

# Strategies for the Production of High Solids Acrylic/Methacrylic Core-Shell Latices

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**ABSTRACT:** Well-defined poly(butyl acrylate)/poly(methyl methacrylate) (PBA/PMMA) core shell particles with a moderately high solid content (49%) and particle diameters of less than 200 nm were prepared via seeded emulsion polymerization with a redox initiator and an anionic surfactant. Low-viscosity (less than 150 cps at 20 s<sup>-1</sup>) latex products were obtained by controlling the particle size distribution to within

certain limits. Polymerization conversion and kinetics were followed gravimetrically and were adjusted so as to obtain recipes that could be scaled-up for industrial production. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2668–2676, 2010

**Key words:** core-shell latex; emulsion polymerization; high solid content; latex stability; production

## INTRODUCTION

Poly(butyl acrylate)/poly(methyl methacrylate) (PBA/PMMA) core shell latexes are widely used in various industrial applications as impact modifiers as well as for applications requiring improved properties such as water resistance, weather resistance, spoil resistance, radiation resistance, tensile strength, impact strength, and adhesive strength with respect to random copolymers. Property enhancement is primarily caused by the morphology of the particles. In core shell particles, one often has grafting or interpenetration of the core and shell polymers of the structured latex that make its response to external stimuli different from that of random copolymers.<sup>1,2</sup> For instance, it has been shown experimentally that with the addition of a certain amount of core-shell particles to a PVC homopolymer increases the impact strength of the resulting product by a factor of 5 with respect to that of the untoughened PVC.<sup>3</sup>

In the specific case of impact modifiers, the core needs to be made of a highly elastic material such as poly(butyl acrylate) (PBA) or poly(butyl acrylate-butadiene) (pBA-BD) to provide resistance to shock, whereas a fine PMMA shell enhances the compatibility with the matrix (eg, polyvinyl chloride [PVC]) and the toughness of the material.<sup>4,5</sup> The dynamic mechanical property improvements of an impact modifier directly depend on the properties of the

rubbery core (eg, its MWD and degree of cross linking), the thickness of the PMMA shell (as thin as practical) and particle size distribution of the latex (as well-defined as possible, and preferably no bigger than 200 nm). The shell thickness of a core shell impact modifier is found to be the single most important factor in the toughening of rigid PVC.<sup>6</sup> If the shell is too thick, a hard core (high modulus) of these core/shell particles results, and the rubbery nature required for an impact modifier is lost.<sup>6</sup> On the other hand, when the shell is too thin, the shell layer is simply unable to fully protect and cover the inner rubbery core during vigorous processing conditions.<sup>6</sup> On the basis of these facts and considering the final particle size, the volume of the PMMA shell made in our process was chosen to be 10% of that of the PBA core particles.

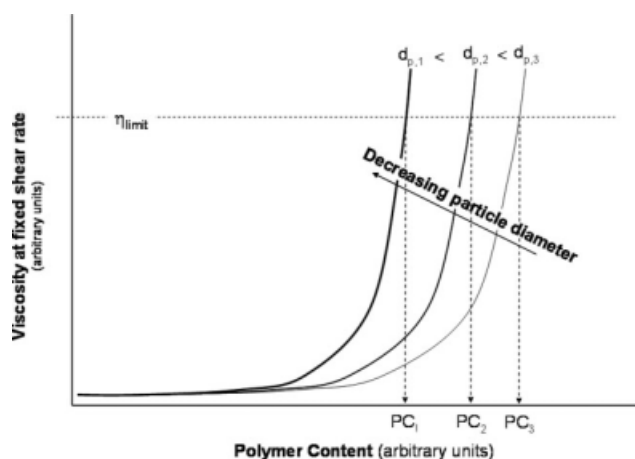
From the point of view of efficient production, increasing the solid content of a commercial product while maintaining reaction rates and the major polymer properties has obvious economic advantages. However, this must be done while maintaining a low macroscopic viscosity to ensure ease of handling and application.

Different experimental procedures have been described in the literature to synthesize latexes with high solid content. In many occasions high solid content latexes have been made by creating a bimodal particle size distribution<sup>7,8</sup> and/or by using larger average particle sizes.<sup>1,8–12</sup> However, in the specific case of an impact modifying core-shell polymer neither of these options is permissible since one needs a latex with small, well-defined particles in order to obtain acceptable impact properties, so one

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needs to work with monomodal systems. In addition there will be an upper limit of operability and on product quality set by the viscosity. This is illustrated in Figure 1. If one wishes to produce a latex with a fixed viscosity,  $\eta_{\text{limit}}$  then for a fixed concentration of surfactant and other ionic species, a higher volume fraction of polymer (Polymer Content; PC) can be obtained for larger particles. In other words, a latex with an average size of  $d_{p,3}$  can have the same viscosity as a latex with an average size  $d_{p,1}$  but more polymer per unit volume of latex.

At low solids (e.g.,  $PC \ll PC_1$ ), the particles have relatively weak interactions, so the viscosity remains low regardless of the size of the particles. As the PC increases  $\eta$  increases slowly at first, then more and more rapidly as one approaches its maximum value (ie, where the particles begin to touch). As PC approaches its limiting value,  $\eta$  increases extremely quickly because the particles interact more. The influence of particle size on the viscosity comes from the fact the polymer particles must be stabilized, usually by a surfactant (or combination of surfactants) but occasionally by the negative charges coming from an initiator like a persulfate. In Figure 1 it was assumed that the three lattices were stabilized in an identical manner. In this case the thickness of the stabilizing layer (eg, electronic double layer for an ionic surfactant) will be the same in all three cases. Thus, the volume fraction occupied by this layer will be relatively greater for smaller particles. This means that small particles (in this sense the particles plus the stabilization layer) will come into contact with each other at much lower solid contents than will larger ones. As the viscosity will be higher when neighboring particles interact, one will therefore start to see an increase in the macroscopic viscosity of a latex at lower solid contents for smaller particles. This has been discussed in a number of



**Figure 1** Dependence of viscosity of a latex upon its solid content for a monomodal product of different particle sizes (with identical stabilization conditions).

articles, and the reader is referred to Refs. <sup>12</sup> and <sup>13</sup> for a more detailed discussion.

Different attempts have been made to synthesize controlled particle size and/or high solid core shell particles.<sup>1,4,5,8,11</sup> However, in each attempt, either low particle size (<100 nm) or high solid content (>40%) has been achieved (not both). For example, Landier et al.<sup>4</sup> have achieved core shell particles of 79 nm and 38% solid. Yao and coworkers<sup>5</sup> generated core shell particles of 400–500 nm. High solid content (60 wt %) core shell particles of ~ 260 nm have been achieved by Gou et al.<sup>1</sup> High solid content (70 wt %) core shell particles with a bimodal size distribution (589 and 80 nm) have been achieved by Ai et al.<sup>8</sup> Anionic surfactants have been used to develop monodisperse low particle size core-shell particles<sup>14–17</sup> but at low solid contents. Aguiar et al.<sup>11</sup> have achieved 40% solid and 30-nm core shell particles by microemulsion polymerization obviously with high emulsifier concentration than will be acceptable for a commodity product such as impact modifiers.

The application in which we are interested in this report requires that we generate small, monodispersed latex core-shell particles of PBA/PMMA (<200 nm) at a solid content that is as high as possible. In other words, we tried to achieve both high solid and low particle diameter monodisperse core shell particles. The solid content needed to be at least 45% (v/v) but with a viscosity less than 150 cps at a shear of 20 s<sup>-1</sup>. This means that we need to study the influence of the stabilization system (here sodium dodecyl benzene sulfonate [SDBS] for different quality-related reasons) in the particle generation process.

If one considers the aforementioned discussion, this means that we will attempt to develop a process with an average particle size of 150–200 nm and will use different concentrations of buffers and anionic surfactants to adjust the thickness of the stabilization layer around the particles to respect both the solid content/viscosity constraint on the one hand, and the need for stability on the other.

The most important parameter in determining the particle size of an emulsion copolymerization of this type is the concentration of anionic surfactant. A low content (0.2 wt %) of SDBS has been used by Yuan et al.<sup>17</sup> in the synthesis of monodispersed hollow polymer particles of MMA-BA-MAA in the size range of 500–600 nm and the CMC of SDBS as reported by them is  $\sim 22.8 \times 10^{-4}$  mol/L. As the required particle size is in between 150 and 200 nm in our process, 0.55 wt % of SDBS was used in the optimum conditions.

As our target total solid content was more than 45%, a seeded semi-batch emulsion polymerization was used here. Schneider et al.<sup>13</sup> showed that the formation of fine particles in a bimodal latex was

detrimental to the observed viscosity. Because our target is a monomodal latex, and we need to control the viscosity, it is important to avoid the production of a population of fine particles. Therefore, to inhibit the formation of new particles during seed polymerization,<sup>18</sup> an oil soluble redox initiator was used.

## EXPERIMENTAL

### Materials

Butyl acrylate (BA99+% from ACROS, Illkirch Cedex, France) and methyl methacrylate (MMA 99+% from ACROS) were used as received. The sodium salt of dodecyl benzene sulfonic acid (SDBS 80% from FLUKA) was used as the anionic surfactant and the amount of SDBS mentioned in the recipes always refers to total surfactant weight (active matter + additional water). The redox initiator was tertiary butyl hydrogen peroxide (TBHP diluted at 70% in water from JANSSEN) coupled with iron (II) sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ; from Sigma-Aldrich; Lyon, France), sodium formaldehyde sulfoxylate (SFS from Sigma-Aldrich) and disodium ethylene diamine tetra acetic acid (EDTA from Sigma-Aldrich). Disodium hydrogen phosphate ( $\text{Na}_2\text{HPO}_4$  from Sigma-Aldrich) was used as a buffer to control the thickness of the electronic double layer around the particles. Deionized water was used throughout the work.

### Emulsion preparation and polymerization

One series of polymerizations was conducted in a 200-mL jacketed glass reactor connected to a heated

water bath for temperature control. A second series was performed in a 1000-mL jacketed glass reactor. Each reactor was equipped with an anchor stirrer, a reflux condenser, nitrogen inlet and outlet, and a valve on the bottom to remove the latex. The major stages of the experimental procedure were as follows:

1. Batch process to form an initial, well-defined seed of pBA particles that are the core.
2. Semicontinuous feed of BA to increase solid concentration.
3. Second semicontinuous feed of MMA to create shell.

A summary of the different runs (all batch) performed in the 200-mL reactor is provided in Table I. The purpose of these runs was to form an initial, well-defined seed of PBA.

The procedure was as follows: SDBS, SFS, and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  were dissolved in water at 50°C. BA was added to the aqueous phase while stirring. The organic phase and aqueous phase were stirred further for 30 min. The reaction mixture was purged with nitrogen for 30 min. The reaction was initiated by adding an aqueous solution of TBHP continuously and the reaction temperature was 50°C. Samples were occasionally withdrawn for analysis. Other variants of these semi-batch recipes were used throughout the course of this work, and in order to facilitate the discussion they will be presented at the pertinent spot during the discussion of results. In each case the recipe will be the same with one or two variations as described in the text.

TABLE I  
Experimental Runs of Batch Process<sup>a</sup>

Run	Mass H <sub>2</sub> O (g)	Mass BA (g)	Mass SDBS (g)	Mass SFS (g)	Mass FeSO <sub>4</sub> ·7H <sub>2</sub> O (g)	Mass TBHP (g)	Mass EDTA (g)	Mass Na <sub>2</sub> HPO <sub>4</sub> (g)
1	90	40	0.125	0.080	0.050	0.004	—	—
2	90	40	0.425	0.080	0.050	0.004	—	—
3	130	80	3.250	0.130	0.080	0.004	—	—
4	140	80	3.250	0.260	0.160	0.008	0.518	—
5	140	80	3.250	0.260	0.160	0.100	0.518	—
6	140	85	3.250	0.260	0.160	0.100	0.518	—
7	140	85	2.250	0.260	0.160	0.100	0.518	—
8	140	85	1.750	0.260	0.160	0.100	0.518	—
9	140	85	1.000	0.260	0.160	0.100	0.518	—
10	140	85	1.000	0.260	0.160	0.100	0.518	3.300
11	140	85	1.000	0.260	0.160	0.100	0.518	1.000
12	140	85	1.000	0.260	0.160	0.100	0.518	0.500
13	140	85	1.500	0.260	0.160	0.100	0.518	1.000
14	140	85	1.500	0.260	0.160	0.100	0.518	0.750
15	140	85	1.500	0.260	0.160	0.100	0.518	0.250
16	140	85	1.500	0.180	0.080	0.100	0.250	0.250

<sup>a</sup> The given amount of TBHP was mixed with 10 mL of water in the runs 1–3 and with 20 mL of water in the rest of runs; the flow rate of TBHP was 3 mL/h; stirring rate 230 rpm.

**TABLE II**  
Monomer Conversion (%) of Final Latexes  
of the Runs 1–6

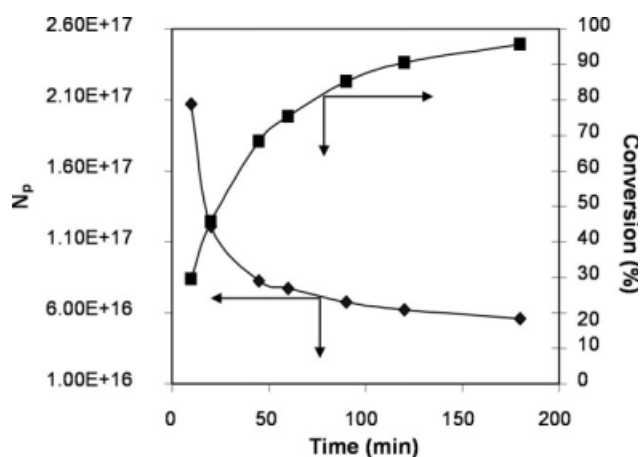
Run	% Conversion of monomer
1	70
2	80
3	95
4	94
5	95
6	100

Conversions were measured by gravimetry. Dynamic light scattering was used to measure the particle size. Average particle sizes ( $D_p$ ) were measured by particle size analyzer (ZETASIZER 1000HS<sub>A</sub>). Average particle sizes reported here are the averages of 10 measurements per sample. Full particle size distributions were measured with a COULTER LS 230. Transition electronic microscopy (TEM; PHILIPS-CM 120) was operated at 80 kV to obtain the TEM images of latex. The viscosity was measured by Rheometric Scientific Viscometer (RFSIII) at 25°C. pH was measured by LPH 330T pH meter.

## RESULTS AND DISCUSSION

### pBA seed optimization

A simple calculation can be used to show that if we wish to attain at least 45% solid content, it is necessary to start with a seed of particles having an average diameter of around 100 nm. In the recipes shown in Table I, we chose to run a batch reaction with approximately 30–40% solids (solid contents much higher than this are difficult to initiate in a controlled manner<sup>19</sup>). However, it appeared to be



**Figure 2** The evolution of the number of polymer particles and overall conversion during the seed generation phase with time.

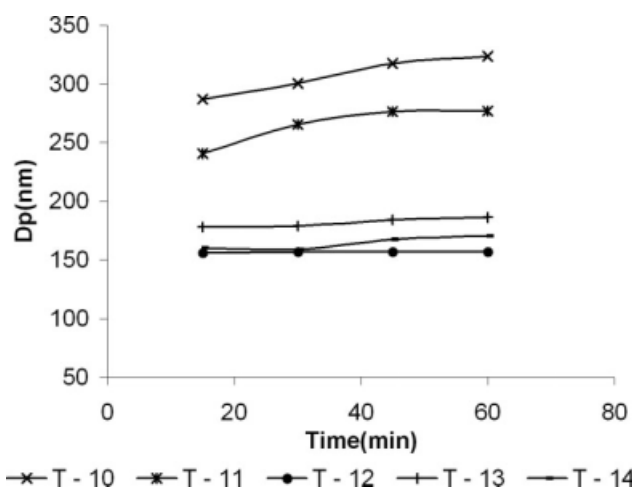
**TABLE III**  
Particle Size of Final Latexes of the Runs 7–15

Run	7	8	9	10	11	12	13	14	15
$D_p$ (nm)	77	80	85	325	275	160	180	175	125

very difficult to attain the high levels of conversion of BA required to make a core-shell latex with a well-defined morphology (generally the core conversion should be well above 90%, and preferably above 95%) even after three hours of reaction. Table II summarizes the monomer conversion of final latexes of runs 1–6.

As shown in Figure 2 the number of particles per liter of emulsion,  $N_p$  of the Run 3 drops sharply after the beginning of the reaction. This indicates that the particles were under-stabilized. To overcome this problem, different strategies were tested: increasing the surfactant concentration, introducing EDTA to the recipe and increasing the concentration of TBHP, staged feed of a concentrated solution of the redox components was added at intervals of one hour from the beginning of the reaction. We will briefly discuss the implications of each below.

The objective of increasing the quantity of surfactant was to increase the number of polymer particles stabilized at the end of the reaction and hence increase the rate of polymerization. By adding 26 times more surfactant compared with the first run, the percentage coverage of particles by surfactant could be increased from 9 to approximately 40% by the third run. Although  $N_p$  could be increased to



**Figure 3** The increase of particle size with the introduction of buffer; T-10 to T-14 refer to the experiments performed under the Runs 10–14; the amount of buffer for the Runs 10–14 was 3.30, 1.00, 0.50, 1.00, and 0.75 g, respectively; the amount of surfactant for the Runs 10–12 was 1.00 g and for the Runs 13–14 was 1.50 g.

TABLE IV  
Analysis of Experimental Results of the Batch Experiment Run 16

Time (min)	$D_p$ (nm)	$N_p$ (L)	TSC% (theoretical)	TSC% (actual)	% Conversion of monomer	% Coverage of $N_p$ by surfactant
15	95.9	1.60E+17	42.1	38.8	92	22.4
30	98.2	1.58E+17	42.1	40.8	97	21.6
45	101	1.46E+17	42.1	41.1	97.6	22.1
60	102	1.47E+17	41.5	41.2	99	21.9
120	102	1.47E+17	41.0	41.0	100	21.7

$10^{17} \text{ L}^{-1}$  from  $10^{16} \text{ L}^{-1}$  by adding additional surfactant, the maximum monomer conversion achieved was 95%.

Adding EDTA to the initiator system helped increase the stability of  $\text{Fe}^{2+}$  ions through the formation of EDTA- $\text{Fe}^{2+}$  complex, thereby avoiding the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ . However, despite multiplying the concentration to TBHP by as much as a factor of 5, complete conversion of monomer was still not reached. This indicates that the efficiency of the redox reaction does not depend only on the quantity of TBHP and the presence of EDTA. Chen et al.<sup>20</sup> showed that the decomposition rate of a hydrophobic oxidant is proportional to the  $\text{Fe}^{2+}$  concentration and the SFS concentration decreases logarithmically with increasing  $\text{Fe}^{3+}$  concentration during the redox reaction. Therefore the concentration of SFS,  $\text{FeSO}_4$ , and EDTA all directly influence the efficiency of the redox reaction. By separately preparing the redox mixture of SFS,  $\text{FeSO}_4$ , and EDTA and adding as a concentrated solution, the efficiency of the redox reaction could be increased and hence complete monomer conversion was obtained after the first hour of the reaction. The relevant recipe is depicted in Table I under run 6.

### pBA seed concentration

Once a recipe suitable for producing seed latex with the desired criteria has been identified, the main focus was to increase the total solid content of the latex while respecting the constraints on particle size. Different procedures such as increasing the monomer quantity, lowering the surfactant concentration and addition of a buffer were tested in the successive runs to increase the particle size and total solid content of the latex as rapidly as possible. Table III summarizes the particle size ( $D_p$ ) of final latexes of the Runs 7–15.

Increasing the concentration of surfactant did not help to significantly increase monomer conversion. We therefore lowered the amount of SDBS from 3.25 g to 1.00 g, which was enough to maintain the percentage coverage of latex by surfactant at  $\sim 25\%$ . Although keeping the surfactant concentration at a minimum level helps to avoid the undesirable effects caused by excess surfactant, the expected increase of particle size could not be achieved, ie, the particle size could not be increased to 100 nm. We therefore introduced disodium hydrogen phosphate as a buffer to control the thickness of the electronic double layer and hence increase the particle size.

TABLE V  
Optimization of Seed, SDBS, and BA Amounts<sup>a</sup>

	Run 17	Run 18	Run 19	Run 20	Run 21
Batch seed creation					
Water (g)	140	140	140	140	140
BA (Seed; g)	65	24	26	30	30
SDBS (g)	1.50	1.50	1.50	1.60	1.70
SFS (g)	0.13	0.13	0.13	0.13	0.13
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (g)	0.08	0.08	0.08	0.08	0.08
EDTA (g)	0.25	0.25	0.25	0.26	0.27
TBHP (g)	0.10	0.10	0.10	0.10	0.10
$\text{Na}_2\text{HPO}_4$ (g)	0.25	0.25	0.25	0.26	0.26
Duration (minutes)	30	30	30	30	30
Semicontinuous particle growth and concentration					
BA (feed; g)	32	73	77	80	90
Feed flow (mL/min)	12	27.80	29	30	33.30
Feed duration (min)	150	150	150	180	180
Catalyst mop up (min)	30	30	30	30	30

<sup>a</sup> The given amount of TBHP was mixed with 20 mL of water and the flow rate of TBHP was 3 mL/h; The given amount of SFS,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and EDTA were dissolved in 5 mL of water and added at the beginning of reaction; stirring rate 240 rpm.

**TABLE VI**  
Experimental Results of Runs 17–21

Run	%TSC	$D_p$ (nm)	Viscosity (cps at 20 s <sup>-1</sup> )
17	43.5	85	90
18	43.3	84	90
19	44.6	88	100
20	46	105	102.5
21	48	112	950

Introducing a buffer increases the ionic strength of the medium and hence lowers the amount of repulsion between polymer particles. The dependence of thickness of electronic double layer on ionic strength of the medium can be illustrated by Eq. (1).

$$\delta_E = \sqrt{\frac{\epsilon k_B T}{8\pi e^2 N_A I}} \quad (1)$$

Where  $\delta_E$  is the thickness of the electronic double layer,  $\epsilon$  the permittivity of the continuous medium (water),  $k_B$  the Boltzman constant,  $T$  the absolute temperature,  $e$  the charge of a single electron,  $N_A$  is Avogadro's number, and  $I$  is the ionic strength.

It should be clear that the amount of buffer one can use will be a trade off between increasing the solid content by compressing the electronic double layer, yet maintaining an adequate level of stability. If the double layer is compressed by adding buffer, then we will experience agglomeration of polymer particles and the particle size increases. This could be a positive effect in the sense that it would be an extra parameter in addition to the feed rate of monomer to control growth and solid content independently (to within reason). Nevertheless care must be

taken since an overly rapid increase of particle size this way could lead to the formation of undesirable coagulum.

Figure 3 and Table III show that the particle size increased rapidly with the introduction of buffer. This is most likely to due a loss of stability because of the compression of the double layer around the particles. This is corroborated by the fact that a so much coagulum formed during the first 60 min of the reaction that it was not possible to proceed with the reaction beyond this point. The relevant experimental recipes are described in Table I.

By regularly reducing the concentration of buffer a balance between the buffer and surfactant could be achieved so that uncontrolled coagulation could be avoided. The pH of latex synthesized under optimum conditions was about 7. The experimental results of the final successful run performed under batch process are illustrated in Table IV, and the relevant recipe is described in Table I under Run 16. It should be noted that the concentration of each of SFS, FeSO<sub>4</sub>, and EDTA was lowered in Run 16 by 50% compared with Run 15 to control the rate of polymerization. The solid content achieved under the batch process was 41% and semicontinuous feed of BA was used to increase the solid concentration further according to our strategy. The seed in these runs is based on Run 16. The recipes used in the semicontinuous feed of BA are summarized in Table V. The experimental results of these runs are summarized in Table VI. It should be noted that a sharp increase of viscosity could be observed when the total solid content was 48%.

The objective of the next series of runs was to increase the particle size by increasing the buffer

**TABLE VII**  
Experimental Runs<sup>a</sup> Performed to Increase the Particle Size by Optimization of Na<sub>2</sub>HPO<sub>4</sub>

	Run 22	Run 23	Run 24	Run 25
Batch seed creation				
Water (g)	140	140	140	140
BA (Seed; g)	27.50	27.50	27.50	27.50
SDBS (g)	1.60	1.60	1.60	1.60
SFS (g)	0.13	0.13	0.13	0.13
FeSO <sub>4</sub> ·7H <sub>2</sub> O (g)	0.08	0.08	0.08	0.08
EDTA (g)	0.26	0.26	0.26	0.26
TBHP (g)	0.10	0.10	0.10	0.10
Na <sub>2</sub> HPO <sub>4</sub> (g)	0.40	0.80	1.00	1.40
Duration (minutes)	30	30	30	30
Semicontinuous particle growth and concentration				
BA (feed; g)	82.50	82.50	82.50	82.50
Feed flow (mL/min)	30.50	30.50	30.50	30.50
Feed duration (min)	180	180	180	180
Catalyst mop up (min)	30	30	30	30

<sup>a</sup> The given amount of TBHP was mixed with 20 mL of water and the flow rate of TBHP was 3 mL/h; The given amount of SFS, FeSO<sub>4</sub>·7H<sub>2</sub>O and EDTA were dissolved in 5 mL of water and added at the beginning of reaction; stirring rate 240 rpm.

**TABLE VIII**  
Experimental Results of the Runs 22–25

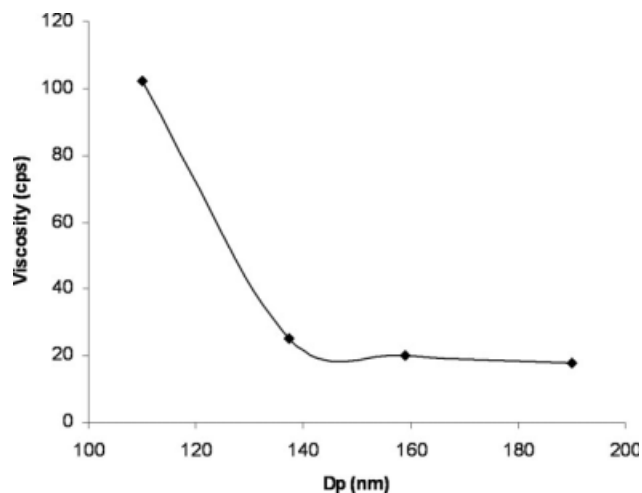
Run	%TSC	$D_p$ (nm)	Viscosity (cps at $20 \text{ s}^{-1}$ )
22	46.8	110	102
23	46.4	137	25
24	46.3	159	20
25	46.3	190	18

quantity and thereby decrease viscosity. The recipes used are summarized in Table VII. The particle size could be increased by increasing the buffer quantity. It appears that no limited or controlled flocculation of the particles occurred even though the quantity of buffer was regularly increased because only 25% of monomer was charged as the seed. The experimental results of these runs are summarized in Table VIII and the variation of viscosity with particle size of the Runs 22–25 is graphically illustrated in Figure 4.

By increasing the particle size by  $\sim 80$  nm, viscosity could be lowered by about 84 cps for the similar solid content of 46%. The increase of particle size also increases the stability of latex due to the increasing percentage coverage of latex with increased particle size.

### PMMA shell production

According to our strategy, the synthesis of PMMA shell around PBA core was the next step. The rec-



**Figure 4** Variation of viscosity with particle size for the Runs 22–25. In all these runs, the total solid content was kept at approximately the same value (46%) but particle size of final latexes were different. Therefore the curve illustrates the dependence of viscosity on particle size independent of the solid content. The shear rate for the viscosity measurements was  $20 \text{ s}^{-1}$ .

ipes used in the incorporation of MMA are summarized in Table IX. Because we used the 1000-mL reactor for these experiments, the recipes used in 200-mL reactor were directly scaled up by a factor of 5. The quantities of seed were adjusted to reflect the conditions of Run 25. MMA was fed at the end of

**TABLE IX**  
Experimental Runs of Semicontinuous Feed of MMA<sup>a</sup>

	Run 26	Run 27	Run 28	Run 29
Batch seed creation				
Water (g)	282	282	282	282
BA (Seed; g)	56	56	56	56
SDBS (g)	3.26	3.26	3.26	3.26
SFS (g)	0.12 <sup>i</sup> & 0.14 <sup>ii</sup>	0.12 <sup>i</sup> & 0.14 <sup>ii</sup>	0.12 <sup>i</sup> & 0.14 <sup>ii</sup>	0.12 <sup>i</sup> & 0.14 <sup>ii</sup>
FeSO <sub>4</sub> ·7H <sub>2</sub> O (g)	0.05 <sup>i</sup> & 0.05 <sup>ii</sup>	0.05 <sup>i</sup> & 0.05 <sup>ii</sup>	0.05 <sup>i</sup> & 0.05 <sup>ii</sup>	0.05 <sup>i</sup> & 0.05 <sup>ii</sup>
EDTA (g)	0.25 <sup>i</sup> & 0.30 <sup>ii</sup>	0.25 <sup>i</sup> & 0.30 <sup>ii</sup>	0.25 <sup>i</sup> & 0.30 <sup>ii</sup>	0.26 <sup>i</sup> & 0.30 <sup>ii</sup>
TBHP (g)	0.20	0.20	0.20	0.20
Na <sub>2</sub> HPO <sub>4</sub> (g)	2.85	2.60	2.25	2.25
Duration (minutes)	30	30	30	30
Semicontinuous particle growth and concentration				
BA (feed; g)	168	168	168	168
Feed flow (mL/min)	85	85	85	85
Feed duration (min)	150	150	150	150
MMA (feed; g)	22.4	22.4	22.4	22.4
Feed flow (mL/min)	43	43	43	43
Feed duration (min)	30	30	30	30
Catalyst mop up (min)	30	30	30	30

<sup>a</sup> The given amount of TBHP was mixed with 40 mL of water and the flow rate of TBHP was 6 mL/h; the initial amounts (indicated by "i") of SFS, FeSO<sub>4</sub>·7H<sub>2</sub>O and EDTA were dissolved in 8 mL of water, and the second quantity of these same components (indicated by "ii") were dissolved in 5 mL of water; the first solution of redox components was added at the beginning of reaction and the second solution was added at 1.5 h from the beginning of reaction; stirring rate 240 rpm.

TABLE X  
Experimental Results of the Runs 26–29

Run	%TSC	$D_p$ (nm)	Viscosity (cps at $20 \text{ s}^{-1}$ )
26	48.6	231	27.5
27	48.2	229	26.3
28	48.4	193	29.7
29	48.7	195	28

BA feed and the flow rate of MMA was half of the BA flow rate. The experimental results of these runs are summarized in Table X. The increase of particle size and narrow particle size distribution (Fig. 5 shows that the volume and number average distributions are very similar) of these latexes suggest that no secondary nucleation occurred during the MMA feed under the flow rate used and PMMA acts as a shell to PBA core. The increase of particle size with the incorporation of MMA could be lowered to 200 nm by lowering the buffer quantity from 2.85 to 2.25 g. The core-shell morphology of the final latex was verified by TEM as shown in Figure 6.

The aim of preparation of two different concentrated redox components was to control the rate of polymerization ( $R_p$ ) and hence control the heat generation. By adding the diluted redox mixture at the beginning of reaction,  $R_p$  could be controlled during the first 1.5 h of the reaction and by adding the concentrated redox mixture secondly the complete conversion of monomers could be achieved at the end of reaction. Figure 7 illustrates the control of mono-

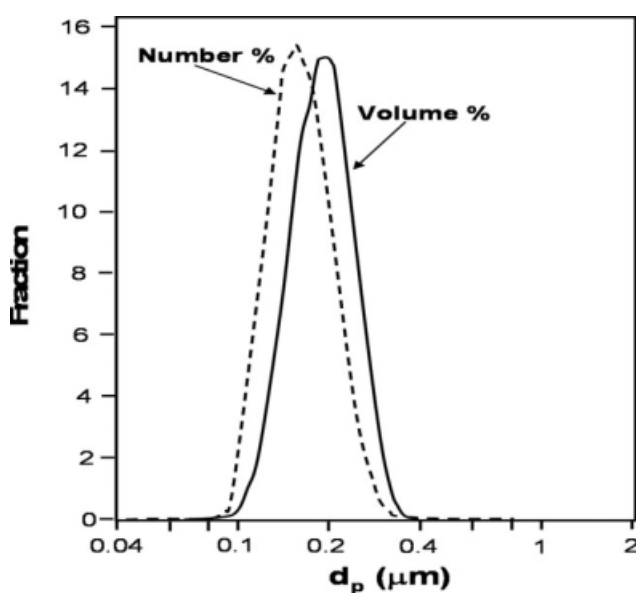


Figure 5 Particle size distribution by volume and number for the run 29 and the similar distribution could be observed for all the latexes synthesized under optimum conditions.

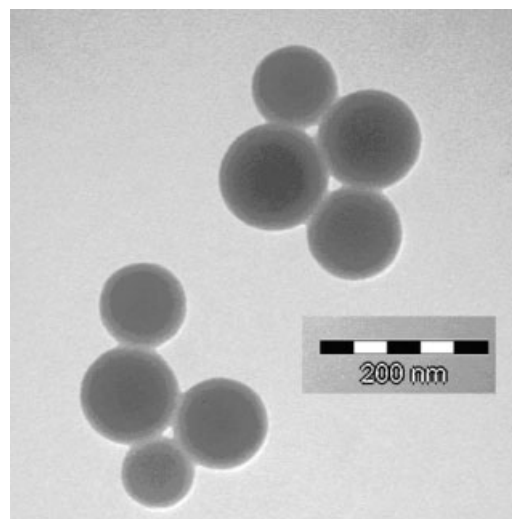


Figure 6 TEM image of core-shell latex of the Run 29.

mer conversion during the semi-batch feed step by this way.

The TEM image clearly shows that the particles do not form a film, but rather maintain a spherical morphology at room temperature. Given that the glass transition temperature of the PBA core is  $-52^\circ\text{C}$ , this means that there is a well defined PMMA shell around the particles.

## CONCLUSION

Well-defined PBA/PMMA core shell latexes could be synthesized via seeded emulsion polymerization using a redox initiator and an anionic surfactant. The quality parameters of the final latex were: total solid content 49%; viscosity 26.3–29.7 cps at a shear rate of  $20 \text{ s}^{-1}$ ; particle size  $\sim 200 \text{ nm}$ .

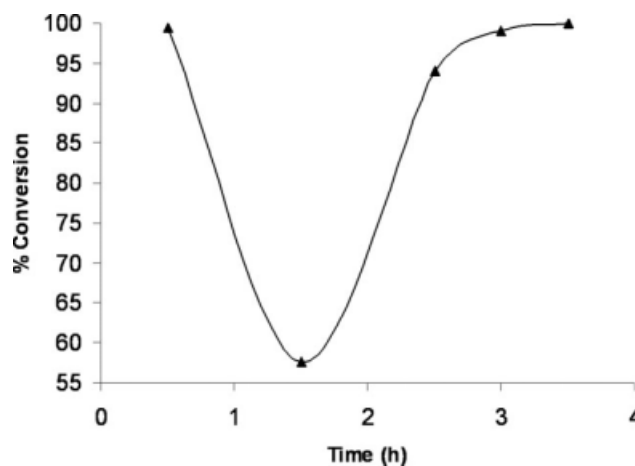


Figure 7 Variation of instantaneous monomer conversion with time for the Run 29; the diluted redox mixture was added at the beginning of reaction and the concentrated redox mixture was added at 1.5 h. The rate of polymerization was controlled by controlling the redox flux.



The sharp increase of viscosity of the latex with increasing solid content could be controlled by controlling the particle size with the introduction of a buffer. As the ionic strength of the medium was increased in the presence of buffer, the repulsions between polymer particles were lowered, particle size increased and the electronic double layer was compressed. As a result the interactions between particles were lowered and hence high solid content with low viscosity could be achieved while maintaining the narrow particle size distribution.

Finally, the rate of polymerization was controlled considering the large scale industrial application by controlling the initiator radical concentration. By adding the diluted redox mixture at the beginning of reaction, rate of polymerization could be controlled during the initial stages of the reaction and with the addition of strong redox mixture the complete monomer conversion could be achieved at the end of reaction.

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