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Particle Size Distributions in Electrosterically Stabilized Emulsion Polymerization Systems: Testing the "Mid-Chain-Radical" Hypothesis

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ABSTRACT: It has been found [Thickett, S. C.; Gaborieau, M.; Gilbert, R. G. *Macromolecules* **2007,** *40*, 4710−4720] that rate and characterization data on the seeded growth of latex particles electrosterically stabilized by a "hairy layer" of anchored poly(acrylic acid) (pAA) can be qualitatively and quantitatively explained by mechanistic events involving mid-chain radicals (MCRs). A considerable range of data was found to be consistent with the supposition that these MCRs are formed by abstraction on the pAA during polymerization, and are slow to propagate but quick to terminate, and thus are a cause of radical loss; they may also undergo β-scission leading to secondary particle formation. Results are reported here for four additional types of experiments on the evolution of the particle size distribution (PSD) in these systems; all these experiments have the potential to refute the mechanistic hypothesis. The experiments comprise (i) evolution of the PSD of small particles, (ii) evolution of the PSD in a bimodal system (competitive growth), (iii) growth rates of separate experiments of small and large particles with the same total amount of pAA, and (iv) the amount of secondary nucleation (formation of small particles) with both pAA and also with poly(ethylene oxide) steric stabilizers. In each case, the data are qualitatively and quantitatively consistent with the predictions of the mid-chain-radical mechanisms and thus support the general applicability of this effect.

Introduction

Emulsion polymerization is a widely used industrial process, and industrial recipes frequently contain steric[1] and/or electrosteric stabilizers[2] for colloidal stability.[3–5] These stabilizers comprise polymers or oligomers which are either chemically anchored to the particle or strongly adsorb onto it and which include a neutral (steric) or ionizable (electrosteric) hydrophilic polymer moiety forming a "hairy layer" on the outside of the particle. An example of a steric stabilizer is provided by stabilizers involving poly(ethylene oxide); an example of electrosteric stabilizers is afforded by recipes which include a water-soluble monomer, especially acrylic acid, in the monomer mix, and thus the final latex particles include poly(acrylic acid) moieties (as part of a blocky copolymer with hydrophobic monomers). Despite their industrial importance, there have been few studies of such systems which were able to provide unambiguous mechanistic information on how these stabilizers affect the rather complex set of processes involved in latex particle formation and growth.

The major reason for this lack was that these hairy layers are often polydisperse and hard to characterize. The situation changed with the means of making latexes stabilized by well-characterized and controllable hairs synthesized with controlled radical polymerization, e.g., using the "RAFT-in-emulsion" controlled radical polymerization technique.[6] Other techniques of making well-defined particle morphologies with electrosteric stabilization, such as using nonreactive amphiphilic block copolymers, can also be used. A new set of mechanisms has recently been put forward[7–9] to explain a range of kinetic and characterization data for such model electrosterically stabilized latexes. It was also suggested that these mechanisms can explain a number of common observations (such as the ease of secondary nucleation) in (electro)sterically stabilized systems which are not well characterized.

In essence, these mechanisms are the following, as summarized in Figure 1:

- A mid-chain radical (MCR) is formed on the backbone of the hairy layer by an abstraction reaction with any of several radical species, such as those arising in the aqueous phase formed directly from initiator and those arising from transfer reactions within the particle.
- An MCR, being a tertiary radical, is slow to propagate and quick to terminate.
- Termination events are possible between an MCR and both entering radicals and radicals formed by transfer within the particle which would otherwise have exited (by diffusion away from the particle into the aqueous phase).
- An MCR can undergo β-scission, forming a hydrophilic oligoradical species which can enter the aqueous phase and participate in events which can lead to secondary nucleation. It should be noted that this postulated does not imply that a single polyAA chain is able to nucleate and stabilize a new polymer

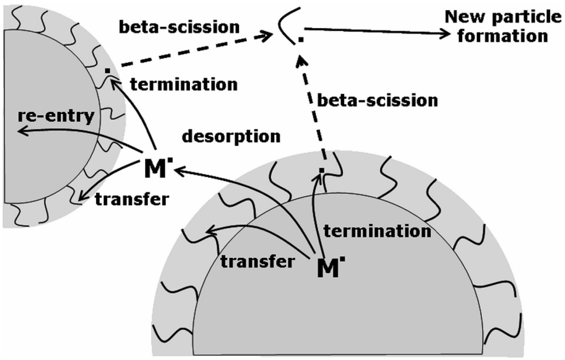

Figure 1. Schematic of the variety of reactions considered significant in the newly developed mid-chain-radical mechanism to interpret the kinetics of electrosterically stabilized emulsion polymerization systems. The additional mechanisms of importance (on top of the standard mechanisms that govern electrostatically stabilized latex systems) are transfer to the stabilizing hair, termination with a mid-chain radical, and β-scission of a mid-chain radical.

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particle through secondary nucleation. In reality, many fragmented chains may assemble and associate, much like the "coagulative" step in the homogeneous nucleation mechanism. This does however serve as an excellent starting point for modeling this process.

The data leading to the deduction of the MCR mechanism, where appropriate, used latexes with well-characterized hairs (made by controlled radical polymerization[6–8]) and again, where appropriate, comparison with equivalent latexes either electrostatically stabilized or electrosterically stabilized without controlled hairs ('uncontrolled' latexes). The experiments comprised the following:

- Rate data in seeded systems: growth of the particles with well-characterized and essentially monodisperse (and controllable) "hairs". These rate data included both steady-state rates with chemical initiator and "relaxation" experiments, which measure the rate of polymerization after initiation by γ radiolysis, following removal from the radical source.
- Molecular weight distribution and NMR data in both bulk (solution) polymerization models of the "hairy layer" environment and of the seeded particles.

The objective of the present paper is to implement a number of experiments, given in the next section, which are qualitatively different from those types of experiments from which the MCR effects were inferred: specifically, experiments involving the particle size distributions (PSDs) of this type of system. As will be seen, each of these types is such that various qualitative or semiquantitative predictions of the MCR mechanism can be tested.

The emphasis in the present paper is on whether qualitative and semiquantitative results contradict the predictions of the mid-chain-radical effect. Because the experiments used here are quite different in type from those from which the effect was deduced, each of the new set of experiments has the potential to qualitatively refute the postulate. Such exacting tests are not often possible in emulsion polymerizations because of the complexity of the system.

Of less importance, but nevertheless significant, is seeing whether quantitative models can be found, with a minimum of adjustable parameters whose values have a wide uncertainty, which can give quantitative accord with the observations. The reason that these tests of the postulated effect are of secondary importance is because there is significant uncertainty in values of parameters which cannot be determined accurately and reliably from independent experiments, and so being able to find reasonable values which give acceptable accord with experiment when used in quantitative models is much less convincing of the applicability of the postulates than are results of experiments which could provide qualitative refutation.

The present studies are all for systems with a pre-existing electrosteric stabilizer layer, with subsequent particle growth being in the presence of added hydrophobic monomer (styrene) but without any of the monomer in the hairy layer, viz., acrylic acid. Moreover, the latexes have been purged of residual monomers prior to the seeded growth measurements. That is, the data are for emulsion polymerization of a hydrophobic monomer in a seeded system comprising polymers of the same hydrophobic monomer and the hydrophilic monomer which is the principal component of the stabilizing hairs.

Choice of Experiments with Potential for Refutation

The four types of particle size experiments to be performed here are now examined with a view to seeing whether there is in each the potential for qualitative refutation of the MCR hypothesis.

An important preliminary point is that modeling studies[7] have indicated that the MCR effects are most prominent for small particles, if one compares large and small particles which have the same number of total hairs, e.g., as would be the case where the larger particles have been grown from the smaller ones. The reason for this is simply that the density of monomer units per unit particle surface area is less in the case of the larger particles, and thus there is a reduction in the rate of effects arising from MCR-originating reactions of the monomer units. This is most manifest in the observation[7–9] of large reduction in the rate of growth of (small) electrosterically stabilized particles compared to the observed growth rate of particles of the same size stabilized by ionic surfactants.

Evolution of Size Distribution of Small Particles. The first type of measurement involves measurement of the PSD of a small hairy particle as it undergoes further polymerization. It is well-known and accepted[3] that, in general, as a seed latex is polymerized the number PSD (the number of particles of a given size) becomes narrower. This however is only well established for electrostatically stabilized systems. It will now be seen that the behavior for growth of small electrosterically stabilized particles is predicted to show the reverse behavior: they should become broader.

The reason for this prediction is as follows. A PSD has a finite width; i.e., some particles are larger than others. The MCR effects lead to radical loss because of the presence of termination with the slowly propagating MCR. These effects will be diminished for the larger particles in a PSD, given that the total number of hairs per particle remains the same. With this loss mechanism diminished for larger particles, these larger particles are predicted to grow more quickly than smaller ones. Therefore, the resultant number PSD should broaden. Eventually of course the particles will all become sufficiently large (say, ~60 nm or bigger in diameter) so that the effect is negligible for all of them, whereupon the normal effect of the number PSD becoming narrower in time (while the volume PSD might become broader) will dominate.

This narrowing seen in systems of "ordinary" size particles is well understood (see, e.g. ref 3): in a system where particles grow uniformly in volume, then while the PSD in terms of *volume* remains of constant width, the distribution in terms of *number* (which differs by a factor of d(volume)/d(radius) = $4\pi r^2$) becomes narrower because of the division by an increasing value of r^2. For later use, the relation between the number and volume particle size distributions ($n_N(r)$ and $n_V(V)$, the number of particles with unswollen radius r and unswollen volume V, respectively) is

$$n_N(r) = 4\pi r^2 n_V(V) \tag{1}$$

Thus, the first qualitative prediction of the MCR mechanism, with the potential to refute this supposition, is that the PSD of a sufficiently small particle stabilized by pAA hairs should show an increasing polydispersity in the PSD time evolution.

Rate of Growth of Large Particles. On the basis of the preceding argument, "large" particles stabilized with the same total number of hairs per particle should essentially obey the rate predicted by well-established mechanistic models for an electrostatically stabilized particle of the same size. This is quite different from what has been seen in studies of the polymerization rates of small particles, which are much slower than an equivalent electrostatically stabilized equivalent (i.e., where both systems have the same particle size and particle number density).

This is the second prediction of the MCR mechanism, with the potential to refute this mechanistic supposition.

Competitive Growth. A competitive growth experiment[10] involves examining the time evolution of the PSD of a bimodal PSD, made by mixing two monomodal samples with sufficiently different sizes. Proper data interpretation[11] requires taking into account the fate of exited radicals. Exit (desorption) in electrosterically stabilized particles has been shown to arise from a transfer-diffusion mechanism,[12,13] whereby free radical activity in the particle is transferred to an entity such as a monomeric radical; this can diffuse out of the particle into the water phase before it could undergo propagation within the originating particle. (If it underwent propagation, it would become so hydrophobic as to be unable to exit.) Once in the water phase, this radical may undergo a number of fates, the most likely of which for many systems[14,15] (including the present case of styrene) is to enter another particle: "re-entry".[16,17] Radical loss by exit in such a system is thus kinetically second order in $\bar{n}$ because the probability of exiting is proportional to $\bar{n}$, and the probability of this radical entering a particle which already contains a growing radical is also proportional to $\bar{n}$. This second-order behavior is termed "limit 2a".[3,18]

When MCR effects are significant, the dominant fate of a transferred radical, once it enters the hairy layer in what would be a prelude to exit in an electrostatically stabilized particle, becomes termination rather than diffusion through the layer. Thus, it is predicted that when MCR effects are significant, radical loss by exit becomes kinetically first-order with respect to $\bar{n}$ (denoted "limit 1" behavior[3,18]).

Competitive growth experiments can give the size dependence of the rate coefficient of capture for *z*-meric radicals and have shown[11] that the capture rate coefficient of aqueous-phase radicals of sufficiently high degree of polymerization so as to irreversibly enter the latex particles ("*z*-mers"[19]) is proportional to the radius of the particle, as expected if this capture is diffusion-controlled. (It is noted parenthetically that strictly speaking this should be the radius of the particle plus hairy layer, but for the present systems, simple estimates[20] suggest this increases the size by ~10%.) Hence, the third prediction from the MCR mechanisms, with the potential to refute this mechanistic supposition, is that the size dependence of the entry rate coefficient deduced from a competitive growth experiment should proportional to radius *if* it is assumed that radical loss is first-order in $\bar{n}$ for the smaller component and is second-order for the larger component.

Secondary Nucleation. The MCR effects also include β-scission of a MCR formed by chain transfer leading to migration of a polymeric species into the aqueous phase that aids the onset of particle nucleation. This occurrence of secondary nucleation during seeded polymerization would be immediately apparent in the particle size distribution. Thus, secondary nucleation would be much more extensive in a latex with an electrosteric stabilizer than in an equivalent one (same particle size and particle number density) where the stabilization is electrostatic.

The fourth prediction of the MCR hypotheses, with the potential to refute the hypotheses, is thus that new particle formation should occur extensively in a sterically stabilized system under some conditions where this does not happen in an equivalent electrostatically stabilized one.

Data Treatment

A summary of key kinetic concepts is presented here as needed for qualitative and semiquantitative data interpretation.

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

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{k_\mathrm{p} C_\mathrm{p} N_\mathrm{p}}{n_\mathrm{M}{}^0 N_\mathrm{A}} \bar{n} \tag{2}$$

where x is the fractional conversion to polymer, k_p the propagation rate coefficient (known accurately for styrene[21,22]), C_p the monomer concentration inside the particles (well-known for styrene[23]), $n_\mathrm{M}{}^0$ the initial monomer concentration per unit volume of aqueous phase, N_p the particle number per unit volume of aqueous phase, and N_A the the Avogadro constant. Equation 1 is used to determine $\bar{n}$ in systems where no secondary nucleation is observed. In the case of emulsion polymerization systems that commence in Interval II[3] (that is, where the particle interior and aqueous phase are saturated with monomer with monomer droplets present in the system), there is typically a lengthy period where the polymerization rate is constant and the steady-state value of $\bar{n}$, $\bar{n}_\mathrm{ss}$, can be determined directly from the above equation. The systems are designed so that it is expected that they obey "zero-one" kinetics,[3] i.e., that there is effectively "instantaneous" termination when a radical enters a particle already containing a growing free radical. Thus, in a zero-one system the average number of radicals per particle is always $\leq {}^1/_2$.

In a zero-one system the value of $\bar{n}$ is determined by the rate coefficients for radical entry (ρ) and radical exit (k), together with the fate of exited radials. The generally accepted mechanism for radical entry into a latex is particle is control by aqueous phase growth, proposed by Maxwell et al.[19] (the "Maxwell–Morrison" model). Here propagation of initiator-derived radicals with the small amount of monomer present in the aqueous phase takes place in the aqueous phase until a critical degree of polymerization z is reached, after which rapid (and irreversible) entry takes place. This degree of polymerization corresponds to when the radical becomes surface-active and has an affinity for the particle surface. For styrene with persulfate initiator, $z \sim 2-3$.[8,19,24]

Competitive Growth Experiments. "Competitive growth" experiments (the seeded polymerization of a bimodal particle size distribution) were pioneered by Vanderhoff et al.;[10] correct data interpretation[11] requires taking into account the fate of exited free radicals.

While the Maxwell–Morrison model assumption that the entry of a *z*-mer into a particle is not rate determining and is thus independent of particle size *in a monomodal latex*, in a bimodal (or polydisperse) latex, it is likely that the rate coefficient for entry of *z*-mers into small particles will be different from that into large ones. It has been established by γ-radiolysis relaxation experiments that the exit rate coefficient k also depends on particle size. Competitive growth experiments were used[11] to show that the entry step (once a radical reaches the critical degree of polymerization z) has a rate coefficient proportional to the radius of the particle that the radical is encountering; as now detailed, this requires careful attention to data reduction to take into account the fate of exited free radicals.

The experiment and data treatment are as follows. A bimodal latex is made by synthesizing two latexes of differing sizes, mixing them together, and then polymerizing them further in seeded experiments. By measuring the PSD, the increase in size of each component is then obtained. As long as the system remains in interval II (where the polymerization rate is constant), the value of $\bar{n}_\mathrm{ss}$ for each of the two sizes j = "big" and "small" can be found from the following equation:

$$\bar{n} = \frac{\frac{4}{3}\pi(r_{\mathrm{f},j} - r_{\mathrm{i},j}) d_\mathrm{p} N_\mathrm{A}}{k_\mathrm{p} C_\mathrm{p} M_0 t_\mathrm{s}} \tag{3}$$

where $r_{\mathrm{i},j}$ and $r_{\mathrm{f},j}$ are the initial and final particle sizes respectively of component j, d_p the density of the polymer, M_0 the molecular weight of the monomer, and t_s the time period between the start of the reaction and the time that sampling took place (all other parameters as defined previously). The rate coefficients for radical entry for both latexes (denoted ρ_large and ρ_small) can be found from the values of $\bar{n}_\mathrm{ss}$ for the two latexes, with the important step of considering whether true desorption and re-entry of exited radicals takes place. It is these rate coefficients which are expected to be proportional to particle radius.

The expressions for obtaining ρ_{large} and ρ_{small} depend on the assumed fate of exited free radicals from each component. The expressions for when it is assumed that *both* obey either limit 1 (complete termination) or limit 2a (complete re-entry) have been given by Morrison et al.[11] In this work the corresponding mixed-limit expressions, when all radicals formed by transfer in the smaller particles terminate in the hairy layer (limit 1) while all exited particles from the larger particles re-enter, are derived in the Supporting Information:

$$\rho_{\mathrm{small}} = \frac{k_{\mathrm{tr}} C_{\mathrm{p}} \bar{n}_{\mathrm{small}}}{1 - 2\bar{n}_{\mathrm{small}}} \tag{4}$$

$$\rho_{\mathrm{large}} = \frac{k_{\mathrm{tr}} k_{\mathrm{dM,large}}}{k_{\mathrm{p}}^{1}} \frac{\bar{n}_{\mathrm{large}}^{2}}{1 - 2\bar{n}_{\mathrm{large}}} \tag{5}$$

Here $k_{\mathrm{dM,large}}$ is the rate coefficient for desorption of a monomeric radical from a large particle, which can either be obtained from an independent γ-radiolysis relaxation experiment or reliably estimated from the diffusion model.[15]

Secondary Nucleation. The present studies of secondary nucleation are in the absence of surfactant. Under those circumstances, the only way that secondary nucleation can occur is through homogeneous nucleation.[13,25,26] In this mechanism, an initiator-derived radical propagates with the small amount of monomer in the aqueous phase, but propagation continues beyond the length z (where surface activity is attained) to a length j_{crit}—the critical chain length before the growing oligomer is no longer soluble in the aqueous phase. This oligomer undergoes a coil-to-globule transition to form a new ("precursor") particle. The value of j_{crit} for styrene with persulfate initiator is ~5.[19]

This mechanism has been well studied for electrostatically stabilized emulsion systems, and reliable models have been given[3,27–30] for predicting conditions where extensive secondary particle formation will occur. Significant secondary nucleation has been frequently observed (see, e.g., refs 7 and 9) in polymerically stabilized emulsion systems (both sterically and electrosterically stabilized) under conditions where the homogeneous nucleation mechanism predicts that essentially no new particle formation should take place. The MCR effect, particularly the β-scission component, implies that extensive secondary particle formation (as seen in the PSD) should be seen for pAA-stabilized particles under some conditions where experiment and/or reliable predictive models show that negligible new nucleation occurs for an equivalent electrostatically stabilized one.

Experimental Section

All experiments were performed at 323 K unless stated otherwise.

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) 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 hydrogen carbonate (Sigma Aldrich), butanone (Sigma Aldrich), and sodium dodecyl sulfate (SDS, Sigma Aldrich) were used as received. All water used in this work was high-purity deionized water (Milli-Q).

Electrosterically Stabilized Seed Latex Synthesis. The synthesis and characterization of electrosterically stabilized seed latexes with hydrophilic stabilizers of controlled length using the "RAFT-in-emulsion"[6] process was the same as presented previously;[20] published procedures[20] were also followed to remove residual RAFT agent. The average particle size of latexes ST5 and ST10 (stabilized with hairs of approximate degree of polymerization 5 and 10, respectively) were particularly small (swollen radius 22 nm); samples of these latexes were further polymerized with styrene to create larger particles (denoted ST5L and ST10L, respectively). Measured particle numbers (N_{p}) were as follows: ST5, 9.7×10^{18} L^{-1}; ST10, 9.6×10^{18} L^{-1}; ST5L, 4.9×10^{17} L^{-1}; ST10L, 9.1×10^{17} L^{-1}. The latexes were pH-adjusted so that the final pH was 7. Typically, the synthesis resulted in a final pH of the resultant latex that was ~7.

Chemically Initiated Dilatometry. This technique was used to measure the rate of growth of small and large seed latexes. For both the set of small and large seed latexes, 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 then heated to 323 K. Stirring was ceased, and the reaction vessel was evacuated again to remove dissolved oxygen.

In a separate vessel an aqueous initiator solution of KPS was prepared. 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 between initiators.

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 the PSD obtained using hydrodynamic chromatography (HDC; Polymer Laboratories PSDA) to ensure the validity of the kinetic analysis as well as to consider the behavior and resultant PSD of the small seed latex population.

Competitive Growth Experiments. Samples of ST5 and ST5L (as well as ST10 with ST10L) were mixed, with the amount of each latex added chosen such that the number of particles from each population was approximately equal. The mixed latex was sparged with high-purity N_2 and raised to 323 K under constant magnetic stirring. Styrene was added to the mixed latex to ensure saturation of the particle interior and aqueous phase, and polymerization was initiated by injection (1 mL) of an aqueous KPS solution at an appropriate concentration. Three different initiator concentrations were chosen spanning 2 orders of magnitude. Samples (2 mL via syringe) were drawn at either 5000 or 10 000 s after commencement of polymerization, the sample was inhibited with a hydroquinone solution, and the PSD was determined by HDC. Transmission electron microscopy (TEM) images were obtained and used to produce PSDs to ensure the validity of HDC analysis. (Obtaining the distribution via HDC is significantly quicker and allows for convenient comparison but must be confirmed by a more rigorous method.) TEM samples were prepared by depositing a dilute sample of the latex onto a carbon-coated Cu grid and dried at ambient temperature. Images were acquired using the Philips CM120 Biofilter (120 kV) at the Electron Microscope Unit at The University of Sydney.

"Uncontrolled" Seeded Emulsion Polymerization Experiments (for Secondary Nucleation Testing). An electrosterically stabilized latex prepared by conventional free-radical emulsion polymerization was prepared and diluted to four different final particle concentrations (N_{p}) spanning an order of magnitude. The synthetic procedure for the seed latex was equivalent to that used for the "high coverage" latex synthesized by Vorwerg[31] (where

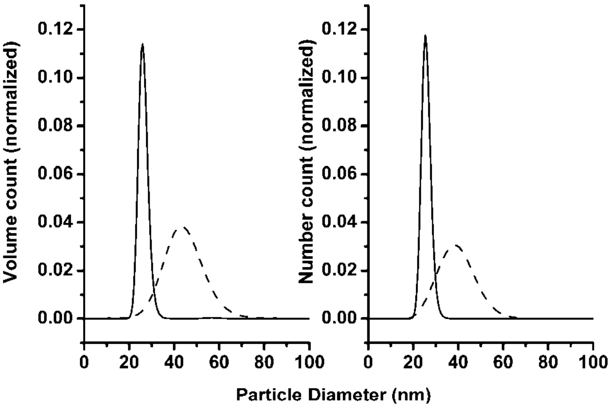

Figure 2. Volume (left) and number (right) distributions, obtained by HDC, of polystyrene latex stabilized by poly(acrylic acid) of average DP = 10 units, before and after seeded polymerization. Seed distribution is shown with a solid line, and the resultant distribution is shown with a dashed line. Polymerization took place with an initiator concentration of [KPS] = 0.3 mM, polymerization took place over 4 h, and sample for HDC analysis was taken at 20% fractional conversion.

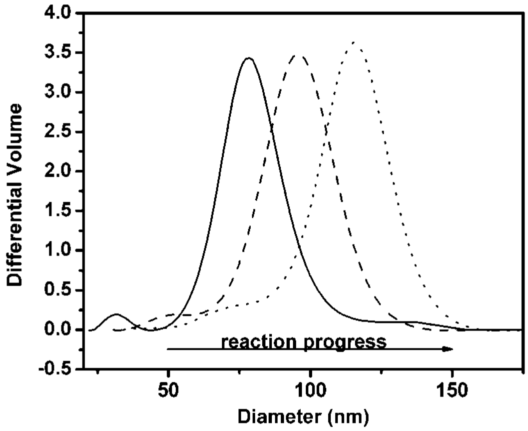

Figure 3. Evolution of particle size distribution (PSD, volume distribution) as obtained by HDC for the ST5/ST5L competitive growth experiment ([KPS] = 10 mM). Distributions shown are as follows: starting distribution (solid line), distribution after 5000 s polymerization (dashed line), and distribution after 10 000 s polymerization (dotted line). The small peak at low particle sizes represents the "small latex" population (distribution confirmed by TEM).

the polyAA represents 15% w/w of the total polymer present); this was chosen as the seed latex as the final value of N_p (5.4×10^{17} L^{-1}, unswollen average radius = 31.2 nm) was much lower than that for latexes made by the "RAFT-in-emulsion" method.[6] Seeded experiments were performed with styrene at 323 K, using an initiator concentration of [KPS] = 1 mM. The four latexes were then analyzed by HDC in order to determine the final PSD and the ratio of new to old particles.

Results and Discussion

PSD of Small Electrosterically Stabilized Latexes. Figure 2 shows the normalized volume and number PSDs of the ST10 latex both before and after a seeded polymerization experiment. The final PSD exemplified here is particularly broad. The weight-average particle diameter from the PSD, 43 nm (number-average 35 nm), is quite close to the predicted average size for the conclusion of this reaction (33 nm). This is an unusual result, as typically PSDs become narrower as the distribution is polymerized further. This does however agree with our qualitative predictions of the behavior of these electrosterically stabilized systems and thus supports the MCR hypothesis. It is also possible to claim that this behavior is due to a significant difference in the diffusion characteristics of radicals entering and exiting particles of different sizes stabilized in this manner. This is indeed true but cannot be the dominant effect; radical exit in these systems was originally explained through a "restricted diffusion" effect,[20] but it was shown in later work[7] that reactions within the hairy layer were much more likely than successful desorption through the hairy layer.

Rate of Growth of Large Particles. In the previous published work on this topic,[8] it was evident that very small poly(styrene) latexes stabilized by poly(acrylic acid) exhibited very small values of $\bar{n}_{ss}$ across a wide range of initiator concentrations—values that were much lower than predicted by the theory for electrostatically stabilized latexes, where no MCR effects are taken into account. The qualitative argument given in the Introduction, as well as quantitative modeling,[7] indicates that as the particle size is increased (all other parameters being held constant), the value of $\bar{n}_{ss}$ would increase up to the "electrostatically stabilized" value as the additional loss terms of transfer/termination became insignificant.

The latex used (ST5L) was stabilized by polyAA chains of average degree of polymerization = 5 and the swollen radius was 46 nm, to compare with the growth rate of the small particles with the same total number of $(AA)_5$ hairs, (ST5, swollen radius 22 nm). Much larger values of $\bar{n}_{ss}$were found for this latex (see Table 1). These values are also very close to the "limit 2a" values predicted for electrostatically stabilized latexes,[19] unlike the small seed latexes stabilized in the same manner. Since this model has been found to give reliable predictions, especially for styrene systems, this indicates that the effect of radical loss through chain transfer to polyAA is strongly reduced to the point of being insignificant when large seed latexes are used. This further supports the MCR hypotheses (and a possible means of model refutation has been rejected) and suggests that the unusual kinetic behavior of electrosterically stabilized latexes is restricted to very small particles.

Competitive Growth Experiments. The evolution of the PSD in a typical experiment is shown in Figure 3, while the measured $\bar{n}_{ss}$ data for both latexes are presented in Table 2. The maxima from the bimodal PSDs are used for the particle size of both the small and large particle population, rather than attempting to separate the observed PSD at longer times into separate small and large components by some sort of deconvolution. While not ideal, the small particle population was too difficult to resolve into an unambiguous component at long reaction times.

As demonstrated experimentally by Morrison,[11] the ratio of entry rate coefficients of the two latexes is approximately equal to the ratio of the particle radii (consistent with diffusion control) when limit 2a re-entry kinetics are assumed. This limit 2a is predicted not to hold for the electrosterically latexes considered here. Indeed, when its applicability is assumed in the data

Table 1. Comparison between Experimental Values of $\bar{n}_{ss}$ for Latexes ST5 and ST5L and Model Values Obtained by the Electrostatic Kinetic Model for Particles of That Size

	ST5 (small seed latex)		ST5L (large seed latex)	
[KPS] (M)	$\bar{n}$ (experiment)	$\bar{n}$ (electrostatically stabilized model[3])	$\bar{n}$ (experiment)	$\bar{n}$ (electrostatically stabilized model[3])
1.51×10^{-4}	2.7×10^{-3}	0.055	0.069	0.067
1.06×10^{-3}	6.0×10^{-3}	0.058	0.15	0.16
1.34×10^{-2}	1.8×10^{-2}	0.067	0.33	0.27

Table 2. Particle Size (from Maxima in PSD) and Data from Competitive Growth Experiments for the ST5+STL5 and ST10/STL10 Bimodal Latexes (for 5000 s Polymerization Time) from Figure 3 (All Sizes Are Diameters, nm)

	ST5+ST5L		
[KPS]	0.1 mM	1 mM	10 mM
	small component		
initial size	24.6	24.6	24.6
final size	30.4	35.1	41.3
$\bar{n}_{ss}$	6.5×10^{-4}	1.9×10^{-3}	3.4×10^{-2}
	large component		
initial size	74.9	74.9	74.9
final size	81.4	85.3	91.2
$\bar{n}_{ss}$	1.4×10^{-3}	5.9×10^{-3}	1.3×10^{-1}
	ST10+ST10L		
[KPS]	0.1 mM	1 mM	10 mM
	small component		
initial size	19	19	19
final size	27.9	32.4	37.4
$\bar{n}_{ss}$	1.1×10^{-3}	2.2×10^{-3}	1.6×10^{-2}
	large component		
initial size	55.8	55.8	55.8
final size	60.6	66.7	71.5
$\bar{n}_{ss}$	4.3×10^{-3}	1.2×10^{-2}	7.7×10^{-2}

processing for these experiments, the ratio of the entry rate coefficients then inferred from the data becomes substantially smaller than the ratio of the radii (Figure 4). This ratio is physically hard to justify. The use of "first-order" loss kinetics in the data processing from these experiments gives a ratio of rate coefficients which is large (note the logarithmic scale in Figure 4). This is also hard to justify physically.

The extended kinetic model[7] suggests that larger particles (such as the size of the ST5L and ST10L latexes used here) are more likely to exhibit re-entry kinetics due to the reduced stabilizer concentration on the particle surface reducing the likelihood of a transfer/termination event, while smaller particles are likely to exhibit limit 1 behavior. Using the model developed in that work, which allows the likelihood of transfer/termination vs desorption to be considered, the entry rate coefficients for both particle populations was calculated. The ratio of entry rate coefficients was much closer to the ratio of the diffusion-limited entry terms (which is slightly larger than the ratio of the radii, due to differences in diffusion coefficients through hairy layers of different density) of the large and small polymer particles (Figure 5). This is as expected from diffusion-limiting entry of *z*-mers, which is readily physically justified, especially as it was found to hold for large particles. This again provides another piece of experimental evidence to suggest that the MCR mechanism is real and dominates in systems where the average particle size is small (below 35 nm swollen radius), and the particle surface is densely covered.

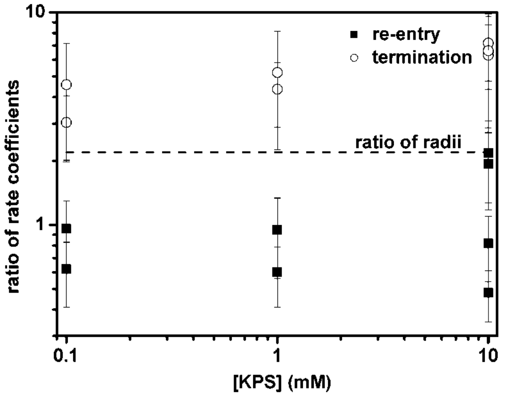

Figure 4. Ratio of entry rate coefficients from competitive growth experiments assuming limit 2a kinetics (re-entry of exited monomeric radicals) (filled squares) and complete aqueous-phase termination (open circles) as a function of initiator concentration, from Table 2. Note the logarithmic *y*-axis.

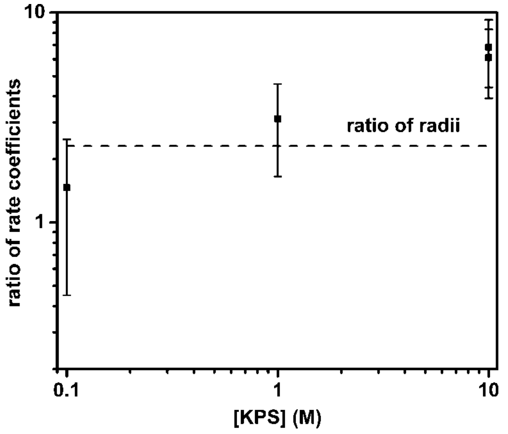

Figure 5. Ratio of entry rate coefficients from competitive growth experiments assuming successful exit (desorption) only takes place from large particles, from Table 2.

It is also apparent from the data that the polydispersity of the volume distributions of the smaller populations increases with polymerization, whereas that of the larger does not show much change. The same is true for the equivalent number distributions (omitted for clarity). As explained in the section on Choice of Experiments, it can be seen that in fact this initially surprising result is in fact consistent with the qualitative predictions of the MCR mechanism.

Although it is tempting to model the full PSD to attempt a quantitative fit of these competitive growth data, this would in fact merely be a curve-fitting exercise. There are two reasons for this. First, while the method used to determine PSDs experimentally here, HDC, produces reliable mean size and standard deviation values, the deconvolution algorithm used in the data processing of the instrument, a variant of the Ishige method,[32] is sensitive to small uncertainties, including baseline subtraction, and thus while the observed broadening is certainly semiquantitatively correct, the precise PSD is subject to quite high uncertainty. Second, the modeling used here perforce contains some parameters whose values cannot be fixed with sufficient precision to produce a quantitatively reliable PSD.

Secondary Nucleation. Figure 6 shows the observed ratio of new to old particles observed with hairy particles made in an "uncontrolled" manner as outlined in the Experimental Section. The latex was chosen to mimic the recipe used by Vorwerg.[31] These results are compared to those predicted by modeling for equivalent electrostatically stabilized ones. A number of models have been developed for this purpose,[3,27–30] and for this system all give effectively the same result, viz., that the homogeneous nucleation mechanism which successfully predicts the occurrence of extensive secondary nucleation in electrostatically stabilized systems over a wide range of particle number predicts a result many orders of magnitude less than that observed in the corresponding electrosterically stabilized one, for all particle numbers examined.

Figure 6 shows that the actual amount of secondary particle formation in a systems stabilized with pAA hairs is orders of magnitude more than in a corresponding electrostatically stabilized one. This is consistent with the predictions of the MCR processes, which again supports this mechanism. No attempt was made to see whether the new particles contained or were

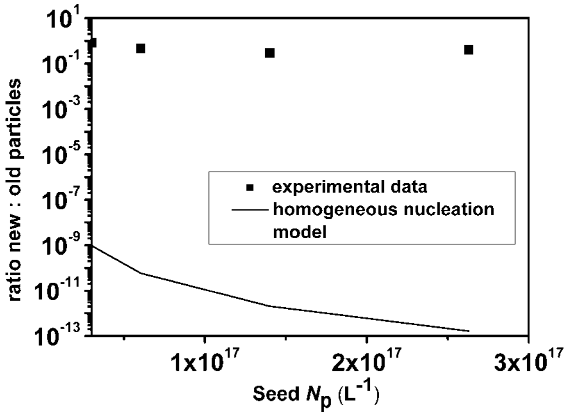

Figure 6. Ratio of new to old particles as a function of seed N_p observed experimentally (points) for an "uncontrolled" electrosterically stabilized system (points) and that predicted by the homogeneous nucleation model[27] for equivalent electrostatically stabilized ones (line). Conditions for polymerization are outlined in the Experimental Section; [KPS] = 1 mM, polymerization time = 3 h.

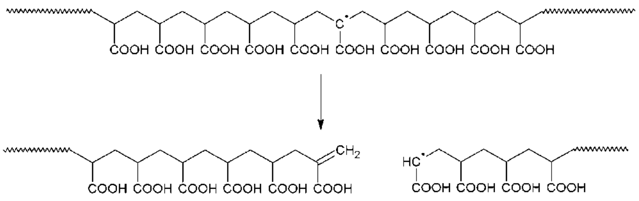

Figure 7. β-scission in poly(acrylic acid).

stabilized by polyAA. However, the main conclusion from this work is that significantly more particles were formed via secondary nucleation (by many orders of magnitude) than predicted by the governing particle formation mechanisms for electrostatically stabilized latexes under the same conditions.

Modeling

As stated, there are a number of parameters whose values are uncertain in modeling systems of this complexity, and thus modeling studies in themselves cannot be used to produce definitive conclusions (as distinct from the qualitative and semiquantitative results of the preceding section, where any of the types of experiments had the potential to refute the MCR hypotheses). Nevertheless, it is useful to see whether modeling with the best available estimates of parameters can produce results which are consistent with the data. Any such agreement is then supportive of the overall conclusions.

Full details of the models are given in the Supporting Information. A summary is given below.

Modeling of Rates. The dominant radical loss mechanisms has been suggested previously to be transfer to poly(acrylic acid) and termination with the resultant MCR.[7] β-scission (see Figure 7) is now included in the kinetic scheme as a possible fate for a formed MCR, which is known to occur for poly(acrylic acid), even at ambient temperatures.[33] Here it is postulated that β-scission of a MCR is mechanistically important in the creation of new particles. This is shown schematically in Figure 1 and is dubbed the "fragmentation nucleation" mechanism. As a simplistic first approximation, it is assumed that every β-scission event leads to the formation of a new particle; this is included in the steady-state rate of new particle formation. (It should be pointed out that the true mechanism of particle formation via secondary nucleation in these systems, whatever it may be, would involve more than just the β-scission event of one polyAA chain.) Full details of this modeling are given in the Supporting Information.

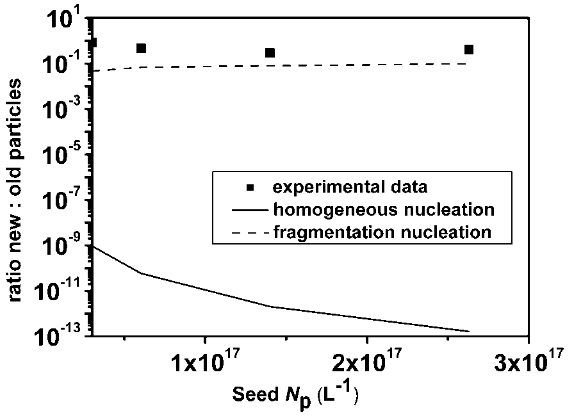

Figure 8. Ratio of new to old particles as a function of number density of particle in the seed; points shown here represent experimental data (filled squares), fragmentation nucleation model results (dashed line), and homogeneous nucleation results (solid line).

Sensitivity analyses were also performed. In these, the value of the rate coefficient of β-scission (k_{beta}) was allowed to vary over 11 orders of magnitude. This was done because there is little consistency in the literature regarding the rate coefficients for β-scission in acrylate systems. Peck[34] observed no β-scission for butyl acrylate (BA) systems at 75 °C, while Junkers[35] observed MCR formation in BA systems (which could potentially undergo β-scission) at temperatures as "low" as 80 °C. Four orders of magnitude exist between the values obtained by Busch[36] and Rantow[37] for high-temperature BA polymerization systems where the resultant molecular weight distribution was used to infer information regarding k_{beta}. Data for polyAA itself were found using pulse radiolysis[33] and ESR[38] at room temperature and pressure, and the values of k_{beta} varied between 10^{-1} and 10^{2} s^{-1}. Recent ESR work by Sato and co-workers[39] on the monomer ethylhexyl acrylate has yielded a value of k_{beta} $\sim 4 \times 10^{-2}$ s^{-1} at room temperature. This substantial variation is most likely due to the fact that these rate coefficients have to be indirectly inferred from other data; however, it would seem that β-scission occurs to a greater extent in polyAA than poly(butyl acrylate). The sensitivity analysis reported in the Supporting Information is designed to reflect the lack of precision with respect to this quantity, and it can be seen that no qualitative mechanistic conclusions change when this parameter is varied.

Rates: Comparison with Experiment. Using this model, comparison was made to the experimental results presented earlier in this paper where an "uncontrolled" electrosterically stabilized latex was used as a seed to determine the amount of secondary nucleation seed in these systems as a function of seed N_p. The results of this are shown in Figure 8. As can be seen, the "fragmentation nucleation" model provides a result that is much closer to the experimental result than that given by the homogeneous nucleation mechanism that governs corresponding electrostatically stabilized systems.

Modeling of Full PSDs. The time evolution of the full PSD of an electrosterically stabilized latex was modeled using a variant of the code originally developed by Coen et al.[27] Additions to this code (including transfer to poly(acrylic acid), termination with a MCR, and β-scission of the resultant MCR) were included, and the experimental conditions used by Vorwerg were modeled by using appropriate input parameters. The details of this code are given in the Supporting Information. Once again it was assumed that every β-scission event led to the creation of a new particle.

PSDs: Comparison with Experiment. The final PSD of one of the experimental samples discussed earlier was compared to

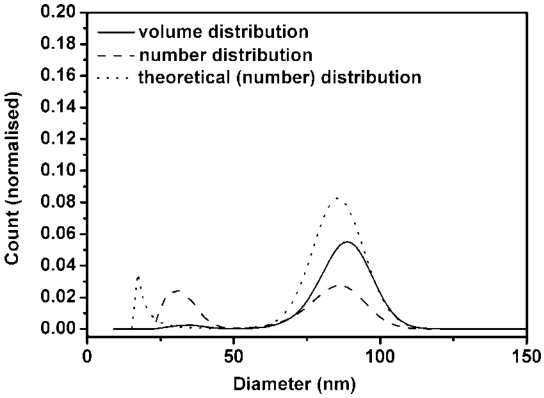

Figure 9. Experimental and modeled PSDs of electrosterically stabilized latex (measured by HDC which provides volume distribution) after further polymerization with styrene, [KPS] = 1 mM. New particles are shown by the new population at small particle sizes. Number density of seed particles = 2.5×10^{17} L^{-1}.

the theoretical one. These distributions are shown in Figure 9. As can be seen, both distributions are bimodal due to the presence of secondary nucleation. The diameter to which the seed latex population has grown is well modeled, although the size of the new population of particles is underestimated. This is most likely due to various approximations regarding the size of a newly formed particle that are not necessarily physically reasonable. However, it can be seen that good semiquantitative agreement is obtained through this modeling. Although parameter values could be chosen to give agreement with experiment, this would be no more than a curve-fitting excerise.

Discussion and Conclusions

The inclusion of β-scission of a MCR as a reaction that is involved in particle formation in electrosterically stabilized emulsion systems can qualitatively explain a number of observations (and can be modeled with reasonable parameter values leading to agreement with experiment).

However, several points of conjecture remain.

The first is whether or not there is simply enough material "fragmented" into the aqueous phase that would lead to particle formation. β-scission of a MCR relies first upon the formation of a MCR, which (in our model) is assumed to take place via hydrogen abstraction with an exiting monomeric radical. An exiting radical can only be formed by transfer to monomer; all of these events occur on different time scales and rely on one another to take place. This ultimately yields a concentration of fragmented species (either radicals or unsaturated chains) that is very low.

Second, the issue as to what happens to the fragmented species must be addressed. The model presented here has worked at the upper bound assumption that every fragmentation event leads to particle nucleation. However, in reality a hydrophilic polymer chain residing in the aqueous phase is highly unlikely to participate in particle formation at all. If encounter with an aqueous-phase oligomer were to take place (such as propagation or termination), the species formed would possibly be a surface-active species composed of polyAA and poly(styrene). This might possibly lead to particle formation through in-situ micellization.

One piece of supporting evidence for the fragmentation nucleation model is that β-scission is pH-dependent. The work of von Sonntag[33] demonstrated that β-scission is common at neutral and high pH, while the reaction is suppressed at pH = 4 and below. Interestingly, at low pH Vorwerg did not observe any secondary nucleation in seeded experiments.[31] If β-scission is a key step in particle nucleation in these systems, then these results agree with the hypothesis. No work was done here with regards to variation of pH of latexes synthesized by controlled-radical techniques due to colloidal stability issues (and the very low degree of polymerization of the stabilizing chains). However, this remains an important, and poorly understood, area of research in emulsion polymerization.

The proposed mechanism can also be applied to any sterically or electrosterically stabilized emulsion system where the stabilizer has labile hydrogen atoms that are susceptible to chain transfer to polymer, not solely polyAA systems as have been studied here. For example, evidence has been put forward that it applies to systems stabilized with poly(ethylene oxide);[7] however, the competition between β-scission and termination in these systems is unclear.

The results represent somewhat of a conundrum for the chemist attempting to optimize reaction conditions by minimizing secondary nucleation. Small electrosterically stabilized particles (with corresponding high N_p values) will help minimize secondary nucleation; however, densely packed "hairy layers" ensure that transfer/termination (if the stabilizer is able to undergo hydrogen-atom abstraction) will be the dominant loss mechanism, and a reduced reaction rate will be seen. Larger particles (with more sparsely covered surfaces) give faster reaction rates (due to higher values of $\bar{n}$); however, secondary nucleation due to a reduced N_p is more likely. Ideally, a balance should be found—small particles with a minimum amount of employed stabilizer or stabilizers that are unable to undergo abstraction would be recommended. It is also conceivable that additional control over the resultant PSD could be achieved through addition of the acrylic acid comonomer later in the reaction profile when designing systems with anchored stabilizers. Further tests of these postulated mechanisms could be carried out by adsorbing known amounts of amphiphilic block copolymers onto the surface of "large" electrosterically stabilized latexes to modify the surface packing density and seeing how the resultant kinetic profile changes as a function of surface coverage.

In conclusion, carefully designed experiments involving the seeded emulsion polymerization of model electrosterically stabilized latexes stabilized by well-defined blocks of poly(acrylic acid) has provided further supporting evidence to the postulate that chain transfer to the poly(acrylic acid) stabilizing chain occurs under certain conditions. Previously, only very small particles tested experimentally (where the particle surface was densely covered by poly(acrylic acid)) demonstrated this phenomenon; however, the model developed to interpret this data as a function of particle size revealed that this process was no longer significant once the particles were beyond a particular critical size.

The particle size distribution (PSD) of small electrosterically stabilized seed latexes were considered both before and after seeded emulsion polymerization experiments. It was seen that the PSD became significantly broader at the conclusion of the reaction, which was highly unusual but in qualitative agreement with the mechanistic postulates put forward with regards to these systems. This behavior is attributed to the large particles within the seed PSD population growing more rapidly than the smaller population due to a diminished effect from the particle-size-dependent loss mechanisms of transfer/termination to the polyAA hairs on the particle surface.

The polymerization of larger seed latexes stabilized in this manner (>35 nm swollen radius) demonstrated significantly increased values of the steady-state average number of radicals per particle ($\bar{n}_{ss}$) compared to the original "small" latexes, with the experimentally obtained values in very good agreement with the "limit 2a" predicted values for styrene emulsion systems. This was attributed to the less densely covered particle surface leading to a lack of "transfer" sites that an exiting radical could encounter during desorption, essentially returning the kinetics to "normal".

Competitive growth experiments (where a bimodal particle size distribution was polymerized) were also in support of the postulate that the exit mechanism is only complicated by chain transfer for small particles. The ratio of the entry rate coefficients into both the small and large particles should be equivalent to the ratio of the radii of the particles assuming that the entry event is so fast to be diffusion-controlled; however, this was only able to be obtained given when exit was not permitted to take place from the small particle population in the data analysis. This again supports the notion that "true" exit (i.e., desorption into the aqueous phase) only takes place from larger electrosterically stabilized particles, with significant implications for the very small particles often used as seed latexes in industrial formulations for adhesives, paints, and surface coatings.

Finally, a postulate has been put forward to explain the unusually large amounts of secondary nucleation exhibited in emulsion polymerization systems stabilized in this manner. This mechanism, dubbed the "fragmentation nucleation" mechanism, is readily included in standard models to interpret the rate of particle formation and growth in such systems, whereby the β-scission of a mid-chain radical (MCR) is considered to be a significant mechanistic event in the particle formation process. Using reasonable values of the rate coefficient of β-scission in acrylate systems and a minimum of model-based assumptions, it was shown that the amount of newly formed particles in a seeded experiment was significantly increased relative to the homogeneous nucleation mechanism. Both steady-state modeling and time-dependent particle size distribution (PSD) modeling demonstrated good agreement with experiment and may go some way to explaining this hitherto poorly understood area of emulsion science. While MCR effects are only significant for small latexes particles, this is of particular importance to industry because all latex products grown with electrosteric stabilizers start out very small (either as seed or ab initio), even though the final product is usually much larger.

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Supporting Information Available: The background to emulsion polymerization kinetics, the relevant governing evolution equations for $\bar{n}$, details of the theory of competitive growth experiments, and the theory of particle formation as well as details as to the procedures used to develop the FORTRAN code to model the β-scission postulate. This material is available free of charge via the Internet at http://pubs.acs.org.

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