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### In-Situ Synthesis of PBA-*graft*-PMMA Copolymers to Be Used as Compatibilizing Agents in PBA/PMMA Composite Latex Particles via the Macromonomer Method

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## **IN-SITU SYNTHESIS OF PBA-*graft*-PMMA COPOLYMERS TO BE USED AS COMPATIBILIZING AGENTS IN PBA/PMMA COMPOSITE LATEX PARTICLES VIA THE MACROMONOMER METHOD**

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### **ABSTRACT**

The concept of using block or graft copolymers as compatibilizing agents for immiscible polymer phases was applied to the preparation of composite latex particles with a controlled core/shell morphology. Graft copolymers of poly(*n*-butyl acrylate) (PBA) and poly(methyl methacrylate) (PMMA) were prepared in-situ during the PBA seed particles synthesis via miniemulsion polymerization of *n*-butyl acrylate (*n*-BA) in the presence of different PMMA macromonomers. The copolymers are to be used as compatibilizing agents to improve the coverage between phases in PBA/PMMA core/shell-type composite latex particles. By

varying the amount and the molecular weight of the macromonomer, the macromonomer method allows control over the structure of the graft copolymers. Changes in particle size averages and size distributions, effective surface area of surfactant coverage on the particle surface, and oil/water phase interfacial tensions were measured as a function of the ratio between added macromonomer and *n*-BA. Copolymer latexes of *n*-BA and methyl methacrylate (MMA) monomers, synthesized under similar conditions, were compared with PBA particles prepared in the presence of PMMA macromonomers in all of the above experiments. Experimental results suggest that the PBA particle's surface was modified by the presence of graft copolymer of *n*-BA and PMMA macromonomer at the interface.

## INTRODUCTION

Composite latex polymers possess properties that cannot be achieved either by physical blending of the constituent polymers or by copolymerization of the corresponding monomers in the same proportion. These polymers are typically prepared by seeded emulsion polymerization, from which a variety of morphological features can be obtained [1]. The core/shell definition for these latexes, where a first-stage polymer particle is engulfed with a second polymer type, could be considered as an idealized representation of the particle morphology based upon sequential monomer addition. Transition morphologies such as hemispherical particles, raspberry, sandwich, mushroom, and confetti-like structures are often reported. Design and control of latex particle morphology are often crucial in order to fulfill end-use requirements for these materials.

Many polymerization parameters and conditions are known to affect the composite particle morphology. Basically, these factors fall into two broad categories: thermodynamic and kinetic [2-4]. The thermodynamic factors determine the stability of the ultimate particle morphology according to the minimum surface free energy change principle. Nevertheless, kinetic factors such as viscosity of polymerization loci (degree of polymer crosslinking) and mode of second-stage monomer addition determine the ease with which such a thermodynamically preferred morphology can be achieved [4-8].

Based on thermodynamic analysis and mathematical modeling, a seeded polymerization system tends to reach the lowest energy state, the one with the lowest total interfacial energy. The interfacial tension between the two polymer phases and the interfacial tension between each phase and the aqueous medium are the key factors governing the type of composite particle morphology [1-4]. A number of researchers have proposed methods to modify the interfacial tension between the aqueous phase and the polymer phases using different types and amounts of surfactant [9], or different types and amounts of initiator [3, 10, 11]. In this research project, for a given polymer pair (PBA and PMMA) we are trying to control the degree of polymer/polymer phase separation and increase the coverage of seed polymer in composite latex particles using a compatibilizing agent as a modifier of polymer<sub>1</sub>/polymer<sub>2</sub> interfacial tensions.

A compatibilizing agent is a material used to bring two or more incompatible polymers into a stable blend through molecular blending. Typically the name refers to block or graft copolymers possessing either segments with chemical structures or solubility parameters similar to those of the polymers being blended. They may be preformed and added to the mixture of the polymers undergoing blending or may be generated in situ by the reaction between co-reactive functional groups on the polymers. The compatibilizing agents act as a polymeric surfactant in that they locate at the interface of two incompatible polymer phases, lowering the interfacial tension and possibly promoting the interfacial adhesion between immiscible phases.

For the preparation of graft copolymers, typically two methods are known: initiation of new chains on the main polymer chain, or deactivation of living polymer chains by a polymer backbone. In the first method, to control molecular weight of grafts and branching distribution, rapid initiation is essential, but functional groups that meet this requirement are difficult to find. Moreover, the formation of the second monomer homopolymer is unavoidable. The latter method is more direct. However, only a limited number of monomers copolymerize anionically to living species. Besides, this method cannot be handled easily in industry because of the purity requirements and the obliged use of a solvent. Furthermore, the branching reactions are reduced by the shielding effects.

More recently, copolymerization of a macromonomer and comonomer has been introduced as a novel method to prepare graft copolymers. Macromonomers are linear polymeric or oligomeric species which, because of the presence of a reactive end group, have the potential either to polymerize with themselves or to copolymerize with other monomers. (The words "macromonomer" and "macromer" are often used interchangeably, although the latter term was employed originally as a trademark to describe macromonomers discovered by Milkovich and Chiang [12].) The most common reactive end group is a vinyl group that can participate in free-radical polymerization. In principle, the formation of graft copolymers by the macromonomer technique is advantageous because of the wide variety of macromonomers and comonomers available. The method offers control over the graft length, since the molecular weight of the starting macromonomer can be preselected. In addition, the number of grafts per polymer chain can be controlled by adjusting the macromonomer to comonomer molar ratio.

Based on the type of macromonomer available, the composite system to be studied in this project is the poly(*n*-butyl acrylate)/poly(methyl methacrylate) (PBA/PMMA) composite system. In-situ compatibilizing agents are prepared by emulsion copolymerization of *n*-butyl acrylate (*n*-BA) in the presence of PMMA macromonomer (Fig. 1), using the terminal double bonds of the macromonomer chains to incorporate them into the PBA particles. The PMMA macromonomers

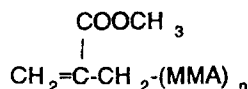


FIG. 1. Structure of PMMA macromonomer.  $n = 4-150$ .

used were prepared by free-radical polymerization of methyl methacrylate (MMA) monomer in the presence of a cobalt complex catalytic chain-transfer agent [13–16]. Composite latexes of PBA/PMMA will be prepared by seeded emulsion polymerization using PBA seed particles in which PMMA macromonomers were incorporated. Based on the hydrophilicity of the monomers, it is anticipated that the graft copolymers will be preferentially partitioned at the polymer/water interface of the seed PBA particles because of their relatively more hydrophilic PMMA branches. These copolymers on the surface of the seed particles will decrease the interfacial tension between PBA and PMMA phases during the second-stage polymerization, leading to an improved coverage of the core particles by the shell polymer.

## EXPERIMENTAL

### Materials

*n*-BA and MMA monomers (Aldrich) were washed with 10% aqueous sodium hydroxide solution, followed by distilled-deionized water, dried overnight (at 4°C) with anhydrous sodium sulfate (100 g/L), and finally passed through a column packed with the inhibitor remover (Aldrich). The monomers were stored at 4°C prior to use. The PMMA macromonomer ( $M_w$   $1.3 \times 10^3$  g/mol, DuPont) was received as a solution in methyl ethyl ketone and air-dried before use. All other PMMA macromonomers (DuPont), sodium lauryl sulfate (Henkel), hexadecane (Aldrich), potassium persulfate (Fisher), toluene (Aldrich), isopropanol (Aldrich), and phosphotungstic acid (Fisher) were used as received.

### Emulsion Copolymerization of *n*-BA and PMMA Macromonomer

Conventional emulsion polymerization based on Maxwell's recipe [17] for monodispersed particle size distribution of PBA particles had been used previously at the Emulsion Polymers Institute to incorporate PMMA macromonomer onto PBA particles [18]. The resulting latexes had a large amount of coagulum because the polymer chains of the macromonomer could not transport through the aqueous phase to the loci of polymerization and precipitate out of the emulsion system. Schulz et al. also found the same result in the emulsion copolymerization of polystyrene macromonomer and butyl and ethyl acrylates [19]. They suggested that emulsion copolymerization of macromonomer and comonomer could occur only when the reaction locus is in the monomer droplet. Ugelstad, El-Aasser, and Vanderhoff [20] have shown that when very small monomer droplets are formed in emulsion, they may become the main locus for particle nucleation and polymerization. The polymerization in these small emulsion droplets has come to be known as "mini-emulsion polymerization."

Miniemulsions are relatively stable oil-in-water emulsions with droplet diameters in the submicron size range (50–500 nm). These emulsions are prepared by shearing a system containing oil phase, water, surfactant, and additionally, a "cosurfactant." The "cosurfactant" is introduced into the monomer droplets to retard substantially the diffusion of monomer out of these monomer droplets. The small size of monomer droplets enables them to compete with micelles (if any) and

TABLE 1. Miniemulsion Polymerization Recipe for Preparing PBA Seed Latexes Containing PMMA Macromonomers<sup>a</sup>

Ingredients	Weight, g
<i>n</i> -BA + PMMA macromonomer <sup>b</sup>	20.00
DDI water	80.00
Hexadecane (20 mM) <sup>c</sup>	0.3623
Sodium lauryl sulfate (5 mM) <sup>c</sup>	0.1153
Potassium persulfate (3 mM) <sup>c</sup>	0.0649

<sup>a</sup>Batch polymerization, 70°C, 24 hours.

<sup>b</sup>Weight ratio of PMMA macromonomer:*n*-BA was varied based on equal molar ratio.

<sup>c</sup>Based on aqueous phase.

become the main locus of particle nucleation by capturing the radicals or oligo-radicals formed in the aqueous phase.

Miniemulsion polymerization was used to prepare the PBA seed latexes in the presence and absence of the PMMA macromonomers. In order to concentrate on the effect of the macromonomers, the ratio of surfactant (sodium lauryl sulfate, SLS), cosurfactant (hexadecane), and initiator (potassium persulfate) to the oil phase (*n*-BA and PMMA macromonomer) was kept constant. The variables to be studied are the differences in the molecular weight of the macromonomer and the ratio of the macromonomer to *n*-BA monomer. In addition, *n*-BA and MMA copolymer latexes were also prepared using the same recipe and procedure. The miniemulsion recipe is given in Table 1.

The process for incorporating the macromonomer into PBA latex particles is as follows. The appropriate amounts of *n*-BA monomer, PMMA macromonomer, and hexadecane were mixed overnight at room temperature using a magnetic stirrer. This oil phase was then added to an aqueous solution of SLS and stirred for 15 minutes before homogenizing. The homogenization was carried out using a Sonifier Disruptor W-350 (Branson Sonic Power) at a power level of 7 and pulsed for 1 minute at 50% duty cycle. The resulting miniemulsion was then polymerized in 4 oz bottles in a bottle polymerizer. The bottles were first flushed with nitrogen gas, next potassium persulfate solution was added, and the bottles were tumbled end-over-end at approximately 30 rpm in a water bath kept at 70°C for 24 hours.

## Characterization and Testing

### Monomer Conversion

At the end of the polymerization, the degree of *n*-BA monomer conversion was determined by the solids content and confirmed by gas chromatography (Hewlett-Packard Model 5890 Gas Chromatograph). For the gas chromatography (GC), 0.1 g of latex sample was mixed with 1 g toluene and 0.5 g isopropanol. 0.15 μL of this mixture was injected into the GC to obtain the area ratio of *n*-BA to isopropanol from the output. The actual monomer amount was determined from a

calibration curve of *n*-BA monomer. The results obtained show no monomer peaks, confirming a complete conversion as expected from the initial gravimetry results.

### Particle Size

The final latex particle sizes and particle size distributions were determined using the transmission electron microscope (TEM). A sample of the latex was initially diluted with a 2% aqueous solution of phosphotungstic acid which was used as a negative staining agent. A drop of this dilute latex was placed on a carbon-coated Formvar film deposited on an aluminum grid and examined in the cold stage (liquid nitrogen temperature) of a Phillips 300 Transmission Electron Microscope at 80 kV. For each sample several micrographs were taken from different locations on the grid at 11,000 magnification. The particle size distribution was determined by measuring approximately 1500 particles per sample using a Zeiss Mop-3 Digital Analyzer.

Due to the breadth of the size distributions and the softness of the particle, capillary hydrodynamic fractionation (CHDF 1100, Matec Applied Science) was chosen to confirm the TEM particle size averages and size distributions. Later on, the CHDF was also used as a method to compare the particle size averages and size distributions of PBA prepared in the presence of PMMA macromonomers and those of *n*-BA/MMA copolymer latexes. CHDF samples were prepared by diluting the latexes to 2% solids, sonifying them in a sonifier bath (Commonwealth Scientific) to break up any aggregates, and filtering these latexes before injection.

### Soap Titration

Partitioning of the compatibilizing agents in the PBA particles was investigated by the soap titration method. 100 mL of each latex (of known polymer content) was conductometrically titrated with an SLS solution of known concentration at room temperature, using the YSI model 32 conductance meter. At least three titrations were measured for each sample. By determining the amount of emulsifier adsorbed onto the latex particles per unit weight of polymer at the critical micelle concentration (CMC) and the average surface area of the particles (based on the surface-volume average particle diameters), one can calculate for the effective surface area per molecule of surfactant at the complete particle surface saturation (CMC of the surfactant). This effective surface area per molecule,  $A_s$ , can be related to the polymer/water interfacial tension and to the polarity of the polymer particle surface [21].

### Interfacial Tension

The interfacial properties between the monomer(s) phase and the water phase were examined by the drop-volume method. The monomer(s) phase consisted of *n*-BA mixed with hexadecane, and *n*-BA mixed with hexadecane and PMMA macromonomer or MMA monomer. [For the mixtures of *n*-BA, hexadecane, and MMA monomer, the SLS solution was prepared using water presaturated with MMA monomer. This step was done to avoid any further solubilization of the MMA monomer in the water phase which may alter the equilibrium at the water/monomer(s) interface.] The procedure consisted of the formation of SLS aqueous solution drops

suspended in the monomer(s) phase at the end of a glass capillary whose tip was perfectly wetted by the aqueous solution. The drops were then allowed to fall, and the volume per drop was determined. At least 10 drops were measured for each sample. For each measurement the interface was created at a constant rate yielding a minimum time of 3 minutes selected for drop detachment at the lowest interfacial tension. The constant rate of the drop formation was obtained by connecting the capillary to a syringe pump (Harvard Apparatus-22) set at a constant delivering rate. The interfacial tensions were calculated using the following expression:

$$\gamma = V_d(\rho_2 - \rho_1)980F/r \quad (1)$$

where  $\gamma$  is the interfacial tension (dyne/cm),  $V_d$  is the drop volume ( $\text{cm}^3$ ),  $\rho_1$  and  $\rho_2$  are the monomer phase density and surfactant solution density, respectively ( $\text{g}/\text{cm}^3$ ), 980 is the gravitational constant (cm/s),  $F$  is the drop volume correction factor, and  $r$  is the radius of the capillary (cm). The densities were measured by the DA-210 density meter (Kyoto Electronics) which measures the natural oscillation period of the sample at a specified temperature. The value of the drop volume correction factor was obtained as a function of  $r/V_d^{1/3}$  from the table of Lando and Oakley [22].

## RESULTS AND DISCUSSION

### PBA/PMMA Macromonomer Copolymer Latex Particle Size Averages and Particle Size Distributions

Figure 2 shows the examples of TEM micrographs of PBA homopolymer latex particles (A) and PBA latex particles prepared in the presence of PMMA macromonomer (B). The measured particle number-average diameters and polydispersity indexes (TEM) are given in Fig. 3(A) and 3(B), respectively. Particles of PBA latexes containing macromonomer are smaller in size but broader in their size distributions as compared to PBA homopolymer latex particles. The size average and polydispersity index of these particles varied according to the amount and molecular weight of the macromonomer used in a given recipe. For the same molar ratio of macromonomer and *n*-BA, the particle size average and the polydispersity index decreased as the macromonomer molecular weight increased. For the same macromonomer used, the particle size average decreased and the polydispersity index increased as the amount of PMMA macromonomer increased. In summary, the size average decreased as the weight ratio of PMMA macromonomer:*n*-BA monomer increased and the polydispersity index increased as the molar ratio of PMMA macromonomer:*n*-BA increased, especially for the latexes prepared with the lower molecular weight PMMA macromonomers. CHDF data display similar features with the TEM data, i.e., particle sizes decreasing with higher weight ratio of macromonomer and *n*-BA. However, the particle sizes obtained from the CHDF were smaller in general, which could be explained by the flattening on the grid of latex particles when they were examined under the electron beam in the TEM. Table 2 shows the comparison between some of the TEM to the CHDF particle size data.

The resulting changes in the average size and size distribution of the PBA particles, determined by both the TEM and the CHDF, suggest that the MMA units from the graft copolymer of PBA and PMMA macromonomer partition close



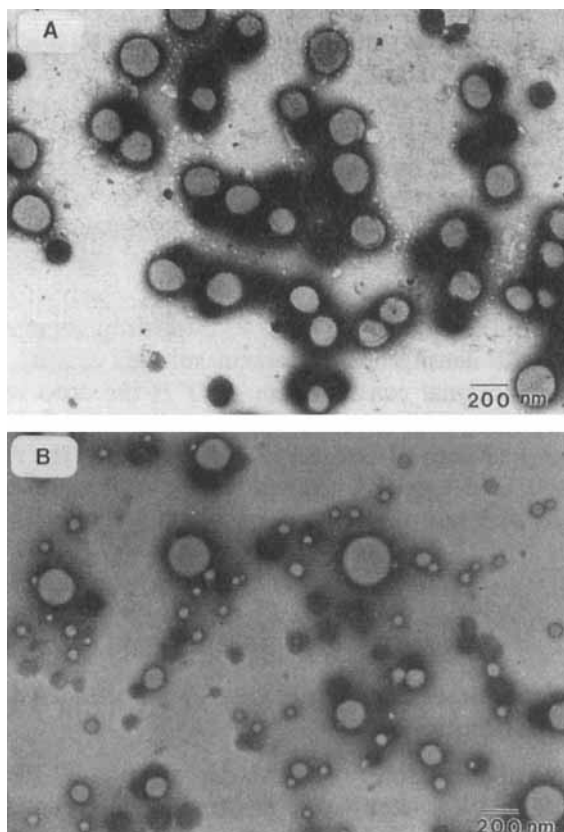


FIG. 2. TEM micrographs of (A) PBA homopolymer latex particles, and (B) PBA latex particles prepared in the presence of PMMA macromonomer (20% weight macromonomer based on *n*-BA, macromonomer  $M_w = 1.3 \times 10^3$  g/mol).

to the particle surface and thereby increase the hydrophilicity of the particle. In addition, the radical capture efficiency of the monomer droplets may have been increased because of the presence of the macromonomer chains in these droplets as suggested by Miller et al. [23, 24]. Future work must be done to clarify the role of the macromonomer in miniemulsion polymerization.

To verify that the changes in particle average diameter and size distribution of the PBA latexes synthesized in the presence of PMMA macromonomer were due to the surface modification by the graft copolymer, the particle size averages and size distributions of these latexes were then compared with those of *n*-BA/MMA copolymer latexes. Instead of a graft copolymer, a random copolymer is expected to be formed by *n*-BA and MMA monomers copolymerization.

Figure 4 compares the number-average diameters (A) and the percent standard deviations (B) of the PBA latexes prepared using the same recipe containing MMA monomer with those containing the PMMA macromonomer. When MMA monomer was used, both particle number-average diameters and percent standard

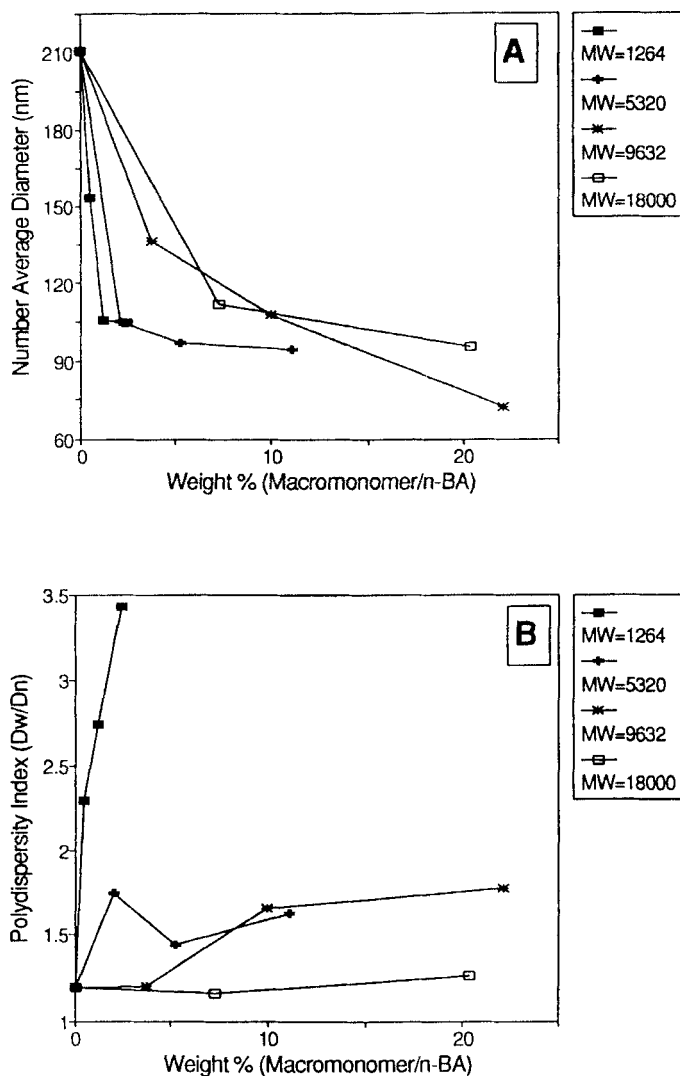


FIG. 3. (A) Number-average diameters, and (B) polydispersity indexes ( $D_w/D_n$ ) of the PBA seed particles prepared in the presence of various molecular weights and concentrations of PMMA macromonomers.

deviations did not vary with the increase in MMA/*n*-BA ratio. On the contrary, the particle size averages decreased significantly and the particle size distributions increased notably with increasing PMMA macromonomer/*n*-BA ratio. A suggested explanation for this behavior is the differences in the chain conformations. A random copolymer formed from the copolymerization of *n*-BA and MMA monomer cannot partition at the particle surface to increase the MMA unit concentration as efficiently as does the graft copolymer formed by the copolymerization of *n*-BA and

TABLE 2. Comparison of Particle Size Averages and Polydispersity Indexes Measured by TEM and by CHDF

Sample	Particle size averages, nm			PDI ( $D_w/D_n$ )
		Number	Weight	
PBA homopolymer latex	TEM	211	250	1.19
	CHDF	189	285	1.28
<i>n</i> -BA/PMMA macromonomer copolymer latex (0.049% weight macromonomer based on <i>n</i> -BA)				
Macromonomer $M_w$ , g/mol				
$1.3 \times 10^3$	TEM	154	352	2.29
	CHDF	187	285	1.53
$5.3 \times 10^3$	TEM	105	185	1.75
	CHDF	112	159	1.42
$9.6 \times 10^3$	TEM	137	164	1.20
	CHDF	98	238	2.43
$1.8 \times 10^4$	TEM	112	130	1.16
	CHDF	90	115	1.28

PMMA macromonomer, and does not modify the particle surface properties as much.

### Partitioning of Compatibilizing Agent in PBA Particles

In an aqueous solution, the driving force for the adsorption of a surfactant molecule such as SLS at the polymer-water interface is the favorable free-energy change associated with the transfer of the hydrocarbon portion of the surfactant molecule from the aqueous phase to the interface [25]. Since Paxton suggested that the area per molecule of a surfactant on a polymer surface can give some information as to the polarity of the polymer surface [26], several workers have attempted to correlate the area per molecule of a surfactant on a polymer surface to the polarity of the surface. Vijayendran used the surfactant molecule as a probe to investigate the nature of the polymer surface by relating the saturation adsorption of the surfactant molecule to the polarity of the polymer surface [21]. Here we used Vijayendran's approach to relate the observed differences in the adsorption of a surfactant molecule to the polarity of the PBA particle surface when the PBA latexes were prepared in the presence of the macromonomer.

Table 3 reports the values of the effective cross-sectional area per molecule ( $A_s$ ) of SLS on PBA latex particles at surface saturation. As was reported for many

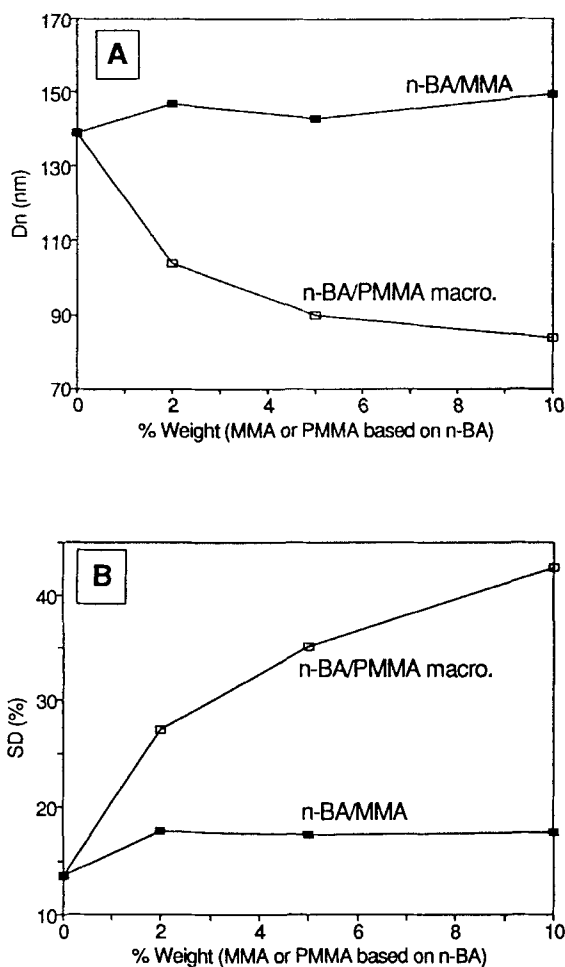


FIG. 4. (A) Number-average particle diameters, and (B) percent standard deviations on the PBA seed latexes prepared with MMA monomer and with PMMA macromonomer;  $M_w$  of PMMA macromonomer =  $5.3 \times 10^3$  g/mol.

other latexes [21, 26], an increase in  $A_s$  values is directly proportional to an increase in the surface polarity of the latex particles. The values of  $A_s$  for the PBA homopolymer latex prepared by conventional emulsion polymerization correspond well with the values found in the literatures. However, the  $A_s$  values for SLS adsorbed onto the PBA latexes prepared by miniemulsion polymerization were lower than those obtained for adsorption onto the PBA conventional latex. This is indicative of a more hydrophobic surface, possibly due to the presence of the hexadecane cosurfactant (used in miniemulsion polymerization) close to the surface of the particle.

The values of  $A_s$  increase only slightly when MMA monomer was copolymerized with *n*-BA, resulting from the increase in the hydrophilicity of the polymer

TABLE 3. Effective Surface Area Per Molecule of SLS (at the CMC of SLS) on Latex Particles

Latex	Macromonomer					Literature values, Å <sup>2</sup>
	<i>M<sub>w</sub></i> (g/mol)	%Weight macromonomer based on n-BA	<i>D<sub>s-v</sub></i> <sup>a</sup> nm	PDI <sup>b</sup>	<i>A<sub>s</sub></i> <sup>c</sup> Å <sup>2</sup>	
PBA homopolymer						
PBA conventional			139	1.2	50 ± 1	62 [27, 28], 56 [29]
PBA miniemulsion			197	1.4	34 ± 2	
n-BA/MMA random copolymer						
BM10		11.11	193	1.4	41 ± 3	
n-BA/PMMA macromonomer copolymer (0.048% mole macromonomer based on n-BA)						
M248	4.8 × 10 <sup>2</sup>	0.185	224	1.7	43 ● 3	
M212	1.3 × 10 <sup>3</sup>	0.485	204	1.7	36 ± 4	
M236	3.6 × 10 <sup>3</sup>	1.398	188	2.0	44 ± 1	
M253	5.3 × 10 <sup>3</sup>	2.041	131	1.2	51 ± 1	
M296	9.6 × 10 <sup>3</sup>	3.560	111	1.2	57 ± 3	
n-BA/PMMA macromonomer copolymer (0.267% mole macromonomer based on n-BA)						
M1036	3.6 × 10 <sup>3</sup>	7.611	149	2.3	56 ± 3	
M1053	5.3 × 10 <sup>3</sup>	11.110	143	1.3	56 ± 3	
PMMA homopolymer						
PMMA			108	1.1	92 ± 10	57 [30], 100 [31], 79 [29, 32], 152 [33], 133 [34]

<sup>a</sup>Volume-surface diameters determined by TEM.<sup>b</sup>Polydispersity indexes determined by TEM.<sup>c</sup>Area/molecule of SLS, values averaged from three measurements.

particles brought on by the presence of MMA monomer units in the random copolymer. A larger increase in  $A_s$  was attained when PMMA macromonomer was copolymerized with *n*-BA, even at much lower weight ratios than in the random copolymer. This increase in the  $A_s$  values become more obvious at higher weight ratios of macromonomer and *n*-BA. These values suggest that the graft copolymer of PBA and PMMA macromonomer partitions close to the particle surface, enriching it with MMA units, thereby altering the surface of the seed latex particles. In a random copolymer, the MMA units are distributed over the length of the entire molecule, while each branch of a graft copolymer can act as random coils of PMMA chains. Thus at the same ratio of MMA and *n*-BA units, more MMA units from the graft copolymer than from the random copolymer can partition at the particle surface.

Considering the broadness of the particle size distribution, especially for latexes prepared with lower molecular weight macromonomers, the  $A_s$  values can give qualitative information on the partitioning of the MMA units from the graft copolymer at the particle interface. By increasing the PMMA macromonomer weight ratio up to 3–4% based on *n*-BA, one can observe an increase in  $A_s$  values of SLS adsorbed on the particle surface. These values indicate a continuous enrichment of the interphase zone with PMMA chains, independent of the molecular weight of the PMMA macromonomers. Above this concentration, the  $A_s$  values remain almost unchanged. These constant values of  $A_s$  suggest that at the particle interface the maximum packing density of the PMMA chains was reached. By further increasing the concentration of PMMA macromonomer, most of the graft copolymers will reside inside the PBA particles. Furthermore, these results suggest that the polarity of the particle surface is affected by the overall concentration of MMA units on the surface, not by the number of branch sites or the graft lengths.

### Interfacial Tension between Monomer/Water Phase

To explain the reduction in particle size of PBA seed latexes synthesized in the presence of PMMA macromonomer, the estimation of changes in particle surface hydrophilicity was obtained via interfacial tension measurements of monomer/water phases. Figure 5 shows a plot of interfacial tension as a function of the weight percent of MMA monomer or PMMA macromonomer based on *n*-BA. While the difference in the interfacial tensions was rather insignificant for mixtures of *n*-BA and MMA monomer at various comonomer ratios, a decrease was obvious when PMMA macromonomer was mixed with *n*-BA. This reduction of the interfacial tension can be explained by the rearrangement of the more hydrophilic PMMA macromonomer molecules at the oil/water interface, whereas the smaller MMA molecules are distributed uniformly in the *n*-BA monomer phase. The displacement of the *n*-BA monomer molecules at the interface between monomer and water by the PMMA macromonomer molecule increases the interface polarity and decreases the interfacial tension between the oil/water phases. The changes are more apparent for the lower molecular weight macromonomers, possibly since shorter PMMA chains can rearrange easier at the oil/water interface and, for the same weight ratio, the number of polymer chains is larger compared to that of high molecular weight PMMA macromonomers.

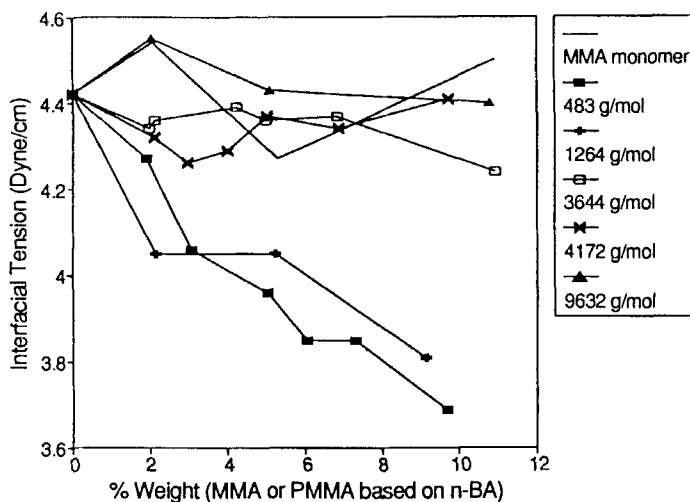


FIG. 5. Variation of monomer/water phase interfacial tension as a function of weight ratio of MMA monomer or PMMA macromonomer:*n*-BA at 24°C.

## CONCLUSIONS

Well-defined graft copolymers were successfully prepared in-situ by miniemulsion copolymerization of *n*-BA and PMMA macromonomers during PBA seed latex synthesis. These graft copolymers act as a compatibilizing agent for PBA seed and PMMA shell during second-stage polymerization. By varying the ratio of macromonomer and *n*-BA, we changed the polymer/polymer interfacial tensions and thus improved the coverage of seed polymer in composite latex particles. The influence of the amount of PMMA macromonomer (macromonomer to comonomer molar ratio, and macromonomer molecular weight) on changing the average sizes and size distributions of PBA seed latex particles has been studied by TEM and CHDF. The partitioning of the compatibilizing agents has been studied by the soap titration method. From the decrease in particle size averages and the increase in the  $A_1$  values compared to the PBA homopolymer latex, it was concluded that the particle's surface was modified by the presence of *n*-BA/PMMA macromonomer copolymers at the interface. To explain the reduction in particle size averages of PBA seed latexes formed in the presence of PMMA macromonomer, estimation of increases in particle surface hydrophilicity was obtained via interfacial tension measurements of monomer/water phases. The decrease in the interfacial tension suggested the partitioning of MMA units from the PMMA macromonomer at the oil/water interface. From all of the above experiments, the *n*-BA/PMMA macromonomer copolymer latexes were proved to be different from *n*-BA/MMA copolymer latexes. From the latter case random copolymers were formed, thus the MMA molecules were distributed randomly along the main polymer chain and were not able to alter the surface of the PBA particles.

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