Stability of Carboxylated Poly(butyl acrylate) Latices during Semibatch Emulsion Polymerization

C. S. CHERN and F. Y. LIN

Department of Chemical Engineering, National Taiwan Institute of Technology, Taipei, Taiwan 106, Republic of China

SYNOPSIS

The stability of latex particles in the semibatch emulsion polymerization of butyl acrylate (BA) in the presence of 0–10% acrylic acid (AA) was investigated. The amount of coagulum (i.e., large flocs caused by intensive coagulation) can be greatly reduced by an increase in the concentration of sodium lauryl sulfate (SLS) in the monomer emulsion feed. On the other hand, increasing the concentration of SLS in the initial reactor charge can result in an increase in the percentage of the particle volume change (i.e., a measure of the degree of limited flocculation) later in the process. Both the scrap and percentage of the particle volume change increase with an increase in the electrolyte concentration. Both the coagulation and secondary nucleation process can result in a significant deviation from the Novak model. Experimental data also show that latex particles comprising pure BA can lose their stability rapidly at higher total solids content because of the crowding effect. Incorporation of only 5% AA into the emulsion polymers greatly improves the latex stability. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Emulsion polymerization involves the propagation reaction occurring in compartmentalized, monomer-swollen polymer particles dispersed in water. These submicron particles can collide with one another by Brownian motion or mechanical agitation, and they tend to coagulate due to the attractive van der Waals force. The latex stability can be achieved by using an anionic surfactant, such as sodium lauryl sulfate, (SLS) which can provide a heterogeneous reaction system with a potential energy barrier against coagulation. The potential energy barrier is attributed to the repulsive force between the negatively charged electric double layers of the dispersed particles. Emulsion polymerization can be accomplished by using a batch, semibatch, or continuous process. Among these processes, semibatch emulsion polymerization is the most widely used technique for the production of coatings, adhesives, and synthetic rubbers. This is due to the fact that heat transfer in large scale reactors is rather limited; furthermore,

the semibatch process can be effective in controlling the physical properties of the latex products.

The size of the emulsion polymer particles can have an important effect on the quality of the products. Recently, Chern and Hsu[1] studied the effects of various reaction variables on the particle nucleation and growth processes for semibatch emulsion polymerization of acrylic monomers. It was found that the concentration of sodium lauryl sulfate (SLS) in the initial reactor charge was the most important parameter in determining the final latex particle size. Growth of the particles via conversion of the imbibed monomer to polymer in the particles will cause an increase in the particle surface area during the monomer addition period. The newly created particle surfaces require more surfactant in order to maintain an adequate colloidal stability. Thus, the primary function of SLS in the monomer emulsion feed is to stabilize the growing particles. Adding extra SLS to the reaction system during the monomer feed also can lead to formation of a second crop of primary particles (secondary nucleation). Secondary nucleation can reduce the average particle size and broaden the size distribution. Therefore, more polymer–water interfacial area is generated, and the particles need more surfactant to pre-

vent them from coagulation. Furthermore, the emulsion polymer particles can grow in size by mild aggregation of a few particles in order to maintain an appreciable colloidal stability. For example, the tremendous particle surface area generated during the particle nucleation period can result in a lower particle surface charge density and, hence, a lower potential energy barrier against flocculation. Therefore, the repulsive force among the interactive particles is not high enough to prevent these particles from flocculation. Such a flocculation process can result in a decrease in the total particle surface area and, consequently, increase the particle surface charge density. Thus, the flocculation process will diminish when the particle surface charge density increases to a critical level and most of the flocculated particles still can be stably dispersed in water. Such a limited flocculation process[2-4] can make the task of particle size control more difficult. On the other hand, intensive coagulation can lead to formation of large flocs (i.e., coagulum or scrap), which can cause problems to the plant production and increase the product cost. Therefore, a better understanding of the effects of important reaction variables on the latex stability during polymerization is essential for successful product development and production.

Chern et al.[2] have demonstrated that a number of events, including the growth of the particles via propagation or limited flocculation, secondary nucleation, and severe coagulation, can take place simultaneously in the semibatch emulsion polymerization of acrylic monomers. The effects of several reaction parameters on the latex stability were studied by analyzing the data of scrap (attributed to intensive coagulation) and the percentage of the particle volume change (attributed to limited flocculation). The percentage of the particle volume change (ΔV) during the monomer addition period can be calculated as follows[2]:

$$\Delta V = [(d_f/d_f')^3 - 1] \times 100\% \qquad (1)$$

where d_f is the particle diameter of the latex product determined by the dynamic light scattering method. The parameter d_f' is the particle diameter of the latex product calculated according to a mass balance [see eq. (2)] if both secondary nucleation and limited flocculation do not occur during the monomer addition period. For example, if the parameters d_{15} (nm) and N_p are the particle diameter and total number of particles, respectively, of the latex sample taken immediately before the start of the monomer emulsion feed, W_m (g) is the total weight of the fed

monomer, and ρ (g/cm^3) is the density of polymer, then d_f' can be calculated according to the following equation:

$$d_f' = [d_{15}^3 + 6 \times 10^{21} W_m/(\pi \rho N_p)]^{1/3} \qquad (2)$$

The work of Chern et al.[2] led to the conclusion that the amount of coagulum formed by intensive coagulation decreased with an increase in the concentration of SLS in the monomer emulsion feed. On the other hand, increasing the concentration of SLS in the initial reactor charge can result in an increase in ΔV due to limited flocculation later in the process. Both the amount of coagulum and ΔV will increase with an increase in the electrolyte concentration. Within the range studied (500–800 rpm), the agitation speed was found to be unimportant to the coagulation process. Their experimental data also indicate that the polymer particles can lose their stability rapidly above 40% total solids content because of the crowding effect. Similarly, Masa et al.[5] used both the scrap and percentage of the particle size change data to investigate the chemical stability of latex products.

As mentioned above, a latex product consists of innumerable submicron polymer particles dispersed in water. These particles are generally stabilized by anionic surfactants. Nevertheless, the surfactant molecules remaining in the latex product can have a negative effect on the application properties such as adhesion of the pressure-sensitive adhesives and film formation and water resistance of the coating materials because the small and mobile surfactant molecules tend to migrate to the surface layer of the polymeric film. One approach to overcome the surfactant migration problem is to reduce the level of surfactant used in the recipe. However, the latex stability can be greatly reduced, and a significant amount of coagulum can form during the monomer addition period. Snuparek[6] and Snuparek and Tutalkova[7] studied semibatch emulsion polymerization of acrylic monomers, and their experimental data showed that incorporation of a small amount of acrylic acid (AA) into the emulsion polymers increased the latex stability significantly. The ionized carboxyl group ($-COO^-$) that is chemically incorporated into the emulsion polymer can increase the particle surface charge density and, therefore, enhance the repulsive force among the interactive particles. Chern et al.[8,9] studied the effects of different functional monomers such as AA and methacrylic acid (MAA) on the physical properties of the carboxylated poly(butyl acrylate) latices produced by a semibatch process. Again, the concentration of SLS

in the initial reactor charge was shown to be the most important parameter in determining the final particle size. The carboxylic monomer AA is the most efficient functional monomer to help nucleate and stabilize the latex particles during polymerization. In addition, their experimental data on the particle size distribution, the molecular weight distribution, and the level of polyelectrolyte that can be detected in water strongly suggest that the aqueous phase reaction should play an important role during the particle nucleation period.

The objective of this work was to study the effects of various reaction parameters on the latex stability during the semibatch emulsion polymerization of butyl acrylate (BA) in combination with a small amount of AA. Both the percentage of the particle volume change and coagulum collection were used to quantify the effects of the parameters chosen for study. The results obtained from this work should be useful to the tape and label industries.

EXPERIMENTAL

Materials

The chemicals used were butyl acrylate (Formosa Plastics Co.), acrylic acid (Formosa Plastics Co.), sodium lauryl sulfate (Henkel Co.), sodium persulfate (Riedel-de-Haen), sodium bicarbonate (Riedel-de-Haen), sodium hydroxide (Riedel-de-Haen), hydrochloric acid (Nacalai Tesque, Inc.), sodium chloride (Riedel-de-Haen), nitrogen (Ching-Feng-Harng Co.), and deionized water (Barnsted, Nanopure Ultrapure Water System, specific conductance < 0.057 μS/cm). The primary monomer BA was distilled under reduced pressure before use. All other chemicals were used as received.
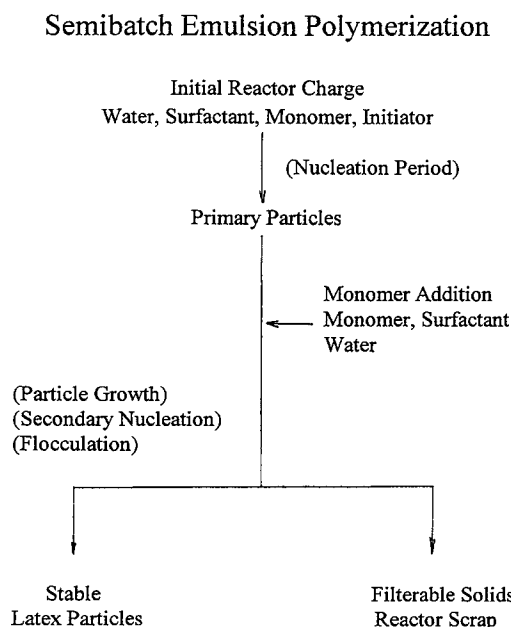
Polymerization Process

Polymerization was carried out in a 1 liter glass reactor equipped with a four-bladed fan turbine agitator, a thermometer, and a reflux condenser. The polymerization procedure is described as follows. All process water, along with the initial surfactant, sodium bicarbonate, and monomers, were charged to the reactor at room temperature. The initial reactor charge was purged with nitrogen for 10 min to remove the dissolved oxygen, while the reactor temperature was brought to 80°C. The reaction was then initiated by adding the initiator solution to the reactor. After 15 min, the monomer emulsion was fed to the reactor over 180 min by an FMI pump. Po-

lymerization temperature was kept at 80°C throughout the reaction. After the end of the monomer emulsion feed, the reaction system was maintained at 80°C for 30 min to reduce the level of the residual monomer. The reaction scheme is shown in Figure 1. The theoretical total solids content at the end of the reaction is 40% unless stated otherwise.

Characterization

The finished latex product 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. The data on the particle size distribution were obtained from dynamic light scattering (DLS, Otsuka Photal LPA-3000/3100). The zeta potential (ζ) of the latex particles was determined by Malvern's Zetamaster. For appropriate measurements, the latex product with a volume of 0.05 mL was diluted with 100 mL water to adjust the number of photons counted per sec (cps) to a proper value of around 5000–15,000. The dilution water had the same pH and conductivity as the original latex product. The pH and conductivity of the dilution water were adjusted by using HCl, NaOH, and NaCl. Hence, the latex particles should be exposed to a similar aqueous environment as compared to the original latex product after sample

Figure 1 Scheme of semibatch emulsion polymerization.

preparation. Five measurements were made for each latex sample, and the average of these five measurements was reported as the ζ of the finished product.

RESULTS AND DISCUSSION

First, we used a fractional two-level factorial design (five variables, 16 experiments, plus one for the midpoint) to study the effects of important reaction variables on the latex stability during polymerization. The variables selected for study were

(1) the concentration of SLS in the initial reactor charge (0.005–0.5%, based on the weight of water in the initial reactor charge);

(2) the concentration of SLS in the monomer emulsion feed (0.13–1%, based on total monomer);

(3) the weight percentage of AA in the monomer mixture (0.1–10% of total monomer);

(4) $[N_a^+]$, that is, the electrolyte concentration (0.174–0.6%, based on the weight of total water); and

(5) the agitation speed (400–800 rpm).

In the designed experiments, $[N_a^+]$ in the initial reactor charge was maintained constant by means of NaCl. The remaining NaCl, required to adjust the finished latex product to the designed electrolyte concentration, was placed in the monomer emulsion feed. The initiator concentration was constant (0.25%, based on the weight of water in the initial reactor charge) throughout this work. A typical recipe for the semibatch emulsion polymerization of BA with various levels of AA is shown in Table I.

To test the batch-to-batch variations, the midpoint experiment (recipe: 0.2525% SLS in the initial reactor charge; 600 rpm; 0.565% SLS in the monomer emulsion feed; $[Na^+]$ = 0.387%; and 5.05% AA) was carried out twice. The average particle size of the finished latices was 153.7 ± 0.7 nm, and the reproducibility of the runs was very good. The filterable solids collected from the 200-mesh screen were insignificant for all experiments in the factorial design. Thus, the data of scrap presented in this work is only the 40-mesh coagulum plus the scrap adhering to the agitator, thermometer, and reactor wall. The experimental data obtained from the factorial design are compiled in Table II. In the factorial design, the overall average amount of scrap of the designed experiments is 0.747 wt %, based on total

Table I   A Typical Recipe for Semibatch Emulsion Polymerization of BA with Various Levels of AA in the Fractional Two-Level Factorial Design

	Chemicals	Weight (g)
Monomer emulsion feed	H_2O	80.00
	NaCl	0.39
	SLS	0.29
	BA	210.79
	AA	0.21
Initial reactor charge	H_2O	242.00
	SLS	0.013
	NaCl	0.26
	$NaHCO_3$	0.66
	BA	11.56
	AA	0.01
Initiator solution	H_2O	15.00
	$Na_2S_2O_8$	0.65
Total Weight (g)	561.83	
Total Solids Content (%)	40.02	

solids, and the overall average percentage of the particle volume change (ΔV) is 151.5%. Table III summarizes the calculated standardized effects of each variable on the latex stability in the factorial design.

The level of coagulum formed during polymerization, for example, will decrease 0.414% with respect to the overall average of scrap when the concentration of SLS in the initial reactor charge increases from the lowest level (0.005%) to the highest level (0.5%). On the other hand, the parameter ΔV will increase 159.9% with respect to the overall average of ΔV when the concentration of SLS in the initial reactor charge increases from the lowest level (0.005%) to the highest level (0.5%). The electrolyte concentration ($[Na^+]$) shows a significant effect on both the scrap and ΔV. Thus, the ionic strength should play an important role in the coagulation process. The ionic strength will not only determine the quantity of scrap formed inside the reactor but also cause the particle size of the latex product to deviate from the designed value.

As shown in Table III, the amount of scrap can be reduced significantly when the concentration of SLS in the monomer emulsion feed is increased. This result is due to the fact that the surfactant gradually added to the reaction medium will cause the surface charge density on the growing particles to increase and, thus, greatly improve the latex stability. Furthermore, the standardized effects of the agitation speed and the weight percentage of AA in the monomer mixture indicate that the

Table II Experimental Data Obtained From the Two-Level Factorial Design

$X_1, X_2,$ X_3, X_4, X_5	d_{15} (nm)	d_f (nm)	d'_f (nm)	Total Scrap (%)	ΔV (%)
−, −, −, −, +	154.3	470.7	413.4	0.88	47.5
+, −, −, −, −	36.9	79.5	98.7	0.67	−47.8
−, +, −, −, −	138.3	384.9	369.2	0.22	12.9
+, +, −, −, +	38.7	75.7	103.4	0.01	−60.9
−, −, +, −, −	159.1	237.2	426.4	0.43	−82.8
+, −, +, −, +	41.5	91.5	111.2	1.19	−44.3
−, +, +, −, +	144.4	244.2	385.9	0.21	−74.5
+, +, +, −, −	37.2	83.6	99.3	0.06	−40.2
−, −, −, +, −	143.7	499.8	382.8	2.89	122.6
+, −, −, +, +	53.7	291.3	142.8	0.26	751.1
−, +, −, +, +	144.5	247.5	385.6	0.23	−73.7
+, +, −, +, −	33.5	189.2	89.4	0.10	848.0
−, −, +, +, +	146.2	338.7	389.5	4.62	−34.2
+, −, +, +, −	33.2	171.9	88.8	0.35	624.8
−, +, +, +, −	142.2	312.5	379.6	0.35	−44.2
+, +, +, +, +	35.5	162.1	94.8	0.56	400.5
0, 0, 0, 0, 0	39.7	154.7	106.0	0.21	211.1
0, 0, 0, 0, 0	40.2	152.7	107.3	0.20	188.2
			−	+	0
X_1 SLS in the initial reactor charge (%)			0.005	0.5	0.2525
X_2 SLS in the monomer feed (%)			0.005	0.5	0.2525
X_3 AA in the monomer mixture (%)			0.1	10	5.05
X_4 [Na$^+$] (%)			0.174	0.6	0.387
X_5 Agitation speed (rpm)			400	800	600

scrap increases and ΔV decreases when either variable changes from the minus level to the plus level, although the magnitude of each effect is smaller. The finding that the amount of scrap formed during the reaction increases when the amount of AA changes from the minus level to the

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

	Standardized Effect	
Variable	Scrap (%)	ΔV (%)
SLS in IRC (%)[a]	−0.414	159.9
SLS in MEF (%)	−0.597	−23.1
AA (%)	0.157	−55.9
[N$_a^+$] (%)	0.356	180.3
Agitation speed (rpm)	0.181	−30.1
Overall average	0.747	151.5

[a] IRC = the initial reactor charge; MEF = the monomer emulsion feed.

plus level seems to be beyond expectation. As mentioned above, the carboxylic monomer AA has been shown to be the most efficient one to help nucleate and stabilize the latex particles during the semibatch emulsion polymerization.[8] This seeming contradiction can be explained in the following discussion.

Based on the above factorial design, the following empirical, predictive equation for the formation of coagulum was developed.

$$\text{Total Scrap } (\%) = 0.21 - 0.4144X_1$$
$$- 0.5969X_2 + 0.1569X_3 + 0.3556X_4$$
$$+ 0.1806X_5 + 0.3794X_1X_2 - 0.01688X_1X_3$$
$$- 0.4381X_1X_4 - 0.07563X_1X_5$$
$$- 0.07938X_2X_3 - 0.2631X_2X_4$$
$$- 0.1456X_2X_5 + 0.1431X_3X_4 + 0.4931X_3X_5$$
$$+ 0.06688X_4X_5 + 0.6044X_3^2 \qquad (3)$$

where the concentration of SLS in the initial reactor charge, the concentration of SLS in the monomer emulsion feed, the weight percentage of AA in the monomer mixture, the electrolyte concentration, and the agitation speed are abbreviated by X_1, X_2, X_3, X_4, and X_5, respectively. Figure 2 shows a typical parametric contour plot of scrap constructed from the predictive equation. In this contour plot, the agitation speed and [Na$^+$] were set at 600 rpm and 0.387%, respectively. The weight percentage of AA in the monomer mixture was set at 0.1, 5.05, and 10% for Figures 2(a–c, respectively). The abscissa represents the concentration of SLS in the monomer emulsion feed, and the ordinate represents the concentration of SLS in the initial reactor charge. Considering, for example, the curve with the amount of scrap equal to 0.7%, the concentration of SLS in the monomer emulsion feed required to maintain the same latex stability should increase with a decrease in the concentration of SLS in the initial reactor charge. The contour plot also indicates that, at a constant concentration of SLS in the initial reactor charge, the amount of scrap is greatly reduced when the concentration of SLS in the monomer emulsion feed increases. Similarly, at a fixed concentration of SLS in the monomer emulsion feed, the amount of scrap is reduced when the concentration of SLS in the initial reactor charge increases.

Figures 2(a) and (b) show that the curve with the amount of scrap equal to 0.7% shifts toward the bottom left corner when the weight percentage of AA in the monomer mixture increases from 0.1 to 5.05%. This kind of behavior suggests that less surfactant (both in the initial reactor charge and in the monomer emulsion feed) is required to maintain the same latex stability when a higher weight percentage of AA in the monomer mixture is used. Increasing the quantity of AA can increase the particle surface charge density and, therefore, increase the repulsive force among the interactive particles. On the other hand, the curve with 0.7% scrap shifts toward the upper right corner this time when the weight percentage of AA in the monomer mixture increases from 5.05 to 10% [see Figures 2(b), (c)]. In this manner, more surfactant is required to maintain the same latex stability at a very high AA concentration, which is probably due to the increased concentration of polyelectrolyte in the aqueous phase.[9] It is postulated that the abundant, ionized polyelectrolyte in water can compress the electric double layer of the particles and, consequently, decrease the potential energy barrier against co-
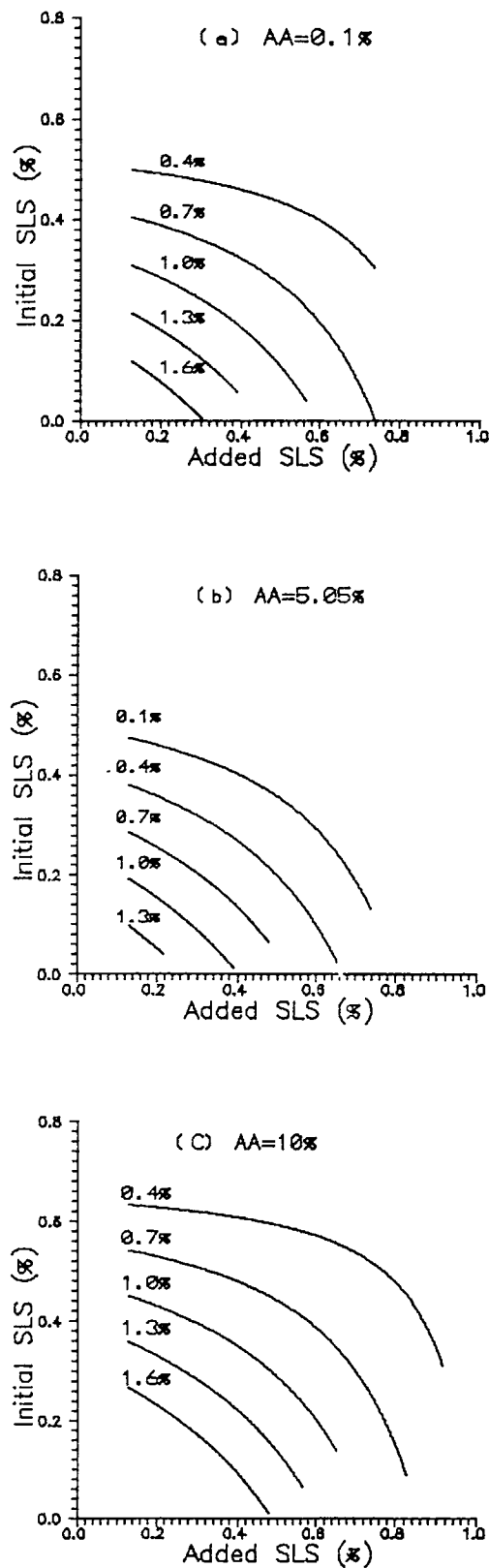
Figure 2 Contour plot of the scrap. Agitation speed = 600 rpm. [Na$^+$] = 0.387%. Weight percentage of AA in the monomer mixture: (a) 0.1%; (b) 5.05%; (c) 10%.

agulation. Another possible explanation is that the higher the concentration of the hydrophilic AA unit on the particle surface, the less the amount of SLS adsorbed on the particle surface. Thus, the latex stability can be greatly reduced as a result of the decreased repulsive force among the interactive particles.

The percentage of the polymer particle volume change (ΔV) is influenced significantly by both the concentration of SLS in the initial reactor charge and $[N_a^+]$. The parameter ΔV increases with an increase in the concentration of SLS in the initial reactor charge. The positive and large standardized effect associated with the concentration of SLS in the initial reactor charge strongly suggests that the limited flocculation process can occur during the monomer emulsion feed period when the concentration of SLS in the initial reactor charge is high. This can be explained by the fact that the number of primary particles nucleated increases with an increase in the concentration of SLS in the initial reactor charge. The tremendous particle surface area thus generated will lead to a lower particle surface charge density and, hence, a lower potential energy barrier against flocculation. Thus, the repulsive force among the interactive particles is not high enough to keep these particles from flocculation. Such a flocculation process will result in a decrease in the total particle surface area and, consequently, increase the particle surface charge density. Since the concentration of SLS in the initial reactor charge is quite high, the flocculation process will diminish when the particle surface charge density increases to a critical level and most of the flocculated particles still can be stably dispersed in water. The work of Fitch[3] and Fitch and Tsai[4] also supports such a limited flocculation process. In addition, the parameter ΔV increases rapidly with increasing $[Na^+]$ since the increased electrolyte concentration can compress the electric double layer of the particles and, hence, reduce the repulsive force among the interactive particles according to DLVO theory.[10,11] This action, in turn, can increase the degree of limited flocculation during the monomer emulsion feed period. Other parameters such as the agitation speed, the concentration of SLS in the monomer emulsion feed, and the weight percentage of AA in the monomer mixture show very little effect on ΔV.

Again, based on the factorial design, a predictive equation can be developed for ΔV, and it is shown below.

$$\Delta V(\%) = 211.1 + 159.8500X_1 - 23.0625X_2$$
$$- 55.9125X_3 + 180.3125X_4 - 30.1125X_5$$
$$+ 6.0125X_1X_2 - 12.7875X_1X_3$$
$$+ 171.8875X_1X_4 - 12.1875X_1X_5$$
$$- 4.6750X_2X_3 - 18.6500X_2X_4$$
$$- 43.0250X_2X_5 - 31.7250X_3X_4$$
$$+ 3.8500X_3X_5 - 33.3250X_4X_5 - 67.0500X_3^2 \quad (4)$$

Figure 3 shows the parametric contour plot of ΔV according to the predictive equation. The agitation speed and the concentration of SLS in the monomer emulsion feed were set at 600 rpm and 0.565%, respectively, in this figure. The weight percentage of AA in the monomer mixture was set at 0.1, 5.05, and 10% for Figures 3(a)–(c), respectively. The abscissa represents the concentration of SLS in the initial reactor charge, and the ordinate represents the concentration of Na^+ in water. At a fixed ionic strength, ΔV increases with an increase in the concentration of SLS in the initial reactor charge. The parameter ΔV also increases with an increase in the electrolyte concentration when the concentration of SLS in the initial reactor charge remains constant. The contour plots with the weight percentage of AA in the monomer mixture equal to 0.1 and 5.05% also show similar trends [see Figs. 3(a) and (b)]. On the other hand, Figures 3(b) and (c) show that all of the curves shift significantly toward the upper right corner when the weight percentage of AA in the monomer mixture increases from 5.05 to 10%. This observation implies that a higher concentration of SLS in the initial reactor charge (i.e., a larger number of primary particles or greater particle surface area generated during the particle nucleation period) or a higher electrolyte concentration is required to maintain the same level of ΔV when the weight percentage of AA in the monomer mixture increases from 5.05 to 10%. Therefore, the limited flocculation process becomes less important when the weight percentage of AA in the monomer mixture is relatively high.

Three formulae (high, medium, and low levels of scrap) were then selected to verify the predictive equations developed for the amount of scrap formed during the reaction. The agitation speed and $[Na^+]$ were fixed at 600 rpm and 0.387%, respectively, in this series of experiments. The formulae and results are summarized in Table IV. The experimental data show that the predictive equation for the scrap works pretty well. The amount of scrap first decreases and

(a) AA=0.1%

(b) AA=5.05%

(c) AA=10%
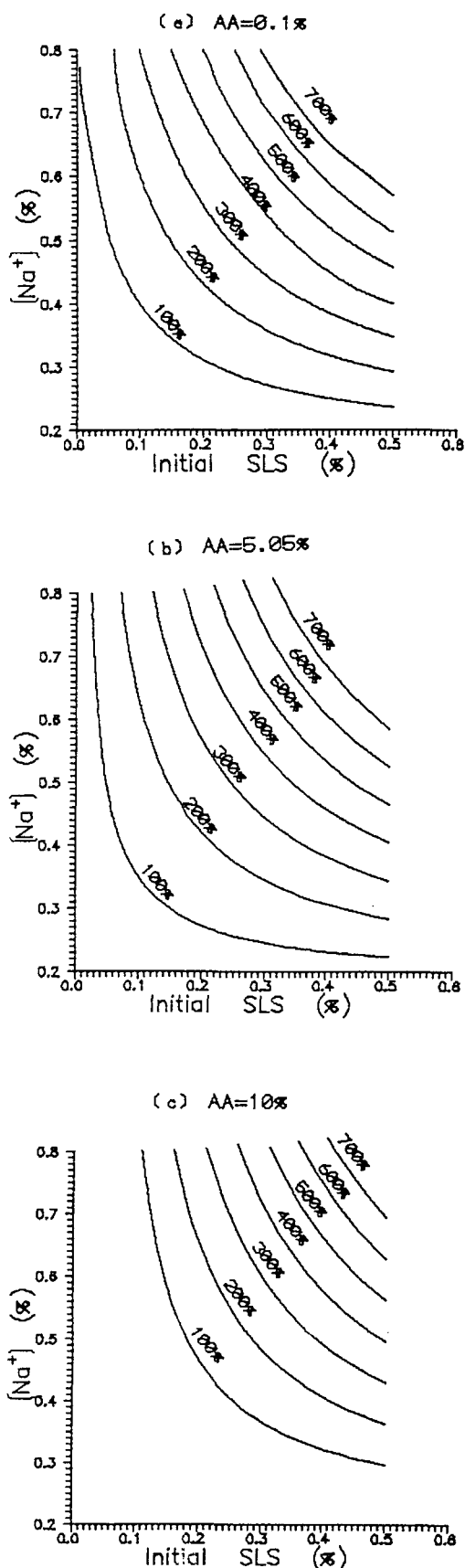
then increases with an increase in the weight percentage of AA in the monomer mixture, which is in agreement with the results obtained from the above factorial design. On the other hand, the deviation between the predicted and experimental data for ΔV is greater in this series, but the trend is still correct. The larger deviation observed for ΔV implies that the limited flocculation process is very sensitive to the reaction environment. Hence, it is very difficult to control the particle size if the limited flocculation process plays an important role during the semibatch emulsion polymerization. Please note that there is no apparent correlation between the scrap and ΔV data. Table IV also shows that the ζ of the latex particles decreases with an increase in the weight percentage of AA in the monomer mixture. This observation is probably caused by the fact that the particles are covered by a very hydrophilic polymer layer that can shift the shear plane toward the bulk solution and, consequently, reduce the ζ of the particles. Furthermore, the decreased particle size (i.e., the increased particle surface area) with increasing weight percentage of AA in the monomer mixture can cause a decrease in the particle surface charge density and thereby reduce the ζ of the particles.

Novak,[12] based on the coagulative nucleation mechanism, developed a model to study the particle nucleation and growth processes for semibatch emulsion polymerization of acrylic monomers. The model assumes that the precursor particles (ca. 2 nm) are first generated by phase separation of the oligomeric radicals in water. These precursor particles, although completely covered with surfactant, are extremely unstable due to the very large radius of curvature and they can aggregate rapidly until a stable (primary) particle size is achieved. The number of primary particles generated during nucleation is determined by the amount of surfactant available to stabilize the particle–water interfacial area generated. The remaining polymerization is simply the growth of the primary particles via the propagation reaction. Secondary nucleation and flocculation are assumed to be negligible throughout the monomer addition period. The Novak model predicts that the slope of the $\log(d_f)$ versus $\log(1/G_a)$ plot should be 0.333. The parameter d_f is the final latex particle size and G_a is the amount of surfactant used during

Figure 3 Contour plot of the percentage of the particle volume change. Agitation speed = 600 rpm. Concentration of SLS in the monomer emulsion feed = 0.565%. Weight percentage of AA in the monomer mixture: (a) 0.1%; (b) 5.05%; (c) 10%.

Table IV Experiments Designed to Verify the Scrap and ΔV Predictive Equations Derived From the Factorial Design

|	High	Medium	Low
Formulations			
SLS in IRC (%)[a]	0.35	0.36	0.40
SLS in MEF (%)	0.16	0.30	0.40
AA (%)	10	0.1	5.05
Results:			
Final latex product			
d_f (nm)	144	171	161
pH	3.2	6.4	3.6
Conductivity (μS/cm)	7460	6770	6920
ζ (mV)	−18	−52	−32
Scrap			
Prediction (%)	1.3	0.7	0.1
Experiment (%)	1.96	0.61	0.13
Error (%)	51	−13	30
ΔV			
Prediction (%)	168	285	315
Experiment (%)	290	351	473
Error (%)	72	24	50

[a] IRC = the initial reactor charge; MEF = the monomer emulsion feed; agitation speed = 600 rpm; [Na$^+$] = 0.387%.

the particle nucleation period (i.e., the concentration of SLS in the initial reactor charge in this work).

Three series of experiments were carried out to study the effects of the carboxylic monomer AA on the particle size of the finished latex product by means of the Novak model. The weight percentage of AA in the monomer mixture was kept constant at 5%, the concentration of SLS in the initial reactor charge was varied between 0.01 and 1%, the concentration of SLS in the monomer emulsion feed was kept constant at 2.5% to maintain an appreciable latex stability during polymerization, the agitation speed was 600 rpm, and the total solids content was 40% at the end of polymerization throughout the following three series of experiments. In the first series (designated as the Novak series), the total [N_a^+] was kept constant at 0.286%, based on the weight of total water shown in the recipe. The concentration of N_a^+ in the initial reactor charge was also kept constant by using NaCl. The remaining NaCl required to adjust the finished latex product to the designed ionic strength was placed in the monomer emulsion feed. The results of the Novak series are shown as the triangular data points in Figure 4. The straight line obtained from the least-squares best-fit method has a slope of 0.295, which is quite close to the value (0.333) predicted by the Novak model. The deviation between the experi-

mental data and the Novak model is most likely caused by incorporation of 5% AA into the emulsion polymers. The negatively charged carboxyl group derived from AA can help nucleate and stabilize the primary particles, especially when the concentration of SLS in the initial reactor charge is very low (or the parameter $1/G_a$ is very high).[8] Thus, the final latex particle size d_f at high $1/G_a$ is lowered more than that at low $1/G_a$. In this way, the slope of the $\log(d_f)$ versus $\log(1/G_a)$ plot can be reduced to a smaller value. The corresponding scrap, ΔV, and ζ, data as a function of $1/G_a$ are shown in Figures 5–7, respectively. Both the scrap and ΔV data show that all latices involved in the Novak series are very stable. In addition, the ζ of the particles remains relatively constant (−45 ± 5 mV) throughout the range of $1/G_a$ in the Novak series. The relatively constant ζ data imply that the number of latex particles produced in the semibatch emulsion polymerization can be regulated by the concentration of SLS in the initial reactor charge and the concentration of SLS in the monomer emulsion feed. Such a regulation mechanism can result in comparable particle surface charge densities and, thereby, a relatively constant ζ of the particles at the end of polymerization.

The second series was designed to study the effect of the coagulation process on the final latex particle size. The total [N_a^+] was kept constant at a relatively high level (0.8%) to induce the coagulation events. Again, the concentration of N_a^+ in the initial reactor
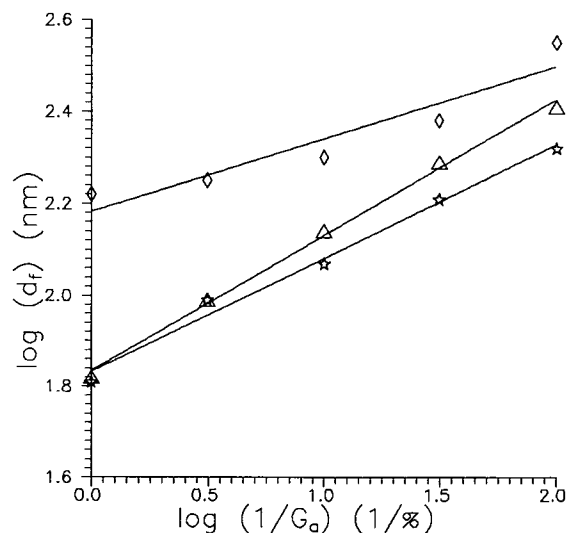
Figure 4 Final particle size versus reciprocal of the concentration of SLS in the initial reactor charge: (△) Novak series; (◇) flocculation series; (✩) secondary nucleation series.
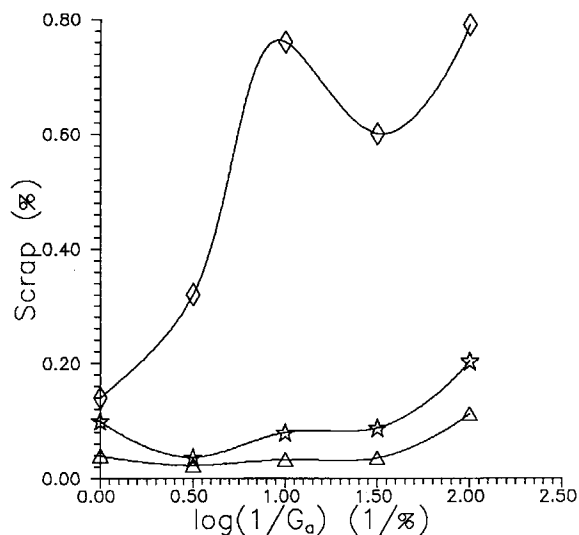
Figure 5 Scrap versus reciprocal of the concentration of SLS in the initial reactor charge: (△) Novak series; (◇) flocculation series; (☆) secondary nucleation series.

charge was kept constant by using NaCl. The remaining NaCl required to adjust the finished product to the designed ionic strength was placed in the monomer emulsion feed. The results of the coagulation series are shown as the diamond data points in Figure 4. The straight line obtained from the least-squares best-fit method has a slope of 0.158, which is much lower than the value predicted by the Novak model. Comparing the experimental data with the Novak series, 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, which is consistent with the scrap and ΔV data shown in Figures 5 and 6. For very small d_f or very small $1/G_a$ (e.g., $d_{15} = 30$ nm, and $d_f = 163$ nm), the formation of scrap was insignificant in comparison with the percentage of the particle volume change. Thus, it can be concluded that limited flocculation predominates throughout the reaction due to the tremendous particle surface area generated during the particle nucleation period. As discussed above, the limited flocculation process can lead to a decrease in the total particle surface area and, consequently, an increase in the particle surface charge density. On the other hand, for very large d_f or very large $1/G_a$ (e.g., $d_{15} = 133$ nm and $d_f = 353$ nm), the amount of scrap was relatively high; whereas ΔV was very low, as shown in Figures 5 and 6. This is because the total particle surface area generated during the particle nucleation period is quite small in this case, and the resultant particle surface charge density is high enough to withstand floccu-

lation. Nevertheless, approximately 0.8% of the polymer particles still can be coagulated to form large flocs under the influence of NaCl addition and intensive mechanical agitation. For the run between the two limiting cases, both the scrap and ΔV data are important in evaluating the latex stability during polymerization. For the coagulation series, the ζ of the particles decreases significantly with an increase in $1/G_a$. This observation, again, supports the above conclusion that the extent of limited flocculation increases with a decrease in d_f (or $1/G_a$). The greater the degree of limited flocculation, the greater the reduction in the total particle surface area and hence the higher the ζ of the particles.

In the last series designed for studying the secondary nucleation effect, an extra shot of the anionic surfactant SLS (1 wt %, based on total water in the reactor before the start of the monomer emulsion feed) was charged to the reactor 36 min after the start of the monomer emulsion feed in order to initiate the secondary nucleation process. Sodium chloride was not used to adjust the ionic strength of the reaction medium; as a result, the total $[N_a^+]$ was 0.35% in this series of experiments. The results of the secondary nucleation series 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 0.248. For very small d_f or very small $1/G_a$ (e.g., $d_{15} = 29$ nm, and $d_f = 69$ nm), the deviation between the experimental data and the Novak model is nil. This result can be explained by the fact that

Figure 6 Percentage of the particle volume change versus reciprocal of the concentration of SLS in the initial reactor charge: (△) Novak series; (◇) flocculation series; (☆) secondary nucleation series.

Figure 7   Zeta potential of the particles versus reciprocal of the concentration of SLS in the initial reactor charge: ($\triangle$) Novak series; ($\Diamond$) flocculation series; ($\star$) secondary nucleation series.

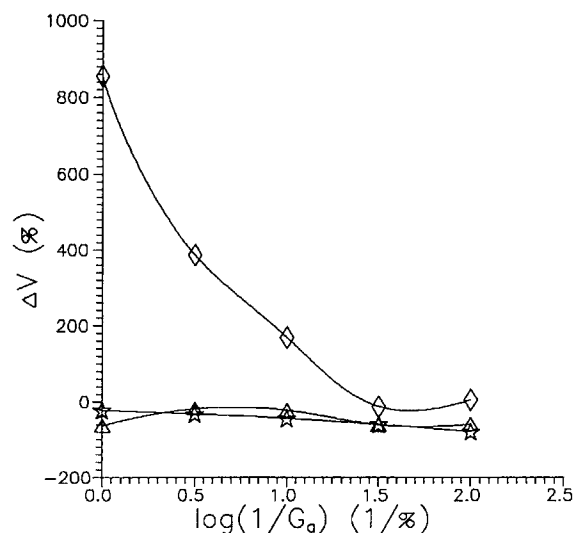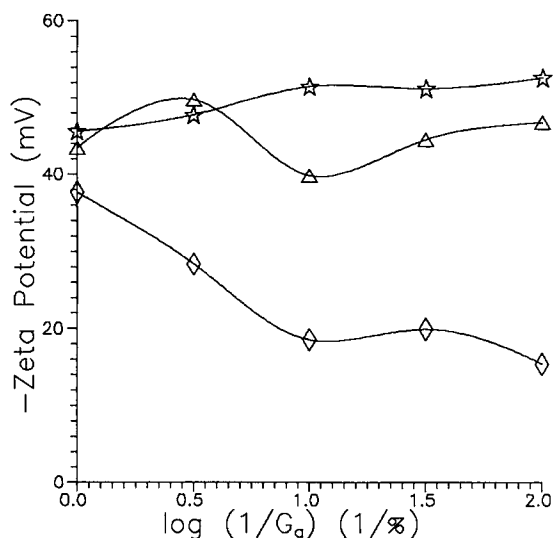the enormous particle–water interfacial area associated with a small particle size latex will efficiently absorb the primary particles formed by the secondary nucleation process. On the other hand, for very large d_f or very large $1/G_a$ (e.g., $d_{15} = 134$ nm and $d_f = 209$ nm), the number of primary particles nucleated during the early stage of polymerization is relatively small. Therefore, the total particle surface area is not high enough to absorb the newly created primary particles after the extra shot of the surfactant. However, the degree of secondary nucleation observed in this experiment is not very significant, probably due to the still relatively small particle size latex and, thus, the relatively high total particle surface area (also see the ΔV data shown in Figure 6). Like the Novak series, the ζ of the particles does not change very much (-49 ± 4 mV) throughout the range of $1/G_a$ in the secondary nucleation series, as shown in Figure 7. It is interesting to note that the coagulation series and the secondary nucleation series just sit on the opposite sides of the line obtained from the Novak series.

Finally, the effect of total solids content on the latex stability was investigated. The average interparticle distance (H) is a measure of the interaction among the latex particles. Chern et al.[2] showed that the calculated relatively mean free path length between two particles (H/r) decreased rapidly with increasing total solids content, and the curves with various seed particle sizes coincided with one another for the seeded semibatch emulsion polymer-

ization process. Thus, at a fixed total solids content, the smaller the seed particles, the smaller the value of H for the stationary particle packing. This result implies that the reaction system with the smallest seed particle size should be the most crowded. Furthermore, the parameter H/r decreases rapidly with increasing total solids content. This trend suggests that the higher the total solids content, the more crowded the reaction system (i.e., the greater the interaction among the particles), which is supported by the experimental data of Chern et al.[2] They showed that the viscosity of the latex that reflected the degree of interaction among the particles increased 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 was greater than the one prepared with the large seed particles. Furthermore, they found that the rate of change in the viscosity with total solids content increased rapidly above 40% total solids content. Thus, it was concluded that the crowding effect could not be ignored for high solids latices.

In this work, two seed latices were then prepared to investigate the impact of total solids content on the latex stability in the seeded semibatch emulsion polymerization of BA/AA (95/5). The particle size of the two seed latices are 79 nm (recipe: 0.249% SLS in the initial reactor charge) and 186 nm (recipe: 0.033% SLS in the initial reactor charge), respectively. For comparison, a seeded semibatch emulsion polymerization of pure BA was also included in this series of experiments. The resultant latex product has a particle size of 186 nm (recipe: 0.033% SLS in the initial reactor charge), and it has the same particle surface charge density contributed by SLS as the seed latex with a composition of BA/AA (95/5) and a particle size of 186 nm. The total solids content was 8.7% just before the start of the monomer addition. There was no surfactant fed to the reactor during the monomer addition period for the purpose of enhancing the effect of total solids content. Figure 8 shows the d_f versus total solids content data. The corresponding scrap and ΔV data as a function of total solids content are shown in Figures 9 and 10, respectively.

It is shown in Figure 8 that the final latex particle size d_f increases significantly with an increase in the total solids content for the run with a composition of BA/AA (100/0) and a seed particle size of 186 nm. The increased d_f with total solids content can be attributed to polymerization of the imbibed monomer in the particles during the monomer addition period. This is because the magnitude of ΔV is quite small, and ΔV remains relatively unchanged
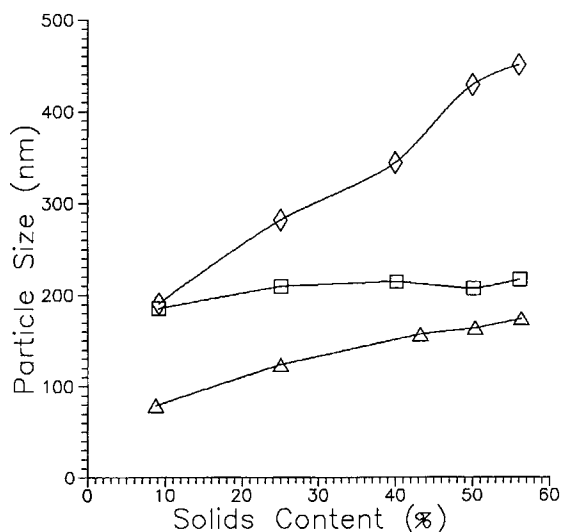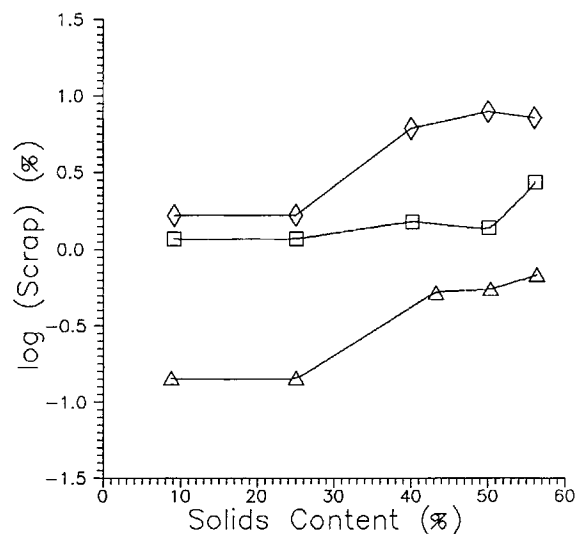
Figure 8 Latex particle size versus total solids content, polymer composition, and seed particle size: ($\triangle$) BA/AA = 95/5, 79 nm; ($\square$) BA/AA = 95/5, 186 nm; ($\lozenge$) BA/AA = 100/0, 186 nm.

Figure 9 Scrap versus total solids content, polymer composition, and seed particle size: ($\triangle$) BA/AA = 95/5, 79 nm; ($\square$) BA/AA = 95/5, 186 nm; ($\lozenge$) BA/AA = 100/0, 186 nm.

throughout the reaction (see Figure 10). The relatively small and constant ΔV indicates that the limited flocculation process is not important in the semibatch emulsion polymerization of pure BA in the presence of large seed particles. The amount of scrap in logarithmic scale remains unchanged before 25% solids content. The reaction system then starts to lose its colloidal stability, and the amount of scrap continues to increase thereafter (see Figure 9), presumably due to both the enhanced crowding effect and the decreased particle surface charge density with total solids content. In addition, it was observed that the ζ of the particles remained relatively constant and it fluctuated between -75 and -87 mV during polymerization.

In comparison with the latex prepared with a composition of BA/AA (100/0) and large seed particles (186 nm), the d_f of the latex product prepared with a composition of BA/AA (95/5) and small seed particles (79 nm) increases more slowly with increasing total solids content (see Figure 8) because, in this case, more seed particles are available for polymerizing the feed monomer. Furthermore, the latex is much more stable than the one prepared with a composition of BA/AA (100/0) and large seed particles (186 nm), as shown by the scrap and ΔV data in Figures 9 and 10. The ζ data (-51 ± 5 mV) are not sensitive to changes in the total solids content.

It is interesting to note that the d_f of the latex particles prepared with a composition of BA/AA (95/

5) and large seed particles (186 nm) does not change very much with an increase in the total solids content (see Figure 8). The reason for this observation is that a second crop of primary particles nucleates during the monomer addition period because AA can help nucleate and stabilize the latex particles. In addition, the total particle surface area associated with the very large seed particles is insufficient to absorb the newly created primary particles. This
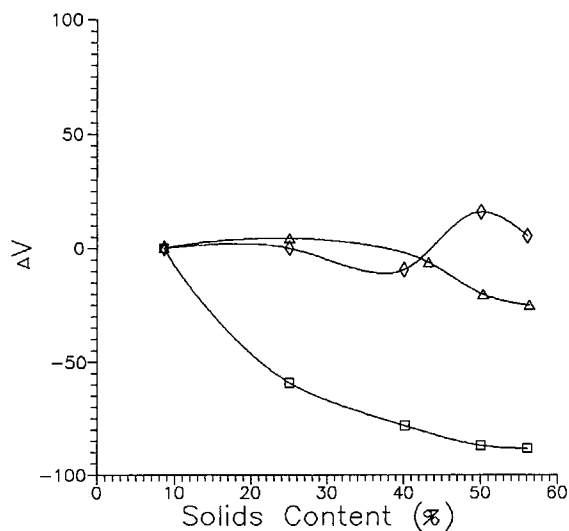
Figure 10 Percentage of the particle volume change versus total solids content, polymer composition, and seed particle size: ($\triangle$) BA/AA = 95/5, 79 nm; ($\square$) BA/AA = 95/5, 186 nm; ($\lozenge$) BA/AA = 100/0, 186 nm.

postulation is further supported by the ΔV data shown in Figure 10. Again, the ζ of the particles (-50 ± 4 mV) does not change very much with changes in the total solids content.

CONCLUSIONS

A two-level factorial design was used to investigate the effects of a number of reaction parameters on the latex stability during the semibatch emulsion polymerization of BA in combination with various levels of AA. The amount of coagulum (i.e., large flocs caused by intensive coagulation) and the percentage of the particle volume change (i.e., a measure of the degree of limited flocculation) were employed to study the latex stability during the reaction. The results showed that the amount of scrap was greatly reduced when the concentration of SLS in the monomer emulsion feed was increased. Increasing the concentration of SLS in the initial reactor charge resulted in an increase in the percentage of the particle volume change due to the limited flocculation process. Both the scrap and percentage of the particle volume change were shown to increase with an increase in the electrolyte concentration. The designed experiments also showed that the amount of scrap increased and the percentage of the particle volume change decreased when the agitation speed or the weight percentage of AA in the monomer mixture increased, but the effects were not significant.

Both coagulation and secondary nucleation resulted in a significant deviation from the simple Novak model, which was developed to predict the particle nucleation and growth processes for semibatch emulsion polymerization of acrylic monomers. Finally, experimental results showed that the amount of scrap increased significantly with an increase in the total solids content in the semibatch emulsion polymerization of pure BA, especially when the total solids content was high. On the other hand, incorporation of only 5% AA into the emulsion polymer greatly improved the latex stability during the reaction.

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