Synthesis and Characterization of Poly(butyl acrylate–methyl methacrylate)/Polyaniline Core–Shell Latexes

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ABSTRACT: Poly(butyl acrylate–methyl methacrylate) [P(BA–MMA]/polyaniline (PANI) core–shell complex particles were synthesized with a two-step emulsion polymerization method with P(BA–MMA) as the core and PANI as the shell. The first step was to prepare P(BA–MMA) latex particles as the core via soapless emulsion polymerization. The second step was to prepare P(BA–MMA)/PANI core–shell particles. Sodium dodecyl sulfate was fed into the P(BA–MMA) emulsion as a surfactant, and this was followed by the addition of the aniline monomer. A bilayer structure of the surfactant over the surfaces of the core particles was desired so that the aniline monomer could be attracted near the outer surface of the core particles. In some cases, dodecyl benzene sulfonic acid was added after 2 h when the polymerization of aniline was started. The final product was the desired core–shell particles. The morphology of P(BA–MMA) and P(BA–MMA)/PANI particles was observed with transmission electron microscopy. The thermal properties were studied with thermogravimetric analysis and differential scanning calorimetry. Furthermore, conductive films made from the core–shell latexes were prepared, and the electrical conductivities of the films were studied. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 823–830, 2007

Key words: conducting polymers; core-shell polymers; emulsion polymerization

INTRODUCTION

Conducting polymers have been used widely by industry recently. They mainly consist of conjugating polymers. Organic conducting polymers have better processability and lower costs than inorganic conducting materials. Among conducting polymers, polyaniline (PANI) has been extensively studied because it is easy to prepare and exhibits good environmental stability. However, PANI is nearly insoluble and hence has poor processability, which is due to its rigid, conjugated double-bond backbone. PANI is only slightly soluble in a limited number of solvents, such as dimethylformamide, *N*-methylpyrrolidone, concentrated sulfuric acid, *m*-cresol, and chloroform.[1,2]

The typical synthesis of conductive PANI is usually performed by the chemical oxidative polymerization of monomers in an aqueous solution;[3] a protonic acid and an oxidizing agent are involved in this method as well. Other methods such as emulsion polymerization,[4–7] the polymerization of aniline in micelles,[8,9] and reversed microemulsions[10] for preparing PANI have been reported recently. An alternative way of preparing colloidal conducting polymers involves coating latex particles with a thin layer of conjugated polymers to form conductive composites with a core–shell morphology, including PANI-coated polystyrene with some appropriate surfactants and a sufficient amount of PANI. A core–shell morphology[11–13] and polypyrrole-coated poly(butyl methacrylate)[14] also improve the processability and provide high conductivity with a low conducting-polymer loading. Another way of improving the processability of PANI is to synthesize a composite of PANI and poly(4-styrenesulfonic acid) (PSS) by the polymerization of aniline in the presence of PSS.[15–17]

In another approach, polymer blends have been used with the aim of making films with better processability. Composite films based on PANI and nylon 6 have been reported to have conductivities of ∼ 0.2 S/cm,[18] and water-soluble PANI blended with poly(ethylene glycol) resulted in a conductivity of ∼ 0.1 S/cm.[19] Polymer/inorganic nanoparticle composite such as PANI/silica composites have also been reported to have conductivities of ∼ 2.9 S/cm.[20]

Previously, we successfully prepared core–shell polystyrene/PANI and silica/polystyrene/PANI composite particles and described their properties.[21,22] A polymer with a lower glass-transition temperature was desired to facilitate film formation and improve the processability of core–shell composite particles. Therefore, in this article, we demonstrate the synthesis of core–shell PANI colloids by using cationic poly(butyl acrylate–methyl methacrylate) [P(BA–MMA)] latexes as the core particles. The morphology of the particles has been examined with transmission electron

TABLE I
Reaction Conditions for Preparing P(BA–MMA) Core Latexes

	B5M5	B6M4	B7M3	B8M2
BA (mL)	20	24	28	32
MMA (mL)	20	16	12	8
EGDMA (mL)	1.8	1.8	1.8	1.8
Distilled water (mL)	760	760	760	760
AIBA (g)	1.08	1.08	1.08	1.08

microscopy (TEM). The thermal and conductive properties of the core–shell particles have also been investigated. The effect of adding dodecyl benzene sulfonic acid (DBSA) on the properties of the core–shell films is also discussed.

EXPERIMENTAL

Materials

Butyl acrylate (BA), methyl methacrylate (MMA), ethylene glycol dimethacrylate (EGDMA), 2,2′-azobis(isobutyramidine)dihydrochloride (AIBA), aniline, DBSA, sodium dodecyl sulfate (SDS), and ammonium peroxide (APS) were obtained from Acros Organics (Geel, Belgium) and used as received.

Preparation of the P(BA–MMA) latex

The BA and MMA monomers and crosslinking agent EGDMA (5 wt % with respect to the monomers) were mixed with 760 mL of distilled water. The reaction vessel was then heated to 70°C and purged with nitrogen. The initiator AIBA was added to the vessel at 70°C with vigorous stirring at 400 rpm. The polymerization was allowed to proceed for 3 h before cooling to room temperature. The conditions employed for the polymerization are summarized in Table I.

Preparation of the P(BA–MMA)/PANI latex

In this part, 50 mL of the P(BA–MMA) latex was diluted with 100 mL of distilled water, acidified with HCl to pH 0.7, and mixed with 0.3 g of SDS. Aniline was added to the mixture and stirred for 2 h before the initiator APS was added to start the polymerization. The reaction was allowed to proceed for 3 h at room temperature. In some cases, 15 mL of a 0.01M DBSA solution was added after 2 h when the reaction started. The conditions used for the reaction are summarized in Table II.

Characterization

The morphology of the latex was examined with TEM (H-7100, Hitachi, San Diego, CA). The particle size distribution was investigated with dynamic light scattering (DLS; Zetasizer 3000HS, Malvern, Worcester-

shire, UK). The thermal properties were examined with differential scanning calorimetry (DSC; DSC 2010, PerkinElmer, Wellesley, MA) and thermogravimetric analysis (TGA; TGA-7, PerkinElmer). Both TGA and DSC analysis were performed with nitrogen gas purging and a heating rate of 10°C/min. P(BA–MMA)/PANI latexes were coated on poly(ethylene terephthalate) (PET) films by dip coating. The surface electrical resistance of the P(BA–MMA)/PANI films made from the core–shell latexes was measured with a standard four-probe technique at room temperature, and the thickness of the films was determined with an α-step surface profiler (Alpha-Step 500 surface profiler, Tencor, San Jose, CA). Then, the electrical conductivity (ρ) of the films was determined as follows:

$$\rho = \frac{t}{RA} \qquad (1)$$

where t is the thickness of the film, R is the surface electrical resistance, and A is the cross-sectional area of the film.

RESULTS AND DISCUSSION

The nomenclature of our samples can be explained with the following examples. For the core P(BA–MMA) particles, for example, B7M3 was a mixture of 70% BA monomer and 30% MMA monomer. For the core–shell P(BA–MMA)/PANI particles, for example, B7M3A5 indicated that we used B7M3 as the core and added 5 wt % aniline with respect to the core particles; B7M3A5D was synthesized in the same way as B7M3A5, but a DBSA solution was added after 2 h when the polymerization of aniline started.

The TEM micrographs of the P(BA–MMA) core particles are illustrated in Figure 1. The particle sizes of the P(BA–MMA) particles were around 170–200 nm. As the content of BA increased, the boundary of the particles became indistinct, and the size of the particles increased, except for sample B6M4.

TABLE II
Reaction Conditions for Preparing P(BA–MMA)/PANI Core–Shell Latexes

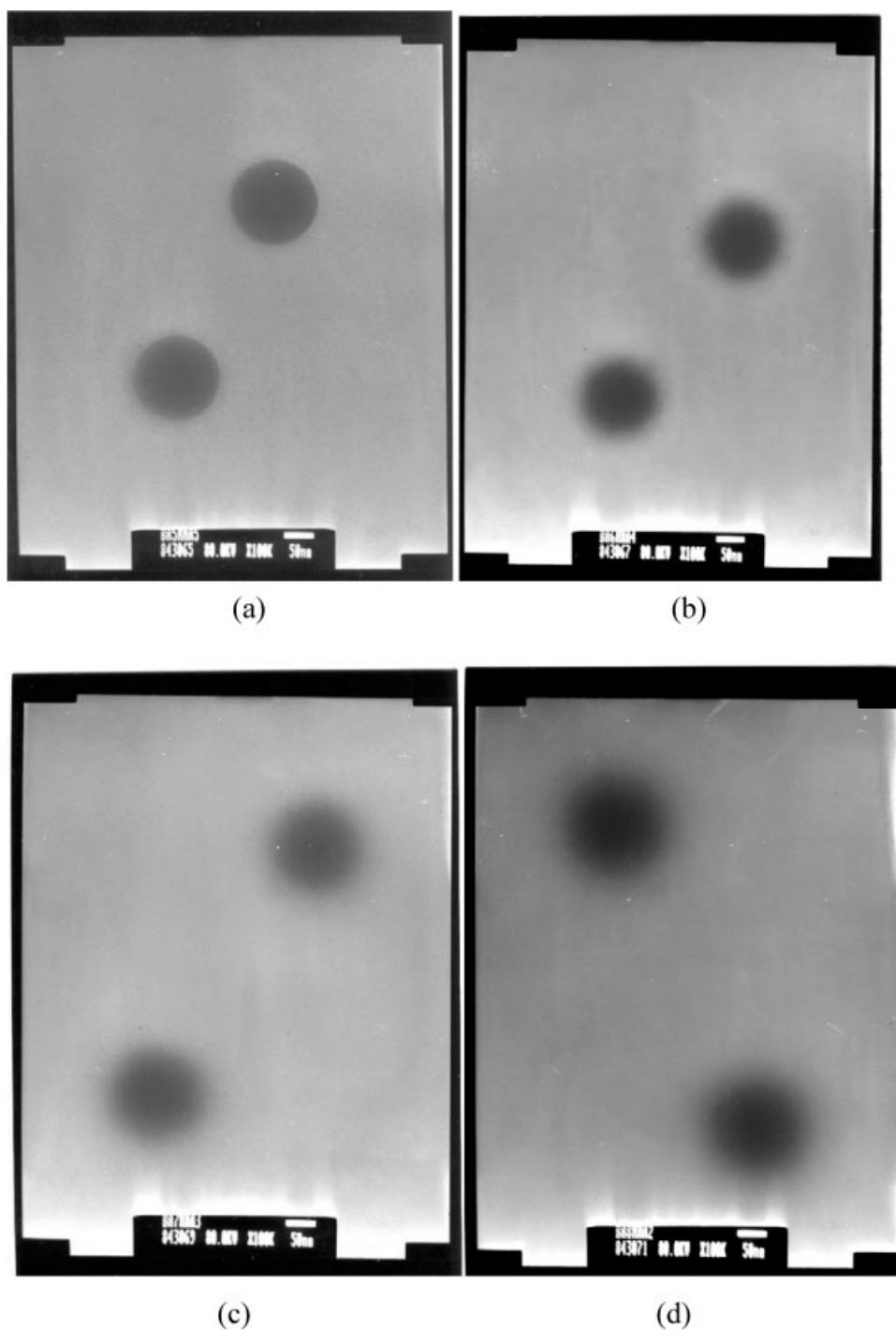|	B5M5	B6M4	B7M3	B8M2
P(BA–MMA) core latex (mL)	50	50	50	50
Aqueous HCl (g)	3.09	3.09	3.09	3.09
Distilled water (mL)	100	100	100	100
SDS (g)	0.3	0.3	0.3	0.3
Aniline 3 wt % (μL)	65	65	65	65
APS (g)	0.165	0.165	0.165	0.165
Aniline 5 wt % (μL)	110	110	110	110
APS (g)	0.277	0.277	0.277	0.277
Aniline 10 wt % (μL)	209	209	209	209
APS (g)	0.52	0.52	0.52	0.52
DBSA (g)	0.0483	0.0483	0.0483	0.0483

Figure 1 TEM photographs of P(BA–MMA) core latexes: (a) B5M5, (b) B6M4, (c) B7M3, and (d) B8M2.

Figure 2 shows the TEM micrographs of the P(BA–MMA)/PANI core–shell particles. After PANI was coated onto the P(BA–MMA) core particles, the core–shell structure of the particles could be clearly seen. Each particle had two color zones. The lighter one in the center area was core polymer P(BA–MMA). The darker part around the core polymer was PANI. The core–shell particles were around 200–400 nm and were larger than the P(BA–MMA) core particles because particle coagulation occurred during the process of PANI synthesis under a more acidic condition. The particle coagulation was more significant when the BA content was increased. Moreover, as the amount of aniline introduced increased, PANI coated on the P(BA–MMA) core became more uniform and thicker. However, if the amount of aniline reached 10 wt %, the chance of self-nucleation of aniline was high, and some PANI precipitated on the bottom of the reactor.
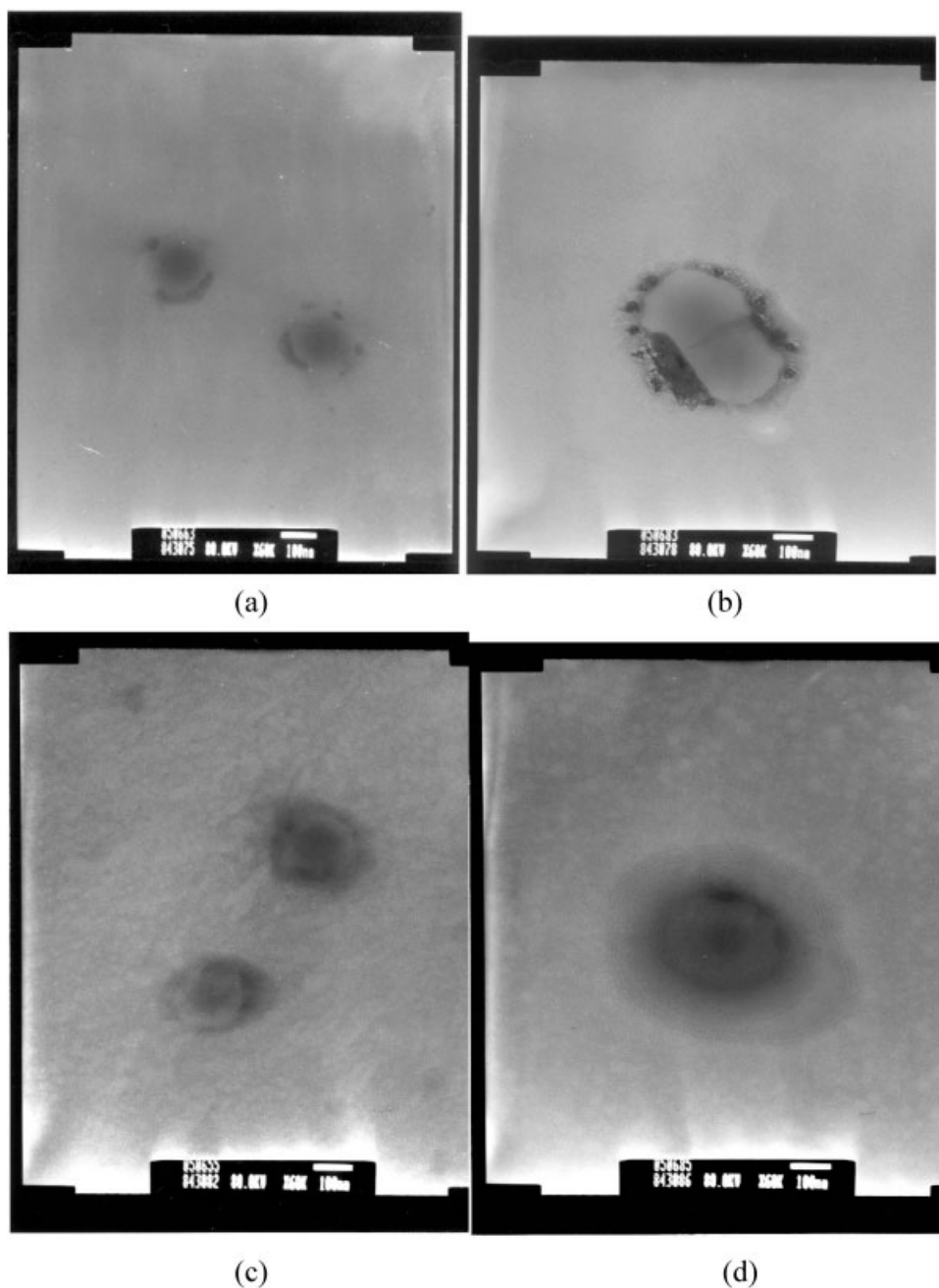
Figure 2 TEM photographs of P(BA–MMA)/PANI core–shell latexes: (a) B6M4A3, (b) B8M2A3, (c) B6M4A5, and (d) B8M2A5.

When DBSA was added during the polymerization of aniline, the product emulsion became more stable. This was because DBSA could act as a surfactant and help particles disperse better. As shown in Figure 3, the P(BA–MMA) core was coated with PANI very well, and the boundary of the core in the TEM photographs was even clearer. Even if some particles coagulated, there was still a PANI domain between them, which showed that the nonconducting cores were separated. We could conclude that adding DBSA was able to increase the stability of the core–shell particles in the emulsion. On the other hand, these emulsions were analyzed with a light scattering analyzer, and the results are shown in Figures 4 and 5. The size distributions were between 200 and 500 nm. The average size of the P(BA–MMA)/PANI core–shell particles measured by DLS was close to that observed by TEM in Figure 3. As the content of BA increased, the average size of the core–shell particles increased. Figures 4 and 5 also show that a small number of particles coagulated with one another, and a few very large particles (>1000 nm) were detected in the DLS measure-
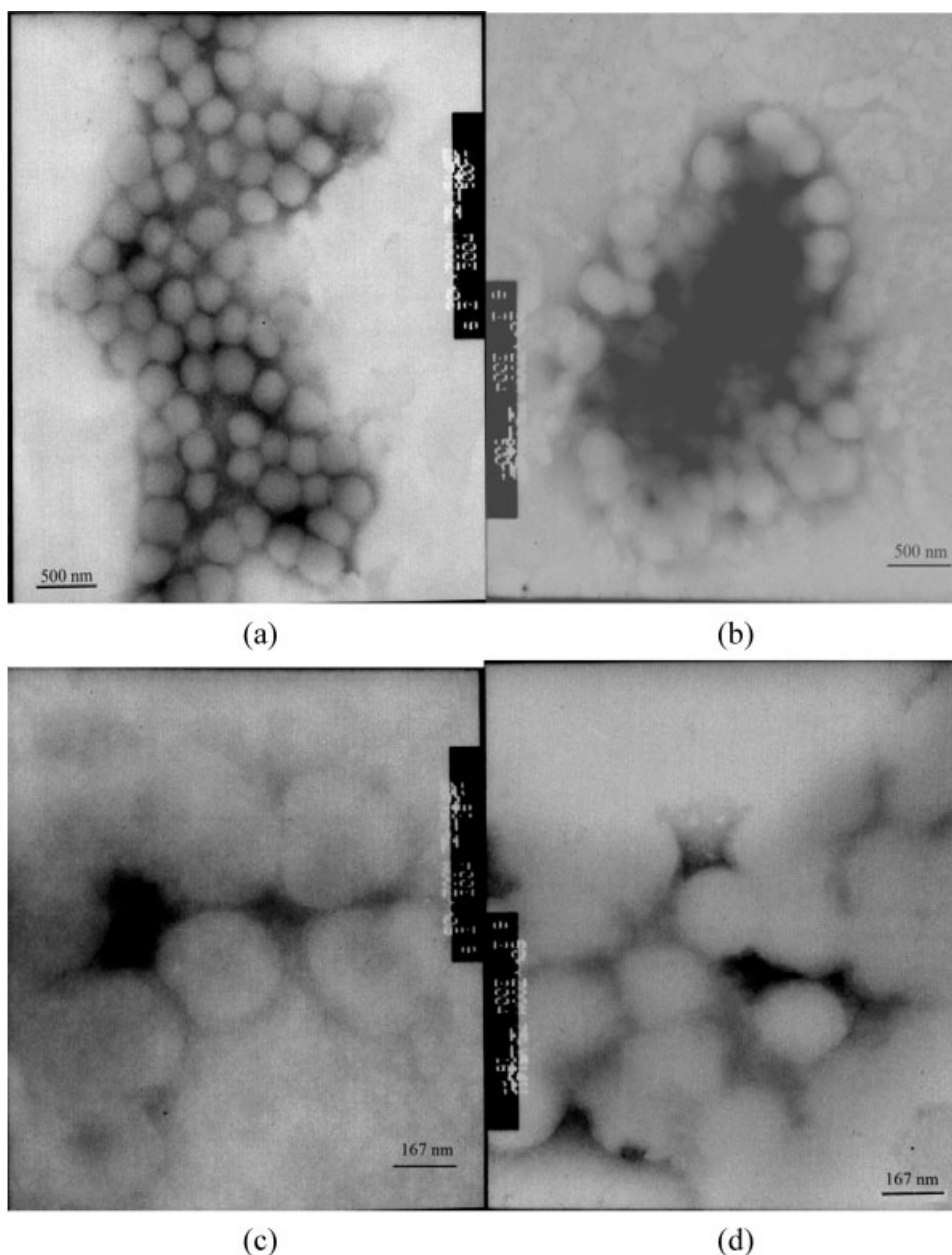
Figure 3 TEM photographs of P(BA–MMA)/PANI core–shell latexes with DBSA added: (a) B5M5A5D, (b) B6M4A5D, (c) B7M3A5D, and (d) B8M2A5D.

ments, especially for the system containing 3 wt % aniline monomer, because when the content of aniline was low in the emulsion, the coagulation of the P(BA–MMA) core particles occurred under the acidic condition quickly before PANI was coated.

Figures 6 and 7 show the thermal degradation properties of the P(BA–MMA) core particles and P(BA–MMA)/PANI composite particles measured by TGA. For the P(BA–MMA) core particles, as shown in Figure 6, decomposition began at about 300°C, and no residual weight was obtained above 600°C. For the P(BA–MMA)/PANI core–shell particles, as shown in Figure 7, the decomposition temperature increased, and dif-

ferent residual weight percentages referring to the amount of aniline in the composite particles were obtained. For example, in B5M5A10, the residual weight percentage was as high as 10 wt %, whereas it was 8 wt % in B5M5A5 and 5 wt % in B5M5A3. The increase in the aniline content increased the residual weight percentage. However, as the content of BA in the core increased, this tendency became less obvious, and finally in those with B8M2 cores, the residual weight percentages at 800°C were almost zero. In the system with B8M2 as the core, the glass-transition temperature was far below room temperature. PANI had more interaction with core particles through the coagu-
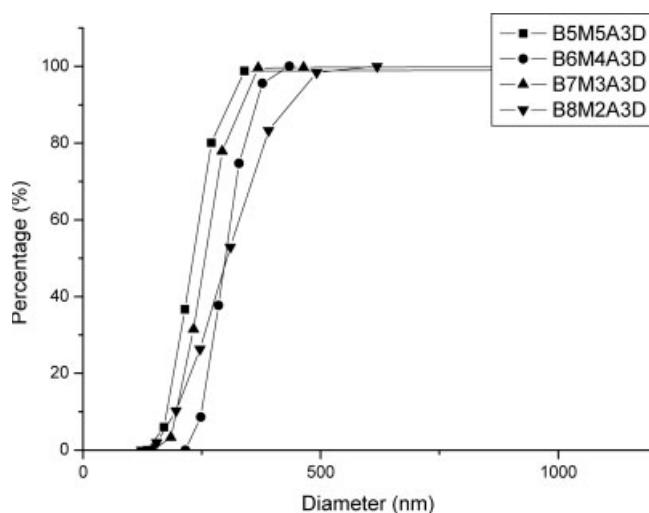
Figure 4 Light scattering size analysis of P(BA–MMA)/PANI core–shell latexes with 3 wt % PANI and DBSA added.

lation, deformation, and fusion of particles. The zero residual weight percentage implied that a mutual interaction between PANI and the core particles occurred significantly during the heating process of TGA.

The DSC results for the P(BA–MMA) and P(BA–MMA)/PANI latex particles are shown in Table III. First, the glass-transition temperatures of the P(BA–MMA) cores depended on the composition of both the BA and MMA monomers. For different contents of BA, we got −25°C for B8M2, −17°C for B7M3, 12.5°C for B6M4, and finally 40°C for B5M5. As expected, the glass-transition temperature decreased when more BA monomer was added. If the glass-transition temperature is below room temperature, it means that a sample itself can form a film simply under room tem-
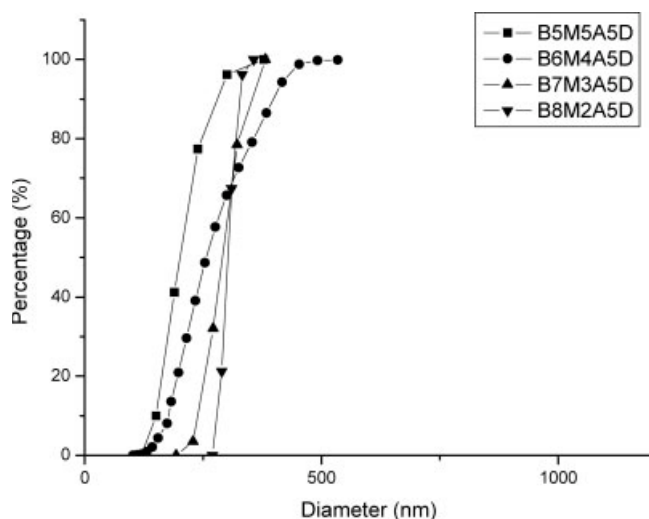

Figure 5 Light scattering size analysis of P(BA–MMA)/PANI core–shell latexes with 5 wt % PANI and DBSA added.

perature, and the film will possess toughness to fit our demand for the final products. After PANI was coated, only one glass-transition temperature was observed, and the glass-transition temperature of the core–shell particles increased slightly compared with the corresponding glass-transition temperature of the core particles because the chain motion of the core component was constrained by PANI. PANI did not show the glass-transition temperature in the DSC measurement; therefore, only the glass-transition temperature of the core polymer could be seen.

The P(BA–MMA)/PANI latex was coated on a PET film, and the surface electrical resistance was measured by standard four-probe technology to obtain the conductivity of each film. In Table IV, the conductivity of the core–shell particles did not increase significantly with a higher aniline load. When no DBSA was added during the polymerization of aniline, considering core–shell particles with B5M5 and B6M4 as cores, we could see that the conductivities decreased when the aniline weight percentage increased from 3 to 5 wt % but increased when the aniline load was increased from 5 to 10 wt %. For core–shell particles with B7M3 and B8M2 as cores, the conductivities increased when the aniline concentration increased from 3 to 5 wt % but decreased with further increases in aniline from 5 to 10 wt %. For those with 10 wt % aniline, secondary nucleation of aniline took place, and phase separation occurred in the film. This was why there was not much improvement in the conductivity observed when more aniline was introduced. In a comparison of samples loaded with 3 wt % aniline, the conductivity of the films was better with cores of B5M5 and B6M4, whereas in a comparison of samples with 5 wt % aniline, better conductivity was obtained with cores of B7M3 and B8M2. As the content of BA in the core increased, the conductivity of the P(BA–MMA)/PANI
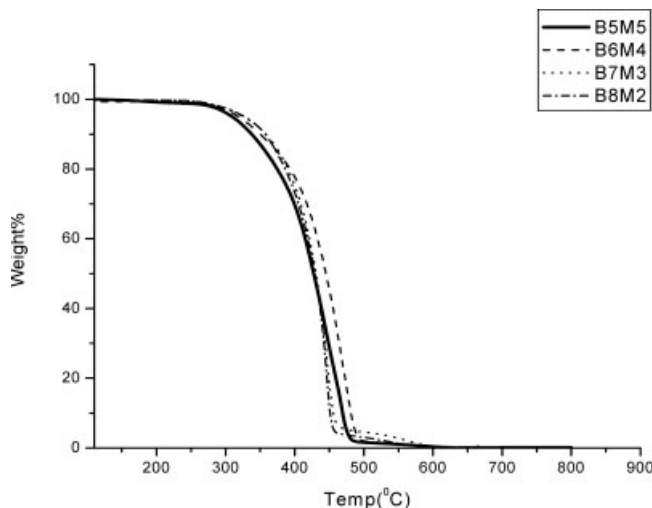

Figure 6 TGA curves of P(BA–MMA) core particles with different compositions.
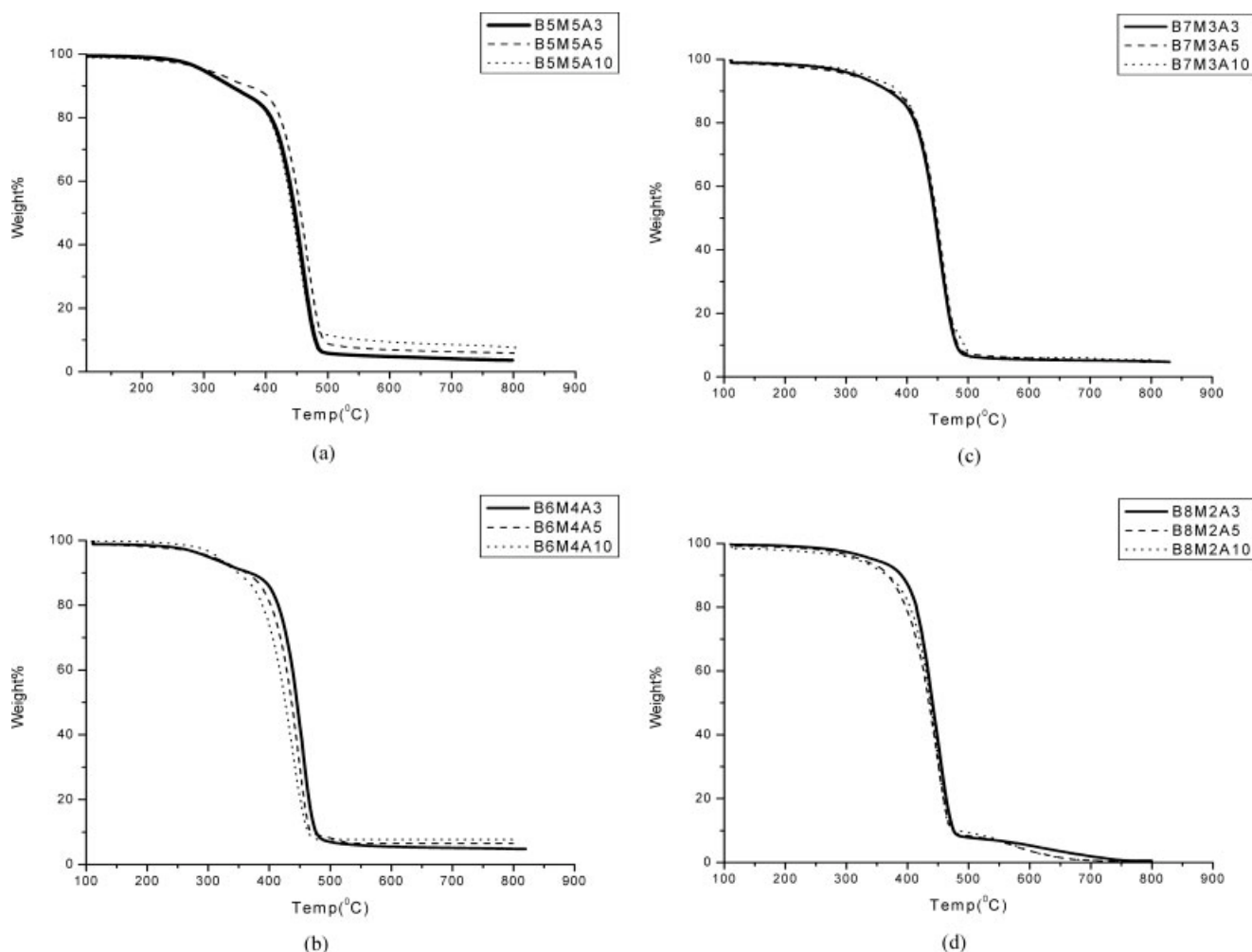
Figure 7   TGA curves of P(BA–MMA)/PANI core–shell particles with different compositions.

film decreased slightly first (from B5M5 to B6M4) but increased again with more BA existing in core (B8M2). Two factors were considered to cause this result: particle coagulation of the latex and film formation. A higher content of BA enhanced the particle coagulation, which deteriorated the conductivity of the film. However, the flexibility of the latex particles facilitated film formation, which led to better conductivity of the conducting film. As we could see, if the loading of aniline was only 3 wt %, aniline was not sufficient to form a uniform shell coating over particles. However, with 10 wt % aniline loaded, self-nucleation of aniline could exist and result in phase separation and a nonuniform shell coating. In our

experiments, when no DBSA was added, B8M2A5 provided the best conductivity, as high as 1.835×10^{-2} S/cm.

Finally, adding DBSA during aniline polymerization was found to efficiently improve the conductivity of the film formed. The conductivities increased from several times to more than 100 times, as shown in Table IV. DBSA could act as both dopant and surfactant for PANI and help core–shell particles disperse better in the emulsion, as shown in our TEM photographs, and therefore led to better conductivity. The conductivities obtained were 0.16, 0.133, and 0.15 S/cm for samples B5M5A5D, B5M5A10D, and B7M3A5D, respectively.

TABLE III
Glass-Transition Temperatures of P(BA–MMA) and P(BA–MMA)/PANI Latex Particles Determined by DSC

	B8M2	B7M3	B6M4	B5M5	B8M2A5	B7M3A5	B6M2A5	B5M5A5
Glass-transition temperature (°C)	−25	−17	12.5	40	−23.5	−16	15	40

TABLE IV
Conductivity (S/cm) of P(BA–MMA)/PANI Films
with Different Compositions

	PANI		
	3 wt %	5 wt %	10 wt %
No DBSA added			
B5M5	3.31×10^{-3}	1.11×10^{-3}	3.03×10^{-3}
B6M4	1.92×10^{-3}	2.10×10^{-4}	1.02×10^{-3}
B7M3	7.80×10^{-4}	4.22×10^{-3}	2.78×10^{-4}
B8M2	1.44×10^{-3}	1.835×10^{-2}	8.17×10^{-4}
DBSA added			
B5M5	9.10×10^{-4}	0.160	0.133
B6M4	3.23×10^{-3}	6.05×10^{-2}	5.3×10^{-3}
B7M3	5.09×10^{-2}	0.150	3.68×10^{-3}
B8M2	1.63×10^{-2}	2.27×10^{-2}	2.14×10^{-2}

CONCLUSIONS

In this work, different compositions of P(BA–MMA) latex particles were synthesized and used as cores, and then PANI was synthesized as a shell over the core particles. According to TEM photographs, the core particles had an average size of 170–200 nm, and the core–shell particles had an average size of 200–400 nm. The TGA results showed that the core particles had decomposition temperatures beginning at about 300°C and had no residual weight after 600°C, whereas the core–shell particles showed a higher decomposition temperature and left char yields even after 800°C. DSC results showed us the change in the glass-transition temperature for cores of different compositions. Among them, B7M3 and B8M2 had glass-transition temperatures noticeably lower than room temperature. After PANI was coated, the glass-transition temperature of the core–shell particles increased slightly in comparison with the corresponding glass-transition temperature of the core particles. Finally, the core–shell latexes were coated on PET films by dip coating, and their conductivities were measured. Adding DBSA during the polymerization of aniline effectively increased the conductivities of the films by up to 2 orders. The conductivities obtained were 0.16, 0.133, and 0.15 S/cm for samples B5M5A5D, B5M5A10D, and B7M3A5D, respectively.

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