Synthesis and Characterization of Amphiphilic Heterograft Copolymers with PAA and PS Side Chains via “Grafting From” Approach

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ABSTRACT: The amphiphilic heterograft copolymers poly(methyl methacrylate-co-2-(2-bromoisobutyryloxy)ethyl methacrylate)-graft-(poly(acrylic acid)/polystyrene) (P(MMA-co-BIEM)-g-(PAA/PS)) were synthesized successfully by the combination of single electron transfer-living radical polymerization (SET-LRP), single electron transfer-nitroxide radical coupling (SET-NRC), atom transfer radical polymerization (ATRP), and nitroxide-mediated polymerization (NMP) via the “grafting from” approach. First, the linear polymer backbones poly(methyl methacrylate-co-2-(2-bromoisobutyryloxy)ethyl methacrylate) (P(MMA-co-BIEM)) were prepared by ATRP of methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) and subsequent esterification of the hydroxyl groups of the HEMA units with 2-bromoisobutyl bromide. Then the graft copolymers poly(methyl methacrylate-co-2-(2-bromoisobutyryloxy)ethyl methacrylate)-graft-poly(t-butyl acrylate) (P(MMA-co-BIEM)-g-PtBA) were prepared by SET-LRP of t-butyl acrylate (tBA) at room temperature in the presence of 2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPO), where the capping efficiency of TEMPO was so high that nearly every TEMPO trapped one polymer radicals formed by SET. Finally, the formed alkoxy-amines via SET-NRC in the main chain were used to initiate NMP of styrene and following selectively cleavage of t-butyl esters of the PtBA side chains afforded the amphiphilic heterograft copolymers poly(methyl methacrylate-co-2-(2-bromoisobutyryloxy)ethyl methacrylate)-graft-(poly(t-butyl acrylate)/polystyrene) (P(MMA-co-BIEM)-g-(PtBA/PS)). The self-assembly behaviors of the amphiphilic heterograft copolymers P(MMA-co-BIEM)-g-(PAA/PS) in aqueous solution were investigated by AFM and DLS, and the results demonstrated that the morphologies of the formed micelles were dependent on the grafting density. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 4146–4153, 2011

INTRODUCTION Over the past few decades, amphiphilic graft copolymers have attracted considerable attention from polymer chemists because of their unique chemical and physical properties as well as their potential applications in drug delivery,1 tissue engineering,2 nanotechnology,3 polymer-hybrid nanocomposites,4 and supermolecular science.5 Since then, a variety of amphiphilic graft copolymers have been reported including the copolymers with one kind of side chains6–8 and the copolymers with various architecture and composition side chains, such as star-graft,9–11 block-graft,12–14 V-shaped graft,15–21 heterograft,22–25 and heterograft block structure.26–28 Generally, three strategies are utilized to synthesize amphiphilic graft copolymers: “grafting through,” “grafting onto,” and “grafting from”. By combining different polymerization techniques with three aforementioned synthetic strategies, a few of amphiphilic heterograft copolymers have been synthesized. Neugebauer et al. synthesized an amphiphilic heterograft copolymer with hydrophilic poly(ethylene glycol) side chains and hydrophobic octadecyl side chains by atom transfer radical polymerization (ATRP) via grafting through method.22 Riva et al. synthesized a amphiphilic heterograft copolymer with poly(ε-caprolactone) (PCL) and poly(ethylene oxide) (PEO) side chains by combining the grafting onto process based on atom transfer radical addition and the grafting from process by ATRP.24 Matyjaszewski reported the synthesis of poly[2-(trimethylsilyl)oxy]ethyl methacrylate co-poly(ethylene glycol) methyl ether methacrylate] (P(BPEM-co-PEOMA)) by ATRP via grafting through method. After transformation of 2-(trimethylsilyl)oxy)ethyl methacrylate (HEMA-TMS) units to 2-(2-bromopropionyloxy)ethyl methacrylate (BPEM), the resulting poly(PBPEM-co-PEOMA) initiates ATRP of nBA to afford a amphiphilic heterograft copolymer [poly(BPEM-co-PEOMA)-g-PnBA] with PnBA and PEO side chains.25 However, in all these cases, tedious steps were needed to separate the residue macromonomers or side chains from the final products.
Compared with two other methods, grafting from is the highly desirable method to synthesize the amphiphilic heterograft copolymers due to the relatively simple purification process. Thus, seeking a facile and convenient route to the amphiphilic heterograft copolymers is a fascinating subject for polymeric chemists.

Single electron transfer-living radical polymerization (SET-LRP), reported by Percec and coworkers in 2006, is a new LRP technique with a good prospect, and a series of well-defined polymers have already been synthesized successfully using SET-LRP at very mild reaction conditions. Our group reported a new coupling reaction termed single electron transfer-nitroxide radical coupling (SET-NRC). This reaction has the attributes of “click” reactions and has been used as a powerful tool in macromolecular modification and preparation of complex macromolecular architecture. In this article, the amphiphilic heterograft copolymers P(MMA-co-HEMA)-g-(PAA/PS) were synthesized by the combination of SET-LRP, SET-NRC, ATRP, and nitroxide-mediated polymerization (NMP) via the grafting from method (Scheme 1). All of the intermediates and final products were characterized with 1H NMR spectra and gel permeation chromatography (GPC). Moreover, the self-assembly behavior of the amphiphilic heterograft copolymers P(MMA-co-BIEM)-g-(PAA/PS) was also investigated by atomic force microscopy (AFM) and dynamic light scattering (DLS).

**EXPERIMENTAL**

**Materials**

2-Hydroxyethyl methacrylate (HEMA, 98%, J&K) was distilled under reduced pressure before use. Styrene [St, >99.5%, Sinopharm Chemical Reagent (SCR)] was washed with 10% NaOH aqueous solution and water three times.
successively, then dried over CaH₂ and distilled under reduced pressure. t-Butyl acrylate (tBA, 99%, SCR) and methyl methacrylate (MMA, 99%, SCR) were dried with CaH₂ over night and distilled before use. CuBr (95%, SCR) was stirred overnight in acetic acid, filtered, washed with ethanol and diethyl ether successively, and dried in vacuo. Copper powder (99%, Aldrich) was sealed in toluene and used without further purification. N,N,N',N''-pentamethylethylenetetramine (PMDETA, 99%, Aldrich), 2,2'-bipyridyl (bpy, 99%, Aldrich), 2-bromoisobutyryl bromide (98%, Aldrich), and trifluoroacetic acid (TFA, 99%, SCR) were used as received without further purification. Tetrahydrofuran (THF, 99%, SCR) was refluxed and distilled from potassium naphthalenide solution. Benzyl 2-bromoisobutyrate was synthesized according to the literature. All other reagents and solvents were used as received except for declaration.

Characterization

Gel permeation chromatography (GPC) was performed on an Agilent 1100 with a G1310A pump, a G1362A refractive-index detector, and a G1343A variable-angle detector, with THF as the eluent at a flow rate of 1.0 mL/min at 35 °C. Polystyrene standards were used for calibration. ¹H NMR spectra were recorded on a Bruker (500 MHz) NMR instrument using CDCl₃ and DMSO-d₆ as the solvent. Hydrodynamic diameter of the micelles was measured at concentrations of 0.1 mg/mL in aqueous solution on ALV/5000E laser light scattering spectrometers at scattering angle of 90 °C and temperature of 25 °C. AFM images were acquired in tapping mode by using a Nanoscope IV from Digital Instruments. For AFM observations, the samples were prepared by casting and drying the solution on freshly cleaved mica at room temperature.

Synthesis of the Linear Random Copolymer

P(MMA-co-HEMA) (1)

A typical polymerization procedure of P(MMA₁₅₂-co-HEMA₁₆) (Scheme 1) was described as follows: CuBr (283 mg, 0.197 mmol), bpy (61.6 mg, 0.395 mmol), benzyl 2-bromoisobutyrate (51.1 mg, 0.198 mmol), HEMA (2.0 mL, 16.5 mmol), MMA (8.7 mL, 82.5 mmol), and methanol (10 mL) were added to a Schlenk flask. The mixture was degassed by three freeze-pump-thaw cycles. Next, the reaction vessel was placed in an oil bath at 50 °C. After 5 h, the polymerization was terminated by quenching in liquid nitrogen followed by exposure to air. The polymer solution was diluted with THF and passed through a neutral alumina column to remove the copper catalyst. The solution was concentrated under reduced pressure, and the residue was precipitated twice in cyclohexane. The purified product was dried under vacuum until constant weight ($M_{n,\text{NMR}} = 17,300; M_{n,\text{GPC}} = 21,000, M_w/M_n = 1.14$).

Synthesis of P(MMA-co-BIEM) (2)

In a typical procedure, P(MMA₁₅₂-co-HEMA₁₆) (2.00 g, containing 1.63 mmol —OH; Scheme 1), triethylenediamine (1.13 mL, 8.12 mmol), and 30 mL dry THF were added to a round-bottomed flask. After cooling to 0 °C in an ice-water bath, 2-bromoisobutyryl bromide (1.00 mL, 8.12 mmol) was added dropwise to the rapidly stirring solution over 30 min. The reaction was performed for 1 h at 0 °C, and 24 h at room temperature. After most of the solvent was removed on a rotary evaporator, the concentrated solution was poured directly into water. The precipitate was dissolved in a small amount of THF and reprecipitated in water. The resulting precipitate was collected and dried at 35 °C under vacuum.

Synthesis of P(MMA-co-BIEM)-g-PtBA by SET-NRC and SET-LRP (3)

A typical polymerization procedure was described as follows. P(MMA₁₅₂-co-BIEM₁₆) (Scheme 1); 0.502 g, containing 0.392 mmol —Br), 2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPO; 33.6 mg, 0.196 mmol), tBA (1.2 mL, 8.28 mmol), PMDETA (67.5 mg, 0.196 mmol), and acetone (2 mL) were added to a Schlenk flask, and the reaction mixture was degassed by three freeze-pump-thaw cycles. Then nanosized Cu(0) (25.0 mg, 0.392 mmol) was introduced into the reaction system followed by another three freeze-pump-thaw cycles. Then the reaction vessel was immersed into an oil bath at 25 °C and lasted for 7 h. The polymerization was terminated via exposure to air and dilution with THF. The polymer solution was passed through a neutral alumina column to remove the copper complex. After most of the solvent was removed by evaporation, the residue was precipitated twice in the mixed solvent of methanol and water (v/v, 1:1). The purified product was dried under vacuum until constant weight ($M_{n,\text{NMR}} = 53,700; M_{n,\text{GPC}} = 48,100, M_w/M_n = 1.16$).

Synthesis of P(MMA-co-HEMA)-g-(PtBA/PS) by NMP (4)

A typical polymerization procedure was described as follows. The solution of P(MMA₁₅₂-co-BIEM₁₆)-g-PtBA₁₈ (0.600 g, 0.0168 mmol; Scheme 1) and styrene (4 mL) was added to a Schlenk flask and degassed by three freeze-pump-thaw cycles. The polymerization reaction was performed at 120 °C for 2.5 h and then was stopped by cooling to room temperature. The crude product was precipitated twice in the mixed solvent of methanol and water (v/v, 1:1). The purified product was dried under vacuum until constant weight ($M_{n,\text{NMR}} = 53,800; M_{n,\text{GPC}} = 65,900, M_w/M_n = 1.18$).

Cleavage of PS Side Chains from P(MMA-co-BIEM)-g-(PtBA/PS)

The copolymer P(MMA₁₀₇-co-BIEM₂₈)-g-(PtBA₁₅/PS₁₉) (0.2 g) was dissolved in 50 mL THF, to which 20 mL of KOH aqueous solution (1 M) was added. The mixture was refluxed for 3 days and then evaporated to dryness. The residue was dissolved with CH₂Cl₂ and washed with water. The organic layer was collected, concentrated under reduced pressure, and then precipitated in methanol. The obtained product was dried under vacuum.

Hydrolisis of P(MMA-co-BIEM)-g-(PtBA/PS)

A typical polymerization procedure was described as follows. The graft copolymers P(MMA₁₅₂-co-BIEM₁₆)-g-(PtBA₁₈/PS₂₁) (0.207 g, containing 0.390 mmol t-butyl ester groups) was dissolved in dry dichloromethane (20 mL) and TFA (0.30 mL, 3.90 mmol) was added. The solution was stirred at room temperature for 1 day. After a part of the solvent was
removed by evaporation, the copolymers P(MMA-co-HEMA)-
\textit{g}-(PAA/PS) was obtained by pouring the concentrated solu-
tion into petroleum ether. The resulting precipitate was col-
lected and dried under vacuum.

**Self-assembly of the Amphiphilic Heterograft Copolymers
P(MMA-co-HEMA)-\textit{g}-(PAA/PS)**

In a typical procedure, 10 mg of the copolymer P(MMA152-
co-HEMA16)-\textit{g}-(PAA/PS) was dissolved in mixed solvent of
5 mL DMF and 5 mL THF, and 20 mL of deionized water was
slowly added to the above solution at a rate of one drop ev-
every 15 s by a microsyringe under rapidly stirring. The solu-
tion was dialyzed against deionized water using a dialysis
bag (MW cutoff 14 kDa). After 2 days, the micelle solution
was transferred to a 100-mL flask, and deionized water was
added to make the concentration of micelle solution to be
0.1 mg/mL.

**RESULTS AND DISCUSSION**

**Synthesis of the linear polymer backbones
P(MMA-co-BIEM)**

As summarized in Table 1, two P(MMA-co-HEMA) copoly-
mers with different compositions were synthesized by ATRP
of MMA and HEMA at 50 °C using benzyl 2-bromoisobuty-
rate as initiator and CuBr/bpy as catalyst. The phenyl group
on the initiator can be used to calculate the degree of poly-
merization (DP) of the random copolymer by \textit{1}H NMR. A typ-
ical \textit{1}H NMR spectrum of P(MMA152-co-HEMA16) is given in
Figure 1(A) (the number of subscript stands for the DP of
each monomer). The DP of MMA and HEMA repeating units
in main chains were derived from the relative integration ra-
tio of peaks (a) at 7.41 ppm, (b) at 3.99 ppm, and (c) at
3.50 ppm, assigned to the phenyl ring protons (C\textit{6}H\textit{5}CH2O\textit{A})
and methylene protons (HOCH\textit{2}C\textit{H}2OCO\textit{A}) of

![FIGURE 1](https://www.materialsviews.com/)

**TABLE 1** Characterization of the Amphiphilic Heterograft Copolymers P(MMA-co-BIEM)-\textit{g}-(PAA/PS)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Backbone M\text{M}a \text{A}</th>
<th>Backbone HEMA</th>
<th>Side Chains tBA</th>
<th>Side Chains St</th>
<th>\textit{M}_a a (KDa)</th>
<th>\textit{M}_b a (KDa)</th>
<th>\textit{M}_w/b \text{M}_a/b</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(MMA152-co-HEMA16)</td>
<td>152</td>
<td>16</td>
<td>0</td>
<td>0</td>
<td>17.3</td>
<td>21</td>
<td>1.14</td>
</tr>
<tr>
<td>P(MMA107-co-HEMA38)</td>
<td>108</td>
<td>28</td>
<td>0</td>
<td>0</td>
<td>14.4</td>
<td>22.6</td>
<td>1.15</td>
</tr>
<tr>
<td>P(MMA152-co-HEMA16)-\textit{g}-(PtBA18)</td>
<td>152</td>
<td>16</td>
<td>18</td>
<td>0</td>
<td>35.7</td>
<td>48.1</td>
<td>1.16</td>
</tr>
<tr>
<td>P(MMA107-co-HEMA38)-\textit{g}-(PtBA18)</td>
<td>108</td>
<td>28</td>
<td>15</td>
<td>0</td>
<td>41.3</td>
<td>59.8</td>
<td>1.16</td>
</tr>
</tbody>
</table>

\textit{a} Measured by \textit{1}H NMR spectroscopy.

\textit{b} Measured by GPC using PS as standard performed in THF.
HEMA units and methyl protons ($\text{CH}_3\text{OCO}$) of MMA units, respectively. The density of the pendant hydroxyl groups can be tuned by the feed ratio of MMA to HEMA. Figure 2 is the GPC diagram, it can be observed that both of the curves of P(MMA$_{152}$-co-HEMA$_{16}$) (A) and P(MMA$_{107}$-co-HEMA$_{28}$) (A') were a single peak with a narrow molecular weight distribution around 1.14, indicating the well control of polymerization.

Esterification of the copolymers P(MMA-co-HEMA) with 2-bromoisobutyryl bromide afforded the copolymers with pendant SET-LRP initiating groups, assigned as P(MMA-co-BIEM). Comparing the $^1$H NMR spectrum of P(MMA$_{152}$-co-BIEM$_{16}$) (B) with that of P(MMA$_{152}$-co-HEMA$_{16}$) (A) in Figure 1, the newly appearing peak (d) at 4.33 ppm is assigned to the methylene protons ($\text{CH}_3\text{BrCCOO}$) of BIEM units. Moreover, the integration of peak (d) is almost equal to that of peak (b), meaning the esterification reaction was performed completely.

Synthesis of the Amphiphilic Heterograft Copolymers P(MMA-co-BIEM)-g-(PAA/PS)

The investigation of our and Monteiro’s groups demonstrated that a carbon-centered radicals generated under SET conditions could be trapped by TEMPO (or TEMPO containing polymers) with approximate diffusion-controlled rates in SET-NRC reaction. Moreover, the formed alkoxyamines can readily decouple to the incipient radicals and parent nitrooxide at elevated temperature. Herein, we designed and synthesized the graft copolymers P(MMA-co-BIEM)-g-PtBA by SET-LRP of tBA using the copolymers P(MMA-co-BIEM) as macroinitiator in the presence of a calculated amount of TEMPO ([TEMPO]/[Br]-1/2 (mol/mol)). In this case, a part of the generated radicals in BIEM units of the main chain by SET would be trapped immediately, and another 50% Br groups of BIEM units would initiate the polymerization of tBA. In this case, the alkoxyamine bonds were stable because of the lower polymerization temperature during SET-LRP, and these bonds can be used as the potential NMP initiating groups for styrene polymerization in the elevated temperature. As shown in Figure 2, the GPC curves of the obtained graft copolymer [Fig. 2(B,B')] clearly shift to the higher molecular weight region compared with that of precursors [Fig. 2(A,A')], and the molecular weight distribution is still narrow (1.15), indicating SET-LRP was successful. In a typical $^1$H NMR spectrum of P(MMA$_{152}$-co-BIEM$_{16}$)-g-PtBA$_{18}$ [Fig. 1(C)], the peaks (e) at 3.95 ppm and (f) at 2.20 ppm corresponding to the methine protons ($-\text{CH}_2\text{CH}(\text{COOC}(\text{CH}_3)\text{Br})$) neighboring terminal bromine and the methine protons ($-\text{CH}_2\text{CH}(\text{COOC}(\text{CH}_3)\text{Br})$) of the PtBA side chains, respectively, were clearly observed. The average DP of PtBA side chains can be calculated by the relative integration of the peaks (e) and (f). Based on the DPs, the molecular weight of the copolymers P(MMA-co-BIEM)-g-PtBA can be calculated according to the following formula:

$$M_\text{n,NMR} = M_\text{n,NMR}^0 + N_{\text{PtBA}} \times DP \times 128$$

where $M_\text{n,NMR}$ is the molecular weight of the copolymers P(MMA-co-BIEM)-g-PtBA; $M_\text{n,NMR}^0$ is the molecular weight of the polymer backbone P(MMA-co-BIEM); $N_{\text{PtBA}}$ is the number of PtBA side chains, and 128 is the molecular weight of the monomer tBA.

The heterograft copolymers P(MMA-co-HEMA)-g-(PtBA/PS) were synthesized by NMP of St using P(MMA-co-HEMA)-g-PtBA as macroinitiator. As shown in Figure 2, both of the
GPC curves of the obtained two polymers P(MMA-co-BIEM)-g-(PtBA/PS) displayed a monomodal peak with narrow molecular weight distribution in the higher molecular weight region, indicating NMP was successful. In a typical \(^1\)H NMR spectrum of P(MMA-co-BIEM)-g-(PtBA/PS) [Fig. 1(D)], the characteristic signal of St repeating units (peak g) at 6.27–7.22 ppm was clearly observed, further demonstrating the successful synthesis of the mixed graft copolymers P(MMA-co-BIEM)-g-(PtBA/PS). The average DP of PS side chains can be calculated by the relative integration of the peaks (g) and (f). And the molecular weight of the copolymers P(MMA-co-BIEM)-g-(PtBA/PS) can be evaluated on the following formula:

\[ M_{n,NMR} = M_{n,NMR0} + N_{PS} \times \text{DP} \times 108 \]  

where \( M_{n,NMR} \) is the molecular weight of the copolymers P(MMA-co-BIEM)-g-(PtBA/PS); \( M_{n,NMR0} \) is the molecular weight of the polymer backbone P(MMA-co-BIEM)-g-PtBA; \( N_{PS} \) is the number of PS side chains, and 108 is the molecular weight of the monomer styrene.

To explore the rate of TEMPO trapping radicals in SET-LRP of tBA, PS side chains were cleaved from the copolymers P(MMA-co-BIEM)-g-(PtBA/PS). In the \(^1\)H NMR spectrum of PS side chains cleaved from the copolymer P(MMA\textsubscript{107}-co-HEMA\textsubscript{28})-g-(PtBA\textsubscript{15}/PS\textsubscript{19}) (Fig. 3), the characteristic signals of the methine protons of tBA units did not observed, that means the rate of TEMPO trapping the radicals was so fast that the radicals generated under SET conditions were capped by TEMPO instantly.

According to the literature, PtBA can be easily hydrolyzed by anhydrous TFA in dichloromethane. By selective hydrolysis of the PtBA side chains, the amphiphilic heterograft copolymers P(MMA-co-BIEM)-g-(PAA/PS) consisting of the hydrophilic PAA and hydrophobic PS segments were obtained. A typical \(^1\)H NMR spectrum of P(MMA\textsubscript{152}-co-HEMA\textsubscript{16})-g-(PAA\textsubscript{16}/PS\textsubscript{21}) is given in Figure 4, it can be observed that the characteristic peak (i) at 12.0–13.0 ppm assigned to the protons of carboxyl groups clearly appeared, revealing that the hydrolysis reaction was successful.

Self-Assembly of the Amphiphilic Heterograft Copolymers P(MMA-co-HEMA)-g-(PAA/PS)

As many other amphiphilic copolymers with different structure, amphiphilic heterograft copolymers could also self-assemble into micellar-like structure in aqueous solution. Figure 5 shows AFM tapping mode height images of the amphiphilic heterograft copolymers P(MMA-co-BIEM)-g-(PAA/PS) on mica surface from dilute solutions. From the images, it was found that the morphologies of the formed micelles were affected by the grafting density of side chains. Spherical micelles were formed from the copolymer P(MMA\textsubscript{152}-co-HEMA\textsubscript{16})-g-(PAA\textsubscript{16}/PS\textsubscript{21}); however, approximately rod-like micelles were formed by the P(MMA\textsubscript{107}-co-HEMA\textsubscript{28})-g-(PAA\textsubscript{15}/PS\textsubscript{19}). In the copolymer backbone with the higher grafting density, the copolymer may be difficult to be coiled as a result of the steric hindrance between graft side chains. The size distributions of the micelles formed by the copolymers P(MMA-co-BIEM)-g-(PAA/PS) were determined by DLS (Fig. 6). From Figure 6, it can be observed

FIGURE 4 \(^1\)H NMR spectrum for P(MMA\textsubscript{152}-co-BIEM\textsubscript{16})-g-(PAA\textsubscript{16}/PS\textsubscript{21}) in the mixed solvent of CDCl\textsubscript{3} and DMSO (v/v, 1:1).

FIGURE 5 AFM images of P(MMA\textsubscript{152}-co-BIEM\textsubscript{16})-g-(PAA\textsubscript{16}/PS\textsubscript{21}) (A) and P(MMA\textsubscript{107}-co-BIEM\textsubscript{28})-g-(PAA\textsubscript{15}/PS\textsubscript{19}) (B) on the surface of mica.
that the size distribution of the micelles for P(MMA107-co-BIEM28)-g-(PAA15/PS19) was symmetrical. However, for the P(MMA152-co-BIEM16)-g-(PAA18/PS21), the size distribution was anomalous. The DLS results are basically consistent with that of AFM.

CONCLUSIONS

A facile and convenient route for the synthesis of the amphiphilic heterograft copolymers via grafting from method was provided, which was based on the combination of SET-LRP and NMP polymerization techniques. The polymer backbones P(MMA-co-BIEM) with pendant bromine groups were first synthesized. Then in the presence of TEMPO ([TEMPO]/[−Br]:1/2 (mol/mol)), nearly half of Br groups were capped by TEMPO and the graft half of Br groups was used to initiate the polymerization of tBA by SET, the trapping efficiency of TEMPO is extremely high. The amphiphilic heterograft copolymers P(MMA-co-BIEM)-g-(PAA/PS) was obtained by using the resultant alkoxyamines to initiate NMP of styrene at the elevated temperature and followed by selective hydrolysis of PtBA side chains. The self-assembly behaviors of the mixed amphiphilic graft copolymers P(MMA-co-BIEM)-g-(PAA/PS) confirmed that the morphologies of the formed micelles changed from spherical to approximately rod-like with increasing the grating density.

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REFERENCES AND NOTES