Electrosteric Stabilization with Poly(Acrylic) Acid in Emulsion Polymerization: Effect on Kinetics and Secondary Particle Formation

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ABSTRACT: A kinetic study of seeded emulsion polymerization using seed latices electrosterically stabilized with poly(acrylic acid) was performed. Data were obtained at 50 °C for the steady-state rate of polymerization initiated with persulfate and for the non-steady-state relaxation initiated using γ-radiolysis; conditions were chosen so the system obeyed "zero−one" kinetics (when entry of a radical into a particle already containing a growing radical leads to instantaneous termination). The relaxation data directly measure the rate coefficient k for radical exit (desorption) from particles, which in combination with the steady-state rate then yields the rate coefficient for radical entry, ρ. Electrosterically stabilized particles were synthesized from well-characterized seed (made with ionic surfactant) by second-stage polymerization of a small amount of styrene and acrylic acid. Two degrees of surface coverage were employed using 5 and 15 wt % acrylic acid. The low-coverage particles were much more colloidally stable than the polystyrene latices stabilized by initiator fragments and adsorbed surfactant but the behavior of k and ρ was the same as that of the ionically stabilized seed. The colloidal stability of the high-coverage latices was strongly pH-dependent, with high stability at high pH. These latices exhibited strongly reduced k (by a factor of about 3) at low pH but ρ was only slightly lower compared to the ionically stabilized seed. At high and neutral pH, kinetic parameters could not be determined for the highly covered particles because of secondary nucleation; however, a decreased rate was observed with increasing pH, despite an increase in particle number, indicating a reduced ρ. Thus, extensive electrosteric stabilizer seems to reduce entry and exit rate coefficients, although to a lesser extent than reported in an earlier preliminary study (Coen et al., *Macromolecules* 1996, **29**, 5128). For sparsely electrosterically stabilized particles, the dependences of ρ and k on particle size and (for ρ) initiator concentration were in accord both with those observed for ionically stabilized ones and with the values predicted from models for these processes (transfer diffusion for k and "propagation to z-mer" for ρ).

Introduction

Hydrophilic carboxylic monomers such as acrylic acid (AA) are often employed in polymer colloid formulations to impart colloidal stability, freeze−thaw stability, and improved film forming properties.[1] Another function of such monomers is as bonding agents in latex-based paper coatings. The carboxylic acid comonomer forms a major component of water-soluble chains on the surface of the latex particle, providing both steric and electrostatic stabilization of the colloid (hence, "electrosteric stabilization"[2,3]). This surface coating of hydrophilic chains is often referred to as a "hairy layer". Typically, a small amount of the hydrophilic monomer is copolymerized with hydrophobic monomers such as styrene or butyl acrylate (BA). For a better control of latex synthesis and end-use properties, it is desirable to understand the effect these electrosteric stabilizers have on the rate of reaction and degree of secondary nucleation (formation of new particles in a semicontinuous seeded emulsion polymerization). A crop of small secondary particles can alter the film-forming and rheological properties of the product, making it less suitable for its intended applications; a reduced rate of reaction can lead to a buildup of monomer in a starve-feed semicontinuous polymerization that may adversely affect the resulting particle size distribution and copolymer composition.

Much experimental work has been done on the kinetic aspects of these copolymerizations, with the objective of predicting the copolymer composition, molecular weight distributions, reaction rate, particle size, and particle number.[4−8] Two of the important rate coefficients governing these quantities are those for entry of radicals into, and exit (desorption) of radicals from, particles. Mechanistic studies of emulsion polymerization have led to the development of quantitative models describing these processes for ionically stabilized latices.[9] As both entry and exit involve transport of radicals (or radical activity) between the particle and water phase, it is possible that the presence of an electrosteric stabilizer will bring about a significant effect on their mechanisms and rate coefficients compared to the situation with simple ionic stabilizers. The objective of the present paper is to extend knowledge of these processes for electrosterically stabilized particles.

Experimental techniques for obtaining the rate coefficients for entry and exit have been developed.[9] The methodology employs appropriate rate data in seeded emulsion polymerizations, wherein secondary particle formation is avoided, and thus the kinetics of particle growth can be separated from those of particle formation. Entry and exit rate coefficients can best be found with this methodology using particular types of rate data for so-called "zero−one" systems; an emulsion polymerization follows zero−one kinetics when intraparticle termination is not rate determining: i.e., when entry of a radical into a particle already containing a growing radical leads to instantaneous termination. Such systems always have an average number of radicals per particle ($\bar{n}$) less than $^1/_2$, although it is emphasized that having $\bar{n} \leq {}^1/_2$ is a necessary but certainly not sufficient condition for zero−one kinetics.[9] For a styrene seeded emulsion polymerization at 50 °C, it has been established both theoretically[10,11] and ex-

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perimentally[12] that this condition is fulfilled for particles of diameter below ~100 nm.

To compare like with like, the ideal experimental study would be a comparison between series of particles which are identical in every respect except the presence and extent of electrosteric stabilizer. In the present study, this is implemented using the technique of Coen et al.,[8] in which a seed particle is made with an ionic surfactant, and then a small amount of second-stage polymerization is carried out with acrylic acid and styrene monomers. The resulting increase in size of the seed is relatively small, and hence one can meaningfully compare entry and exit rate coefficients obtained for the parent ionically stabilized seed and for the electrosterically stabilized particles from this second step.

There are three possible ways in which an electrosteric stabilizer might affect entry and exit: changes in surface charge (which might change the rate coefficient for entry of a charged radical), changes in the viscosity in the interfacial region (which might slow the diffusion of an entering or exiting radical), and possible radical reactions (e.g., transfer of radical activity of an entering or exiting radical to a component of the electrosteric stabilizer). There have been numerous published results on such effects on the rate of emulsion polymerization. Adams et al.[13] reported no effect of surface charge on the rate coefficient for entry in a series of studies on ionically stabilized styrene particles, while Penboss et al.[14] provided data which suggested insignificant effects of the charge on the entering species. These results were subsequently used to develop what has become a widely accepted model for this process,[15] discussed later in the present paper. In a previous study,[8] the effect of electrosteric stabilization by a poly(acrylic acid) (pAA) stabilizer on entry and exit rates was examined for latices which were essentially the same except for being stabilized by either ionic surfactant or by an electrosteric stabilizer. In this early study, it was reported that entry and exit rate coefficients were reduced by an order of magnitude at neutral pH; there was no significant effect on the overall rate of polymerization, which was interpreted as being because the reported reductions coincidentally were of similar size. Teyssié and co-workers[16] found that the rate was increased when a charged block copolymer was used as surfactant in combination with an initiator of like charge; however, that work considered ab initio and not seeded polymerizations, making it difficult to isolate any effects of the stabilizer on mechanisms. Cheong and Kim[17,18] investigated the effect of surface charge derived from styrenesulfonate on the rate of seeded polymerization. They observed a reduction in rate and the occurrence of secondary nucleation as surface charge was increased. However, the particle sizes employed in that work were such that the system was probably above the zero−one limit.

In this article, a more detailed investigation of the pAA stabilizer system is undertaken involving variation of the degree of surface coverage, dependence on pH, surface characterization by conductivity titration, stability measurement, and particle size analysis by transmission electron microscopy (TEM). The electrosterically stabilized particles used in this study were made by a two-stage procedure[8] in which the parent polystyrene seed latex was swollen with styrene monomer and then polymerized in the presence of aqueous-phase acrylic acid. The pH was not adjusted in these experiments: acrylic acid polymerizes more rapidly at low pH[19] and at high pH the charges on the AA moieties would keep a much larger proportion of growing p(AA/styrene) chains fully solubilized and prevent it from grafting to the hydrophobic particle surface.

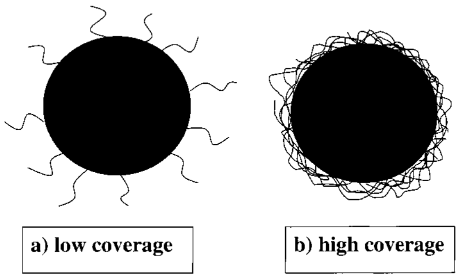

Figure 1. Schematic representation of low and high coverage of an electrosteric stabilizer. The high-coverage structure also depends on pH, the right-hand image representing the case of low pH with a contracted layer.

In addition to measurement of the entry and exit coefficients, surface characterization of the particles is performed to estimate the surface coverage of acrylic acid. The amount of charge on the particles was obtained from conductivity titrations and the colloidal stability was quantified through measurement of the critical coagulation concentration (CCC). The stability of carboxylic-acid-stabilized latices is expected to be pH dependent. The particles used in this work are not an ideal model system with well-defined surface characteristics but bear a close resemblance to electrosterically stabilized latices prepared in industry (i.e., by copolymerizing carboxylic acids with other monomers).

Two different particle size ranges are used, approximately 45 and 95 nm in diameter. For the smaller particles, the experiments can be done at high particle density and in interval 2 (polymerization in the presence of monomer droplets but without new particle formation) as the masses of polymer and added monomer are still relatively small. While it is essential for the methodology employed that secondary particle formation be avoided, the detection of secondary particles is difficult when they are of similar size to the seed. For this reason larger seeds with the same surface characteristics were made so that secondary particle formation could be more easily detected.

The effect of a hairy layer on the kinetics will depend on its structure (Figure 1). It is therefore instructive to consider the number of acrylic acid units necessary to create a dense layer on the surface of the particle that could capture radicals diffusing in and out of the particle. Entering radicals are assumed to be charged growing radical oligomers while exiting radicals are most likely monomeric species.[9] It is possible to calculate the surface charge density of a latex that contains 2 wt % of acrylic acid. For a diameter of 50 nm, this would result in a surface charge density of 23.5 μC cm^{-2} (or 6.8×10^{-19} m^2 per charge/acrylic acid unit). If all carboxyl groups were situated on the surface, this would amount to a dense layer. However, in a particle made as described here, the AA is mostly incorporated in long chains attached to the particle surface. Thus, even at 2 wt % incorporation of AA, a picture similar to that shown in Figure 1b emerges: if the pAA chains are close-packed on the surface, one might suppose that they offer no more impediment to the entry of a short radical than would happen with that radical in the interior of a particle, and simple calculations (using $r^2 = 6Dt$) show that this in turn is very rapid. That is, there is probably still enough space between the pAA chains for radicals to diffuse in and out of the particle unhindered. The immobilization of water by the pAA in the layer is unlikely to be strong enough to slow the transport of radicals in and out of the particle. While the macroscopic viscosity of polyacrylate gels differs significantly from that for aqueous solutions, this does not influence the diffusion coefficients of uncharged species (e.g., 4-hydroxy-TEMPO).[20,21] This is probably due to the existence of channels filled with the solution and trapped in the structure of the gel. Diffusion of small molecules in pAA gels of low concentration is controlled by the microscopic viscosity of the system, which is close to that of the solvent of the solution immobilized in the gel network.[21] The diffusion of small molecules in hydrogels has generally been found to decrease with increasing cross-link density and size of entering molecule.[22−24] However, the hairy layer around the particles considered here is not cross-linked and can only be effective on a microscopic scale if it has a high polymer volume fraction. Therefore, it is expected that radical diffusion through the pAA chains is not rate-determining for latices with low coverage. There would also be a charge repulsion effect at high pH but it has been reported that particles covered with different amounts of ionic surfactant behave identically,[13] although admittedly this study was for very limited systems. From this it was concluded that there is no electrostatic barrier of a charged species into a charged particle. Thus, a higher coverage than 2 wt % is required to give a "dense" layer of pAA (with thickness of several nanometers) that significantly impedes the transport of radicals across the particle interface (see Figure 1b). For this case a reduced rate of exit of uncharged radicals might be expected due to slow diffusion. The behavior of entering radicals is more complex since they are both charged and surface-active. With increasing pH the charge repulsion by the pAA chains of like charge increases and the hydrophobicity of the surface (necessary for adsorption) decreases. Both trends might reduce the rate of entry into the particle with increasing pH.

Particles with two degrees of coverage (5 and 15 wt % AA monomer, based on polymer weight) were prepared for this study. Since only a fraction of the AA used is incorporated into the particle due to termination in the aqueous phase, the amount of grafted AA was expected to be lower. The actual surface coverage and effect on stability were then measured experimentally.

Styrene as monomer and polystyrene as polymer were used because styrene is kinetically well characterized and polystyrene can be imaged by TEM without staining or deformation in the electron beam.

Theory

Theoretical Background for Deducing Rate Coefficients from Rate Data. The measurable rate of reaction R_p in a seeded emulsion polymerization is described by

$$R_p = k_p \frac{N_c}{N_A} \bar{n} C_p \tag{1}$$

where N_c = number of particles per unit volume of aqueous phase, N_A = Avogadro's constant, k_p = propagation rate coefficient, $\bar{n}$ = average number of radicals per particle, and C_p = monomer concentration in the latex particles. Equation 1 is used to obtain $\bar{n}$ from experimental rate data, for systems where N_c remains constant, i.e., a seeded emulsion polymerization in the absence of secondary nucleation. For styrene at 50 °C, $k_p = 2.6 \times 10^2$ dm^3 mol^{-1} s^{-1},[25] and the saturation value of C_p is 5.8 mol dm^{-3}.[12] It has been shown that for styrene most monomeric exiting radicals re-enter another particle and remain there (limit 2b).[9] One then has[9]

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

where ρ is the pseudo-first-order entry rate coefficient giving the number of entry events per particle per unit time (the sum of components derived from chemical or radiolytic initiation, $\rho_{\text{initiator}}$, and spontaneous or "thermal" initiation, ρ_{thermal}), and k is the rate coefficient for exit of monomeric radicals per particle. The value of k is obtained from the conversion/time data of the γ relaxation experiment. Radiolytically initiated polymerization can be switched on and off by removing the source; in a relaxation experiment the conversion as a function of time t from the in-source steady state to the out-of-source steady state is measured and fitted to eq 2 to yield k (and ρ_{thermal}), as described elsewhere.[9] The second and subsequent relaxations from the source will be free of inhibitor and equilibration artifacts.

The ρ value is then obtained from the steady-state value of $\bar{n}$ determined in the chemically initiated experiment, $\bar{n}_{ss}$, by using the value of k from the relaxation experiments together with the steady-state form of eq 2:

$$\rho_{\text{initiator}} + \rho_{\text{thermal}} = \frac{2k\bar{n}_{ss}^{\,2}}{1-2\bar{n}_{ss}} \tag{3}$$

Current Models for Entry and Exit. Extensive experimental data for electrostatically stabilized particles have supported the validity of the following models for the entry and exit rate coefficients.[9] The mechanism for exit in such systems has been found to be transfer to a monomeric radical which can either diffuse out of the particle through the water phase (with diffusion coefficient D_w) or propagate (with rate coefficient k_p^1), in which case it cannot exit. This yields[26]

$$k = \frac{3D_w}{r_s^{\,2}} \frac{k_{tr}}{k_p^1} \frac{C_w}{C_p} \tag{4}$$

where r_s is the swollen radius of the particle, k_{tr} the transfer rate coefficient, and C_w the monomer concentration in the water phase.

The mechanism for entry in an electrostatically stabilized latex involves the following aqueous-phase events:[15]

$$\text{initiator} \rightarrow \text{I}^\bullet \tag{5}$$

$$\text{I}^\bullet + \text{M} \rightarrow \text{IM}^\bullet \rightarrow\rightarrow \text{IM}_n^{\,\bullet} \longrightarrow \text{IM}_z^{\,\bullet} \tag{6}$$

$$\text{IM}_n^{\,\bullet} + \text{IM}_m^{\,\bullet} \rightarrow \text{termination}, \quad n,m < z \tag{7}$$

$$\text{IM}_z^{\,\bullet} + \text{particle} \rightarrow \text{entry} \tag{8}$$

Here M is a monomer unit in the water phase. The oligomer chains IM$_i$ either terminate in the aqueous

Table 1. Polystyrene Seed Preparation

	sample			
	PS1	PS2	PL1	PL2
water (g)	300	300	300	620
$NaHCO_3$ (g)	1	1	0.6	1
AMA80 (g)	14.4	7.45	4.01	11.35
styrene (g)	33	50	50	300
$K_2S_2O_8$ (g)	2	0.74	0.5	1
polymerization temp (°C)	80	85	85	85
d_N (nm)	36	42	85	94
d_W (nm)	38	44	86	96
polydispersity index	1.05	1.05	1.01	1.02

phase or continue growing to the length z at which they become surface active, enter a particle, and start the polymerization; step 8 is so fast as not to be rate-determining for electrostatically stabilized particles. If it is assumed that the propagation and termination rate coefficients in eqs 6 and 7 are independent of chain length and that the initial propagation step ($I^\bullet + M$) is also very fast, an analytical solution for $\rho_{initiator}$ can be found:

$$\rho_{initiator} = \frac{2k_d\,[I]\,N_A}{N_c}\left\{\frac{\sqrt{2k_d\,[I]\,k_{t,w}}}{k_{p,w}\,C_w}+1\right\}^{1-z} \qquad (9)$$

where [I] is the initiator concentration and k_d is its dissociation rate coefficient and the subscript "w" indicates the water phase. Note for later purposes that the mechanism given above, with step 8 being so fast as not to be rate-determining, implies that $\rho_{initiator}$ is independent of particle size *provided* that one is comparing systems with the same N_c and [I]. This apparently surprising result (implied by the theory) has been confirmed experimentally for electrostatically stabilized latexes,[8] and is reflected in the lack of size dependence in eq 9. Equations 4 and 9 will be used in this work to calculate benchmark theoretical values for comparison with the experimental ones. It has been shown that for polystyrene latices this model provides satisfactory agreement with experiment. The model can be quantitatively improved by allowing the water-phase propagation rate coefficients to vary with chain length for the first one or two monomer units, as is physically reasonable.

Experimental Section

Polystyrene seed latices were prepared following standard procedures.[13] Monomer, surfactant, and $NaHCO_3$ buffer (Table 1) were emulsified in a 1 L glass reactor equipped with a stainless steel stirrer. Sufficient water was retained for the initiator to be dissolved in a separate container, and the initiator was added after the temperature had reached the desired value. Heat evolution was observed as the temperature increased 10 min after addition of initiator. The reaction mixture was left at the appropriate temperature for approximately 4 h, upon which the conversion was determined gravimetrically and found to be ~100%. The latex was then dialyzed for 5 days against distilled water, and filtered through glass wool to remove any coagulum. Significant amounts of coagulation were observed when dialysis continued longer than 5 days. The electrosterically stabilized latices were made by grafting polymeric stabilizer onto the surface of the polystyrene particles (see Table 2 for the recipes). The general procedure was as follows: styrene monomer was allowed to swell the latex overnight in the presence of Aerosol-MA 80 (dihexyl sulfosuccinate) surfactant. The latex was then brought to the reaction temperature and AA was added, followed several minutes later by the initiator solution. To produce highly covered particles, the AA was added manually in fractions over 2 h (see Table 2), so as to keep the aqueous concentration of AA low in order to reduce homopolymerization. The reaction vessel was purged with nitrogen throughout the reaction. After 4 h the reaction was stopped and the product was dialyzed against deionized water for at least a week. No coagulation was observed on prolonged dialysis. Dialysis alone was used to purify the latices (except PLAL); ion exchange was only used to convert it into the H^+ form, as described by Blackley.[1]

Table 2. Synthesis of Electrosterically Stabilized Seeds

	sample			
	PSAL	PLAL	PSAH	PLAH
mass dry polymer (g)	4.8	4.95	4.3	6.8
seed name	PS2	PL1	PS2	PL2
N_c (10^{17} dm^{-3})	12	1.5	11	1.6
styrene (g)	1.4	1.8	6.7	5.53
AMA80 (g)	0.1	0.1	0.1	0.1
$K_2S_2O_8$ (g)	0.006	0.006	0.03	0.03
polymerization temp (°C)	50	50	70	70
AA (g)	0.35	0.3	2.2[a]	2[b]
d_N (nm)	46	94	52	104
d_W (nm)	49	95	57	105
polydispersity index	1.06	1.01	1.08	1.01

[a] Was added over 1.5 h. [b] Was added in two parts: 1 g at the start and the rest after 1 h.

Styrene (Fluka) was purified of inhibitor by running through a column filled with basic alumina. The monomer then was stored at 4 °C. Acrylic acid was kindly supplied by Nuplex Australia and was subjected to four freeze–thaw cycles to remove the inhibitor. Potassium persulfate, potassium chloride and Aerosol MA 80 (AMA 80, disodium dihexyl sulfosuccinate, National Starch and Chemicals) were used without further purification.

To measure the effect of the electrosteric stabilizer on kinetics, seeded emulsion polymerizations using the latices described above were performed and followed by automated dilatometry. These runs were done at 50 °C using persulfate or ^{60}Co-γ radiation as initiator. Latex, monomer, surfactant, and other additives (NaOH or HNO_3 to adjust the pH) were placed in the reaction vessel and left to swell the particles under ambient conditions for at least 8 h. The surfactant concentration in these recipes was below the critical micelle concentration (cmc) of the surfactant (10^{-2} mol dm^{-3} for AMA 80[27]). The mixture was then heated to slightly above the reaction temperature and degassed under vacuum. In chemically initiated experiments, the initiator was added as a solution in 1 mL of distilled water after the temperature was adjusted to 50 °C. For γ-relaxation experiments, the reaction mixtures were prepared in the same way without the addition of chemical initiator. In these experiments the system is allowed to reach a steady state in the source initiated by ^{60}Co radiation. The dilatometer is then removed from the source so that the initiation stops virtually instantaneously, and the system relaxes to a new steady state where the rate of reaction is determined by the rates of thermal entry and exit.

Figure 2 shows two individual relaxations from the γ experiments; $\bar{n}$ is plotted instead of conversion as this way of presenting the data is more sensitive to fluctuations. It can be seen that the system relaxes from the in-source steady state to another steady state, which is caused by thermal polymerization (recall the discussion of $\rho_{initiator}$ and $\rho_{thermal}$ above). From the postrelaxation steady state, it is possible to extract values for $\rho_{thermal}$. The exit rate coefficient to describe this process of radical loss from the particles is obtained from the corresponding conversion–time data. To see whether the experimental results can be well described by eq 2, a theoretical curve was generated by integration of that equation with the k and $\rho_{thermal}$ values obtained by data fitting (Figure 2). The agreement between the recalculated values of $\bar{n}$ and those obtained directly from experiment is satisfactory. For each run the vessel was reinserted into the source up to four times to obtain the exit rate coefficient for successive insertions.

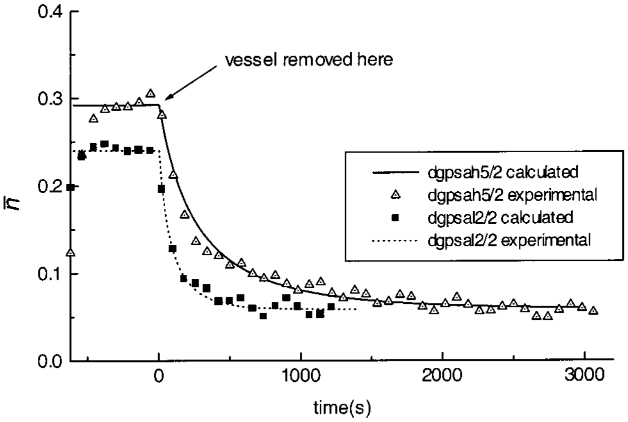

Figure 2. Two relaxations from the in-source to the out-of-source steady state in a γ-relaxation experiment; the vessel was removed from the source at $t = 0$ s (see arrow). The calculated curves were generated with values for ρ and k obtained from the relaxation data using the slope and intercept method.[9]

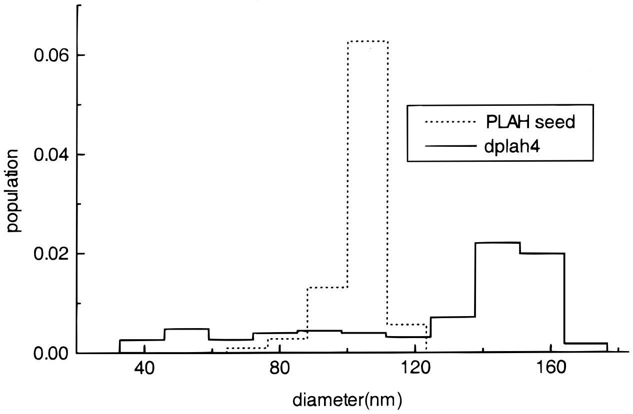

Figure 3. Normalized particle size distributions of the high-coverage large seed PLAH and the resulting latex after a kinetic run at high pH using that seed. Particles generated by secondary nucleation are clearly discernible.

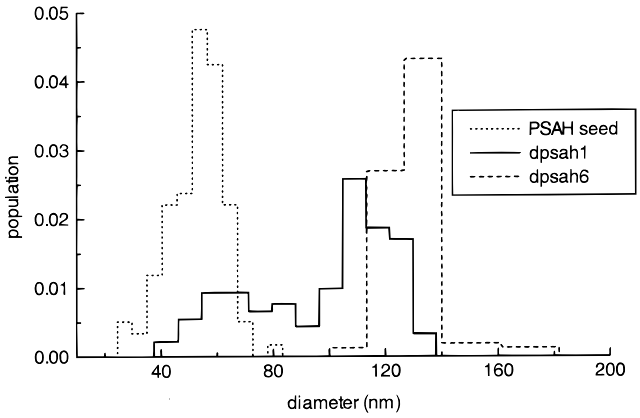

Figure 4. Normalized particle size distributions of the high-coverage small seed PSAH and the resulting latices after kinetic runs at high and low pH using that seed. At neutral pH there appears to be secondary particle formation while there is none at low pH.

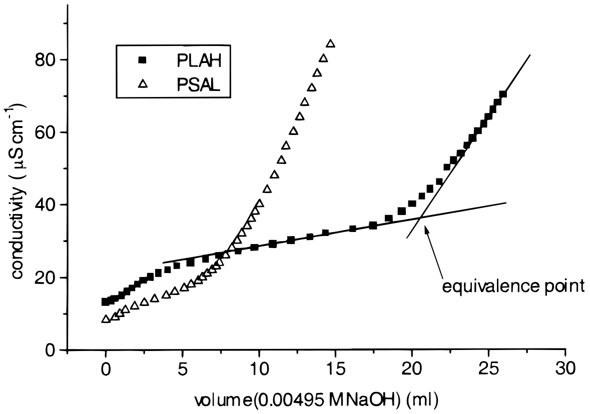

Figure 5. Conductivity titration curves of a low (PSAL) and high-coverage (PLAH) seed.

The amount of monomer chosen was such that the reaction started in Interval 2, i.e., monomer droplets were present at the beginning of the reaction. The particle density for small seed particles was high (above 10^{17} dm^{-3}) in order to avoid secondary particle formation and to give faster rates of polymerization and hence less fluctuation in the data. For the larger seeds the particle concentration had to be lower (about 2×10^{16} dm^{-3}) to operate in interval II.

The pH of the reaction mixtures was adjusted by adding dilute solutions of NaOH or HNO_3. All runs were performed at 50 °C.

Particle sizes distributions (PSDs) of the seeds and the resulting latices after the kinetic runs were obtained using TEM. Between 50 and 200 particles were counted for each sample and used for the calculation of the number- and weight-averaged diameters and the polydispersity. Secondary particle formation after a kinetic run was detected if the PSD was bimodal, i.e., an additional peak at small particle sizes was present. Other indications of secondary nucleation were broad particle size distributions (polydispersity >1.1) and lower than expected experimental diameter averages of the product latex; depending on how much the latex had grown, (secondary) particles smaller than the seed were also clearly visible in the TEM micrographs. In all cases used to extract rate coefficients, the distribution was unimodal. Figures 3 and 4 show normalized PSDs for some latices.

The surface charge was measured by conductivity titration using a conductivity meter (Extech) and a syringe pump (Kent Scientific Corp.). A known amount of latex was treated overnight with an excess of Dowex mixed-bed ion-exchange resin to convert it into the protonated form. After the latex was filtered off, it was titrated with 0.00495 M NaOH at approximately 0.5 wt % with the conductivity being measured. As acrylic acid is a weak acid, only a low proportion of protons are replaced by metal cations during titration as the pH increases. The electrical conductivity increases with progressive neutralization as the concentration of metal cations is being increased, with almost no change in the very low concentration of highly conductive hydrogen ions.[1] This behavior corresponds to the region of the curve having a small positive slope (unlike the conductivity titration of strong acids where the slope before the equivalence point is negative resulting in a V-shaped curve). When neutralization is complete, the positive slope increases, because the concentration of hydroxide ions as well as that of the metal cations is now increasing. Hence, the transition between the two slopes observed in the plot of conductivity as a function of volume of NaOH was taken as the equivalence point of the titration for particles with mostly weakly acidic groups on the surface (see Figure 5). Using the particle size and solids content previously determined that this value can be converted into the surface charge density. It is likely that strong acid groups were not visible because they were swamped by the large number of weak acid groups. The low charge is in agreement with theoretical considerations about the maximum amount of charges generated by the initiator when the low initiator efficiency of styrene is taken into account.

The stability against electrolyte was determined by time-dependent UV spectroscopy using the following standard procedure for determining the CCC. Constant volumes of dilute latex (solid content approximately 0.1 wt %) and electrolyte

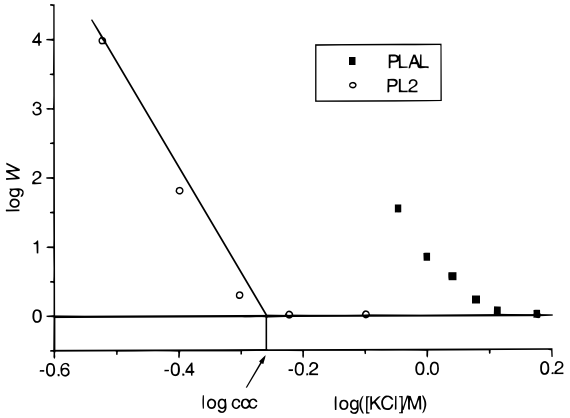

Figure 6. CCC measurement of a polystyrene seed (PL2) and of the large low-coverage seed (PLAL) which shows a higher CCC.

solution (KCl) were mixed in a spectrophotometer cell and the increase in turbidity followed at 680 nm. The initially linear slope of the turbidity vs time curves[28,29] at different electrolyte concentrations was used to obtain the transition from fast (diffusion-controlled) to slow coagulation. For the small particle sizes (about 45 nm diameter) it was not possible to measure the fast coagulation rate accurately due to its high rate. The slope of the turbidity vs time curve was estimated from the high turbidity value at the start of the measurement and the short time lag between addition of the electrolyte and data collection (about 1 s). However, the onset of slow coagulation could still be clearly seen. Plotting the stability ratio *W* (defined as the ratio of slow to fast coagulation rates) as a function of the electrolyte concentration in a double logarithmic plot allowed the CCC to be determined (Figure 6).

The pH of the latices was adjusted to 10 for the CCC measurements to ensure that all carboxyl groups were deprotonated, to give the maximum stabilizing effect. The ionic strengths after adjustment to pH 10 were found to be negligible compared to the CCC values. Some measurements at low pH were also carried out.

Results and Discussion

Surface Characteristics. Results for the surface characteristics of the AA stabilized latices are given in Table 3. It can be seen that a low coverage of pAA gives a significant increase in stability compared to the parent polystyrene latex, with CCCs approximately twice as high. The CCC for PL1 was not measured but is assumed to be in the same range as that of the other polystyrene latices. The particles with high AA content are more stable at high pH but much less stable at low pH. This is exemplified by the low CCC of PLAH at pH 3, well below that of the polystyrene latices. This may be due to bridging flocculation, as at low pH the pAA chains are protonated, become more hydrophobic, and can adsorb onto multiple particle surfaces: the adsorption of pAA onto oxide surfaces has been studied in relation to the use of pAA as flocculant.[30] It has been found that adsorption correlates with the positive (opposite) charge of the metal oxide.[31] However, some specific adsorption was also found at the isoelectric point of the oxide; this could also apply to the polymeric surface of the latex particles considered here. The steric stabilization effect is lowered at low pH because the solubility of pAA in water is less than at high pH.[1] While still swollen with water, pAA becomes insoluble when most of the carboxyl groups are protonated. A small degree of stability is provided by the remaining sulfate groups stemming from the initiator decomposition, although even these are partially shielded.

Table 3. Surface Charge and Colloidal Stability Data

sample	surface charge, μC cm^{-2}	CCC, mol dm^{-3}
PS1		0.48
PS2	0.6	0.51
PL2	0.2	0.6
PSAL	11.2	1.27
PLAL	5.6	1.25
PSAH	52	>1.5
PLAH	82	>1.5 (*p*H 10); 0.103 (*p*H 3)

The surface charge on the bare polystyrene latices was too low to stabilize the particle sufficiently: these latices showed coagulation when dialyzed for longer than 5 days. The amount of initiator used could not provide enough charges to stabilize the particle considering the low initiator efficiency of styrene.[15] The stability seen in the CCC measurement is therefore mostly due to surfactant still adsorbed on the surface rather than stemming from initiator-derived surface charge. The amount of surfactant still left on the particles can be calculated using the Langmuir adsorption isotherm. If sample PS2 (Table 1) is taken as an example, the amount of surfactant left on the particle surface after dilution for the CCC measurement can be calculated with the following parameters (equilibrium constant K and maximum coverage are the values for SDS reported by Ahmed:[32] total surface area = 6841 m^2, $K = 2350$ L mol^{-1}, and maximum coverage = 3.95×10^{-6} mol m^{-2}). If it is assumed that 1 g of surfactant is left after dialysis, the surface charge resulting from the adsorbed surfactant molecules changes from 3.65 to 1.87 μC cm^{-2} when diluted by a factor of 200. The exact amount of surfactant left after dialysis is not known but this calculation shows that dilution to a solids content of about 0.1% changes the amount of adsorbed surfactant by only a factor of 2.

From the surface charge values for the pAA-stabilized latices, it is apparent that the actual charge grafted onto the surface is only a small fraction of the amount of AA monomer actually polymerized in making the electrosteric stabilizer. The theoretical maximum for surface coverage is 72 μC cm^{-2} for PSAL and 120 μC cm^{-2} for PLAL. This means that between 5 and 10% of the AA used was incorporated in the surface of the seed. The rest of the AA presumably homopolymerized in the aqueous phase. The water-soluble polymer formed was then removed during dialysis. Slavinski et al.[33] examined the grafting of AA onto a polystyrene latex under conditions similar to those employed in this paper (70 °C, $\sim 2 \times 10^{16}$ dm^{-3} seed particles, 0.01 M persulfate, 0.077 M acrylic acid), and found that the amounts grafted varied between 36 and 57% at low pH. Since even less AA was found to have been grafted in the surface modification in our experiments, it is unlikely that free pAA was titrated under these conditions. While large chains may not be removed by diffusion through the pores of the dialysis tube, it was noted in the present work that no increase in viscosity was observed when the pH of the latex was raised. This is taken as evidence that there were only negligible amounts of high molar mass pAA in the latex serum. As a further check on the correctness of the interpretation adopted here, latex PLAL was subjected to ultrafitration using a membrane with a 50 nm pore size, which could be expected to be permeable to free pAA. Since the charge density obtained for PLAL was about the same as that of PSAL, it is concluded that the analysis of the dialyzed samples gave correct answers at the level of accuracy required

Table 4. γ Relaxation Experiments for Latices without Electrosteric Stabilizer (Small Particles: PS1, PS2; Large Particles PL1, PL2), with Low Coverage of Electrosteric Stabilizer (PSAL, PLAL) and with High Coverage (PSAH)

run	latex	pH	k_{exp}, s^{-1}	k_{calc}, s^{-1}	ρ_{thermal}, s^{-1}
Ionically Stabilized					
dgps15	PS1	6.5	0.032	0.039	0.000075
dgps24	PS2	6.5	0.033	0.027	0.000014
dgps28	PS2	3	0.030		0.000014
dgpl12	PL1	6.5	0.012	0.0066	0.00083
dgpl22	PL2	6.5	0.0052	0.0056	0.00039
Electrosterically Stabilized					
Low Surface Coverage					
dgpsal1	PSAL	6.5	0.021	0.024	0.000082
dgpsal2	PSAL	3	0.021		0.00015
dgpsal4	PSAL	10.5	0.015		0.000037
dgplal2	PLAL	6.5	0.0052	0.0054	0.00031
High Surface Coverage					
dgpsah0	PSAH	5.5	0.012	0.018	0.000037
dgpsah5	PSAH	4.2	0.0061		0.000055
dgpsah4	PSAH	10.5	(0.021)[a]		

[a] Secondary nucleation observed.

Table 5. Chemical Dilatometry Runs with Polystyrene Latices (No Electrosteric Stabilizer)

sample	N_{c}, 10^{17} dm^{-3}	[I], mM	$\bar{n}$ exp	$\bar{n}$ calc	$\rho_{\mathrm{initiator}}$, s^{-1}	ρ_{calc}, s^{-1}
PS1	4.5	0.52	0.083	0.088	0.00046	0.00073
	4.5	2	0.15	0.13	0.00183	0.0018
	2.1	11	0.23	0.26	0.00623	0.011
PS2	1.7	0.59	0.24	0.17	0.0071	0.0023
	1.6	9.6	0.30	0.30	0.015	0.013
PL1	0.4	1.0	0.39	0.41	0.0162	0.013
PL2	0.25	0.95	0.45	0.45	0.019	0.020

Table 6. Chemical Dilatometry Runs with Latices Prepared with 5 wt % AA (Low Surface Coverage)

run	sample	pH	N_{c}, 10^{17} dm^{-3}	[I], mM	$\bar{n}_{\mathrm{exp}}$	$\bar{n}_{\mathrm{calc}}$	$\rho_{\mathrm{initiator}}$, s^{-1}	ρ_{calc}, s^{-1}
dplal1	PLAL	6.5	0.18	0.48	0.49	0.44	0.125−0.02	0.017
dpsal1	PSAL	6.5	1.94	0.95	0.24	0.19	0.0045	0.0026
dpsal2		3	1.94	0.61	0.18	0.16	0.0021	0.0019
dpsal3		10.5	1.95	0.60	0.22	0.16	0.0027	0.0019

for interpreting the kinetics. Reinforcing this interpretation is the observation that AA partitions into the particle at low pH to some extent[34] and can polymerize there. In the case of the high coverage latices, unreacted AA may also be present (individual monomer conversions after the surface modification were not measured).

The experimental surface charge values for the highly covered samples may underestimate the degree of coverage, because not all charges are equally accessible in a titration. The buried carboxyl groups closer to the surface are more difficult to titrate than those on chains extended into solution in a direct titration starting at acidic pH.[35]

Rate Coefficients. Tables 4−8 and Figures 7−10 give the rate coefficients for entry and exit for the electrosterically stabilized latices, together with those for the uncovered polystyrene latices for comparison. The experimental ρ values in Tables 5−7 have been converted to $\rho_{\mathrm{initiator}}$ by subtracting ρ_{thermal}. Calculated values for $\rho_{\mathrm{initiator}}$ are also given in Figure 8. While experimental uncertainties are not quoted for any of these quantities, since each is the result of an individual measurement rather than repeated measurements on the same sample, the scatter in data points in the figures gives an indication of the uncertainty.

Table 7. Chemical Dilatometry Runs with Latices Prepared with 15 wt % AA (High Surface Coverage), with ρ and $\bar{n}$ Values

run	sample	pH	N_{c}, 10^{17} dm^{-3}	[I], mM	$\bar{n}_{\mathrm{exp}}$	$\bar{n}_{\mathrm{calc}}$	$\rho_{\mathrm{initiator}}$, s^{-1}	ρ_{calc}, s^{-1}
dpsah3	PSAH	4.0	2.24	8.0	0.38	0.30	0.0078	0.0083
dpsah6	PSAH	4.4	0.72	8.0	0.44	0.39	0.019	0.026
dpsah7	PSAH	5.1	0.73	0.73	0.34	0.27	0.0042	0.0058
dpsah9	PSAH	4.3	0.73	0.75	0.40	0.28	0.0098	0.0061

It is apparent that the ρ values for latex PS2, which is “uncoated” (i.e., only electrostatically stabilized), are higher than those for the other polystyrene latices and for the pAA-stabilized latices with low coverage. This is presumably due to a slight overestimate of the particle size resulting in an underestimation of the particle number and hence an increase in the calculated apparent $\bar{n}$. (There is always an uncertainty when measuring very small particle sizes; with small particles a typical deviation of 1 or 2 nm in the average diameter can result in a significant change in N_{c} and $\bar{n}$.) This difference cannot be due to the slightly larger size of the latex (see eq 9 and ensuing discussion thereafter). Apart from this, the entry and exit coefficients are in good agreement with theory and with experimental values obtained for similar particles.[9]

The values of ρ and k were compared with those expected from theory, eqs 9 and 4, with the following parameters, all of which have been determined from independent experiments as referenced: $D_{\mathrm{w}} = 1.5 \times 10^{-5}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$,[36] $D_{\mathrm{mon}} = 1.3 \times 10^{-5}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$,[37] $C_{\mathrm{w}} = 4.3 \times 10^{-3}$ M,[38] $k_{\mathrm{tr}} = 9.3 \times 10^3\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$,[39] $k_{\mathrm{p}}^1 = 1.2 \times 10^3\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$,[9] $k_{\mathrm{p}} = k_{\mathrm{p,w}} = 260\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\mathrm{s}^{-1}$,[25] $k_{\mathrm{t,w}} = 4 \times 10^9\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$,[9,15,40−42] $C_{\mathrm{p}} = 5.8$ M,[12] $w_{\mathrm{p}} = 0.35$ (in Interval 2, this value of w_{p} follows by mass conservation from the value of C_{p}[9]), $z = 2$,[15] and $k_{\mathrm{d}} = 1.2 \times 10^{-6}\ \mathrm{s}^{-1}$.[43] The calculated values of ρ and k are given in Tables 4 and 5 and in Figures 7−9.

Tables 4 and 6 show the data for latices with low surface coverage of pAA. It is evident that the rate coefficients for exit and entry at the same pH values are essentially the same as those obtained for the polystyrene seed stabilized only by initiator fragments and adsorbed surfactant. For both types of particle surface the experimental $\bar{n}$ and ρ values are in agreement with the theoretical predictions of the ab initio model. A low coverage apparently stabilizes the particles but does not affect the transport of radicals in and out of the particles. The value of ρ for run dplal1 (seed PLAL, Table 6), however, shows a large deviation from the theoretically predicted value. This is probably because in a system where $\bar{n}$ is close to 0.5, there is considerable uncertainty in the experimental value of ρ inferred from a value of k and the experimental $\bar{n}$ (see eq 3). The agreement in $\bar{n}$ is satisfactory but the value of ρ inferred from eq 3 varies between 0.125 and 0.02 with a 10% uncertainty in the value of $\bar{n}$.

The value of k for the small, high-coverage particles (PSAH) was measured in the γ relaxation experiment at different pH, but secondary nucleation was avoided only at low pH. Because of this occurrence of secondary nucleation, no data could be obtained for k for pHs of 8 and 10. Kinetic parameters for the larger size latex (PLAH) could not be used because the $\bar{n}$ values inside the γ-source were slightly above 0.5, indicating that the system was no longer zero−one. This is in accordance with the radius measurement of 52 nm, slightly above

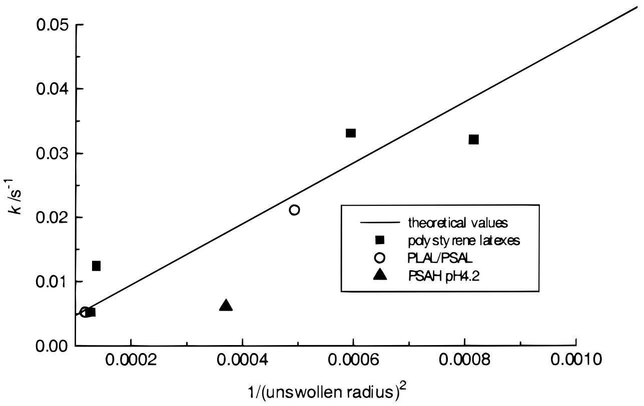

Figure 7. Exit rate coefficients k obtained from γ relaxations, and calculated values from eq 4 with parameter values given in the text.

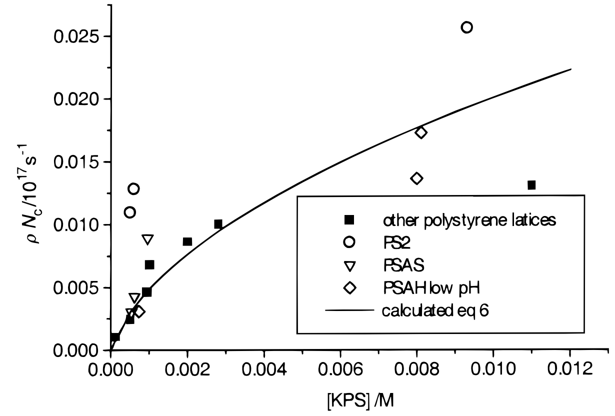

Figure 8. Product of $\rho_{\mathrm{initiator}}$ and particle density. Equation 9 shows that plotting $\rho_{\mathrm{initiator}}N_c$ enables runs done at different N_c values to be compared. The theoretical values were calculated with eq 9 and the parameter values given in the text.

the zero–one limit for styrene of about 50 nm at 50 °C.[10,11] At low pH the apparent value of k was less than the theoretical value, while at high pH, secondary nucleation was observed, similar to what occurred with latex PSAH.

The exit rate coefficient of the PSAH latex decreased as the pH was lowered toward the pK_a of AA (see Figure 9). This is in accord with the possibility, discussed above, that the pAA layer would result in significantly reduced rates of diffusion of the exiting radical.

It is not clear if this reduction becomes even greater at lower pH values. At pH 3 a very low steady-state rate was observed in the γ source and no exit rate coefficient could be measured. The same observation was made in chemical runs at pH 3 for both particle sizes. Experiments with a bare polystyrene seed (to exclude the possible effect of low pH on initiator decomposition) and ab initio (unseeded) runs in the presence of pAA homopolymer (to exclude the possible effect of dissolved pAA on the propagation of oligomers) both gave much higher reaction rates. The most likely reason for the low rate at pH 3 is aggregation of the latex particles, greatly reducing the effective particle number. Evidence for this is given by large aggregates clearly visible in TEM micrographs of the samples (swollen with monomer for 10 h) before and after dilatometry runs at low pH. Such aggregates were not observed after runs under any other conditions. The latices after these experiments did not appear to be coagulated completely with the formation of large flocs of coagulum, the coagulation or coalescence of the swollen particles occurring only up to a certain aggregate size. This agglomeration under the influence of a good solvent for the polymer is well-known and indeed has been used to increase the average size of latices to improve flow behavior at high solid content.[1] The agglomeration stops at a certain particle size when enough stabilizer is present to cover the reduced surface area of the latex. These observations support the low value for the CCC that was found for PLAH at pH 3.

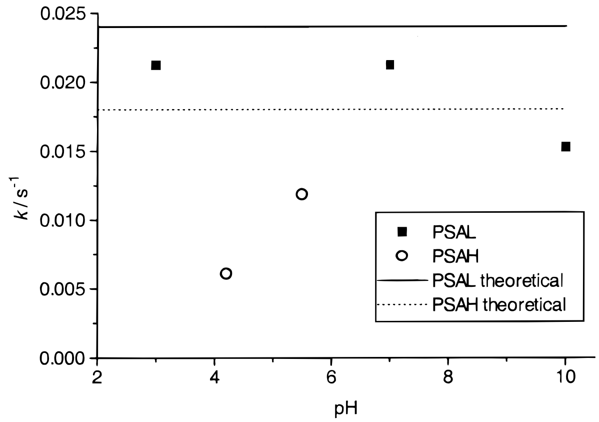

Figure 9. Exit rate coefficients as a function of pH for the small low-coverage (PSAL) and small high-coverage latices (PSAH). Calculated values are those predicted from eq 4 (recall this equation gives reliable predictions for latices which are ionically stabilized—see Figure 7).

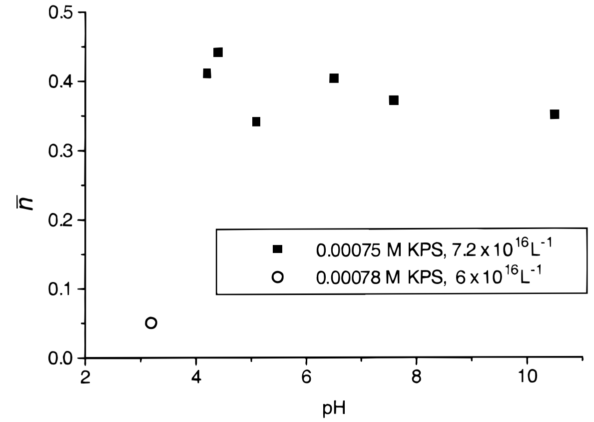

Figure 10. Apparent $\bar{n}$ values as a function of pH for the small high-coverage latex (PSAH). These $\bar{n}$ values only serve to illustrate the rate of polymerization as a function of pH.

Exit appears to be slowed in these systems, but this is only measurable at low pH when entry is fast enough for secondary particle formation to be avoided. Entry does not seem to be slowed at low pH. There is a slight decrease in ρ at low pH (see Table 7, cf. the polystyrene data in Table 5) but the apparent $\bar{n}$ values increase slightly as pH is lowered (see Figure 10). It must be emphasized that the $\bar{n}$ values in runs with secondary nucleation (see Table 8) are not true values but only measures of the rate of reaction. Since the overall rate of reaction decreases at higher pH despite a higher particle number, the entry rate coefficient must be lower. However, a possible reduction in the adsorption of the growing oligomers (i.e., lower entry rate coefficient due to the increasingly hydrophilic surface and reduced tendency of the surface active oligomer to adsorb) was reflected only in a slightly lower rate of reaction at high pH. The effect of the pAA layer appears to be stronger

Table 8. Chemical and γ Dilatometry Runs with Latices Prepared with 15 wt % AA (High Surface Coverage), Secondary Nucleation Data[a]

run	sample	pH	N_c, 10^{17} dm^{-3}	[I], mM	$\bar{n}_{exp}$	secondary nucleation	d_N, nm	d_W, nm	polydispersity	d_{th}, nm
dgpsah0	PSAH	5.5	1.4	(γ)		no	92	97	1.06	91
dgpsah4		10.6	1.1	(γ)		yes	66	80	1.21	81
dgpsah5		4.2	1.1	(γ)		no	97	105	1.08	101
dgplah0	PLAH	10	0.26	(γ)		yes	103	121	1.17	130
dgplah1		4.4	0.25	(γ)		no	140	142	1.02	143
dpsah1	PSAH	6.7	1.16	7.7	0.38	yes	97	112	1.15	113
dpsah3		4.0	2.24	8.1	0.38	no	104	106	1.02	100
dpsah4		8.5	0.71	11	0.42	yes	126	134	1.07	130
dpsah5		3.4	0.60	7.8	0.05	coalescence				
dpsah6		4.4	0.72	8.0	0.44	no	128	129	1.01	124
dpsah7		5.1	0.73	0.73	0.34	no	126	131	1.04	125
dpsah8		7.6	0.73	0.75	0.37	no	124	127	1.03	127
dpsah9		4.3	0.70	0.70	0.41	no	136	140	1.02	138
dpsah10		10.5	0.74	0.74	0.35	yes	126	134	1.07	137
dpsah11		6.5	0.70	0.77	0.403	no	137	145	1.05	138
dplah1	PLAH	2.9	0.27	0.96	0.05	coalescence				
dplah2		10.5	0.24	0.93	0.58	yes	121	139	1.15	175
dplah4		9.5	0.24	0.11	0.35	yes	125	146	1.16	165
dplah8		2.6	0.25	1.1	0.05	coalescence				
dplah9		4.2	0.29	2.9	0.53	no	194	198	1.02	199

[a] The $\bar{n}_{exp}$s in this table are apparent values calculated under the assumption that the particle number does not change.

for exit than for entry for sample PSAH at low pH. Now it will be recalled that exit and entry are fundamentally different processes. The former involves an uncharged monomeric radical and the latter an oligomeric species with (in the present case) a sulfate end group. The diffusion of the z-meric oligomer may be slowed but this would have no effect on entry because it is not the rate-limiting step of the entry process. It is also possible (although unlikely) that there is a reduction in the entry rate coefficient which is less apparent than that for the exit, due to an overestimate of the particle size.

These results seem to contradict those published in a preliminary study from this group[8] on pAA electrosterically stabilized particles, where reduced exit rate coefficients were reported at neutral but not at low pH, and where there was a large reported reduction for the equivalent of low-coverage systems, an effect not found here. The procedure was similar to that used to produce the low-coverage particles in the present study, although since the surfaces of the latices used in that study were not characterized by CCC or by surface charge, it is difficult to say how they compare with those used here. However, the steady-state chemically initiated rates found by Coen et al.[8] were the same as those for the polystyrene particles without electrosteric stabilizer, consistent with the results given here for low surface coverage. It is also worth mentioning that the check for secondary nucleation was done using CHDF (capillary hydrodynamic fractionation) and not TEM. Small secondary particles in the presence of larger ones are difficult to pick up by the UV detector used in the CHDF instrument because of their small extinction cross section.[44] In addition, close examination of the actual relaxation data of Coen et al. reveals that there was a high uncertainty in the values of the exit rate coefficient for coated particles, and the large effect of electrosteric stabilizer reported in this earlier work might in actuality not be significantly different from uncoated ones, within this uncertainty.

Secondary Particle Formation. To assess the extent of secondary nucleation and coalescence, the measured number- and weight-average particle sizes were compared with theoretically calculated diameters for the respective final conversions. For these calculations a monodisperse seed latex was assumed. Broader polydispersities and smaller experimental particle sizes than expected were taken as an indication of secondary particle formation. This is evident in runs done at high pH (e. g. dpsah10) and/or high initiator concentration (dpsah4, dpsah1). In the runs done with the larger seed (PLAH), a secondary population of small particles was easily distinguishable with TEM. The experimental diameters are also much smaller than the theoretical ones for these experiments. On the other hand, polymerizations with the smaller seed gave a broad distribution with smaller than expected averages but no easily distinguishable population of small particles. The extent of secondary particle formation observed in this work was such that the number of particles thought to have formed during the kinetic run was 50% or less of the primary particle number.

Secondary nucleation in systems below the cmc is thought to occur by homogeneous nucleation:[45,46] z-mers in the aqueous phase propagate to higher chain lengths instead of entering a particle until they reach a critical chain degree of polymerization, j_{crit}, whereupon they become insoluble and form precursor particles that grow into latex particles. While secondary nucleation was clearly observed in this work, no significant reduction was found in ρ in those runs with constant particle number. Another reason for increased secondary nucleation as pH is raised could be that added or in situ surfactant building up during the run is adsorbed to a lesser extent than at low pH (note that while the system always remained below the cmc, there was some added surfactant present in the kinetic runs to emulsify the monomer). While it has been shown that charge repulsion of the negatively charged oligomers by different amounts of adsorbed surfactant does not result in reduced entry rate coefficients,[13] there may be stronger repulsion with a partially ionized pAA layer extending into space.

The same trend as with PSAH was observed in the case of the larger seed (PLAH): secondary nucleation was present at neutral or high pH but did not occur under acidic conditions. Table 8 contains some data for chemical runs that illustrate this situation. Similarly, in γ-runs with this latex, no particles were formed at low pH while the particle number did not remain constant at high pH. These runs are not included as the system was not governed by zero−one kinetics, making extraction of ρ and k from the data much less unambiguous.

It is conceivable that primary particles could still be formed in the systems where no secondary nucleation is observed and that these colloidally unstable primary particles then flocculate onto preexisting seed (akin to the "colloidal entry" mechanism which has been proved[13] to be inapplicable to simple anionically stabilized systems). However, there is no reason to assume that primary particles formed under acidic conditions would be less stable than at high pH (they should be stabilized by strongly acidic sulfate groups derived from initiator); the levels of added surfactant and ionic strength would be similar in both cases. If colloidal entry were operative at low pH, it would then also happen at high pH instead of secondary particle formation; however, this is contrary to observation. This reasoning reinforces the conclusion that reduced entry/oligomer adsorption at high pH is the reason for secondary nucleation.

Conclusions

Electrosterically stabilized latices with different amounts of stabilizer on the surface were prepared by grafting pAA on a swollen polystyrene seed using 5 or 15 wt % acrylic acid to give two levels (high and low) of surface coverage.

The systems used for kinetic analysis were zero−one systems (termination was not rate determining). Initiation was either by persulfate or γ-radiation; the latter allows the direct measurement of radical loss from the particles. Surface titration was used to determine the surface charge densities. The CCC was measured to assess stability toward electrolyte.

Significant differences were observed between low-coverage (charge densities below 12 μC cm^{-2}) and high-coverage (above 50 μC cm^{-2}) particles. Neither the entry nor exit rate coefficients, and hence, the overall rates of seeded emulsion polymerizations are greatly affected by the presence of a low-coverage grafted pAA layer. For high-coverage particles, there is a significant reduction in exit, but not of entry, at low pH (i.e., below pH 5, when the electrosteric stabilizer is not fully ionized). Such electrosteric stabilization also has an effect on secondary particle formation, depending on the amount of stabilizer and the pH.

The low-coverage latices showed increased stability toward electrolyte at high pH but no difference in their polymerization kinetics compared to the polystyrene latices. The surface coverage of pAA is not dense enough to slow the transport of radicals across the particle interface of these latices. This result is in agreement with consideration of the structure of the hairy layer. For this degree of coverage no effect of the electrosteric stabilizer is expected as far as secondary nucleation and rate of reaction are concerned.

The high-coverage latices on the other hand were very stable at high pH (for which the CCC was above 1.5 M in KCl) but much less stable than a polystyrene seed at low pH. They also exhibited a significantly reduced exit coefficient and a slightly reduced entry rate at low pH compared to bare polystyrene particles. At pH 3, a very low rate of polymerization was observed that could be shown to be due to coalescence of the latex to aggregates; i.e., the effective particle number was very low. For pH > 6, no kinetic parameters could be measured, as secondary particle formation occurred under those conditions. However, despite an increase in particle number, a somewhat reduced rate of reaction was found at high pH that can be explained by a reduced rate of entry of charged surface-active oligomers into the highly charged poly(acrylic acid) stabilized latices at high pH. Another possible reason for the observed secondary nucleation is reduced adsorption of added and in situ surfactant onto the charged particles at high pH. This is consistent with the idea that at high pH the surface of the pAA-covered particles is very hydrophilic and therefore less attractive for the surface-active oligomers.

An interesting area for future research could be the investigation of the effect on the kinetics of a layer of grafted poly(ethylene glycol) chains. Such stabilizers can be made with well-defined chain length, e.g., by using poly(ethylene glycol) chains capped with polymerizable acrylate units as comonomers. Another potentially interesting system would be latices covered by a layer of cross-linked poly(N-isopropylacrylamide). Such a system would be more like a core−shell particle where the radicals would have to diffuse through the gellike shell into the core.

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