

Stability of Acrylic Latices in a Semibatch Reactor

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SYNOPSIS

The effects of various reaction variables on the stability of acrylic latices in a semibatch reactor were investigated by measuring the amount of coagulum formed and particle volume changes caused by limited flocculation. The amount of coagulum could be reduced significantly with an increase in the level of sodium lauryl sulfate (SLS) in the monomer emulsion feed. An increase in the amount of SLS in the initial reactor charge resulted in an increase in the particle volume change due to limited flocculation later in the process. The larger the ratio of methyl methacrylate (MMA) to butyl acrylate (BA) in the copolymer, the greater the amount of coagulum produced. Both coagulum and particle volume change increased with an increase in the electrolyte concentration. Within the range studied (500–800 rpm), the agitation speed was not important to the coagulation process. Experimental data also indicated that the polymer particles could lose their stability rapidly above 40% total solids content because of the crowding effect. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Semibatch emulsion polymerization is one of the most important processes for the production of coatings, adhesives, thermoplastics, and synthetic rubbers because heat transfer in large scale reactors is limited and semibatch processes can be effective in controlling latex properties. Emulsion polymerization is a heterogeneous system in which most of the propagation reaction occurs in the segregated particles dispersed in water. These tiny particles (ca. 50–1000 nm in diameter) collide with each other frequently and tend to coagulate due to the attractive van der Waals forces. Stability against coagulation can be achieved by the addition of an anionic surfactant that imparts repulsive forces between similarly charged electric double layers to the polymer particles.

The size distribution of the latex particles, for example, is a property that can have a significant effect on the quality of the products. Aggregation of particles during the reaction will make the task of particle size control more difficult. Removal of coagulum from the latex products by filtration is nec-

essary, since the coagulum produced by the loss of stability has a negative effect on application properties. In addition, the reactor needs to be shut down for cleaning when polymer on the wall accumulates to an unacceptable level. Both factors will cause plant production problems and increase the product cost. Thus, a knowledge of the effects of important reaction variables on the latex stability is essential for successful product development and production.

THEORETICAL BACKGROUND

Classical von Smoluchowski flocculation theory¹ considers monodisperse particles whose motion is governed by Brownian motion and applies diffusion theory to develop an equation for the rate of doublet formation. If the latex is under the influence of mechanical agitation a velocity gradient will develop and will increase both force and frequency of collisions. Such a shear-induced coagulation process has been treated and an infinite series of first-order ordinary-differential equations, which takes into account individual particle-to-particle collisions, has been developed.^{2,3}

Latex particles can be adsorbed at the air-liquid interface according to a Langmuir adsorption isotherm. At the interface, coagulation of the adsorbed

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particles can take place according to zeroth-order kinetics if the concentration of particles is high enough.⁴ Such a mechanism is recognized as surface coagulation.⁵ Lowry et al.⁴ studied the kinetics of agitation-induced coagulation of high-solids latices. They assumed that the Brownian coagulation was insignificant and the surface coagulation followed zeroth-order kinetics. The following equation was developed to describe the coagulation process.

$$dC/dt = P_1 + P_2C - P_3C \quad (1)$$

where C is the fraction of particles coagulated and t is the coagulation time. $P_1 = B + K_s$, $P_2 = K' - B$, $P_3 = K' = 4\dot{\gamma} Z/3W$, $B = 4\dot{\gamma} \Phi/\pi W$, and $K_s = A_s/V(K_0/K_2^2 C_0)$. $\dot{\gamma}$ is the shear rate, Φ is the volume fraction of particles, W is the stability factor, K_s is the surface coagulation rate constant, A_s/V is the surface area-to-volume ratio, K_0 is the global surface coagulation rate constant, K_2 is the Langmuir adsorption constant, C_0 is the initial concentration of particles, and Z is a proportionality constant.

The stability factor (W) is related to the total potential energy of interaction between two particles (V_t).⁶ V_t equals the sum of the potential energy of van der Waals attraction (V_a) and the potential energy of electrostatic repulsion (V_r) according to DLVO theory.^{7,8} V_t can be considered as a potential energy barrier against coagulation. V_a is dependent on the particle size and interparticle distance. V_r is a function of the latex particle size, interparticle distance, zeta-potential of the particles, and electrolyte concentration.

In general, the average interparticle distance will become an important factor in interaction between two particles (as reflected in the latex viscosity) only when the solids content is high. The height of the energy barrier will increase with an increase in the zeta-potential of the particles. An increase in the electrolyte concentration will compress the electric double layer of the particles and reduce the repulsive force between two particles. This action can result in a decrease in the latex stability. As to the particle size, it shows a 2-fold effect on the coagulation process. The shear-induced collision frequency is proportional to the cube of particle radius, whereas the stability factor is approximately proportional to the particle radius.

During monomer addition, growth of the latex particles via polymerization of the absorbed monomer will result in an increase in the particle surface area. The newly created particle surface requires more surfactant to maintain adequate latex stability.

Chern and Hsu¹⁰ studied semibatch emulsion copolymerization of methyl methacrylate (MMA) and butyl acrylate (BA). It was found that the anionic surfactant, sodium lauryl sulfate (SLS), in the initial reactor charge had the largest influence on the number of particles generated. The amount of SLS in the monomer emulsion feed did not show any significant effect on the particle size of the finished batch and its primary function was to stabilize the growing particles. Adding SLS to the reactor during the monomer feed can cause secondary nucleation (i.e., formation of a second crop of primary particles). Secondary nucleation will reduce the average particle size and broaden the size distribution. Moreover, it will create more polymer-water interfacial area. Thus, the reaction system needs more surfactant for appropriate stability.

Coagulation of particles by mechanical agitation will lead to the formation of filterable solids and reactor scrap. However, not all flocculation events will result in the formation of coagulum. In addition to the conversion of monomer to polymer inside the particles, these particles can grow through a limited flocculation process and yet these particles can be still stable enough to remain in the aqueous phase. Thus, determination of filterable solids and reactor scrap alone is not sufficient to quantify the extent of coagulation. In the study of chemical stability of latices, Masa et al.¹¹ added monovalent counterions to the samples. They found that the particle size increased significantly. When both divalent and trivalent counterions were used in the experiments, rapid formation of coagulum was observed. If no appreciable coagulum was found in the sample, the percent change in particle size was used as a measure of the latex stability. In other experiments the amount of coagulum collected was used to assess latex stability.

The objective of this work was to study the effects of various reaction parameters on the coagulation process for emulsion copolymerization of MMA and BA in a semibatch reactor. We will use both particle volume change caused by limited flocculation and coagulum collection to investigate the effects of various parameters on the latex stability. The percent particle volume change during monomer addition can be calculated as follows:

Percent particle volume change

$$= [(d_f/d'_f)^3 - 1] \times 100\% \quad (2)$$

where d_f is the measured particle diameter of the final latex. The parameter d'_f is the calculated par-

ticle diameter of the final latex if both secondary nucleation and limited flocculation do not occur during monomer addition. For example, if d_{15} (nm) and N_p are the particle diameter and total number of particles, respectively, of the sample taken immediately before the start of monomer emulsion feed, W_m (g) is the total weight of fed monomer, and ρ (g/cm³) is the density of polymer, then d'_f can be calculated according to the following equation:

$$d'_f = [d_{15}^3 + 6 \times 10^{21} W_m / (\pi \rho N_p)]^{1/3} \quad (3)$$

EXPERIMENTAL

The chemicals used were methyl methacrylate (Kaohsiung Monomer Co.), butyl acrylate (Formosa Plastics Co.), sodium lauryl sulfate (Henkel Co.), sodium persulfate (Riedel-de-Haen), sodium chloride (Riedel-de-Haen), nitrogen (Ching-Feng-Harg Co.), and deionized water (Barnsted, Nanopure Ultrapure Water System). All chemicals were used as received.

Polymerization was carried out in a 1-L glass reactor equipped with a four-bladed fan turbine agitator, a thermometer, and a condenser. A conventional semibatch emulsion polymerization process begins with a large portion of water along with some surfactant and monomer charged to the reactor, followed by heating the initial reactor charge to the reaction temperature (80°C in this work). The initial reactor charge is purged with nitrogen (for 10 min in this work) while the reactor is brought to 80°C. The initiator solution is then added to the reactor to start the reaction. After a short period of time (15 min in this work) for nucleation of polymer particles, the remaining monomer and other ingredients such as water and surfactant are fed to the reactor over several hours (3 h in this work). Polymerization temperature is kept constant throughout the reaction. After the end of monomer feed, the reactor temperature is maintained at the same temperature (for 30 min in this work) to reduce the residual monomer to an acceptable level. The reaction scheme is shown in Figure 1. The theoretical total solids content at the end of reaction was 45% unless stated otherwise.

The finished batch was filtered through 40-mesh (0.42-mm) and 200-mesh (0.074-mm) screens in series to collect the filterable solids. Scrap adhering to the agitator, thermometer, and reactor wall was also collected. Total solids content was determined by the gravimetric method. Particle size distribution data were obtained from dynamic light scattering

Semibatch Emulsion Polymerization

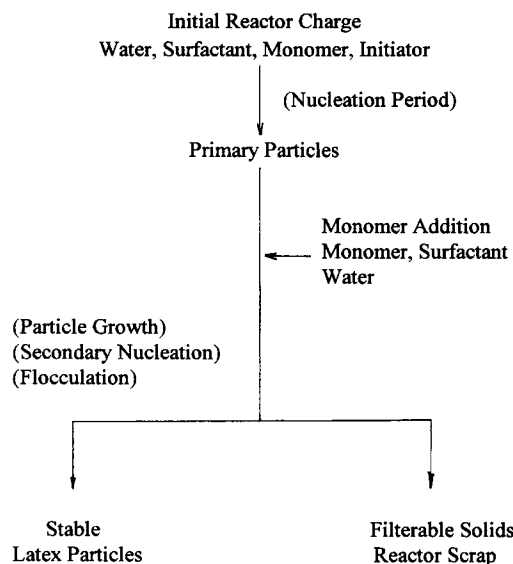


Figure 1 Scheme of semibatch emulsion polymerization.

(DLS, Otsuka Photal LPA-3000/3100) and transmission electron microscopy (TEM, Hitachi H-7100). The zeta-potential of latex particles was determined by the instrument Otsuka Photal LEZAI-600. The latex sample was diluted with deionized water to adjust the number of photons counted per sec (cps) to a proper value of around 5000–15,000 for zeta-potential measurement. The latex viscosity was measured with a cone and plate viscometer (Brookfield, Model LVT). The latex surface tension was determined by a Face, CBVP-A3 surface tension meter.

RESULTS AND DISCUSSION

A fractional two-level factorial design (5 variables, 16 experiments) was employed to study the effects of important reaction variables on the latex stability. The variables selected for study were (1) the concentration of SLS in the initial reactor charge (0.01–0.5 wt % based on water present in the initial reactor charge), (2) the agitator speed (500–800 rpm), (3) the concentration of SLS in the monomer emulsion feed (0.5–1.0 wt % based on water present in the initial reactor charge), (4) $[Na^+]$, that is, the electrolyte concentration (0.107–0.6 wt % based on total water), and (5) the weight percent MMA in the monomer mixture (30–70 wt % of total monomer). In the designed experiments, $[Na^+]$ in the initial

Table I A Typical Recipe for the Semibatch Emulsion Copolymerization of MMA/BA in the Factorial Design

	Chemicals	Weight (g)
Monomer emulsion feed	H ₂ O	80.00
	NaCl	0.30
	SLS	1.54
	BA	88.50
	MMA	206.50
Initial reactor charge	H ₂ O	285.30
	SLS	0.03
	NaCl	0.30
	BA	4.05
	MMA	9.46
Initiator solution	H ₂ O	15.00
	Na ₂ S ₂ O ₈	0.45
Total weight (g)		691.43
Total solids content (%)		45.00

reactor charge was maintained constant by means of sodium chloride. The remaining sodium chloride required to adjust the finished batch to the designed electrolyte concentration was placed in the monomer emulsion feed. The initiator concentration was constant (0.15 wt % based on water present in the initial reactor charge) throughout this work. A typical recipe for the semibatch emulsion copolymerization of MMA/BA is shown in Table I.

The reactivity ratios of MMA and BA are 0.92 and 0.13, respectively.¹² According to the copolymer composition equation,¹³ the mole fractions of MMA in the copolymer are 0.55, 0.66, and 0.78 for the recipes with MMA/BA ratios equal to 30/70, 50/50, and 70/30, respectively (i.e., the mole fractions of MMA in the monomer emulsion feed are 0.35, 0.56, and 0.75, respectively). Thus, the less reactive monomer (BA) may build up during semibatch emulsion copolymerization of MMA and BA. As a result, the polymer formed near the particle surface layer toward the end of polymerization may be rich in BA regardless of the MMA/BA ratio in the monomer emulsion feed. Nevertheless, all experiments in the factorial design were estimated to be operated around the monomer-starved condition (i.e., rate of polymerization > rate of monomer addition) based on the copolymerization rate equation developed by Hamielec.¹⁴ Such a monomer-starved condition will suppress the shift in the polymer composition during the reaction. Thus it is reasonable to assume that the polymer composition on the particle surface is similar to the MMA/BA ratio in the monomer emulsion feed.

The filterable solids collected from the 200-mesh screen were nearly nil for all experiments. Thus the data for scrap presented are only the 40 mesh coagulum plus the scrap adhering to the agitator, thermometer, and reactor wall. In the factorial design, the overall average amount of scrap of the 16 experiments is 0.437 wt % based on total solids and the overall average particle volume change is 662.7%. Table II shows the calculated standardized effects of each variable on the latex stability in the factorial design. The amount of coagulum produced, for example, will decrease 0.132% when the level of SLS in the initial reactor charge changes from the minus level (0.01 wt %) to the plus level (0.5 wt %). The electrolyte concentration shows a significant effect on both scrap and particle volume change. Thus, the ionic strength plays a very important role in the coagulation process. The ionic strength will not only determine the level of scrap formed inside the reactor, but also cause the particle size of the finished latex to deviate from the designed value.

The amount of scrap produced during the reaction drops rapidly with increasing SLS in the monomer emulsion feed. This is because the surfactant gradually added to the reaction system will increase the surface charge density on the growing particles and, consequently, improve the latex stability. The polymer composition is also an important factor in determining the extent of coagulum formation. As the ratio of MMA to BA increases from 30 : 70 to 70 : 30, the increase in scrap cannot be ignored. This observation is perhaps related to the surface area occupied by an SLS molecule on PMMA particles (0.79 nm²) as compared to PBA particles (0.56 nm²).¹⁵ The higher the concentration of MMA units on the particle surface, the less the amount of SLS adsorbed on the surface. Thus, the latex stability decreases as a result of the reduced repulsive force be-

Table II Calculated Standardized Effects of Each Variable on the Latex Stability in the Fractional Two-Level Factorial Design

Variable	Standardized Effect	
	Scrap (%)	Particle Volume Change (%)
SLS in IRC (%)	-0.132	1085.5
Agitation speed (rpm)	0.068	-213.5
SLS in MEF (%)	-0.634	-310.7
[Na ⁺] (%)	0.593	1267.9
MMA : BA	0.486	208.7

IRC, initial reactor charge; MEF, monomer emulsion feed.

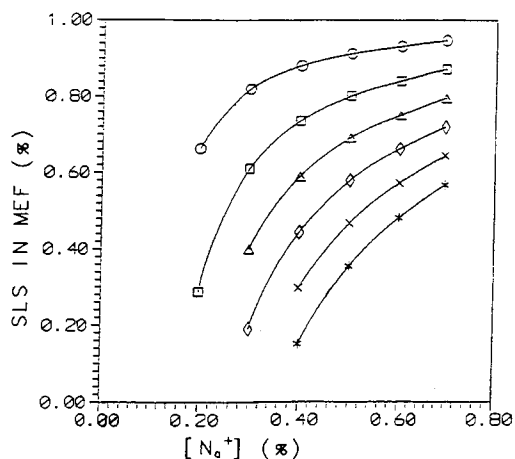


Figure 2 Contour plot of scrap: SLS in initial reactor charge = 0.25%, 600 rpm, and MMA/BA = 50/50. Scrap (○) 0.1%, (□) 0.3%, (△) 0.5%, (◇) 0.7%, (×) 0.9%, (*) 1.1%.

tween two particles. Neither the concentration of SLS in the initial reactor charge nor the agitation speed seems to have much effect on the formation of scrap.

Based on the factorial design, we derived a predictive equation for the coagulum formation. Figure 2 shows a typical parametric contour plot of scrap constructed from the predictive equation. In this plot, the concentration of SLS in the initial reactor charge, the agitation speed, and the ratio of MMA to BA were set at 0.25%, 600 rpm, and 50 : 50, respectively. Considering, for example, the curve with scrap equal to 0.5%, the level of SLS in the monomer emulsion feed required to maintain the same latex stability should increase with an increase in the electrolyte concentration. The contour plot also indicates that at a constant ionic strength, the scrap is reduced when the level of SLS in the monomer emulsion feed increases. Similarly, at a constant level of SLS in the monomer emulsion feed, the scrap is reduced when $[Na^+]$ decreases.

Polymer particle volume change is influenced significantly by both $[Na^+]$ and the level of SLS in the initial reactor charge. The particle volume change increases with an increase in the level of SLS in the initial reactor charge. This can be explained by the fact that the number of primary particles nucleated increases with an increase in the level of SLS in the initial reactor charge. The tremendous particle surface area thus generated will lead to a lower surface charge density and, hence, a lower potential energy barrier against flocculation. Thus the repulsive force between two particles is not high enough to keep these particles from flocculation. Such a flocculation process will result in a

decrease in the particle surface area and, consequently, increase the surface charge density. Since the level of SLS in the initial reactor charge is quite high, the flocculation process will cease when the surface charge density increases to a certain level and most of the flocculated particles still can be stably dispersed in water. The work of Fitch and Tsai¹⁶ also supports such a limited flocculation process. Other parameters such as the agitation speed, the level of SLS in the monomer emulsion feed, and the ratio of MMA to BA show very little effect on the particle volume change.

A parametric contour plot of particle volume change is shown in Figure 3. The agitation speed, the level of SLS in the monomer emulsion feed, and the ratio of MMA to BA were set at 600 rpm, 0.75%, and 50 : 50, respectively, in this figure. The contour plots at different levels of SLS in the monomer emulsion feed show similar trends. At a fixed ionic strength, the particle volume change increases with an increase in the level of SLS in the initial reactor charge. The particle volume change also increases with an increase in the electrolyte concentration when the level of SLS in the initial reactor charge is kept constant.

We then chose three points (i.e., high, medium, and low levels) each to verify the predictive equations developed for the scrap and particle volume change, respectively. The formulations and results are summarized in Tables III and IV. Table III shows that the predictive equation for the scrap works pretty well. In addition, it is observed in this series

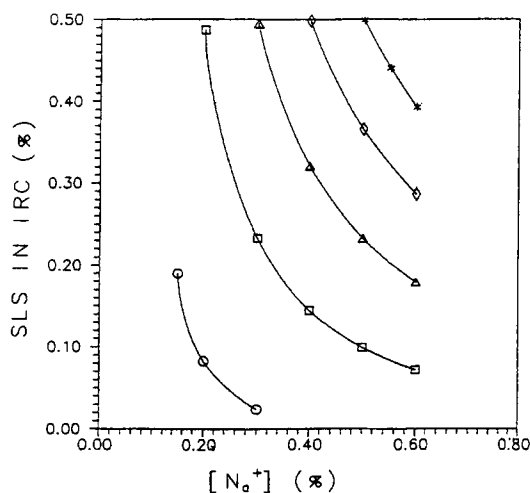


Figure 3 Contour plot of particle volume change: 600 rpm, SLS in monomer emulsion feed = 0.75%, and MMA/BA = 50/50. Particle volume change (○) 100%, (□) 500%, (△) 1000%, (◇) 1500%, (*) 2000%.

Table III Experiments Designed to Verify the Scrap Predictive Equation

	High	Medium	Low
Formulations			
SLS in MEF (%)	0.55	0.74	0.93
[Na ⁺] (%)	0.56	0.37	0.17
Results			
Prediction (%)	1.60	0.71	0.11
Experiment (%)	1.21	0.61	0.13
Error (%)	-24	-14	18
Particle volume change (%)	1316	284	9

SLS in IRC = 0.25%; MMA/BA = 70/30.

of experiments that the greater the scrap, the greater the particle volume change.

As shown in Table IV, the predictive equation for the particle volume change underpredicts the experimental data. The deviation between the predicted and experimental data is much greater in this series, but the trend is correct. This behavior implies that the limited flocculation process is very sensitive to the reaction environment and a minor change in the environment might cause the flocculated particles to be converted into coagulum. Thus, it is very difficult to control the particle size if the limited flocculation process is significant. The scrap collected in this series is not very high (0.14–0.29%) and there is no apparent correlation between scrap and particle volume change.

Based on the coagulative nucleation mechanism, Novak¹⁷ developed a simple model to describe the particle nucleation and growth in semibatch emulsion polymerization of acrylic monomers. In the model development, it was assumed that the precursor particles (ca. 2 nm) were first formed by phase separation of oligomeric radicals in the aqueous phase. These precursor particles, although completely covered with surfactant, were extremely unstable and they rapidly aggregated until a stable (primary) particle size was achieved. The number of primary particles generated during nucleation was governed by the amount of surfactant available to stabilize the generated interfacial area. The remainder of polymerization was simply the growth of primary particles via the propagation reaction. Secondary nucleation and flocculation were assumed to be negligible throughout monomer addition. The Novak model predicts that the slope of the $\log(d_f)$ -vs- $\log(1/G_s)$ plot should be $\frac{1}{3}$ where d_f is the final particle size and G_s is the amount of surfactant used during nucleation (i.e., the level of SLS in the initial reactor charge in this work).

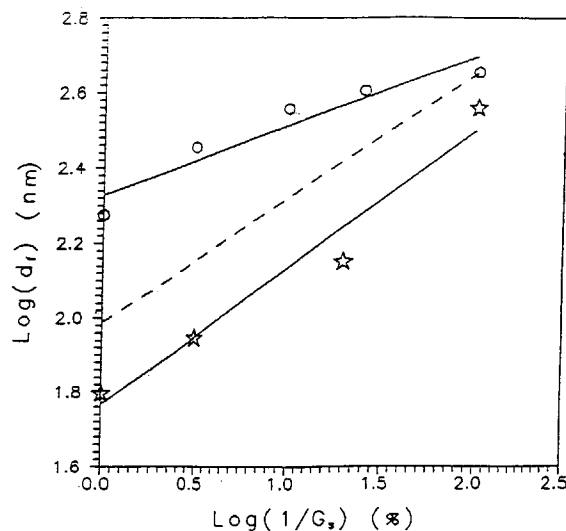
Table IV Experiments Designed to Verify the Predictive Equation For Particle Volume Change

	High	Medium	Low
Formulations			
SLS in IRC (%)	0.45	0.36	0.25
[Na ⁺] (%)	0.54	0.45	0.33
Results			
Prediction (%)	1975	1294	612
Experiment (%)	1143	1032	178
Error (%)	-42	-20	-71
Scrap (%)	0.14	0.29	0.26

SLS in MEF = 0.75%; MMA/BA = 50/50.

Two series of experiments were carried out to study the effects of flocculation and secondary nucleation on the final particle size by means of the Novak model. In the first series, the level of SLS in the initial reactor charge was varied between 0.01 and 1%, whereas the level of SLS in the monomer emulsion feed was kept constant at 0.5%. The total [Na⁺] in the recipe was kept constant at 0.6%. As before, [Na⁺] in the initial reactor charge was also kept constant by using sodium chloride. The remaining sodium chloride required to adjust the finished batch to the designed ionic strength was placed in the monomer emulsion feed.

The results are shown as the circular data points in Figure 4. The straight line obtained from the least squares best fit method has a slope of 0.185, which is much lower than the value predicted by the Novak

**Figure 4** Final particle size versus reciprocal of SLS level in initial reactor charge: (---) Novak model, (O) flocculation series, (☆) secondary nucleation series.

model. The experiment with d_f equal to 451 nm (determined by dynamic light scattering) produced the lowest amount of scrap (0.038%) and particle volume change (51.7%) and it was also the most stable latex in this series. Thus, for comparison, we drew a straight line with a slope of $\frac{1}{3}$ through this data point, as shown by the dashed line in Figure 4. Comparing the experimental data with the Novak model, it can be seen that the deviation increases with a decrease in d_f . This observation suggests that the extent of limited flocculation increases with a decrease in d_f . This is supported by the particle volume change data shown in Figure 5. As $1/G_s$ increases (i.e., d_f increases), the particle volume change decreases monotonically.

Also shown in Figure 5 is the amount of scrap formed during the reaction. A maximum amount of scrap is observed at a value of d_f close to 400 nm. The data for the zeta-potential of the latex particles as a function of $1/G_s$ for the samples taken immediately before the start of monomer emulsion feed and the final latex products are shown in Figure 6. Examining Figures 4–6 leads to the conclusion that for very small d_f (i.e., very small $1/G_s$), the formation of scrap is insignificant in comparison with the particle volume change. Thus, the limited flocculation process predominates during monomer addition and, hence, the decreasing particle surface area causes an increase in the zeta-potential of the particles (see Fig. 6). On the other hand, for very large d_f (i.e., very large $1/G_s$), both scrap and particle volume changes are very low. The latex particles are rather stable throughout the reaction and a decrease in the zeta-potential of the particles is expected due to the

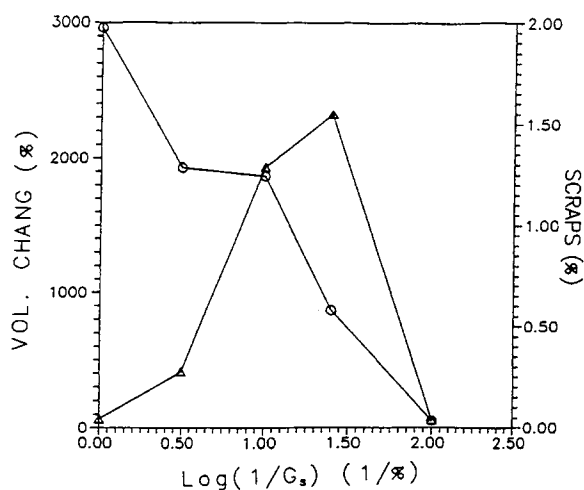


Figure 5 Particle volume change or scrap versus reciprocal of SLS level in initial reactor charge: (○) particle volume change, (△) scrap.

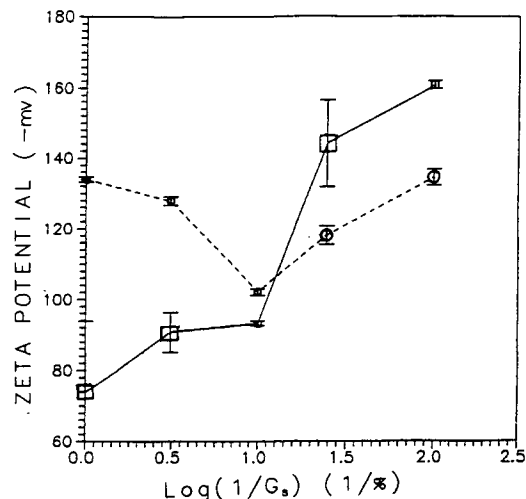


Figure 6 Zeta-potential versus reciprocal of SLS level in initial reactor charge: (□) sample taken immediately before start of monomer emulsion feed, (○) final latex.

growing particle surface area (see Fig. 6). For the run between the two limiting cases discussed above, both scrap and particle volume change are important in evaluating the latex stability. The zeta-potential of the particles does not change very much as polymerization proceeds (see Fig. 6).

In the second series designed for the secondary nucleation effect, again the level of SLS in the initial reactor charge was varied between 0.01 and 1%, and the level of SLS in the monomer emulsion feed was kept constant at 0.5%. An extra shot of SLS (1 wt % based on total water present in the reactor before the start of monomer emulsion feed) was charged to the reactor 36 min after the start of monomer emulsion feed in order to initiate the secondary nucleation. Sodium chloride was not used to adjust the ionic strength of the reaction medium. The results are shown as the star data points in Figure 4. The straight line obtained from the least-squares best fit method has a slope of 0.380, which is slightly greater than the value predicted by the Novak model. It is interesting to note that the two designed series sit on opposite sides of the line predicted by the Novak model. The data for scrap and particle volume change in the secondary nucleation series, listed in Table V, shows that the latex particles are pretty stable during the monomer emulsion feed and the negative values of particle volume change for all runs provide evidence for secondary nucleation.

The TEM photograph in Figure 7(B) shows that a large number of small particles, not found in the sample taken immediately before the start of monomer emulsion feed [see Fig. 7(A)], surround the large

Table V Experiments Designed to Study the Effect of Secondary Nucleation on the Novak Model

d_f (nm)	Scrap (%)	Particle Volume Change (%)
364	0.028	-3.5
142	0.047	-26.0
89	0.047	-32.9
63	0.069	-10.9

particles for the run with d_f equal to 364 nm. These tiny particles were generated by secondary nucleation. Figure 7(C), for the run with d_f equal to 89 nm, shows agglomeration during TEM sample preparation for the sample taken immediately before the start of monomer emulsion feed, and we were unable to obtain a photograph without such agglomeration. The average particle size of this sample, determined by dynamic light scattering, is 39 nm. In contrast to Figure 7(B), only a few very small particles can be observed in Figure 7(D). This can be explained by the fact that the enormous interfacial area associated with a small particle size latex (e.g., $d_f = 89$ nm) will efficiently absorb the primary particles formed by secondary nucleation.

Finally, we studied the effect of total solids content on the latex stability. The average interparticle distance (H) is a measure of the interaction between two particles. For monodisperse colloidal systems, H is a function of total solids content according to the following equation:¹⁸

$$H/r = 2[(74 \rho_p/w_p)^{1/3} - 1] \quad (4)$$

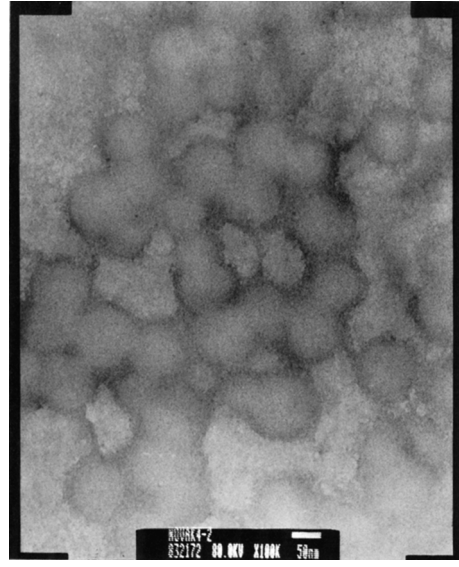
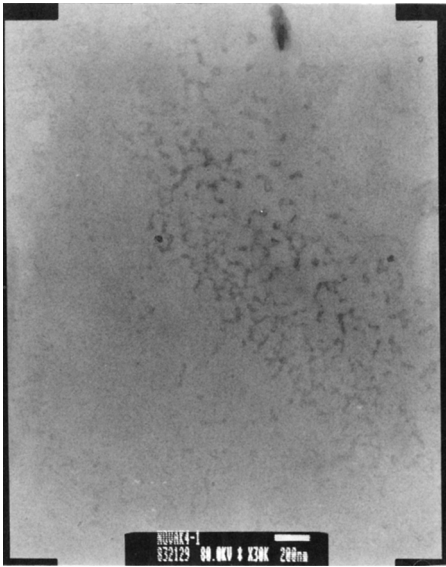
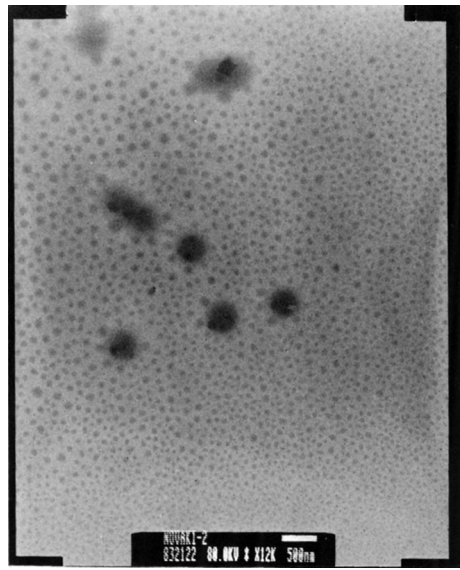
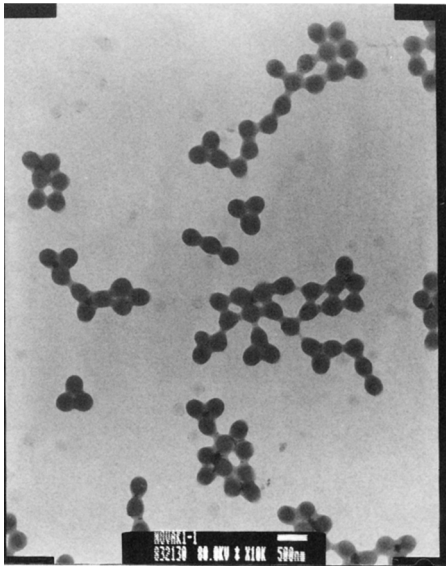
where r is the particle radius, ρ_p is the polymer density, and w_p is the weight percent particles in the latex, which is linearly proportional to total solids content. Figure 8 shows the calculated relationship between the relatively mean free path length between two particles (H/r) and total solids content for seeded semibatch emulsion polymerization. The weight percent of seed particles based on total polymer was kept constant (3%) and the seed particle size was varied from 50 to 200 nm. All three curves coincide. Since different seed particles were employed in these runs, the smaller the seed particles, the smaller the value of H for the stationary particle packing. Thus, the reaction system with the smallest seed particle size should be the most crowded. In addition, H/r decreases with an increase in the total solids content and, consequently, the higher the total

solids content, the more crowded the system (i.e., the greater the interaction between two particles).

We then prepared two seed latices to investigate the impact of total solids content on the latex stability. The average particle sizes for the seed latices are 79 and 180 nm, respectively. The total solids content was 8.7% just before the start of monomer addition. There was no surfactant fed to the reactor during the monomer addition for the purpose of enhancing the effect of total solids content. Figure 9 shows the data for viscosity-vs-total solids content. As expected, to reflect the degree of interaction between two particles, the viscosity increases with an increase in the total solids content. At a fixed total solids content, the viscosity of the latex prepared with the small seed particles is greater than the one prepared with the large seed particles. More importantly, the rate of change in viscosity increases rapidly above 40% total solids content. This result implies that the crowding effect cannot be ignored for high solids latices.

The amount of scrap produced at various levels of total solids content is shown in Figure 10. Similar to the viscosity profiles, the amount of scrap increases with an increase in the total solids content and the rate of change in scrap increases rapidly above 40% total solids content. However, the latex prepared with the small seed particles is more stable than the one prepared with the large seed particles. This seems to be in conflict with the viscosity data shown in Figure 9. This contradiction suggests that the crowding effect is not the only parameter that determines the coagulation behavior. In most cases, the data of particle volume change shown in Figure 11 are less than zero. It is unlikely that secondary nucleation took place during the monomer feed because the surfactant feed was not incorporated into the process. The negative values of particle volume change might be caused by coagulation of the larger particles of a normally distributed population because, as mentioned above, the shear-induced collision frequency is proportional to the cube of particle radius. This could shift the average particle size slightly toward the lower end.

The data for the zeta-potential of the particles as a function of the total solids content are shown in Figure 12. Both the small and large latex particles display similar behavior. The zeta-potential of the particles first decreases with increasing total solids content due to the growing particle surface area. The reaction system starts to coagulate after a minimum zeta-potential (ca. -120 mV) is reached at about 25% total solids content. As a result, the zeta-potential of the particles increases toward the end of



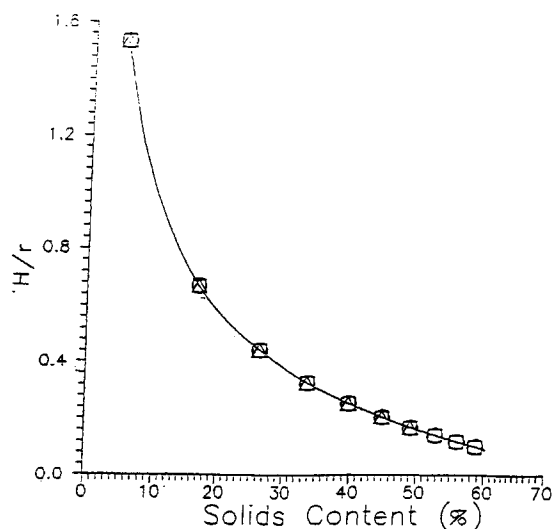


Figure 8 Calculated relatively mean free path length between two particles versus total solids content: seed particle size (O) 50 nm, (□) 100 nm, (Δ) 200 nm.

crease in the concentration of SLS at the air-water interface because the particle-water interface, air-water interface, and water are in equilibrium. Thus, the constancy of the air-water surface tension data cannot serve as supporting evidence for the adsorption of surfactant derived from the coagulated particles onto the surviving particle surfaces.

In general, it is desirable to design a latex product containing as low surfactant as possible to improve the water resistance and minimize the surfactant migration problem for many industrial applications such as caulks and sealants, coatings, and pressure-sensitive adhesives. However, inadequate stabil-

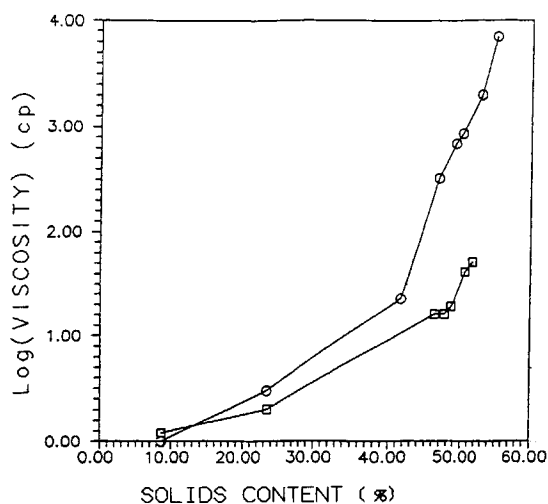


Figure 9 Viscosity versus total solids content: seed particle size (O) 79 nm, (□) 180 nm.

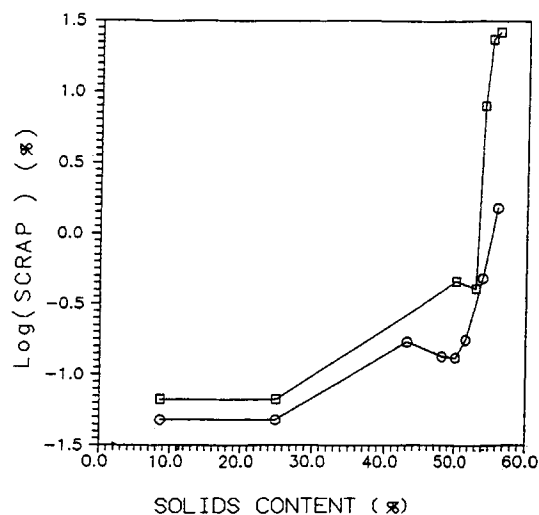


Figure 10 Scrap versus total solids content: seed particle size (O) 79 nm, (□) 180 nm.

zation of the particles will result in the formation of filterable solids and reactor scrap, which often becomes a barrier against successful product scale-up. Furthermore, the problem of controlling the latex particle size due to the limited flocculation process is also a concern in product development. The dilemma between the product properties and smooth plant production places a challenge in front of colloidal chemists. As demonstrated in this study, events including the particle growth via propagation or limited flocculation, secondary nucleation, and coagulation can take place simultaneously during semibatch emulsion polymerization and the interplay among various reaction parameters is very complicated.

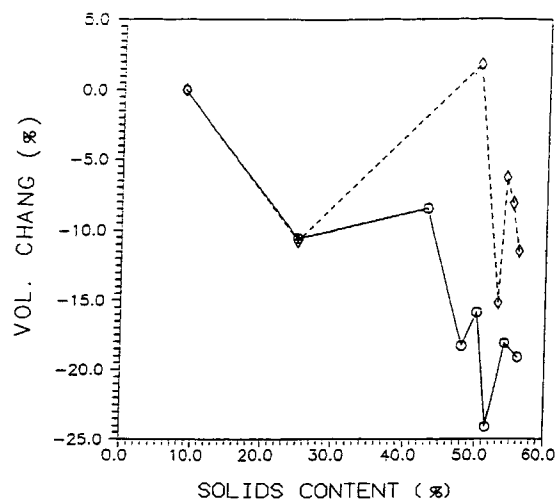


Figure 11 Particle volume change versus total solids content: seed particle size (O) 79 nm, (□) 180 nm.

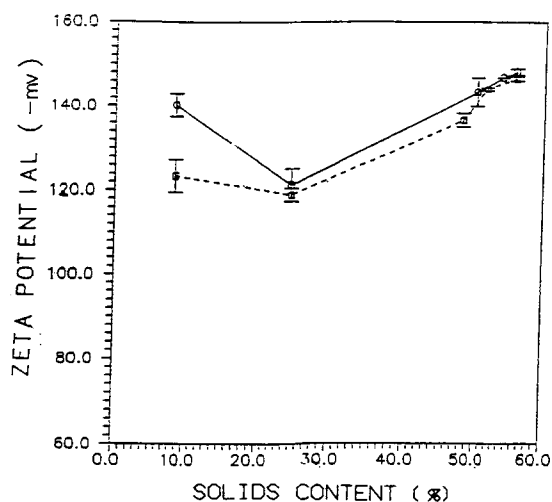


Figure 12 Zeta-potential versus total solids content: seed particle size (O) 79 nm, (□) 180 nm.

CONCLUSIONS

In the semibatch emulsion copolymerization of MMA and BA, events including the particle growth via propagation or limited flocculation, secondary nucleation, and coagulation can take place simultaneously. The effects of various reaction parameters on the latex stability were investigated by analyzing the data of coagulation scrap and particle volume change attributed to limited flocculation.

Both scrap and particle volume changes were shown to increase with an increase in the electrolyte concentration. The amount of scrap was greatly reduced when the level of SLS in the monomer emulsion feed increased. Increasing the level of SLS in the initial reactor charge resulted in an increase in the particle volume change due to the limited flocculation process. The designed experiments also showed that the greater the ratio of MMA to BA, the greater the amount of scrap formed during polymerization. Within the range of experimental conditions, the scrap increased and the particle volume change decreased with an increase in the agitation speed, but the effects were not significant.

Experimental results also showed that the amount of scrap increased with an increase in the total solids content. More importantly, the rate of change in scrap increased rapidly above 40% total solids content. Finally, both limited flocculation and secondary nucleation resulted in deviation from the simple Novak model, which was developed to predict the particle nucleation and growth for semibatch emulsion copolymerization of acrylic monomers.

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