

# New Route to Monodispersed Amphiphilic Core-Shell Polymer Nanoparticles: Polymerization of Styrene from $\alpha$ -Methylstyrene-Containing Macroinitiator

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**ABSTRACT:** A novel method has been developed to prepare amphiphilic core-shell polymer nanoparticles via polymerizations of styrene (St) initiated by hydrophilic  $\alpha$ -methylstyrene (AMS)-containing prepolymers. AMS-containing prepolymers were first synthesized by soap-free emulsion copolymerization of AMS, butyl acrylate (BA), and acrylic acid (AA) and then were kept at 90°C to generate free radicals on the AMS segments, which subsequently initiate the polymerization of St. Thus, well-defined, amphiphilic core-shell nanoparticles, ranging from 126 to 282 nm in diameter, were produced in the absence of surfactant. The St conversion, molecular weights, and size of products strongly depended on the AMS-containing prepolymer

concentration and the AMS content of it. Transmission electron microscopic (TEM) images of the particles clearly show well-defined core-shell morphologies where PSt cores are coated with hydrophilic AMS-containing prepolymer shells. The amphiphilic core-shell nanoparticles can be produced in high concentrations (up to 25% solids content). This new method is scientifically and technologically significant because it provides a commercially viable route to a wide variety of novel amphiphilic core-shell nanoparticles. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4121–4126, 2012

**Key words:**  $\alpha$ -methylstyrene; macroinitiator; soap-free emulsion polymerization; core-shell nanoparticle

## INTRODUCTION

Core-shell latex particles, consisting of polymer shells outside and different polymer cores inside, attract increasing research attention for they often improve physical and chemical properties. The versatility of these particles determined their wide range of applications in chemical, biological, and pharmaceutical industries,<sup>1</sup> for example, in nanophase domains,<sup>2</sup> processing aid,<sup>3</sup> etc.

Core-shell particles are usually synthesized by at least a two-stage emulsion polymerization.<sup>4–6</sup> Generally, at the first stage, the cores of these latex particles are obtained; and for the second stage of the polymer-

ization, the production of the shell is to be accomplished by two different addition routes of monomers, which are continuous addition process (dropwise method),<sup>7–11</sup> and batch process (swelling method).<sup>12,13</sup> To date, numerous people<sup>14–17</sup> successfully prepared core-shell latex particles by classical emulsion polymerization techniques. Khan et al.<sup>7</sup> synthesized a series of core-shell latex particles, containing a PBA/MMA/MAA core inside and a PSt/AN, PBA/MMA shell outside. Li et al.<sup>18</sup> prepared amphiphilic core-shell polymer nanospheres via graft copolymerization, which is a new and efficient method.

In this study, we report on a novel method for preparation of core-shell particles. Recently, we were able to successfully prepare block copolymers with  $\alpha$ -methylstyrene (AMS)-containing macroinitiators both in bulk and solution. At an appropriate temperature, the AMS-containing macroinitiator was believed to decompose into chain free radicals,<sup>19,20</sup> and these radicals, in turn, enabled the subsequent polymerization of the new monomer by free radical polymerizations, giving rise to block copolymers. The formation of block copolymers by simply heating a preformed polymer containing AMS units in the presence of a second monomer is somewhat like the 1,1-diphenylethene (DPE) method.<sup>21–25</sup> In the

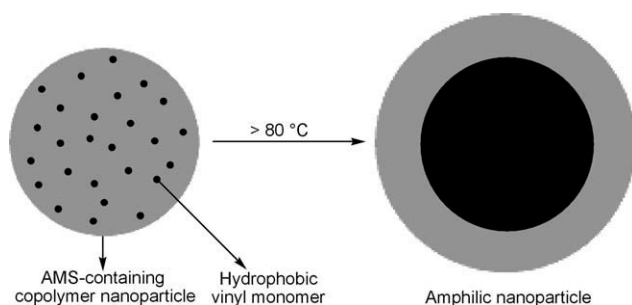
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**Figure 1** Schematic representation of the formation of amphiphilic core-shell nanoparticles.

present article, core-shell particles with hydrophobic polymer PSt as core and hydrophilic polymer poly (AMS-*co*-BA-*co*-AA) (PABA) as shell were prepared by a two-stage emulsion polymerization. The monomer BA was chosen for the reason that it could be copolymerized with kinds of monomers to synthesize kinds of copolymers, which can be used in coating, adhesive, etc. At the first stage, the PABA shell was prepared by soap-free emulsion polymerization, unlike common polymerizations, in which the core was always prepared first.<sup>26,27</sup> At the second stage, this hydrophilic AMS-containing prepolymer acted as macroinitiator. It was heated to generate macro-radicals on the AMS segments, which subsequently initiate the polymerization of St in the preformed particle. The PSt core thus obtained is covalently bonded with the hydrophilic AMS-containing prepolymer shell (Fig. 1). The effects of various polymerization conditions have also been investigated in this present work.

## EXPERIMENTAL

### Materials

$\alpha$ -Methylstyrene (AMS, Alfa Aesar), acrylic acid (AA, Aldrich), and butyl acrylate (BA, Aldrich) were distilled under vacuum. Styrene (St) was purchased from Beijing Chemical Reagent Corp. and was distilled under reduced pressure before use. Ammonium persulfate (APS) was purchased from Alfa Aesar and used as received. Aqueous ammonia was purchased from Beijing Chemical Reagent Corp. and used as received.

### Instruments

An FT-IR spectrometer (Hitachi 270-50) was used to detect the functional groups of the nanoparticles. The dried products were ground with KBr and pressed into tablet. Molecular weights and molecular weight polydispersities ( $M_w/M_n$ ) of the copolymers were determined by GPC (Waters 515-2410 system) calibrated by using polystyrenes as standards and

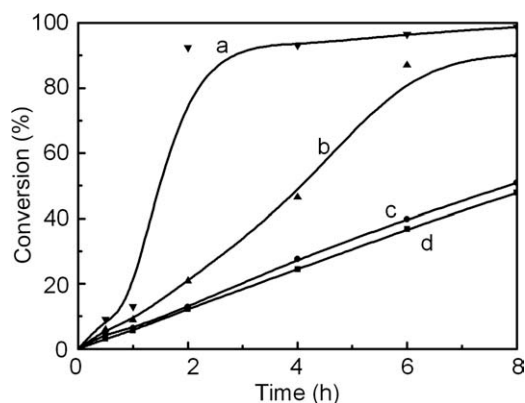
THF as an eluent. The particle size distribution was determined at 25°C in deionized water using a Zeta-PALS particle sizer (Brookhaven Instruments Co.). The particle morphology was characterized by transmission electron microscopy (TEM). XPS analysis was carried out on an ESCALAB 250 spectrometer using a monochromatized Al K $\alpha$  X-ray source at a constant analyzer.

### Synthesis of poly(AMS-*co*-BA-*co*-AA) (PABA) macroinitiator latex

Degassed water was introduced under Ar in the polymerization reactor. Distilled BA, AA, AMS, and ammonia solution buffer (25% in water) were charged under vigorous stirring and purged with argon. The mixture was kept at 45°C for a certain time to make all the monomers mixed thoroughly, and then heated to reaction temperature of 70°C. The polymerization was started by dropping slowly over a period of 10 min APS dissolved in water. After 24 h the polymerization was stopped. The percent conversion of monomers was determined gravimetrically.

### Synthesis of amphiphilic core-shell particles

After removing the residual APS and monomers by dialysis for several days, the PABA emulsion was mixed with purified St monomer in a water-jacketed flask equipped with a condenser, a magnetic stirrer, and an argon inlet. The stirred mixture was purged with argon for 20 min. No extra initiator was added, and the mixture was heated at 90°C for 4 h under argon. The percent conversion of St was determined gravimetrically. The obtained product was dried in a vacuum oven at 60°C until the weight was constant. Core-shell latex particles were characterized by Zeta-PALS particle sizer and transmission electron



**Figure 2** Dependence of monomers conversion as function of time in the polymerization of BA, AA, and AMS (AA/(AMS+BA) = 1/6 (mol/mol); APS/monomers = 11.2% (w/w); T = 70°C); (a) AMS/BA = 1/6; (b) AMS/BA = 1/2; (c) AMS/BA = 1/1; (d) AMS/BA = 2/1.

TABLE I  
Comparison of the Polymer Particle Diameters

Run	Step 1: PABA particles			Step 2: PSt/PABA core-shell particles			
	Monomer ratio [AMS]/[BA]	DPABA (nm)	$M_n$ , PABA (g/mol) <sup>a</sup>	DPS/PABA (nm)	PDI	CSt (%)	$M_n$ , PS/PABA (g/mol) <sup>a</sup>
1	1 : 10	215	57,400	282	0.069	73.5%	77,100
2	1 : 2	137	31,300	199	0.033	78.6%	67,300
3	1 : 1	109	13,600	137	0.014	79.6%	29,500
4	2 : 1	107	12,900	135	0.005	98.1%	28,700

<sup>a</sup> Values measured by GPC, calibrated with polystyrene standards.

microscopy (TEM) to determine particle size, particle polydispersity index (PDI), and morphology. And samples incorporating a PSt core and a PABA shell were synthesized.

## RESULTS AND DISCUSSION

### Synthesis and characterization of PABA macroinitiator latex

A series of reactions was conducted at 70°C for 24 h. Monomers feeds ranged in composition from AMS/BA = 1/10 to 2/1 (mol/mol), while the ratio of AA to above two monomers was 1/6 (mol/mol). Monomers conversion was determined by gravimetry on small emulsion samples withdrawn at regular time intervals. Figure 2 reports that as AMS content of the feed increases, the copolymerization rate and the monomers conversion decrease. With the concentration of AA constant, when the ratio AMS/BA increased from 1/6 to 2/1 (mol/mol), the monomers conversion decreased from 100 to 40% in 8 h. A similar behavior was observed in solution copolymerization of AMS and other monomers.<sup>19,20</sup> The nanoparticle size was determined by ZetaPALS particle sizer. From Table I, the particle size also reduced with the AMS content of the feed increased. These phenomena could be attributed to depropagation of AMS units or penultimate group effects to the steric restrictions on the placement of successive AMS units in the copolymer.<sup>28,29</sup> Table I also shows that the presence of AMS influences the molecular weight of the resulting copolymers. The number-average molecular weight ( $M_n$ ) of the copolymers reduced as  $f_{AMS}$  increased. With  $f_{AMS}$  increased from 0.078 to 0.571, the  $M_n$  of the copolymer reduced from 57,400 to 12,900 g/mol. These molecular weights are clearly higher than those observed in solution copolymerization,<sup>19,20</sup> which was caused by the low termination reaction rate of emulsion polymerization. Since AMS causes a drastic decrease in both the rate of polymerization and the average degree of polymerization, a conclusion can be drawn that the kinetic chain with a terminal AMS-radical would rather terminate with another radical or

transfer to a monomer than propagate in emulsion copolymerization.

### Synthesis and characterization of amphiphilic core-shell particles

PABA latex obtained above was diluted with water, and the new monomer St was then added into the reaction system, stirred at 90°C for 4 h under argon.

The FTIR spectra of the PABA prepolymer and the PSt/PABA copolymer are given in Figure 3. The phenyl peaks at 1947  $\text{cm}^{-1}$ , 1597  $\text{cm}^{-1}$ , 758  $\text{cm}^{-1}$ , and 680  $\text{cm}^{-1}$  are much more attractive in the spectrum of the PSt/PABA copolymer, than in the one of the PABA prepolymer. It thus demonstrated the St monomer did polymerize in the second stage polymerization.

From Table I, under the same conditions, the St monomer conversion increased as the AMS content of PABA macroinitiator increased. In contrast to the conversion, the molecular weight of block copolymer reduced when the AMS content of PABA macroinitiator increased. It agrees well with the preparation of block copolymers using AMS macroinitiators in solution, and the polymerization occurred at the AMS sites.<sup>20</sup> Only one peak was observed in the GPC spectrum of the products resulted from the second step polymerization of St (Fig. 4), and the

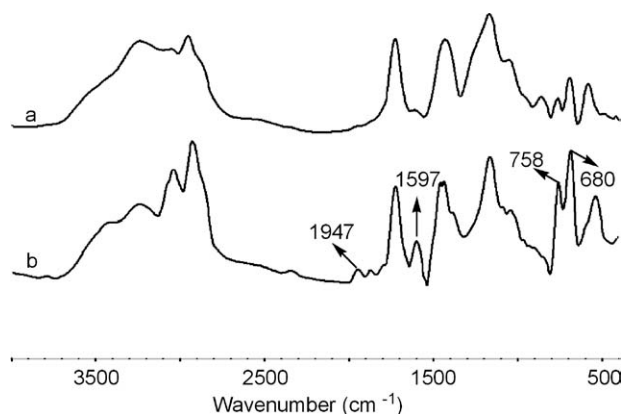
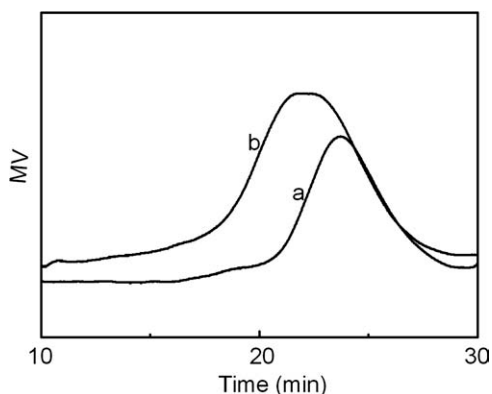


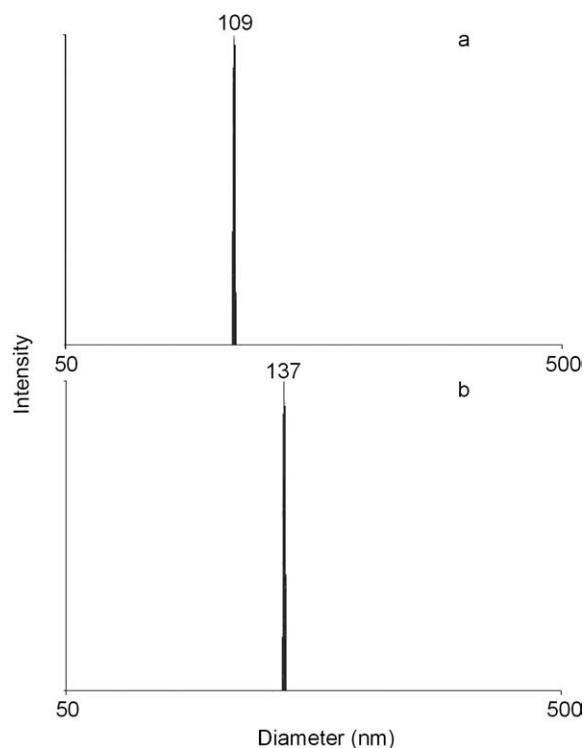
Figure 3 FT-IR spectra of (a) PABA prepolymer and (b) PSt/PABA copolymer.



**Figure 4** GPC spectra of (a) PABA and (b) PSt/PABA copolymer.

molecular weight of PS/PABA copolymer is larger than that of the original polymer PABA. This phenomenon further proved that the second step polymerization can only be initiated by PABA.

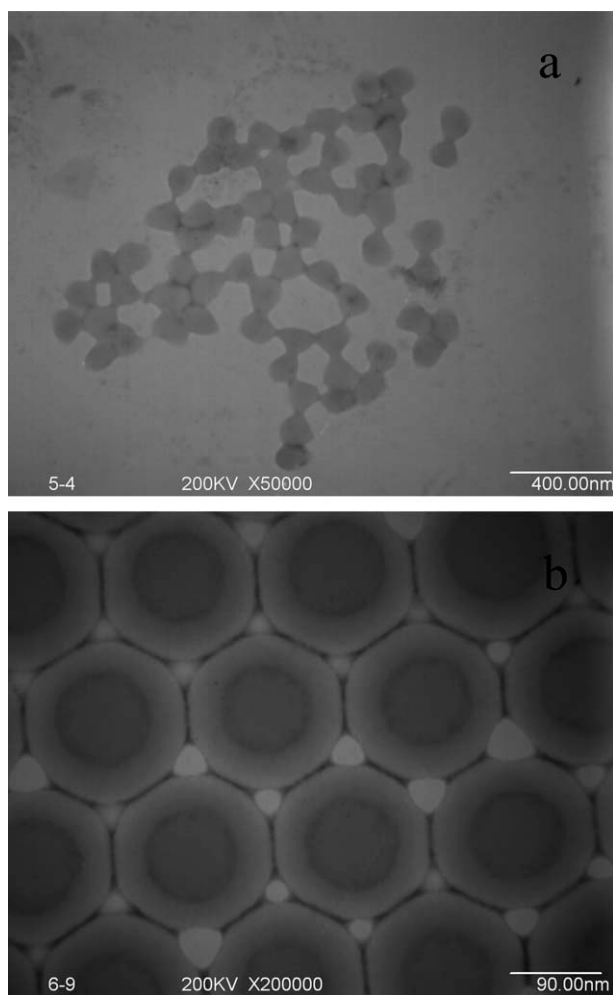
As predicted in Table I, the average size of PABA prepolymer particles obtained during the first stage of polymerization ranged between 107 and 215 nm. Average particle sizes increased after adding the St monomer in the second stage. Final particle sizes in the range of 126–282 nm in diameter were obtained.



**Figure 5** Particle size distribution histograms of (a) PABA prepolymer (AA/(AMS+BA) = 1/6 (mol/mol); APS/monomers = 11.2% (w/w);  $T = 70^{\circ}\text{C}$ ; AMS/BA = 1/1 (mol/mol)) and (b) core-shell copolymer (PSt/PABA = 3 : 2 (w/w),  $T = 90^{\circ}\text{C}$ ).

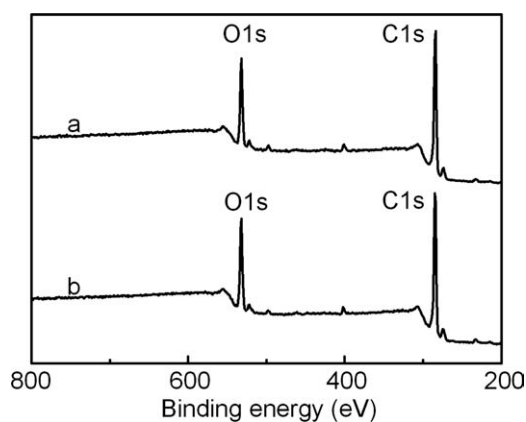
Figure 5 shows representative particle size distribution histograms of the PABA prepolymer and final copolymer particles. Both histograms indicate very narrow particle size distributions, indicating the average particle size increased monotonically.

Figure 6 shows typical TEM images of the PABA nanoparticles, and the PSt/PABA core-shell latex particles consisted of 60 wt % PSt and 40 wt % (speculated by the monomer conversions in both two stage polymerizations). In each case, uniform particles were obtained with a mean particle diameter of 109 nm and 137 nm, respectively. After PABA nanoparticles reacted with St, the particle size became larger, and the core-shell structure was obvious. The gray outside indicated PABA shell, while the dark inside indicated PSt core. At the mean time, no remaining PABA nanoparticles were observed, indicating that all the PABA particles had turned to be core-shell particles during the second stage polymerization.



**Figure 6** TEM pictures of (a) PABA prepolymer particles (scale bar = 400 nm) (AA/(AMS+BA) = 1/6 (mol/mol); APS/monomers = 11.2% (w/w);  $T = 70^{\circ}\text{C}$ ; AMS/BA = 1/1 (mol/mol)) and (b) core-shell copolymer particles (scale bar = 90 nm) (PSt/PABA = 3 : 2 (w/w),  $T = 90^{\circ}\text{C}$ ).



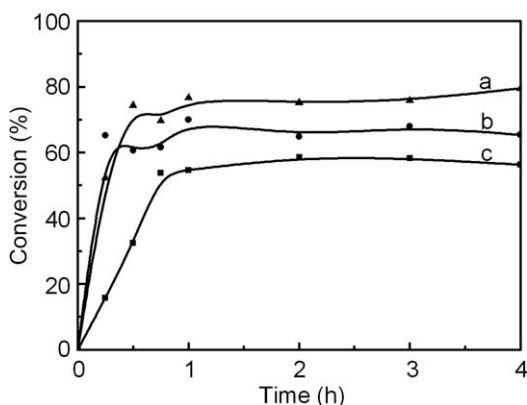


**Figure 7** XPS spectra for (a) PABA particle surfaces and (b) PSt/PABA core-shell particle surfaces.

XPS was employed to further determine the composition of the particle surface. It has a typical sampling depth of 2–5 nm. Figure 7 compares the XPS spectrum for the PABA prepolymer with that for the core-shell copolymer. The major peak component at the binding energy (BE) of approximately 284.6 eV was assigned to the C1s, and the minor peak component at the BE of 533.8 eV was attributed to O1s. If the shell consisted of PSt, the relative oxygen atomic concentration would be much lower than that of the PABA particle surfaces. However, as a result of the XPS spectra, the relative atomic concentrations of oxygen of the PABA particle surfaces and the core-shell particle surfaces were 18.8% and 18.2%, which were almost the same, providing a strong support for the conclusion that the shell was consisted of the PABA prepolymer.

#### Effect of PABA macroinitiator concentration

Figure 8 shows the results of the percent conversions of St with respect to different PABA prepolymer



**Figure 8** Dependence of monomer conversion as function of time in the polymerization of St initiated by PABA ([St] = 5.71% (wt %);  $T = 90^{\circ}\text{C}$ ): (a) [PABA] = 10.65% (wt %); (b) [PABA] = 7.11% (wt %); (c) [PABA] = 1.78% (wt %).

**TABLE II**  
Particle Diameters ( $M_n$  of PABA = 13,600 g/mol, DPABA = 109 nm, [St] = 5.71% (wt %),  $T = 90^{\circ}\text{C}$ , reaction time = 4 h)

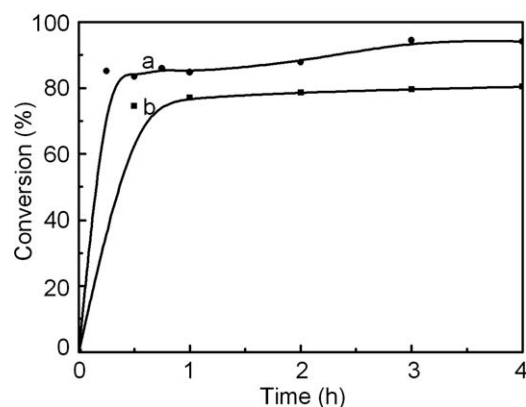
Run	PABA concentration (wt %)	$M_n$ , PS/PABA (g/mol) <sup>a</sup>	DPS/PABA (nm)	PDI
1	1.78	62,800	179	0.005
2	7.11	29,500	137	0.014
3	10.65	28,000	126	0.017

<sup>a</sup> Values measured by GPC, calibrated with polystyrene standards.

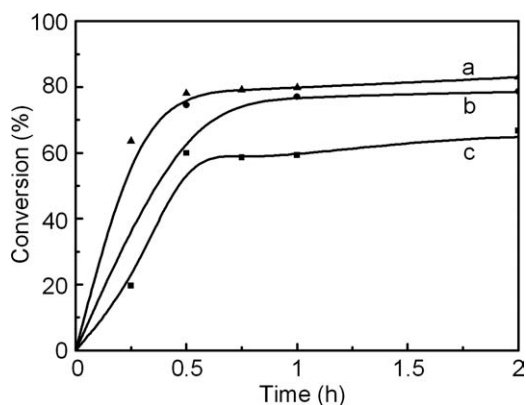
concentrations. When the PABA prepolymer concentration increased from 1.78% to 10.65%, the polymerization rate got accelerated, and the percent conversion of St was improved from 58.5% to 79.6%. Combined with the discussion about the effect of the remaining APS initiator, it can be further sure that PABA prepolymer did work as the macroinitiator during the second step polymerization. The increase of PABA macroinitiator concentration also had an influence on the particle diameter. The effective diameter of core-shell nanoparticles reduced from 179 to 126 nm, as the PABA macroinitiator concentration increased from 1.78% to 10.65% (Table II). As the macroinitiator concentration increased, the amount of particles where the second stage polymerization would occur also increased, by which the quantity of St monomer dispersed into every particle would reduce, causing the reduction of core-shell particle diameter.

#### Effect of the reaction temperature

It was found that the temperature had to be higher than  $80^{\circ}\text{C}$  to achieve a reasonable conversion in 4 h. Figure 9 shows the effect of reaction temperature



**Figure 9** Dependence of monomer conversion as function of time in the polymerization of St initiated by PABA ([PABA] = 3.55% (wt %); [St] = 5.71% (wt %)): (a)  $T = 95^{\circ}\text{C}$ ; (b)  $T = 90^{\circ}\text{C}$ .



**Figure 10** Dependence of monomer conversion as function of time in the polymerization of St initiated by PABA ([PABA] = 3.55% (wt %); [St] = 5.71% (wt %);  $T = 90^{\circ}\text{C}$ ): (a)  $t = 60$  min; (b)  $t = 20$  min; (c)  $t = 0$  min.

on the percent conversion St. When the reaction temperature increased from 90 to  $95^{\circ}\text{C}$ , the polymerization rate was also enhanced. When the temperature was set at  $95^{\circ}\text{C}$ , the percent conversion of St achieved 94.4% in less than half an hour, while the particle size almost kept constant, around 200 nm.

#### Effect of the swelling time of the monomer St

During the second step polymerization of St, after the prepared PABA emulsion was diluted with certain amount of water, stirred for 20 min, St was added. Then the whole reaction system was stirred for a certain time to make the St monomer disperse into the PABA particles, where the polymerization would occur. The dispersion time did influence the polymerization process (Fig. 10). Increasing the swelling time from 0 to 60 min, the percent conversion of St was improved from 66.8% to 86.1% in 2 h.

### CONCLUSIONS

Core-shell PS/PABA was prepared by a two-stage soap-free emulsion polymerization. Hydrophilic AMS-containing copolymer particles were first synthesized, and then underwent reaction in the presence of St to generate amphiphilic copolymer particles. During the reaction, AMS-containing copolymers were supposed to be both macroinitiator and surfactant. Since no small molecular initiator and surfactant were added in the second step, this process appears to be amenable to the commercial production of a wide variety of novel amphiphilic core-shell nanomaterials with different sizes, compositions, structures, and functions. Important features

include nanoparticle diameters ranging from 126 to 282 nm, narrow particle size distributions, covalent bonding between the core and shell, the ability to tailor the core diameter and shell thickness, the use of aqueous based chemistry, and a simple synthetic approach. These new materials should be extremely useful in a wide range of applications. Further studies in this direction are currently in progress.

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