One-Pot Preparation of ABA-Type Block-Graft Copolymers via a Combination of ''Click'' Chemistry with Atom Transfer Nitroxide Radical Coupling Reaction

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ABSTRACT: A new strategy for the one-pot preparation of ABA-type block-graft copolymers via a combination of Cu-catalyzed azide-alkyne cycloaddition (CuAAC) "click" chemistry with atom transfer nitroxide radical coupling (ATNRC) reaction was reported. First, sequential ring-opening polymerization of 4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (GTEMPO) and 1-ethoxyethyl glycidyl ether provided a backbone with pendant TEMPO and ethoxyethyl-protected hydroxyl groups, the hydroxyl groups could be recovered by hydrolysis and then esterified with 2-bromoisobutyryl bromide, the bromide groups were converted into azide groups via treatment with NaN_3. Subsequently, bromine-containing poly(tert-butyl acrylate) (PtBA-Br) was synthesized by atom transfer radical polymeriza-

tion. Alkyne-containing polystyrene (PS-alkyne) was prepared by capping polystyryl-lithium with ethylene oxide and subsequent modification by propargyl bromide. Finally, the CuAAC and ATNRC reaction proceeded simultaneously between backbone and PtBA-Br, PS-alkyne. The effects of catalyst systems on one-pot reaction were discussed. The block-graft copolymers and intermediates were characterized by size-exclusion chromatography, ^{1}H NMR, and FT-IR in detail. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 5430–5438, 2010

KEYWORDS: atom transfer radical polymerization; block copolymers; graft copolymers; "click" chemistry; atom transfer nitroxide radical coupling

INTRODUCTION The copolymers with well-defined architectures show some novel properties stemming from their unique structures, such as block,[1] star[2] and graft.[3] Nowadays, these copolymers have been attracting much interest, because there has been wide application of well-defined polymeric architectures in industry.[4] Block-graft copolymer, consisting of block and graft structures, is a new kind of copolymer because of their ability to arrange the different side chains on backbone accurately, such as the hard graft chain outside and soft chain inside.[5] Up to now, few works have reported ABA-type block-graft copolymers, because the synthesis of these copolymers is still a challenge.[5–7]

Generally, there are three strategies for graft copolymer: "grafting from,"[8,9] "grafting through"[10,11] and "grafting onto".[12,13] The "grafting onto" strategy shows a promising prospect because the backbone and side chains could be prepared separately with controllable molecular parameters. However, low grafting efficiency was usually a basic drawback, and looking for synthetic route with high efficiencies and simplicity in practice was always an essential work.

Recently, one-pot methods have gained attention in polymer science[14–19] because of their simple operation procedure. Up to now, several graft copolymers with different structures

have been prepared using a one-pot procedure. Wooley et al. synthesized a core-shell brush by ring-opening metathesis and reversible addition-fragmentation chain transfer copolymerization.[15] Ochiai et al. reported the one-pot synthesis of graft copolymer by a combination of free radical polymerization and polyaddition.[18] Wang et al. prepared amphiphilic centipede-like brush copolymers by a one-pot synthesis strategy combining ring-opening polymerization (ROP) and "click" reaction.[19] However, the "grafting from" strategy was usually adopted in these works, and the accurate control of molecular weight and the chain structure in these cases is still questionable. In this presentation, "grafting onto" strategy is adopted by using two coupling reactions in one pot.[16]

Fortunately, Cu-catalyzed azide-alkyne cycloaddition (CuAAC) "Click" chemistry is researched intensively due to their high specificity, quantitative yields and near-perfect fidelity in the presence of most functional groups,[20–24] which proved to be a powerful tool for synthesis of graft copolymers.[25–29] As a novel coupling reaction, atom transfer nitroxide radical coupling (ATNRC) reaction between 2,2,6,6-tetramethyl-piperidine-1-oxyl (TEMPO) and in situ generated radicals by atom transfer radical polymerization[30] (ATRP) had been intensively investigated and developed.[31] Percec reported

single electron transfer living radical polymerization (SET-LRP),[32–44] which provides a new strategy to generate macro-radicals. The macro-radicals generated by SET mechanism are trapped by nitroxide radicals, and the coupling reaction was termed as single electron transfer nitroxide radical coupling (SETNRC) reaction.[45–47] Using nitroxide radical coupling (NRC) reaction, some block,[45,48] star-shaped,[46,47,49,50] and graft copolymers[31,51] were constructed successfully. Our previous works ever described the use of one-pot technique combining CuAAC "Click" chemistry with ATNRC reaction to prepare copolymers of the block[48] and star[50] structures in high efficiency. Therefore, it is promising to apply them for preparation of block-graft copolymer by one-pot.

In this work, the ABA-type block-graft copolymer was prepared via the one-pot reaction by a combination of CuAAC with ATNRC. The catalyst system of $CuBr/Cu^0$/PMDETA was used in the reaction, which is the better system compared with the CuBr/PMDETA.

EXPERIMENTAL

Materials

2,2-dimethyl-1,3-propanediol (Acros Organics) was dried *in vacuo* at 50 °C for 24 h. 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%; SCR), propargyl bromide (99%), N,N-dimethylformamide (DMF, 99%) and dimethyl sulfoxide (DMSO; 98%) were dried over CaH_2 and distilled under reduced pressure before use. CuBr (95%) was stirred overnight in acetic acid, filtered, washed with ethanol and diethyl ether successively, and dried *in vacuo*. Copper powder (Cu^0, 99%, Aldrich) N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA, Aldrich), ethyl 2-bromoisobutyrate (EBiB, Aldrich) were used as received. And other reagents were all purchased from SCR and purified by standard methods.

Diphenylmethyl potassium (DPMK) solution was freshly prepared according to the literature,[52] the concentration was 0.75 mol/L. 4-Glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (GTEMPO) was synthesized according to our previous work.[53] and 1-ethoxyethyl glycidyl ether (EEGE) was synthesized from glycidol (Gly) and ethyl vinyl ether according to Fitton et al.[54]

Synthesis of the Poly(EO-*co*-EEGE)-*b*-Poly(EO-*co*-GTEMPO)-*b*-Poly(EO-*co*-EEGE) Backbone with Pendant TEMPO and Ethoxyethyl-Protected Hydroxyl Groups

The copolymer poly(EO-*co*-EEGE)-*b*-poly(EO-*co*-GTEMPO)-*b*-poly(EO-*co*-EEGE) was prepared through sequential anionic ROP. The typical procedure is described as follows: Into a 150-mL dried stainless steel kettle, the anhydrous 2,2-dimethyl-1,3-propanediol (0.28 g, 2.69 mmol) dissolved in mixed solvents of DMSO and tetrahydrofuran (THF) (v/v: 3/2, 60 mL), a solution of DPMK in THF (3.59 mL, 2.69 mmol)

were slowly introduced. Then GTEMPO (3.68 g, 16.2 mmol) and EO (8.2 mL, 162 mmol) were added, and the solution was stirred at 55 °C for 48 h. After the kettle was cooled to −20 °C, EEGE (3.4 mL, 24.2 mmol) and EO (12.3 mL, 242 mmol) were introduced into kettle under magnetic stirring, and the solution was again maintained at 55 °C for another 48 h. The final polymer was purified by dissolution/precipitation with methylene chloride/ petroleum ether (60–90 °C) twice. The red viscous product poly(EO-*co*-EEGE)-*b*-poly(EO-*co*-GTEMPO)-*b*-poly(EO-*co*-EEGE) was dried *in vacuo* at room temperature (22.38 g, yield: 89.5%). ^1H NMR (CD_3OD), in the presence of calculated amounts of $HCOONH_4$ and Pd/C, δ ppm: 0.9 (s, 6H, —C(CH_3)$_2$—), 1.1–1.32 (complex, 18H, CH_3CH$_2$O—, —CH(CH_3)— of EEGE and —CH_3 of GTEMPO), 1.43, 1.91 (complex, 4H, —CH_2— of GTEMPO), 3.25 (s, 4H, —C(CH$_3$)$_2$CH_2O—), 3.5–3.8 (m, 17H, —CH_2CH_2O— of PEO, —CH—, —OCH_2CH(CH$_2$)— of GTEMPO, and —OCH_2CH(CH$_2$)—, CH$_3$CH_2O— of EEGE), 4.7 (—OCH(CH$_3$)O—of EEGE), $M_{n,NMR}$: 9,900 g/mol. Size-exclusion chromatography (SEC), M_n: 9,800 g/mol, polydispersity index (PDI): 1.12.

Synthesis of Poly(EO-*co*-AiBGE)-*b*-Poly(EO-*co*-GTEMPO)-*b*-Poly(EO-*co*-AiBGE) Backbone with Pendant TEMPO and Azide Groups

Poly(EO-*co*-AiBGE)-*b*-poly(EO-*co*-GTEMPO)-*b*-poly(EO-*co*-AiBGE) was obtained by transforming the EEGE units (on poly(EO-*co*-EEGE)-*b*-poly(EO-*co*-GTEMPO)-*b*-poly(EO-*co*-EEGE)) into glycidol (Gly) units by hydrolysis, then into 2-bromoisobutyryloxyglycidyl ether (BiBGE) by esterification and 2-azideisobutyryloxyglycidyl ether (AiBGE) by azidation, respectively.[28]

The typical preparation procedure for Poly(EO-*co*-Gly)-*b*-poly(EO-*co*-GTEMPO)-*b*-poly(EO-*co*-Gly) (according to literature.[28]): Poly(EO-*co*-EEGE)-*b*-poly(EO-*co*-GTEMPO)-*b*-poly(EO-*co*-EEGE) ($M_{n,NMR}$: 9800 g/mol, 5 g) was mixed with formic acid (60 mL), the solution was stirred at room temperature for 30 min and then evaporated under reduced pressure vacuo 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 mol/L). The red copolymer poly(EO-*co*-Gly)-*b*-poly(EO-*co*-GTEMPO)-*b*-poly(EO-*co*-Gly) was obtained by separation of the formed salts and precipitation in cold petroleum ether (60–90 °C) twice and dried under vacuum at 40 °C till to a constant weight (4.6 g, yield: 92%). ^1H NMR (CD_3OD), in the presence of calculated amounts of $HCOONH_4$ and Pd/C, δ ppm: 0.9 (s, 6H, -C(CH_3)$_2$-), 1.18, 1.43, and 1.91 (complex, 16H, —CH_2—, —CH_3 of GTEMPO), 3.25 (s, 4H, —C(CH$_3$)$_2$CH_2O—), 3.5–3.8 (m, 15H, —CH_2CH_2O—, —CH_2CH(CH$_2$OH)O— of PEO, and —CH—, —OCH_2CH(CH$_2$)— of GTEMPO). $M_{n,cal}$: 9300 g/mol.

The typical preparation procedure for Poly(EO-*co*-BiBGE)-*b*-poly(EO-*co*-GTEMPO)-*b*-poly(EO-*co*-BiBGE): dried poly(EO-*co*-Gly)-*b*-poly(EO-*co*-GTEMPO)-*b*-poly(EO-*co*-Gly) ($M_{n,cal}$ 9300 g/mol, 4 g, 4.4 mmol hydroxyl groups) was dissolved in anhydrous pyridine (100 mL), then 2-bromoisobutyryl bromide (0.82 mL, 6.6 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 poly(EO-co-BiBGE)-b-poly(EO-co-GTEMPO)-b-poly(EO-co-BiBGE) with red color was obtained with the yield of 85%. ^{1}H NMR (CD$_3$OD), in the presence of calculated amounts of HCOONH$_4$ and Pd/C, δ ppm: 0.9 (s, 6H, —C(CH$_3$)$_2$—), 1.18, 1.43, and 1.91 (complex, 16H, —CH$_2$—, —CH$_3$ of GTEMPO), 1.94 (s, 6H, —C(CH$_3$)$_2$Br), 3.25 (s, 4H, —C(CH$_3$)$_2$CH$_2$O—), 3.5–3.8 (m, 13H, —CH$_2$CH$_2$O— —CH$_2$CH(CH$_2$—)O— of PEO, and —CH—, —CH$_2$CH(CH$_2$)O— of GTEMPO), 4.13–4.42 (m, 2H, —CH$_2$OCOC(CH$_3$)$_2$Br). $M_{\text{n,cal.}}$: 10,800 g/mol.

The typical preparation procedure for poly(EO-co-AiBGE)-b-poly(EO-co-GTEMPO)-b-poly(EO-co-AiBGE) (according to the literature[28]): Poly(EO-co-BiBGE)-b- poly(EO-co-GTEMPO) -b-poly(EO-co-BiBGE) (1.5 g, 1.4 mmol bromide atoms) was dissolved in DMF (20 mL), then NaN$_3$ (0.91 g, 14 mmol) was added and stirred for 24 h at room temperature. The polymer solution was passed through a short column of neutral alumina to remove the formed salt. After removal of DMF under reduced pressure, the copolymer poly[(EO-co-AiBGE)-b-poly(EO-co-GTEMPO)-b-poly(EO-co-AiBGE) was recovered by precipitation into petroleum ether, then stored at −20 °C before use. Yield: 80%. $M_{\text{n,cal.}}$: 10,500 g/mol. FT-IR (cm^{-1}): 1121 (—C—O—C—), 1726 (—COO—), 2108 (—N$_3$).

Synthesis of Bromine-Containing Poly(*tert*-Butyl Acrylate) (P*t*BA-Br)

To a 50-mL ampoule, EBiB (0.254 mL, 1.72 mmol), CuBr (0.172 g, 1.2 mmol), PMDETA (0.25mL, 1.2 mmol), and *t*BA (26 mL, 179 mmol) in acetone (26 mL) were charged, and then the mixture was vacuumed by three freeze-pump-thaw cycles and left under nitrogen. The ampoule was immersed in oil bath at 60 °C for 4.5 h and stopped by dipping the ampoule into liquid nitrogen. The reaction mixture was diluted with THF and filtered through an activated neutral alumina column to remove the copper salts. The polymer precipitated in CH$_3$OH/H$_2$O (v/v = 1/1) was collected and dried at 40 °C in vacuum for 4 h. ^{1}H NMR (CDCl$_3$), δ (ppm): 1.13 (s, 6H, —C(CH$_3$)$_2$—P*t*BA), 1.20–2.29 (m, 15H, CH$_3$CH$_2$O—, —CH$_2$CH—, and —C(CH$_3$)$_3$ of P*t*BA), 4.05–4.15 (m, 3H, CH$_3$CH$_2$O— and —CH—Br). $M_{\text{n NMR}}$: 3100 g/mol, Conversion: 21.6%. SEC, M_{n}: 3,100 g/mol, PDI: 1.09. FT-IR (cm^{-1}): 1726 (—COO—).

Synthesis of Alkyne-Containing Polystyrene (PS-alkyne)

First, the poly(styryl)lithium (PS$^-$Li$^+$) prepared using butyl lithium as initiator for anionic polymerization of St was capped by EO to form the functionalized PS with an active hydroxyl group at ω-end (PS—OH) according to literature.[55] SEC, M_{n}: 1900 g/mol, PDI: 1.08.

Then, PS-alkyne was prepared by the nucleophilic substitution reaction between active hydroxyl group and propargyl bromide: To a 250 mL dried ampoule, PS—OH ($M_{\text{n,SEC}}$: 1900 g/mol, 8 g, 4.21 mmol) and THF (60 mL) were added. Then the system was bubbled with N$_2$ and DPMK solution was introduced until the solution was turned into reddish-brown. After the ampoule was placed in ice bath, propargyl bromide

(1.87 mL, 2.5 g, 21 mmol) was added dropwise during 2 h, and the reaction was continued for 24 h at room temperature. The PS-alkyne was obtained by separation of the formed salts and precipitation in cold methanol twice, and dried under vacuum at 40 °C for 12 h until constant weight (7.76 g, yield :97.0%). ^{1}H NMR (CDCl$_3$) δ (ppm): 0.80 (m, 3H, CH$_3$CH$_2$—), 1.26–2.1 (m, 3H, —CHCH$_2$— of PS), 3.05–3.30 (m, 2H, —CH$_2$CH$_2$O—), 3.84–4.18 (m, 2H, —OCH$_2$C≡CH), 6.30–7.30 (m, 5H, C$_6$H$_5$—), $M_{\text{n NMR}}$: 2,100 g/mol. SEC, M_{n}: 1,900 g/mol, PDI: 1.07. FT-IR (cm^{-1}): 3300 (—C≡CH).

One-Pot Synthesis of ABA-Type Block-Graft Copolymer [Poly(EO-*co*-AiBGE)-*g*-PS]-*b*-[Poly(EO-*co*-GTEMPO)-*g*-P*t*BA]-*b*-[Poly(EO-*co*-AiBGE)-*g*-PS] ((PEO-*g*-PS)-*b*-(PEO-*g*-P*t*BA)-*b*-(PEO-*g*-PS))

Typically, the reaction in the presence of CuBr/Cu^0/PMDETA was carried out using the following procedure: Into a 50-mL ampoule, poly(EO-*co*-AiBGE)-*b*-poly(EO-*co*-GTEMPO)-*b*-poly (EO-*co*-AiBGE) ($M_{\text{n cal}}$: 10,500 g/mol, 0.1 g, 9.5 × 10^{-3} mmol), P*t*BA-Br ($M_{\text{n NMR}}$: 3100 g/mol, 0.227 g, 0.073 mmol, [TEMPO]:[Br] = 1:1.2), PS-alkyne ($M_{\text{n NMR}}$: 2100 g/mol., 0.242 g, 0.115 mmol, [azide]:[alkyne] = 1:1.2), CuBr (0.112 g, 0.786 mmol), Cu^0 (0.05 g, 0.786 mmol), PMDETA (0.164 mL, 0.786 mmol), and DMF (6 mL) were charged. The reaction mixture was then vacuumed by three freeze-pump-thaw cycles and purged with N$_2$, heated to 90 °C for 24 h and then immersed in liquid nitrogen. After evaporation of DMF, the reaction mixture was diluted with THF and passed through an activated neutral alumina column to remove the copper salts. The crude product was dissolved in cyclohexane, then petroleum ether was added slowly to the solution under continuous agitation at room temperature until the polymer precipitate instantaneously. The backbone of graft copolymer [Poly(EO-*co*-AiBGE)-*g*-PS]-*b*-[poly(EO-*co*-GTEMPO)-*g*-P*t*BA]-*b*-[poly(EO-*co*-AiBGE)-*g*-PS] showed the same structure as PEO, so it is named as (PEO-*g*-PS)-*b*-(PEO-*g*-P*t*BA)-*b*-(PEO-*g*-PS) briefly. The latter was collected by centrifugation and dried *in vacuo*. ^{1}H NMR (CDCl$_3$), δ (ppm): 0.7–1.18 (m, 24H, CH$_3$CH$_2$— of PS, CH$_3$CH$_2$OCOC(CH$_3$)$_2$— of P*t*BA, —CH$_3$ of GTEMPO), 1.2–2.1 (m, 14H, —CH$_2$CH— of PS, —CH$_2$CH— and —C(CH$_3$)$_3$ of P*t*BA), 2.2 (s, 1H, —CH$_2$—CH— of P*t*BA), 3.0–3.23 (m, 2H, —OCH$_2$CH$_2$—PS), 3.5–3.8 (m, 13H, —CH$_2$CH$_2$O—, —CH$_2$CH(CH$_2$—)O— of PEO, and —CH—, —OCH$_2$CH(CH$_2$)— of GTEMPO), 4.05–4.15 (s, 2H, CH$_3$CH$_2$O— of P*t*BA), 4.2–4.45 (m, 2H, —CH$_2$OCOC(CH$_3$)$_2$-triazole ring), 4.55–4.7 (s, 2H, —OCH$_2$-(4-triazole), 6.3–7.3 (m, 5H, C$_6$H$_5$- of PS), 7.7 (s, 1H, —CH— of triazole ring). SEC, M_{n}: 19,800 g/mol, PDI: 1.13. FT-IR(cm^{-1}): 1146 (—C—O—C—), 1454, 1494, 1601 (aromatic, —C—C—) and 1726 (—COO—) 3027 (aromatic, —C—H).

By varying molecular weight (M_{n}) of side chains and catalyst systems(CuBr/Cu^0/PMDETA, CuBr/PMDETA), a series of block-graft copolymers were prepared.

Characterizations

SEC was performed in THF at 35 °C with an elution rate of 1.0 mL/min on an Agilent1100 with a G1310A pump, a G1362A refractive index detector and a G1314A variable
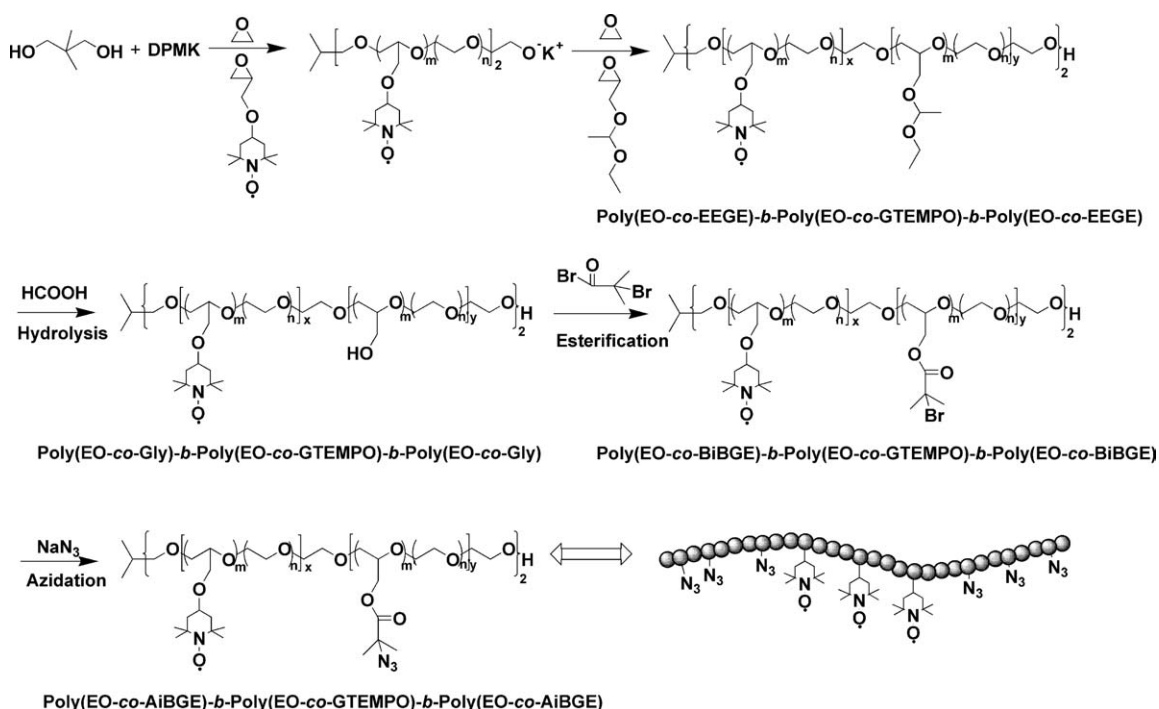
SCHEME 1 Schematic synthesis route of the backbone Poly(EO-*co*-AiBGE)-*b*-Poly(EO-*co*-GTEMPO)-*b*-Poly(EO-*co*-AiBGE).

wavelength detector. One 5 μm LP gel column (500 Å, 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) were calibrated by PS standard samples. The injection volume was 20 μL, and the concentration was 5 mg/mL. ^{1}H NMR spectra were recorded at room temperature by a Bruker (500 MHz) spectrometer using tetramethylsilane as the internal standard and deuterated chloroform (CDCl$_3$) as the solvent, except for the GTEMPO-containing copolymers; which were determined in deuterated methanol (CD$_3$OD) with stoichiometric ammonium formate (HCOONH$_4$) and the catalyst palladium on carbon (Pd/C). Fourier transform infrared (FT-IR) spectra were recorded on a Magna-550 FT-IR spectrometer (NaCl tablet).

RESULTS AND DISCUSSIONS

Preparation and Characterization of Poly(EO-*co*-AiBGE)-*b*-Poly(EO-*co*-GTEMPO)-*b*-Poly(EO-*co*-AiBGE) Backbone with Pendant TEMPO and Azide Groups

The procedure for synthesis of PEO backbone was described in Scheme 1. The backbone poly(EO-*co*-EEGE)-*b*-poly(EO-*co*-GTEMPO)-*b*-poly(EO-*co*- EEGE) was successfully prepared through the sequential anionic copolymerization of EO and GTEMPO, EO, and EEGE using DPMK and 2,2-dimethyl-1,3-propanediol as coinitiator, and a mixture of DMSO and THF (v/v: 3/2) as solvent. The SEC curve C of poly[(EO-*co*-EEGE)-*b*-poly(EO-*co*-GTEMPO)-*b*-poly(EO-*co*-EEGE) in Figure 1 showed a monomodal peak with PDI of <1.12.

Because of the paramagnetism of the pendant TEMPO radicals, the ^{1}H NMR was carried out in deuterated methanol in

the presence of stoichiometric HCOONH$_4$ and catalytic Pd/C for the reduction of the TEMPO radicals to corresponding oximes. The structure of copolymer poly(EO-*co*-EEGE)-*b*-poly(EO-*co*-GTEMPO)-*b*- poly(EO-*co*-EEGE) was confirmed by ^{1}H NMR spectrum (Fig. 2). Clearly, the EEGE in the copolymer can be confirmed by the signal at 4.7 ppm (—OCH(CH$_3$)O—), and the signals at 1.18, 1.43, and 1.91 ppm (—CH_2—, —CH_3 of GTEMPO) showed the extisence of GTEMPO. The methyl protons (—C(CH_3)$_2$—) of 2,2-dimethyl-1,3-propanediol were detected at 0.9 ppm. Therefore, the number of EEGE (N_{EEGE}: 8.2), GTEMPO (N_{GTEMPO}: 6.4) and EO
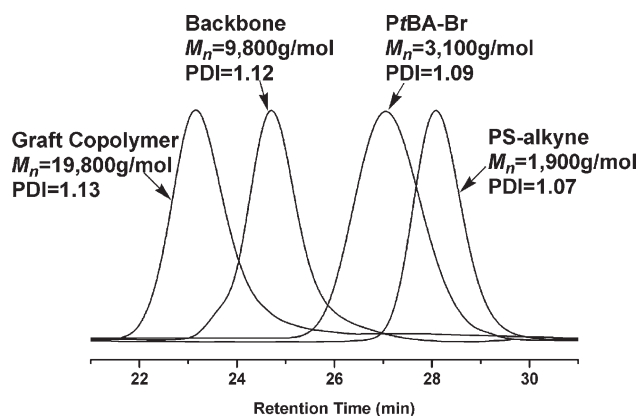

FIGURE 1 SEC traces of (A) PS-alkyne, (B) P*t*BA-Br, (C) Backbone poly(EO-*co*-EEGE)-*b*-poly(EO-*co*-GTEMPO)-*b*-poly(EO-*co*-EEGE), and (D) Graft copolymer (PEO-*g*-PS)-*b*-(PEO-*g*-P*t*BA)-*b*-(PEO-*g*-PS).
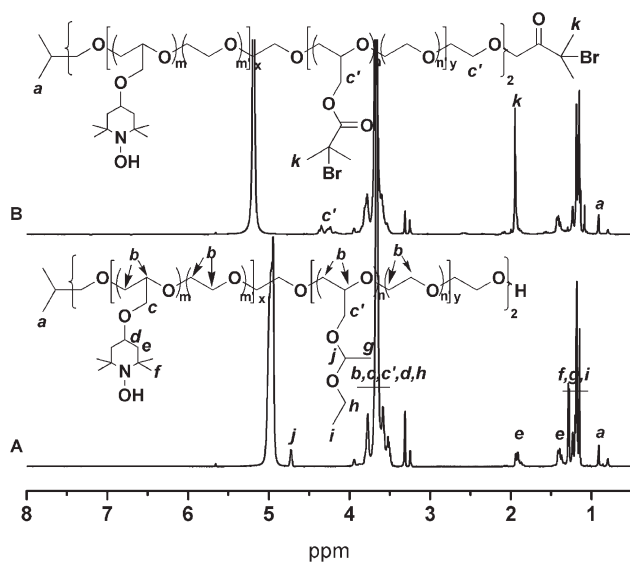
FIGURE 2 ^{1}H NMR spectra of (A) poly(EO-*co*-EEGE)-*b*-poly(EO-*co*-GTEMPO)-*b*-poly(EO-*co*-EEGE), and (B) poly(EO-*co*-BiBGE)-*b*-poly(EO-*co*-GTEMPO)-*b*-poly(EO-*co*-BiBGE)] in the presence of Pd/C and HCOONH$_4$, (solvent: CD$_3$OD).

(N_{EO}: 161.5) in poly(EO-*co*-EEGE)-*b*-poly(EO-*co*-GTEMPO)-*b*-poly(EO-*co*-EEGE) can be calculated using the following eqs 1–3, respectively.

$$N_{EEGE} = \frac{6A_j}{A_a} \tag{1}$$

$$N_{GTEMPO} = \frac{6(A_{f+g+i} - 6A_j)}{12A_a} \tag{2}$$

$$N_{EO} = \frac{6(A_{b+c+c'+d+h} - 7N_{EEGE} - 6N_{GTEMPO})}{4A_a} \tag{3}$$

where A_a, A_{f+g+i}, A_j, $A_{b+c+c'+d+h}$ were the integral areas of corresponding protons at 0.9 ppm, 1.1–1.32 ppm, 3.5–3.8 ppm, 4.7 ppm in ^{1}H NMR (Fig. 2). The molecular weight of poly(EO-*co*-EEGE)-*b*-poly(EO-*co*-GTEMPO)-*b*-poly(EO-*co*-EEGE) ($M_{n\,NMR}$: 9,900 g/mol) could also be calculated by eq 4:

$$M_{nNMR} = 104 + 44 \times N_{EO} + 146 \times N_{EEGE} + 228 \times N_{GTEMPO} \tag{4}$$

where the values of 104, 44, 146, and 228 were the molecular weight of 2,2-dimethyl-1,3-propanediol, EO, EEGE and GTEMPO, respectively.

The EEGE units on poly(EO-*co*-EEGE)-*b*-poly(EO-*co*-GTEMPO)-*b*-poly(EO-*co*-EEGE) were hydrolyzed and turned into glycidol units. The complete removal of the 1-ethoxyethyl groups was confirmed by completely disappearance of the signal assigned to the 1-ethoxyethyl group (—OCH(CH$_3$)O—) of EEGE at 4.70 ppm. The formed poly[(EO-*co*-Gly)-*b*-(EO-*co*-GTEMPO)-*b*-(EO-*co*-Gly)] was then esterified by the reaction of recovered hydroxyl groups on

glycidol units with 2-bromoisobutyryl bromide, and the esterification efficiency (E.F.$_{esterification}$: 98.8%) of the copolymer poly(EO-*co*-BiBGE)-*b*-poly(EO-*co*-GTEMPO)-*b*-poly(EO-*co*-BiBGE), could be calculated by eq 5:

$$\text{E.F.}_{(esterification)} = \frac{\frac{A_{c'}}{2}}{\frac{A_a}{6}(N_{EEGE} + 2)} \times 100\% \tag{5}$$

where A_a and $A_{c'}$ were the integral areas of corresponding protons at 0.9 ppm (glycidol C(CH_3)$_2$glycidol), 4.13–4.42 ppm (—CH_2OCOC(CH$_3$)$_2$Br), respectively. And the others were the same as defined before.

Finally, the pendant bromide atoms of poly(EO-*co*-BiBGE)-*b*-poly(EO-*co*-GTEMPO)-*b*-poly(EO-*co*-BiBGE) were easily and completely transformed to azides by a nucleophilic substitution reaction with NaN$_3$ in DMF at room temperature.[28,50] Then the copolymer poly(EO-*co*-AiBGE)-*b*-poly(EO-*co*-GTEMPO)-*b*-poly(EO-*co*-AiBGE) with multiple TEMPO and azide groups was obtained. FT-IR spectrum of poly(EO-*co*-AiBGE)-*b*-poly(EO-*co*-GTEMPO)-*b*-poly(EO-*co*-AiBGE) was shown in Figure 3. The characteristic bands of azide at 2108 cm^{-1} could be easily observed, which confirmed the successful of azidation.

Preparation and Characterization of P*t*BA-Br and PS-Alkyne

The precursor P*t*BA-Br was synthesized by typical ATRP using EBiB as initiator and CuBr/PMDETA as catalyst (Scheme 2). By controlling the conversion (under 30%), the P*t*BA with high bromination degree at chain end could be obtained,[56] and two P*t*BA-Br samples with different M_n were obtained by stopping the reaction at different times (Table 1). Two characteristic peaks could be observed in ^{1}H NMR spectrum of P*t*BA-Br (Fig. 4): the resonance signal for
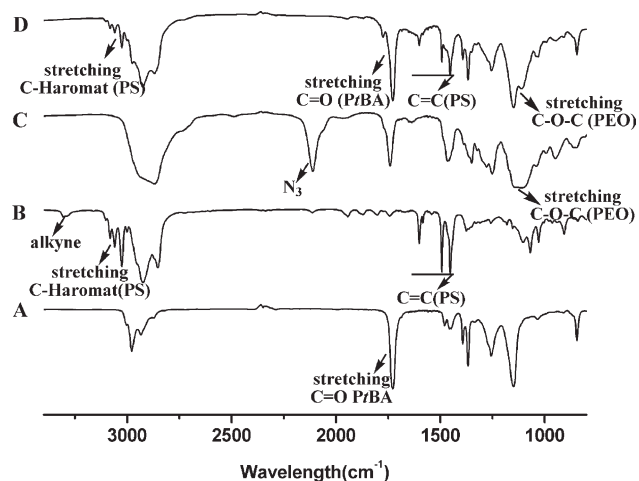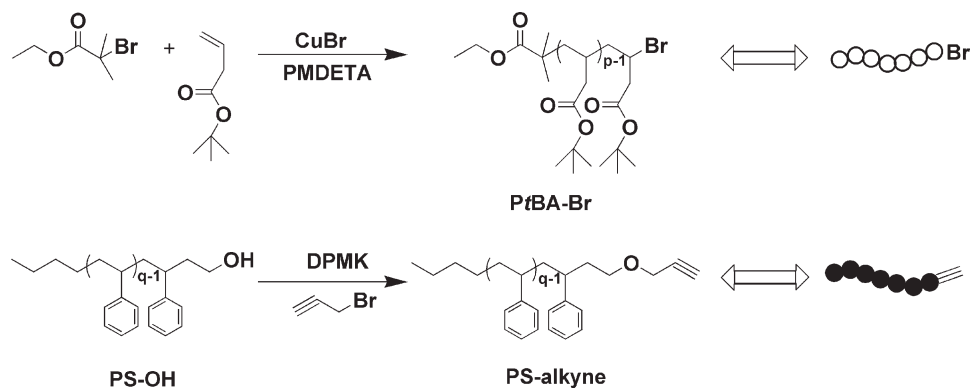

FIGURE 3 FT-IR spectra of (A) P*t*BA-Br, (B) PS-alkyne, (C) backbone poly(EO-*co*-AiBGE)-*b*-poly(EO-*co*-GTEMPO)-*b*-poly(EO-*co*-AiBGE), and (D) graft copolymer (PEO-*g*-PS)-*b*-(PEO-*g*-P*t*BA)-*b*-(PEO-*g*-PS).

SCHEME 2 The synthesis of precursors P*t*BA-Br and PS-alkyne.

methine protons of P*t*BA-Br occurs at 2.2 ppm, the methine resonance for —C**H**—Br functional group and the methylene resonances for the CH$_3$C**H**$_2$O— group from EBiB were observed at 4.05–4.15 ppm. Thus, the average degree of polymerization (DP) of P*t*BA-Br was derived from the integrated area ratio of peaks at 4.05–4.15 ppm and 2.2 ppm (Table 1).

The preparation of PS-alkyne was illustrated in Scheme 2. First, the poly(styryl)lithium (PS$^-$Li$^+$) was capped by EO to form the functionalized polymer PS—OH, which had an active hydroxyl group at ω-end. Subsequently, the propargyl group was introduced to ω-end of PS—OH by the nucleophilic substitution reaction between active hydroxyl group and propargyl bromide at 0 °C. From ^{1}H NMR spectrum (Fig. 4), a new peak at 3.84–4.18 ppm was observed after the hydroxyl group was transformed into alkyne group, which was an indicative of the formation of PS-alkyne by the functionalization of PS-OH with propargyl bromide. The functionality efficiency and the average DP of PS-alkyne can be calculated based on ^{1}H NMR data, respectively (Table 1).

Monomodal curves for P*t*AB-Br and PS-alkyne with low PDIs were illustrated in Figure 1, which also confirmed the successful synthesis of precursors (Table 1).

Preparation and Characterization of Block-Graft Copolymers (PEO-*g*-PS)-*b*-(PEO-*g*-P*t*BA)-*b*-(PEO-*g*-PS) by One-Pot Method

The block-graft copolymer was prepared by mixing PS-alkyne, P*t*BA-Br and backbone poly(EO-*co*-AiBGE)-*b*-poly(EO-*co*-GTEMPO)-*b*-poly(EO-*co*-AiBGE) with the definite ratio in an ampoule by one pot (Scheme 2), the effects of molecular weight of precursors and catalyst systems on copolymers were discussed (Table 2).

In this system, alkyne group at PS end would couple with azide on backbone to form triazole ring,[21] whereas the macroradicals generated at P*t*BA-Br end were trapped by the stable nitroxide radicals of TEMPO on backbone to form alkoxyamines,[31] thus the block-graft copolymer was prepared. The crude product could be purified by dissolution/precipitation with cyclohexane/petroleum ether to remove unreacted P*t*BA-Br and PS-alkyne. Figure 1 showed the SEC curve of block-graft copolymer (PEO-*g*-PS)-*b*-(PEO-*g*-P*t*BA)-*b*-(PEO-*g*-PS) (sample **G4** in Table 2) after purification, which showed a Gaussian distribution with narrow PDI and meant that the excess PS and P*t*BA precursor were completely removed.

TABLE 1 The Data for Precursors P*t*BA-Br and PS-Alkyne

Sample	$M_{n,\,SEC}$[a] (g/mol)	PDI[a]	$M_{n,\,NMR}$[b] (g/mol)	DP[c]	E.F. (%)[d]
P*t*BA1	1700	1.10	1700	11.8	
P*t*BA2	3100	1.09	3100	22.5	
PS1	1900	1.07	2100	18.6	98.8
PS2	4300	1.03	4300	40	99.1

[a] Measured by SEC in THF with linear PS as standard.
[b] Calculated from ^{1}H NMR data. The formulas displayed as follow: $M_{n,NMR(PtBA)} = 128 \times DP + 195$, $M_{n,NMR(PS)} = 104 \times DP + 140$, where DP represent the average degree of polymerization of P*t*BA-Br or PS-alkyne.
[c] DP is Average degree of polymerization of St or *t*BA, calculated from the ^{1}H NMR data. The formulas displayed as follow: $DP_{tBA} = \frac{3A_b}{A_{a,c}}$, $DP_{st} = \frac{2A_f}{5A_d}$, where $A_{a,c}$, A_b, A_d, and A_f represent the integral areas of corresponding protons in ^{1}H NMR (Fig. 4).
[d] E.F. is the efficiency of functionalization of PS end groups, calculated from ^{1}H NMR data on the formula: $E.F._{\cdot propargyl} = \frac{A_e}{A_d}$, where A_d and A_e represent the integral areas of corresponding protons in ^{1}H NMR. (Fig. 4).
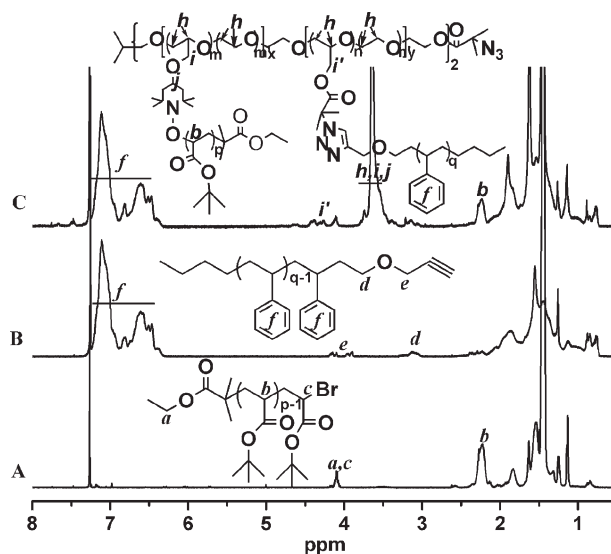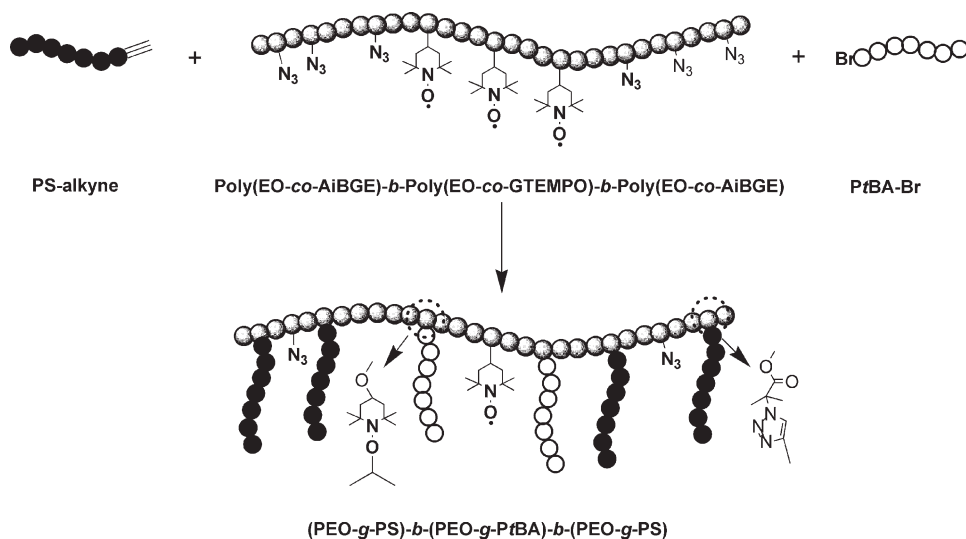

FIGURE 4 ^{1}H NMR spectra of (A) P*t*BA-Br, (B) PS-alkyne, and (C) (PEO-*g*-PS)-*b*-(PEO-*g*-P*t*BA)-*b*-(PEO-*g*-PS) (solvent: CDCl$_3$).

PS-alkyne **Poly(EO-co-AiBGE)-b-Poly(EO-co-GTEMPO)-b-Poly(EO-co-AiBGE)** **PtBA-Br**

(PEO-g-PS)-b-(PEO-g-PtBA)-b-(PEO-g-PS)

SCHEME 3 The synthesis of ABA-type block-graft copolymers (PEO-g-PS)-b-(PEO-g-PtBA)-b-(PEO-g-PS) by one-pot Method.

The ^{1}H NMR spectrum of graft copolymer (PEO-g-PS)-b-(PEO-g-PtBA)-b-(PEO-g-PS) was depicted in Figure 4, in which three main regions can be observed. The typical methine group protons (—CH$_2$CH—) of PtBA at 2.2 ppm, the phenyl group (C$_6$H$_5$—) of PS at 6.30–7.30 ppm and the methylene/methine protons of backbone at 3.5–3.8 ppm were detected respectively, and these results confirmed the coupling reaction was proceeded successfully. The structure of (PEO-g-PS)-b-(PEO-g-PtBA)-b-(PEO-g-PS) was also supported by FT-IR spectra (Fig. 3). Compared with the FT-IR spectra of backbone(C), precursor PtBA-Br (A) and PS-alkyne (B), for (PEO-g-PS)-b-(PEO-g-PtBA)-b-(PEO-g-PS) (D), the characteristic signal of azide at 2108 cm^{-1} disappeared, the signals of PS at 1454, 1494, 1601, and 3027 cm^{-1} appeared and the intensity of signal from PtBA segments C=O stretching at 1726 cm^{-1} increased.

The efficiency of CuAAC "Click" chemistry (E.F.$_{CuAAC}$) in the synthesis of block-graft copolymer could be calculated according to the integrated area of resonance signal for PS segment to PEO segment in ^{1}H NMR, and the efficiency of

ATNRC reaction (E.F.$_{ATNRC}$) was calculated according to that of PtBA segment to PEO segment using the corresponding eqs 6 and 7, respectively:.

$$\text{E.F.}_{\cdot\text{CuAAC}} = \frac{\dfrac{A_f}{DP_{st} \times 5 \times 10.1}}{\dfrac{A_{h+i+j}}{709}} \times 100\% \qquad (6)$$

$$\text{E.F.}_{\cdot(\text{ATNRC})} = \frac{\dfrac{A_b}{DP_{tBA} \times 1 \times 6.4}}{\dfrac{A_{h+i+j}}{709}} \times 100\% \qquad (7)$$

where, DP_{St}, DP_{tBA}, were the average DP of St, tBA. The values of 10.1 and 6.4 were numbers of azide and TEMPO groups on backbone, respectively. The value of 709 was the number of protons at 3.5–3.8 ppm on each backbone. A_b, A_{h+i+j}, and A_f, were the integral areas of corresponding protons resonance signal at 2.2 ppm, 3.5–3.8 ppm, and 6.3–7.3 ppm in ^{1}H NMR (Fig. 4). All the data of block-graft copolymers were summarized in Table 2.

TABLE 2 The Data for One-Pot Preparation of ABA-Type Block-Graft Copolymer[a]

Sample	Side Chain Composition	Catalyst System	M_n[b] (g/mol)	PDI[b]	E.F. (%)[c] CuAAC	E.F. (%)[c] ATNRC
G1	PS1/PtBA1	CuBr/PMDETA	17,900	1.13	84.8	82.8
G2	PS1/PtBA1	CuBr/Cu^0/PMDETA	17,500	1.13	77.1	89.8
G3	PS1/PtBA2	CuBr/PMDETA	20,300	1.12	86.9	58.8
G4	PS1/PtBA2	CuBr/Cu^0/PMDETA	19,800	1.13	74.6	73.2
G5	PS2/PtBA2	CuBr/Cu^0/PMDETA	25,700	1.09	78.0	62.6

[a] Experimental conditions: [TEMPO]:[Br]=1:1.2, [azide]:[alkyne]=1:1.2, [TEMPO]:[azide]:[CuBr]::[PMDETA] =64:101:825:825. [CuBr]:[Cu^0]=1:1, when Cu^0 was applied.
[b] Measured by SEC in THF with linear PS as standard.
[c] E.F. is the coupling efficiency of CuAAC or ATNRC, Calculated from ^{1}H NMR data in eq 6 and 7 in text, respectively.

A series of side chains with different chain lengths were used to evaluate the relationship between the molecular weight and the coupling efficiency. When molecular weight of PtBA-Br decreased, the efficiency of ATNRC increased to 89.8%, but the molecular weight of PS-alkyne did not exert effect on the efficiency of CuAAC in our experiment conditions. However, it was found that the efficiency of ATNRC would reduce somewhat with the molecular weight increase of PS-alkyne, the cause may be that: once some PS side chains were grafted on backbone outside, there would be a certain steric hindrance exerted on grafting of the PtBA side chains onto the middle part of backbone.

Effect of Catalyst Systems on Efficiencies of ATNRC

Comparing G1 with G2, and G3 with G4 in Table 2, respectively, the efficiencies of ATNRC under CuBr/Cu^0/PMDETA were higher than that under CuBr/PMDETA, which meant that the concentration of PtBA macroradicals in the presence of CuBr/Cu^0/PMDETA were much higher than that in the presence of CuBr/PMDETA under the same conditions, and the CuBr/Cu^0/PMDETA system is a better choice for ATNRC than the CuBr/PMDETA system. In ATNRC reaction, the generation of macro-radicals was a key step. When CuBr/PMDETA system was used, CuBr participating in ATNRC reaction could not be regenerated as that in ATRP, but was consumed with reaction going. Thus the concentration of the macroradicals was dropped down with the consumption of CuBr and Cu(II) was accumulated.[31] However, when the Cu(0) was added to the catalyst system, the efficiency of NRC was raised. In the presence of CuBr/Cu^0/PMDETA system, ATNRC and SETNRC may occur simultaneously. SETNRC may work to produce the macroradicals in the presence of Cu(0)/PMDETA, and Cu(II) formed by ATNRC would react with Cu(0) to disproportionate to Cu(I), so the ATNRC could be carried out continuously. It may be the cause for the increase of coupling efficiency in CuBr/Cu^0/PMDETA system, but we don't know which mechanism would play the main role. The relative research is undergoing.

CONCLUSIONS

In summary, a new strategy for one-pot synthesis of ABA-type block-graft copolymer via a combination of CuAAC "Click" chemistry with ATNRC reaction was presented. The Cu(0) added in the one-pot reaction showed a positive influence on the NRC reaction. The one-pot reaction in the presence of CuBr/Cu^0/PMDETA could be conducted with high efficiency, so this synthesis route is a versatile and simple strategy for preparation of copolymer with well-defined architecture.

REFERENCES AND NOTES

1 Kim, S. O.; Solak, H. H.; Stoykovich, M. P.; Ferrier, N. J.; de Pablo, J. J.; Nealey, P. F. Nature 2003, 424, 411–414.

2 Li, Z. B.; Kesselman, E.; Talmon, Y.; Hillmyer, M. A.; Lodge, T. P. Science 2004, 306, 98–101.

3 Yan, Q.; Yuan, J. Y.; Zhang, F. B.; Sui, X. F.; Xie, X. M.; Yin, Y. W.; Wang, S. F.; Wei, Y. Biomacromolecules 2009, 10, 2033–2042.

4 Destarac, M. Macromol React Eng 2010, 4, 165–179.

5 Miura, Y.; Satoh, K.; Kamigaito, M.; Okamoto, Y.; Kaneko, T.; Jinnai, H.; Kobukata, S. Macromolecules 2007, 40, 465–473.

6 Qin, S. H.; Matyjaszewski, K.; Xu, H.; Sheiko, S. S. Macromolecules 2003, 36, 605–612.

7 Christodoulou, S.; Iatrou, H.; Lohse, D. J.; Hadjichristidis, N. J Polym Sci Polym Chem 2005, 43, 4030–4039.

8 Borner, H. G.; Beers, K.; Matyjaszewski, K.; Sheiko, S. S.; Moller, M. Macromolecules 2001, 34, 4375–4383.

9 Cheng, G. L.; Boker, A.; Zhang, M. F.; Krausch, G.; Muller, A. H. E. Macromolecules 2001, 34, 6883–6888.

10 Tsukahara, Y.; Mizuno, K.; Segawa, A.; Yamashita, Y. Macromolecules 1989, 22, 1546–1552.

11 Neugebauer, D.; Zhang, Y.; Pakula, T.; Matyjaszewski, K. Macromolecules 2005, 38, 8687–8693.

12 Deffieux, A.; Schappacher, M. Macromolecules 1999, 32, 1797–1802.

13 Ryu, S. W.; Hirao, A. Macromolecules 2000, 33, 4765–4771.

14 Durmaz, H.; Dag, A.; Altintas, O.; Erdogan, T.; Hizal, G.; Tunca, U. Macromolecules 2007, 40, 191–198.

15 Cheng, C.; Khoshdel, E.; Wooley, K. L. Macromolecules 2007, 40, 2289–2292.

16 Dag, A.; Durmaz, H.; Demir, E.; Hizal, G.; Tunca, U. J Polym Sci Polym Chem 2008, 46, 6969–6977.

17 Wolf, F. F.; Friedemann, N.; Frey, H. Macromolecules 2009, 42, 5622–5628.

18 Ochiai, B.; Kato, Y.; Endo, T. Macromolecules 2009, 42, 8001–8002.

19 Yuan, Y. Y.; Du, Q.; Wang, Y. C.; Wang, J. Macromolecules 2010, 43, 1739–1746.

20 Huisgen, R. Angew Chem Int Ed 1963, 2, 633–645.

21 Kolb, H. C.; Finn, M. G.; Sharpless, K. B. Angew Chem Int Ed 2001, 40, 2004–2021.

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

23 Meldal, M.; Tornoe, C. W. Chem Rev 2008, 108, 2952–3015.

24 Lodge, T. P. Macromolecules 2009, 42, 3827–3829.

25 Helms, B.; Mynar, J. L.; Hawker, C. J.; Frechet, J. M. J. J Am Chem Soc 2004, 126, 15020–15021.

26 Tsarevsky, N. V.; Bencherif, S. A.; Matyjaszewski, K. Macromolecules 2007, 40, 4439–4445.

27 Gao, H. F.; Matyjaszewski, K. J Am Chem Soc 2007, 129, 6633–6639.

28 Luo, X. L.; Wang, G. W.; Pang, X. C.; Huang, J. L. Macromolecules 2008, 41, 2315–2317.

29 Goldmann, A. S.; Walther, A.; Nebhani, L.; Joso, R.; Ernst, D.; Loos, K.; Barner-Kowollik, C.; Barner, L.; Muller, A. H. E. Macromolecules 2009, 42, 3707–3714.

30 Wang, J. S.; Matyjaszewski, K. J Am Chem Soc 1995, 117, 5614–5615.

31 Fu, Q.; Lin, W. C.; Huang, J. L. Macromolecules 2008, 41, 2381–2387.

32 Percec, V.; Guliashvili, T.; Ladislaw, J. S.; Wistrand, A.; Stjerndahl, A.; Sienkowska, M. J.; Monteiro, M. J.; Sahoo, S. J Am Chem Soc 2006, 128, 14156–14165.

33 Lligadas, G.; Percec, V. J Polym Sci Polym Chem 2007, 45, 4684–4695.

34 Lligadas, G.; Rosen, B. M.; Bell, C. A.; Monteiro, M. J.; Percec, V. Macromolecules 2008, 41, 8365–8371.

35 Lligadas, G.; Percec, V. J Polym Sci Polym Chem 2008, 46, 2745–2754.

36 Rosen, B. M.; Percec, V. Chem Rev 2009, 109, 5069–5119.

37 Rosen, B. M.; Lligadas, G.; Hahn, C.; Percec, V. J Polym Sci Pol Chem 2009, 47, 3940–3948.

38 Rosen, B. M.; Jiang, X.; Wilson, C. J.; Nguyen, N. H.; Monteiro, M. J.; Percec, V. J Polym Sci Polym Chem 2009, 47, 5606–5628.

39 Nguyen, N. H.; Rosen, B. M.; Lligadas, G.; Percec, V. Macromolecules 2009, 42, 2379–2386.

40 Nguyen, N. H.; Rosen, B. M.; Jiang, X.; Fleischmann, S.; Percec, V. J Polym Sci Polym Chem 2009, 47, 5577–5590.

41 Jiang, X.; Fleischmann, S.; Nguyen, N. H.; Rosen, B. M.; Percec, V. J Polym Sci Polym Chem 2009, 47, 5591–5605.

42 Jiang, X. A.; Rosen, B. M.; Percec, V. J Polym Sci Polym Chem 2010, 48, 2716–2721.

43 Jiang, X.; Rosen, B. M.; Percec, V. J Polym Sci Polym Chem 2010, 48, 403–409.

44 Fleischmann, S.; Rosen, B. M.; Percec, V. J Polym Sci Polym Chem 2010, 48, 1190–1196.

45 Fu, Q.; Zhang, Z. N.; Lin, W. C.; Huang, J. L. Macromolecules 2009, 42, 4381–4383.

46 Kulis, J.; Bell, C. A.; Micallef, A. S.; Jia, Z. F.; Monteiro, M. J. Macromolecules 2009, 42, 8218–8227.

47 Kulis, J.; Bell, C. A.; Micallef, A. S.; Monteiro, M. J. J Polym Sci Polym Chem 2010, 48, 2214–2223.

48 Lin, W. C.; Fu, Q.; Zhang, Y.; Huang, J. L. Macromolecules 2008, 41, 4127–4135.

49 Liu, C.; Pan, M. G.; Zhang, Y.; Huang, J. L. J Polym Sci Polym Chem 2008, 46, 6754–6761.

50 Fu, Q.; Wang, G. W.; Lin, W. C.; Huang, J. L. J Polym Sci Polym Chem 2009, 47, 986–990.

51 Li, Y. G.; Zhang, Y. Q.; Yang, D.; Li, Y. J.; Hu, J. H.; Feng, C.; Zhai, S. J.; Lu, G. L.; Huang, X. Y. Macromolecules 2010, 43, 262–270.

52 Francis, R.; Taton, D.; Logan, J. L.; Masse, P.; Gnanou, Y.; Duran, R. S. Macromolecules 2003, 36, 8253–8259.

53 Jia, Z. F.; Fu, Q.; Huang, J. L. Macromolecules 2006, 39, 5190–5193.

54 Fitton, A. O.; Hill, J.; Jane, D. E.; Millar, R. Synthesis-Stuttgart 1987, 1140–1142.

55 Wei, J.; Huang, J. L. Macromolecules 2005, 38, 1107–1113.

56 Lutz, J. F.; Matyjaszewski, K. J Polym Sci Polym Chem 2005, 43, 897–910.