

# Synthesis and Characterization of Functionalized Polymer Latex Particles Through a Designed Semicontinuous Emulsion Polymerization Process

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**ABSTRACT:** Monodispersed noncarboxylated and carboxylated poly(*n*-butyl methacrylate-*co*-*n*-butyl acrylate) latices were synthesized with a well-defined semicontinuous emulsion polymerization process. A modified theory to correlate the polymerization rate to the instantaneous conversion of the monomer or comonomer mixture was developed. The resulting equation was used to determine the maximum polymerization rate only below or equal to which the polymerization could be operated in the highly monomer-starved regime, which corresponded to an instantaneous conversion of 90% or greater. Experimental data from reaction calorimetry supported that the polymerization was under highly monomer-starved conditions when the model latices were synthesized with the modified model. The estimation of the average number of free radicals per latex particle ( $\bar{n}$ ) during the feeding stage revealed that  $\bar{n}$  was as high as 1.4 in the actual polymerization, which showed that the original selection of 0.5 as the  $\bar{n}$  value was not accurate

in the developed model. From the conductimetric titration experiments, we found that most of the carboxyl groups from the methacrylic acid (MAA) were buried inside the latex particles, and the surface carboxyl group coverage increased as the MAA concentration in the comonomer feed increased. The glass-transition temperatures of the synthesized polymers were close to the designed value from the Pochan equation, and only one glass transition was observed in the polymer samples in the differential scanning calorimetry measurements, indicating a homogeneous copolymer composition in the functionalized shell. Particle size characterization and transmission electron microscopy confirmed the uniformity in the latex particle size. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 248–256, 2005

**Key words:** calculations; emulsion polymerization; functionalization of polymers; modeling

## INTRODUCTION

Synthetic latices consisting of colloiddally dispersed polymer particles, which can be prepared by tightly controlled emulsion polymerization techniques, are frequently encountered in the modern world. They are produced in large quantities and are employed in many applications, including rubber, plastics, coatings, and adhesives. Among them, functionalized latices are of special importance because they can provide unique properties to the resulting materials by varying the type of functional groups, the concentration of the functional groups, and their location in the particles.<sup>1–6</sup>

Semicontinuous processes are the most widely used processes in the industry to produce polymer latices, especially functionalized latex particles, because of their several advantages over batch processes: first,

they can effectively reduce the monomer or comonomer holdups in the reactor. This facilitates heat transfer and improves operation safety. Second, they can efficiently control the copolymer composition by changing the comonomer feed strategy and/or the (co)monomer feed rates ( $R_m$ 's). In a batch process, copolymer composition drift is inevitable as long as there is a difference in monomer reactivities.<sup>7</sup> Semicontinuous processes also have a strong influence on the control of the resulting latex particle morphologies, which can impart different properties for end-use applications. One way to prepare functionalized latex particles is to copolymerize functional comonomers with the backbone (co)monomers.<sup>8–11</sup> However, as it has been pointed out in a previous article,<sup>12</sup> past studies describing the preparation of functionalized latex particles with a semicontinuous emulsion polymerization process have been empirical in nature and have only allowed for the control of one experimental parameter at a time. In the same study,<sup>12</sup> a theoretical model was developed to design semicontinuous processes with well-defined particle structures.

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In this study, a modification to the original model was developed to consider monomer swelling effects in polymer particles during the feed stage of the semicontinuous processes. The accuracy of  $R_m$  prediction, from the modified model to maintain monomer-starved conditions, was tested with reactor calorimetry. The synthesized latices were also used to study the influence of the latex particle surface characteristics on film formation from pigmented latex systems. To separate out the effects of particle size, surface charge, and glass-transition temperature ( $T_g$ ) on the binder performance, we needed to control each. For this, the requirements were that (1) the particles had to be uniform in size despite their functionality, (2) there had to be independent control of the particle size and the density of the surface functional groups, and (3) the particles had to have the same  $T_g$  regardless of their functionality.

## EXPERIMENTAL

### Materials

We purified *n*-Butyl methacrylate (BMA), *n*-butyl acrylate (BA), and methacrylic acid (MAA) monomers (Sigma-Aldrich, Milwaukee, WI; reagent-grade) by passing them through columns filled with an appropriate inhibitor-removal packing material (Sigma-Aldrich, Somerville, NJ). Sodium lauryl sulfate (SLS; Fisher Scientific, Pittsburgh, PA; reagent-grade) and potassium persulfate (KPS; Sigma-Aldrich, Milwaukee, WI; reagent-grade) were used as received without further purification. A cationic ion-exchange resin (20–50 mesh; AG 50W-X4, Bio-Rad Co., Hercules, CA) and an anionic ion-exchange resin (20–50 mesh; AG 1-X4, Bio-Rad) were cleaned by the method suggested by van den Hul and Vanderhoff.<sup>13</sup>

### Latex synthesis

Model latex synthesis was performed in a 1000-mL, four-necked flask equipped with a reflux condenser, a nitrogen gas inlet tube, a polytetrafluoroethylene stirrer (~230 rpm), and three feed tubes for the monomer, surfactant, and initiator solution. The noncarboxylated and carboxylated model poly(*n*-butyl methacrylate-*co*-*n*-butyl acrylate) [P(BMA/BA)] copolymer latices were prepared by a conventional semicontinuous emulsion polymerization process at 80°C. Table I gives a typical recipe for the synthesis of the P(BMA/BA) latex particles with a designed size around 150 nm in diameter. For the synthesis of the carboxylated P(BMA/BA) latices, MAA was added into the comonomer mixture (the weight fractions of MAA, BMA, and BA were adjusted according to the desired MAA weight fraction and  $T_g$ ), which was fed into the reactor. The initial 1.5-h period of the polymerization

**TABLE I**  
General Recipe for the Synthesis of Noncarboxylated and Carboxylated P(BMA/BA) Latex Particles with a Designed Size of 150 nm at 80°C

Seed stage				
BMA (g)				26.25
BA (g)				8.75
DI water (g)				450.00
KPS (g)				0.40
SLS (g)				1.00
		MAA (wt %)		
Feed stage	0	1	3	6
BMA (g)	215.0	206.42	190.30	166.14
BA (g)	71.70	80.68	91.00	106.46
MAA (g)	0	2.90	8.70	17.4
DI water (g)	50.00	50.00	50.00	50.00
KPS (g)	0.40	0.40	0.40	0.40
SLS (g)	2.44	2.44	2.44	2.44

was the seed stage. About 10% of the monomer mixture (BMA/BA = 75/25 w/w) was used in the seeding stage. After the seeds were almost fully formed (~98% conversion as determined by gravimetry), the remaining monomer mixture of BMA, BA, and/or MAA (for carboxylated latex particles); surfactant; and initiator solution was separately fed into the reactor at constant rates with two syringe pumps (Harvard Apparatus 22, Holliston, MA). When the feeds were finished, the reaction was allowed to continue for another 2 h, and the latex was then cooled to room temperature and filtered. Well-defined latex particles with larger particle sizes (250 and 450 nm) could be synthesized with this process.

The kinetics of the emulsion copolymerization of BMA and BA, with the recipe shown in Table I, was determined at 80°C with a Mettler RC1 reaction calorimeter (Columbus, OH) equipped with a 1-L MP10 reactor, a pitched impeller blade, and a baffle. The procedure with the Mettler RC1 reaction calorimeter for making the seed latex was as follows. First, the surfactant, SLS, was dissolved in deionized (DI) water and charged into the MP10 reactor. Nitrogen was passed through the reactor for 10 min with stirring at 100 rpm. The comonomers, BMA and BA, were then added, the reactor was sealed, and a first calibration was performed at 25°C to determine the heat-transfer coefficient through the wall of the reactor. The reactor temperature was then ramped to 80°C in 10 min, and a second calibration was carried out. The initiator, KPS, dissolved in 5 g of DI water, was then injected. During the reaction, samples (2 mL) were withdrawn regularly from the reactor. After the end of the reaction, a final calibration was then conducted. For all semicontinuous emulsion copolymerizations in RC1, similar calibration steps were taken, and a feed pump

(Gamma 4-W metering pump, model G1201T/W, ProMinent, Heidelberg, Germany) needed to be programmed to control the feed rate of the comonomer mixture. The surfactant and initiator feeds were provided with a programmable syringe pump (Harvard Apparatus 22).

### Latex characterization

In this study, ion-exchange resins were used to remove the surfactants and electrolytes from the latices. After the treatment of the analytical-grade anionic and cationic ion-exchange resins according to the method suggested by van den Hul and Vanderhoff,<sup>13</sup> the cationic resin and anionic resin were mixed at a weight ratio of 51:49 just before they were used. Latex samples were diluted to approximate 5% solid content. The ratio of the solid polymer to the mixed resins was 1:1 (w/w), and the mixture was stirred with a magnetic bar for 2 h. The conductance of the latex was measured after each ion-exchange cycle. This ion-exchange procedure was repeated until the conductance of the latex remained constant (a typical value was  $\sim 8 \mu\text{S}$ ). This procedure often required five ion-exchange cycles.

The particle size and particle size distribution were measured by capillary hydrodynamic fractionation (CHDF; model 1100, Matec Applied Sciences, Northborough, MA). All samples were prepared by dilution of the original sample to approximately 1% solid and were sonified in a sonifier bath (Commonwealth Scientific, Alexandria, VA) to break up any colloidal aggregates and filtered through a syringe filter (25-mm high-performance liquid chromatography (HPLC) syringe filter, Alltech Associates, Inc., Deerfield, IL) before injection into the CHDF instrument.

The  $T_g$ 's of the BMA/BA copolymers were measured by differential scanning calorimetry (DSC; DSC 2920 scanning calorimeter, TA Instruments, New Castle, DE). Experiments were performed over a temperature range of  $-40$  to  $250^\circ\text{C}$  with a heating rate of  $10^\circ\text{C}/\text{min}$ .

Latex particles were observed by transmission electron microscopy (TEM; Phillips 400T (Eindhoven, The Netherlands)). For TEM analysis, a negative stain (2% uranyl acetate) was used along with cold-stage conditions.

The concentrations of carboxyl groups on the surface of the particles and inside the particles were determined by a conductometric titration technique. The surface carboxyl group densities were determined by conductometric titration of the cleaned latex samples. The number of carboxyl groups in the aqueous phase was determined by conductometric titration of the serum separated from the latex by ultracentrifugation (L8-M Ultracentrifuge, Beckman, Fullerton, CA; the conditions were 37,000 rpm,  $4^\circ\text{C}$ , and 10 h). The num-

ber of buried carboxyl groups was calculated by subtraction of the number of carboxyl groups on the surface of the latex particles and in the aqueous phase from the total carboxyl group content in a given recipe.

## RESULTS AND DISCUSSION

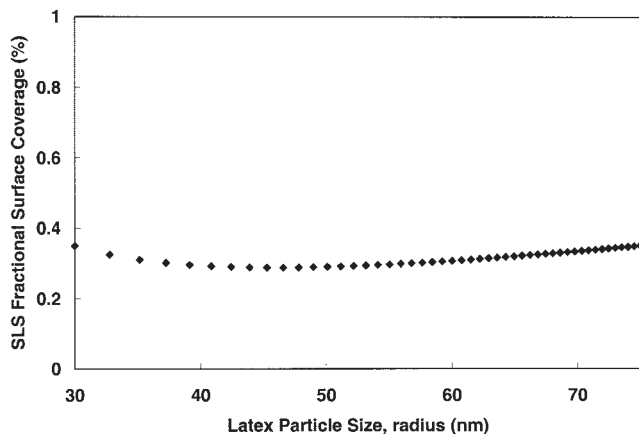
### Surfactant amount calculation

During the feeding stage, one important problem is the determination of the required amount of surfactant to be added to provide a sufficient stability to the latex system and yet prevent secondary nucleation. Tang et al.'s model<sup>1</sup> was used to calculate the amount of surfactant needed in the feeding stage ( $W$ ). The following equation was used:

$$W = \frac{6^{2/3} \pi^{1/3} N_p^{1/3} V_{a0}^{1/3} M_s}{N_A a_s \rho^{2/3}} (\text{Total polymer weight})^{2/3} + \frac{(\text{Aqueous phase weight}) M_s}{1000} \quad (1)$$

where  $N_p$  is the particle number concentration in terms of the initial volume of the aqueous phase (number/mL),  $V_{a0}$  is the initial volume (before feeding) of the aqueous phase (mL),  $M_s$  is the molecular weight of the surfactant (288 g/mol for SLS),  $N_A$  is Avogadro's number ( $6.022 \times 10^{23} \text{ mol}^{-1}$ ),  $a_s$  is the particle surface area occupied by each surfactant molecule at 100% surface coverage ( $56 \text{ \AA}^2$  for this specific system<sup>14</sup>),  $\rho$  is the BMA/BA copolymer density ( $1.037 \text{ g/cm}^3$  in this case), and cmc is the critical micelle concentration ( $7.0 \text{ mM}$  for SLS).<sup>15</sup>

The calculated  $W$  from eq. (1) represents the upper limit of the amount of surfactant to be used in a polymerization below which, theoretically, there should be no secondary nucleation. A practical level for the amount of surfactant to be added in the feeding stage is 35% of the total amount of surfactant for 100% surface coverage (at the cmc in aqueous phase) to retain the stability of the latex particles and to prevent limited coagulation from taking place during the feed stage. Later, this amount of surfactant was verified to be enough to maintain the stability of the latex system during the feed stage by the latex particle size analysis. Also, a linear feed scheme was used here for the surfactant addition during the feed stage of the semi-continuous emulsion polymerization. As shown in Figure 1, when the linear surfactant feed scheme was adopted, the theoretical SLS fractional surface coverage was close to 35% during the feed stage; even some deviation appeared in the beginning of the surfactant feed.



**Figure 1** Theoretical SLS fractional surface coverage as a function of latex particle radius during the semicontinuous emulsion polymerization of BMA/BA.

### $R_m$ calculation

#### Model development

In a previous study,<sup>12</sup> a model was developed to correlate the polymerization rate ( $R_p$ ) to the instantaneous conversion of the monomer or comonomer mixture. The model can help determine the maximum polymerization rate ( $R_p^{Max}$ ) below or equal to which monomer-starved conditions can be achieved. The  $R_p^{Max}$  calculated from the model can serve as a useful guide for selecting the appropriate monomer or comonomer mixture feed rate corresponding to the required instantaneous conversion. In turn, the surfactant feed rate can be determined accordingly because it is dependant on  $R_m$  ( $\text{g s}^{-1} \text{cm}^{-3}$ ). In this study, a modification to the original model was developed to account for the swelling effects of the monomer in the existing polymer particles during the feed process. Here, *instantaneous conversion* was defined as the ratio of the amount of polymer in the system at any instant to the total amount of monomer added up to that point, including the monomer in the seed stage.<sup>16</sup>

In a semicontinuous emulsion polymerization process, the monomer concentration in the polymer particles ( $[M_p]$ ;  $\text{mol/cm}^3$ ), can be expressed as

$$[M_p](t) = \frac{(W_0 + R_m t)[1 - c(t)]}{1/6\pi D_{vs}^3 N_p M_0} \quad (2)$$

where  $W_0$  is the initial polymer weight in the system (g),  $t$  is the feeding time (min),  $c(t)$  is the fractional instantaneous conversion,  $D_{vs}$  is the volume-average diameter of the swollen polymer particle (cm), and  $M_0$  is the molecular weight of the monomer (or comonomer mixture; g/mol).

The total volume of polymer particles could be expressed in the form

$$1/6\pi D_{vus}^3 N_p = \frac{(W_0 + R_m t)c(t)}{\rho_p} \quad (3)$$

where  $D_{vus}$  is the volume-average diameter of unswollen polymer particles (cm) and  $\rho_p$  is the density of polymer ( $\text{g/cm}^3$ ).

When eqs. (2) and (3) are combined,  $[M_p]$  is then

$$[M_p](t) = \frac{[1 - c(t)]\rho D_{vus}^3}{c(t)M_0 D_{vs}^3} \quad (4)$$

with the assumption that the volume of monomer swollen particles is equal to the volume of polymer plus that of unreacted monomer

$$\frac{D_{vus}^3}{D_{vs}^3} = \frac{1}{1 + \frac{\rho_p[1 - c(t)]}{\rho_m c(t)}} \quad (5)$$

where  $\rho_m$  is the density of monomer or comonomer mixture ( $\text{g/cm}^3$ ). Hence,  $[M_p]$  is a function of  $c(t)$  in the form of

$$[M_p](t) = \frac{[1 - c(t)]}{c(t) + \frac{\rho_p}{\rho_m}[1 - c(t)]} \frac{\rho_p}{M_0} \quad (6)$$

Therefore, in the growth stage of conventional emulsion polymerization,  $R_p$  ( $\text{mol s}^{-1} \text{cm}^{-3}$ ) has a general form, which could be written as

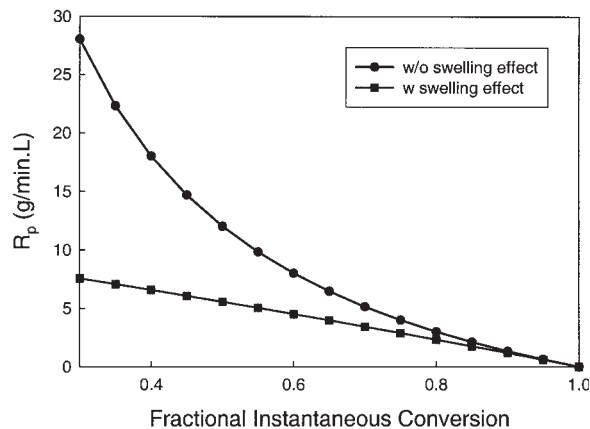
$$\begin{aligned} R_p &= k_p \frac{\bar{n}}{N_A} N_p [M_p](t) \\ &= k_p \frac{\bar{n}}{N_A} N_p \frac{[1 - c(t)]}{c(t) + \frac{\rho_p}{\rho_m}[1 - c(t)]} \frac{\rho_p}{M_0} \quad (7) \end{aligned}$$

where  $k_p$  is the propagation rate coefficient ( $\text{L mol}^{-1} \text{s}^{-1}$ ) and  $\bar{n}$  is the average number of free radicals per polymer particle.

The original model without consideration of the swelling effects of the monomer to the polymer particles is

$$R_p = k_p \frac{\bar{n}}{N_A} N_p [M_p](t) = k_p \frac{\bar{n}}{N_A} N_p \frac{[1 - c(t)]}{c(t)} \frac{\rho_p}{M_0} \quad (8)$$

Figure 2 illustrates the difference between the two models. As shown, the two models predicted very closely the values of  $R_p$  when the instantaneous conversion was higher than 85%; when the instantaneous conversion becomes lower, for example, smaller than 70%, the modified model (taking into consideration of the swelling effects of the monomers) gave a consid-



**Figure 2** Reaction rate versus instantaneous conversion from two models for the synthesis of P(BMA/BA) latex particles:  $N_p = 1.213 \times 10^{17} \text{ L}^{-1}$ .

erably lower value than the previous model. However, in this study, the two models gave similar predictions on  $R_p$  because high instantaneous conversions ( $>90\%$ ) were required to obtain latex particles with monodisperse particle sizes and controlled copolymer compositions.

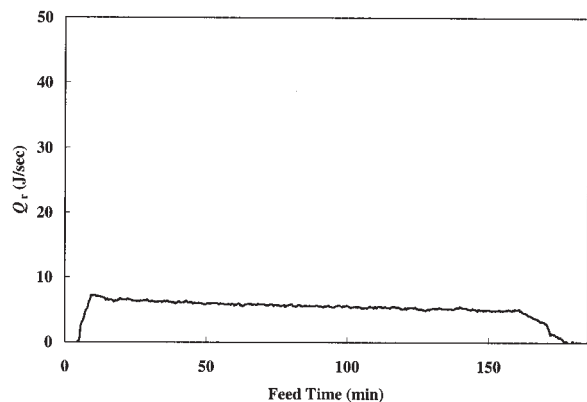
*Monomer-starved conditions* are generally defined as the conditions under which the instantaneous conversion is greater than 90%.<sup>7</sup> Then, from eq. (7), one can obtain the maximum value of  $R_p$  by choosing  $c(t) = 0.90$ . For different  $N_p$  values, different values of  $R_p^{Max}$  were obtained, only at or below which monomer-starved conditions [i.e.,  $c(t) \geq 0.9$ ] could be reached. The actual  $R_m$  selected should be lower than or at least equal to  $R_p^{Max}$  to maintain highly monomer-starved conditions.

#### Evaluation of the model

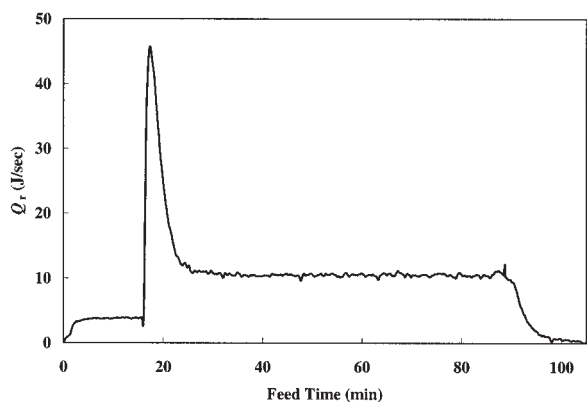
It is of practical interest to confirm the validity of eq. (7). To determine if the reaction was monomer-starved, three different feeding rates from the same general recipe (Table I) for the synthesis of noncarboxylated P(BMA/BA) were evaluated. Three rates were examined: 0.60 mL/min, which was well below  $R_p^{Max}$  and also the actual feed rate used in the synthesis of latex particles of 150 nm in diameter; 1.49 mL/min, which was  $R_p^{Max}$  calculated from eq. (7) according to its  $N_p$ ; and 3.62 mL/min, which was more than two times  $R_p^{Max}$ . The semicontinuous reaction with the feed rate of 0.60 mL/min was run with an agitation speed of 230 rpm. For the semicontinuous reaction with a feeding rate of 1.49 mL/min, the agitation rate was also set as 230 rpm initially. However, after 17 min of the comonomer feeding, a clear monomer layer was observed on the top of the reaction fluid. To achieve a more homogeneous comonomer distribution in the reactor, the agitation rate was increased to 500 rpm.

For the same reason, the semicontinuous reaction with a feed rate of 3.62 mL/min was run with an agitation rate of 500 rpm.

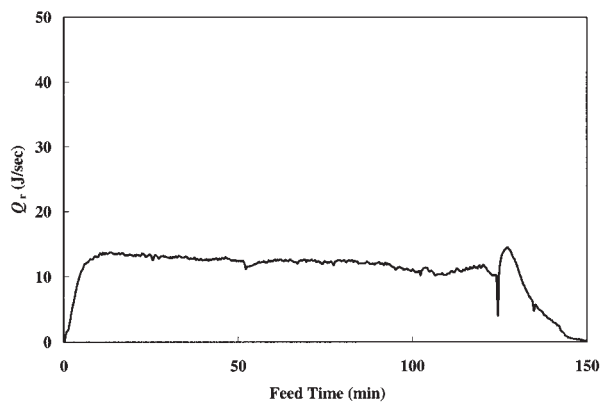
The heat profiles of the three semibatch copolymerization reactions are shown in Figure 3. Figure 4 illus-



(a)



(b)



(c)

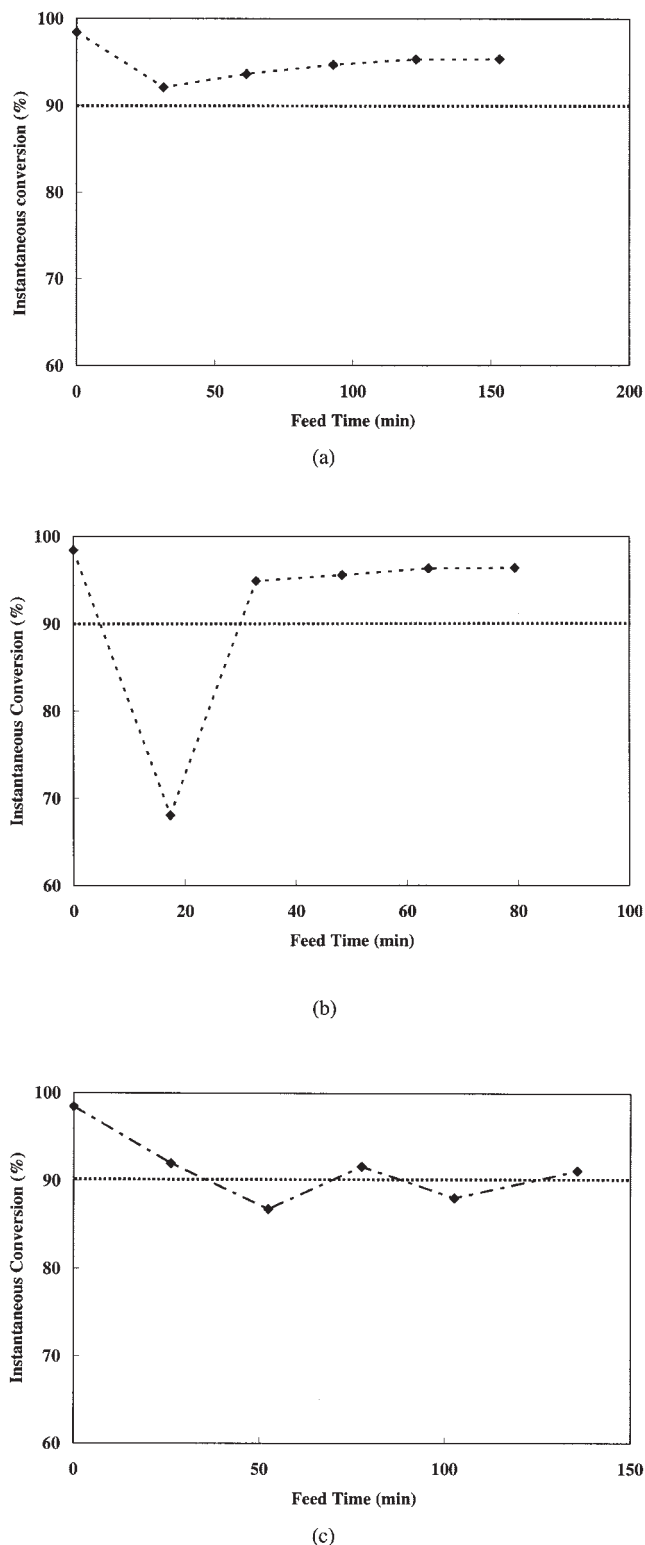
**Figure 3**  $Q_r$  versus reaction time for the semicontinuous emulsion copolymerization of BMA/BA ( $T_r = 80^\circ\text{C}$ ):  $R_m =$  (a) 0.60 mL/min at 230 rpm, (b) 1.49 mL/min at 230 rpm for the first 17 min and 500 rpm for the rest of the reaction, and (c) 3.62 mL/min at 500 rpm;  $T_r =$  reactor temperature.

trates the instantaneous conversions in the three reactions as a function of the feed time. Instantaneous conversion was obtained from gravimetric data of samples taken during the course of the semicontinuous copolymerization. Clearly, the reaction with a feed rate of 0.60 mL/min had an instantaneous conversion higher than 90% all the time during the feed stage [Fig. 3(a)]. As shown Figure 3(b), the instantaneous conversion at 17 min was lower than 90%. This was because of poor mixing in the reaction system at that time, as mentioned previously. After the agitation rate was increased from 230 to 500 rpm, the comonomer was distributed uniformly in the reactor. This led to a faster consumption of the accumulated comonomer by the existing particles, which resulted in a peak in the heat profile of the reaction. Other than that short period of time, the instantaneous conversion was greater than 90% for the reaction. Hence, the reactor was operated in the highly monomer-starved regime at  $R_m$  values of either 0.60 or 1.49 mL/min. However, when the feed rate was increased to 3.62 mL/min [Fig. 3(c)], the reaction somehow deviated, although not very far, from monomer-starved conditions because the instantaneous conversion was lower than 90% at some points in the reaction.

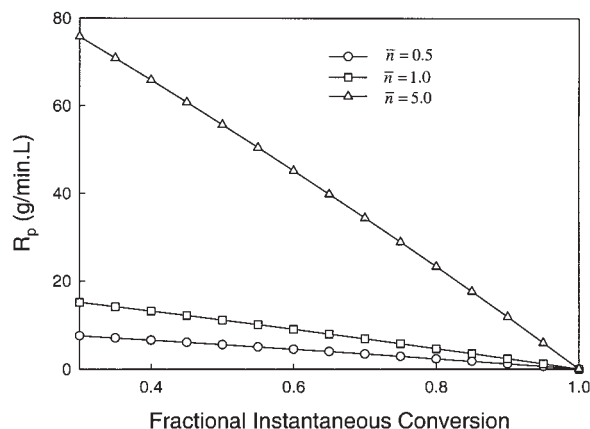
RC1 experimental data indicated that at the feed rate that was chosen for the model latex synthesis, 0.60 mL/min, the reaction was well within the monomer-starved regime. However, some experimental results were not expected from the model. Although the maximum rate calculated from eq. (7) was 1.49 mL/min, the reaction carried out at a feed rate of 3.62 mL/min, which was more than twice as much as the  $R_p^{Max}$  that the model predicted, was still very close to the highly monomer-starved region. This suggests that there might have been some errors in the model when the parameters were chosen.

#### Effects of $\bar{n}$

In the calculation of the model, the value of  $\bar{n}$  was set as 0.5. According to Lovell,<sup>7</sup> in a semibatch process, although  $N_p$  can be kept constant with a sufficiently large seed particle number concentration and through the correct selection of the amount of surfactant present (or added during the addition of monomer), it is unreasonable to expect  $\bar{n}$  to remain constant as the particle volumes increase. Indeed, recent real-time electron spin resonance experimental studies have shown that  $\bar{n}$  increases with conversion and can take on very high values during semicontinuous processes; for some systems, such as methyl methacrylate (MMA), it can be much higher than 100.<sup>17</sup> Figure 5 shows the different reaction rates that were calculated by the selection of different values of  $\bar{n}$  in the model. Therefore, it was necessary to find out the actual value of  $\bar{n}$  from the kinetics study and reevaluate the ratio-



**Figure 4** Instantaneous conversion as a function of feed time for the semibatch emulsion copolymerization of BMA/BA ( $T_r = 80^\circ\text{C}$ ):  $R_m =$  (a) 0.60 mL/min at 230 rpm, (b) 1.49 mL/min at 230 rpm for the first 17 min and 500 rpm for the rest of the reaction, and (c) 3.62 mL/min at 500 rpm.



**Figure 5** Reaction rate versus instantaneous conversion in the synthesis of P(BMA/BA) latex particles, with the effects of  $\bar{n}$  shown.

nality of the choice of 0.5 for the  $\bar{n}$  value. RC1 is a powerful tool in kinetics studies because it can provide  $R_p$  directly from the heat profile of the reaction, compared with other indirect methods of determining reaction rate, such as from conversion (gravimetry method). The continuous heat of reaction ( $Q_r$ ) versus time curves were obtained directly from the RC1 evaluation software, and  $R_p$  was calculated with the following equation:

$$R_p = \frac{Q_r}{V_{\text{H}_2\text{O}}\Delta H} \quad (9)$$

where  $Q_r$  is the heat of the reaction (J/s),  $V_{\text{H}_2\text{O}}$  is the volume of DI water in the recipe (L), and  $\Delta H$  is the heat of polymerization of the monomer (or comonomer; J/mol).

In the estimation of the  $\bar{n}$  value for this copolymerization system, an assumption was made: the heat of copolymerization [ $\Delta H_{\text{copolymerization}}$  (kJ/mol)] was equal to the sum of the heat of homopolymerization [ $\Delta H_{i,\text{homopolymerization}}$  (kJ/mol)] of the monomer times their molar fraction ( $M_i$ ) in the comonomer mixture:

$$\Delta H_{\text{copolymerization}} = \sum_{i=1}^n M_i \Delta H_{i,\text{homopolymerization}} \quad (10)$$

The  $\Delta H$  values of BMA and BA were 57.5 and 78 kJ/mol,<sup>18,19</sup> respectively. The BMA/BA comonomer mixture was fed into the reactor in at a weight ratio of 3:1 (a molar ratio of 73:27); therefore, the heat of copolymerization was calculated as 63.0 kJ/mol from the assumption made previously. Accordingly, the average rate of copolymerization was obtained from the equation with the average  $Q_r$  and the volume of initial DI water in the system known. Then,  $\bar{n}$  value were calculated from eq. (7) for the three different feed rates

**TABLE II**  
Characterization of Noncarboxylated and Carboxylated P(BMA/BA) Latex Particles with a Designed Diameter of 150 nm and with a  $T_g$  of 273 K

		MAA (wt %)			
		0	1	3	6
Particle size	$D_w$ (nm)	156.9	146.8	136.9	162.1
	$D_n$ (nm)	152.5	145.4	134.2	157.0
	PDI	1.03	1.01	1.02	1.03
	$T_g$ (K)	274.2	271.4	273.0	276.9
	pH of latex	2.5	2.3	2.2	2.1

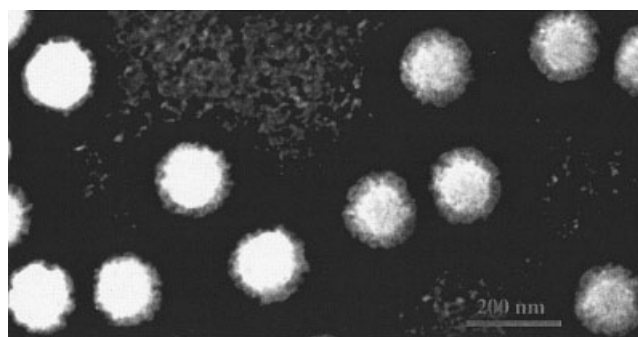
$D_w$  = weight-average diameter,  $D_n$  = number-average diameter; PDI ( $=D_w/D_n$ ) = polydispersity index.

0.60, 1.49, and 3.62 mL/min. The  $\bar{n}$  values were 0.6, 1.3, and 1.4, respectively. The plateau value of  $\bar{n}$  seemed to result from the balance between the increasing initiator flow due to the increasing feeding rate and the increasing termination rate caused by the viscosity decreases due to the holdup of monomer in the latex particles. This simple estimation indicated that it was not rational to set  $\bar{n}$  as 0.5 during the course of semicontinuous polymerization. Doing so introduced errors to the prediction results of the model. In the actual situation,  $\bar{n}$  was as high as 1.3–1.4, which explains why the system was still operating under a monomer-starved regime even at high feed rate of 3.62 mL/min (much higher than the predicted value of 1.49 mL/min).

### Characterization of latex particles

#### Particle sizing

With the feed rates being well-controlled, a homogeneous copolymer composition and monodisperse particle size could be expected and was achieved. The uniformity in particle size, as shown in Table II, reflected a constant particle number, indicating that there was no secondary nucleation or limited aggre-



**Figure 6** TEM micrographs of carboxylated P(BMA/BA) latex particles (with 1 wt % MAA in the comonomer feed; number-average particle diameter ( $D_n$ ) = 145 nm).

gation. Also, this confirmed the validity of the linear feeding scheme of the surfactant.

Figure 6 shows the TEM micrographs of the copolymer latex particles. In the micrograph, the monodispersity of the copolymer latex particles is evident. Under the cold-stage conditions, the latex particle edges were gray compared with the white bulk part of the particles due to precipitation of the staining agent, uranyl acetate, on the latex particles.

### $T_g$ control in the design of the recipe

To keep the  $T_g$  of the resulting copolymer well below room temperature (the designed  $T_g$  of the copolymer was 273 K) for the later room-temperature film-formation study, a calculation was made to determine the composition of the comonomer feed when different amounts of MAA were added into the system.

In this study, the Pochan et al.<sup>20</sup> equation was used to calculate the  $T_g$  of the copolymer:

$$\ln T_g = \sum_{i=1}^3 M_i \ln T_{gi} \quad (11)$$

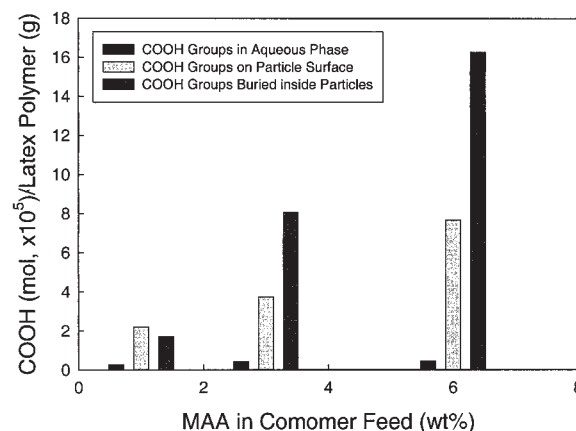
where  $M_i$  is the mass fraction of monomer  $i$  in the comonomer feed and  $T_{gi}$  (K) is the glass-transition temperature of the homopolymer of monomer  $i$ .

From the *Polymer Handbook*,<sup>21</sup> the  $T_g$ 's of BA, BMA, and MAA homopolymers were 219, 295, and 501 K, respectively.

The comonomer ratio (BMA/BA) used during the feed stage was calculated with the Pochan equation when the weight fraction of MAA in the feed mixture was known. From the DSC measurements, only one glass transition was found for all of the synthesized polymers. Table II compares the actual DSC data obtained from the resulting copolymers and the designed  $T_g$ 's. Clearly, the actual  $T_g$  of the polymers was very close to the designed value.

### Distribution of carboxyl groups in the latices

Figure 7 shows the distribution of carboxyl groups in the copolymer latex particles with diameters of 150 nm. As shown by these results, there was a small amount of MAA present in the aqueous phase. However, compared with the number of carboxyl groups that remained on the particle surface and inside the particles, the amount of MAA in the aqueous phase was relatively small, which indicated that the partitioning of MAA was more into the copolymer latex particles. As the concentration of MAA in the comonomer feed increased, the percentage of MAA in the water phase decreased. Also, the absolute amount of carboxyl groups located on the particle surface also



**Figure 7** Distribution of carboxyl groups of the cleaned P(BMA/BA) latex samples, with a designed latex particle size of 150 nm.

increased with increasing MAA concentration in the comonomer feed. More importantly, the surface coverage increased with the increasing amount of MAA in the comonomer feed. On the basis of these observations, it is reasonable to state that the introduction of the MAA monomer as the source of carboxyl functional groups resulted in a uniform distribution of carboxyl groups in the particles. This uniform distribution was considered mainly due to the relatively low water solubility of MAA and the low pH of the latex system.

According to Lovell,<sup>7</sup> the distribution of the acid monomer was primarily influenced by factors such as (1) the partitioning of the monomer between the aqueous and oil phases, (2) the reactivity ratios for copolymerization, (3) the physical state of the particles, and (4) the emulsion polymerization process used. Among all the factors, partitioning played a major role. In view of this, polymerizations were normally run with the aqueous phase at pH < 4 [the pH of the P(BMA/BA) latex was around 2–3; Table II] so that the comonomer was present in its acid form, which thereby shifted the partitioning equilibrium toward higher concentrations of acid comonomer in the latex particles and reduced the probability of homopolymerization of the acid comonomer in the aqueous phase.

### Final conversion of the synthesis

According to the experimental procedure for the copolymer synthesis, a 2-h “cookout” time is always necessary for each single copolymerization to ensure the comonomer mixture was nearly fully converted to copolymer. All of the final conversion values of the copolymerization reactions were between 98 and 100%.



## CONCLUSIONS

A modified theoretical model was developed to predict the maximum reaction rate under which monomer-starved reaction conditions could be achieved in a semicontinuous emulsion polymerization. The experimental data showed that the synthesis of the mono-dispersed noncarboxylated and carboxylated P(BMA/BA) latices were operated in a highly monomer-starved regime. Estimation of  $\bar{n}$  during the feed stage revealed that  $\bar{n}$  was as high as 1.4 in the actual polymerization. This indicated that the setting of the  $\bar{n}$  value as 0.5 originally in the model was not accurate.

Model latices were characterized in terms of particle size,  $T_g$ , and functional group distribution. TEM and CHDF results confirm the uniformity in the latex particle size. Conductimetric titration experiments disclosed the uniform distribution of functional groups in the latex particles.  $T_g$  measurements verified the designed  $T_g$ . The fact that only one  $T_g$  was observed indicated a homogeneous copolymer composition.

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