymerization is denoted CT1 and the sample after styrene polymerization is denoted CT2. Quantitative solution-state NMR spectra were recorded on a Bruker Avance 300 spectrometer at Larmor frequencies of 300.13 MHz for $^1$H and 75 MHz for $^{13}$C. The samples were left to evaporate at room temperature then dissolved in $D_2O$ (10% w/w for CT1, lower for CT2) and measured at 60 °C. For $^1$H spectra, 4 transients were recorded with 7.9 $\mu$s 90° pulse and a relaxation delay of 5 s. The spectra were calibrated with respect to the residual water signal at 4.79 ppm. $^{13}$C spectra were recorded using a 6 $\mu$s 90° pulse and a relaxation delay of 10 s, with 192 transients for CT1 (31 min) and 5585 transients for CT2 (15 h 30 min).

Solid-state NMR spectra of CT1 and CT2 were recorded on a Bruker Avance 300 spectrometer at Larmor frequencies of 300.13 MHz for $^1$H and 75 MHz for $^{13}$C. The samples were packed in a 4 mm o.d. $ZrO_2$ rotor and spun at 4.5 MHz MAS. Spectra were recorded at room temperature. For $^1$H spectra, 16 transients were recorded with a 5.6 $\mu$s 90° pulse and a relaxation delay of 20 s. $^{13}$C single-pulse excitation (SPE-MAS) spectra were recorded using a 5.5 $\mu$s 90° pulse and a relaxation delay of 20 s, with 1220 transients for CT1 (6 h 50) and 3048 transients for CT2 (17 h 06). A $^{13}$C cross-polarization (CP-MAS) spectrum of CT1 was recorded using a contact time of 10 ms and a relaxation delay of 5 s with 1024 transients (1 h 30 min).

## Results and Discussion

**Inhibition by polyAA.** The postulate at the heart of the explanation of the apparent contradictory mechanistic behavior of the polymerically stabilized latexes studied previously is that the polyAA chains on the particle surface undergo rapid chain transfer, affecting the overall kinetics and providing another two loss mechanisms (transfer and termination with the resultant MCR formed). One simple approach to test this postulate involved the addition of fully ionized oligoAA to the aqueous phase of an electrostatically stabilized polystyrene latex (a system that displays well understood kinetics), with subsequent seeded dilatometric experiments performed with chemical initiation (persulfate). It was seen that significant inhibition/induction times were observed when the oligoAA was added to the aqueous phase of the conventional styrene emulsion (up to 5 h 30 min at the lowest initiator concentration; see Figure 1). This would suggest that the oligoAA is acting as a degradative chain transfer agent,[17] with initiator-derived radicals undergoing chain transfer in the aqueous phase, forming a MCR that does not reinitiate quickly (but may terminate other radicals, providing a rationale for the observed inhibition times).

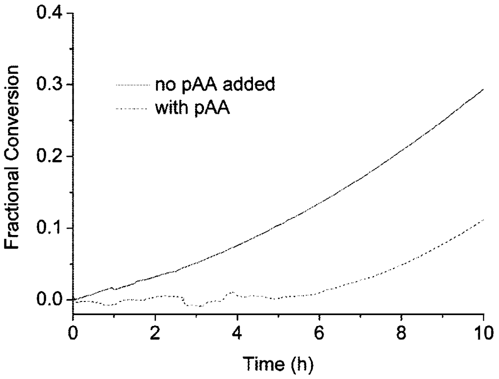

**Figure 1.** Polymerization rate of seeded styrene emulsion polymerization in the presence of added pAA, showing significant inhibition periods for the polymerization of conventionally stabilized polystyrene latex in the presence of short-chain polyAA in the water phase.

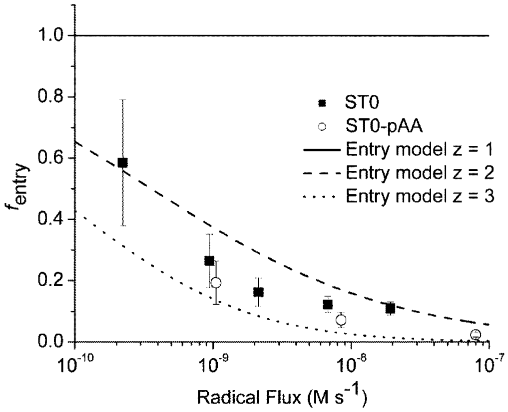

**Figure 2.** Comparison of radical entry efficiencies ($f_{entry}$) for the conventionally stabilized ST0 latex (treated as second order loss, filled squares) and the same latex with added polyAA (treated as first order loss, open circles) for persulfate-initiated experiments; also shown are predicted values for the entry mechanism assuming $z = 1$ (solid line), $z = 2$ (dashed line), and $z = 3$ (dotted line).

There was also an observed reduction in the steady-state $\bar{n}$ ($\bar{n}_{ss}$) relative to that in the absence of any added oligoAA; however this reduction was not as marked as that seen in the electrosterically stabilized latexes studied previously (most likely because the AA in that case provides a dense layer on the surface of the particle restricting true radical exit, whereas when added to the entire aqueous phase there is no significant "local" concentration of AA units). Determination of radical entry efficiencies ($f_{entry}$, the fraction of radicals generated by initiator that eventually enter a particle) in these experiments only yielded good agreement with the accepted entry mechanism[6] for electrostatically stabilized styrene systems when first-order loss kinetics (limit 1) were used[11] (see Figure 2), again suggesting that exiting monomeric radicals lose radical activity (either by transfer or termination) during an encounter with an AA unit (this time in the aqueous phase rather than on the particle surface).

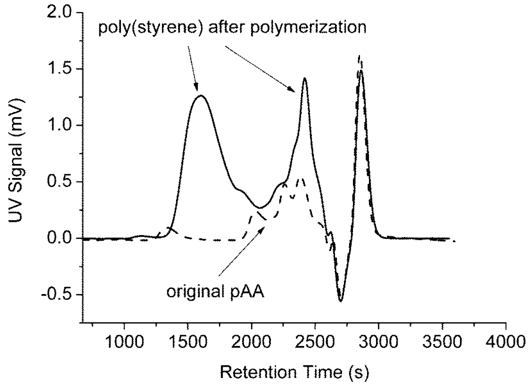

**Figure 3.** SEC chromatogram of poly(acrylic acid) (dashed line) and the resultant SEC distribution after polymerization of bulk styrene in the presence of this polymer (solid line).

The "chain transfer" experiments originally performed[11] to prove the concept of polyAA acting as a chain transfer agent in the polymerization of styrene were reconsidered by using size exclusion chromatography (SEC) and nuclear magnetic resonance spectroscopy (NMR) to analyze the resultant polymer to potentially observe any "branching" off the polyAA, a phenomenon that would result from the termination of a growing polystyrene radical and a MCR on the polyAA backbone. The SEC chromatogram demonstrated that, besides the peak corresponding to the homopolymer of polystyrene (albeit at a much lower molecular weight than expected, indicating being formed in the presence of a chain transfer agent), the peaks corresponding to the low molecular weight polyAA have increased in intensity, possibly due to the attachment (via termination with a MCR) of a short polystyrene oligomer (see Figure 3). This provides indirect, qualitative evidence for MCR and branch formation.

**Detection of Poly(acrylic acid-*g*-styrene) by NMR.** $^{13}C$ solution-state NMR was used aiming at quantifying the amount of quaternary carbons due to grafting of polystyrene onto oligoAA. $^{13}C$ NMR can in principle be used for the direct detection of the quaternary carbon of the branching/grafting point at 49 ppm.[14] Oligo(acrylic acid) produced by radical polymerization is expected to exhibit some branching,[14] even for degrees for polymerization as low as 5. Thus, the detection of grafting points of styrene on oligo(acrylic acid) could thus only be done by comparing the intensity of the signals at 49 ppm for samples CT1 and CT2, before and after styrene polymerization. The free oligo(acrylic acid) CT1 readily dissolved in $D_2O$ at 10% w/w without the need for any additional base to assist dissolution, and its $^{13}C$ NMR spectrum of CT1 exhibits a signal at 49 ppm (Figure 4). The sample CT2 was added to $D_2O$ at a target of 10% w/w, with the intent that the free polystyrene would not dissolve but the polyAA with any short polystyrene branches would do so; any undissolved polymer was removed by filtration. Unfortunately the $^{13}C$ signal-to-noise ratio obtained for CT2 in 15 h 30 min was too low to detect a possible signal for the quaternary carbon of (Figure 4). Indeed, the $^{13}C$ spectrum of CT2 recorded over 15 h 30 min had a significantly poorer signal-to-noise ratio than that of CT1 recorded over 31 min (Figure 4). The $^{1}H$ spectrum of CT2 also had a poorer signal-to-noise ratio than that of CT1. A simple recovery experiment demonstrated that less than 3% of the original polymer of CT2 actually dissolved in the $D_2O$, giving too low a concentration to measure a signal successfully. This recovery experiment however yielded a very powerful result, given that 66% of the polymer sample was comprised of AA that should readily dissolve in water. It is therefore postulated that so many transfer/termination events take place along each polyAA chain that the polymer becomes essentially water-insoluble, supporting our original hypothesis.

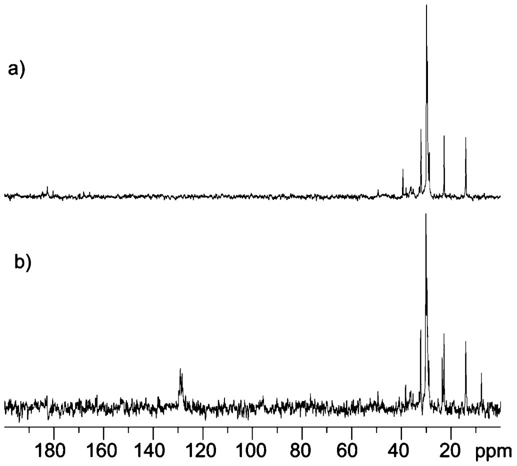

**Figure 4.** $^{13}C$ solution-state spectra of samples (a) CT1 and (b) CT2 in $D_2O$ at 60 °C.

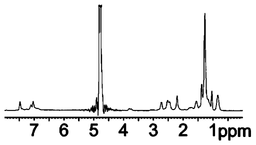

**Figure 5.** $^{1}H$ solution-state spectrum of sample CT2 in $D_2O$ at 60 °C.

**Table 1. Parameters Used in the Newly Developed Electrosteric Kinetic Model**

| parameter | value (units) |
|---|---|
| $Z$ | 2 |
| $k_p$ | 260 $M^{-1}$ $s^{-1}$ |
| $k_p{}^1$ | 4 $k_p$ |
| $k_d$ | $4 \times 10^{-6}$ $s^{-1}$ |
| $k_t$ | $1.75 \times 10^{9}$ $M^{-1}$ $s^{-1}$ |
| $k_{tr}$ | $9.3 \times 10^{-3}$ $M^{-1}$ $s^{-1}$ |
| $C_w$ | $4.3 \times 10^{-3}$ M |
| $C_p$ | 7.1 M |
| $N_p$ | $9.66 \times 10^{18}$ $L^{-1}$ |
| $r_s$ | 22.8 nm |
| $\delta$ | 1.25 nm |
| $D_w$ | $1.3 \times 10^{-9}$ $m^2$ $s^{-1}$ |
| $D_h$ | $7.2 \times 10^{-11}$ $m^2$ $s^{-1}$ |
| $k_{abs}$ | $8.4 \times 10^{5}$ $M^{-1}$ $s^{-1}$ |
| $k_{trAA}$ | $2.1 \times 10^{3}$ $M^{-1}$ $s^{-1}$ |
| [AA] | 0.23 M |
| $\Phi_{HL}$ | 0.02 |

Interestingly, both $^{1}H$ and $^{13}C$ NMR spectra of CT2 exhibit significant aromatic signals for polystyrene at 6.8 to 7.6 and 125 to 130 ppm respectively (Figures 4 and 5 and Table 5 for chemical shift assignment). These cannot arise from styrene monomer, as no double bond signal at 5.2−5.7 and 113 ppm is observed, or from poly(acrylic acid) or dodecanethiol. However, oligomers of styrene without a polar headgroup are insoluble in water when their degree of polymerization (DP) exceeds 2.[6,18] Thus, the observed polystyrene signals cannot come from dissolved oligostyrene homopolymer, but are expected to come from oligostyrene or polystyrene chains covalently grafted to water-soluble species such as oligo(acrylic acid). Thus, the $^{1}H$ and $^{13}C$ solution-state NMR indicate the presence of poly(acrylic acid-*g*-styrene) via the presence of polystyrene in water at 60 °C.

As only part of CT2 dissolves in $D_2O$, a comparison between CT1 and only a part of CT2 with solution-state NMR would be meaningless. However, solid-state NMR spectra of the samples

**Table 2. Comparison between Experimental Data Collected by Vorwerg for Uncontrolled Electrosterically Stabilized Latexes and Model Values Determined in this Work**

"Low Coverage" AA Latex ($1.94 \times 10^{17}$ L$^{-1}$)

| | $\bar{n}$ | | $\rho$ | | $k$ (limit 2a) | |
|---|---|---|---|---|---|---|
| [KPS] (M) | experiment | model | experiment | model | experiment | model |
| $6 \times 10^{-4}$ | 0.2 | 0.259 | $2.4 \times 10^{-3}$ | $1.9 \times 10^{-3}$ | $5.2 \times 10^{-3}$ | $7.1 \times 10^{-3}$ |

"High Coverage" AA Latex ($7.3 \times 10^{16}$ L$^{-1}$)

| | $\bar{n}$ | | $\rho$ | | $k$ (limit 2a) | |
|---|---|---|---|---|---|---|
| [KPS] (M) | experiment | model | experiment | model | experiment | model |
| $7.5 \times 10^{-4}$ | 0.37 | 0.26 | $7 \times 10^{-3}$ | $5.31 \times 10^{-3}$ | $1.2 \times 10^{-2}$ | $1.8 \times 10^{-2}$ |
| $8 \times 10^{-3}$ | 0.42 | 0.403 | $1.34 \times 10^{-2}$ | $1.9 \times 10^{-2}$ | $1.2 \times 10^{-2}$ | $1.3 \times 10^{-2}$ |

**Table 3. Comparison between Experimentally Determined Limit 1 Exit Rate Coefficients (*k*) for Electrosterically Stabilized Latexes Made by the RAFT-in-Emulsion Method and Those Determined by the Electrosteric Kinetic Model in This Work**

| latex | $k$ (limit 1, experimental) | $k$ (limit 1, theoretical model) |
|---|---|---|
| ST5 | $6.76\ (\pm 1.32) \times 10^{-3}$ | $6.99 \times 10^{-3}$ |
| ST10 | $5.12\ (\pm 1.7) \times 10^{-3}$ | $7.11 \times 10^{-3}$ |
| ST20 | $5.05\ (\pm 1.37) \times 10^{-3}$ | $7.90 \times 10^{-3}$ |

**Table 4. Comparison between Experimental Values of $\bar{n}_{ss}$ for the ST5L Latex and Model Values Obtained by the Electrosteric Kinetic Model for Particles of that Size**

| [KPS] (M) | $\bar{n}$ (experiment) | $\bar{n}$ (electrosteric model) |
|---|---|---|
| $1.51 \times 10^{-4}$ | 0.069 | 0.067 |
| $1.06 \times 10^{-3}$ | 0.145 | 0.162 |
| $1.34 \times 10^{-2}$ | 0.33 | 0.269 |

**Table 5. Chemical Shift Assignment for $^{1}$H and $^{13}$C NMR Spectra of OligoAA,[14] Polystyrene,[31] Dodecanethiol,[32] and AIBN Fragment[32]**

| nucleus | $\delta$ (ppm) | assignment |
|---|---|---|
| $^{1}$H | 0.84 | dodecanethiol, $CH_3$-$(\mathit{CH}_2)_{11}$-S-oligoAA |
| | 1.04 | oligoAA, $CH_2$ |
| | 1.1 to 1.6 | dodecanethiol, $CH_3$-$(\mathit{CH}_2)_{10}$-$CH_2$−S-oligoAA |
| | 1.7 to 1.9 | polystyrene backbone and AIBN $CH_3$ |
| | 2.20 | oligoAA, CH |
| | 2.4 to 2.8 | dodecanethiol, $C_{11}H_{23}$-$\mathit{CH}_2$-S-oligoAA |
| | 4.79 | residual water |
| | 7.0 to 7.5 | polystyrene, aromatic $^{1}$H |
| $^{13}$C | 7.7 | ?? |
| | 14.0 | dodecanethiol, $\mathit{CH}_3$-$(CH_2)_{11}$-S-oligoAA |
| | 22.8 | dodecanethiol, $CH_3$-$\mathit{CH}_2$-$(CH_2)_{10}$-S-oligoAA |
| | 23.5 | AIBN fragment, $CH_3$ |
| | 25 | oligoAA, $CH_2$ |
| | 28 to 31 | dodecanethiol, $CH_3$-$(\mathit{CH}_2)_{10}$-$CH_2$−S-oligoAA |
| | 32.2 | dodecanethiol, $CH_3$-$(CH_2)_{10}$-$\mathit{CH}_2$-S-oligoAA |
| | 35 to 40 | oligoAA, $CH_2$, and polystyrene, backbone |
| | 49 | oligoAA, quaternary carbon |
| | 128 to 130 | PS, aromatic $^{13}$C |
| | 183 | oligoAA, C═O |

can provide useful information. $^{13}$C CP-MAS and $^{13}$C SPE-MAS spectra recorded on sample CT1 exhibited similar resolution. Because of the non-quantitative character of $^{13}$C CP-MAS spectra, it was decided to record $^{13}$C SPE-MAS spectra of the samples (Figure 6). Because of the lower resolution of these spectra compared to the solution-state ones, the signals of the backbone $^{13}$C of polystyrene at 40−47 ppm (Table 5) overlap with the region in which the quaternary carbon of the grafting point is expected. Thus, no easy quantification of a possible grafting signal at 49 ppm could be obtained by $^{13}$C solid-state NMR at room temperature. $^{13}$C solid-state NMR could be tried on the molten sample, following the method used for successful quantification of branching in poly(alkyl acrylates),[19] but it is beyond the scope of the present work.

**Secondary Nucleation in Electrosterically Stabilized Emulsion Systems.** It is well-known[2,3,5] that seeded polymerization experiments involving electrosterically stabilized emulsions are often plagued by secondary nucleation (that is, the formation of new particles). This problem is not unique to systems stabilized by acrylic acid, but also other common stabilizers such as poly(ethylene oxide). Secondary nucleation in seeded systems below the critical micelle concentration (cmc) of the stabilizing agent (not applicable in the case of electrosteric systems where the stabilizer is grafted onto the particle surface and is not free to micellize in the aqueous phase) is assumed to take place through "homogeneous nucleation" ; however the amount of new particles seen in polyAA[3] and PEO-stabilized systems[20] (this last reference is an unpublished report, requisite details of which are given below) are orders of magnitude higher than that predicted by this model. The work reported by Hammond[20] involved Interval II seeded dilatometric studies of a PEO-stabilized polystyrene latex (particle number $N_p = 5 \times 10^{16}$ L$^{-1}$, swollen radius 66 nm, molecular weight of the stabilizing PEO block $2 \times 10^4$, [KPS] = 0.6 mM), experiments that exhibited extensive secondary nucleation; a ratio of new−old particles of 0.45 was observed, orders of magnitude higher than predicted for such conditions using conventional models.[5]

It is postulated here that a MCR formed by the rapid transfer/abstraction reactions in the hairy layer will undergo $\beta$-scission (well-known for poly(alkyl acrylates)),[21,22] leading to either a secondary radical or polymer with an unsaturated end group breaking off from the particle surface and moving into the aqueous phase. This species could, upon further reaction (such as termination with an initiator-derived oligomer) form a species analogous to the precursor particle involved in homogeneous nucleation (see, e.g., the literature overview by Gilbert[5]) leading to secondary nucleation. A simple experiment involving the reaction of poly(acrylic acid) in water with potassium persulfate revealed that, after 24 h at 323 K, only a tiny percentage of the original chain population remained with a significant population appearing at lower molecular weights (see Figure 7). This indicates the reasonable rapidity of $\beta$-scission and chain fragmentation, an area that merits further research.

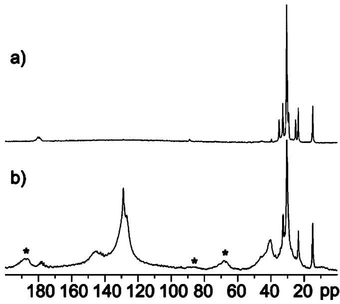

**Figure 6.** $^{13}$C solid-state spectra of samples CT2 at 4.5 kHz MAS and room temperature: (a) SPE-MAS and (b) CP-MAS. The asterisks indicate spinning side bands.

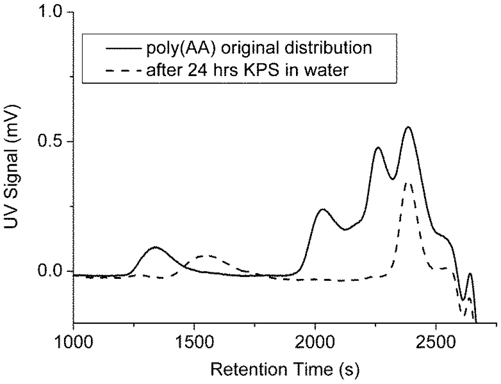

**Figure 7.** SEC chromatogram of poly(acrylic acid) before (solid line) and after (dashed line) treatment with potassium persulfate in water for 24 h, 323 K.

The ability to cross-link PEO has also been described in the literature[23] through the use of functional peroxides, the cross-linking taking place after radicals are formed by hydrogen abstraction reactions. It is also quite possible that $\beta$-scission is an important mechanism in PEO-stabilized systems, again explaining the extreme amounts of secondary nucleation in such systems.

It is also worth noting that Vorwerg only observed secondary nucleation at neutral and high pH in electrosterically stabilized emulsion systems. The pulse radiolysis work of von Sonntag[22] demonstrated that, in the case of poly(acrylic acid) in water, $\beta$-scission is the most likely fate of a polymer chain bearing a MCR at neutral pH, while under acidic conditions recombination or cross-linking is dominant. This in agreement with the postulate that $\beta$-scission of stabilizing chains at neutral pH is a major factor in the extensive secondary nucleation often seen in electrosterically stabilized systems. This is a significant area of future research with substantial implications for a large number of industrial emulsion polymer formulations.

**An Extended Kinetic Model.** While the claim that the polyAA hairy layer acts as an extremely efficient chain transfer agent/termination site is plausible, the original treatment of the rate coefficient data for these electrosterically stabilized latexes was inconsistent.[10,11] The data for radical exit were interpreted in terms of a "restricted" diffusion process, while radical entry results were explained on the basis that an exited radical will encounter a polyAA "hair" before reentry. Both cannot be correct in themselves, or rather, neither can happen to the exclusion of the other. This is because interaction with the hairy layer will occur in both directions, especially as the first postulate happening in isolation involves second-order loss of desorbed radicals, while the other involves first-order loss. To resolve this contradiction, an extended kinetic model that explains both sets of results is now put forward.

Much of the data against which used in the new development have been given previously.[10,11] In brief, using the "RAFT-in-emulsion" technique,[12] polystyrene latexes stabilized by 5, 10, and 20 AA units were synthesized; the unswollen particle diameter for all three latexes was approximately 21 nm. Particle growth in these latexes was measured using these latexes as seed. That is, the seed was swollen with monomer, and second-stage growth was initiated with an appropriate initiator, with the rate being followed dilatometrically. Two initiating systems were used: persulfate (for which the steady-state rate was used), and $\gamma$-radiolysis wherein the reactor was removed from the radiation source after an appropriate time and watching the rate decrease in the absence of new radicals ("relaxation mode" ), which gives a direct measure of the rate of radical loss.

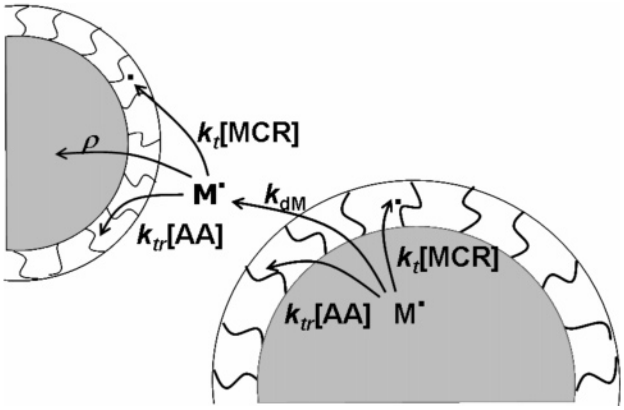

**Figure 8.** Various fates of an exiting monomeric radical both within the particle interior as well as in the aqueous phase for electrosterically stabilized systems. Reactions of this radical within the particle interior (such as propagation and termination) are omitted for clarity.

The model now presented is an extension of the currently accepted emulsion polymerization kinetic equations that, to date, give excellent quantitative agreement with experiment for electrostatically stabilized systems. For convenience, the hairy layer is taken to be comprised of polyAA, unless specified otherwise. The width of the hairy layer (denoted $\delta$) was estimated as described previously.[10] The values of $\delta$, the average DP of the stabilizing block and the number of stabilizing chains per particle are combined to yield the local acrylic acid concentration in the hairy layer ([AA]), details of which are given in the Supporting Information.

The treatment given here assumes ideal partitioning of the total aqueous phase radical concentration. The local acrylic acid concentration [AA] provides a concentration of possible transfer/abstraction sites. It is assumed that every AA group has one site where transfer/abstraction can take place, although pulse radiolysis experiments by von Sonntag et al.[22] demonstrated that MCRs form at sites both $\alpha$ and $\beta$ to the carboxylic acid group in significant amounts − so it is possible that every AA group may yield up to two active sites for transfer/termination. The rate coefficient for hydrogen-atom abstraction by an aqueous phase radical (the population of which comprising sulfate ion radicals and oligomers with sulfate end groups of DP less than $z$) was chosen to be $k_{abs} = 8.4 \times 10^5$ M$^{-1}$ s$^{-1}$, a lower-bound value taken from measurements[24] of the rate coefficient of hydrogen atom abstraction using sulfate radical ions. A sensitivity analysis was employed to determine the effect on the results when the value of $k_{abs}$ was varied.

With the new mechanisms deduced here, the fate for a monomeric radical formed by transfer to polymer within a particle is now complicated by reaction pathways additional to those in electrostatically stabilized systems:[8] it can propagate in the particle interior, desorb into the hairy layer and undergo a transfer reaction with an AA unit, desorb into the hairy layer and undergo termination with a midchain radical (MCR), or completely desorb through the hairy layer and out into the aqueous phase. These various fates are shown in Figure 8. Successful desorption into the aqueous phase to form an exited radical (denoted E$^\bullet$) allows reentry kinetics to be considered, where the equivalent reactions can take place—an exited radical can successfully reenter or again undergo a transfer or termination event.

The aqueous-phase chemistry is assumed to be that proposed by Maxwell et al.,[6] in that an entering radical is a surface-active oligomer of critical DP $z$. However as $z$-mers interact with the particle surface in the process of entry, the transfer and termination reactions within the hairy layer are included in the evolution equation for this species. MCRs within the polyAA hairy layer are allowed to propagate within this model (they are likely to, albeit slowly as has been seen with alkyl acrylates);[25] however, the local radical concentration will not be changed by a propagation event, and the monomer concentration is likely to be low in the hairy layer.

To model kinetic parameters such as the steady-state value of $\bar{n}$ and the entry and exit rate coefficients $\rho$ and $k$, the evolution equations for the zero-one kinetic model[8] for the populations of $N_0$ (the number of particles containing no radicals), $N_1^{\mathrm{m}}$ (particles containing one monomeric radical), and $N_1^{\mathrm{p}}$ (particles containing one polymeric radical) have been modified to account for the additional reactions with the polyAA hairy layer. The equations now are

$$\frac{\mathrm{d}N_0}{\mathrm{d}t} = \rho(N_1^{\mathrm{p}} + N_1^{\mathrm{m}} - N_0) + k_{\mathrm{dM,HL}}N_1^{\mathrm{m}} + \boldsymbol{P_{\mathrm{des}}(k_{\mathrm{trAA}}[\mathrm{AA}]N_1^{\mathrm{m}} + 2k_{\mathrm{t}}[\mathrm{MCR}]N_1^{\mathrm{m}})} \quad (1)$$

$$\frac{\mathrm{d}N_1^{\mathrm{m}}}{\mathrm{d}t} = \rho_{\mathrm{re}}N_0 - \rho N_1^{\mathrm{m}} - k_{\mathrm{dm,HL}}N_1^{\mathrm{m}} + k_{\mathrm{tr}}C_{\mathrm{p}}N_1^{\mathrm{p}} - k_{\mathrm{p}}^{1}C_{\mathrm{p}}N_1^{\mathrm{m}} - \boldsymbol{P_{\mathrm{des}}(k_{\mathrm{trAA}}[\mathrm{AA}]N_1^{\mathrm{m}} + 2k_{\mathrm{t}}[\mathrm{MCR}]N_1^{\mathrm{m}})} \quad (2)$$

$$\frac{\mathrm{d}N_1^{\mathrm{p}}}{\mathrm{d}t} = \rho_{\mathrm{I}}N_0 - \rho N_1^{\mathrm{p}} - k_{\mathrm{tr}}C_{\mathrm{p}}N_1^{\mathrm{p}} - k_{\mathrm{p}}^{1}C_{\mathrm{p}}N_1^{\mathrm{m}} \quad (3)$$

where the newly added terms are presented in bold; the other terms in the above equations correspond to the model used to describe the behavior in electrostatic systems.[8] (Note that in eq 3, the symbol $\rho_{\mathrm{I}}$ refers to the entry rate coefficient for initiator-derived oligomers and thermally generated radicals, as these entering species are generally oligomeric in length. $\rho$ refers to the total entry rate coefficient, which includes reentry). To an excellent approximation one has $N_1^{\mathrm{p}} = \bar{n}$. [MCR] = concentration of MCRs within the hairy layer, $k_{\mathrm{trAA}}$ = rate coefficient for transfer of a styrene radical to a polyAA backbone site (determined in separate chain transfer experiments[11] to be approximately 2100 $\mathrm{M}^{-1}\ \mathrm{s}^{-1}$ at 323 K), $k_{\mathrm{t}}$ = bimolecular rate coefficient for termination between a MCR and a monomeric styrene radical, $k_{\mathrm{dM,\ HL}}$ = rate coefficient for complete (restricted) desorption of a monomeric radical through the hairy layer and into the aqueous phase, and $P_{\mathrm{des}} = k_{\mathrm{dM}}/(k_{\mathrm{dM}} + k_{\mathrm{p}}^{1}\mathrm{C_p})$ is the probability that a monomeric radical actually goes from the particle interior to the hairy layer. The expression used to calculate $k_{\mathrm{dM,HL}}$ was given previously[10] and is a function of $D_{\mathrm{h}}$, the diffusion coefficient of a monomeric radical in the hairy layer (a function of the weight fraction of polymer in the hairy layer, $w_{\mathrm{p}}$). The other parameters, $k_{\mathrm{p}}^{1}$, $k_{\mathrm{p}}$and $k_{\mathrm{tr}}$ correspond to the rate coefficients of propagation of a monomeric radical, propagation of any other radical species, and transfer to monomer respectively.

The fate of an exited radical is now considered. Its reentry rate coefficient $\rho_{\mathrm{re}}$ is given by $k_{\mathrm{re}}[\mathrm{E}^\bullet]$, where $k_{\mathrm{re}}$ is the Smoluchowski expression for a diffusion-controlled reaction, and one has

$$\frac{\mathrm{d}[\mathrm{E}^\bullet]}{\mathrm{d}t} = k_{\mathrm{dM,HL}}N_1^{\mathrm{m}}\frac{N_{\mathrm{p}}}{N_{\mathrm{A}}} - k_{\mathrm{re}}[\mathrm{E}^\bullet]\frac{N_{\mathrm{p}}}{N_{\mathrm{A}}} - k_{\mathrm{t}}[\mathrm{E}^\bullet][\mathrm{T}^\bullet] - k_{\mathrm{trAA}}[\mathrm{AA}][\mathrm{E}^\bullet] - 2k_{\mathrm{t}}[\mathrm{MCR}][\mathrm{E}^\bullet] \quad (4)$$

where $[\mathrm{T}^\bullet]$ is the total aqueous-phase radical concentration, given by the sum of the concentrations of the initiator-derived oligomers as well as the exited radical concentration. Specification of the MCR concentration ([MCR]) within the hairy layer was achieved by applying the steady-state approximation to an evolution equation whereby MCRs are generated only through abstraction with radicals in the hairy layer and terminated by any other radical (see Supporting Information). An iterative numerical approach can also be used and is given in the Supporting Information; however, the qualitative results of the model are unchanged.

If we include transfer and termination of monomeric styrene radicals with AA units and MCRs (which has to be preceded by diffusion into the hairy layer from the particle interior), then the full zero-one limit expression for the time evolution of $\bar{n}$ is

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = \rho(1 - 2\bar{n}) - k_{\mathrm{tr}}\mathrm{C_p}\left(\frac{k_{\mathrm{dM}}\bar{n} + \mathrm{P_{des}}(k_{\mathrm{trAA}}[\mathrm{AA}] + k_{\mathrm{t}}[\mathrm{MCR}])}{k_{\mathrm{dM}}\bar{n} + k_{\mathrm{p}}^{1}\mathrm{C_p} + \mathrm{P_{des}}(k_{\mathrm{trAA}}[\mathrm{AA}] + k_{\mathrm{t}}[\mathrm{MCR}])}\right)\bar{n} \quad (5)$$

The loss term in eq 5 is essentially the microscopic rate coefficient term with both a first-order and a second-order component. The numerator of the above fraction is the key determinant in which limit is most appropriate—the larger of the two terms will dictate the order of the loss mechanism (i.e., if $k_{\mathrm{dM}}\ \bar{n}$ is the larger term, the system is essentially second-order, while if $P_{\mathrm{des}}(k_{\mathrm{trAA}}[\mathrm{AA}] + k_{\mathrm{t}}[\mathrm{MCR}])$ is larger, the system is equivalent to a first-order loss mechanism).

Having a general expression which can be first- or second-order in the loss of exited radicals, depending on the sizes of the various kinetic parameters, opens the ways to resolving the anomaly discussed in the Introduction. From this global model, two limiting expressions for the exit rate coefficient $k$ can be described:

$$\text{Limit 1:}\quad k_1 = k_{\mathrm{tr}}\mathrm{C_p}\left(\frac{\mathrm{P_{des}}(k_{\mathrm{t}}[\mathrm{MCR}] + k_{\mathrm{trAA}}[\mathrm{AA}])}{k_{\mathrm{p}}^{1}\mathrm{C_p} + \mathrm{P_{des}}(k_{\mathrm{t}}[\mathrm{MCR}] + k_{\mathrm{trAA}}[\mathrm{AA}])}\right) \quad (6)$$

$$\text{Limit 2a:}\quad k_{2\mathrm{a}} = \frac{k_{\mathrm{dM}}k_{\mathrm{tr}}}{k_{\mathrm{p}}^{1}} \quad (7)$$

For the sake of completeness, the termination term can be included in the limit 2a expression,[8] as it does not become vanishingly small at bigger particle sizes, but it will only change the obtained value of $k$ by ~15−20%.

The steady-state forms of eqs 1−3, 4 and the modified equations for the Maxwell−Morrison entry mechanism (including transfer/termination in the hairy layer for $z$-mers) were solved iteratively for a given initiator concentration to determine the steady-state values of $\bar{n}$ and $\rho$. Using these two values, first and second-order exit rate coefficients ($k_1$ and $k_{2\mathrm{a}}$) were determined from the two applicable time evolution equations. From this, a comparison with experimental data previously obtained was then made.

**Comparison with Experimental Results. 5AA Stabilized Latex.** The values of the various parameters used in the modeling performed in this work are listed in Table 1. The experimental $\bar{n}_{\mathrm{ss}}$ for the polystyrene latex stabilized by polyAA oligomers of average DP 5 (the latex denoted ST5) initiated by persulfate were compared to model values across 2 orders of magnitude of initiator concentration. The comparison between experimental and model values can be seen in Figure 9.

As can be seen, there is good semiquantitative agreement between the experimental and model $\bar{n}_{\mathrm{ss}}$, regarded as satisfactory,

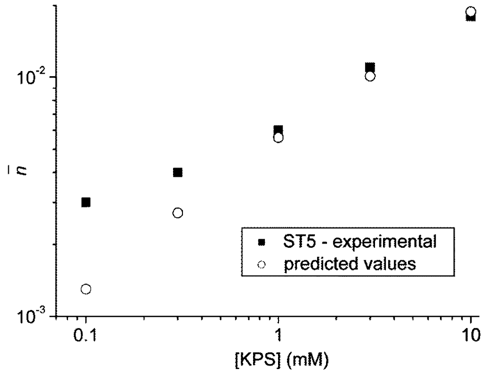

**Figure 9.** Comparison between $\bar{n}_{ss}$ values obtained for the ST5 latex via experiment (black squares) and those obtained from the new kinetic model calculations (open circles).

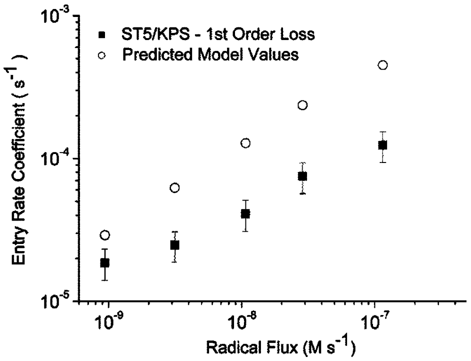

**Figure 10.** Comparison of radical entry rate coefficients obtained for the ST5 latex assuming first-order loss (black squares) and those obtained from the new kinetic model (open circles).

considering a minimal of model-based assumptions have been made. Most importantly, the general observed trend of extremely low values of $\bar{n}_{ss}$ seen experimentally is replicated by the model results − the expected values of $\bar{n}_{ss}$ for this latex system assuming "normal" styrene emulsion kinetics[5] are of the order of 0.05−0.07, much higher than those calculated here. The reason for this dramatic reduction is that the value of $N_1^m$ is significantly reduced by the addition of the extra loss terms (through transfer with a polyAA site or termination with a resultant MCR). As the particles considered in this work are small (swollen radius = 22 nm), the local concentration of AA units in the hairy layer is high, making transfer/termination much more likely than desorption of a monomeric radical into the aqueous phase (i.e., $P_{des}(k_{trAA}[AA] + k_t[MCR]) \gg k_{dM}\bar{n}$). This reduces the exited radical concentration [E$^\bullet$] (the ratio [E$^\bullet$]/[T$^\bullet$] is a factor of 10 smaller in the electrosterically stabilized system ST5 when compared to an electrostatically stabilized latex of the same size) indicating a much smaller exited radical population that can potentially reenter, ensuring that the value of $\bar{n}_{ss}$ remains low.

The calculated steady-state values of the entry rate coefficient $\rho$ (and subsequently the entry efficiency $f_{entry}$) from this model are very close to those found experimentally when assuming first-order loss kinetics, and are in good agreement with the accepted "control by aqueous phase growth" entry mechanism (see Figures 10 and 11). This is strong supporting evidence for the use of limit 1 kinetics during the experimental data processing to calculate experimental entry rate coefficients.[11] The "normal" values of $\rho$ and $f_{entry}$ can be rationalized by considering the likely fates for a surface active $z$-mer, namely entry into a particle or transfer/termination on the particle surface. The likelihood of a $z$-mer undergoing an entry event (given by the pseudo-first-order rate coefficient $k_eN_p/N_A$) is several orders of magnitude more likely than a transfer/termination event on the particle surface prior to entry, making any change to the overall entry rate coefficient $\rho$ essentially insignificant (any significant competition between entry and a loss event on the particle surface only occurs at particle sizes that are extremely small (10 nm swollen radius), and would be difficult to synthesize). The same can be said for the kinetics of reentry: an exited radical will most likely reenter, but very few radicals actually escape from a particle into the aqueous phase in the first place.

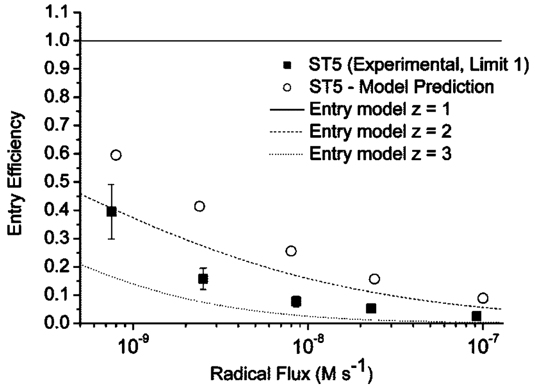

**Figure 11.** Comparison of radical entry efficiencies obtained for the ST5 latex assuming first-order loss (black squares) and those obtained from the new kinetic model (open circles).

From the model values of $\rho$ and $\bar{n}_{ss}$, exit rate coefficients were calculated from the appropriate limiting forms: limit 1 and limit 2a kinetics. It was shown that physically realistic values of $k$ (that were also consistent with experiment) are only found when limit 1 kinetics are used, due to the linear dependence with respect to $\bar{n}$.

A sensitivity analysis of the model in question was performed by varying three of the critical input parameters: $k_{abs}$ (the abstraction rate coefficient), $D_h$ (the diffusion coefficient within the hairy layer), and $k_d$ (the decomposition rate coefficient of initiator) were all varied by up to a factor of 10 to ensure the consistency of the results and their subsequent explanation. A full account of this analysis is given in the Supporting Information. It was seen that while the model is sensitive to the size of the transfer/abstraction rate coefficient (essentially the key process in the different mechanism at play in these electrosterically stabilized systems), the use of physically reasonable values for all parameters chosen (the lower bound for $k_{abs}$ from experiments involving hydrogen abstraction via sulfate ion radicals)[24] suggests that the conclusions drawn from this model are valid.

A long-chain limit value of $k_{trAA}$ (the transfer rate coefficient in styrene polymerizations while using polyAA as a chain transfer agent) was measured in separate bulk experiments;[11] if we consider that the transfer rate coefficient for a monomeric radical scales analogously to the situation involving propagation of radicals[26−28] then we obtain a value of $k_{trAA}$ that is large enough ($2.1 \times 10^4$ M$^{-1}$ s$^{-1}$) to account for observed results (low $\bar{n}$, apparent first-order loss kinetics) without the need to consider MCRs being formed by abstraction reactions involving radicals with a sulfate end group. It should be noted that this process is kinetically equivalent to the postulated mechanism put forward in this paper, and all of the results presented remain unchanged.

**Model Behavior as a Function of Particle Size.** The model was used to make predictions for the behavior of electrosterically stabilized latexes as a function of size, while the total solids content of the latex was held constant. It can be seen intuitively

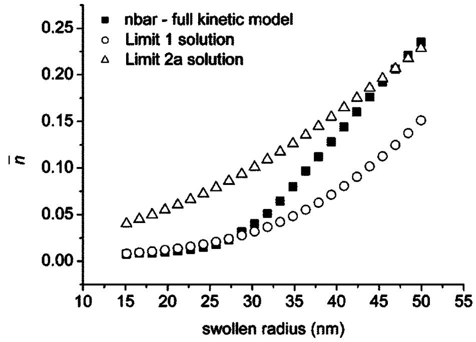

**Figure 12.** Variation of $\bar{n}_{ss}$ ([KPS] = 1 mM) as calculated by the electrosteric kinetic model for a 10% solids latex (filled squares) as a function of particle size, with comparison to the limit 1 solution (open circles) and limit 2a solution (open triangles) for such systems.

that as the size of the polystyrene core becomes larger, the volume fraction of the aqueous phase that exists within the hairy layer ($\Phi_{HL}$) decreases significantly. The increased surface area per particle means that each polyAA chain occupies more surface area, and that the local [AA] concentration is reduced. This decreases the likelihood of a transfer or abstraction, resulting in a reduction in the steady-state midchain radical concentration ([MCR]).

Calculations were performed for a seed latex with a solids content of 10% w/w, stabilized by polyAA chains of average DP = 5. The experimentally determined quantity of 220 stabilizing chains per particle was used in this modeling. The persulfate concentration was held constant at $10^{-3}$ M, while the swollen particle radius was allowed to vary from 15 to 50 nm. All other parameters used were as reported in Table 1. Estimates were made for $D_h(r_s)$, the diffusion coefficient of a monomeric radical within the hairy layer, based on a value determined from the literature[29] ($D_h = 7.2 \times 10^{-11}$ m$^2$ s$^{-1}$ for particles of swollen radius 22 nm, as used in the experimental work on radical exit[10] for these systems) and the known variation of the diffusion coefficient $D$ of a radical in polymer solutions of differing $w_p$.[30] The sensitivity analysis performed on this model demonstrated little variation when the value of $D_h$ was varied by up to a factor of 10, indicating that the precision in this parameter is not critical.

The $\bar{n}_{ss}(r_s)$ results from these calculations (see Figure 12) are quite informative. Very small particles gave values of $\bar{n}_{ss}$ that were similar to those predicted by limit 1 kinetics for an electrostatically stabilized system of identical particle size, but as the particle size increased the value of $\bar{n}_{ss}$ converged toward the limit 2a limit for the same quantity. This suggests a crossover in the applicable limit in these systems at an intermediate particle size (approximately 35 nm swollen radius) for constant total solids, whereby particles larger than this crossover point essentially obey "expected" styrene emulsion kinetics and the effect of the hairy layer is no longer seen.

This observed limit crossover can be rationalized by comparing the size of the two differing loss mechanisms in these systems: the first-order loss term (transfer or termination) and the second-order loss term (desorption from the particle). For very small particles, the densely packed hairy layer makes rapid abstraction and subsequent termination highly likely, while the sparsely covered surface of a larger electrosterically stabilized latex means that successful desorption is more likely than encountering an AA unit or a MCR. The relative sizes of these terms are seen in Figure 13Using the new limit 1 expression, we obtain a small value of $k_1$ for a particle of the size used in the corresponding experimental work (22 nm swollen radius). This is because "true escape" rarely happens: most monomeric radicals that actually enter into the hairy layer will be terminated rather than diffuse into the aqueous phase. This value of $k$ is similar to the restricted diffusion model developed initially[10] to explain the observed results; the agreement between this model and experiment is shown in Table 3.

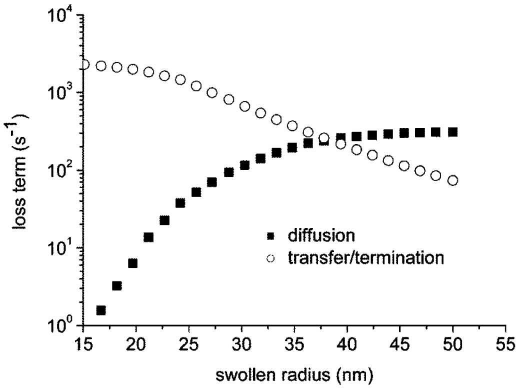

**Figure 13.** Comparison of diffusion (filled squares) and transfer/termination (open circles) loss terms as a function of particle size within the electrosteric kinetic model (10% w/w latex).

It can be seen that the agreement is very good. The model developed predicts an increase in $k$ with hair length on the particle surface; however this increase (from 5 to 20 AA units) leads to only a slight increase in $k$. Within experimental uncertainty, this model fits the values found from first-order fitting of $\gamma$-relaxation experiments. (The slope/intercept results from $\gamma$-relaxation experiments are also very similar in terms of the obtained $k$ values).

**Reconsideration of Previous Experimental Data.** While the experimental data collected using "model" systems made by the RAFT-in-emulsion process is useful to make comparisons with the kinetic model developed for electrosterically stabilized systems, a crucial component of modeling the kinetics of these systems is to consider those synthesized without the use of a control agent, i.e., free-radically synthesized electrosterically stabilized latexes. Such latexes were used in the kinetic studies of Coen[2] and Vorwerg,[3] where the main complication was that there was then (and now) no means to accurately characterize or determine the nature of the hairy layer. Using the more accurate experimental data of Vorwerg, an attempt was made to characterize the seed latexes used in that work along the lines developed in the model reported in this paper; using an estimate of the width of the hairy layer at $\delta = 2.5$ nm, parameters such as [AA] and $\Phi_{HL}$ were able to be estimated from the recipe for the seed latex syntheses. Both the "low coverage" latex (5% w/w AA) and "high coverage" latex (15% w/w AA) were of the order of 35−40 nm swollen radius, placing them in the "crossover" region (see Figure 12) somewhat between limit 1 and limit 2a. It can be seen in Table 2 that the general treatment developed within this kinetic model is able to predict the values of $\bar{n}_{ss}$, $\rho$ and the limit 2a $k$ value of Vorwerg (who treated his data assuming limit 2a kinetics) to within 20−30%, an excellent result considering the small number of adjustable parameters within the model. It should therefore be possible to predict the overall kinetics (and the appropriate limit to use) for any electrosterically stabilized latex given a reasonable knowledge of the width and density of the hairy layer on the particle surface, an extremely powerful result for such systems as such analysis has never before been possible.

In summary, the complete description given here shows that for small particles (i.e., the early stages of the reaction for particle growth, including growth from a small seed, which is a widely used industry practice), the overall kinetics follow first-order radical loss of exited radicals:

$$\frac{d\bar{n}}{dt} = \rho(1 - 2\bar{n}) - k_1\bar{n} \quad (8)$$

with $k_1$ given by eq 6. For larger particles, which is most of the period of growth of a latex particle, the overall kinetics follow second-order loss of exited radicals:

$$\frac{d\bar{n}}{dt} = \rho(1 - 2\bar{n}) - 2k_{2a}\bar{n}^2 \quad (9)$$

with $k_{2a}$ given by eq 7. In each case, the loss rate coefficient includes the new effects revealed in the present paper, and slowed diffusion in the hairy layer. Equations 8 and 9 provide simple means of extracting entry and exit rate coefficients from appropriate rate data in systems obeying these limits. For particle growth between these limits, the complete description, eq 5, must be used.

## Conclusions

In order to explain a significant contradiction in kinetic data collected experimentally for styrene latexes stabilized by grafted polyAA, the postulate of significant additional reactions between exiting radicals and the polyAA hairy layer, namely transfer via hydrogen-atom abstraction and termination with a resultant MCR, has been put forward. Through separate experiments, it has been proven that low molecular weight polyAA can act as a degradative chain transfer agent, also acting as an inhibitor in electrostatically stabilized seeded styrene emulsion experiments. Through SEC and NMR spectroscopy, evidence of polystyrene branch formation off the polyAA chain was detected, giving strong support to the midchain radical hypothesis.

After qualitative evidence to support the existence of the transfer and termination reactions put forward to potentially explain the highly unusual kinetic behavior seen experimentally, an extended kinetic model was developed for the kinetic equations long used to rationalize the kinetics of electrostatically stabilized emulsion systems, by including additional terms such as transfer and termination involving MCRs. With a minimal number of adjustable parameters and physically reasonable values for the rate coefficients of hydrogen-atom abstraction in these systems, this limit-free modeling provided excellent agreement with experimental kinetic data for the steady-state polymerization rate as well supporting the first-order loss mechanism proposed experimentally. It was seen that, for small particles such as those studied experimentally in the present paper, a densely packed hairy layer on the particle surface ensured that an exiting monomeric radical would have radical transfer or termination (both first-order loss mechanisms with respect to the average number of radicals per particle) as the dominant loss mechanism over “classical” desorption followed by reentry (a second-order loss mechanism). The model revealed that, beyond a critical particle size (approximately 35 nm swollen radius for the systems examined here), the system behaves “as expected”—desorption and reentry are the dominant loss mechanism due to the decreased likelihood of encountering an AA unit.

The inclusion of transfer and termination with AA units on the particle surface was included in the mechanism of homogeneous nucleation in an attempt to account for the significant amounts of secondary nucleation seen in seeded electrosterically stabilized experiments. These terms did not significantly increase the likelihood of secondary nucleation, but it was postulated that $\beta$ scission of polyAA chains bearing a midchain radical may lead to fragmented radicals in the aqueous phase that could act as a potential nucleation site for new particles. Experiments involving aqueous solutions of polyAA in the presence of persulfate revealed extensive chain fragmentation at neutral pH, supporting the hypothesis. Similar mechanisms may also pertain to other steric stabilizers such as those based on poly(ethylene oxide). It is hoped that further work will reveal the mechanism behind the vast amounts of new nucleation seen in these systems, providing a solution to a problem that plagues these industrially significant systems.

While the new effects are only manifest for relatively small (electro)sterically stabilized particles, the importance of this result lies in the fact that many industrially significant systems employ very small, electrosterically stabilized seed latexes—the kind that would be subject to the additional loss mechanism of transfer or termination. This rate reduction early in the growth of these seed latexes, and knowing the reasons behind secondary particle formation which can ruin a batch of latex, have significant implications for the development and improvement of industrial products and processes.

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**Supporting Information Available:** Text detailing the method of calculating the local acrylic acid concentration within the hairy layer is provided, as well as the mathematics (steady-state and full numerical iterative treatment) of determining the midchain radical concentration. and a sensitivity analysis (including figures) of the developed model with respect to important numerical parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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