

Colloidal Stability of High-Solids Polystyrene and Polyvinyl Acetate Latices

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ABSTRACT: Commercial emulsion polymerization processes are often done with high-solids recipes (e.g., about 50 wt % monomer), resulting in relatively viscous, pseudo-plastic reaction mixtures. The change in rheological behavior during high-solids emulsion polymerization complicates the operation in terms of imperfect mixing, increasing heat transfer resistance and reactor fouling. In this article, we report the influence of solids content on the colloidal stability of polystyrene (PS) and polyvinyl acetate (PVAc) latex systems. For the systems investigated, solids content up to 50 wt % had no influence on the colloidal stability of the latex. The influence of recipe on colloidal stability is more pronounced than the influence of operating conditions. Brownian coagulation dominates over shear coagulation for both low- and high-solids systems, although in some cases the operating conditions appear to have some effect on the course and outcome of high-solids emulsion polymerization. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1780–1791, 1999

Key words: colloidal stability; styrene; vinyl acetate; high-solids emulsion polymerization

INTRODUCTION

Industrial emulsion polymerization is usually performed with high-solids recipes. One advantage of producing high-solids latices is that there is little or no need to remove water after polymerization¹ when the latices are applied as such. However, the production of high-solids latices is more complicated than low-solids latices in terms of the rheology and flow of the reaction mixture.² Even though coagulation phenomena have been studied extensively, little attention has been paid to coagulation in complex high-solids latex systems in stirred tanks under reaction conditions.³ Building on an earlier article on the coagulation

behavior of 25 wt % latex systems,⁴ this article reports the results of an experimental study on the colloidal stability of high-solids polystyrene (PS) and polyvinyl acetate (PVAc) latices.

Colloidal Stability

In emulsion polymerization with ionic surfactants, colloidal stability of the polymer particles in the latex system is governed mainly by electrostatic repulsion. If the surface charge density falls below a critical value, then the colloidal stability of the system is lost, leading to coagulation of the latex particles. Previous work performed in our laboratory⁴ revealed that physicochemical factors related to the emulsifier and electrolyte concentration completely govern the colloidal stability of electrostatically stabilized latex systems in stirred tanks. No influence was observed on pro-

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cess conditions in terms of scale, tank configuration, impeller speed and type, and energy dissipation. The results point to Brownian coagulation as the dominating mechanism for coagulation. In this article we report the differences in colloidal stability of high-solids PS and PVAc latices. The experimental results are discussed in terms of adsorption of emulsifier onto polymer particles, as well as steric stabilization.

Adsorption of Emulsifier on Latex Particle Surfaces

The adsorption of emulsifier on the surface of polymer particles often governs the stability of the latex system.⁵ The area occupied by one emulsifier molecule, A_E [$\text{m}^2/(\text{mol emulsifier})$], is affected by the emulsifier used, temperature, electrolyte concentration, particle size, and nature of the polymer surface.⁶ According to Gu et al.,^{7,8} surfactant adsorption differs for low and high surface concentrations of emulsifier. At low surface concentrations, the emulsifier is adsorbed through emulsifier particle surface interactions. Single emulsifier molecules adsorb on the particle surface.⁹ At higher surface concentrations, hydrophobic interactions of the adsorbed surfactant molecules come into play.⁸ The emulsifier molecules adsorb cooperatively,⁹ favoring so-called surface micellization.⁷ The adsorption isotherm of emulsifier on the surface of latex particles can take various forms, including Langmuir (L type), S-shaped (S type), and LS type.⁷ The adsorption of sodium dodecyl sulfate on PS particles obeys Langmuirian behavior,⁵ whereas the adsorption isotherm for PVAc latices is of the S type, characteristic of adsorption on a porous substrate or absorption of emulsifier by the substrate.^{5,10} For polymerization of polar monomers, the polar groups of macromolecules near the particle surfaces tend to orient toward the aqueous phase,^{10,11} and so they also act as stabilizers.

The A_E value of a particular surfactant in a latex system depends strongly on the nature of the polymer particle surface.^{12,13} A_E increases with increasing polarity of the particle surface.¹²⁻¹⁵ As polarity of the polymer surface increases, the density of the adsorbed emulsifier on the particle surface decreases, resulting in decreased colloidal stability.¹⁶ The higher the polarity of the polymer particle surface, the stronger the mutual affinity between the emulsifier molecules themselves as compared to the affinity between the surfactant and the particle surface.⁶

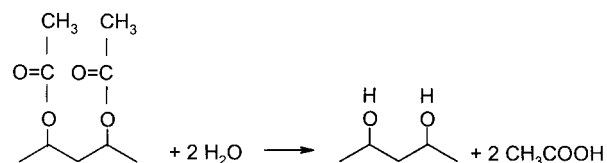


Figure 1 Schematic view of the hydrolysis of vinyl acetate groups into vinyl alcohol groups and acetic acid.

Despite the diminished stabilization by the surfactant, polar polymer particles may exhibit self-stabilization due to the orientation of the polar groups of the polymer at the particle surface.¹³

Steric Stabilization

In addition to electrostatic stabilization originating from the anionic emulsifier used, PVAc particles may also exhibit steric stabilization. At the surface of the PVAc particles, partial hydrolysis of acetate groups into hydroxyl groups may occur, as shown in Figure 1. The partially hydrolyzed PVAc at the particle surface shows some resemblance to the PVAc (anchor polymer) used in combination with polyvinyl alcohol (stabilizing moiety) to provide steric stabilization in aqueous dispersions, as discussed by, for example, Napper¹⁷ and Blackley.¹⁸

Steric stabilization of colloidal particles is governed by macromolecules that are chemically or physically attached to the particle surfaces.^{17,19} Steric stabilization has both entropic and enthalpic (osmotic) origins.²⁰ The steric interaction energy can be regarded as the sum of the volume restriction interaction, caused by the loss of configurational freedom of the attached chains, V_{fr} , and the osmotic interaction, which results from an increase in the local concentration of attached chains close to the particle surface, V_{os} .^{21,22} The combination of electrostatic and steric stabilization is often referred to as *electrosteric* stabilization.^{19,21} The overall potential energy is assumed to be the sum of all attractive and repulsive contributions²¹:

$$V_{tot} = V_{VDW} + V_E + V_S = V_{VDW} + V_E + V_{fr} + V_{os} \quad (1)$$

where V_{VDW} is Van der Waals attraction, V_E is electrostatic repulsion, and V_S is steric repulsion.

Steric stabilization requires that the attached stabilizing molecules (e.g., macromolecular chains) have certain characteristics:

- The macromolecules should form a layer thickness δ , for which the distance 2δ is sufficient to substantially reduce the effect of the Van der Waals attraction.²³
- The macromolecular layer should have sufficient density to provide steric interference.¹⁸
- One end of the macromolecules must stay firmly attached to the surface.²³
- The macromolecular chains should be sufficiently solvated by the dispersing medium¹⁸ for emulsion polymerization mixtures, the water molecules of the continuous phase.

The various types of steric stabilizers include nonionic surfactants, random coil polymers, linear block copolymers, brush copolymers, grafted polymer chains, and globular molecules.²³ For steric stabilization, the orientation as well as the degree of surface coverage of the attached chains are both important.^{20,21} In the case of vinyl alcohol segments on PVAc particles, the polymer chains are irreversibly bound to the surface. For terminally attached isolated chains, two limiting cases are considered: the “mushroom” structure and the “pancake” structure, where the chain revisits the surface.²⁴ When the average chain density on the surface increases and chain overlap occurs, the structure becomes stretched into a brush.^{19,24} Romero-Cano et al.²¹ studied the colloidal stability of PS particles with polyethylene oxide chains on the surface as steric stabilizers. Their results point to a conformational change resulting in an extension of the chains when the chain length of the surfactant molecules increases. This conformational change gives improved colloidal stability due to the greater distance between the chain end and the particle surface. Romero-Cano et al.²¹ also found that a more hydrophobic surface provides a more extended conformation, resulting in better colloidal stability. According to Walker and Grant,²⁰ both chain length and flexibility affect the conformation of the macromolecules at the particle surface and thus the colloidal stability of the system. Liu et al.²⁵ studied the colloidal stability of PS particles synthesized with macromonomer polyethylene oxide as a polymerizable stabilizer and found that only a small fraction of the particle surface need be covered with macromolecules to provide sufficient steric stability of the latex system.

Steric stabilization also depends on the relative size of the PVAc particles as compared to the size

of the stabilizing vinyl alcohol segments.^{20,23} Only if the particle size is considerably larger than the radius of gyration of the macromolecules will steric stabilization occur.

Electrostatic and steric stabilization differ in several ways:

- Sterically stabilized dispersions are relatively insensitive to the presence of electrolyte as compared to electrostatically stabilized systems.¹⁷ Steric stabilizers can be effective at high electrolyte concentrations where electrical double layers are shielded to such an extent that they are almost unable to provide colloidal stability.¹⁸ However, when the polymer chain is charged and/or the particle surface carries a charge, both electrolyte and pH become important for the electrosteric stability (both electrostatic and steric interactions) of the colloidal system.^{20,24}
- Steric stabilization is more sensitive than electrostatic stabilization to temperature.¹⁸
- Steric stabilization is usually equally effective at either high or low solids content.^{17,26} Due to the interactions between the charge clouds of the electrical double layers surrounding the particles, increasing the solids content leads to a considerably more pronounced increase in viscosity for electrostatically stabilized latex systems than for sterically stabilized latex systems.
- When the interparticle distance decreases (by an increase in solids content), steric repulsion begins quite suddenly, whereas electrostatic repulsion operates over rather long distances.²³ There is little steric repulsion between the attached chains on different particles when they are far apart; but once the layers approach each other, a sudden increase in the repulsion force occurs.

High-Solids Emulsion Polymerization

Typical recipes for commercial emulsion polymerization processes contain 50 wt % of monomer, resulting in a high-solids latex product. In contrast with low-solids emulsion polymerization, the apparent viscosity of the reaction mixture increases significantly with conversion during high-solids emulsion polymerization in a batch process. The product is a viscous pseudoplastic latex.² The difference between high- and low-sol-

ids polymerization is due to the higher final solids content (50 wt % versus, e.g., 15wt % of polymer), as well as a greater increase in solids content during *ab initio* emulsion polymerization.

Considering the colloidal stability of high-solids latices, the average interparticle distance becomes an important factor in the interaction between two particles.²⁷ At high solids content, the classical DLVO (Deeaguin, Landau, Verwey, Overbeek) theory is no longer applicable,²⁸ and multiparticle interactions must be taken into account.²⁹ The presence of particles surrounding two interacting particles reduces the total interaction energy between the latter and thus increases the probability of coagulation.²⁸

Reactor Fouling

Reactor fouling often occurs during high-solids emulsion polymerization at about 60–70% conversion.² Two types of fouling can be distinguished: coagulum formation in the latex, and polymer buildup on the reactor wall, impeller, and baffles.³⁰ Reactor fouling causes several problems in the production of latices³ It decreases the yield of the latex produced,³⁰ increases the heat transfer resistance to the reactor wall, and affects the quality and properties of the final latex product.³¹ Reactor fouling also increases the frequency of reactor shutdowns for cleaning.²⁷

Formation of microscopic and/or macroscopic coagulum in the latex results from the loss of particle colloidal stability.³⁰ Once a floc is formed, it quickly aggregates with polymer particles to form more coagulum.³² Coagulum can also result from entry of radicals into separate layers of monomer, causing bulk polymerization.³⁰ A few very large particles, incidentally formed by droplet polymerization, may act as nuclei for coagulum formation.³³ Coagulum is formed relatively easily at low surface coverage, as well as at high electrolyte and particle concentrations.³⁴ Hydrophobicity of the monomer/polymer in the reacting system may also play a role in coagulum formation.³¹ A significant segment of the particle surface may have a hydrophobic, “nonwetttable” character for particles with a low density of the surface ionic groups.³⁵ Particles with such hydrophobic areas may associate with each other, thus minimizing their contact surface with water.³⁵

Coagulum formation increases considerably above 40 wt % solids content.²⁷ According to Chern et al.,²⁷ the impeller speed has no signifi-

cant influence. Kusters³⁶ studied the influence of the hydrodynamics on the turbulent aggregation of 1 μm PS particles in baffled turbine agitated vessels. Interest focused on the dependence of aggregate size on stirrer speed, solids concentration, destabilizer concentration, and vessel size. The results showed that a dynamic equilibrium exists between aggregate growth in zones of low turbulent shear stress (i.e., circulation zone) and break-up of aggregates in zones of high shear stress (i.e., impeller region). The question is how important the break-up mechanism is for the formed coagulum during emulsion polymerization. Kemoun et al.³⁷ studied the influence of hydrodynamics on the aggregation of clay in agitated vessels. In contrast with the findings of Chern et al.,²⁷ their results point to a dynamic equilibrium between aggregate size and local hydrodynamic conditions. A high stirrer speed corresponds with large average floc sizes. Considerably smaller floc sizes were measured at the impeller discharge flow locations than elsewhere in the vessel. Extrapolation of these results to emulsion polymerization systems suggests that the energy dissipation distribution influences the formation of coagulum. Because the energy dissipation distribution appears to be independent of vessel size at constant power input,³⁹ coagulum formation is expected to be scale independent. Large radial-flow impellers, which produce a relatively uniform power input,³⁸ are probably more suitable for preventing coagulum formation than small axial-flow impellers.

The polymer on the reactor wall, impeller, and baffles results from surface polymerization³⁰ and/or deposition of polymer particles.⁴⁰ Polymer buildup depends on the characteristics of the vessel surface, among other factors. Glass-lined reactors are less sensitive to polymer deposition than stainless steel reactors.³⁰

Surface polymerization is related to the smoothness of the reactor surfaces, because scratches provide prime locations for the fixation of polymer or radical carrying oligomeric species.³⁰ Wetting of the reactor surface by the monomer/polymer phase is facilitated by surface roughness.³⁰ Because scale-up with geometric similarity decreases the ratio of surface area and reactor volume, the effect of polymer buildup on the yield and properties of the latex product becomes less important on a larger scale, although in industrial emulsion polymerization, the inevitable

Table I Polystyrene and Polyvinyl Acetate Seed Latices

Seed Latex	PS I	PS II	PVAc I	PVAc II
X_{final} [-]	0.97	0.84	0.92	0.97
$d_{p,v}$ [nm]	38.0	57.7	130	150
N [10^{21} l/m ³]	10.8	2.66	0.250	0.170
C_{Na^+} [kmol/m ³]	0.12	0.12	0.074	0.078
C_{E} [kmol/m ³]	0.12	0.12	0.017	0.020
θ [-]	0.72	0.81	0.25	0.34

cleaning of reactor surfaces is still a significant problem.

Concerning the deposition of particles on the reactor surface, three phenomena are involved: deposition, blocking (i.e., collisions between free particles and deposited particles resulting in a particle flux away from the surface), and detachment.⁴⁰ The mechanism of particle deposition is governed by the physicochemical properties of the latex and surface of the equipment used, as well as the hydrodynamic conditions in the stirred latex.⁴⁰ Van der Waals, electrostatic, and hydrophobic interactions play a role in the deposition of colloidal particles onto equipment surfaces.⁴⁰

To minimize reactor fouling during high-solids emulsion polymerization, good temperature control and proper latex stability are essential. In addition, smooth reactor surfaces and proper procedures when adding ingredients are necessary.

EXPERIMENTAL

The experimental setup of the equipment and coagulation experiments were as described in detail in an earlier article.⁴ The colloidal stability of PS latices was studied during seeded emulsion polymerization. The stability of PVAc latices was studied with swelling experiments⁴ as well as with *ab initio* emulsion polymerization experiments. Reaction calorimetric studies revealed that the nucleation period of vinyl acetate emulsion polymerization is independent of the stirrer speed,⁴¹ provided that the stirrer speed is equal to or higher than the lowest impeller speed for sufficient emulsification. In that case, it is relevant to study the aspects of colloidal stability of PVAc particles in the later stages of polymerization by *ab initio* emulsion polymerization. Note that in seeded emulsion polymerization of vinyl acetate,

it is very difficult to avoid homogeneous secondary nucleation. Secondary nucleation can hardly be controlled and would seriously hamper interpretation of the experimental results of a study on colloidal stability. Therefore, in our experiments *ab initio* emulsion polymerization was performed to study the colloidal stability of PVAc latices during reaction.

The recipes and characteristics of the seed latices used in this study are given in Tables I and II. On the 1.85 dm³ scale, the torque exerted on the impeller shaft was measured by a Staiger Mohilo torque meter, installed between the motor and the impeller shaft. The power (P) transferred into the reaction mixture by the impeller is directly related to the torque on the impeller shaft. P can also be estimated from the dimensionless power number, the impeller speed and diameter, and the density of the liquid in the tank.^{2,42} The power number of each impeller was determined from torque measurements in glycerol water mixtures. Although in principle the power number is a function of the Reynolds number,⁴² the variations in power number with Reynolds number during high-solids emulsion polymerization have been shown to be rather limited.² Therefore, the power number is assumed to be constant during the polymerizations.

RESULTS AND DISCUSSION

Colloidal Stability of PS Latices

An overview of the seeded emulsion polymerization experiments of styrene is given in Table III. Concerning the influence of recipe on the colloidal stability of PS latices, two parameters were investigated: electrolyte concentration and solids content. Figure 2 shows that electrolyte concentration had a considerable influence on the colloidal stability of the seeded 35 wt % solids content

Table II Overview of the Recipes Used for the Emulsion Polymerization Experiments

Component	S 1	S 2	S 3	VAc 1
ϕ [-]	0.25	0.35	0.50	0.25
C_{E} [kmol/m ³]	0.013	0.02	0.081	0.020
C_{I} [kmol/m ³]	0.010	0.010	0.010	0.020
C_{B} [kmol/m ³]	0.0090	0.0090	0.0090	0.0090
C_{Na^+} [kmol/m ³]	0.18	0.18/0.25	0.18	0.078

Table III Overview of the Seeded Emulsion Polymerization Experiments of Styrene

Experiment	Seed	Recipe	Reactor (dm ³)	Stirrer	N_i (rpm)	$\varepsilon_{av,power}^a$ (W/kg)	$\varepsilon_{av,torque}^b$ (W/kg)
1	PS I	S2	0.935	1/3T	500	0.17	—
2	PS I	S2	0.935	1/3T	500	0.17	—
3	PS I	S1	0.935	1/3T	500	0.17	—
4	PS I	S3	0.935	1/3T	500	0.17	—
5	PSII	S3	0.935	1/3T	500	0.17	—
6	PSII	S3	0.935	1/3T	700	0.47	—
7	PSII	S3	0.935	1/3T	900	1.0	—
8	PSII	S3	1.85	1/3T	796	0.96	0.93
9	PSII	S3	1.85	1/2T	396	0.85	0.80
10	PSII	S3	1.85	1/3P	1314	2.2	1.9
11	PSII	S3	1.85	1/2P	653	1.6	1.5

^a Calculated with $\varepsilon_{av,power} = P/M_{rm}$ with $P = N_p \rho_{rm} N_i^3 d^5$; N_p (0.935 dm³): 1/3 T = 5.0; N_p (1.85 dm³): 1/3 T = 5.2, 1/2 T = 4.9, 1/3 P = 2.6, 1/2 P = 2.1.

^b Calculated with $\varepsilon_{av,torque} = P/M_{rm}$ with $P = 2\pi N_i T$.

emulsion polymerization. Reactor fouling and a significant broadening of the particle size distribution were observed for polymerizations with

$C_{Na^+} = 0.25$ kmol/m³_w and conversions higher than 60%. This reactor fouling and the broadening of the particle size distribution may be caused by some limited coagulum formation. Compared to the influence of electrolyte concentration on the seeded 25 wt % solids content emulsion polymerization of styrene, reported earlier,⁴ emulsion polymerizations with higher solids content have shown to be more sensitive to electrolyte in terms of reactor fouling. High-solids emulsion polymerization of styrene needs a robust recipe (i.e., a low electrolyte concentration) to guarantee colloidal stability during reaction.

To study the colloidal stability of PS latices during emulsion polymerization without the confusing effects of reactor fouling, the overall electrolyte concentration in the recipe was set to 0.18 kmol/m³_w. Figure 3 shows that the influence of solids content on colloidal stability is not significant, within the limits of experimental error. Particle growth and development of particle size distribution were approximately the same for the three polymerization experiments. Note that in the later stages of the 50 wt % solids content emulsion polymerization, some scattering in the data points was observed. This scattering probably resulted from the more complicated sampling necessitated when relatively viscous, pseudoplastic reaction mixtures are involved. It can be concluded that in the cases where recipes were chosen with low or moderate (up to 0.18 kmol/m³_w) electrolyte concentrations, the colloidal stability of the PS latex was not affected by the solids content.

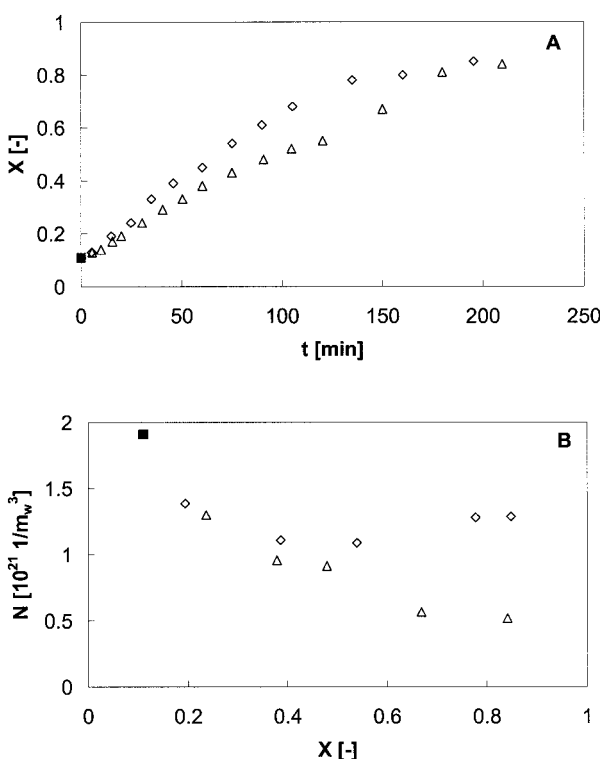


Figure 2. Influence of electrolyte concentration on the colloidal stability of PS latices during seeded emulsion polymerization of styrene. (a) Conversion time history; (b) particle number as a function of conversion. ■: seed latex PS I; ◇: exp 1, $C_{Na^+} = 0.18$ kmol/m³_w; △: exp 2, $C_{Na^+} = 0.25$ kmol/m³_w.

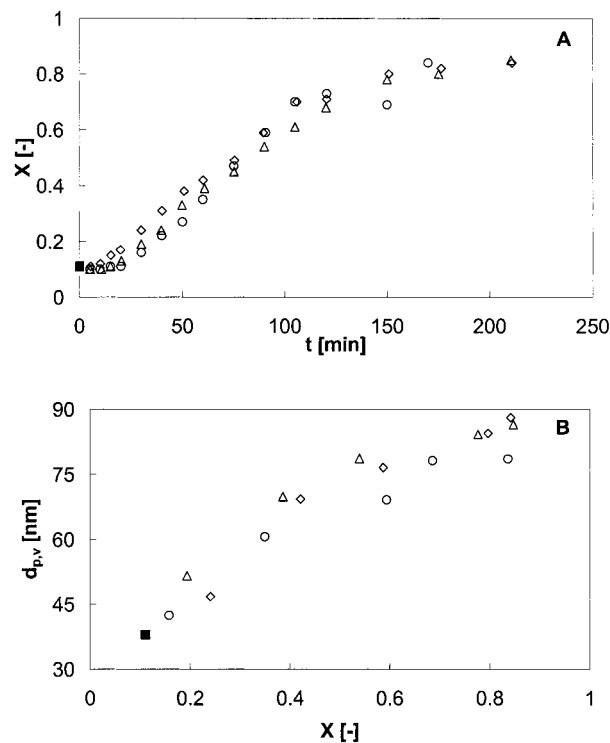


Figure 3 Influence of solids content on the colloidal stability of PS latices during seeded emulsion polymerization of styrene. (a) Conversion time history; (b) particle size as a function of conversion. ■: seed latex PS I; ◇: exp 3, $\phi = 0.25$; △: exp 1, $\phi = 0.35$; ○: exp 4, $\phi = 0.50$.

Figures 4 and 5 illustrate the effects of operating conditions (impeller speed, type, and diameter) on the colloidal stability of 50 wt % solids content emulsion polymerizations. The results shown in Figure 4 indicate that impeller speed has no significant influence on the colloidal stability of high-solids latices. No differences in development of particle size distribution between the three experiments were observed until 50–60% conversion. At the end of the polymerization, however, the amount of reactor fouling increased with stirrer speed. Thus, impeller speed may have a slight affect on the particle size (distribution) for high-solids emulsion polymerization. The sudden increase in polymerization rate at the end of experiment 5 may point to the gel effect.

Figures 5(a) and (b) show that the colloidal stability of high-solids PS latices is not affected by the impeller type and diameter. During the polymerization experiments shown in Figures 5(a) and (b), the torque on the impeller shaft was also measured. Figure 5(c) shows the mean energy

dissipation $\epsilon_{av,torque}$ calculated from the torque exerted on the impeller shaft. In the beginning of the polymerization $\epsilon_{av,torque}$ agrees reasonably well with the mean energy dissipation calculated from the power number, $\epsilon_{av,power}$; see Table III. Figure 5(c) shows that at about 60% conversion, $\epsilon_{av,torque}$ starts to deviate from $\epsilon_{av,power}$. The increase in $\epsilon_{av,torque}$ indicates the extent of reactor fouling. From these results, it follows that the impeller type and diameter significantly affect the extent of reactor fouling. Note that the impeller speeds for the different impeller types were chosen such that the mean energy dissipation is not constant for the four experiments; see Table III. The pitched-blade impeller with the smallest diameter induced the largest amount of reactor fouling, whereas the large Rushton turbine impeller caused the least amount of fouling. These results confirm the expectation mentioned earlier that at constant mean energy dissipation, large

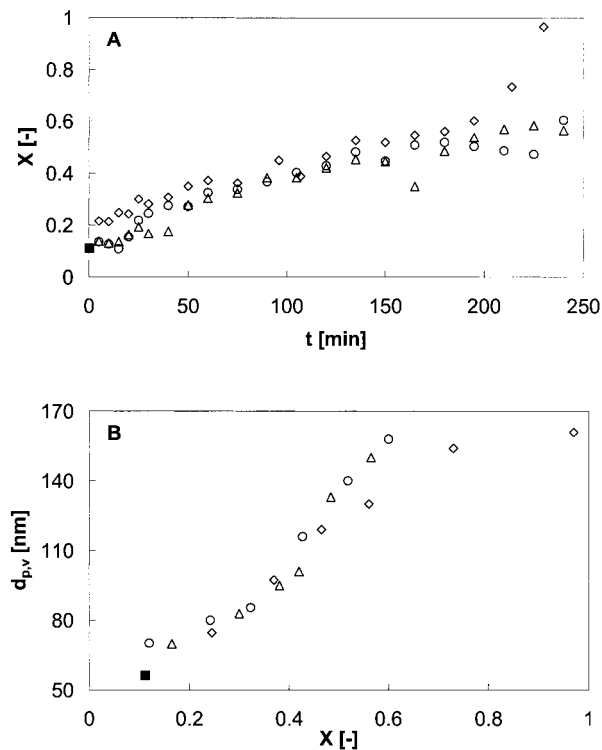


Figure 4 Influence of impeller speed on the colloidal stability of PS latices during seeded emulsion polymerization of styrene, stirred with a Rushton turbine impeller. (a) Conversion time history; (b) particle size as a function of conversion. ■: seed latex PS II; ◇: exp 5, $N_i = 500$ rpm; △: exp 6, $N_i = 700$ rpm; ○: exp 7, $N_i = 900$ rpm.

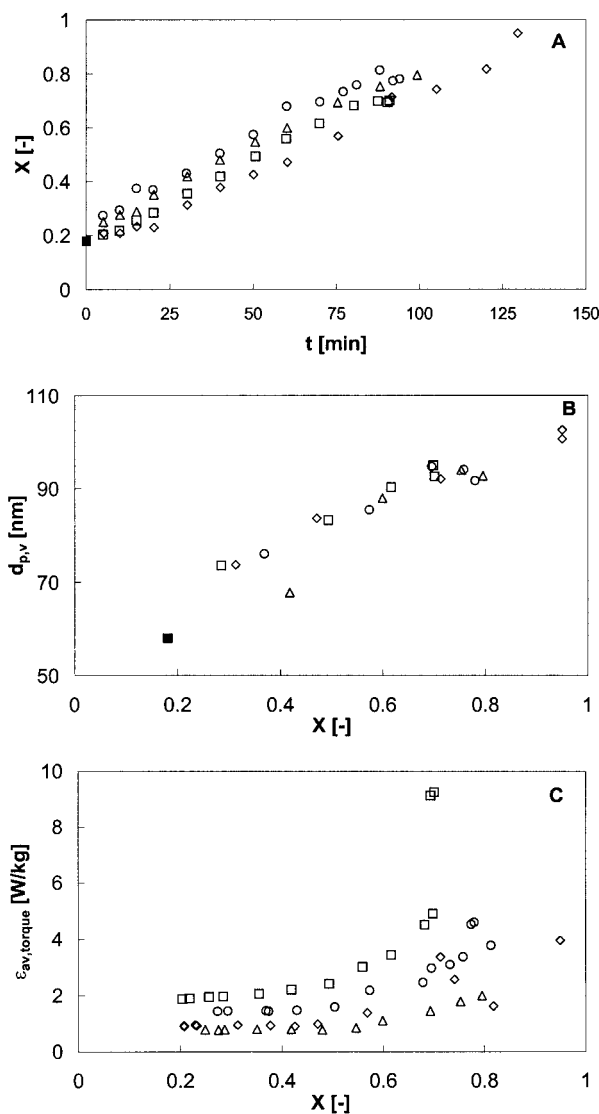


Figure 5 Influence of impeller type and diameter on the colloidal stability of PS latices during seeded emulsion polymerization of styrene. (a) Conversion time history; (b) particle size as a function of conversion (c) Energy dissipation as a function of conversion. ■: seed latex PS II; ◇: exp 8, 1/3 T; △: exp 9, 1/2 T; □: exp 10, 1/3 P; ○: exp 11, 1/2 P (see list of nomenclature).

radial-flow impellers, which generate relatively uniform power input, are most suitable for avoiding reactor fouling. In contrast to the small polymer particles formed by emulsion polymerization eventually followed by limited coagulation, flocs formed by coagulum formation may become significantly larger than the Kolmogorov microscale of isotropic turbulence. For particles or aggregates larger than the Kolmogorov microscale,

shear coagulation may become more dominant. Because shear coagulation is affected by the energy dissipation (distribution) in the vessel,⁴ it is very likely that variations in energy dissipation distribution induced by different impeller speeds, type, or diameter will influence the extent of reactor fouling.

Colloidal Stability of PVAc Latices

To investigate the colloidal stability of PVAc latices, both swelling experiments⁴ and *ab initio* emulsion polymerization experiments were performed. Table IV gives an overview of the PVAc experiments. Note that the solids content of the swelling experiments (experiments 12–21) was calculated based on the mass fraction of monomer-swollen polymer particles in the dispersion.

The influence of recipe during swelling experiments was studied by variation of emulsifier concentration (Fig. 6) and solids content (Fig. 7). Figure 6 shows that emulsifier concentration strongly affects the colloidal stability of PVAc latices. For increasing electrolyte concentrations, the latex with the higher emulsifier concentration is able to maintain a higher particle number, until the electrostatic stabilization is lost at about $C_{\text{Na}^+} = 0.30 \text{ kmol/m}^3$. For $C_{\text{Na}^+} \geq 0.30 \text{ kmol/m}^3$, steric stabilization is dominant in stabilizing the particles. Because the same seed latex was used for both experiments, the effect of steric stabilization appeared to be the same and, consequently, the particle size and number become approximately equal for high electrolyte concentrations.

Apart from a different starting point due to the variation in solids content, Figure 7(a) does not show any influence of solids content on the colloidal stability. At high electrolyte concentration where only steric stabilization is operative, all three experiments shown in Figure 7(b) reach the same stable particle number.

Figure 8 illustrates the influence of operating conditions, in terms of impeller speed and reactor scale, on the colloidal stability of high-solids PVAc latices. A different seed latex was used for the experiment on a 7.48 dm³ scale. This experiment (experiment 21; see Table IV) started, of course, with a different particle number. The final particle number of a stable latex due to steric stabilization was also different, because the amount and characteristics of the vinyl alcohol blocks on the

Table IV Overview of the Experiments with Vinyl Acetate

Experiment	Seed/Recipe	Reactor (dm ³)	Stirrer	N_i (rpm)	Solids (%)	$\varepsilon_{av,power}$ (W/kg)
12	PVAc I	0.935	1/3T	500	25	0.17
13	PVAc I	0.935	1/3T	500	25	0.17
14	PVAc I	0.935	1/3T	500	35	0.17
15	PVAc I	0.935	1/3T	500	50	0.17
16	PVAc II	0.935	1/3T	500	50	0.17
17	PVAc II	0.935	1/3T	700	50	0.47
18	PVAc II	0.935	1/3T	900	50	1.0
19	PVAc II	1.85	1/3T	467	50	0.19
20	PVAc II	1.85	1/3T	841	50	1.1
21	PVAc I	7.48	1/3T	500	50	0.62
22	VAc 1	0.935	1/3T	500	25	0.17
23	VAc 1	0.935	1/3T	900	25	1.0
24	VAc 1	1.85	1/3T	429	25	0.15
25	VAc 1	1.85	1/3T	771	25	0.87
26	VAc 1	7.48	1/3T	477	25	0.54

surface of the PVAc particles was not the same as in the experiments performed with seed latex PVAc II. Figure 8 clearly shows that impeller speed and reactor scale did not influence the colloidal stability of PVAc latices.

Figure 9 presents several *ab initio* 25 wt % solids content emulsion polymerization experiments of vinyl acetate with varying impeller speeds and degrees of reactor scale. Despite considerable experimental error in the emulsion polymerizations of vinyl acetate collected in Figure 9, the results of the polymerization experiments agree with the results of the swelling ex-

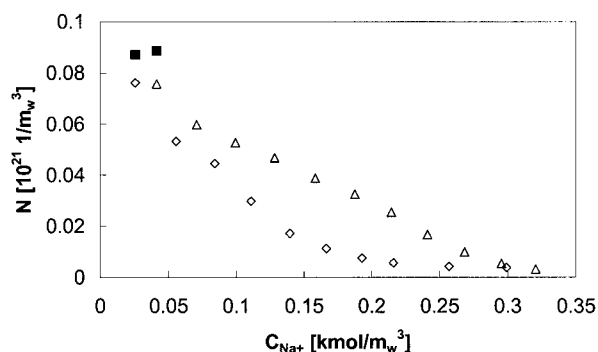


Figure 6 Influence of emulsifier concentration on the colloidal stability of PVAc latices during swelling experiments. Particle number as a function of electrolyte concentration. ■: seed latex PVAc I; ◇: exp 12, $C_E = 0.0060$ kmol/m_w³; △: exp 13, $C_E = 0.021$ kmol/m_w³.

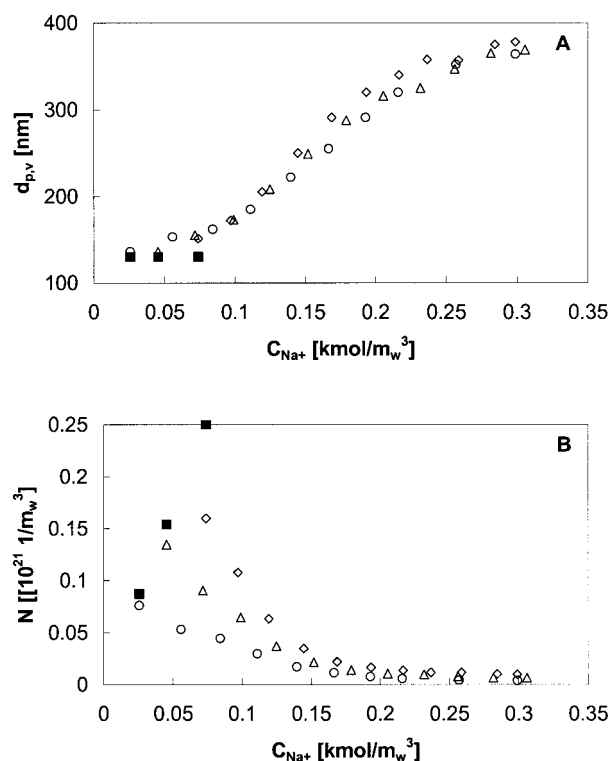


Figure 7 Influence of solids content on the colloidal stability of PVAc latices during swelling experiments. (a) Particle size as a function of electrolyte concentration; (b) particle number as a function of electrolyte concentration. ■: seed latex PVAc I; ◇: exp 13, $\phi = 0.25$; △: exp 14, $\phi = 0.35$; ○: exp 15, $\phi = 0.50$.

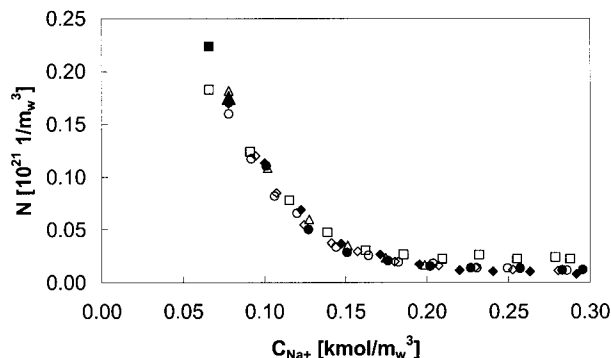


Figure 8 Influence of impeller speed and reactor scale on the colloidal stability of PVAc latices during swelling experiments. Particle number as a function of electrolyte concentration. ■: seed latex PVAc I; ▲: seed latex PVAc II; ◇: exp 16, $N_i = 500$ rpm, $V_r = 0.935$ dm³; △: exp 17, $N_i = 700$ rpm, $V_r = 0.935$ dm³; ○: exp 18, $N_i = 900$ rpm, $V_r = 0.935$ dm³; ◆: exp 19, $N_i = 467$ rpm, $V_r = 1.85$ dm³; ●: exp 20, $N_i = 841$ rpm, $V_r = 1.85$ dm³; □: exp 21, $N_i = 500$ rpm, $V_r = 7.48$ dm³.

periments reported by Kemmere et al.⁴ In both swelling experiments⁴ and polymerizations, the colloidal stability of 25 wt % PVAc latices was not significantly affected by impeller speed and scale of operation.

CONCLUSIONS

In line with the earlier study on colloidal stability of 25 wt % PS and PVAc latices,⁴ this study on the colloidal stability of 50 wt % latices shows that recipe has more influence than operating conditions on colloidal stability. Brownian coagulation dominates over shear coagulation even for systems of up to 50 wt % solids content. The following conclusions can be drawn:

- High-solids (i.e., 50 wt %) emulsion polymerization of styrene appears to be more sensitive to electrolyte in terms of reactor fouling than low solids (i.e., 25 wt %) emulsion polymerization.
- At moderate electrolyte concentrations, the colloidal stability of PS latices is not affected by the solids content up to 50 wt %.
- The operating conditions in terms of impeller speed, type, and diameter does not affect the colloidal stability of PS latices during high-solids emulsion polymerization.

- The operating conditions appear to have some influence on the extent of reactor fouling. Turbine impellers appear to be more suitable for clean operation than pitched-blade impellers.
- Concerning PVAc latices during swelling experiments, the emulsifier and electrolyte concentration have considerable influence on the colloidal stability in the electrostatic stabilization regime, whereas solids content and operating conditions have no influence.
- In line with the swelling experiments, the *ab initio* emulsion polymerization experiments of vinyl acetate showed no clear dependency of colloidal stability on operating conditions.

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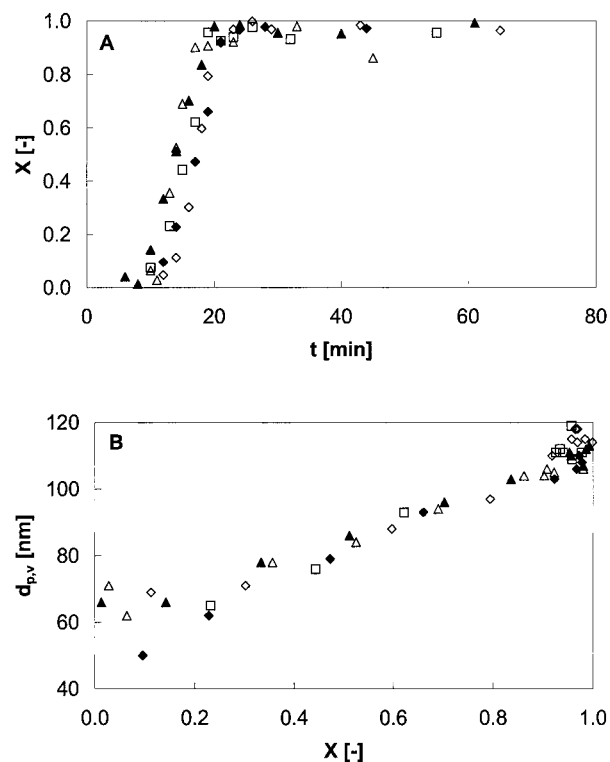


Figure 9 Influence of impeller speed and reactor scale on the colloidal stability of PVAc latices during *ab initio* emulsion polymerization of vinyl acetate. (a) Conversion time history; (b) particle size as a function of conversion. ◆: exp 22, $N_i = 500$ rpm, $V_r = 0.935$ dm³; ▲: exp 23, $N_i = 900$ rpm, $V_r = 0.935$ dm³; ◇: exp 24, $N_i = 429$ rpm, $V_r = 1.85$ dm³; △: exp 25, $N_i = 771$ rpm, $V_r = 1.85$ dm³; □: exp 26, $N_i = 477$ rpm, $V_r = 7.48$ dm³.

contribution to this work, and also acknowledge the useful comments provided by Prof. D. Thoenes.

NOMENCLATURE

ϕ	Mass fraction monomer in the recipe (-)
θ	Fractional surface coverage (-)
ρ_{rm}	density of reaction mixture (kg/m^3)
$\varepsilon_{\text{av,power}}$	mean energy dissipation based on power number (W/kg)
$\varepsilon_{\text{av,torque}}$	mean energy dissipation based on torque measurement (W/kg)
$[\frac{1}{2}]P$	45° pitched six-blade impeller with $d = [\frac{1}{2}]D$
$[\frac{1}{2}]T$	Rushton turbine impeller with $d = [\frac{1}{2}]D$
$[\frac{1}{3}]P$	45° pitched six-blade impeller with $d = [\frac{1}{3}]D$
$[\frac{1}{3}]T$	Rushton turbine impeller with $d = [\frac{1}{3}]D$
A_E	area occupied by one emulsifier molecule (m^2/mol)
C_B	buffer concentration (kmol/m_w^3)
C_E	overall emulsifier concentration (kmol/m_w^3)
C_I	initiator concentration (kmol/m_w^3)
C_{Na^+}	overall electrolyte concentration (kmol/m_w^3)
d	impeller diameter (m)
D	vessel diameter (m)
$d_{p,v}$	volume average particle size (m)
M_{rm}	mass of reaction mixture (kg)
N	particle number ($1/\text{m}_w^3$)
N_i	impeller speed (1/s)
N_p	power number (-)
P	power input (W)
T	torque (N m)
t	time (sec)
V_E	electrostatic repulsion energy (J)
V_{os}	osmotic interaction energy (J)
V_r	reactor volume (m^3)
V_S	steric repulsion energy (J)
V_{tot}	overall potential energy (J)
V_{VDW}	Van der Waals attraction energy (J)
V_{vr}	volume restriction interaction energy (J)
X	conversion (-)
X_{final}	conversion of product latex (-)

REFERENCES

1. Leiza, J. R.; Sudol, E. D.; El-Aasser, M. S. *J Appl Polym Sci* 1997, 64, 1797.

2. Kemmere, M. F.; Meuldijk, J.; Drinkenburg, A. A. H.; German, A. L. *Polym React Eng* 1998, 6, 243.
3. Lowry, V.; El-Aasser, M. S.; Vanderhoff, J. W.; Klein, A.; *J Appl Polym Sci* 1984, 29, 3925.
4. Kemmere, M. F.; Meuldijk, J.; Drinkenburg, A. A. H.; German, A. L. *J Appl Polym Sci* 1998, 69, 2409.
5. Ahmed, S. M.; El-Aasser, M. S.; Micale, F. J.; Poehlein, G. W.; Vanderhoff, J. W. in *Polymer Colloids II*; Fitch, R. M., Ed.; Plenum: New York, 1980; p. 265.
6. Piirma, I.; Chen, S. R. *J Colloid Interface Sci* 1980, 74, 90.
7. Zhu, B. Y.; Gu, T. *Adv Colloid Interface Sci* 1991, 37, 1.
8. Gu, T.; Zhu, B. Y.; Rupprecht, H. *Progr Colloid Polym Sci* 1992, 88, 74.
9. Brown, W.; Zhao, J. *Macromolecules* 1993, 26, 2711.
10. Verezhnikov, V. N.; Kashlinskaya, P. E.; Lozhkina, S. A. *Kolloidn Zh* 1993, 55, 194.
11. Yeliskeeva, V. I.; Petrova, S. A.; Zuikov, A. V. *J Polym Sci, Polym Symp* 1973, 42, 63.
12. Vijayendran, B. R. in *Polymer Colloids II*; Fitch, R. M., Ed.; Plenum: New York, 1980; p. 209.
13. Vijayendran, B. R. *J Appl Polym Sci* 1979, 23, 733.
14. Paxton, T. R. *J Colloid Interface Sci* 1969, 31, 19.
15. Zuikov, A. V.; Vasilenko, A. I. *Kolloidn Zh* 1975, 37, 640.
16. Vasilenko, A. I.; Zuikov, A. V.; Eliseeva, V. I. *Kolloidn Zh* 1983, 45, 858.
17. Napper, D. H. *Polymeric Stabilization of Colloidal Dispersions*; Academic Press: New York, 1983.
18. Blackley, D. C. *Polymer Latices*; Science; Technology, 2nd ed.; Chapman and Hall: New York, 1997; Part I.
19. Hiemenz, P. C.; Rajagopalan, R. *Principles of Colloid Surface Chemistry*, 3rd ed.; Marcel Dekker: New York, 1997; Chap.13.
20. Walker, H. W.; Grant, S. B. *Colloids Surf, A* 1998, 135, 123.
21. Romero-Cano, M. S.; Martin-Rodriguez, A.; Chauveteau, G.; de las Nievas, F. J. *J Colloid Interface Sci* 1998, 198, 273.
22. van de Pas, J. C. Ph.D. Thesis, State University Groningen, The Netherlands, 1993.
23. Ottewill, R. H. in *Emulsion Polymerization*; Emulsion Polymers; Lovell, P. M. and El-Aasser, M. S., Eds.; Wiley: New York, 1997; Fig. 3.37.
24. Fler, G. F.; Cohen-Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgrove, T.; Vincent, B. *Polymer at Interfaces*; Chapman and Hall: New York, 1993; Fig. 8.2.1.
25. Liu, J.; Gan, L. M.; Chew, C. H.; Quek, C. H.; Gong, H.; Gan, L. H. *J Polym Sci, Part A: Polym Chem* 1997, 35, 3575.

26. Russel, W. B.; Saville, D. A.; Schowalter, W. R. *Colloidal Dispersions*; Cambridge, U. K.: Cambridge University Press, 1989.
27. Chern, C. S.; Hsu, H.; Lin, F. Y. *J Appl Polym Sci* 1996, 60, 1301.
28. Hsu, J. P.; Liu, B. T. *J Phys Chem* 1998, 102, 334.
29. SenGupta, A. K.; Papadopoulos, K. D. *J Colloid Interface Sci* 1998, 203, 345.
30. Vanderhoff, J. W. in *Emulsion Polymers, Emulsion Polymerization*; Bassett, D. R., Hamielec, A. E., Eds.; ACS Symposium Series 165; American Chemical Society: Washington, DC, 1981; p. 199.
31. Kostansek, E. C. *Trends in Polymer Science (TRIP)* 1996, 11, 383.
32. Lowry, V.; El-Aasser, M. S.; Vanderhoff, J. W.; Klein, A.; Silebi, C. A. *J Colloid Interface Sci* 1986, 112, 521.
33. Rodrigues, J.; Schork, F. J. *J Appl Polym Sci* 1997, 66, 1317.
34. Chern, C. S.; Kuo, Y. N. *Chem Eng Sci* 1996, 51, 1079.
35. Sjöblom, J. *Emulsions, Emulsion Stability*; Marcel Dekker: New York, 1996; Chap. 2.
36. Kusters, K. A. Ph.D. Thesis, Eindhoven University of Technology, The Netherlands, 1991.
37. Kemoun, A.; Lusseyran, F.; Skali-Lami, S.; Mahouast, M.; Mallet, J.; Lartiges, B. S.; Lemelle, L.; Bottero, J. Y. in *Proceedings of the 9th European Mixing Conference, 1997*, 52, 33.
38. Henzler, H. J.; Biermann, A. *Chem -Ing -Tech* 1996, 68, 1546.
39. Schoenmakers, J. H. A.; Wijers, J. G.; Thoenes, D. in preparation.
40. van de Ven, T. G. M. *Colloids Surf, A* 1998, 138, 207.
41. Kemmere, M. F.; PhD Thesis, 1999; Eindhoven University of Technology, The Netherlands.
42. Bates, R. L.; Fondy, P. L.; Corpstein, R. R. *Ind Eng Chem, Process Des Dev* 1963, 2, 310.