Synthesis and Characterization of Model Carboxylated Latexes for Studies of Film Formation from Latex Blends

JIANSHENG TANG, VICTORIA L. DIMONIE, ERIC S. DANIELS, ANDREW KLEIN, MOHAMED S. EL-AASSER

Emulsion Polymers Institute and Department of Chemical Engineering, Lehigh University, Room D-325, Iacocca Hall, 111 Research Drive, Bethlehem, Pennsylvania 18015

ABSTRACT: Poly(*n*-butyl methacylate-co-*n*-butyl acylate) [P(BMA/BA)] soft latexes (carboxylated and noncarboxylated) were synthesized using a semicontinuous emulsion polymerization process that was designed on the basis of a theoretical calculation to determine the suitable surfactant [i.e., sodium dodecyl sulfate (SDS)], monomer, and water feed rates to maintain a constant particle number throughout the polymerization (guaranteeing monodispersity in the particle size), to obtain a homogeneous copolymer composition, and to independently control the particle size and carboxyl group concentration. The experimental results support the theoretical calculation. The surface coverage of the carboxyl groups present on the soft latex particles ranges from 7.6 to 21.9% for a series of latexes with particle sizes around 120 nm. In another series of latexes, the particle size was varied over a range from 120 to 450 nm. Monodisperse carboxylated polystyrene hard latexes were synthesized by shot growth (batch) and semicontinuous processes. The shot growth method is somewhat inflexible in providing more choices in surfactant, particle size, and surface carboxyl coverage. A semicontinuous process designed using a similar method used for the synthesis of P(BMA/BA) latexes successfully eliminated the drawbacks of the shot growth process. In this way, the changes in the surface carboxyl coverage (varies from 0 to 77.2%) was independent of the particle size, which was precisely controlled by the amount of styrene fed under suitable styrene and SDS feed rates. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 644–659, 2000

Key words: carboxylated latex particles; monodisperse latex particles; poly(*n*-butyl methyacrylate-co-*n*-butyl acrylate); polystyrene; semicontinuous emulsion polymerization

INTRODUCTION

Latex blending, especially blends of hard and soft latex particles, is an attractive strategy to develop new durable coatings with very good mechanical properties and with zero volatile organic compounds (VOCs). It is envisioned that the soft latex particles (i.e., low glass transition temperature, T_g) will deform and form a continuous film with embedded hard latex particles (high T_g) whose presence will impart desirable mechanical or optical properties.[1–3] Polymer latex blends are thus expected to offer a compromise between latexes that have good mechanical properties and those that are good film formers.[4,5] Therefore, academic research to understand the fundamental parameters governing film formation and their relationship to mechanical and other properties of zero VOC films was initiated. This paper describes the synthesis and characterization of model carboxylated latexes that are to be used for studies of the influence of the particle surface characteristics on

film formation from hard/soft latex blends (carboxylated and noncarboxylated).

The following are the parameters that influence film formation from hard/soft latex blends and the properties and morphologies of the latex blend films: geometrical parameters (e.g., particle size and particle size ratio between component latex particles), physical parameters (e.g., glass transition temperature, volume fraction, and compatibility), chemical parameters (e.g., surface charge and surface functional groups), or environmental parameters (e.g., drying temperature, humidity, and air velocity). While the strategy of using latex blends is being actively investigated in industry, theoretical studies are just beginning. Several papers have reported on investigations concerned with the influence of some of the geometrical or physical parameters such as particle size and T_g on film formation or film properties.[1,6,7] However, few papers have reported on studies of the influence of the surface properties of latex particles in latex blends, which we think would play an important role in influencing the film formation and the properties of latex blend films. Thus, the surface characteristics of latex particles are of great interest.

The incorporation of functional groups (e.g., carboxyl groups) into latex particles is a common method to alter the surface properties of the latex particles,[8–11] which were also used here to change the surface properties of model latex particles for studies on film formation from latex blends consisting of polystyrene (PS) hard and poly(n-butyl methacrylate-co-n-butyl acrylate) copolymer [P(BMA/BA)] soft latex particles. Since many parameters may influence the film formation from latex blends, as mentioned above, the isolation of the specific parameter of interest, i.e., the surface properties of latex particles, from the other parameters described previously is necessary. Therefore, it is necessary to vary one parameter without affecting the others during the synthesis of the model latex particles. The requirements for the latex particles synthesized here are the following: (1) the particles have to be monodisperse in size, (2) a range of particle sizes is needed, (3) there should be independent control of the particle size and carboxyl group concentration, and (4) the copolymer composition should be homogeneous. Thus, success in the synthesis of well-defined model carboxylated latexes is the critical step for the subsequent studies of film formation from latex blends. The synthesis processes developed here can be used to prepare carboxylated monodisperse latex particles with homogeneous copolymer composition (if copolymer latex) while varying only the carboxyl group concentration on the particles and keeping all the other particle characteristics constant.

EXPERIMENTAL

Materials

n-Butyl methacrylate (BMA), n-butyl acrylate (BA), styrene (St), and methacrylic acid (MAA) monomers (Aldrich; reagent grade) were purified by passing them through columns filled with an appropriate inhibitor removal packing (Aldrich). Maleic acid (MA; Aldrich; analytical grade), sodium dodecyl sulfate (SDS; Fisher Scientific; reagent grade), Aerosol MA-80 (Cytec Industries), potassium persulfate (KPS; Aldrich; reagent grade), sodium bicarbonate (Aldrich; reagent grade), uranyl acetate (UAc; Fluka; reagent grade), and cesium hydroxide (CsOH; Aldrich; reagent grade) were used as received without further purification. Cationic ion exchange resin (AG 50W-X4, 20~50 mesh; Bio-Rad Company) was extensively washed with deionized water before use. Anionic ion exchange resin (AG 1-X4, 20 ~ 50 mesh, Bio-Rad Company) was converted from its chloride form to its hydroxide form with 3N aqueous sodium hydroxide solution and then completely washed with water just before use. Serum replacement cells were also used to preclean some of the latexes.[12]

Latex Synthesis

Noncarboxylated and Carboxylated P(BMA/BA) Soft Latex Particles

All syntheses were performed in a 500-mL four-neck flask equipped with a reflux condenser, nitrogen gas inlet tube, poly(tetrafluoroethylene) (PTFE) stirrer (~230 rpm), and two feed tubes for monomer and surfactant solution, respectively. The P(BMA/BA) copolymer latex was prepared by a conventional semicontinuous emulsion polymerization process at 80°C. Table I gives a typical recipe for the synthesis of the noncarboxylated P(BMA/BA) latexes. For the synthesis of carboxylated P(BMA/BA) latexes, MAA was added into the monomer mixture (the weight fractions of MAA, BMA, and BA are adjusted according to the desired carboxyl group concentration and T_g), which was fed into the reactor (Table II). The

Table I   Typical Recipe for the Synthesis of P(BMA/BA) Copolymer Latex Using a Semicontinuous Emulsion Polymerization Process at 80°C[a]

Ingredient	Amount (g)
Seed stage	
n-Butyl methacrylate	5.25
n-Butyl acrylate	1.75
Potassium persulfate	0.08 (3.29 mM)[b]
Sodium dodecyl sulfate	0.20 (7.72 mM)[b]
Deionized (DI) water	90.00
Feed stage	
Monomer mixture	
n-Butyl methacrylate	43.00
n-Butyl acrylate	14.34
Surfactant solution	
Sodium dodecyl sulfate	1.20
Deionized water	50.00

[a] BMA : BA (wt) = 3 : 1; the ratio can be adjusted according to the T_g desired.
[b] Concentrations based on aqueous phase.

initial 1.5-h period of the polymerization is the seed stage. Ten percent of the monomer mixture (BMA/BA = 75/25 wt/wt) was used in the seed stage. After the seed was almost fully formed (~95% conversion), the remaining monomer mixture of BMA, BA, and/or MAA (for carboxylated

latex particles) and surfactant solution were separately fed into the reactor at constant rates (i.e., 0.26 mL/min for the monomer mixture and 0.23 mL/min for the surfactant solution) using two syringe pumps (Harvard Apparatus 22). Samples were taken from the reactor every half-hour during feeding. The particle size and conversion for each sample were monitored. When the feeds were finished, the reaction was allowed to continue for another 2 h, and the latex was then cooled to room temperature.

Noncarboxylated and Carboxylated PS Latex Particles

PS latex particles were prepared by batch (shot growth and normal batch) and conventional semicontinuous emulsion polymerization processes. The syntheses of PS (both noncarboxylated and carboxylated) by a semicontinuous process were performed in a similar manner to the methods described above. The difference is that in the syntheses of PS latex particles, the monomer feed was divided into two stages. The first stage is the styrene feed stage, while the second feed stage is comprised of a mixture of St and MAA monomers, which results in the formation of a thin polymer shell layer about 3 nm in thickness around the seed latex particles. In the shot growth process, the polymerization was carried out in 200 cm³

Table II   Recipe for the Synthesis of Carboxylated P(BMA/BA) Copolymer Latexes Using a Semicontinuous Emulsion Polymerization Process at 80°C

Ingredient	Weight Fraction	Amount (g)
Seed stage		
n-Butyl methacrylate	0.75[a]	5.25
n-Butyl acrylate	0.25[a]	1.75
Potassium persulfate		0.08 (3.29 mM)[b]
Sodium dodecyl sulfate		0.20 (7.72 mM)[b]
Deionized water		90.00
Feed stage		
Monomer mixture		57.34
n-Butyl methacrylate	0.742–0.436[a]	
n-Butyl acrylate	0.247–0.497[a]	
Methacrylic acid	0.0112–0.0668[c]	
Surfactant solution		
Sodium dodecyl sulfate		1.20
Deionized water		50.00

[a] Based on monomer charged.
[b] Concentrations based on aqueous phase.
[c] Based on monomer feed; adjusted according to the desired concentration of carboxyl groups and T_g.
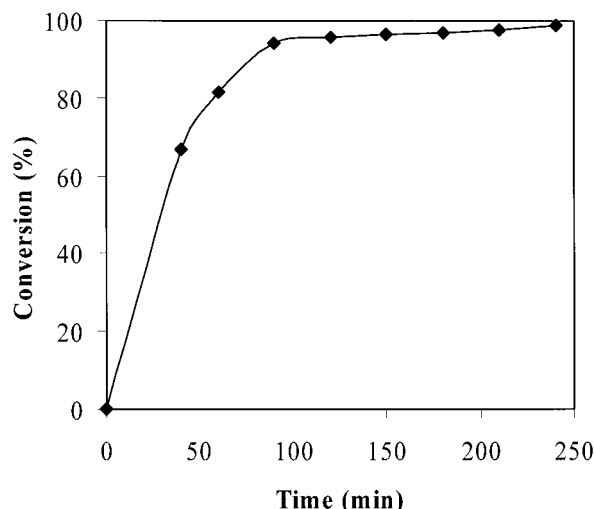
Figure 1   Conversion vs reaction time curve for the batch emulsion polymerization of styrene at 70°C.

pressure bottles. There were two stages for feeding the reactants. In the initial stage, specific amounts of styrene, surfactant (Aerosol MA-80), sodium bicarbonate, and deionized water were charged into the bottles. The contents of each bottle were purged with nitrogen using a hypodermic needle inserted through a rubber gasket in the bottle cap. The required amount of initiator solution (KPS) was purged with nitrogen and injected into each bottle using a hypodermic syringe. The bottles were placed in cloth jackets,

placed in the bottle polymerizer unit, and rotated end-over-end in a thermostated bath heated at 70°C for 1.5 h. At this time, the conversion of styrene reached 95% according to a conversion vs. time curve, which was determined independently (Fig. 1). At this point, specific amounts of Aerosol MA-80, sodium bicarbonate, KPS, styrene, maleic acid, and deionized water were injected into each bottle. The reactions were continued for 13.5 h. A normal batch process was carried out for comparison with the shot growth method using a similar recipe (Table III) to that used in the shot growth synthesis, but adding all the ingredients batchwise into the reactor before the polymerization was initiated.

Characterization

For the transmission electron microscopy (TEM) experiments, a Philips EM400T microscope was used at an acceleration voltage of 100 kV. For the PS hard particles, the latex was first highly diluted with deionized water, and then dried on a copper grid, and imaged with the TEM. For the P(BMA/BA) soft particles, a cold-stage TEM attachment with liquid nitrogen coolant was employed to maintain the soft particles in their original spherical shapes. The particles were treated with a 2 wt % aqueous solution of UAc as a negative stain. A 2 wt % aqueous solution of CsOH was utilized to selectively stain the acid groups.

Table III   General Recipe and Conditions for the Synthesis of Carboxylated Polystyrene Latex Using the Shot Growth Method

Ingredient	Amount (g)
First stage	
Styrene	20.5
Aerosol MA (100%)	0.75 (39.0 mM)[a]
Sodium bicarbonate	0.05 (11.9 mM)[a]
Potassium persulfate	0.05 (3.70 mM)[a]
Deionized water	50.0
Temperature and time of polymerization	70°C, 1.5 h
Maleic acid	0.5–2.0 (115–460 mM)
Second stage (shot growth)[b]	
Styrene	1.80–3.29
Total amount of Aerosol MA, sodium bicarbonate, KPS, and DI water (wt ratio = 15 : 1 : 1 : 983)	9.41
Temperature and time of polymerization	70°C, 13.5 h

[a] Concentrations based on aqueous phase.
[b] Common ingredients in the shot growth stage: 0.1388 g Aerosol MA (100%); 0.0097 g sodium bicarbonate; 0.0095 g KPS; 9.25 g DI water.

The particle size and particle size distribution were measured by capillary hydrodynamic fractionation (Model 1100, Matec Applied Sciences) and dynamic light scattering (Nicomp Submicron Particle Sizer, Model 370). All samples were sonified in a sonifier bath (Commonwealth Scientific) to break up any latex particle aggregates before particle size measurement was carried out.

The surface carboxyl group densities were determined by conductometric titration using cleaned latex samples. The quantity of carboxyl groups in the aqueous phase was determined by the conductometric titration of the serum separated from the latexes by ultracentrifugation (L8-M Ultracentrifuge, Beckman). The amount of the carboxyl groups buried within the latex particles was calculated by subtracting off the carboxyl groups present on the latex particle surfaces and in the aqueous phase from the total carboxyl group content in a given recipe.

RESULTS AND DISCUSSION

Preparation of Noncarboxylated and Carboxylated P(BMA/BA) Latex Particles

The requirements for the latex particles to be used in this film formation study from latex blends are that (1) the particles should be uniform in size, (2) they should be available in varying particle sizes, (3) their surfaces should be well characterized, and (4) there should be independent control of the particle size and the density of the surface functional groups. Well-designed methods to prepare the particles are necessary to meet these requirements.

For the BMA/BA copolymerization system, the reactivity ratios of the two monomers are quite different ($r_{BMA} = 2.2$, $r_{BA} = 0.3$–50°C).[13] If a batch polymerization method were used to prepare the copolymer with 75 wt % of PBMA (73 mole %), the copolymer composition would be heterogeneous, drifting from ~80% initially to 0% of PBMA as the conversion increases based on the composition curve (Fig. 2). The heterogeneous composition would make it difficult, or even impossible, to investigate the parameters governing the film formation from latex blends. Therefore, well-designed semicontinuous processes, under monomer-starved polymerization conditions, should be applied to this system to control all the aforementioned parameters and obtain well-defined model latex particles.
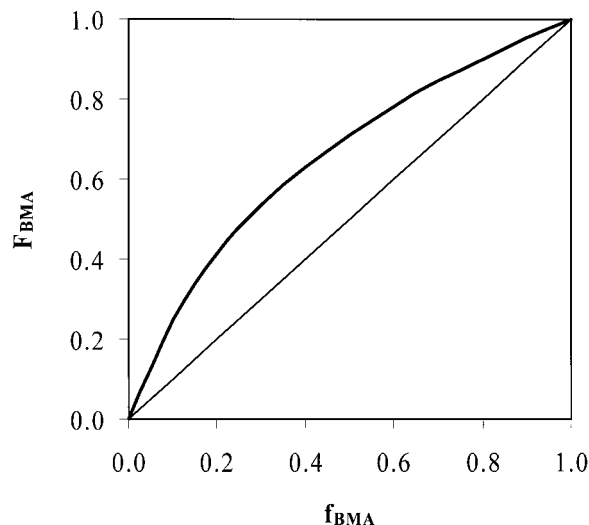

Figure 2 Composition curve of the BMA/BA copolymerization system. F_{BMA} is the mole fraction of BMA in the copolymer, and f_{BMA} is the mole fraction of BMA in the monomer mixture: points falling above the 45° line would indicate that BMA is more reactive than BA in the copolymerization system.

Synthesis of Noncarboxylated P(BMA/BA) Latex Particles

Here, a theoretical calculation was initially used instead of an experiment to choose a surfactant addition rate that provides a suitable surfactant concentration to both stabilize the latex particles and also to prevent secondary nucleation. This is the prerequisite for obtaining monodisperse particles. The following model was used for this calculation.

The assumptions used for this calculation are that (1) monolayer adsorption of surfactant (i.e., SDS used here) occurs on the latex particle surfaces and (2) when SDS reaches 100% monolayer coverage on the particle surface, it reaches the CMC in the aqueous phase simultaneously.

At any given feed time t (min), an equation can be established based on a mass balance:

$$R_m \cdot t \cdot P + W_{m_0} \cdot P_0 = \frac{1}{6} \cdot \pi \cdot D_v^3 \cdot \rho \cdot N_p \cdot V_{a_0} \quad (1)$$

where R_m is the feeding rate for the monomer mixture (g/min), P is the instantaneous conversion (%), W_{m_0} is the weight of monomer used in the seed preparation step (g), P_0 is the conversion at the end of the seeding stage, D_v is the volume-average particle size (cm), ρ is the P(BMA/BA)

copolymer density whose value was derived from the data reported by Gilbert[14] using a mixing rule for copolymers (i.e., 1.037 g/cm^3 for 75 wt % of BMA in the copolymers), V_{a_0} is the initial volume (before feeds) of the aqueous phase (mL), and N_p is the particle number concentration in terms of the initial volume of the aqueous phase (constant for each reaction here) at any given time (number of particles/mL).

D_v can be determined by rearranging eq. (1). The total particle surface area S_p (cm^2) can be calculated from the particle diameter and total particle number. Substituting for D_v in eq. (3) from eq. (2) leads to a relation between the total surface area to the macroscopic parameters for semicontinuous polymerization.

$$D_v = \left(\frac{6}{\pi \cdot \rho \cdot N_p \cdot V_{a0}}\right)^{1/3} \cdot (R_m \cdot P \cdot t + W_{m_0} \cdot P_0)^{1/3}$$
(2)

$$S_p = \pi \cdot D_v^2 \cdot N_p \cdot V_{a0}$$
(3)

$$S_p = \frac{6^{2/3} \cdot \pi^{1/3} \cdot N_p^{1/3} \cdot V_{a0}^{1/3}}{\rho^{2/3}} \cdot (R_m \cdot P \cdot t + W_{m_0} \cdot P_0)^{2/3}$$
(4)

Based on assumption (1), the surfactant weight W_s (g) needed for 100% coverage on the particle surface is given by eq. (5):

$$S_p = \frac{W_s}{M_s} \cdot N_a \cdot A_s$$
(5)

where M_s is the molecular weight of surfactant (288 g/mol for SDS), N_a is Avogadro's constant, and A_s is the particle surface area occupied by each surfactant molecule at 100% surface coverage. Here, we take A_s as 56 Å for this specific system.[15]

An expression for W_s can be derived by combining eqs. (4) and (5):

$$W_s = \frac{6^{2/3} \cdot \pi^{1/3} N_p^{1/3} \cdot V_{a0}^{1/3} \cdot M_s}{N_a \cdot A_s \cdot \rho^{2/3}}$$
$$\times (R_m \cdot P \cdot t + W_{m_0} \cdot P_0)^{2/3} \quad (6)$$

From assumption (2), the surfactant concentration in the aqueous phase reaches its critical micellar content (CMC) (6.9 mM for SDS)[16] when it reaches 100% monolayer surface coverage. Therefore, the weight of surfactant in the aqueous
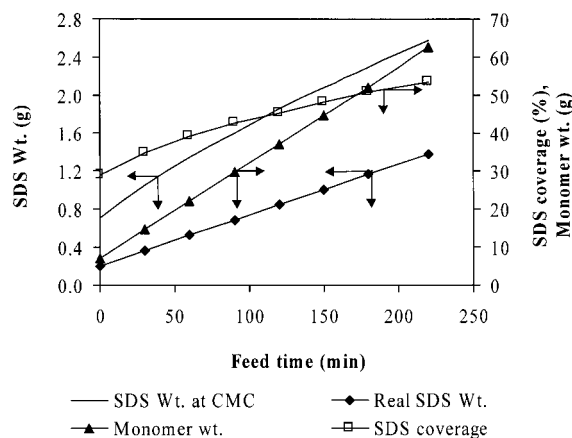

Figure 3 SDS weight (i.e., the amount theoretically calculated to reach the CMC as well as the quantity used in the actual synthesis), monomer weight, and the SDS coverage all as a function of feed time.

phase (W_a) under this condition can be computed by eq. (7). The total surfactant weight (W_E) used to attain 100% coverage on the particle surface should be the sum of W_s and W_a, and is given as eq. (8).

$$W_a = CMC \cdot V_a \cdot M_s = \frac{CMC \cdot (V_{a_0} + R_a \cdot t) \cdot M_s}{1000}$$
(7)

$$W_E = \frac{6^{2/3} \cdot \pi^{1/3} \cdot N_p^{1/3} \cdot V_{a0}^{1/3} \cdot M_s}{N_a \cdot A_s \cdot \rho^{2/3}}$$
$$\times (R_m \cdot P \cdot t + W_{m_0} \cdot P_0)^{2/3}$$
$$+ \frac{CMC \cdot (V_{a_0} + R_a \cdot t) \cdot M_s}{1000} \quad (8)$$

where R_a is the feed rate of water (mL/min).

In eq. (8), the only variable is the feeding time t. Parameters such as R_m, P, and R_a can be held constant. To obtain a homogeneous copolymer composition, a monomer-starved, semicontinuous criterion should be met. From this requirement, R_m can be set according to the analysis of Wessling,[17] who introduced another three assumptions, which are (a) a steady-state exists throughout the feeding period, (b) the amount of monomer dissolved in the aqueous phase is negligible, and (c) the reaction rate (R_p) is approximately equal to the monomer feed rate ($R_p \cong R_m$). Therefore, the predicted polymerization rate can be given by the monomer feed rate (i.e., 0.26 g/min). R_a (i.e., 0.23 mL/min) is set based on the
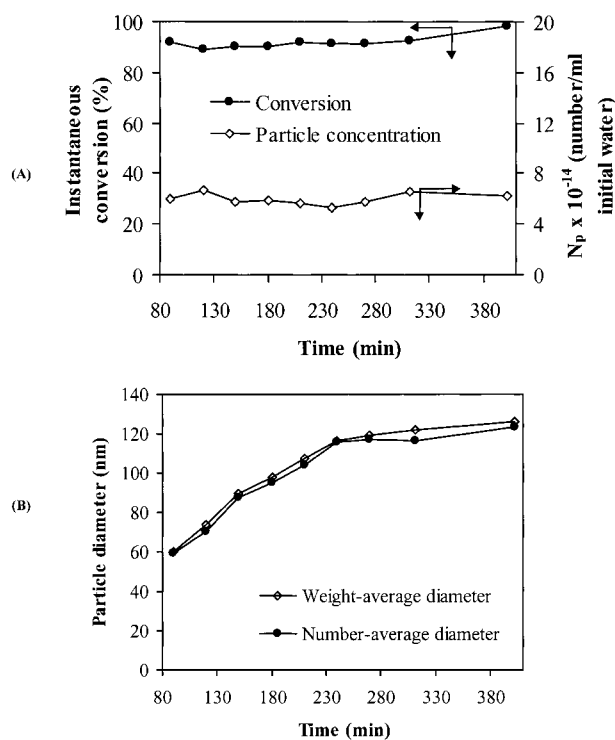
Figure 4 Kinetics of monomer-starved, semicontinuous emulsion polymerization for preparing P(BMA/BA) copolymer soft latex with a particle size of approximately 120 nm.

desired solids content for the final latex obtained. P can be treated as a constant under monomer-starved conditions (i.e., 90%). Now, W_E can be plotted against the feeding time t as shown in Figure 3.

The W_E (SDS wt at CMC) curve represents the upper limit of the amount of surfactant, below which, theoretically, there should be no secondary nucleation. A practical level for surfactant to be added in the seed stage is 35% for the total amount of surfactant necessary for 100% surface coverage (at the CMC in the aqueous phase). Surfactant is initially added at this level and the percentage of surfactant is gradually increased to 55% by the end of the feed. This addition scheme is based on the consideration that the system would be less stable and more surfactant would be needed to stabilize the particles as the solids content and particle size increase. From this percentage, the actual surfactant weight at the end of the feed stage can be calculated. Now, we have two points on the "real" surfactant feed curve. To simplify the experiments, a linear surfactant feed profile was applied, and the slope gives the feed rate. Figure 4 presents the kinetics of an actual typical semicontinuous emulsion polymerization.

Figure 4(A) shows that with the monomer feed rate used, instantaneous conversions are higher than 90%, which means that the monomer-starved requirement was met. This should guarantee a homogeneous copolymer composition.[18] In addition, the particle number remained constant throughout the reaction, which resulted in the monodispersity in particle size [Figure 4(B)]. The monodispersity of these soft particles was also verified by TEM. P(BMA/BA) latexes were negatively stained by UAc and observed in the TEM. A micrograph of these latex particles is presented in Figure 5.

The polymerization illustrated in Figure 4 yielded a well-defined P(BMA/BA) copolymer latex with a particle size of approximately 120 nm. Well-defined latex particles having a larger particle size can by synthesized by the same process by using the final latex obtained from the synthesis illustrated in Figure 4 as seed (i.e., the polymerization shown in Figure 6 yielded ~250 nm particles) or by using the latex obtained from the reaction presented in Figure 6 as seed (i.e., the polymerization depicted in Figure 7 yielded ~450 nm particles) for a subsequent polymerization.

Synthesis of Carboxylated P(BMA/BA) Copolymer Latexes

With the method established for synthesizing noncarboxylated P(BMA/BA) copolymer latexes, the synthesis of carboxylated P(BMA/BA) latexes was greatly simplified. MAA was employed to incorporate carboxyl groups into the latex particles. Similar calculations were used to predict the parameters governing these polymerizations. An-
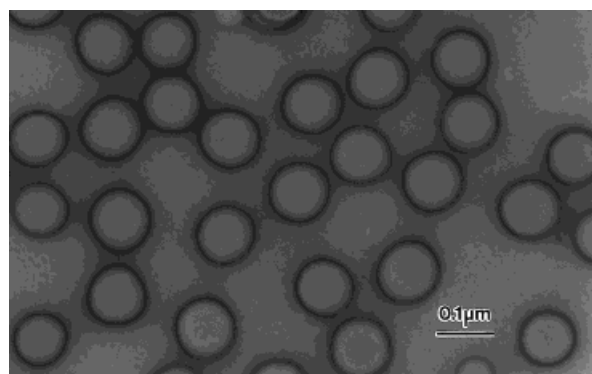

Figure 5 TEM micrograph of P(BMA/BA) soft latex particles; the sample that is the final product from the synthesis depicted in Figure 4 was negatively stained with UAc.
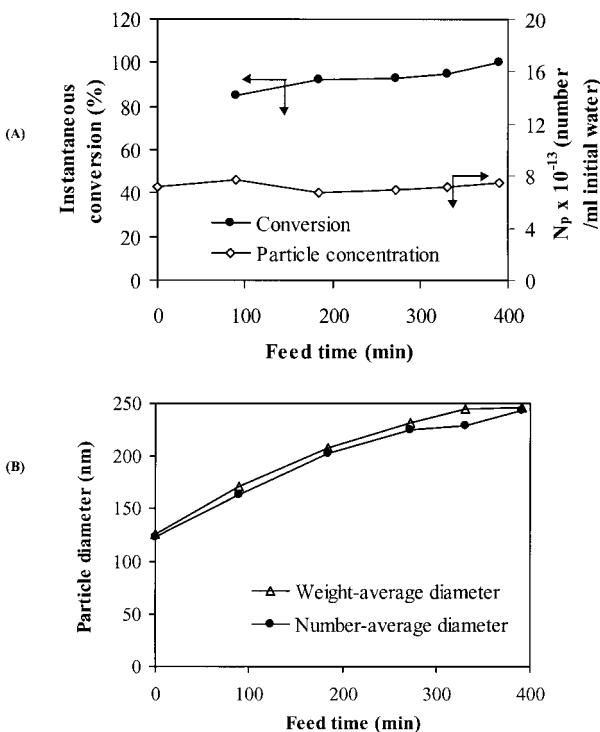
Figure 6 Kinetics of monomer-staved, semicontinuous emulsion polymerization for preparing P(BMA/BA) copolymer latex with particle diameters of approximately 250 nm.

other parameter that should be taken into consideration in this synthesis is the location of the carboxyl groups. This would be controlled by the time when the MAA feed was started. In this case, it was desired to obtain P(BMA/BA) copolymer latexes with carboxyl groups distributed throughout the particles. Thus, the MAA feed was started at the same time as the BMA and BA mixture. Recipes and characterization results are listed in Table IV, and the kinetics of a typical polymerization containing MAA is illustrated in Figure 8.

Well-defined, carboxylated P(BMA/BA) copolymer latexes were also obtained (Fig. 8). The constant particle number indicated that there was no secondary nucleation and coagulation, which was reflected in the monodispersity in the particle size. Constant instantaneous conversions higher than 90% implied a homogeneous composition of the copolymer latex. The characterization results presented in Table IV show that the surface coverage by the carboxyl groups present on the particles increased as the MAA used in the monomer feed increased, while the particle size remained constant. This means that independent control of carboxyl group density in the P(BMA/BA) copolymer latexes was also achieved.

Further characterization gave the distribution of carboxyl groups in different locations in the carboxylated latexes as obtained by conductometric titration of the cleaned latexes (Fig. 9). As was expected, a large quantity of the carboxyl groups were buried inside the particles. Here, the buried carboxyl groups refers to those groups that are localized in the first subsurface layer, second subsurface layer, and in the core of the latex particles.[20] This was also supported by the TEM examination of the carboxylated latex particles that were positively stained by cesium hydroxide for one hour (Fig. 10). The dark rings seen in the micrograph were caused by the formation of cesium carboxylate resulting from the reaction of carboxyl groups with cesium hydroxide. The thick dark rings demonstrate that the carboxyl groups were located in a gradient from the particle surface to regions within the particles. It is desirable for the carboxyl groups to be located uniformly throughout the soft particles for film formation studies from latex blends because the soft particles will deform during film formation and finally form a soft polymer matrix. A better connectivity in the interface between the hard latex particles
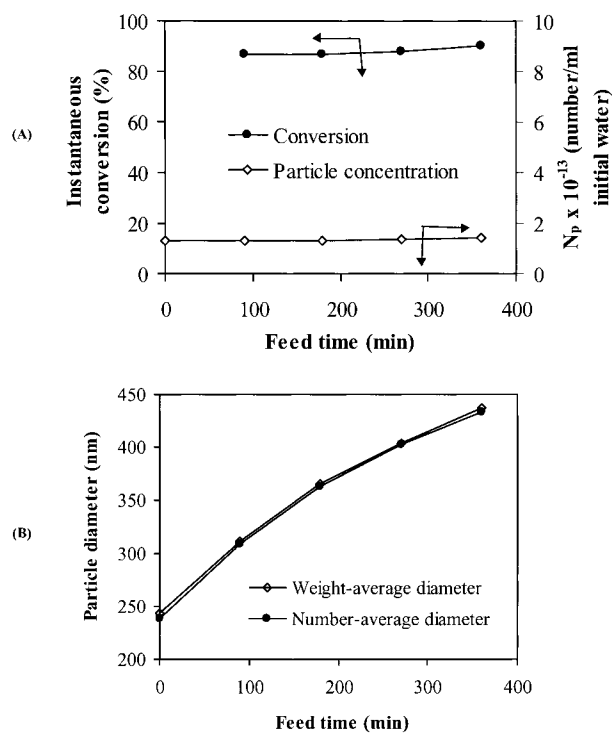

Figure 7 Kinetics of monomer-staved, semicontinuous emulsion polymerization for preparing P(BMA/BA) copolymer latex with particle diameters of approximately 450 nm.

Table IV   Characterization of Carboxylated P(BMA/BA) Copolymer Latexes at 80°C

Sample Code	BBc2	BBc1	BBc3
Wt of seed latex (g)—charged[a]	100.0	100.0	100.0
Components and weight in monomer mixture (g)—fed[b]			
n-Butyl methacrylate	42.78	42.63	41.57
n-Butyl acrylate	14.26	14.25	13.88
Methacrylic acid	0.65	1.94	3.88
% Methacrylic acid	1.0	2.9	5.9
Particle size and distribution			
D_w (nm)	130.8	120.4	118.1
D_n (nm)	129.1	117.3	116.8
PDI (D_w/D_n)	1.013	1.026	1.011
Surface characterization			
$Conc_{COOH}$[c] (mmol/g polymer)	0.105	0.326	0.663
A_{COOH}[d] (Å^2)	118.3	61.3	41.2
COOH coverage (%)[e]	7.6	14.7	21.9

[a] Seed latex was prepared by bottle polymerization over 24 h at 80°C by using the recipe for the seeded stage in Table I: % solids = 7.06%; D_n = 64.8 nm, PDI (=D_w/D_n) = 1.02; 0.08 g of KPS was added into the seed latex before semi-continuous polymerization was begun.
[b] BMA/BA (wt) = 3/1; SDS solution (SDS: 1.20 g, water: 50 g) was fed separately.
[c] The average concentration of the carboxyl groups throughout the latex particles.
[d] The particle surface area occupied by each carboxyl group.
[e] Percentage of the particle surface area covered by carboxyl groups, taking 9 Å^2 as the area for each carboxyl group.[19]

and the soft copolymer matrix would be expected if the carboxyl groups are evenly distributed in the matrix. The concentration of carboxyl groups remaining in aqueous phase was very low and was roughly constant (2~3 mM), which indicates a good partitioning of MAA into the particles.

Preparation of Carboxylated PS Latex Particles

Synthesis via a Batch Process

Since polystyrene is a homopolymer, it is possible to use batch emulsion polymerization processes to prepare monodisperse PS latex particles, while independently controlling the particle size and surface carboxyl group concentration by using a suitable surfactant type and concentration. Here, the normal batch process (i.e., all the ingredients were charged before the polymerization) and a shot growth process are compared for the syntheses of carboxylated PS latex particles using MA as the functional monomer to incorporate carboxyl groups. The surfactant used here is Aerosol MA-80.

Table V lists the characterization results for the carboxylated PS latexes based on the normal batch and shot growth processes. These results show that both methods resulted in latexes with narrow particle size distributions using the reci-

pes shown in Table III. Figure 11 shows a representative TEM micrograph, which confirms that the polystyrene latex with a narrow particle size distribution was achieved by the batch process. From Table V, it was also found that utilizing the shot growth method could meet the requirement of independently controlling the particle size and the concentration of surface carboxyl groups as well as providing narrow particle size distribution latexes. However, in the normal batch polymerization, the particle size changed as the concentration of surface carboxyl group changed. This means that it is hard to independently control the particle size and the concentration of surface carboxyl groups in the normal batch process. The reason for this may be that the large amount of acid used in the recipe overwhelmed the buffer system. Once the MA is added, the polymerization environment is acidic (see pH values given in Table V) and the pH value of the medium decreases as the concentration of MA increases. In the normal batch method, all of the latex particles were formed and grew in the acidic environment with different pH values, while in the shot growth process only around 10% of the styrene (including the portion injected for the second stage reaction) polymerized under acidic conditions. In the shot growth process, the majority of the particles were
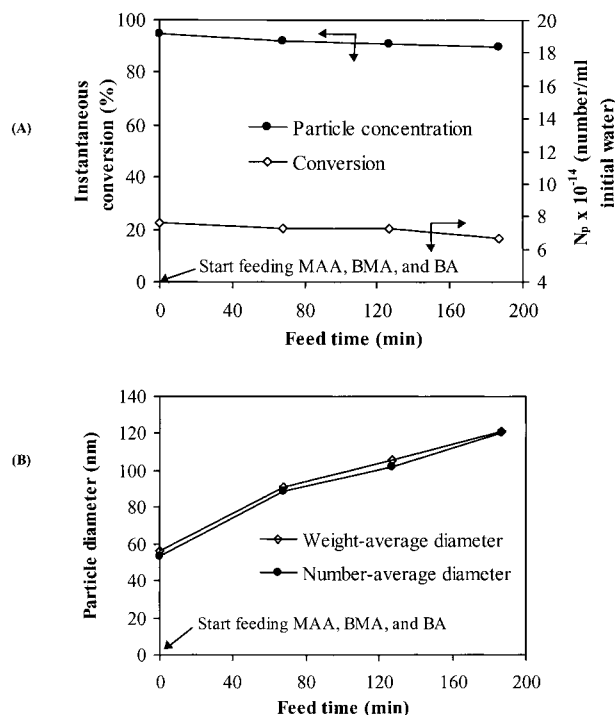
Figure 8 Kinetics of monomer-starved, semicontinuous emulsion polymerization for preparing carboxylated P(BMA/BA) copolymer latexes with a particle diameter of approximately 120 nm (Sample BBc1, see recipe in Table IV).

Figure 10 TEM micrograph of Sample BBc3 (see Table IV) cleaned with ion exchange resin and positively stained with CsOH for one hour.

formed and grew in an identical environment, and the acidic environment only occurred in the later stages of the polymerization, which has little
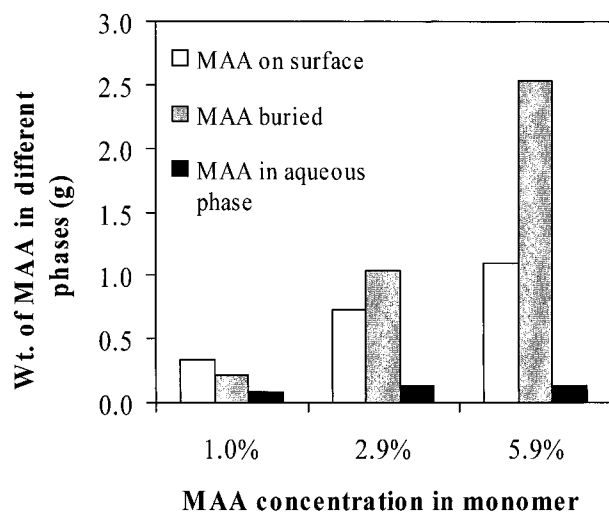

Figure 9 The distribution of carboxyl groups in different locations of the carboxylated P(BMA/BA) copolymer latexes (based on recipes listed in Table IV).
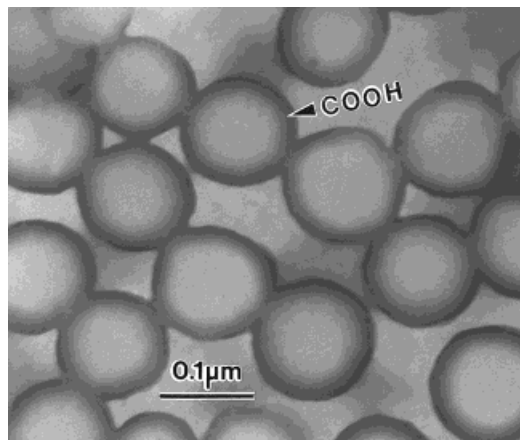
influence on the particle size and size distribution.

Figure 12 shows the conversion of maleic acid (in this section, the conversion of maleic acid is defined as the percentage of the maleic acid that is incorporated into the polystyrene latex particles—inside the particles and on the surface of the particles) as a function of the weight fraction of maleic acid in the monomer feed. These results show that the conversion of maleic acid in either the batch or shot growth process decreases as the weight fraction of maleic acid in the monomer feed increases. These results are in agreement with the copolymerization behavior of itaconic acid with acrylate monomers.[20] The conversion of maleic acid in the normal batch process is greater than that in the shot growth process. This implies that the conversion of maleic acid seems to be dependent on the concentration of styrene because, for the normal batch method, the maleic acid could react from the beginning of the polymerization when there was an initial relatively rich concentration of styrene, while the maleic acid could only react starting in a relatively low concentration of styrene (~95% styrene was already converted at the shot addition point) for the shot growth method. In both processes, the maleic acid may have copolymerized with the styrene in two sites: the aqueous phase and the styrene-swollen particles. Because the reaction medium for maleic acid in the aqueous phase in both processes is almost the same, the conversion of maleic acid was primarily considered to occur via the reaction inside the styrene-swollen particles for the normal batch method because the styrene

Table V Characterization of Carboxylated Polystyrene Latexes Obtained by Batch Emulsion Polymerization Processes

Sample Code	Sooh 6	Sooh 7	Sooh 8	Sooh 9	Sooh 10	Sooh 11	Sooh 12	Sooh 13	Sooh 14
First charge[a]									
Maleic acid (g)	0.000	0.506	1.010	1.504	2.000	—	—	—	—
Styrene (g)	20.50	20.50	20.50	20.50	20.50	20.50	20.50	20.50	20.50
Temp. (°C)	70	70	70	70	70	70	70	70	70
Time (hour)	15	15	15	15	15	1.5	1.5	1.5	1.5
pH[b]	8.19	1.67	1.48	1.35	1.28	8.13	8.08	8.16	8.12
Shot growth[c]									
Maleic acid (g)	—	—	—	—	—	0.500	1.002	1.501	2.003
Styrene (g)	—	—	—	—	—	3.292	2.789	2.303	1.797
Temp. (°C)	—	—	—	—	—	70	70	70	70
Time (hour)	—	—	—	—	—	13.5	13.5	13.5	13.5
pH[d]	—	—	—	—	—	1.73	1.47	1.33	1.22
Characterization									
D_n (nm)	126.5	102.0	100.3	107.5	113.9	135.1	136.5	130.5	131.4
D_w (nm)	130.8	107.4	106.4	112.8	121.5	139.2	140.4	134.7	134.6
PDI	1.034	1.053	1.061	1.049	1.067	1.030	1.029	1.032	1.024
$C_{S,COOH}$[e] (molecule/nm^2)	0.00	0.303	0.381	0.388	0.495	0.308	0.395	0.408	0.557

[a] Common ingredients in first charge: 0.75 g Aerosol MA (100%); 0.05 g NaHCO$_3$; 0.05 g KPS; 50 g deionized water.
[b] The pH values determined at the end of polymerization for samples Sooh6 to Sooh10; determined just before the shot growth for samples Sooh11 to Sooh14.
[c] See Table III for details.
[d] The pH values determined at the end of polymerization.
[e] $C_{S,COOH}$: the surface concentration of carboxyl group.

concentration was high. However, in the shot growth process, the incorporation of the maleic acid into the particles is considered to take place mainly through its copolymerization, with styrene in the aqueous phase forming oligomers, which eventually precipitate onto the particles. As the conversion of maleic acid in the batch process is higher than in the shot growth method, we conclude that the reaction of maleic acid in the
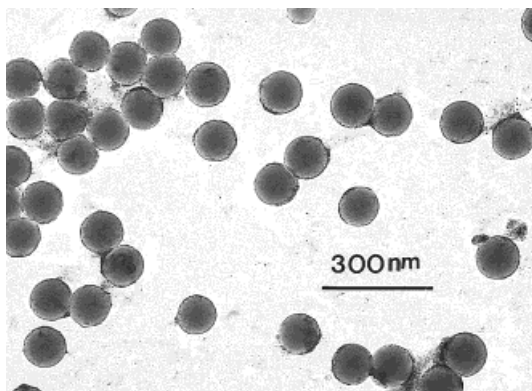
styrene-swollen particles contributed more to the conversion of the maleic acid.

Although the conversion of the maleic acid in the maleic acid in the normal batch method is greater than that in the shot growth process, the surface carboxyl group density of the PS particles obtained by the shot growth method is higher than that of the particles obtained by the normal
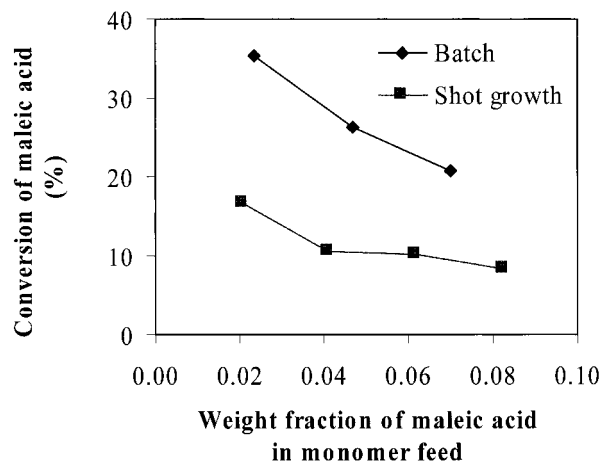

Figure 11 TEM micrograph of carboxylated PS latex particles synthesized by shot growth process; Sample Sooh12 in Table V.

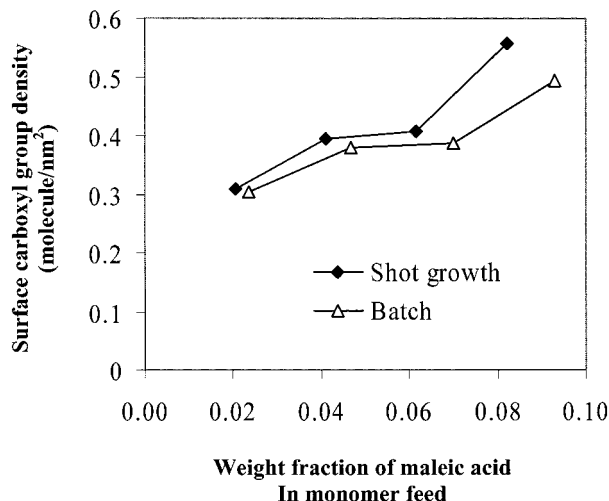**Figure 12** The conversion of maleic acid versus weight fraction of maleic acid in the monomer feed.

Figure 13 The density of surface carboxyl groups versus the weight fraction of maleic acid in the monomer feed.

Synthesis of Carboxylated PS Particle by Semicontinuous Process

Carboxylated polystyrene latexes with narrow particle size distributions and independent control of the surface carboxyl group density have been successfully synthesized by using a shot growth polymerization process (see discussion in last section). The carboxyl groups were incorporated into the latex particles by the copolymerization of maleic acid with styrene in the later stages of the polymerization (after 95% conversion of the initially charged styrene). The motivation driving the development of a semicontinuous process to prepare the same type of particles is that there are some drawbacks in the shot growth process, such that the shot growth method does not meet all the requirements of a model carboxylated PS latex particle for film formation studies. As discussed in the last section, the shot growth process has the following drawbacks besides its advantages in preparing PS latex particles with narrow polydispersity and realizing the independent control on particle size and surface carboxyl group density: (1) the conversion of the maleic acid is low, resulting in a lot of unreacted MA remaining in the aqueous phase, (2) it is hard to incorporate high densities of carboxyl groups on the surface of the PS latex particles, and (3) it is difficult to vary particle size over a broad range while maintaining monodispersity in size. Thus, a more powerful semicontinuous polymerization process is demanded. With a well-designed semicontinuous process, the above drawbacks of the shot growth method could be eliminated. In addition, due to
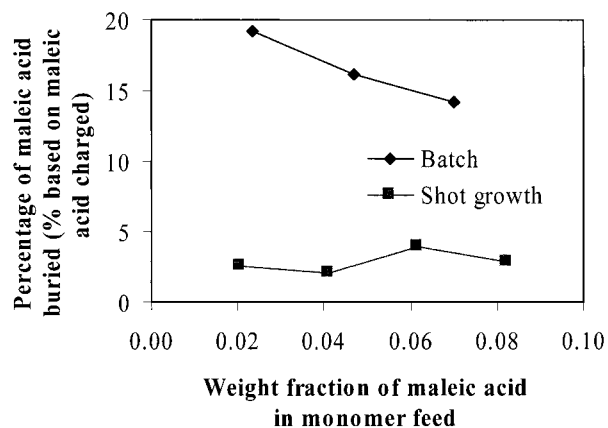
batch process (Fig. 13). This means that most of the incorporated carboxyl groups are located on the particle surface as a result of the shot growth process, while the majority of the carboxyl groups are located inside the particles in the case where the normal batch method was used. By referring to the discussion in the last paragraph, it seems that the maleic acid that was copolymerized in the aqueous phase and then precipitated onto the particles mainly results in the incorporation of the carboxyl groups at the particle surface, while the maleic acid that had polymerized in the styrene-swollen particles resulted in a larger quantity of buried carboxyl groups. Figure 14 shows that utilizing the normal batch process resulted in much more maleic acid becoming buried inside the latex particles compared to the shot growth process. For PS hard latex particles that do not deform or coagulate during the film formation from the hard/soft latex blends, the buried carboxyl groups are not desired because they contribute little to changing the particle surface properties and may also explain why it is hard to independently control the particle size and the surface carboxyl group density (see Table V). Therefore, regarding the surface incorporation of carboxyl groups and the independent control of particle size and surface carboxyl group density, the shot growth process is more efficient than the normal batch method.

Figure 14 Percentage of maleic acid localized on the latex particle surface compared to the total amount of converted maleic acid versus the weight fraction of maleic acid in the monomer feed.

less restrictions in the selection of the surfactant, a well-designed semicontinuous process would use the same surfactant (i.e., SDS) as that used in the synthesis of P(BMA/BA) latex particles and minimize the addition of additives to the aqueous phase. The semicontinuous method, therefore, would result in the formation of low concentrations of ions and carboxyl groups in the form of water-soluble oligomers in the aqueous phase, and at the same time, enable very precise control on the particle size and particle structure (see the following sections). The low and relatively constant concentration of carboxyl groups in the aqueous phase is especially important to the investigation of the relationship of the properties of the latex blend films to the carboxyl group concentration on the latex particles, where cleaned latexes cannot be used. For example, in the investigation of the relationship between the mechanical properties of latex blend films and carboxyl groups present in the latex particles, uncleaned model latexes with high solids contents have to be utilized to cast relative thick films. Therefore, the materials in the aqueous phase, especially the amount of acidic moieties, should be low and relatively constant. The quantity of carboxyl groups in the aqueous phase could be regarded as background noise in the investigation of the influence of carboxyl groups on the mechanical properties of the latex blend films. In choosing a recipe, the following factors should be taken into consideration: (1) to obtain high incorporation of carboxyl groups into the latex particles, a functional monomer with higher oil-solubility and higher reactivity with St, such as MAA, should be utilized; (2) to prevent the carboxyl groups from being neutralized during the emulsion polymerization, sodium bicarbonate (buffer) can no longer be added to the formulation; and (3) to minimize the influence of surfactant on the film formation from latex blends and the properties of the resulting latex blend films, the same surfactant (i.e., SDS) as that used in the syntheses of P(BMA/BA) soft latex particles should be used. This means that we have to use the simplest emulsion polymerization system (i.e., monomer, surfactant, initiator, and water) with a fixed surfactant (SDS) to prepare the model caboxylated PS latex particles with controllable particle size, monodispersity, and independent variability of the carboxyl group content. This makes the design of the semicontinuous process to synthesize carboxylated model PS latex particles more challenging.

Structure Design and Control of Particle Size. By referring to the methods that were developed to synthesize the monodisperse P(BMA/BA) soft model latex particles with homogeneous copolymer composition and independent carboxyl group content, parameters such as monomer feed and SDS feed rates can be calculated to ensure that the emulsion polymerization is performed under conditions free of any particle coagulation and secondary nucleation. Under these conditions, the following relationship can be employed:

$$N_{p,\text{seed}} = \frac{6W_0 \cdot P_{\text{seed}}}{\pi \cdot D_{v_0}^3 \cdot \rho} = N_{p,\text{feed}} = \frac{6W \cdot P_{\text{feed}}}{\pi \cdot D_v^3 \cdot \rho} \quad (9)$$

where $N_{p,\text{seed}}$ and $N_{p,\text{feed}}$ are the total particle numbers at the end of the seed stage and during the feed stage, respectively; W_0 and W are the monomer weights used for the seeding stage and at any point of the feed stage, respectively; D_{v_0} and D_v are the volume-average particle sizes obtained at the end of the seed stage and at any point during the feed stage, respectively; and P_{seed} and P_{feed} are the instantaneous monomer conversions at the end of the seed stage and at any point of the feed stage, respectively.

When polymerization is performed under monomer-starved conditions, P_{seed} is approximately equal to P_{feed}. Therefore, the weight of the monomer fed (W_{feed}) to increase the particle size can be calculated by rearranging the monomer feed rate (R_m) and monomer feed time (t) [eq. (9)} using the following equation:

$$W_{\text{feed}} = R_m \cdot t = W_0 \left[\left(\frac{D_v}{D_{v_0}} \right)^3 - 1 \right] \quad (10)$$

Equation (11) is another form of eq. (10) that is convenient to predict the growth in the particle size as the feed time increases, which is illustrated in Figure 15.

$$D_v = D_{v_0} \cdot \left(\frac{R_m}{W_0} \cdot t + 1 \right)^{1/3} \quad (11)$$

If we want to obtain particles with size D_v, the amount of monomer that needs to be fed into the reactor can be immediately computed by eq. (10), knowing the seed particle size and the amount of monomer that was used in the seed stage (W_0). Under the conditions needed to keep the total particle number constant, the particle size and
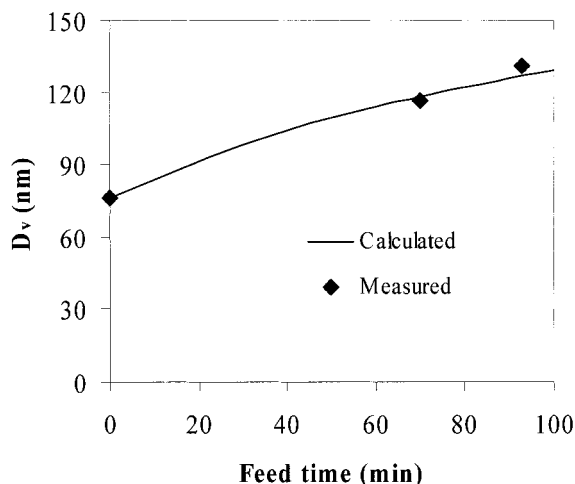
Figure 15 Increase in particle size with feed time under conditions where there is no coagulation or secondary nucleation. Monomer (monomer I or monomer II) was fed into the reactor at a constant rate of 0.3 mL/min, and SDS solution (3.85 wt %) was simultaneously fed into the reactor at a constant rate of 0.114 mL/min. Monomer I is styrene, which was fed into the reactor during the first feed stage (0 to ~70 min). Monomer II is the mixture of styrene and MAA fed into the reactor during the last feed stage to build up the shell thickness (~3 nm thick).

structure can be calculated from eq. (10) or eq. (11). Because PS hard particles do not deform during film formation at room temperature, the carboxyl groups inside the particles will not be able to contact other groups or ions outside the particles. Therefore, it is not necessary to incorporate carboxyl groups inside the PS particles. The structure that we designed for these latex particles consists of a PS core covered by a very thin layer (~3 nm in thickness) of poly(styrene-co-methacrylic acid) [P(S/MAA)] copolymer, which is the layer that contains the carboxyl groups. The composition of the shell polymer can be varied to change the surface carboxyl group concentration. Figure 16 schematically illustrates the structure of the carboxylated PS particle. In the preparation process, the particle size of the seed latex was measured at the end point of the seeding stage, and then the amount of the monomer (i.e., St, monomer I), which was needed to be fed into the reactor to increase the size of the core was calculated. Then, a calculated amount of monomer II (i.e., the mixture of St and MAA) was fed into the reactor to increase the shell thickness to around 3 nm. The SDS solution was fed into the reactor at a constant rate, which was calculated by the

method used for the synthesis of P(BMA/BA) latexes to stabilize the latex particles while either monomer I or monomer II was fed into the reactor (Table VI). The particle size was measured at the end of the seeding stage, at the end of the monomer I feed, and at the end of the polymerization. All of the measured values fell along the theoretically calculated curve [calculated by eq. (11), Fig. 15], which verifies the accuracy of this method in achieving the designed latex particle structure.

Characterization of the Carboxylated PS Latex Particles. Precise control of particle size, particle size distribution, and carboxyl group content was achieved using the method described above. Table VI shows the characterization results for these latex particles. The difference in the particle size of the different latex samples is less than 5 nm. The particles with surface carboxyl group coverage varying from 0 to 77.2% are all monodisperse, demonstrating that the designed semicontinuous process can be successfully used to prepare well-defined model carboxylated PS latex particles by using a simple emulsion polymerization system.

The distribution of carboxyl groups in the latex was analyzed by the conductometric titration of cleaned latexes and the serum separated from the corresponding latexes using an ultracentrifugation technique. The titration of the cleaned latex gives the values of the carboxyl group content on the particle surface, while the titration of the serum yields the carboxyl group content in the aqueous phase. Based on a given recipe (Table VI), the carboxyl group content buried inside the particles can be calculated. A detailed carboxyl group distribution balance can be calculated using these analysis methods, which is presented in Figure 17.

As expected in the latex particle design, the amount of the carboxyl groups remaining in the aqueous phase is low and basically constant (2–3 m*M*), which shows that this contribution to the overall amount of the carboxyl groups can be
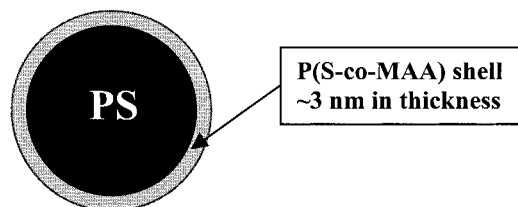

Figure 16 Structure of the desired carboxylated PS latex particle.

Table VI Characterization of Carboxylated PS Latexes Obtained by a Semicontinuous Emulsion Polymerization Process

Sample Code	S16	Sc10	Sc8	Sc11	Sc9I
Weight of seed latex (g)—charged[a]	97.28	97.28	97.28	97.28	97.28
Components weight—fed					
Monomer I					
St (g)	17.79	17.70	21.12	20.98	21.45
SDS solution					
Water (g)	6.47	7.75	7.88	8.70	9.72
SDS (g)	0.26	0.31	0.32	0.35	0.39
Monomer II					
St (g)	0.00	0.31	0.32	0.35	0.39
MAA (g)	0.00	0.52	1.01	1.44	1.97
wt % MAA	0.00	15.0	30.0	45.0	60.0
Characterization					
D_w (nm)	132.9	128.4	131.6	129.8	130.8
D_n (nm)	130.4	125.8	128.8	127.5	127.6
PDI	1.019	1.021	1.022	1.018	1.025
COOH coverage[b] (%)	0.00	12.9	19.1	29.7	65.8

[a] The seed latexes were synthesized at 80°C for 1.5 h with the following recipe: St = 7.00 g, DI water = 90.00 g, KPS = 0.08 g, and SDS = 0.2 g.
[b] Percentage of the particle surface area covered by carboxyl groups, taking 9 Å^2 as the area for each carboxyl group.[19]

treated as background noise in the subsequent investigation of the influence of carboxyl group on the mechanical properties of the latex blend films. Most of the carboxylated PS latexes have the majority of their carboxyl groups present on the outermost surface of the latex particles.
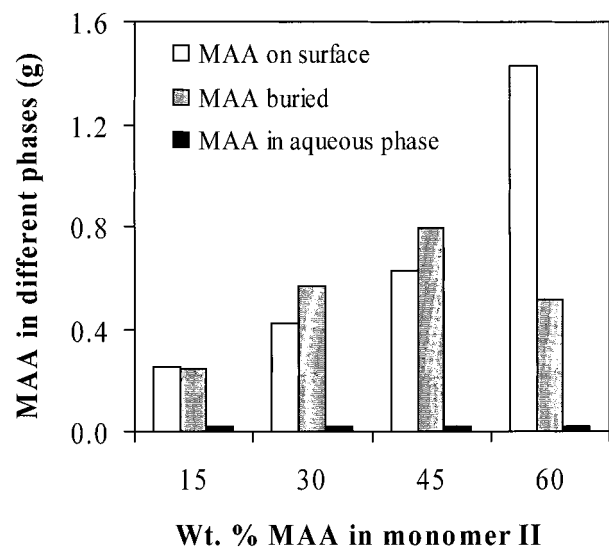

Figure 17 The distribution of carboxyl groups in different locations in the carboxylated PS latex particles (based on the recipes presented in Table VI).

CONCLUSIONS

Theoretical calculations based on a simplified model are helpful for the selection of monomer and surfactant feed rates in a semicontinuous emulsion polymerization process that allows one to maintain a constant particle number throughout the polymerization and results in a homogeneous composition in the copolymer latexes. The noncarboxylated P(BMA/BA) latex particles obtained by this process are monodisperse in size and have a homogeneous copolymer composition. The particle size can vary over a wide range between 120 and 450 nm while maintaining their monodispersity and homogeneity in composition. The model carboxylated P(BMA/BA) latexes have independently adjustable carboxyl group concentrations (from 7.6 to 21.9% in terms of surface carboxyl group coverage, or 0.105–0.663 mmol COOH/g polymer, in terms of the carboxyl group concentration throughout the entire particles) as being monodisperse in size and homogeneous in copolymer composition. In the synthesis of carboxylated P(BMA/BA) latexes, the percentage of the MAA incorporated into the latex particles is high. Only 2–3 mM MAA remains in the aqueous of the carboxylated P(BMA/BA) latexes.

Carboxylated monodisperse PS latex particles with a particle size around 130 nm can be prepared

by either a normal batch or a shot growth process using Aerosol MA-80 as surfactant and MA as the functional monomer used as the source for the carboxyl groups. However, independent control of the surface coverage of the carboxyl groups present on the particle surface can only be achieved by the shot growth method. The percentage of the MA incorporated into latex particles is below 40%. In terms of the incorporation of carboxyl groups onto the surface of the PS latex particles and the independent control of the surface coverage of the carboxyl groups, the shot growth method is more efficient than the normal batch process.

Carboxylated PS latexes with monodisperse particle sizes and independent, variable surface coverage by the carboxyl groups can be synthesized by using a well-designed semicontinuous process with a very simple emulsion polymerization recipe (comprised only of St, SDS, water, and KPS). The calculation used in the synthesis of the P(BMA/BA) soft latexes can also be applied here. By monitoring the seed size as well as the amount of monomer fed under suitable monomer and surfactant feed rates, the final particle size can be precisely controlled with a difference in size between the different samples that was less than 5 nm. Only 2–3 mM MAA remains in the aqueous phase of the final carboxylated PS latexes.

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