

# Characterization of Carboxylated Poly(butyl acrylate) Latices Produced by a Semibatch Process

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## SYNOPSIS

Several carboxylated poly(butyl acrylate) latices prepared by a semibatch emulsion polymerization process were characterized in this study. A significant amount of polyelectrolyte was found in the latex product containing 10% AA, designated as AA10. On the other hand, latices containing 0.1% AA (AA0.1), 0.1% MAA (MAA0.1), and 10% MAA (MAA10) showed very low levels of polyelectrolyte in water. Based on the critical flocculation concentration data, it can be concluded that incorporation of 10% AA or 10% MAA into the emulsion polymers can greatly improve the chemical stability of the latex products, especially at higher pH. The data of the pH and conductometric titration experiments show that the MAA unit can be distributed more uniformly in the latex particles in comparison with the AA unit. This result is further confirmed by determination of the  $T_g$ 's of the emulsion polymers by means of thermally stimulated current (TSC). © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Semibatch emulsion polymerization is a process that has been widely used to manufacture latex products such as coatings, binders, adhesives, and synthetic rubbers. The latex product is a dispersion of innumerable polymer particles in water with the aid of surfactants. Inadequate stabilization of the latex particles often results in the formation of coagulum and, consequently, causes problems to the plant production. Carboxylic monomers such as acrylic acid (AA) and methacrylic acid (MAA) can be incorporated into the polymer particles to improve the latex stability.<sup>1,2</sup> The ionized carboxyl group ( $-\text{COO}^-$ ) that is chemically incorporated into the latex particles can enhance the particle surface charge density and, therefore, increase the repulsive force among the interactive particles.

Greene<sup>3,4</sup> carried out emulsion copolymerization of styrene, butadiene, and a functional monomer (AA or MAA) by using a semibatch process. Distribution of the carboxylic monomer unit in the aqueous phase, in the surface layer of the particles,

and in the interior of the latex particles was found to be 2 : 3 : 1 and 0.1 : 1 : 1 for the latex products containing AA and MAA, respectively. Bassett et al.<sup>5-7</sup> carried out semibatch emulsion copolymerization of acrylic monomers in the presence of AA. They pointed out that distribution of various monomer units in the particles was dependent on the monomer addition method. Verbrugge<sup>8,9</sup> polymerized styrene or acrylic monomers in the presence of MAA and showed that the MAA unit was distributed more uniformly in the particles for the semibatch emulsion polymerization process. Nishida et al.<sup>10</sup> studied the emulsion polymerization of methyl methacrylate in the presence of 5–30% MAA. Their data showed that most of the carboxyl groups derived from MAA were distributed near the particle surface layer for latices prepared batchwise, whereas the way the MAA unit was distributed in the particles was closely related to the composition of the fed monomer for latices prepared by a semibatch process.

Recently, Chern and Lin<sup>11</sup> studied the effects of the functional monomer AA, MAA, or hydroxyethyl methacrylate (HEMA) on the particle nucleation and growth processes for semibatch emulsion polymerization of butyl acrylate (BA). The final latex particle size was found to decrease with an increase

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in the weight percentage of the functional monomer present in the monomer mixture. At a constant level of the functional monomer, the final particle size, in increasing order, is AA < MAA < HEMA. This result suggests that the carboxylic monomer AA should be the most efficient one to nucleate and stabilize the growing latex particles during polymerization. The molecular weight distribution data showed that low molecular weight oligomers do exist during the first 15 min of polymerization. Thus, the aqueous-phase reaction cannot be ignored during the particle nucleation period, especially when the concentration of AA is high. On the other hand, the latex product showed a strong peak associated with high molecular weight polymers. This result indicates that the propagation reaction taking place in the compartmentalized particles becomes predominant after the particle nucleation process has ceased. Thus, the type and concentration of the carboxylic monomers should play an important role in the nucleation and subsequent growth of the particles in the semibatch emulsion polymerization of BA.

The objective of this work was to characterize the carboxylated poly(butyl acrylate) latices produced in a semibatch reaction system. The swelling behavior of the latex particles, zeta potential data, and critical flocculation concentration data were used to characterize the pH-sensitive latices. In addition, the pH and conductometric titration experiments and determination of the amount of polyelectrolyte formed in the aqueous phase and the glass transition temperature ( $T_g$ ) of the carboxylated emulsion polymers were used to investigate the distribution of the AA or MAA unit in the latex products. The results obtained from this work should be useful to understanding the reaction mechanisms involved in the semibatch emulsion polymerization of BA in the presence of a small amount of AA or MAA.

## EXPERIMENTAL

### Materials

The chemicals used were butyl acrylate (BA) (Formosa Plastics Co.), acrylic acid (AA), (Formosa Plastics Co.), methacrylic acid (MAA) (Mitsubishi Rayon), sodium lauryl sulfate (SLS) (Henkel Co.), nonyl phenol-40 (NP-40) mol ethyleneoxide adduct (Union Carbide), 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  $\mu$ S/cm). The monomer BA was distilled under reduced pressure before use. All other chemicals were used as received.

### Polymerization Process

The carboxylated poly(butyl acrylate) latices were prepared in a 1 L reactor equipped with a four-bladed fan turbine agitator, a thermometer, and a reflux condenser. A typical recipe is shown in Table I. The recipe consists of 90% BA and 10% AA in the monomer mixture. The mixed surfactant system includes 0.01% SLS and 0.01% NP-40 in the initial reactor charge (based on the weight of water in the initial reactor charge). The concentrations of the initiator and neutralizing agent (sodium bicarbonate) are 0.25 and 0.15%, respectively, based on the weight of water in the initial reactor charge. The concentration of SLS in the monomer emulsion feed is 2.5%, based on total monomer shown in the recipe, and the agitation speed is 400 rpm.

The polymerization procedure is briefly described below. A large portion of water along with some surfactant and monomer was charged to the reactor, followed by heating the initial reactor charge to the reaction temperature (80°C in this work). The initial reactor charge was purged with nitrogen (for 10 min) while the reactor was brought to 80°C. The initiator solution was then added to the reactor to start the

**Table I** A Typical Recipe for the Semibatch Emulsion Polymerization of BA/AA (90/10)

	AA10	Chemicals	Weight (g)
Monomer emulsion feed		H <sub>2</sub> O	80.00
		SLS	5.67
		BA	185.40
		AA	20.60
Initial reactor charge		H <sub>2</sub> O	450.00
		SLS	0.05
		NP-40	0.05
		NaHCO <sub>3</sub>	0.68
Initial monomer charge		BA	18.85
		AA	2.09
Initiator solution		H <sub>2</sub> O	15.00
		Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	1.15
Total weight (g)			779.54
Total solids content (%)			30.00

reaction. After a short period of time (15 min) for nucleation of polymer particles, the remaining monomer and other ingredients such as water and surfactant were fed to the reactor over several hours (3 h). Polymerization temperature was kept constant throughout the reaction. After the end of the monomer emulsion feed, the reactor temperature was maintained at the same temperature (for 30 min) to reduce the residual monomer to an acceptable level. The theoretical total solids content at the end of the reaction is 30%.

The latex product was then filtered through a 40 mesh (0.42 mm) screen and a 200 mesh (0.074 mm) screen in series to remove the filterable solids. The formulas and some physical properties of the carboxylated poly(butyl acrylate) latices used in this study are summarized in Table II. For comparison, a homopoly(butyl acrylate) latex prepared by the semibatch surfactant-free emulsion polymerization<sup>12</sup> was also included in this work.

### Characterization

The total solids content of the latex sample was determined by the gravimetric method. The latex particle size data were obtained from the dynamic light scattering method (Otsuka, Photal LPA-3000/3100). The glass transition temperature ( $T_g$ ) of the emulsion polymer was measured by means of thermally stimulated current (TSC, Solomat, TSC/RMA). The experimental condition is described as follows: The polymeric film was polarized for 2 min under the condition of 130 and 250°C for the latex samples AA10 and MAA10, respectively, and a polarization field of 100 V/mm. The sample was then brought down to -150°C and was allowed to remain at the freezing temperature for 2 min. Subsequently, the polymer sample was scanned at a rate of 7°C/min.

To determine the amount of polyelectrolyte formed during polymerization, latex products AA0.1, AA10, MAA0.1, or MAA10 (total solids content = 27

± 1%) were centrifuged at 12,000 rpm for 12 h. The supernatant with a volume of 1 mL was then removed and filtered through a membrane with MWCO equal to 10,000 or 100,000 g/mol under centrifugation at 5000 rpm for 30 min, followed by titration with 0.1N NaOH solution.

The pH-dependent properties such as the swelling and zeta potential of the latex particles were determined as follows: Add 0.05 mL latex to 100 mL NaCl aqueous solution (0.01M NaCl, pH 3–11). The pH of the 0.01M NaCl solution was adjusted by using HCl and NaOH. The resultant latex sample has a total solids content of 0.015%. The latex sample was then allowed to stand at room temperature for 24 h before the particle size and zeta potential ( $\zeta$ ) measurements. The  $\zeta$  of the latex particles was measured by a Malvern Zetamaster. Five measurements were made for each latex sample and the average of these five measurements was reported as the  $\zeta$  of the finished product.

The dialyzed latex with a volume of 100 mL and a total solids content of 1.1% was titrated dropwise with the 0.05N NaOH solution to study the distribution of carboxyl groups in the latex particles. Carboxyl group-containing water-soluble oligomers, if any, were assumed to be removed completely by dialysis (MWCO = 12,000–14,000 g/mol). The latex sample was mixed thoroughly by a magnetic stirrer for 30 s and then was allowed to stand at room temperature for 1 min before each pH measurement. The reported value of pH was an average of three measurements. The conductometric titration method<sup>13</sup> was also employed to study the distribution of carboxyl groups in the latex particles. The experiment was carried out by pouring 12 g latex with a total solids content of 17.3% into 500 mL 0.1N NaOH solution. Changes in conductivity with time were then recorded by a conductivity meter (WTW, LF95/SET).

The transmittance of the dialyzed latex sample (total solids content = 0.009%) was measured by a

**Table II** Formulas and Some Properties of the Carboxylated Poly(butyl acrylate) Latices

Sample ID	AA0.1	AA10	MAA0.1	MAA10	PBA <sup>a</sup>
[AA] (%) <sup>b</sup>	0.1	10.0	—	—	—
[MAA] (%) <sup>b</sup>	—	—	0.1	10.0	—
Solids (%)	26.2	28.0	26.7	27.6	37.7
pH	5.4	3.4	5.1	4.3	7.9
$d_f$ (nm) <sup>c</sup>	196	159	218	283	561

<sup>a</sup> PBA is a homopoly(butyl acrylate) latex made by a semibatch surfactant-free emulsion polymerization.

<sup>b</sup> Based on total monomer weight.

<sup>c</sup>  $d_f$  is the final latex particle size.

**Table III** Carboxyl Content in 1 mL Water of the Latex Sample with a Total Solids Content of  $27 \pm 1\%$ 

MWCO (g/mol)	Carboxyl Content (mol)			
	AA0.1	AA10	MAA0.1	MAA10
100,000	$3.61 \times 10^{-6}$	$1.47 \times 10^{-4}$	$1.30 \times 10^{-7}$	$1.20 \times 10^{-6}$
10,000	$3.63 \times 10^{-6}$	$1.20 \times 10^{-4}$	$1.70 \times 10^{-6}$	$1.00 \times 10^{-6}$

spectrophotometer (Metertek SP-810) at 540 nm for determination of the critical flocculation concentration (CFC). The pH and ionic strength of the latex sample were adjusted by using NaOH, HCl, and NaCl. The sample was allowed to stand at room temperature for 1 h before the transmittance measurement unless otherwise stated.

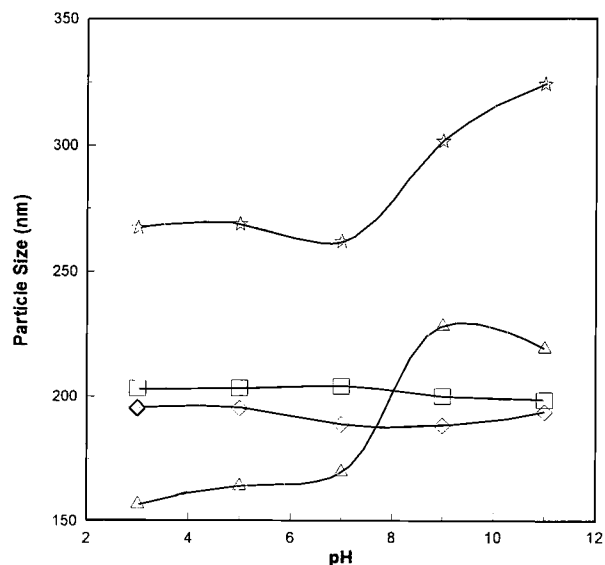
## RESULTS AND DISCUSSION

Based on the molecular weight distribution data, Chern and Lin<sup>11</sup> postulated that a significant amount of polyelectrolyte should have formed during the early stage of polymerization for the poly (butyl acrylate) latex containing 10% AA if the termination and/or chain-transfer reactions occurred in water or at the particle-water interface. The location in which the polyelectrolyte is present in the polymerization system can have an impact on the latex particle size and stability. The ionized polyelectrolyte in water, e.g., can compress the electric double layer of the particles and, therefore, reduce the repulsive force among the interactive particles. This kind of action can reduce the latex stability significantly and this subject will be discussed in a forthcoming article.<sup>14</sup> On the other hand, if the polyelectrolyte is adsorbed onto the particle surface, the surface active species can enhance the particle surface charge density and, consequently, improve the latex stability.

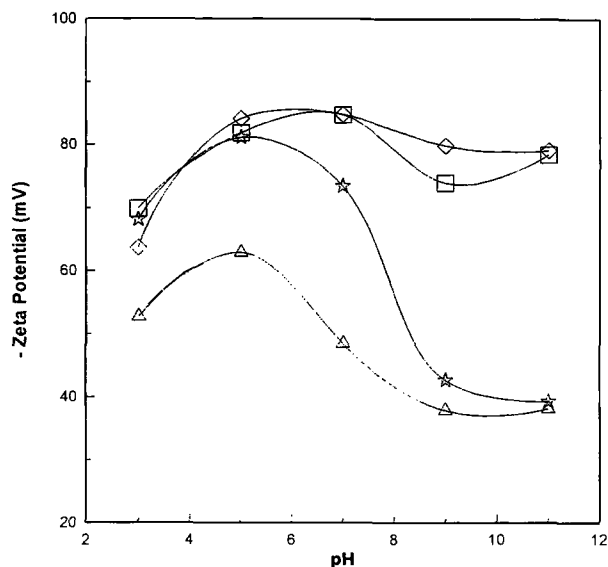
The titration results summarized in Table III show that, indeed, a significant quantity of polyelectrolyte can be found in the latex sample AA10 and the carboxyl content of AA10 is about 40 times greater than that of AA0.1. On the other hand, like the latex sample AA0.1, both MAA0.1 and MAA10 show very low levels of polyelectrolyte in the aqueous phase. This is probably due to the fact that the more hydrophobic MAA can be incorporated into the latex particles more easily. This behavior can result in a reduction in the formation of polyelectrolyte in water. Another possibility for the very low level of polyelectrolyte associated with MAA10 is that the relatively hydrophobic and surface-active polyelec-

trolyte can adsorb strongly on the particle surface. Thus, the probability of finding the polyelectrolyte in water is greatly reduced.

Figure 1 shows the latex particle size data as a function of pH, i.e., the particle swelling behavior. As expected, the particle-size data for both latex samples AA0.1 and MAA0.1 do not change very much with changes in pH. In addition, incorporation of 0.1% AA or 0.1% MAA into the polymerization system leads to comparable particle sizes (ca. 200 nm). On the other hand, the particle size of the latex sample AA10 or MAA10 remains relatively constant before pH 7 and, thereafter, the particle size increases rapidly because of the increased ionization of the carboxyl groups in the particles. Please note that incorporation of 10% AA into the emulsion polymer causes a significant decrease in the particle size as compared to the case of 0.1% AA, whereas incorporation of 10% MAA into the polymer results in an increase in the particle size as compared to the case of 0.1% MAA. The reason why this opposite behavior happens is not clear at this point in time.

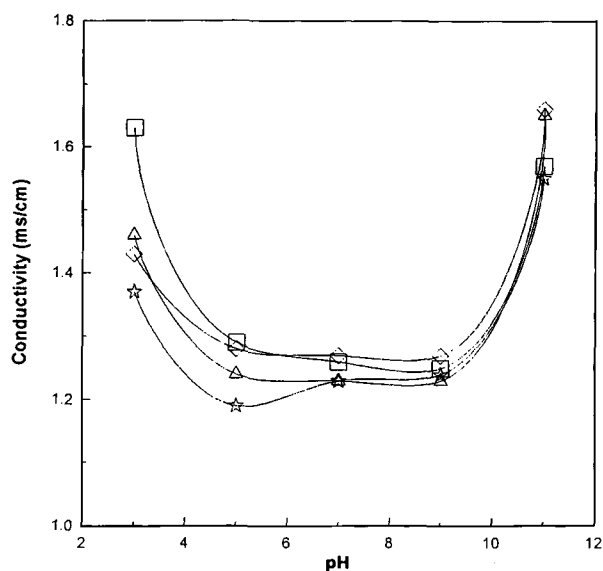


**Figure 1** Latex particle size as a function of pH: (□) AA0.1; (△) AA10; (◇) MAA0.1; (☆) MAA10.



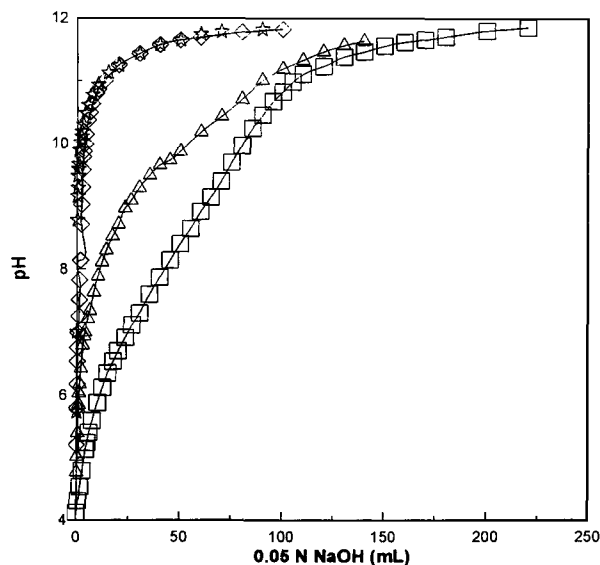
**Figure 2** Zeta potential of the latex particles as a function of pH: (□) AA0.1; (△) AA10; (◇) MAA0.1; (☆) MAA10.

Figure 2 shows the zeta potential ( $\zeta$ ) of the latex particles as a function of pH. The measured conductivity of the latex samples are also shown in Figure 3. It is shown in Figure 2 that for both the latex samples AA10 and MAA10 the  $\zeta$  of the particles first increases to a maximum around pH 5 because the increased ionization of the carboxyl groups with pH can result in an increase in the particle surface charge density and, as a result, the  $\zeta$  of the particles is increased. Another factor is that the conductivity of the latex sample is quite high below pH 4 since the  $H^+$  ion becomes more important in determining the ionic strength of the solution as compared to the 0.01M NaCl solution (see Fig. 3). Thus, the increased ionic strength can compress the electric double layer of the particles and lead to a decrease in  $\zeta$  when pH is decreased. After the maximal point is reached, the  $\zeta$  of the particles then starts to decrease with increasing pH. 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  $\zeta$ . In this range of pH, the increased conductivity with pH (see Fig. 3) also can compress the electric double layer of the particles and cause a decrease in  $\zeta$ . Furthermore, the increased particle size (i.e., the increased particle surface area) with pH (see Fig. 1) can cause a decrease in the particle surface charge density and thereby reduce the  $\zeta$ . For both the latex samples AA0.1 and MAA0.1, the  $\zeta$  data are relatively insensitive to changes in pH and they show a maximum around pH 5-6.

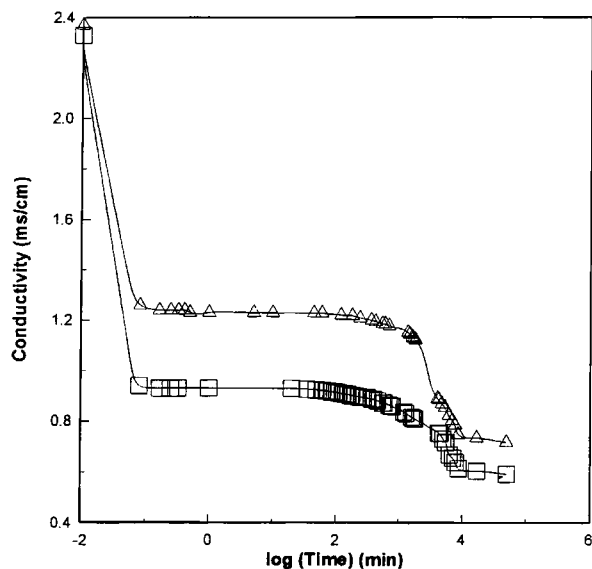


**Figure 3** Conductivity of the latex particles as a function of pH: (□) AA0.1; (△) AA10; (◇) MAA0.1; (☆) MAA10.

Figure 4 shows the titration data of the dialyzed latex samples AA0.1, AA10, and MAA10. For comparison, a blank sample (water) was also included in the pH titration study. The pH curves of the blank sample and AA0.1 are very sharp and they almost coincide with each other. On the other hand, the rate of change in pH with the titration process is slower for the run using AA10 or MAA10. The titration data also show that at a fixed volume of the added 0.05N NaOH solution the pH of the latex



**Figure 4** Titration data of the dialyzed latex samples: (☆) blank sample; (◇) AA0.1; (□) AA10; (△) MAA10.



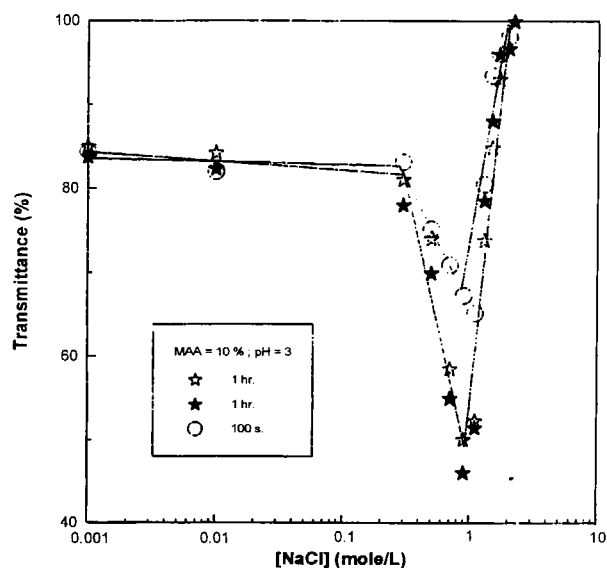
**Figure 5** Conductometric titration data of the dialyzed latex samples: (□) AA10; (△) MAA10.

sample AA10 is always lower than that of MAA10. This result suggests that a large proportion of the carboxyl groups derived from AA is located near the particle surface layer. On the other hand, the more hydrophobic MAA unit can be distributed more uniformly in the particles.

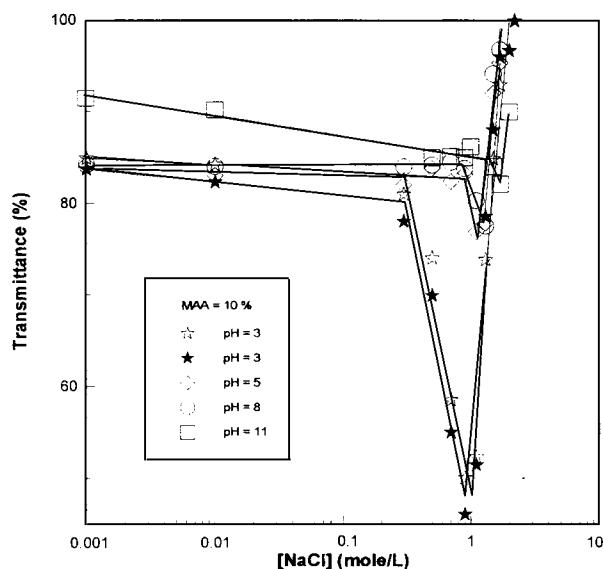
The conductometric titration results shown in Figure 5 also support the above postulation. The conductivity of the latex sample AA10 or MAA10 decreases rapidly during the very early stage of titration (within 1 min) and, thereafter, reaches the first plateau region ( $10^0$ – $10^3$  min). After passing through the first plateau region, the conductivity decreases again ( $10^3$ – $10^4$  min) and finally reaches the second plateau region (greater than  $10^4$  min). The magnitude of the decreased conductivity between the starting point and the first plateau region is attributed to the carboxyl groups remaining in the particle surface layer, whereas that between the first and the second plateau region can be attributed to the detectable carboxyl groups buried inside the particles. Note that the latter conductometric titration process should be diffusion-controlled. Thus, the ratio of the carboxyl groups in the particle surface layer to those in the interior core of the particles is 4.3 : 1.0 and 2.3 : 1.0 for AA10 and MAA10, respectively. This result is consistent with the work of Greene,<sup>3,4</sup> in which distribution of the carboxyl groups in the surface layer of the particles and in the core of the particles is 3 : 1 and 1 : 1 for the semibatch emulsion polymerization system containing AA and MAA, respectively. Clearly, the

MAA unit can be distributed more uniformly in the particles in comparison with the AA unit.

Figure 6 shows the transmittance-vs.- $\log[\text{NaCl}]$  data for the latex sample MAA10 at pH 3, where the parameter  $[\text{NaCl}]$  is the concentration of NaCl. The star data points represent the data obtained from the latex samples which were allowed to stand at room temperature for 1 h before the transmittance measurements. Each experiment was carried out twice and the reproducibility of the experiment was reasonably good. The transmittance of the latex sample maintains a relatively constant value when the value of  $[\text{NaCl}]$  is increased from 0.001 to 0.29M. Subsequently, the transmittance starts to decrease rapidly with increasing  $[\text{NaCl}]$  because of aggregate formation. The point at which  $[\text{NaCl}]$  is equal to 0.29M is thereby identified as the critical flocculation concentration (CFC). Thereafter, the transmittance increases very rapidly with increasing  $[\text{NaCl}]$  as larger flocs start to form and then precipitate under the influence of gravitational force. Thus, the minimal point of the transmittance-vs.- $\log[\text{NaCl}]$  curve can be defined as the critical sedimentation concentration (CSC). Another series of experiments, in which the latex samples were allowed to stand at room temperature for 100 s before transmittance measurements, was carried out and the data also show a similar trend except that the minimal point occurs at a higher value of transmittance. It is also interesting to note that the values of CFC and CSC



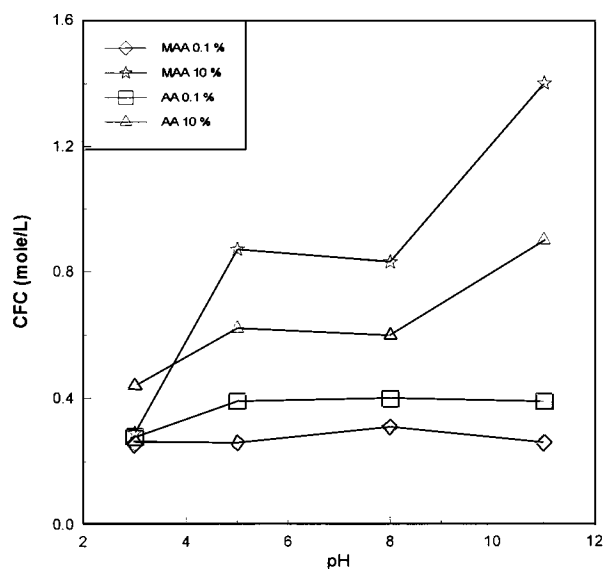
**Figure 6** Transmittance of the latex sample MAA10 at pH 3. The time that the latex sample is allowed to stand at room temperature before the transmittance measurement: (☆, ★) 1 h; (○) 100 s.



**Figure 7** Transmittance of the latex sample MAA10 at various values of pH: (☆) pH 3; (◇) pH 5; (○) pH 8; (□) pH 11.

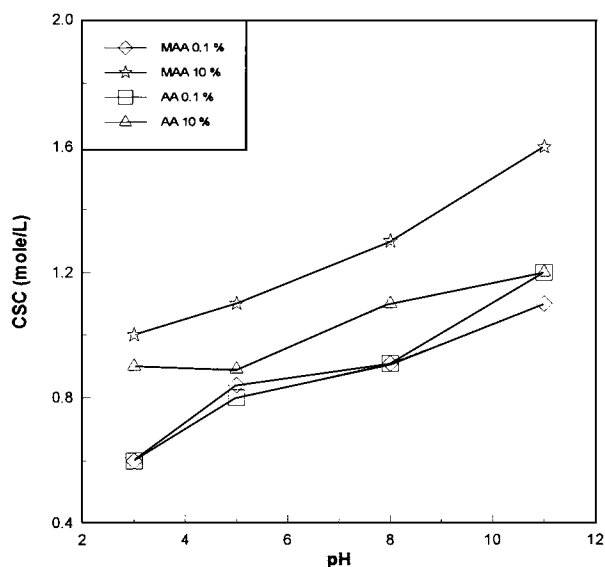
do not change much when the method of sample preparation is modified. To the best of the authors' knowledge, this kind of kinetic behavior regarding determination of the chemical stability of the latex samples has not been reported in the literature.<sup>12,15</sup>

Figure 7 shows the transmittance data of the latex sample MAA10 as a function of [NaCl] at various values of pH. In this series of experiments, the minimal point (CSC) becomes less significant when the pH of the latex sample is increased from 3 to 11. This is probably due to the enhanced stability of the carboxylated latex with increasing pH. The enhanced latex stability can retard the aggregate formation. Thus, the transmittance curve exhibits only a shallow minimum as the sodium salt is continuously added to the latex sample. The transmittance- $[\text{NaCl}]$  curves for MAA0.1, AA0.1, and AA10 at various values of pH also show similar trends. The CFC and CSC data as a function of pH are shown in Figures 8 and 9, respectively. As expected, the magnitude of CFC for the latex sample AA0.1 (or MAA0.1) is smaller than that for AA10 (or MAA10) and the CFC data of the latex sample AA0.1 (or MAA0.1) appear to be relatively insensitive to changes in pH. On the other hand, the CFC for the latex sample AA10 (or MAA10) increases with an increase in pH. At a constant value of pH, the CFC of the latex sample MAA10 is greater than that of AA10 throughout most of the pH range. Thus, it can be concluded that incorporation of 10% AA or 10% MAA into the emulsion polymers can greatly im-

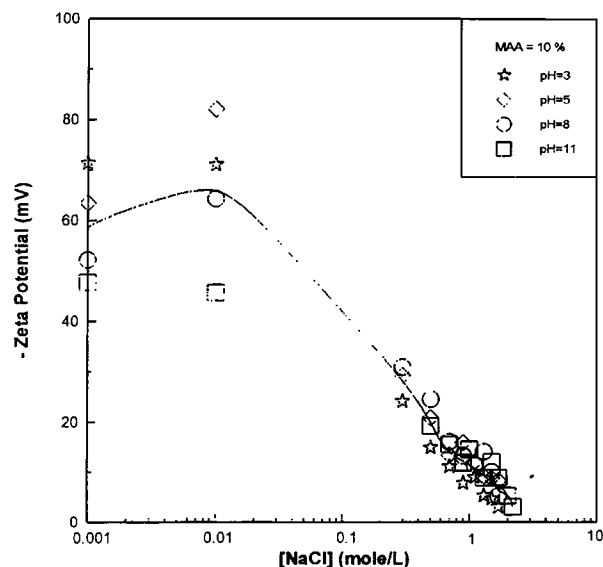


**Figure 8** CFC of the latex sample as a function of pH: (□) AA0.1; (△) AA10; (◇) MAA0.1; (☆) MAA10.

prove the chemical stability of the finished latex products, especially at higher values of pH. Furthermore, the carboxylic monomer MAA seems to be more effective in promoting the chemical stability of the finished products as compared to AA. This result seems to be totally different from the conclusion made by Chern and Lin<sup>11</sup> that the carboxylic monomer AA is the most efficient one to nucleate and stabilize the growing particles during polymerization. The reason for this contradiction is not clear at this point of time, but it is probably related to



**Figure 9** CSC of the latex sample as a function of pH: (□) AA0.1; (△) AA10; (◇) MAA0.1; (☆) MAA10.



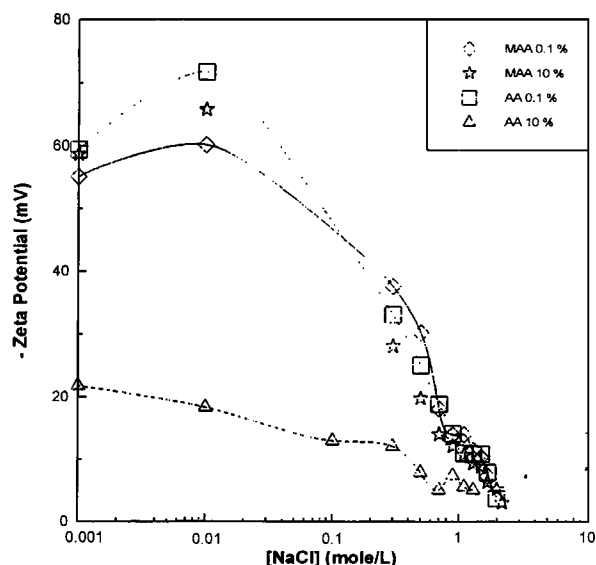
**Figure 10** Zeta potential of the latex sample MAA10 as a function of NaCl concentration at various values of pH: (★) pH 3; (◇) pH 5; (○) pH 8; (□) pH 11.

distribution of the AA or MAA unit in the latex products. The abundant, ionized polyelectrolyte in water, e.g., can reduce the chemical stability of the latex sample AA10. Another possible explanation is that the latex sample AA10 has a smaller particle size (i.e., a larger particle surface area) and, hence, a lower  $\zeta$  of the particles in comparison with MAA. This factor can make the finished product MAA10 more stable than AA10. It is shown in Figure 9 that the CSC of the four carboxylated latices increases with increase in pH. The CSC data of the latex samples AA0.1 and MAA0.1 almost coincide with each other. The CSC of the latex sample MAA10 is, again, greater than that of AA10 throughout the pH range.

Figure 10 shows the  $\zeta$  of the particles for the latex sample MAA10 as a function of [NaCl] at various values of pH. At a value of [NaCl] less than 0.01M, the  $\zeta$  of the particles is very sensitive to changes in pH. In general, the  $\zeta$  of the particles decreases with an increase in pH, probably due to the shift of the shear plane toward the bulk solution. On the other hand, the  $\zeta$  of the particles becomes insensitive to pH at very high values of [NaCl] because in this case the ionic strength plays an important role in determining the  $\zeta$  of the particles. In addition, the  $\zeta$  of the particles first increases to a maximum around 0.01M NaCl and, thereafter, decreases with an increase in [NaCl]. The maximal point can be explained by compression of the shear plane inward when [NaCl] is increased from 0.001 to 0.01M.<sup>16</sup> The  $\zeta$ -vs.- $-\log[\text{NaCl}]$  data for the latex samples MAA0.1,

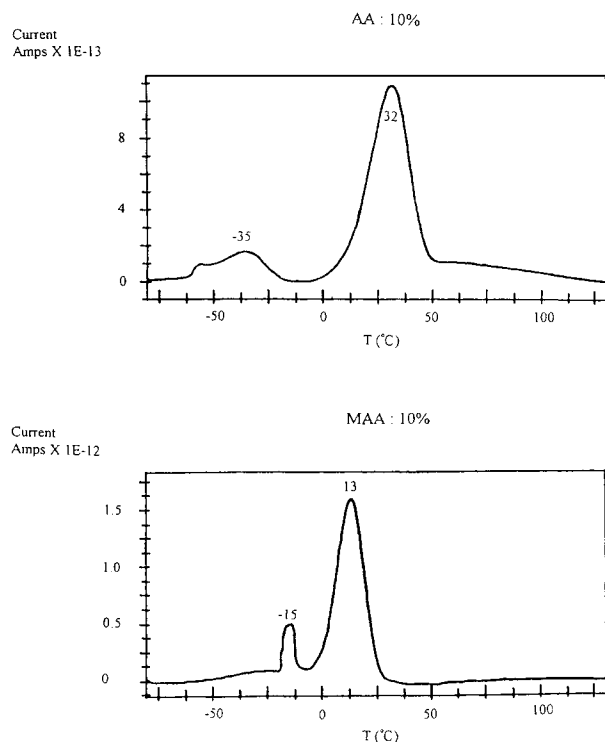
AA0.1, and AA10 at various values of pH also show similar trends. Nevertheless, the  $\zeta$  data for the latex sample AA10 are rather scattered because a bimodal distribution of  $\zeta$  was always observed during the  $\zeta$  measurements and one of the peaks was centered around 0 mV. So far, we have been unable to obtain satisfactory  $\zeta$  data for AA10 and we do not intend to interpret the  $\zeta$  data for AA10 here. Figure 11 shows the overall average of the  $\zeta$  data measured at various values of pH as a function of [NaCl].

Finally, Figure 12 shows the glass transition temperature ( $T_g$ ) data of the dialyzed samples AA10 and MAA10 determined by means of TSC. Each polymer sample was scanned twice and the reproducibility of the spectra was excellent. For comparison, the range of temperature chosen for the latex sample MAA10 in Figure 12(b) is  $-75$  to  $125^\circ\text{C}$  because no transitions was observed above  $125^\circ\text{C}$ . The  $T_g$ 's of the AA, MAA, and BA homopolymers are reported to be 106, 228, and  $-54^\circ\text{C}$ , respectively.<sup>17</sup> For reference, the calculated  $T_g$ 's of the homogeneous copolymers of BA/AA (90/10) and BA/MAA (90/10) are  $-46$  and  $-43^\circ\text{C}$ , respectively, based on the Fox equation.<sup>18</sup> As shown in Figure 12, both the latex samples AA10 and MAA10 display a bimodal distribution. The bimodal distribution implies a non-uniform distribution of the carboxylic monomer unit in the latex particles. Furthermore, the distribution of the latex sample AA10 is broader than that of MAA10. This observation suggests that the BA/MAA polymer particles should be more homoge-



**Figure 11** Zeta potential of the latex particles as a function of NaCl concentration: (□) AA0.1; (△) AA10; (◇) MAA0.1; (★) MAA10.





**Figure 12** Glass transition temperature of the emulsion polymers determined by TSC: (a) AA10; (b) MAA10.

neous in composition than are the BA/AA polymer particles. For the latex sample AA10, e.g., the peak centered around  $-35^{\circ}\text{C}$  can be attributed to the BA/AA copolymer comprising a higher BA concentration, presumably produced inside the latex particles. The other peak centered around  $32^{\circ}\text{C}$  then can be attributed to the BA/AA copolymer comprising a lower BA concentration, presumably formed at the particle-water interface. The physically adsorbed polyelectrolyte that is rich in AA also can contribute to this peak. Note that the magnitude of separation between the two distinct peaks is  $32 - (-35) = 67^{\circ}\text{C}$  [see Fig. 12(a)]. Similarly, the peak centered around  $-15^{\circ}\text{C}$  can be attributed to the BA/MAA copolymer comprising a higher BA concentration, whereas the peak centered around  $13^{\circ}\text{C}$  can be attributed to the BA/MAA copolymer comprising a lower BA concentration for the latex sample MAA10 [see Fig. 12(b)]. However, the magnitude of separation between the two peaks is only  $28^{\circ}\text{C}$ , as compared to  $67^{\circ}\text{C}$  observed for the latex sample AA10. Such a big difference suggests that the fine structure of the AA10 polymer particles is quite different from that of the MAA10 polymer particles. This result, again, supports the above postulation that in comparison with the AA unit the more hydrophobic MAA unit

can be distributed more uniformly in the particles in the semibatch emulsion polymerization of BA.

## CONCLUSIONS

Several carboxylated poly(butyl acrylate) latices produced in a semibatch reaction system were characterized in this work. A significant amount of polyelectrolyte formed in water was found in the latex product containing 10% AA (designated as AA10) and the carboxyl content of AA10 was about 40 times greater than that of the latex product containing only 0.1% AA (AA0.1). On the other hand, both the latices containing 0.1% MAA (MAA0.1) and 10% MAA (MAA10) have very low levels of polyelectrolyte dissolved in the aqueous phase. These results confirm the postulation of Chern and Lin (see Ref. 11).

The swelling behavior of the latex particles, zeta potential, and critical flocculation concentration were determined and the experimental data showed that both the latex samples AA10 and MAA10 were pH-sensitive. On the other hand, the physical properties of the latex samples AA0.1 and MAA0.1 are relatively independent of pH. The CFC of the latex sample AA0.1 (or MAA0.1) is smaller than that of AA10 (or MAA10) and the CFC data of the latex sample AA0.1 (or MAA0.1) appear to be insensitive to changes in pH. On the other hand, the CFC of the latex sample AA10 (or MAA10) increases with increase in pH. Thus, incorporation of 10% AA or 10% MAA into the emulsion polymers can greatly improve the chemical stability of the latex products, especially at higher values of pH. Furthermore, in comparison with AA, the carboxylic monomer MAA is more effective in promoting the chemical stability of the latex products.

The pH and conductometric titration experiments and the glass transition temperature of the carboxylated emulsion polymers were determined to study the distribution of the AA or MAA unit in the latex particles. The results show that the ratio of the carboxyl groups in the particle surface layer to those in the interior core of the particles is about 4.3 : 1.0 and 2.3 : 1.0 for the dialyzed samples AA10 and MAA10, respectively. Thus, the MAA unit can be distributed more uniformly in the latex particles as compared to the AA unit. The  $T_g$  data for the dialyzed samples AA10 and MAA10 determined by TSC do indicate a difference in their fine particle structures. This observation also supports the above postulation based on the pH and conductometric titration data.

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