Macromolecules **2008**, *41*, 4127−4135

One-Pot Synthesis of ABC Type Triblock Copolymers via a Combination of “Click Chemistry” and Atom Transfer Nitroxide Radical Coupling Chemistry

Wencheng Lin, Qiang Fu, Yi Zhang, and Junlian Huang*

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

Received October 30, 2007; Revised Manuscript Received March 21, 2008

ABSTRACT: A new strategy for one-pot synthesis of ABC type triblock copolymers via a combination of “click chemistry” and atom transfer nitroxide radical coupling (ATNRC) reaction was suggested, and poly(*tert*-butyl acrylate)-*block*-polystyrene-*block*-poly(ethylene oxide) (P*t*BA−PS−PEO) and poly(*tert*-butyl acrylate)-*block*-polystyrene-*block*-poly(ϵ-caprolactone) (P*t*BA−PS−PCL) were successfully prepared by this method. The precursors with predetermined number-average molecular weight and low polydispersity indices, such as PS with α-alkyne and ω-bromine end groups, P*t*BA with azide end group, PEO and PCL with a 2,2,6,6-tetramethylpiperidine-1-oxyl end group, were directly prepared by living polymerization technique using the compounds with corresponding functional groups as initiators, and no further modifications of the end groups were needed, except P*t*BA-N_3. The coupling reaction between precursors was carried out in the CuBr/*N,N,N′,N″,N″*-pentamethyldiethylenetriamine system with high efficiencies. The obtained polymers were characterized by FT-IR, ^{1}H NMR, differential scanning calorimetry, and gel permeation chromatography in detail.

Introduction

Molecular design of block copolymers with well-defined architectures is a very important research field.[1] Traditionally, block copolymers with predetermined number-average molecular weight (M_n) and low polydispersity indices (PDI) are always synthesized by two strategies: sequential living polymerizations of different monomers[2,3] or coupling reaction of polymers with preformed functional groups.[4,5] Among various kinds of block copolymer, the ABC type triblock copolymers have attracted much attention for their unique structure with three different homopolymer blocks, leading to potentially interesting properties for possible further applications.[6–9] In order to prepare well-defined ABC type triblock copolymers with predetermined M_n and PDI, living anionic polymerizations are always used.[2,3] However, the rigid conditions and only a few available monomers limited the applications of conventional living anionic polymerizations. As the development of “controlled/living” radical polymerization (CRP), a novel route for synthesis of well-defined triblock copolymer has arisen.

In recent years, CRP techniques have developed rapidly for facile preparation of a variety of polymeric materials with predetermined M_n, low PDI, and high degrees of chain-end functionalization.[10] Compared with conventional living anionic polymerizations, CRP techniques have the advantage of the variety of applicable monomers and more tolerant experimental conditions. The most widely used CRP methods are atom transfer radical polymerization (ATRP),[11–14] reversible addition−fragmentation chain transfer (RAFT) polymerization,[15,16] and nitroxide-mediated polymerization (NMP).[17,18] Especially, ATRP and NMP have proved useful in the synthesis of triblock copolymers.[19–21] The polymers contained terminal halogen groups synthesized by ATRP can be successfully converted to various desired functional chain-end groups through appropriate transformations.[22] For example, a halogen end group of the polymer could be successfully converted to an azide group and then further react with alkynes to form a substituted triazole group, which is termed “click chemistry”.[23]

Click chemistry has been used extensively due to its quantitative yields, high tolerance of functional groups, and insensitivity of the reaction to solvents.[24] The reaction between a terminal alkyne and an azide groups to form a triazole group is the most popular one, which was first studied by Huisgen.[25] Nowadays, click reactions have already been widely used in polymeric science and material,[24] such as the synthesis of linear,[26,27] dendritic,[28,29] cyclic,[30] and star polymers.[22] They are also utilized in functionalized surfaces,[31–33] sugars,[34] probe biological systems,[35,36] and synthesis of synthesize analogues of vitamin D.[37] The great potential of this coupling procedure for the construction of well-defined (functional) polymer architectures was quickly recognized, and it is the subject of intensive research.[38] The fact has showed that it was a wonderful route to use click reaction in synthesis of ABC triblock copolymer.[39] However, the polymers with azide groups are difficult to be reserved because of their photosensitivity, thermal instability, and shock sensitivity. Thus, in the operations of “click” chemistry, special care should be taken. It is obvious that there is a need to look for a strategy to prepare well-defined copolymers with complex structure by the coupling reaction of the more stable and more reactive functional groups than azide.

Matyjaszewski et al.[40] reported the synthesis of several alkoxyamines derived from organic halides and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) or TEMPO derivatives using copper systems. The alkoxyamines bearing different functional groups have been prepared in one simple step with high yield. Now, we are trying to introduce this reaction to the polymer field, and what we care about is whether this coupling reaction with high efficiency would be realized when a polymer containing TEMPO group is mixed with another polymer contained halide group in the presence of CuBr. In this coupling reaction, the terminal bromine groups of the polymers served as oxidant are reduced to bromine anions, and then carbon radicals of polymers are formed; CuBr is served as reductant, and the Cu^{1+} is oxidized to Cu^{2+}. The formed free carbon radicals are immediately captured by the TEMPO radical of another polymer, and a stable bond −C−O− is obtained between the two polymers. This oxido-reduction process is irreversible. The reaction is termed as atom transfer nitroxide

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* Corresponding author: Fax +86-21-65640293; e-mail jlhuang@fudan.edu.cn.

10.1021/ma702404t CCC: $40.75

radical coupling (ATNRC) reaction. Because halide and TEMPO are typical groups for ATRP and NMP, the ATNRC reaction could be widely used in synthesis of a variety of polymers.

Several months ago, Durmaz[41] reported a one-pot synthesis of ABC type triblock copolymers via a combination of click [3 + 2] with Diels−Alder [4 + 2] reactions between maleimide and anthracene groups. However, since the required functional anthryl and maleimide groups for his one-pot reaction are not easy to be prepared, the modification of end groups of each precursor polymer blocks is a time-consuming procedure.

Herein, a new strategy for preparation of the ABC triblock copolymers by the one-pot method is provided, some precursor polymers as poly(ethylene oxide) (PEO) and poly(ϵ-caprolactone) (PCL) with a TEMPO end group, polystyrene (PS) with α-alkyne and ω-bromine end groups, could be prepared simply by the initiators with corresponding functional groups, and the final triblock copolymer poly(*tert*-butyl acrylate)-*block*-polystyrene-*block*-poly(ethylene oxide) (P*t*BA−PS−PEO) and poly(*tert*-butyl acrylate)-*block*-polystyrene-*block*-poly(ϵ-caprolactone) (P*t*BA−PS−PCL) were successfully prepared with high efficiencies via a combination of "click chemistry" and ATNRC reaction.

Experimental Section

Materials. Ethylene oxide (EO, 99.9%, Sinopharm Chemical Reagent) (SCR), *tert*-butyl acrylate (*t*BA, 99%, SCR), ϵ-caprolactone (CL, 99%, SCR), and propargyl alcohol (99%, SCR) were dried by CaH_2 for 48 h and distilled before use. Styrene (St; 99.5%,SCR) purchased from SCR was washed with a 15% NaOH aqueous solution and water successively for three times, dried over anhydrous $MgSO_4$, further dried over CaH_2, and then distilled under reduced pressure twice before use. Diphenylmethylpotassium (DPMK) solution with a concentration of 0.630 mol/L was prepared according to the literature.[42] 4-Hydroxyl-TEMPO (HTEMPO) prepared according to the literature[43] was purified by recrystallization with hexane. CuBr (95%, SCR) was stirred overnight in acetic acid, filtered, washed with ethanol and diethyl ether successively, and dried in vacuo. *N,N,N′,N″,N″*-Pentamethyldiethylenetriamine (PMDETA, 99%), ethyl 2-bromoisobutyrate (EBiB, 98%), and 2-bromoisobutyryl bromide (98%) were purchased from Aldrich and used without further purification. Acetone (99%), tetrahydrofuran (THF, 99%), toluene (99%), pyridine (99%), *N,N*-dimethylformamide (DMF, 99%), and other reagents were all purchased from SCR and purified by standard methods before use.

Measurements. Gel permeation chromatography (GPC) 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 column (molecular range 200−3 × 10^6 g/mol). Polystyrene standards were used for calibration. For PEO, GPC was performed in distilled water 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. ^1H NMR spectra were recorded at room temperature by a Bruker (500-MHz) spectrometer using tetramethylsilane as the internal standard and $CDCl_3$ as the solvent, except for PEO; the latter was determined in deuterated methanol in the presence of stoichiometric ammonium formate ($HCOONH_4$) and the catalyst palladium on carbon (Pd/C). All of the samples were scanned for 128 times, and the sensitivity of the instrument was 0.1% ethylbenzene; NS = 1, LB = 1; S/N = 300:1. FT-IR spectra were obtained on a Magna-550 Fourier transform infrared spectrometer. The differential scanning calorimetry (DSC) analysis was carried out with a Perkin-Elmer Pyris 1 DSC instrument under a nitrogen flow (10 mL/min); all samples were heated from −70 to 140 at 10 °C/ min under a nitrogen atmosphere. The glass transition (T_g) and the melting temperatures (T_m) were calculated as a midpoint and a peak apex of thermograms, respectively. DSC was calibrated for temperature by indium (theoretical: 156.6 °C; measured: 158.344 °C) and zinc (theoretical: 419.47 °C; measured: 423.4666 °C). Heat flow was calibrated by indium (theoretical: 28.45 °C; measured: 26.914 °C; weight: 3.6 mg).

Table 1. Characterization of the Synthetic Alkyne-PS-Br[a]

sample	$M_{n,GPC}$[b] (g/mol)	$M_{n,NMR}$[c] (g/mol)	M_w/M_n[b]	DP[c]
alkyne-PS_A-Br	7 300	6 900	1.10	64
alkyne-PS_B-Br	10 600	10 700	1.08	101

[a] Alkyne-PS-Br: polystyrene with α-alkyne and ω-bromine end groups, obtained by ATRP of St using PgBiB (propargyl 2-bromoisobutyrate) as an initiator, CuBr/PMDETA as a catalyst system at 90 °C. [b] $M_{n,GPC}$ (the GPC number-average molecular weight) and M_w/M_n (molecular weight distribution), measured by GPC in THF with RI detector, calibration with linear PS as standard. [c] $M_{n,NMR}$ (the NMR number-average molecular weight) and DP (number-average degree of polymerization of St), measured by ^1H NMR spectroscopy.

Synthesis of Propargyl 2-Bromoisobutyrate (PgBiB). Propargyl alcohol (5.00 mL, 85.9 mmol) was dissolved in 40.0 mL of pyridine and cooled in an ice−water bath, and a solution of 2-bromoisobutyryl bromide (10.6 mL, 85.9 mmol) in pyridine (10.0 mL) was slowly added under stirring. Then the system was stirred continuously in the cooling bath for 2 h and then at room temperature for another 24 h. After the precipitated pyridine salts were filtered, the solvent was removed on a rotary evaporator. The crude product was distilled under reduced pressure to give the clear liquid of PgBiB with yield of 85.3%. ^1H NMR ($CDCl_3$, δ): 4.71 (2H, C**H**$_2$O), 2.47 (1H, C≡C**H**), and 1.90 (6H, (C**H**$_3$)$_2$C). IR spectrum (neat liquid, KBr plates): 3296 cm^{-1} ($\nu_{\equiv C-H}$), 2132 cm^{-1} ($\nu_{C\equiv C}$), and 1743 cm^{-1} ($\nu_{C=O}$).

Synthesis of PS with α-Alkyne and ω-Bromine (Alkyne-PS-Br). Alkyne-PS-Br was prepared by ATRP of St using PgBiB as an initiator and CuBr/PMDETA as a catalyst. A typical example is as follows: PgBiB (0.180 mL, 1.20 mmol), CuBr (0.0860 g, 0.0600 mmol), PMDETA (0.130 mL, 0.0600 mmol), and St (30.0 mL, 262 mmol) were added to a dry ampule. The reaction mixture was degassed by three freeze−pump−thaw cycles and purged with nitrogen. The ampule was immersed in oil bath at 90 °C for 6 h, then taken from the oil bath, and dipped in liquid nitrogen to stop the polymerization. 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 purified by dissolution/precipitation with THF/cold methanol twice and then dried at 40 °C in vacuum oven for 4 h ($[M]_0/[I]_0 = 220$; conversion = 29.8%; the number-average molecular weight from ^1H NMR ($M_{n,NMR}$) = 6900 (see Figure 4a, eq 1 was used for calculation); the number-average molecular weight from GPC ($M_{n,GPC}$) = 7300 (relative to linear PS standard); molecular weight distribution (M_w/M_n) = 1.10). Two types of alkyne-PS-Br (alkyne-PS_A-Br and alkyne-PS_B-Br) with different M_n were prepared (listed in Table 1). ^1H NMR ($CDCl_3$, δ): 7.23−6.30 (phenyl protons of PS), 4.60−4.30 (C**H**(Ph)−Br, end group of PS), 4.17−3.90 (CH≡C−C**H**$_2$ of initiator PgBiB), 2.50−1.20 (C**H**$_2$C**H**(Ph), repeating unit of PS), 1.14−0.80 (−(CO)−C(C**H**$_3$)$_2$ of initiator PgBiB) (Figure 4a).

Synthesis of P*t*BA with Azide End Group (P*t*BA-N$_3$). P*t*BA with bromine end group (P*t*BA-Br) was prepared by ATRP of *t*BA in acetone, using EBiB as an initiator and CuBr/PMDETA as a catalyst. EBiB (0.150 mL, 1.00 mmol), CuBr (0.144 g, 1.00 mmol), PMDETA (0.210 mL, 1.00 mmol), and *t*BA (18.0 mL, 126 mmol) were dissolved in acetone (18.0 mL). The reaction mixture was degassed by three freeze−pump−thaw cycles and left under nitrogen. The ampule was immersed in oil bath at 60 °C for 6 h, then taken from the oil bath, and dipped in liquid nitrogen to stop the polymerization. The products were diluted with THF, passed through a column chromatograph filled with neutral alumina to remove the copper complex, and precipitated in a cold mixture solution of methanol and H_2O (1/1 v/v). The precipitate was collected and dried at 40 °C in vacuum oven for 4 h ($[M]_0/[I]_0$ =

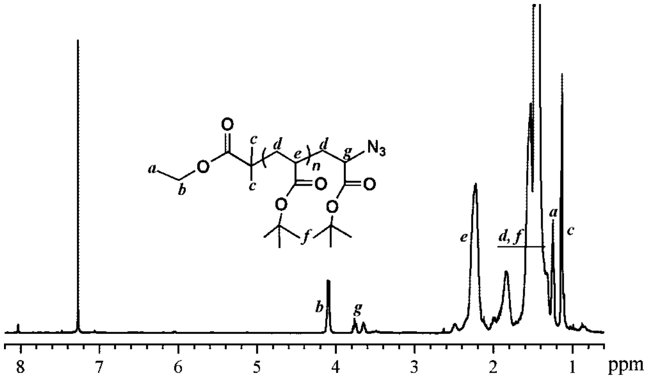


Figure 1. ^{1}H NMR spectrum of the precursor of P*t*BA$_a$-N$_3$.

Table 2. Characterization of the Synthetic P*t*BA-N$_3$[a]

sample	$M_{n,GPC}$[b] (g/mol)	$M_{n,NMR}$[c] (g/mol)	M_w/M_n[b]	DP[c]
P*t*BA$_a$-N$_3$	3000	4000	1.13	30
P*t*BA$_b$-N$_3$	5300	6300	1.10	48

[a] P*t*BA-N$_3$: poly(*tert*-butyl acrylate) with azide end group, obtained by ATRP of *t*BA using EBiB (ethyl 2-bromoisobutyrate) as an initiator, CuBr/PMDETA as a catalyst system at 60 °C. [b] $M_{n,GPC}$ (the GPC number-average molecular weight) and M_w/M_n (molecular weight distribution), measured by GPC in THF with RI detector, calibration with linear PS as standard. [c] $M_{n,NMR}$ (the NMR number-average molecular weight) and DP (number-average degree of polymerization of *t*BA), measured by ^{1}H NMR spectroscopy.

126; conversion = 24.5%; $M_{n,NMR}$ = 3000; $M_{n,GPC}$ = 4000 (relative to linear PS standard); M_w/M_n = 1.13).

Then, the precipitate of P*t*BA-Br (3.60 g, 1.20 mmol) was dissolved in DMF (15 mL), and sodium azide (0.390 g, 6.00 mmol) was added to the solution. The reaction mixture was stirred 24 h at room temperature. Dichloromethane (25.0 mL) was added into the mixture and washed three times with distilled water. The organic layer was dried with anhydrous MgSO$_4$, and the solvent was removed by vacuum. Then the product was collected and dried at 40 °C in vacuum oven for 4 h [(yield = 95.4%; $M_{n,NMR}$ = 3000 (see Figure 1 and eq 2 was used for calculation); $M_{n,GPC}$ = 4000 (relative to linear PS standard); M_w/M_n = 1.13)]. Two types of P*t*BA-N$_3$ (P*t*BA$_a$-N$_3$ and P*t*BA$_b$-N$_3$) with different M_n were prepared (listed in Table 2). ^{1}H NMR (CDCl$_3$, δ): 4.13−4.07 ($CH_3\mathbf{CH_2}O$ of initiator EBiB), 3.81−3.61 ($CH_2\mathbf{CH}-N_3$, end group of P*t*BA), 2.56−2.06 ($CH_2\mathbf{CH}$, repeating unit of P*t*BA), 2.05−1.30 ($\mathbf{CH_2}CH$ and $-(CO)-OC(\mathbf{CH_3})_3$, repeating units of P*t*BA), 1.27−1.20 ($\mathbf{CH_3}CH_2O$ of initiator EBiB), 1.16−1.07 ($-(CO)-C(\mathbf{CH_3})_2$ of initiator EBiB) (Figure 1).

Synthesis of TEMPO End-Functionalized PEO (PEO-TEMPO). PEO-TEMPO was prepared by ring-opening polymerization (ROP) of EO in THF using DPMK and HTEMPO as initiators. In an ampule, the dried HTEMPO (0.690 g, 4.00 mmol) by azeotropic distillation in 30.0 mL of THF was introduced, DPMK solution (1.51 mL, 0.950 mmol) was injected into the ampule under nitrogen by a syringe, and then EO (17.0 mL, 336 mmol) and THF (40.0 mL) were added. The reaction was allowed to proceed at 60 °C for 72 h. At the end of the polymerization, excessive methanol was added to terminate the reaction. After removing the solvent, the mixture was diluted with dichloromethane and precipitated into an excessive amount of diethyl ether for three times. The precipitate was dried in vacuum oven at 40 °C for 24 h, and the pink powder was obtained ($[M]_0/[I]_0$ = 84.0; conversion = 100%; the theoretical M_n ($M_{n,theo}$) = 3900; $M_{n,NMR}$ = 3900 (see Figure 2 and eq 3 was used for calculation); $M_{n,GPC}$ = 3600 (relative to linear PEO standard); M_w/M_n = 1.20). Two types of PEO-TEMPO (PEO$_A$-TEMPO and PEO$_B$-TEMPO) with different M_n were prepared (listed in Table 3). ^{1}H NMR (CD$_3$OD, in the presence of Pd/C and HCOONH$_4$, δ): 3.78−3.60 ($\mathbf{CH_2CH_2}O$, repeating unit of PEO), 1.97−1.92 and 1.44−1.39 ($\mathbf{CH_2}$, methylene protons of TEMPO), 1.19−1.14 ($\mathbf{CH_3}$, methyl protons of TEMPO) (Figure 2).

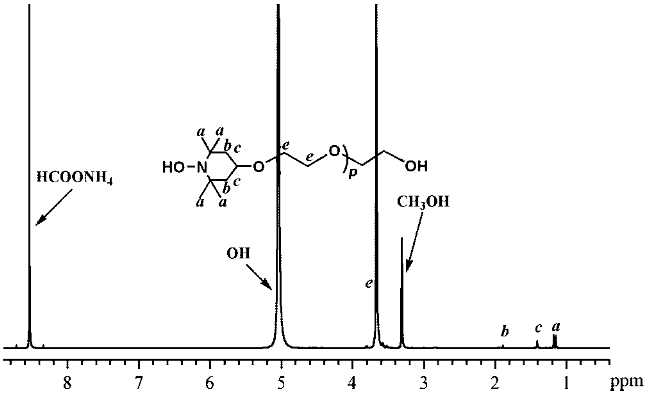


Figure 2. ^{1}H NMR spectrum of PEO$_A$-TEMPO (in the presence of Pd/C and HCOONH$_4$ using CD$_3$OD as solvent).

Table 3. Characterization of the Synthetic PEO-TEMPO[a]

sample	$M_{n,GPC}$[b] (g/mol)	$M_{n,NMR}$[c] (g/mol)	M_w/M_n[b]	DP[c]
PEO$_A$-TEMPO	3600	3900	1.20	84
PEO$_B$-TEMPO	4000	4100	1.05	89

[a] PEO-TEMPO: poly(ethylene oxide) with a 2,2,6,6-tetramethylpiperidine-1-oxyl end group, obtained by ROP of EO in THF using DPMK (diphenylmethylpotassium) and HTEMPO (4-hydroxyl-2,2,6,6-tetramethylpiperidine-1-oxyl) as co-initiators at 60 °C. [b] $M_{n,GPC}$ (the GPC number-average molecular weight) and M_w/M_n (molecular weight distribution), measured by GPC in distilled water with RI detector, calibration with linear PEO as standard. [c] $M_{n,NMR}$ (the NMR number-average molecular weight) and DP (number-average degree of polymerization of EO), measured by ^{1}H NMR spectroscopy.

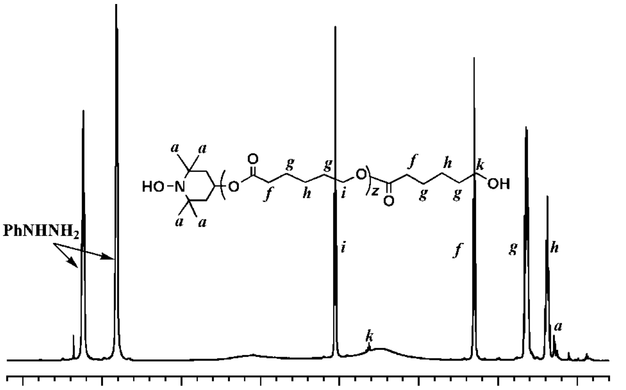


Figure 3. ^{1}H NMR spectrum of PCL-TEMPO (in the presence of phenylhydrazine using CDCl$_3$ as solvent).

Synthesis of TEMPO End-Functionalized PCL (PCL-TEMPO). PCL-TEMPO was prepared by ROP of ϵ-CL in toluene solution using stannous octoate Sn(Oct)$_2$ as a catalyst and HTEMPO as an initiator. The dried HTEMPO (0.190 g, 1.10 mmol) by azeotropic distillation with dry toluene was dissolved in 3.50 mL of toluene, to which CL (4.32 mL, 40.0 mmol) was added. Then a given amount of the catalyst ($[Sn(Oct)_2]/[OH]$ = 0.500) was injected under nitrogen by a syringe. The reaction was allowed to proceed at 100 °C for 24 h. After cooling to room temperature, the products were dissolved in THF and precipitated into an excess amount of methanol. The precipitate was isolated by filtration and dried at room temperature in a vacuum oven for 4 h ($[M]_0/[I]_0$ = 36.4; conversion = 100%; $M_{n,theo}$ = 4300; $M_{n,NMR}$ = 4400 (see Figure 3 and eq 4 was use for calculation); $M_{n,GPC}$ = 7700 (relative to linear PS); M_w/M_n = 1.23). ^{1}H NMR (CDCl$_3$, δ): 4.12−4.02 [$-(CO)-CH_2CH_2CH_2CH_2\mathbf{CH_2}O$, the fifth methylene group connected to carbonyl of repeating unit of PCL], 3.70−3.62 [$-(CO)-CH_2CH_2CH_2CH_2\mathbf{CH_2}OH$, end group of PCL], 2.35−2.24 [$-(CO)-\mathbf{CH_2}CH_2CH_2CH_2CH_2O$, the first methylene group connected to carbonyl of repeating unit of PCL], 1.72−1.56 [$-(CO)-CH_2\mathbf{CH_2}CH_2\mathbf{CH_2}CH_2O$, the second and fourth

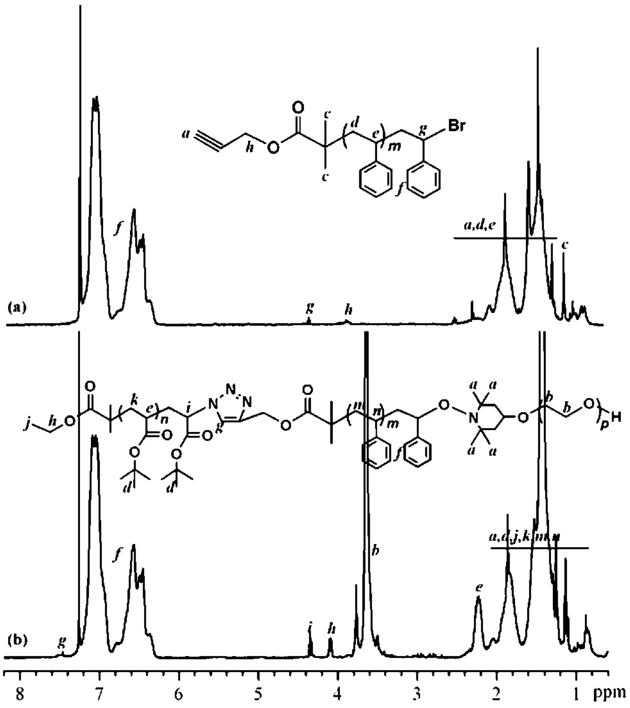


Figure 4. ^{1}H NMR spectrum of (a) alkyne-PS$_A$-Br and (b) P*t*BA$_a$-PS$_A$-PEO$_A$ (using CDCl$_3$ as solvent).

methylene groups connected to carbonyl of repeating unit of PCL], 1.42−1.33 [−(CO)−CH$_2$CH$_2$C**H**$_2$CH$_2$CH$_2$O, the third methylene group connected to carbonyl of repeating unit of PCL], 1.28−1.17 (C**H**$_3$, methyl protons of TEMPO) (Figure 3).

One-Pot Synthesis of P*t*BA−PS−PEO Triblock Copolymer. P*t*BA$_a$-N$_3$ (0.147 g, 0.049 mmol), alkyne-PS$_A$-Br (0.299 g, 0.041 mmol), and PEO$_A$-TEMPO (0.176 g, 0.049 mmol) were dissolved in DMF (10.0 mL) in a dry ampule. CuBr (0.059 g, 0.410 mmol) and PMDETA (0.086 mL, 0.410 mmol) were added, and the reaction mixture was degassed by three freeze−pump−thaw cycles and left under nitrogen. The ampule was immersed in oil bath at 90 °C for 24 h, then taken from the oil bath, and dipped in liquid nitrogen to stop the polymerization. The products were diluted with THF, and solution was passed through alumina column to remove copper salt, precipitated into cold methanol, and dried in vacuum oven at 40 °C for 4 h. The P*t*BA$_a$-PS$_A$-PEO triblock copolymer was obtained (listed in Table 4) [yield = 0.510 g (82.0%); $M_{n,theo}$ = 14 700 (eq 5 was used for calculation); the actual molecular weight ($M_{n,act}$) = 13 800 (see Figure 4b and eq 6 was used for calculation); $M_{n,GPC}$ = 11 500 (relative to linear PS standard); M_w/M_n = 1.08]. Two types of P*t*BA−PS−PEO (P*t*BA$_a$−PS$_A$−PEO$_A$ and P*t*BA$_b$−PS$_B$−PEO$_B$) were obtained using the same procedure (listed in Table 4). ^{1}H NMR (CDCl$_3$, δ): 7.60−7.41 (proton in triazole), 7.26−6.30 (phenyl protons, repeating unit of PS), 4.37−4.30 (P*t*BA-CH$_2$C**H**-triazole), 4.13−4.06 (CH$_3$C**H**$_2$OCO, end group of P*t*BA), 3.82−3.48 (C**H**$_2$C**H**$_2$O, repeating unit of PEO), 2.32−2.16 (CH$_2$C**H**, repeating unit of P*t*BA) (Figure 4b).

One-Pot Synthesis of P*t*BA−PS−PCL Triblock Copolymer. P*t*BA$_b$-N$_3$ (0.470 g, 0.088 mmol), alkyne-PS$_A$-Br (0.460 g, 0.063 mmol), and PCL-TEMPO (0.490 g, 0.0630 mmol) were dissolved in DMF (10.0 mL) in a dry ampule. CuBr (0.0900 g, 0.630 mmol) and PMDETA (0.130 mL, 0.630 mmol) were added, and the reaction mixture was degassed by three freeze−pump−thaw cycles and purged with nitrogen. The ampule was immersed in oil bath at 90 °C for 24 h, then taken from the oil bath, and dipped in liquid nitrogen to stop the polymerization. The products were diluted with THF, and solution was passed through alumina column to remove copper salt, precipitated into methanol, and dried in vacuum oven at 40 °C for 4 h [yield = 1.20 g (84.4%);$M_{n,theo}$ = 17 500 (eq 7 was used for calculation); $M_{n,act}$ = 15 800 (see Figure 7b and eq 8 was used for calculation);$M_{n,GPC}$ = 14 900 (relative to linear PS standard); M_w/M_n = 1.23]. Two types of P*t*BA−PS−PCL (P*t*BA$_b$−PS$_A$−PCL and P*t*BA$_b$−PS$_B$−PCL) were obtained using the same procedure (listed in Table 4). ^{1}H NMR (CDCl$_3$, δ): 7.60−7.41 (proton in triazole), 7.26−6.27 (phenyl protons, repeating unit of PS), 4.17−3.96 [−(CO)−CH$_2$CH$_2$CH$_2$CH$_2$C**H**$_2$O, the fifth methylene group connected to carbonyl, repeating unit of PCL], 3.70−3.60 [−(CO)−CH$_2$CH$_2$CH$_2$CH$_2$C**H**$_2$OH, end group of PCL], 2.50−2.13 (CH$_2$C**H**, repeating unit of P*t*BA and −(CO)−C**H**$_2$CH$_2$CH$_2$CH$_2$CH$_2$O, the first methylene group connected to carbonyl, repeating unit of PCL) (Figure 7b).

Results and Discussion

Synthesis of Precursors with Proper Functional Groups. All of the precursors were prepared by living polymerization with predetermined M_n and low PDI. Alkyne-PS-Br was prepared by ATRP of St using PgBiB as an initiator and CuBr/PMDETA as a catalyst system at 90 °C. The end groups of alkyne and bromine in alkyne-PS-Br were supported by the appearance of signals at 4.17−3.90 ppm (CH≡C−C**H**$_2$, end group of PS) and 4.60−4.30 ppm (C**H**(Ph)−Br, end group of PS) in the ^{1}H NMR spectrum (Figure 4a). Furthermore, −HC≡C of alkyne-PS-Br could easily be detected at 3295 cm^{-1} in the IR spectrum. Two types of alkyne-PS-Br (alkyne-PS$_A$-Br and alkyne-PS$_B$-Br, listed in Table 1) were prepared with different M_n and low PDI. The number-average M_n of alkyne-PS-Br by NMR ($M_{n,NMR}$) was determined by comparing the integrals of the phenyl protons of PS at 7.23−6.30 ppm with that of C**H**(Ph)−Br (end group of PS) at 4.60−4.30 ppm, using eq 1.

$$M_{n,NMR} = \frac{A_f}{5A_g} \times 104 + 205 \tag{1}$$

Here, A_f represents the integral area of the peaks at “f” for phenyl group protons on PS repeating units, A_g represents the integral area of the peaks at “g” for C**H**(Ph)−Br methine group proton on the alkyne-PS-Br end group, and the value 205 is the molecular weight of the initiator PgBiB. The result was almost consistent with the $M_{n,GPC}$ of PS shown in Table 1.

P*t*BA-Br was prepared by ATRP of *t*BA in acetone using EBiB as an initiator and CuBr/PMDETA as a catalyst system at 90 °C; the obtained P*t*BA-Br was reacted with sodium azide in DMF in room temperature. The transformation of bromine to azide group was confirmed by the observation of a signal at 3.81−3.61 ppm (CH$_2$C**H**−N$_3$, end group of P*t*BA) (Figure 1). Furthermore, P*t*BA-N$_3$ displays characteristic stretching band of −N$_3$ which appeared at 2112 cm^{-1} in the IR spectrum. Two types of P*t*BA-N$_3$ (P*t*BA$_a$-N$_3$ and P*t*BA$_b$-N$_3$, listed in Table 2) were prepared with different M_n and low PDI for further use. The $M_{n,NMR}$ of P*t*BA-N$_3$ was calculated taking into account the integrated ratio of peaks at 2.56−2.06 ppm (CH$_2$C**H**, repeating unit of P*t*BA) to 4.13−4.07 ppm (CH$_3$C**H**$_2$O, end group of P*t*BA), using eq 2.

$$M_{n,NMR} = \frac{2A_e}{A_b} \times 128 + 195 \tag{2}$$

Here, A_e represents the integral area of the peaks at “e” for CH$_2$C**H** methine group proton on P*t*BA repeating unit, A_b represents the integral area of the peaks at “b” for CH$_3$C**H**$_2$O methylene group protons on P*t*BA-N$_3$ end group, and the value 195 is the molecular weight of the initiator EBiB.

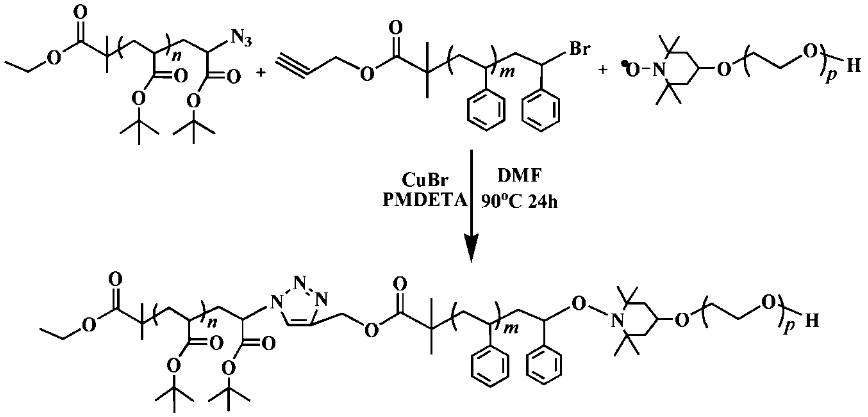
PEO-TEMPO was prepared by ROP of EO in THF using DPMK and HTEMPO as co-initiators at 60 °C. The ^{1}H NMR spectrum of PEO-TEMPO displays characteristic signals of C**H**$_2$ (methylene protons of TEMPO) and C**H**$_3$ (methyl protons of TEMPO) at 1.44−1.39, 1.97−1.92, and 1.19−1.14 ppm (Figure 2). Two types of PEO-TEMPO (PEO$_A$-TEMPO and PEO$_B$-TEMPO, listed in Table 3) were prepared with different M_n and low PDI for further use. The $M_{n,NMR}$ of PEO-TEMPO was

Table 4. One-Pot Synthesis of P*t*BA−PS−PEO/PCL[a]

sample	$M_{n,GPC}$[b](g/mol)	$M_{n,act}$[c](g/mol)	$M_{n,theo}$[d](g/mol)	M_w/M_n[b]	yield (%)	efficiency (%)[e]	
						ATNRC	click
P*t*BA$_a$−PS$_A$−PEO$_A$	11 500	13 800	14 700	1.08	82.0	86.0	89.6
P*t*BA$_b$−PS$_B$−PEO$_B$	15 800	19 600	21 100	1.13	80.9	80.9	87.9
P*t*BA$_b$−PS$_A$−PCL	14 900	15 800	17 500	1.23	84.4	81.6	85.9
P*t*BA$_b$−PS$_B$−PCL	17 700	19 200	21 300	1.13	85.1	80.1	80.7

[a] P*t*BA−PS−PEO/PCL: poly(*tert*-butyl acrylate)-*block*-polystyrene-*block*-poly(ethylene oxide)/poly(ϵ-caprolactone), obtained in the presence of CuBr/PMDETA in DMF at 90 °C. [b] $M_{n,GPC}$ (the GPC number-average molecular weight) and M_w/M_n (molecular weight distribution), measured by GPC in THF with RI detector, calibration with linear PS as standard. [c] $M_{n,act}$ (the actual molecular weight), measured by the ratio of integrated values of the PS to the P*t*BA and the PEO/PCL segments. [d] $M_{n,theo}$ (the theoretical molecular weight), measured by eq 5. [e] Efficiency of ATNRC (atom transfer nitroxide radical coupling) and click reaction, measured by ^{1}H NMR spectrum of the triblock copolymers (see Supporting Information).

Scheme 1. One-Pot Synthesis of P*t*BA−PS−PEO



determined by the ratio of the integrated signals at 3.78−3.60 ppm (C**H**$_2$C**H**$_2$O, repeating unit of PEO) to 1.19−1.14 ppm (C**H**$_3$, methyl protons of TEMPO), using eq 3.

$$M_{n,NMR} = \frac{12A_e}{4A_a} \times 44 + 172 \qquad (3)$$

Here, A_e represents the integral area of the peaks at "e" for **CH**$_2$**CH**$_2$ methylene group protons on PEO repeating unit, A_a represents the integral area of the peaks at "a" for methyl group protons on PEO end group, and the value 172 is the molecular weight of the initiator HTEMPO. The $M_{n,theo}$, $M_{n,NMR}$, and $M_{n,GPC}$ were in good agreement.

PCL-TEMPO was prepared by ROP of CL in toluene using Sn(Oct)$_2$ as a catalyst and HTEMPO as an initiator at 100 °C. TEMPO end group displays a characteristic signal of C**H**$_3$ (methyl protons of TEMPO) at 1.28−1.17 ppm in the ^{1}H NMR spectrum (Figure 3). For the TEMPO radicals, no reliable information could be derived from the ^{1}H NMR measurement because of its paramagnetism. In this work, the ^{1}H NMR spectrum was carried out in deuterated methanol in the presence of stoichiometric HCOONH$_4$ and catalytic Pd/C (or phenylhydrazine). TEMPO radicals on the copolymers were reduced to the corresponding oximes, and clear ^{1}H NMR spectra were then obtained.[44] The $M_{n,NMR}$ of PCL-TEMPO was 4400, which was determined by the ratio of the integrated signals at 2.35−2.24 [−(CO)−C**H**$_2$CH$_2$CH$_2$CH$_2$CH$_2$O, the first methylene group connected to carbonyl, repeating unit of PCL] to 1.28−1.17 ppm (C**H**$_3$, methyl protons of TEMPO), using eq 4.

$$M_{n,NMR} = \frac{12A_f}{2A_a} \times 114 + 172 \qquad (4)$$

Here, A_f represents the integral area of the peaks at "f" for −(CO)−**CH**$_2$CH$_2$CH$_2$CH$_2$CH$_2$O (the first methylene group connected to carbonyl) on PCL repeating unit, A_a represents the integral area of the peaks at "a" for methyl group protons on PCL end group, and the value 172 is the molecular weight of the initiator HTEMPO.

The $M_{n,GPC}$ of PCL-TEMPO was derived as 7700 g/mol; however, the chain structure of PCL is quite different from the PS standard. Thus, the more precise M_n obtained by GPC should use a correction formula:[40,45] $M_{n,PCL} = 0.259M_{n,GPC}^{1.073}$. The calibrated value $M_{n,PCL}$ was 3800, which was almost consistent with the $M_{n,theo}$ and $M_{n,NMR}$ of PCL-TEMPO.

One-Pot Synthesis of P*t*BA−PS−PEO Triblock Copolymer. P*t*BA-N$_3$, alkyne-PS-Br, and PEO-TEMPO were reacted in one pot to obtain the corresponding triblock copolymer P*t*BA−PS−PEO, as shown in Scheme 1. Click reaction between azide end group of P*t*BA-N$_3$ and alkyne functional group of alkyne-PS-Br was performed in the presence of CuBr/PMDETA in DMF at 90 °C. Simultaneously, ATNRC reaction between TEMPO end group of PEO-TEMPO and bromine functional group of alkyne-PS-Br was conducted at the same condition; the obtained P*t*BA−PS−PEO triblock copolymer is listed in Table 4.

The synthesis of P*t*BA−PS−PEO triblock copolymer was characterized by ^{1}H NMR and IR spectra. The crude product of the one-pot reaction was purified by dissolution/precipitation with THF/methanol because the excessive PEO-TEMPO and P*t*BA-N$_3$ could be dissolved in methanol, but P*t*BA-PS-PEO cannot. Comparing the ^{1}H NMR spectra of alkyne-PS-Br with that of P*t*BA−PS−PEO triblock copolymer (Figure 4), the characteristic peak of CH≡C−C**H**$_2$ (end group of PS) at 4.17−3.90 ppm disappeared, and a new signal related to triazole ring at 7.60−7.41 ppm appeared, which proved the click reaction accomplished between azide group and alkyne group. Besides, the characteristic peak of C**H**(Ph)-Br (end group of PS) at 4.60−4.30 ppm disappeared because the signal of the methine group proton shifted to upfield when the Br atom broke off from the alkyne-PS-Br chain. This indicated the ATNRC reaction occurred between bromine group and TEMPO group. Figure 4b also shows the characteristic peaks of phenyl group (repeating unit of PS) at 7.26−6.30, −C**H**$_2$C**H**$_2$O (repeating unit of PEO)

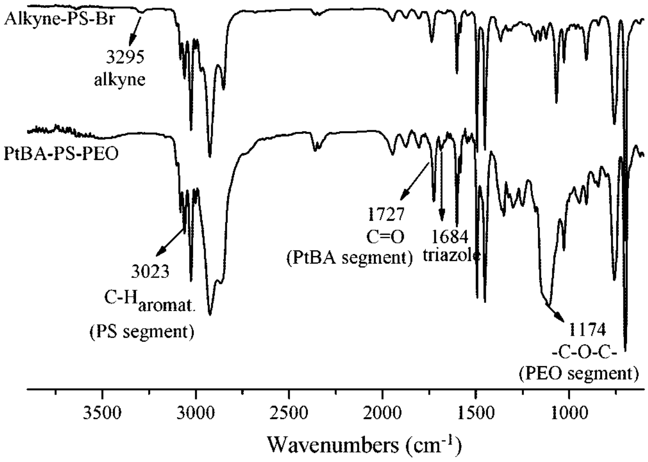


Figure 5. IR spectrum of P*t*BA$_a$–PS$_A$–PEO$_A$ and the corresponding precursor alkyne-PS$_A$-Br.

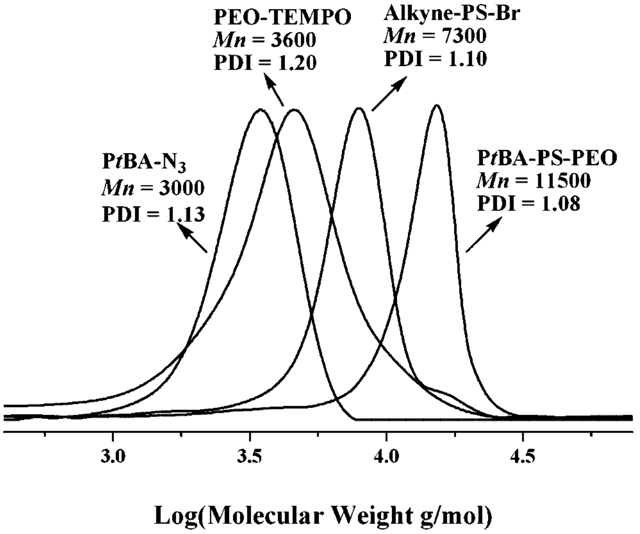


Figure 6. GPC curves of P*t*BA$_a$–PS$_A$–PEO$_A$ and the corresponding precursors P*t*BA$_a$-N$_3$, PEO$_A$-TEMPO, and alkyne-PS$_A$-Br by using RI detector.

at 3.82–3.48 ppm, and –CH$_2$**CH** (repeating unit of P*t*BA) at 2.32–2.16 ppm, which confirmed the successful coupling of P*t*BA-N$_3$ and PEO-TEMPO with alkyne-PS-Br chain.

This one-pot reaction was further supported by the IR spectrum (Figure 5). Compared with the IR spectrum of alkyne-PS-Br, the characteristic signal of –HC≡C at 3295 cm^{-1} disappeared, and a new signal related to triazole ring appeared at 1684 cm^{-1}, which indicated the alkyne group was transformed to triazole group. Furthermore, a characteristic signal of ether bond (–C–O–C–, belong to PEO chain) at 1174 cm^{-1} appeared while the signal of carbonyl (due to P*t*BA chain) at 1727 cm^{-1} enhanced, which was another evidence of the PEO and the P*t*BA chains coupled to PS chain.

In this one-pot reaction, the feeded P*t*BA-N$_3$ and PEO-TEMPO were slightly excessive, compared to that of alkyne-PS-Br. The molar ratio of P*t*BA-N$_3$ to alkyne-PS-Br and PEO-TEMPO was about 1.2:1:1.2. Because P*t*BA-N$_3$ and PEO-TEMPO could be dissolved in methanol completely, the excess amounts of P*t*BA-N$_3$ and PEO-TEMPO could be easily removed from the mixture by precipitation in cold methanol after the one-pot reaction was carried out. The GPC curves of the triblock copolymer and the corresponding precursors showed singlet and low PDI (Figure 6). All the data of the triblock copolymer are summarized in Table 4.

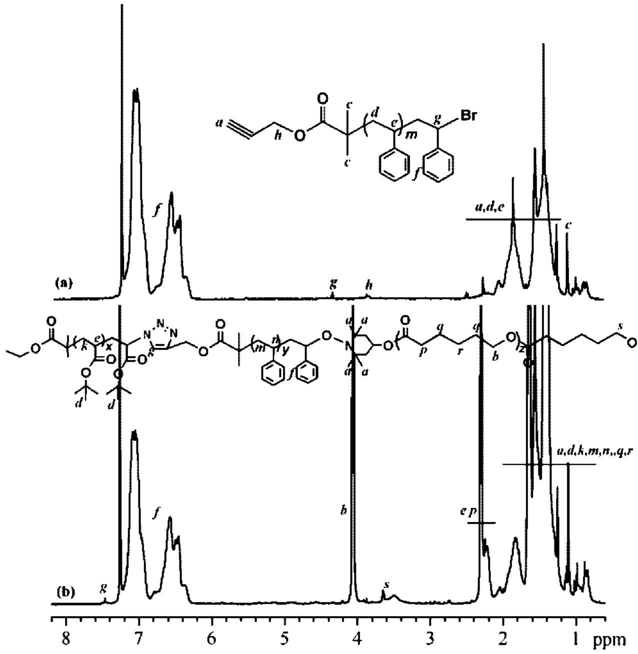


Figure 7. ^{1}H NMR spectra of (a) alkyne-PS$_A$-Br and (b) P*t*BA$_b$-PS$_A$-PCL (CDCl$_3$ as solvent).

The theoretical molecular weight ($M_{n,theo}$) of P*t*BA–PS–PEO could be calculated by the sum of the separate $M_{n,NMR}$ of precursors participated in the reaction, using eq 5.

$$M_{n,theo} = M_{n,NMR}(PtBA\text{-}N_3) + M_{n,NMR}(alkyne\text{-}PS\text{-}Br) + M_{n,NMR}(PEO\text{-}TEMPO) - 80 \quad (5)$$

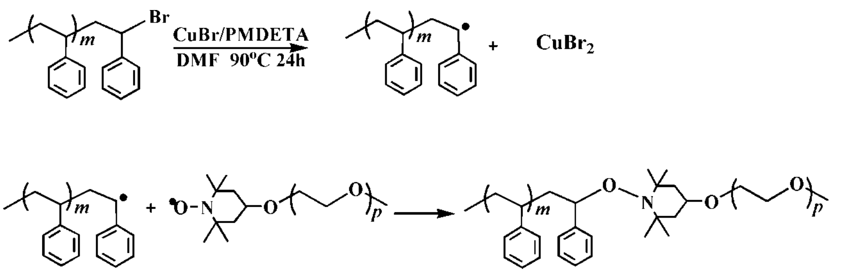
Here $M_{n,NMR}$(P*t*BA-N$_3$), $M_{n,NMR}$(alkyne-PS-Br), and $M_{n,NMR}$(PEO-TEMPO) represented the $M_{n,NMR}$ values of corresponding precursors P*t*BA-N$_3$, alkyne-PS-Br, and PEO-TEMPO which participated in the one-pot reaction; the value 80 was the molecular weight of the leaving group Br atom.

The actual molecular weight ($M_{n,act}$) of triblock copolymer was determined by a ratio of the integration of PS segment to P*t*BA and PEO segment at 7.26–6.30 (phenyl protons, repeating unit of PS) to 2.32–2.16 (CH$_2$**CH**, repeating unit of P*t*BA) and 3.82–3.48 (**CH$_2$**CH$_2$O, repeating unit of PEO) in NMR using eq 6.

$$\begin{aligned} M_{n,act} &= M_{n,NMR}(PtBA) + M_{n,NMR}(PEO) + M_{n,NMR}(PS) \\ &= \frac{5A_e}{A_f} \times \frac{M_{n,NMR}(PS)}{104} \times 128 + \frac{5A_b}{4A_f} \times \frac{M_{n,NMR}(PS)}{104} \times 44 + \\ &\quad M_{n,NMR}(PS) \end{aligned} \quad (6)$$

Here, $M_{n,NMR}$(P*t*BA), $M_{n,NMR}$(PEO), and $M_{n,NMR}$(PS) represent the actual $M_{n,NMR}$ of P*t*BA, PEO, and PS segment in the P*t*BA–PS–PEO triblock copolymer, respectively, where the $M_{n,NMR}$(PS) was equal to $M_{n,NMR}$ of the precursor alkyne-PS-Br which participated the reaction. A_e represents the integral area of the peaks at "e" for CH$_2$**CH** methine group proton on P*t*BA segment, A_f represents the integral area of the peaks at "f" for phenyl group protons on PS segment, and A_b represents the integral area of the peaks at "b" for **CH$_2$**CH$_2$ methylene group protons on PEO segment; the values 104, 128, and 44 were the molecular weights of repeating unit of PS, P*t*BA, and PEO segment, respectively. The efficiencies of the ATNRC and click reactions (listed in Table 4) were calculated by the ratio of PEO and P*t*BA segments to PS segment in the ^{1}H NMR spectrum of triblock copolymer, respectively (see Supporting Information). Compared with the efficiency of click reaction (89.6% and 87.9%, respectively), the efficiency of ATNRC reaction (86.0% and 80.9%, respectively) was a little lower.

Scheme 2. Mechanism of the ATNRC Reaction



And it was very clear that the efficiency for both of ATNRC and click reactions was reduced with the increasing of the molecular weight (compared the efficiencies of the two triblock copolymers (P*t*BA$_a$−PS$_A$−PEO$_A$ and P*t*BA$_b$−PS$_B$−PEO$_B$)).

The mechanism of the ATNRC reaction is shown in Scheme 2. The terminal bromine group of alkyne-PS-Br served as oxidant was reduced to bromine anions, and then secondary carbon radicals of PS were formed; CuBr was served as reductant, the Cu^{1+} was oxidized to Cu^{2+}, and the $CuBr_2$ was formed. The formed carbon-centered radical was immediately captured by the TEMPO radical of PEO-TEMPO, and alkoxyamines were formed between the two polymers. In the ATNRC reaction, CuBr participated in the reaction as reactant, and the reaction is irreversible, which is quite different from the common ATRP.

One-Pot Synthesis of P*t*BA−PS−PCL Triblock Copolymer via a Combination of Click and ATNRC Reaction. P*t*BA-N_3, alkyne-PS-Br, and PCL-TEMPO were reacted to synthesize corresponding triblock copolymer P*t*BA−PS−PCL in one-pot using a combination of click and ATNRC reaction as we described before. Figure 7 shows the characteristic peak of CH≡C−**CH**$_2$ (end group of PS) at 4.17−3.90 ppm disappeared, and a new signal related to the triazole ring at 7.60−7.41 ppm appeared. Besides, the characteristic peak of **CH**(Ph)−Br (end group of PS) at 4.60−4.30 ppm disappeared as the result of ATNRC reaction. Moreover, the characteristic peaks of the phenyl group (repeating unit of PS), −(CO)−CH$_2$CH$_2$-CH$_2$CH$_2$**CH$_2$O** (the fifth methylene group connected to carbonyl, repeating unit of PCL), and CH$_2$**CH** (repeating unit of P*t*BA) at 7.26−6.27, 4.17−3.96, and 2.50−2.13 ppm, respectively, were observed, which confirmed the successful coupling of P*t*BA-N_3 and PCL-TEMPO with alkyne-PS-Br chain in one pot. This one-pot reaction was further supported by IR spectra (Figure 8). Compared with the IR spectra of alkyne-PS-Br, the characteristic signal of −HC≡C at 3295 cm^{-1} disappeared and a new signal related to triazole ring appeared at 1649 cm^{-1}, which indicated the alkyne group was transformed to triazole group. Furthermore, a characteristic signal of the ether bond (−C−O−C−, belong to PCL chain) at 1151 cm^{-1} appeared while the signal of carbonyl group at 1731 cm^{-1} enhanced due to the successful coupling of P*t*BA-N_3 and PCL-TEMPO with alkyne-PS-Br chain.

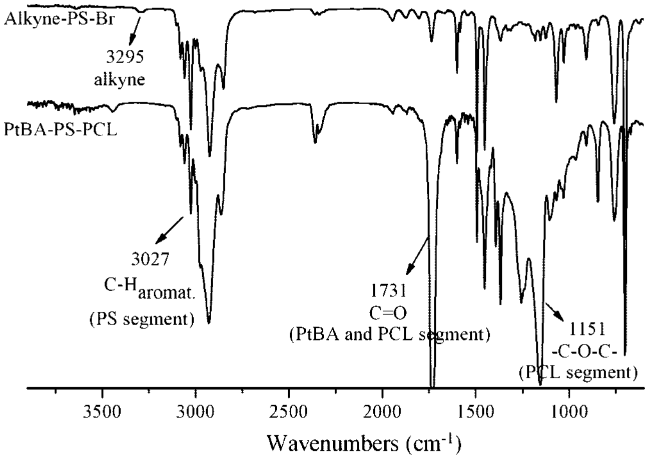


Figure 8. IR spectrum of P*t*BA$_b$−PS$_A$−PCL and the corresponding precursor alkyne-PS$_A$-Br.

The $M_{n,theo}$ of P*t*BA−PS−PCL triblock copolymer was calculated by the sum of the separate $M_{n,NMR}$ of the precursors which participated in the reaction, using eq 7.

$$M_{n,theo} = M_{n,NMR}(PtBA-N_3) + M_{n,NMR}(\text{alkyne-PS-Br}) + M_{n,NMR}(\text{PCL-TEMPO}) - 80 \quad (7)$$

Here, $M_{n,NMR}$(PCL-TEMPO) was the $M_{n,NMR}$ value of the corresponding precursor PCL-TEMPO which participated in the one-pot reaction.

The $M_{n,act}$ of triblock copolymer was determined by a ratio of the integration of PS segment to P*t*BA and PCL segment, using eq 8.

$$\begin{aligned} M_{n,act} &= M_{n,NMR}(PtBA) + M_{n,NMR}(PCL) + M_{n,NMR}(PS) \\ &= \frac{5(A_{e+p} - A_b)}{A_f} \times \frac{M_{n,NMR}(PS)}{104} \times 128 + \\ &\quad \frac{5A_b}{2A_f} \times \frac{M_{n,NMR}(PS)}{104} \times 114 + M_{n,NMR}(PS) \end{aligned} \quad (8)$$

Here, $M_{n,NMR}$(PCL) represents the actual $M_{n,NMR}$ of PCL segment in P*t*BA−PS−PCL triblock copolymer, A_{e+p} represents the integral area of the peaks at “e” and “p” for the CH$_2$**CH** methine group proton on P*t*BA segment and −(CO)−**CH$_2$**CH$_2$CH$_2$CH$_2$CH$_2$O (the first methylene group connected to carbonyl) on PCL segment, respectively, A_f represents the integral area of the peaks at “f” for phenyl group protons on PS segment, A_b represents the integral area of the peaks at “b” for −(CO)−CH$_2$CH$_2$CH$_2$CH$_2$**CH$_2$**O (the fifth methylene group protons connected to carbonyl) on PCL segment, the value 114 is the molecular weight of repeating unit of PCL segment, and others are the same as defined in eq 6. The efficiencies of the ATNRC and click reactions (listed in Table 4) for the synthesis of P*t*BA−PS−PCL were also calculated by the ratio of PCL and P*t*BA segments to PS segment in the ^{1}H NMR spectra of triblock copolymers, respectively (see Supporting Information); the efficiency of ATNRC reaction (81.6% and 80.1%, respectively) was a little lower than that of click reaction (85.9% and 80.7%, respectively). Comparing the efficiencies of the two type triblock copolymers (P*t*BA$_b$−PS$_A$−PCL and P*t*BA$_b$−PS$_B$−PCL), it also showed the efficiency, no matter ATNRC or click reactions, was reduced with the increasing of molecular weight. The GPC curves of the triblock copolymer and the corresponding precursors showed singlet and low PDI (Figure 9). All the data of the triblock copolymers are summarized in Table 4.

Variation of the Thermal Transition Temperature of Triblock Copolymers. Thermal transitions of the triblock copolymers were determined by DSC at a heating rate of 10 °C/min under a nitrogen atmosphere (Figure 10). In the case of

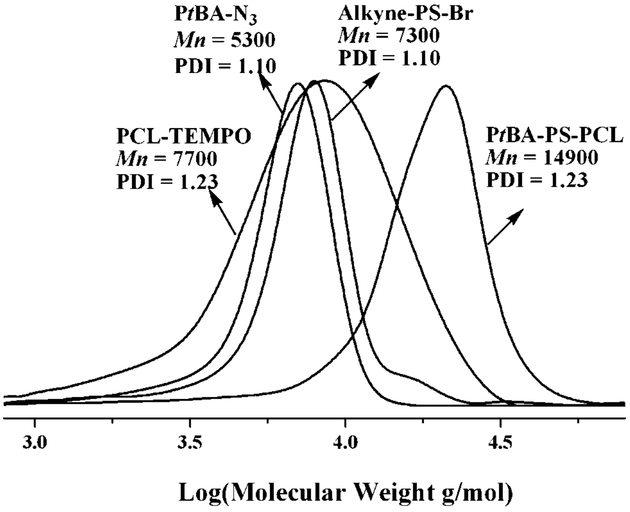


Figure 9. GPC curves of P*t*BA$_b$−PS$_A$−PCL and the corresponding precursors P*t*BA$_b$-N$_3$, PCL-TEMPO, and alkyne-PS$_A$-Br by using an RI detector.

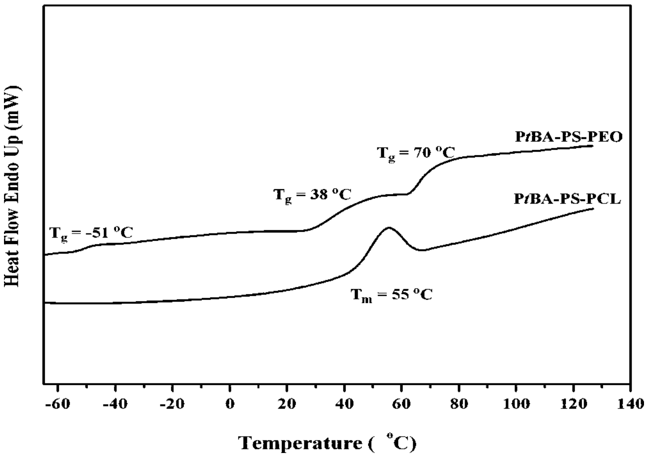


Figure 10. DSC spectra of P*t*BA$_a$−PS$_A$−PEO and P*t*BA$_b$−PS$_A$−PCL (heating rate: 10 °C/min, a nitrogen atmosphere). The glass transition (T_g) and the melting temperatures (T_m) were calculated as a midpoint and a peak apex of thermograms, respectively.

P*t*BA−PS−PEO, three transitions were observed at −51 °C (T_g for the PEO block), 38 °C (T_g for the P*t*BA block), and 70 °C (T_g for the PS block), but the T_gs of their corresponding individual polymers are −61, 38, and 90 °C for PEO,[46] P*t*BA,[47] and PS,[48] respectively. In addition, from a DSC analysis of the P*t*BA-PS-PCL, only one melting transition (T_m) was detected at 55 °C (for PCL block) compared with 45 °C for individual PCL homopolymer,[48] and not any T_g traces for the P*t*BA or PS block could be detected. These examples confirmed that in triblock copolymers the interaction between polymer blocks can affect the segment movement of corresponding polymers, leading to the variation of the T_g and T_m of polymer blocks.

Conclusions

A new strategy for one-pot synthesis of ABC type triblock copolymer via a combination of "click" and ATNRC reaction was provided. All the corresponding precursors, alkyne-PS-Br, P*t*BA-N$_3$, PEO-TEMPO, and PCL-TEMPO, were easily synthesized by living polymerization. The click reaction of a terminal alkyne with an azide group and the ATNRC reaction of the TEMPO group with halide end group were successfully conducted in one pot with high efficiencies.

Acknowledgment. We appreciate the financial support of this research from the Natural Science Foundation of China (No. 20574010).

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

Note Added After ASAP Publication. This article was published ASAP on May 13, 2008. A correction has been made to reference 41. The correct version was published on June 17, 2008.

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MA702404T