One-Pot Synthesis of PS-b-PEO-b-PrBA Triblock Copolymers via Combination of SET-LRP and “Click” Chemistry Using Copper(0)/PMDETA as Catalyst System

Rongkuan Jing, Guowei Wang, Yannan Zhang, and Junlian Huang*

The Key Laboratory of Molecular Engineering of Polymer, State Education Ministry of China, Department of Macromolecular Science, Fudan University, Shanghai 200433, China

Received November 18, 2010; Revised Manuscript Received January 7, 2011

ABSTRACT: Triblock copolymers of polystyrene-block-poly(ethylene oxide)-block-poly(tert-butyl acrylate) (PS-b-PEO-b-PrBA) were prepared via combination of single electron transfer living radical polymerization (SET-LRP) with “click” chemistry using Cu(0)/N,N,N′,N″,N‴-pentamethyldiethylenetriamine (PMDETA) as catalyst system. The ω,ω-heterofunctionalized PEO with an ethoxyl-protected hydroxyl group and an active hydroxyl group was synthesized via anionic ring-opening polymerization (ROP) of ethylene oxide (EO) using potassium 2-(1-ethoxyethoxy)ethoxide as initiator. After further modifications of the end groups, the PEO with alkylne and bromine groups was obtained. Meanwhile, bromine-terminated polystyrene (PS-Br) was synthesized by atom transfer radical polymerization (ATRP), then the bromine end groups were transformed to azide groups by nucleophilic substitution reaction in N,N-dimethylformamide (DMF) in the presence of excessive sodium azide. Lastly, in the presence of Cu(0)/PMDETA, bromine end group of PEO initiated the polymerization of tert-butyl acrylate (tBA) by SET-LRP, the formed Cu(I) in situ was used directly to catalyze the “click” coupling between azide group of PS and alkyn group of PEO. Thus, the triblock copolymers PS-b-PEO-b-PrBA could be prepared by one-pot strategy. The obtained triblock copolymers and intermediates were characterized by SEC, 1H NMR, and FT-IR in detail.

Introduction

Molecular design of block copolymers constitutes a very important research field, because of their great applications in self-assembly. Generally, two strategies were used for the preparation of block polymers: sequential polymerizations of different monomers or coupling reaction of polymers with preformed functional groups. With the fast development of controlled polymerization technique and efficient coupling reaction, various kinds of block copolymers with different compositions were prepared precisely, such as diblock, triblock, and multiblock. Of these block copolymers, ABC triblock copolymers have attracted much attention for their unique structure with three different blocks, which may lead to potentially novel properties for further applications.

Poly(ethylene oxide) (PEO) has been widely used as hydrophilic block in amphiphilic ABC triblock copolymers, owing to its intrinsic properties, such as high polarity, crystallizability, and biocompatibility. Generally, the PEO block is located at the end of ABC triblock copolymer. Herein, exploring a simple and efficient synthetic route of ABC triblock copolymer with PEO as middle block is an attractive work.

It is well-known that 1,3-dipolar cycloaddition (SET-LRP) of azides and alkynes had a dramatic improvement of cycloaddition reaction rate owing to the introduction of Cu(I) catalysis, which was termed as “click” chemistry by Sharpless. The potential of “click” chemistry has been proven by the successful synthesis of copolymers with different architectures such as linear, star, graft, cyclic, and dendritic.

Recently, single electron transfer living radical polymerization (SET-LRP) emerged as a new powerful polymerization technique for the rapid synthesis of tailored polymers with perfect retention of chain-end functionality at room temperature. In SET-LRP, Cu(I) could be generated via the oxidation of Cu(0) by SET mechanism. Therefore, it is promising to utilize Cu(I) generated from Cu(0) in SET-LRP to catalyze the “click” reaction by a one-pot process, which may be used in the synthesis of ABC triblock copolymers.

In the present work, we report a novel strategy combining SET-LRP technique with “click” chemistry using Cu(0)/N,N,N′,N″,N‴-pentamethyldiethylenetriamine (PMDETA) as catalyst system, which was adopted for the synthesis of ABC triblock copolymer polystyrene-block-poly(ethylene oxide)-block-poly(tert-butyl acrylate) (PS-b-PEO-b-PrBA), in which Cu(I) generated in situ by SET mechanism was utilized directly to catalyze “click” chemistry.

Experimental Section

Materials. Ethylene oxide (EO, Sinopharm Chemical Reagent (SCR)) was dried by CaH₂ for 48 h and distilled under N₂ before use. Styrene (St, 99.5%) purchased from SCR was washed with a 15% NaOH aqueous solution and water successively, dried over anhydrous MgSO₄, further dried over CaH₂, and then distilled under reduced pressure twice before use. tert-Butyl acrylate (tBA, 99%, Aldrich), propargyl bromide (99%), and N,N-dimethylformamide (DMF, 99%, SCR) were dried over CaH₂ and distilled under reduced pressure before use. Tetrahydrofuran (THF, 99%, SCR) and pyridine (99.5%, SCR) were refluxed and distilled from sodium naphthalenide solution and sodium, respectively. Toluene (99%, SCR) were dried over CaH₂ 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. Cu(0) (99.9%, Aldrich), 2-bromoisoobutyric bromide (98%, Aldrich), PMDETA (Aldrich), ethyl 2-bromoisoobutyrate (EBB, Aldrich), formic acid, sodium azide (NaN₃, > 98%), and potassium hydroxide (KOH) were used as received. And other reagents were all purchased from SCR and used as received, unless otherwise noted.

Diphenylmethyl potassium (DPMK) solution was freshly prepared by the reaction of potassium naphthalenide with diphenylmethane in THF according to the literature, the concentration was 0.61 M. 2-(1-Ethoxyethoxy)ethanol was synthesized by protecting one hydroxyl group of ethylene glycol with ethyl vinyl ether according to Fittion et al. 33

Synthesis of α-Ethoxyethyl-ω-hydroxyl Poly(ethylene oxide) (EE−PEO−OH). The initiator solution was prepared according to the following procedure: To a 250 mL three-necked glassware were added dry THF (210 mL) and 2-(1-ethoxyethoxy) ethanol (12.7 g, 0.095 mol). With the bubbling of dry nitrogen, potassium (3.9 g, 0.1 mol) with a fresh surface was added. After stirring for 24 h, the solution was filtered and titrated with 0.1 M HCl, and the concentration was 0.45 M. The typical polymerization procedure was performed as follows: A 150 mL kettle was vacuumed at 80 °C for 24 h and cooled to room temperature and then to −20 °C; given volumes of the initiator solution (10.8 mL, 4.9 mmol), EO (44.0 g, 440 mmol), and THF (60 mL) were introduced successively. The system was heated to 60 °C under stirring for 48 h, and the reaction was terminated by the addition of few drops of methanol. The polymer was precipitated via the solvent exchange of the methylene chloride and precipitated into an excessive amount of methanol with a fresh surface. After removing the solvent, the mixture was diluted with diethyl ether three times. The precipitate was dried under vacuum at 40 °C for 30 min under vigorous stirring, and the mixture was stirred at room temperature for another 24 h. The crude product was concentrated and purified by dialysis against water to remove salts, and the final product Br−PEO−alkyne with khaki color was obtained by precipitation in diethyl ether twice and dried under vacuum at 40 °C until constant weight (4.5 g, yield: 91.2%). 1 H NMR (CDCl 3 ), δ (ppm): 0.70−0.99 (9H, −C(CH 3 ) 3−PS), 1.20−2.15 (2H, −CH 2 −CH−of PS), 3.44−3.63 (2H, 2H, −CH 2 −CH−of PS), 4.41−4.52 (2H, −CH(Ph)−Br), 6.30−7.30 (3H, 5H, −C 6 H 5 of PS), Conversion: 14.1%. SEC: Mw 8600 g/mol; PDI: 1.10.

Preparation of α-(2-Bromoisobutyril)-ω-proprargyl Poly(ethylene oxide) (Br−PEO−Alkyn). Heterofunctionalized Br−PEO−alkyne was obtained by nucleophilic substitution of the hydroxyl group (on EE−PEO−OH) into alkyn group, then hydrolysis of the ethoxyethyl group into hydroxy group, and final esterification of the recovered hydroxyl group into 2-bromoisobutyl group, respectively.

The typical preparation procedure for heterofunctionalized α-ethoxyethyl-ω-proprargyl poly(ethylene oxide) (EE−PEO−Alkyn) was as follows. A 250 mL dry round-bottom flask was charged with CuBr/PMDETA (0.144 g, 1.0 mmol) and St (20 mL, 175 mmol) was dissolved in 10 mL of toluene. The mixture was added to a 50 mL Schlenk flask and degassed by three freeze−pump−thaw cycles. The flask was immersed in oil bath at 90 °C for 2.5 h. After quenching the reaction with 10 mL of water, the mixture was stirred at room temperature for another 24 h. The crude product was collected, and the final product was obtained by precipitation in diethyl ether twice and dried under vacuum at 40 °C (1.10 g, 0.42 mmol) was dissolved in 10 mL of DMF; then, 0.1 g of sodium azide (0.273 g, 4.2 mmol) was added to the solution. The mixture was stirred at room temperature overnight. After precipitation into methanol/water mixture (1/1 by volume), the product was collected and dried under vacuum at 40 °C until constant weight (1.05 g, yield: 95.5%). 1 H NMR (CDCl 3 ), δ (ppm): 0.70−0.99 (9H, −C(CH 3 ) 3−PS), 1.20−2.15 (2H, −CH 2 −CH−of PS), 3.44−3.63 (2H, 2H, −CH 2 −CH−of PS), 3.95 (1H, −CH(Ph)−N 3 of PS), 6.30−7.30 (3H, 5H, −C 6 H 5 of PS). SEC: Mw 2600 g/mol; PDI: 1.09.

Synthesis of α-Azide−Poly(Styrene) (PS−N 3 ). First, PS with bromomethyl group (PS−Br) was prepared by ATRP of St in toluene, using EBB as initiator and CuBr/PMDETA as catalyst. EBB (0.15 mL, 1.0 mmol), CuBr (0.144 g, 1.0 mmol), PMDETA (0.21 mL, 1.0 mmol), and St (20 mL, 175 mmol) were dissolved in 10 mL of toluene. The mixture of the solution was stirred at room temperature for another 24 h. The crude product was collected and dried under vacuum at 40 °C for 12 h. 1 H NMR (CDCl 3 ), δ (ppm): 0.70−0.99 (9H, −C(CH 3 ) 3−PS), 1.20−2.15 (2H, −CH 2 −CH−of PS), 3.44−3.63 (2H, 2H, −CH 2 −CH−of PS), 4.41−4.52 (2H, −CH(Ph)−Br), 6.30−7.30 (3H, 5H, −C 6 H 5 of PS), Conversion: 14.1%. SEC: Mw 2600 g/mol; PDI: 1.09.

Then, PS−N 3 was prepared by the nucleophilic substitution reaction transforming active bromine group to azide group. PS−Br (1.10 g, 0.42 mmol) was dissolved in 10 mL of DMF; then, 0.1 g of sodium azide (0.273 g, 4.2 mmol) was added to the solution. The mixture was stirred at room temperature overnight. After precipitation into methanol/water mixture (1/1 by volume), the product was collected and dried under vacuum at 40 °C until constant weight (1.05 g, yield: 95.5%). 1 H NMR (CDCl 3 ), δ (ppm): 0.70−0.99 (9H, −C(CH 3 ) 3−PS), 1.20−2.15 (2H, −CH 2 −CH−of PS), 3.44−3.63 (2H, 2H, −CH 2 −CH−of PS), 3.95 (1H, −CH(Ph)−N 3 of PS), 6.30−7.30 (3H, 5H, −C 6 H 5 of PS). SEC: Mw 2600 g/mol; PDI: 1.09.

Synthesis of PS−H−PEO−H−PrBA. Typically, the reaction was carried out by the following procedure: Into a 50 mL Schlenk flask, Br−PEO−alkyne [Mw SEC: 8600 g/mol] 0.2 g (0.032 mmol), PS−N 3 [Mw SEC: 2600 g/mol] 0.078 g, 0.03 mmol, βBA (0.2 g, 1.54 mmol), PMDETA (0.025 mL, 0.12 mmol), and DMF (4.5 mL) were added. Oxygen was removed from the solution by three freeze−pump−thaw cycles. Cu(0) (0.007 g, 0.11 mmol) was quickly added to the frozen solution and the flask was evacuated, backfilled with N 2 and sealed. The reaction mixture was stirred at room temperature for 24 h and then immersed in liquid nitrogen. After centrifuging, the product was diluted with methylene chloride and passed through an activated neutral alumina column to remove the copper salts. After removal of solvents under reduced pressure, the crude product was extracted with cyclohexane/paraffin ether mixture (1/1 by volume) to remove unreacted PS. After centrifuging, the white product was collected and dried under vacuum at 40 °C.

1 H NMR (CDCl 3 ), δ (ppm): 0.70−0.99 (9H, −C(CH 3 ) 3−PS), 1.20−2.15 (m, 14H, −CH 2 −CH−of PS), 3.44−3.57 (m, −CH 2 −CH−of PEO), 3.50−3.63 (m, −CH 2 −CH−of PEO).
Measurements. SEC was performed on an Agilent 1100 with a G1314A variable-wavelength detector with THF as the eluent at a flow rate of 1.0 mL/min at 35°C. One 5 μm LP gel column (500 E, molecular range 500 – 2 x 10^6 g/mol) and two 5 μm LP gel mixed bed columns (molecular range 200 – 3 x 10^5 g/mol) were calibrated by polystyrene standards. For PEO, SEC was performed in 0.1 M aqueous NaNO₃ at 40°C with an elution rate of 0.5 mL/min with the same instruments, except that the G1314A variable-wavelength detector was substituted by a G1315A variable-wavelength detector with THF as the eluent 0.5 mL/min with the same instruments, except that the G1314A variable-wavelength detector was substituted by a G1315A variable-wavelength detector with THF as the eluent.

Results and Discussion

Synthesis and Characterization of Precursor Polymers Br−PEO−Alkyne and PS−N₃. The process for synthesis of Br−PEO−alkyne was described in Scheme 1. First, EE−PEO−OH was synthesized by the anionic ring-opening polymerization method. The SEC curve of EE−PEO−OH in Figure 1 showed a monomodal peak with PDI of 1.10. Figure 2A showed the ¹H NMR spectrum of EE−PEO−OH. The resonance signals of methyl protons (“a, c”) and methine proton (“d”) in 1-ethoxyethyl group appeared at 1.19–1.30 and 4.66 ppm, respectively, which confirmed the successful synthesis of PEO with ethoxyl-protected hydroxyl group. The alkyne group was introduced to end of EE−PEO−OH by the nucleophilic substitution reaction between active hydroxyl group and propargyl bromide at 0°C. The ¹H NMR spectrum of EE−PEO−alkyne is shown in Figure 2B, two new resonance signals of protons (“f, g”) in propargyl group appeared at 4.20 and 2.44 ppm, after the hydroxyl group was transformed into propargyl group. The efficiency of modification of alkyne group (E.F.(Alkyne)) can be determined on the basis of end group analysis using the following formula 1:

\[
E.F.(\text{Alkyne}) = \frac{6A_f}{2A_{a+c}}
\]  

where \(A_{a+c}\) represents the integral area sum of the methyl protons (“a, c”) in 1-ethoxyethyl group at 1.19–1.30 ppm and \(A_f\) represents the integral area of the methylene protons (“f”) in propargyl group at 4.20 ppm, as shown in Figure 2B. The value of E.F.(Alkyne) is 99.1% (see Table 1, entry P1).

In order to recover the reactive hydroxyl group on EE−PEO−alkyne, the 1-ethoxyethyl group on polymer was removed by hydrolysis in formic acid. The complete removal of the 1-ethoxyethyl group was confirmed by ¹H NMR analysis. As Figure 2C showed that the resonance signals at 4.66 ppm and 1.19–1.30 ppm assigned to the ethoxyl group of EE−PEO−alkyne was then esterified with 2-bromoisobutyryl bromide to obtain Br−PEO−alkyne. The molecular weight of Br−PEO−alkyne determined by
The absorption band at 1726 cm$^{-1}$ showed that heterofunctionalized PEO with low PDI and the band at 3250 cm$^{-1}$ of E.F.(Alkyne) is 99.5% (see Table 1, entry P1).

SEC using PEO as standard was 8600 g/mol with a PDI of 1.10. In $^1$H NMR analysis (Figure 3B), the resonance signal at 1.94 ppm assigned to the methyl protons (“k”) of the 2-bromoiso butyryl group, which confirmed that the reaction was successful. The functionalization efficiency of PEO end groups, calculated from $^1$H NMR data on formulas 1) or (2 in text, respectively.

The precursor PS–Br was synthesized by ATRP using EBiB as initiator and CuBr/PMDETA as catalyst. The reaction was stopped at low conversion (under 30%) to ensure a high degree of bromine chain-end functionality. PS–Br samples with different molecular weights were obtained by stopping the reaction at different time. Then, the terminal bromine groups were transformed into azide groups by the nucleophilic substitution reaction with sodium azide.

The $^1$H NMR spectra of PS–N$_3$ is shown in Figure 3A.

Table 1. Data for Precursor Polymers Br–PEO–Alkyne and PS–N$_3$

<table>
<thead>
<tr>
<th>entry</th>
<th>polymer</th>
<th>$M_n$SEC (g/mol)</th>
<th>PDI</th>
<th>alkyne$^a$</th>
<th>bromine$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>PEO$^b$</td>
<td>8600$^b$</td>
<td>1.10$^b$</td>
<td>99.1</td>
<td>99.5</td>
</tr>
<tr>
<td>P2</td>
<td>PS$_1$$^c$</td>
<td>2600$^c$</td>
<td>1.09$^c$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P3</td>
<td>PS$_2$$^c$</td>
<td>5100$^c$</td>
<td>1.10$^c$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Br–PEO–alkyne. $^b$Determined by SEC, calibrated against PEO standard and 0.1 M NaNO$_3$ as eluent. $^c$PS–N$_3$, obtained via azidation of PS–Br, experimental conditions of PS–Br: [St]:[EBiB]:[CuBr]:[PMDETA] = 175:1:1:1. different molecular weight obtained by stopping at 2.5 and 4 h, respectively. $^d$Determined by SEC using PS as standard and THF as eluent. $^e$The functionalization efficiencies of PEO end groups, calculated from $^1$H NMR data on formulas 1) or (2 in text, respectively.

The precursor PS–Br was synthesized by ATRP using EBiB as initiator and CuBr/PMDETA as catalyst. The reaction was stopped at low conversion (under 30%) to ensure a high degree of bromine chain-end functionality. PS–Br samples with different molecular weights were obtained by stopping the reaction at different time. Then, the terminal bromine groups were transformed into azide groups by the nucleophilic substitution reaction with sodium azide.

The $^1$H NMR spectra of PS–N$_3$ is shown in Figure 3A.

The disappearance of the peak at 4.41–4.52 ppm (the resonance signal of methine proton in $-\text{CH(Ph)}-Br$ functional group) and appearance of a new peak at 3.95 ppm (resonance signal of the methine proton (“g”) in $-\text{CH- (Ph)}-N_3$ functional group) confirmed that the azidation was complete. In typical FT-IR spectrum of PS–N$_3$ (Figure 4A), the observation of the characteristic absorption band at 2108 cm$^{-1}$ further indicated the existence of azide group in the polymer. Table 1 (entry P2, P3) summarized the data of precursor PS–N$_3$, which showed that the precursor polymers were prepared with predetermined molecular weight and low PDI.

**Figure 4. FT-IR spectra of triblock copolymer and its precursor copolymers: (A) PS–N$_3$, (B) Br–PEO–alkyne, and (C) triblock copolymer PS-b-PEO-b-PrBA.**

The disappearance of the peak at 4.41–4.52 ppm (the resonance signal of methine proton in $-\text{CH(Ph)}-Br$ functional group) and appearance of a new peak at 3.95 ppm (resonance signal of the methine proton (“g”) in $-\text{CH- (Ph)}-N_3$ functional group) confirmed that the azidation was complete. In typical FT-IR spectrum of PS–N$_3$ (Figure 4A), the observation of the characteristic absorption band at 2108 cm$^{-1}$ further indicated the existence of azide group in the polymer. Table 1 (entry P2, P3) summarized the data of precursor PS–N$_3$, which showed that the precursor polymers were prepared with predetermined molecular weight and low PDI.

**Synthesis and Characterization of Triblock Copolymers PS-b-PEO-b-PrBA by One-Pot Method.** The one-pot procedure was carried out in presence of Cu(0)/PMDETA at room temperature, in which Br–PEO–alkyne initiated the polymerization of tBA by SET-LRP, in this case, Cu(I) was formed by single electron transfer of Cu(0), then “click” reaction between azide and alkyn functional groups was performed in the presence of Cu(I)/PMDETA (Scheme 2).

A series of triblock copolymers were prepared by varying feeding quantity of tBA monomer and molecular weight ($M_n$) of PS–N$_3$. The concentration of Br–PEO–alkyne was set low to 0.005 M, due to its high molecular weight. The feeding PS–N$_3$ was excessive comparing with Br–PEO–alkyne, the molar ratio was about 1.3/1. The crude product could be purified by extraction with cyclohexane/petroleum ether mixture (1/1 by volume). The SEC curve of triblock copolymer PS-b-PEO-b-PrBA was shown in Figure 1, a Gaussian distribution with narrow PDI was observed, that meant the excess PS precursor was completely removed.

The $^1$H NMR spectrum of triblock copolymer was depicted in Figure 3C, in which three main regions could be observed. The resonance signal at 2.22 ppm assigned to methine protons (“n”) of the tBA units, the signal at 6.30–7.30 ppm assigned to phenyl protons (“l”) of the St units, and the signal at 3.50–3.80 ppm assigned to the methylene protons (“m”) of the EO units were detected, respectively. The appearance of a new resonance signal at 5.07 ppm assigned to the methine proton (“o”) of $-\text{CH(Ph)}-\text{triazole}$ supported the azide group of PS was converted into 1,2,3-triazole group. The resonance signal assigned to the methylene protons (“n”) of the propargyl end group was shifted from 4.20 to 4.62 ppm. All these results indicated the occurrences of

**Figure 3. $^1$H NMR spectra of (A) PS–N$_3$, (B) Br–PEO–alkyne, and (C) PS-b-PEO-b-PrBA (solvent: CDCl$_3$).**
Further evidence for the formation of triblock copolymer were observed in the FT-IR spectrum (Figure 4C). The characteristic absorption band at 3000–3100 cm$^{-1}$ of $\text{C} \equiv \text{H}$ aromat on PS segment, and the characteristic band at 1100–1200 cm$^{-1}$ of $\text{C} = \text{O} - \text{C}$ on PEO segment, could be detected easily. Because of the introducing of PBa segment, the characteristic band at 1726 cm$^{-1}$ in Figure 4C obviously intensified, compared with the spectra of PS$ - N_3$ (Figure 4A) and Br$ - \text{PEO} - \text{alkyne}$ (Figure 4B). Besides, a new absorption band at 1646 cm$^{-1}$ for $\text{C} = \text{N}$ of triazole on the triblock copolymer could also be detected. These results further confirmed the ABC triblock was prepared successfully.

To obtain the number of BrA units on ABC triblock copolymer ($N_{\text{BrA}}$) and coupling efficiency of “click” chemistry (E.F.\textsubscript{Click}), the following formulas 3 and 4 from corresponding integrated area ratio in $^1$H NMR were used, respectively. The data are listed in Table 2.

$$N_{\text{BrA}} = \frac{A_n}{A_j} \times \left( \frac{M_{\text{PEO}}}{44} \times 4 \right)$$

(3)

$$\text{E.F.\textsubscript{Click}} = \frac{A_j}{A_j} \times \left( \frac{M_{\text{PEO}}}{44} \times 4 \right) \times 100\%$$

(4)

where 44 and 104 are the molecular weight of EO and St monomers, respectively. $A_n$ represents the integral area sum of the methine protons (“$n$”) in the BrA units at 2.22 ppm, $A_j$ represents the integral area sum of the methylene protons (“$j$”) at 3.50–3.80 ppm, and $A_r$ represents the integral area sum of the phenyl protons (“$r$”) at 6.30–7.30 ppm in $^1$H NMR spectrum (Figure 3C).

Table 2 summarized all the data of ABC triblock copolymer. The coupling efficiencies of “click” chemistry were relatively high. It was found that when the molecular weight of PS$ - N_3$ increased, the coupling efficiency would reduce somewhat (Table 2, entries T2, T3). The number of BrA units on copolymer could be controlled by varying the feeding quantity of BrA monomer (Table 2, entries T1, T2). The successful synthesis of ABC triblock copolymer PS-b-PEO-b-PBa showed the one-pot technique combining SET-LRP with “click” chemistry in the presence of Cu(0)/PMDETA was feasible.

**Conclusion**

In summary, ABC triblock copolymer with PEO as middle block was successfully synthesized at room temperature via the combination of SET-LRP and “click” chemistry in presence of Cu(0)/PMDETA. The Cu(I) generated from Cu(0) by SET mechanism was utilized smartly to catalyze “click” reaction. The synthetic approach is simple and efficient, which provides a new choice for the synthesis of polymers with more complex microstructures under mild conditions.

**Acknowledgment.** We appreciate the financial support of this research by the Natural Science Foundation of China (No. 20874013) and the Natural Science Foundation of Shanghai (No.08ZR1400800).

**References and Notes**


(9) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. Angew. Chem., Int. Ed. 2002, 41, 2596.