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One-Pot Synthesis of PS-*b*-PEO-*b*-P*t*BA Triblock Copolymers via Combination of SET-LRP and "Click" Chemistry Using Copper(0)/PMDETA as Catalyst System

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ABSTRACT: Triblock copolymers of polystyrene-*block*-poly(ethylene oxide)-*block*-poly(*tert*-butyl acrylate) (PS-*b*-PEO-*b*-P*t*BA) 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 α,ω-heterofunctionalized PEO with an ethoxyethyl-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 alkyne 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 (*t*BA) by SET-LRP, the formed Cu(I) in situ was used directly to catalyze the "click" coupling between azide group of PS and alkyne group of PEO. Thus, the triblock copolymers PS-*b*-PEO-*b*-P*t*BA could be prepared by one-pot strategy. The obtained triblock copolymers and intermediates were characterized by SEC, ^{1}H NMR, and FT-IR in detail.

Introduction

Molecular design of block copolymers constitutes a very important research field,[1] because of their great applications in self-assembly.[2] Generally, two strategies were used for the preparation of block polymers: sequential polymerizations of different monomers[3] or coupling reaction of polymers with preformed functional groups.[4] With the fast development of controlled polymerization technique[5−8] and efficient coupling reaction,[4,9] various kinds of block copolymers with different compositions were prepared preciously, such as diblock,[4] triblock,[10] and multiblock.[11] 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.[12,13]

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.[14−17] The reports about ABC triblock copolymers with PEO as the middle block are much fewer for the difficulty in synthesis.[18,19] 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[20] of azides and alkynes had a dramatic improvement of cycloaddition reaction rate owing to the introduction of Cu(I) catalysis,[21] which was termed as "click" chemistry by Sharpless.[9,22] The potential of "click" chemistry has been proven by the successful synthesis of copolymers with different architectures,[23] such as linear,[16] star,[24] graft,[25,26] cyclic,[27] and dendritic.[28]

Recently, single electron transfer living radical polymerization[8] (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.[8,29−33] In SET-LRP, Cu(I) could be generated via the oxidation of Cu(0) by SET mechanism.[30] 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*-P*t*BA), 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 CaH_2 for 48 h and distilled under N_2 before use. Styrene (St, 99.5%) purchased from SCR was washed with a 15% NaOH aqueous solution and water successively, dried over anhydrous $MgSO_4$, further dried over CaH_2, and then distilled under reduced pressure twice before use. *tert*-Butyl acrylate (*t*BA, 99%, Aldrich), propargyl bromide (99%), and *N*,*N*-dimethylformamide (DMF, 99%, SCR) were dried over CaH_2 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 CaH_2 and distilled before use. CuBr (95%, SCR) was stirred

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overnight in acetic acid, filtered, washed with ethanol and diethyl ether successively, and dried in vacuo. Cu(0) (99%, Aldrich), 2-bromoisobutyryl bromide (98%, Aldrich), PMDETA (Aldrich), ethyl 2-bromoisobutyrate (EBiB, Aldrich), formic acid, sodium azide (NaN_3, >98%), and potassium hydroxide (KOH) were used as received. And other reagents were all purchased from SCR and used as received, unless otherwise noted.

Diphenylmethylpotassium (DPMK) solution was freshly prepared by the reaction of potassium naphthalenide with diphenylmethane in THF according to the literature,[34] 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 Fitton et al.[35]

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, 1.0 mol), 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. After removing the solvent, the mixture was diluted with methylene chloride and precipitated into an excessive amount of diethyl ether three times. The precipitate was dried under vacuum at 40 °C for 12 h, and the white powder was obtained (40.7 g, yield: 91.2%). ^{1}H NMR ($CDCl_3$) δ ppm: 1.19−1.30 (m, 6H, $CH_3CH_2OCH(CH_3)O-$), 3.50−3.80 (m, $-CH_2CH_2O-$ of PEO and CH_3CH_2O-), 4.66 (1H, $CH_3CH_2OCH(CH_3)O-$). Size-exclusion chromatography (SEC): M_n, 8600 g/mol; polydispersity index (PDI), 1.10.

Preparation of α-(2-Bromoisobutyryl)-*ω*-propargyl Poly(ethylene oxide) (Br−PEO−Alkyne). Heterofunctionalized Br−PEO−alkyne was obtained by nucleophilic substitution of the hydroxyl group (on EE−PEO−OH) into alkyne group, then hydrolysis of the ethoxyethyl group into hydroxyl group, and final esterification of the recovered hydroxyl group into 2-bromoiso butyryl group, respectively.[36]

The typical preparation procedure for heterofunctionalized α-ethoxyethyl-*ω*-propargyl poly(ethylene oxide) (EE−PEO−alkyne): To a 250 mL dried ampule were added EE−PEO−OH (10 g, 1.12 mmol) and THF (60 mL). Then the system was bubbled with N_2, and DPMK solution was introduced until the solution turned reddish-brown. After the ampule was placed in ice bath, propargyl bromide (0.5 mL, 0.67 g, 5.60 mmol) was added dropwise during 2 h, and the reaction continued for 24 h at room temperature. The EE−PEO−alkyne was obtained by separation of the formed salts and precipitation in diethyl ether twice, and dried under vacuum at 40 °C until constant weight (9.65 g, yield: 96.5%). ^{1}H NMR ($CDCl_3$) δ ppm: 1.19−1.30 (m, 6H, $CH_3CH_2OCH(CH_3)O-$), 2.44 (t, 1H, $-OCHH_2C{\equiv}CH$), 3.50−3.80 (m, $-CH_2CH_2O-$ of PEO and CH_3CH_2O-), 4.20 (d, 2H, $-OCHH_2C{\equiv}CH$), 4.66 (1H, $CH_3CH_2OCH(CH_3)O-$).

The typical preparation procedure for heterofunctionalized α-hydroxyl-*ω*-propargyl poly(ethylene oxide) (HO−PEO−alkyne): EE−PEO−alkyne (8 g, 0.93 mmol) was mixed with excess formic acid (30 mL), the solution was stirred at room temperature for 30 min and then evaporated under reduced pressure to remove formic acid. After the product was again dissolved in a mixture of dioxane (45 mL) and methanol (25 mL), the solution was alkalized with KOH aqueous solution (pH > 12) and refluxed for 24 h, then neutralized with HCl aqueous solution (1.0 M). The khaki copolymer HO−PEO−alkyne was obtained by separation of the formed salts and precipitation in diethyl ether twice and dried under vacuum at 40 °C until constant weight (7.3 g, yield: 91.3%). ^{1}H NMR ($CDCl_3$) δ ppm: 2.44 (t, 1H, $-OCHH_2C{\equiv}CH$), 3.50−3.80 (m, $-CH_2CH_2O-$ of PEO), 4.20 (d, 2H, $-OCHH_2C{\equiv}CH$).

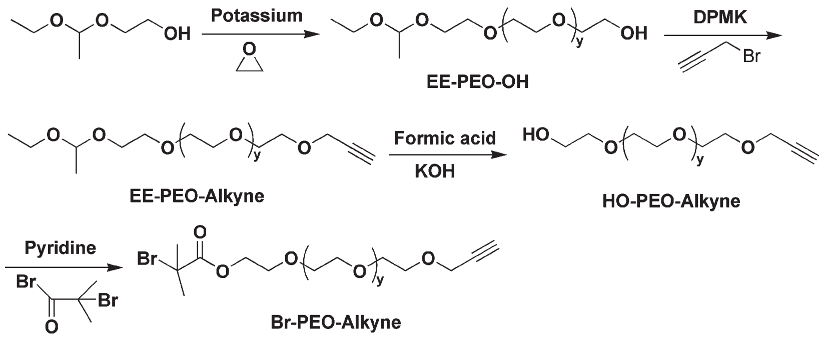
The typical preparation procedure for heterofunctionalized α-(2-bromoiso butyryl)-*ω*-propargyl poly(ethylene oxide) (Br−PEO−alkyne): Dried HO−PEO−alkyne (5 g, 0.58 mmol) was dissolved in anhydrous pyridine (80 mL), then 2-bromoisobutyryl bromide (0.11 mL, 0.87 mmol) was added dropwise at 0 °C for 30 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: 90%). ^{1}H NMR ($CDCl_3$) δ ppm: 1.94 (s, 6H, $-C(CH_3)_2Br$), 2.44 (t, 1H, $-OCHH_2C{\equiv}CH$), 3.50−3.80 (m, $-CH_2CH_2O-$ of PEO), 4.20 (d, 2H, $-OCHH_2C{\equiv}CH$). FT-IR (cm^{-1}): 1100−1200 (−C−O−C−), 1726 (−COO−), 3250 (−C≡CH). SEC: M_n, 8600 g/mol; PDI, 1.10.

Synthesis of *ω*-Azide−Polystyrene (PS−N_3). First, PS with bromine group (PS−Br) was prepared by ATRP of St in toluene, using EBiB as initiator and CuBr/PMDETA as catalyst. EBiB (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 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. The reaction was stopped via dipped in liquid nitrogen. The products were diluted with THF, passed through a column chromatograph filled with neutral alumina to remove the copper complex, and precipitated in cold methanol. The precipitate was collected and dried under vacuum at 40 °C for 12 h. ^{1}H NMR ($CDCl_3$), δ (ppm): 0.70−0.99 (m, 9H, $-C(CH_3)_2-$PS, CH_3CH_2O-), 1.20−2.15 (m, 3H, $-CH_2CH-$ of PS), 3.44−3.63 (m, 2H, CH_3CH_2O-), 4.41−4.52 (m, 1H, $-CH$(Ph)−Br), 6.30−7.30 (m, 5H, $-C_6H_5$ of PS). Conversion: 14.1%. SEC: M_n, 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 (m, 9H, $-C(CH_3)_2-$PS, CH_3CH_2O-), 1.20−2.15 (m, 3H, $-CH_2CH-$ of PS), 3.44−3.63 (m, 2H, CH_3CH_2O-), 3.95 (m, 1H, $-CH$(Ph)−N_3), 6.30−7.30 (m, 5H, $-C_6H_5$ of PS). SEC, M_n: 2600 g/mol, PDI: 1.09. FT-IR- (cm^{-1}): 1454, 1494, 1601 (aromatic, −C−C−), 1726 (−COO−), 2108 (−N_3) and 3000−3100 (aromatic, −C−H).

Synthesis of PS-*b*-PEO-*b*-P*t*BA. Typically, the reaction was carried out by the following procedure: Into a 50 mL Schlenk flask, Br−PEO−alkyne [($M_{n\ SEC}$: 8600 g/mol) 0.2 g, 0.023 mmol], PS−N_3 [($M_{n\ SEC}$: 2600 g/mol) 0.078 g, 0.03 mmol], *t*BA (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 re-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/petroleum 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 (m, 9H, $-C(CH_3)_2-$PS, CH_3CH_2O-), 1.20−2.15 (m, 14H, $-CH_2CH-$ o fPS,

Scheme 1. Schematic Synthesis Route of Br−PEO−Alkyne



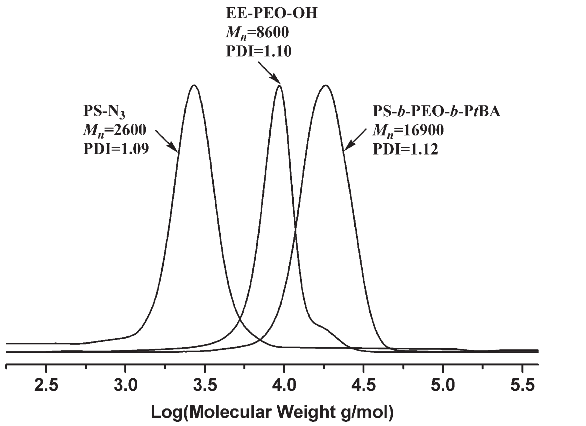


Figure 1. SEC curves of PS−N_3, EE−PEO−OH, and triblock copolymer PS-*b*-PEO-*b*-P*t*BA.

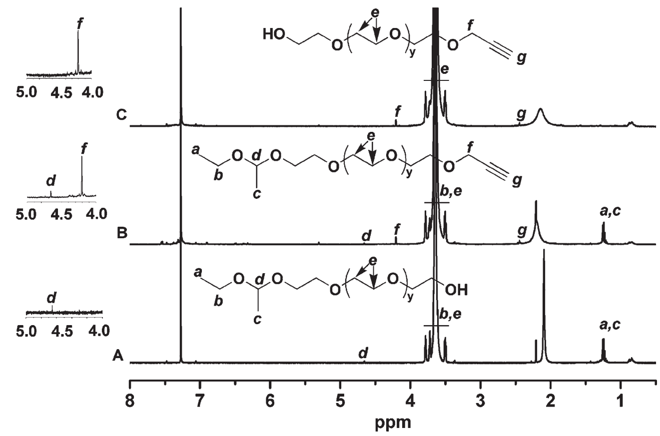


Figure 2. ^{1}H NMR spectra of heterofunctionalized PEO (solvent: $CDCl_3$): (A) EE−PEO−OH, (B) EE−PEO−alkyne, and (C) HO−PEO−alkyne.

−CH_2CH− and −C(CH_3)$_3$ of P*t*BA), 2.22 (s, 1H, −CH_2*CH*− of P*t*BA), 3.50−3.80 (m, −CH_2CH_2O− of PEO), 4.19 (1H, −*CH*-Br of P*t*BA), 4.62 (m, 2H, −CH_2CH_2OCH_2−triazole ring), 5.07 (m, 1H, −*CH*(Ph)−triazole), 6.30−7.30 (m, 5H, C_6H_5 of PS). SEC: M_n, 16 900 g/mol; PDI, 1.12. FT-IR(cm^{-1}): 1100−1200 (−C−O−C−), 1646 (−C═N−), 1726 (−COO−) and 3000−3100 (aromatic, −C−H).

Measurements. SEC was performed on an Agilent 1100 with a G1310A pump, a G1362A refractive-index detector, and 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 500−2×10^4 g/mol) and two 5 μm LP gel mixed bed columns (molecular range 200−3 × 10^6 g/mol) were calibrated by polystyrene standards. For PEO, SEC was performed in 0.1 M aqueous $NaNO_3$ 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 diode-array detector, and PEO standards were used for calibration. ^{1}H NMR spectra were obtained at a DMX500 MHz spectrometer with tetramethylsilane (TMS) as the internal standard and $CDCl_3$ as the solvent. Fourier transform infrared (FT-IR) spectra were recorded on a Magna-550 FT-IR spectrometer (NaCl tablet).

Results and Discussion

Synthesis and Characterization of Precursor Polymers Br−PEO−Alkyne and PS−N_3. 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 of EO with potassium 2-(1-ethoxyethoxy) ethoxide as the initiator and THF as solvent. The SEC curve of EE−PEO−OH in Figure 1 showed a monomodal peak with PDI of 1.10. Figure 2A showed the ^{1}H 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 ethoxyethyl-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 ^{1}H 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.$_{(\text{Alkyne})}$) can be determined on the basis of end group analysis using the following formula 1:

$$\text{E.F.}_{(\text{Alkyne})} = \frac{6A_f}{2A_{a+c}} \quad (1)$$

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.$_{(\text{Alkyne})}$ 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 ^{1}H NMR analysis. As Figure 2C showed that the resonance signals at 4.66 ppm and 1.19−1.30 ppm assigned to the 1-ethoxyethyl group disappeared completely after hydrolysis, so the HO−PEO−alkyne was really formed. The hydroxyl group of HO−PEO−alkyne was then esterified with 2-bromoisobutyryl bromide to obtain Br−PEO−alkyne. The molecular weight of Br−PEO−alkyne determined by

Table 1. Data for Precursor Polymers Br−PEO−Alkyne and PS−N_3

				E.F. (%)	
entry	polymer	$M_{n\ SEC}$ (g/mol)	PDI	alkyne[e]	bromine[e]
P1	PEO[a]	8600[b]	1.10[b]	99.1	99.5
P2	PS1[c]	2600[d]	1.09[d]		
P3	PS2[c]	5100[d]	1.10[d]		

[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.

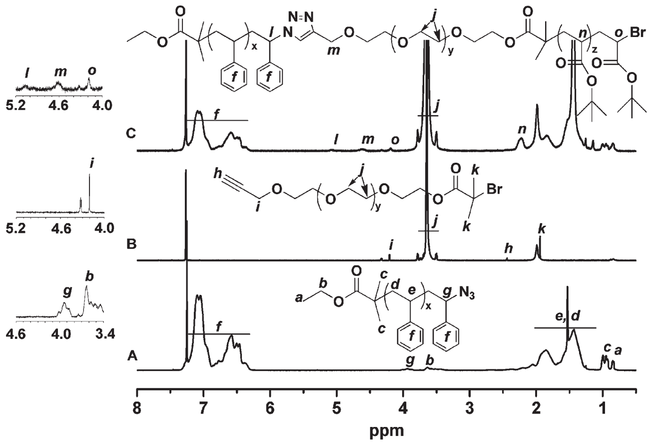


Figure 3. ^{1}H NMR spectra of (A) PS−N_3, (B) Br−PEO−alkyne, and (C) PS-*b*-PEO-*b*-P*t*BA (solvent: $CDCl_3$).

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 2-bromoiso butyryl group appeared after esterification reaction, which confirmed that the reaction was successful. The efficiency of esterification (E.F.$_{(\mathrm{Bromine})}$) can be determined on the basis of end group analysis using the following formula 2:

$$\mathrm{E.F.}_{(\mathrm{Bromine})} = \frac{2A_k}{6A_i} \qquad (2)$$

where A_k represents the integral area of the methyl protons ("k") in 2-bromoiso butyryl group at 1.94 ppm and A_i represents the integral area of the methylene protons ("i") in propargyl group at 4.20 ppm, as shown in Figure 3B. The value of E.F.$_{(\mathrm{Alkyne})}$ is 99.5% (see Table 1, entry P1).

Figure 4B was the FT-IR spectrum of Br−PEO−alkyne. The absorption band at 1726 cm^{-1} of ester bond stretching and the band at 3250 cm^{-1} of alkyne group gave the further support to the existence of 2-bromoiso butyryl and alkyne groups in the polymer. All the data of precursor Br−PEO−alkyne were summarized in Table 1(entry P1), which showed that heterofunctionalized PEO with low PDI was prepared with high functionality efficiencies.

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.[37] 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.

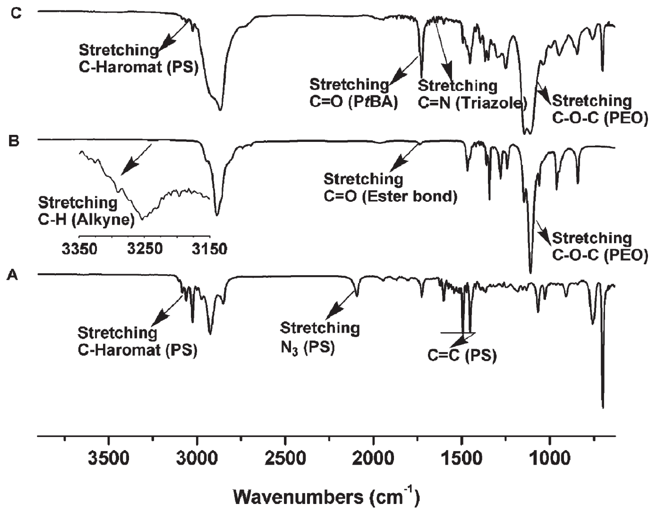


Figure 4. FT-IR spectra of triblock copolymer and its precursor copolymers: (A) PS−N_3, (B) Br−PEO−alkyne, and (C) triblock copolymer PS-*b*-PEO-*b*-P*t*BA.

The disappearance of the peak at 4.41−4.52 ppm (the resonance signal of methine proton in −C***H***(Ph)−Br functional group) and appearance of a new peak at 3.95 ppm (resonance signal of the methine proton ("g") in −C***H***-(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*-P*t*BA 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 *t*BA by SET-LRP,[30] in this case, Cu(I) was formed by single electron transfer of Cu(0), then "click" reaction between azide and alkyne functional groups was performed in the presence of Cu(I)/ PMDETA (Scheme 2).[21]

A series of triblock copolymers were prepared by varying feeding quantity of *t*BA 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*-P*t*BA is 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 *t*BA units, the signal at 6.30−7.30 ppm assigned to phenyl protons ("f") of the St units, and the signal at 3.50−3.80 ppm assigned to the methylene protons ("j") of the EO units were detected, respectively. The appearance of a new resonance signal at 5.07 ppm assigned to the methine proton ("l") of −C*H*(Ph)−triazole supported the azide group of PS was converted into 1,2,3-triazole group. The resonance signal assigned to the methylene protons ("m") of the propargyl end group was shifted from 4.20 to 4.62 ppm. All these results indicated the occurrences of

Scheme 2. Schematic One-Pot Synthesis of PS-*b*-PEO-*b*-P*t*BA via Combination of SET-LRP and "Click" Chemistry

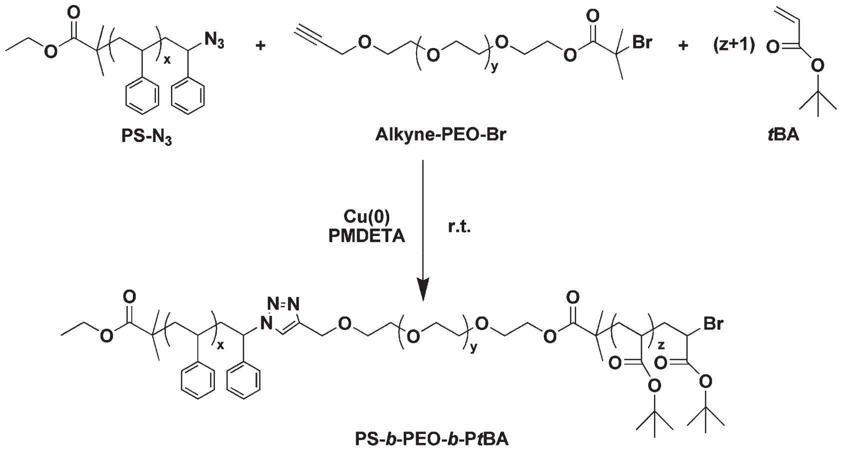


Table 2. Data for One-Pot Synthesis of PS-*b*-PEO-*b*-P*t*BA[a]

entry	*t*BA [M]/[I][b]	PS−N_3	PS-*b*-PEO-*b*-P*t*BA $M_{n,SEC}$[c] (g/mol)	PDI[c]	N_{tBA}[d]	E.F.$_{(Click)}$[e] (%)
T1	67	PS1	16 900	1.12	36.1	95.7
T2	33	PS1	13 800	1.07	15.5	96.4
T3	33	PS2	12 700	1.13	17.5	92.8

[a] Experimental conditions: [Br−PEO−alkyne]:[PS−N_3]:[Cu(0)]:[PMDETA] = 1:1.3:5:5; [Br−PEO−alkyne] = 0.005 M; conducted in DMF at room temperature. [b] Molar ratio of monomer *t*BA and macroinitiator Br−PEO−alkyne. [c] Determined by SEC using PS as standard and THF as eluent. [d] N_{tBA} represents the number of *t*BA units on triblock copolymer, calculated from ^{1}H NMR data on formula 3 in text. [e] E.F.$_{Click}$ represents the coupling efficiency of "click" reaction, calculated from ^{1}H NMR data on formula 4 in text.

SET-LRP and "click" chemistry, and the formation of PS-*b*-PEO-*b*-P*t*BA.

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 −C−H$_{aromat}$ on PS segment, and the characteristic band at 1100−1200 cm^{-1}of −C−O−C− on PEO segment could be detected easily. Because of the introducing of P*t*BA 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−PEO−alkyne (Figure 4B). Besides, a new absorption band at 1646 cm^{-1} for -C=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 *t*BA units on ABC triblock copolymer (N_{tBA}) and coupling efficiency of "click" chemistry (E.F.$_{Click}$), 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.

$$N_{tBA} = \frac{A_n}{A_j} \times \left(\frac{M_{PEO}}{44} \times 4\right) \quad (3)$$

$$E.F._{Click} = \frac{A_f}{A_j} \times \frac{\left(\frac{M_{PEO}}{44} \times 4\right)}{\left(\frac{M_{PS}}{104} \times 5\right)} \times 100\% \quad (4)$$

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 *t*BA 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_f represents the integral area sum of the phenyl protons ("*f*") at 6.30−7.30 ppm in ^{1}H NMR spectrum (Figure 3C).

Table 2 summarized all the data of ABC triblock copolymers. 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 *t*BA units on copolymer could be controlled by varying the feeding quantity of *t*BA monomer.(Table 2, entries T1,T2) The successful synthesis of ABC triblock copolymer PS-*b*-PEO-*b*-P*t*BA 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.

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