One-Pot Synthesis of Heterograft Copolymers via "Graft Onto" by Atom Transfer Nitroxide Radical Coupling Chemistry

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ABSTRACT: Heterograft copolymers poly(4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl-*co*- ethylene oxide)-*graft*-polystyrene and poly(*tert*-butyl acrylate) (poly (GTEMPO-*co*-EO)-*g*-PS/P*t*BA) were synthesized in one-pot by atom transfer nitroxide radical coupling (ATNRC) reaction via "graft onto." The main chain was prepared by the anionic ring-opening copolymerization of ethylene oxide (EO) and 4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (GTEMPO) first, then the polystyrene and poly (*tert*-butyl acrylate) with bromine end (PS-Br, P*t*BA-Br) were prepared by atom transfer radical polymerization (ATRP). When three of them were mixed each other in the presence of CuBr/*N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) at 90 °C, the formed secondary carbon radicals at the PS and P*t*BA chain ends were quickly trapped by nitroxide radicals on poly(GTEMPO-*co*-EO). The heterograft copolymers were well defined by ^{1}H NMR, size exclusion chromatography, fourier transform infrared, and differential scanning calorimetry in detail. It was found that the density of GTEMPO groups on main chain poly(GTEMPO-*co*-EO), the molecular weights of PS/P*t*BA side chains, and the structure of macroradicals can exert the great effects on the graft efficiency. © 2008 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 46: 6770–6779, 2008

Keywords: anionic polymerization; atom transfer nitroxide radical coupling; graft copolymer; ring-opening polymerization

INTRODUCTION

Driven by the challenges and interests, not only the design and synthesis of new types of polymeric materials, but also the modification of existing polymers for new applications have attracted much attentions.[1] One popular modification method is grafting reaction, which can offer the possibility of varying the physical and chemical properties of polymers. Through changes of the nature of the polymer backbone and composition or density of the grafts, the preparations of graft (co)polymers with various architectures, such as star-graft,[2,3] block-graft,[4,5] V-shaped graft,[6–8] and heterograft[9–13] structures have been reported. The interest in heterograft copolymer comes from the unique properties relating to their variety of compositions, such as the combination of a crystallizable and an amorphous side chain,[12] or a hydrophobic and a hydrophilic side chain.[11]

Additional Supporting Information may be found in the online version of this article.

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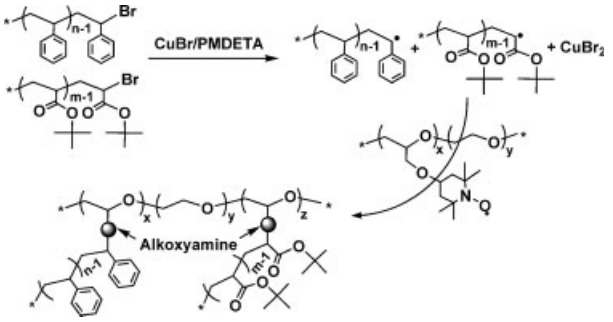
Three different methods have been reported to prepare graft copolymers: (1) "graft from"[10,13,14]; (2) "graft through"[2,12,15]; and (3) "graft onto."[7,16–18] By combining different grafting methods and polymerization techniques, Neugebauer et al. synthesize the heterograft brush with poly(ethylene glycol) methyl ether methacrylate (PEOMA) and octadecyl acrylate (ODA) side chains (poly(PEOMA-*co*-ODA))[12]; Moeller reports the preparation of polyglycidol (PG) main chain with poly(ε-caprolactone-acetyl) (PCL) and poly(methyl methacrylate) (PMMA) or poly(*n*-butyl methacrylate) (PBMA) side chains (PG-*g*-PCL/MMA and PG-*g*-PCL/BMA)[10]; Matyjaszewski reports the synthesis of poly(2-(trimethylsilyloxy) ethyl methacrylate-*co*-PEOMA) (poly(HEMA-TMS)-*co*-PEOMA). After transformation of HEMA-TMS units to 2-(2-bromopropionyloxy) ethyl methacrylate (BPEM), the resulting poly(BPEM-*co*-PEOMA) initiates controlled polymerization of *n*BA. Thus heterograft copolymer with P*n*BA and PEOMA side chains (poly(BPEM-*co*-PEOMA)-*g*-P*n*BA) is obtained.[9] Saha reports the synthesis of mixed arm graft copolymers (PGMA-*g*-PMMA)-*g*-PSt and ((PGMA-*g*-PMMA)-*g*-PSt)-*g*-PBMA,[13] the polymerization is initiated by the Cp_2TiCl-catalyzed radical ring opening of the epoxide group of GMA and is optionally controlled by $CuBr_2$/bipyridyl. All these synthetic strategies need many steps for the separation and purification of intermediates and final products except Neugebauer's "graft through" method, however in this case the gradient not random copolymers were obtained. Thus looking for a facile strategy to synthesize the heterograft copolymers is so fascinating that we are driven by the interests to improve the synthesis techniques.

"Click" chemistry[19] as a facile modification method has been reported and widely applied.[20] However, the azide groups are difficult to be reserved because of their photosensitivity, thermal instability, and shock sensitivity. It is well known the 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as radical scavenger can trap the radicals with high efficiency. If the former was mixed with another kind of macroradicals, then coupling reaction with high efficiency could be carried out.[21,22]

In this article, we report an efficient way for the preparation of heterograft copolymer with polystyrene (PS) and poly(*tert*-butyl acrylate) (P*t*BA) side chains in one-pot via coupling reaction of TEMPO with macroradicals by "graft onto" (Scheme 1). Our work provides a new strategy to prepare well-defined heterograft copolymers with PS and P*t*BA side chains.



Scheme 1. The synthetic mechanism for heterograft copolymers by atom transfer nitroxide radical coupling chemistry.

EXPERIMENTAL

Materials

Ethylene oxide (EO; 96%; 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, then distilled under reduced pressure twice before use. *Tert*-butyl acrylate (*t*BA; 99%; SCR) was dried over CaH_2 and distilled under reduced pressure twice before use. 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) and ethyl 2-bromoisobutyrate (EBiB) were purchased from Aldrich and used without further purification. 2-(2-methoxyethoxyl) ethanol (99%), tetrahydrofuran (THF; 99%), toluene (99%), and other reagents were all purchased from SCR and purified by standard method before use. 4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (GTEMPO) was synthesized according to our previous work,[23] and distilled under a reduced pressure, the fraction at 130 °C/80Pa was collected and recrystallized in hexane at 2 °C twice, mp: 38–39 °C. ^{1}H NMR (500 MHz, sol.: CD_3OD,25 °C, tetramethylsilane as internal standard, in the presence of calculated amounts of $HCOONH_4$ and Pd/C; δ, ppm): 1.18, 1.45, 1.93, and 3.40–3.49 (complex, 17H, —C***H*****$_3$**, —C***H*****$_2$**— and —C***H***— of the TEMPO group); 2.60–2.79 (m, 2H, —OC***H*****$_2$**CH(CH_2)— of the glycidyl ring), 3.31 (m, 1H, —OCH_2C***H***(CH_2) — of the glycidyl ring), 3.62–3.87 (m, 2H, —OCH_2 CH(C***H*****$_2$**)— of the glycidyl ring), 8.53 (—OOC***H*** of $HCOONH_4$). Gas

chromatography: 99%. Mass spectrometry (70 eV) *m/z* (%): 228 [M^+], 172 [$C_9H_{19}NO_2]^+$, 57 [$C_3H_5O]^+$. ELEM. ANAL. Calcd. for $C_{12}H_{22}NO_3$ (228.16): C, 63.13%; H, 9.71%; N, 6.13%. Found: C, 63.02%; H, 9.91%; N, 6.03%.

Measurements

Size exclusion chromatography (SEC) was performed at 35 °C in tetrahydrofuran (THF) with a flow rate of 1 mL/min using an HP1100 system equipped with three Waters Styragel columns (in series, with pore sizes 10^2, 10^3, and 10^4 Å) and a Waters 410 refractive-index detector; monodistributed PS was used as the calibration standard (molecular weight range of the standards is 580–3390,000 g/mol). ^{1}H 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 GTEMPO and the precursor copolymer poly(GTEMPO-*co*-EO), which were determined in CD_3OD in the presence of stoichiometric ammonium formate ($HCOONH_4$) and the catalyst palladium on carbon (Pd/C). Fourier transform infrared (FTIR) spectra were recorded on Magna 550 FTIR instrument; the samples were dissolved in dry THF and then cast onto a NaCl disk to form the film by the evaporation of the solvent under infrared lamp. The differential scanning calorimetry (DSC) analysis was carried out with a PerkinElmer Pyris 1 DSC instrument under a nitrogen flow (10 mL/min); all the samples were heated with the rate of 10 °C/min from −80 °C to 140 °C for the first scan, then cooled with the rate of −10 °C/min until to −80 °C, and the scanning for the second time was followed immediately. The glass transition temperatures (T_g) were measured on the second scan. Electron spin resonance (ESR) was recorded on a Bruker ER200D-SRC spectrometer in CH_2Cl_2. Gas chromatography/mass spectrometry (GC/MS) analysis for GTEMPO was carried out by a Finnigan Voyager system with mass-selective detection operating in electronic ionization. A silica capillary column had dimensions of 30 m ×0.25 mm (i.d.) with a 0.25-μm film thickness (DB-5, Restek). The GC/MS parameters were as follows: the ion source temperature was 200 °C, the carrier gas was helium, the column flow was 1 mL/min, the temperature program was 100–200 °C at 15 °C/min, and splitless injection was used at 250 °C. Ionization was achieved at 70 eV. The conversions were determined by a gravimetric method.

Synthesis of Halogen-Containing PS-Br and P*t*BA-Br by ATRP

The mixture of St (34.3 mL, 300 mmol), EBiB (0.31 mL, 2.1 mmol), CuBr (0.158 g, 1.1 mmol), and PMDETA (0.2 mL, 1.1 mmol) was added to a 100-mL ampoule and degassed by three freeze-pump-thaw cycles. The ampoule was immersed in oil bath at 90 °C for predetermined time, then taken from the oil bath and dipped in liquid nitrogen to stop the polymerization. The products were diluted with THF, the solution passed through a column chromatograph filled with neutral alumina to remove the copper complex before the polymer was precipitated in cold CH_3OH. The precipitate was collected and purified by dissolution/precipitation with THF/cold CH_3OH twice, and then dried at 40 °C *in vacuo*. SEC: PS*1*, M_n: 2100 g/mol, M_w/M_n: 1.10; PS*2*, M_n: 4000 g/mol, M_w/M_n: 1.08. ^{1}H NMR ($CDCl_3$),δ (ppm): 0.70–0.99 (m, 9H, C***H*****$_3$**CH_2O— and —C(C***H*****$_3$**$)_2$—PS introduced by EBiB), 1.20–2.25 (m, 3H, —C***H*****$_2$**CH— of PS), 3.44–3.63 (m, 2H, CH_3C***H*****$_2$**O—), 4.41–4.52 (m, 1H, —C***H***(Ph)—Br), 6.30–7.30 (m, 5H, C_6***H*****$_5$** of PS).

To a 100-mL ampoule, EBiB (0.30 mL, 2 mmol), CuBr (0.216g, 1.5 mmol), PMDETA (0.3 mL, 1.5 mmol), and *t*BA (23 mL, 160 mmol) in 20 mL acetone were charged, then the ampoule was vacuumed by three freeze-pump-thaw cycles in liquid nitrogen, sealed and immersed in oil bath at 60 °C. The reaction was stopped by dipping the ampoule in liquid nitrogen. Crude products were diluted with THF and the solution was filtered through a column chromatograph filled with neutral alumina, the purified P*t*BA was obtained by precipitation in CH_3OH/H_2O (v/v = 1/1). SEC: P*t*BA*1*, M_n: 2000 g/mol, M_w/M_n: 1.10; P*t*BA2, M_n: 4900 g/mol, M_w/M_n: 1.06. ^{1}H NMR ($CDCl_3$),δ (ppm): 1.10–1.30 (m, 9H, C***H*****$_3$**CH_2O— and —C(C***H*****$_3$**$)_2$—P*t*BA introduced by EBiB), 1.30–2.10 (m, 11H, —C***H*****$_2$**CH— and —C(C***H*****$_3$**$)_3$ of P*t*BA), 2.13–2.23 (s, 1H, —CH_2C***H***— of P*t*BA), 4.05–4.15 (m, 3H, CH_3C***H*****$_2$**O— and —C***H***-Br).

Synthesis of Precursor Copolymer Poly(GTEMPO-*co*-EO)

The initiator, potassium 2-(2-methoxyethoxyl) ethanol, was synthesized as follows: To a 150-mL, three-necked flask, 100 mL of dry THF and

6.0 mL (0.075 mol) of 2-(2-methoxyethoxyl) ethanol were added, then 2.1 g (0.054 mol) of potassium with fresh surface was introduced under nitrogen atmosphere. After stirring for 24 h, the solution was filtered and titrated with 0.1 M HCl, the concentration was 0.42 M.

The anionic copolymerization of GTEMPO with EO was carried out by following procedure: The 150-mL kettle was vacuumed at 80 °C for 24 h and cooled to room temperature and then to −20 °C, a given volume of initiator solution and monomers (GTEMPO and EO with different molar ratios) were introduced successively into the kettle under magnetic stirring. The system was heated to 40 °C under stirring for 48 h, and then a few drops of acidified methanol were added to terminate the reaction. Crude products were dissolved in 250 mL deionized water and extracted with CH_2Cl_2 three times. Combined CH_2Cl_2 was dried over anhydrous $MgSO_4$, then the solvents were removed by reduced distillation, the precursor copolymer poly(GTEMPO-*co*-EO) was obtained in a yield of 96%. As the contents of GTEMPO in the copolymer were varied, solid or gum-like products with dark red color were obtained. SEC: A, M_n: 6100 g/mol, M_w/M_n: 1.10, R_f: 1/5 (here R_f is the feed ratio of GTEMPO to EO); B, M_n: 6200 g/mol, M_w/M_n: 1.09, R_f: 1/20. ^{1}H NMR (CD_3OD), in the presence of calculated amounts of $HCOONH_4$ and Pd/C, δ (ppm): 1.18, 1.43, and 1.91(complex, 16H, —C***H*****$_3$** and —C***H*****$_2$**— of the GTEMPO group), 3.37(s, 3H, C***H*****$_3$**O— of the methoxyl group), 3.53–3.78 (m, 10H, —C***H***—, —OC***H*****$_2$**CH(C***H*****$_2$**)— of the GTEMPO group and —OC***H*****$_2$**CH_2— of PEO), 8.53 (—OOC***H*** of $HCOONH_4$). FTIR (cm^{-1}): 1107 (—C—O—C—).

One-Pot Synthesis of Heterograft Copolymer Poly(GTEMPO-*co*-EO)-*g*-PS/P*t*BA

The coupling reaction was carried out as follows: An ampoule charged with precursor copolymer A (M_n: 6100 g/mol, R_G: 1/5.4, here R_G is the measured molar ratio of GTEMPO to EO in copolymer; 0.103 g, 0.017 mmol), PS2 (M_n: 4000 g/mol; 0.4 g, 0.1 mmol), P*t*BA2 (M_n: 4900 g/mol; 0.49 g, 0.1 mmol), CuBr (0.029 g, 0.2 mmol), PMDETA (0.036 mL, 0.2 mmol), and toluene (10 mL) was degassed by three freeze-pump-thaw cycles, placed in oil bath at 90 °C for 24 h, and then immersed in liquid nitrogen. Crude products were diluted with THF and the solution was filtered through a column chromatograph filled with neutral alumina to remove copper complex. The products were extracted with CH_3OH firstly to remove soluble unreacted P*t*BA, and the solid powder was then dissolved in cyclohexane at 40 °C under magnetic stirring. When the solution was cooled to 0 °C, it was turned to turbid and the target products were precipitated as a white gel, while the unreacted PS was still in the solution. After centrifuging, the white gel was collected and dried at 40 °C *in vacuo*. SEC: A2, M_n: 24,900 g/mol, M_w/M_n: 1.09; ^{1}H NMR($CDCl_3$), δ(ppm): 0.70–1.18 (m, 21H, —C***H*****$_3$** of GTEMPO group, —C(C***H*****$_3$**$)_2$—PS and C***H*****$_3$**CH_2O— introduced by EBiB), 1.20–2.15 (m, 14H, —C***H*****$_2$**CH— of PS, —C***H*****$_2$**CH— and —C(C***H*****$_3$**$)_3$ of P*t*BA), 2.20 (s, 1H, —CH_2C***H***— of P*t*BA), 3.53–3.78 (m, 10H, —C***H***—, —C***H*****$_2$**O— of GTEMPO group, —OC***H*****$_2$**CH— of glycidyl ring and —OC***H*****$_2$**CH_2— of PEO), 4.05–4.15 (s, 2H, CH_3C***H*****$_2$**O— introduced by EBiB of P*t*BA side chain), 6.30–7.30 (m, 5H, C_6***H*****$_5$** of PS); FTIR (cm^{-1}): 1146 (—C—O—C—), 1454, 1494, 1601 (—C—C— (aromatic ring)) and 1726 (—COO—).

By varying molecular weight (M_n) of side chains, and density of GTEMPOs on main chain, a series of heterograft copolymers was prepared.

Effect of Reaction Time on the Activity of Macroradicals

Five ampoules charged with the same amounts of poly(GTEMPO-*co*-EO) B (M_n: 6200 g/mol, R_G: 1/22; 0.13 g, 0.021 mmol), PS*2* (M_n: 4000 g/mol; 0.2 g, 0.05 mmol), P*t*BA*2* (M_n: 4900 g/mol; 0.245 g, 0.05 mmol), CuBr (0.014 g, 0.1 mmol), PMDETA (0.018 mL, 0.1 mmol) and toluene (5 mL) were degassed by three freeze-pump-thaw cycles in liquid nitrogen and placed in oil bath at 90 °C. These ampoules were taken from the oil bath at different time intervals as 2, 4, 8, 12, and 24 h and quenched in liquid nitrogen to stop the coupling reaction. The target products were purified as described above and characterized by ^{1}H NMR.

RESULTS AND DISCUSSION

As the "Experimental Section" showed, whole preparation process of final heterograft copolymers can be divided into following steps: synthesis of main chain copolymer poly(GTEMPO-*co*-EO), synthesis of side chains PS-Br and P*t*BA-Br, and coupling reaction between them by one-pot. It could be described as in Scheme 1.

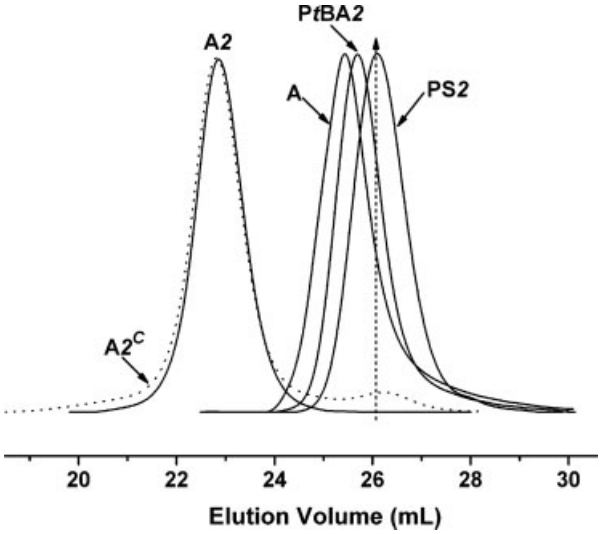


Figure 1. SEC traces of the halogen-containing homopolymers PS*2*, P*t*BA*2*, precursor copolymer A and the heterograft copolymer A2. The dot trace $A2^C$ represents crude products of A2 after extraction with CH_3OH.

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

PS-Br and P*t*BA-Br were synthesized by typical ATRP using EBiB as initiator and CuBr/PMDETA as catalyst. These reactions were stopped at low conversion (<30%) to ensure a high contents of bromines at chain ends.[24] The SEC traces of PS2 and P*t*BA2 were illustrated in Figure 1, the M_w/M_n was less than 1.10. ^{1}H NMR spectrum of PS2 was showed in Figure 2(A). The characteristic resonance signal for the methine group proton (—C***H***(Ph)—Br) at 4.40 ppm ("g") proved the successful preparation of PS-Br.

The average degree of polymerization of St (DP_{St}) was analyzed as eq 1

$$DP_{St} = \frac{9A_{6.3-7.3}}{5A_{0.8-1.1}} \quad (1)$$

Here $A_{0.8-1.1}$ and $A_{6.3-7.3}$ were the integral areas of methyl groups protons ($C\boldsymbol{H_3}CH_2O$— and —$C(C\boldsymbol{H_3})_2$—) and the aromatic protons of PS, respectively. The values of resultant polymers PS1 and PS2 were 20.1 and 38.8, which were consistent with that obtained by SEC. Figure 2(B) showed the ^{1}H NMR spectrum of P*t*BA2. In addition, the unique methine group protone (—C***H***—Br) ("n") and the methylene group protones ($CH_3C\boldsymbol{H_2}O$—) ("i") from EBiB both at 4.05–4.15 ppm were observed. Thus the DP_{tBA} were determined from the ^{1}H NMR spectrum using eq 2

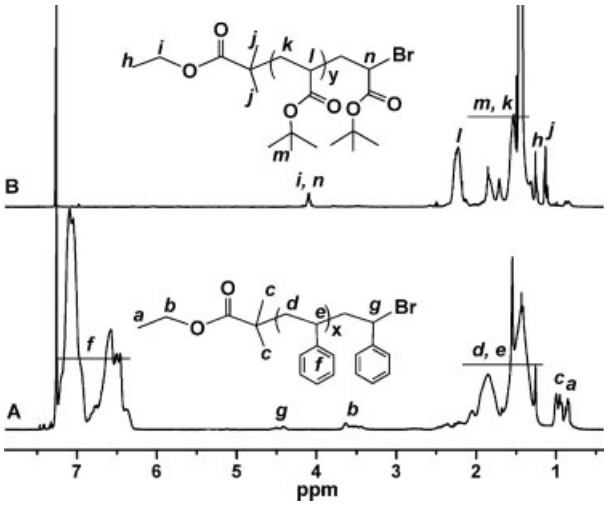


Figure 2. ^{1}H NMR spectra of (A) PS*2* (M_n: 4000 g/mol; solvent: $CDCl_3$) and (B) P*t*BA*2* (M_n: 4900 g/mol; solvent: $CDCl_3$) prepared by ATRP.

$$DP_{tBA} = \frac{3A_h}{A_{4.05-4.15}} \quad (2)$$

Here, A_h was the integral area of the methine group proton (—$CH_2C\boldsymbol{H}$—) ("l") at 2.10–2.29 ppm of P*t*BA. $A_{4.05-4.15}$ were the sum of the integral areas of methylene group protons ($CH_3C\boldsymbol{H_2}O$—) and the methine group protone (—C***H***—Br). The results were 19.6, 40.6 for P*t*BA1 and P*t*BA2, respectively. As it is well known, the structure of P*t*BA is quite different from the PS standard, the actual M_n of P*t*BA would deviate from the value by SEC, especially the DP_{tBA} with high molecular weight was used. All the data of the PS1, PS2, and P*t*BA1, P*t*BA2 were presented in Table 1.

Table 1. Characterization of the Synthetic Halogen-Containing PS-Br and P*t*BA-Br

Exp.	M_n[a] (g/mol)	M_w/M_n[a]	$M_{n\ NMR}$[b] (g/mol)	*DP*[c]
PS1	2100	1.10	2200	20.1
PS2	4000	1.08	4200	38.8
P*t*BA1	2000	1.10	2700	19.6
P*t*BA2	4900	1.08	5400	40.6

[a] Determined by SEC in THF using PS as standard.
[b] Calculated from the ^{1}H NMR data, M_{nNMR} = MW × DP + 195, MW represented the molecular weight of the monomers.
[c] Average degree of polymerization of St or *t*BA, calculated from the ^{1}H NMR data.

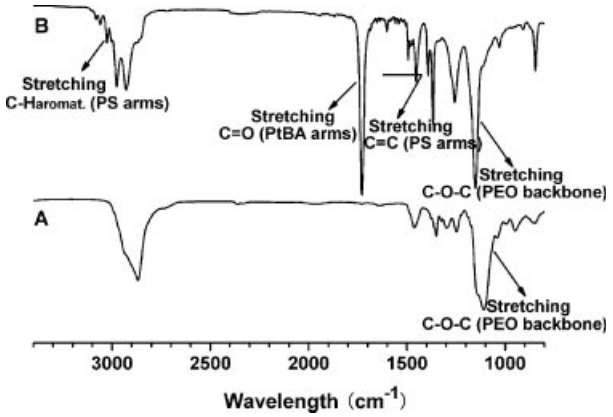


Figure 3. IR spectra of (A) precursor copolymer A and (B) heterograft copolymer A3 (see Table 3).

Synthesis and Characterization of Precursor Copolymer Poly(GTEMPO-*co*-EO)

The monomer GTEMPO was synthesized as previous work reported,[23] and then it was copolymerized with EO by anionic ring-opening polymerization using potassium 2-(2-methoxyethoxyl) ethoxide as initiator at 40 °C. Curve A in Figure 1 was the SEC trace of the precursor copolymer A, the trace showed low M_w/M_n (1.10). FTIR spectrum of precursor copolymer A is shown in Figure 3(A), the characteristic bands of poly(GTEMPO-*co*-EO) segments —C—O—C— stretching at 1107 cm^{-1} could easily be observed. Because of the paramagnetism of the pending TEMPO radicals, the ^1H NMR was carried out in deuterated methanol in the presence of stoichiometric $HCOONH_4$ and catalytic Pd/C, the TEMPO radicals on the copolymers were reduced to corresponding oximes and clear ^1H NMR spectra were then performed [Fig. 4(A)]. The TEMPO groups on poly(GTEMPO-*co*-EO) can be confirmed by the observation of signals at 1.18 ppm (—C***H₃***; "a"), 1.43 and 1.91 ppm (—C***H₂***—; "b"). Moreover, the compositions

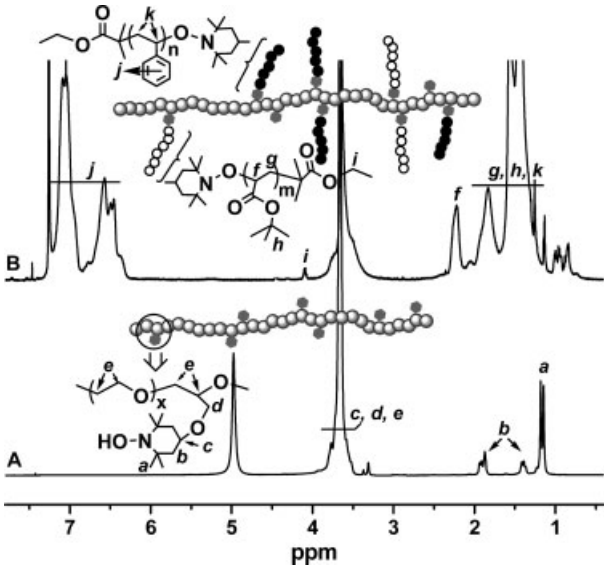


Figure 4. ^1H NMR spectra of (A) poly(GTEMPO-*co*-EO) A (M_n: 6100 g/mol; in presence of Pd/C and $HOOCNH_4$, solvent: CD_3OD) and (B) heterograft copolymer A2 (M_n: 24,900 g/mol; solvent: $CDCl_3$).

of the precursor copolymers could be calculated by eq 3

$$R_G = \frac{2A_a}{6A_{3.5-3.8} - 3A_a} \quad (3)$$

Here, A_a is the integral area of methyl group protons at 1.18 ppm of GTEMPO, $A_{3.5-3.8}$ were the integral areas of all the methine or methylene group protons at 3.53–3.78 ppm. The R_G values were closed to the feed ratio of GTEMPO to EO. All the data of the two copolymers were inserted to Table 2.

Preparation and Characterization of Heterograft Copolymers

Heterograft copolymer poly(GTEMPO-*co*-EO)-*g*-PS/P*t*BA was synthesized by mixing calculated

Table 2. Characterization of the Synthetic Precursor Copolymers Poly(GTEMPO-*co*-EO)

Exp.	R_f[a]	R_G[b]	M_n[c] (g/mol)	M_w/M_n[c]	N_{TEMPO}[d]	Yield %[e]
A	1/5	1/5.4	6,100	1.10	12.9	95%
B	1/20	1/22	6,200	1.09	5.3	96%

[a] Feed ratio of GTEMPO to EO.
[b] Observed molar ratio of GTEMPO to EO, measured by ^1H NMR.
[c] Measured by SEC in THF with linear PS as standard.
[d] Number-average of TEMPO groups on each poly(GTEMPO-*co*-EO) chain, calculated from ^1H NMR data.
[e] The yield of copolymers poly(GTEMPO-*co*-EO), determined by the gravimetric method.

Table 3. Data of Heterograft Copolymers with Same M_n of Side Chains

Exp.	Feed[a] (%) $[TEMPO]_0/[PS2]_0/[PtBA2]_0$	Reaction Time (h)	M_n[b] (g/mol)	M_w/M_n[b]	$M_{n\ NMR}$[c] (g/mol)	Ratio (%) G_{PS}/G_{PtBA}[d]	x_{PS}/x_{PtBA}[e]	y[f]
A1	1/0.30/0.30	24	21,800	1.09	37,200	0.29/0.22	0.96/0.73	0.75
A2	1/0.45/0.45	24	24,900	1.09	47,600	0.38/0.30	0.84/0.67	0.79
A3	1/0.60/0.60	24	32,200	1.13	53,800	0.43/0.35	0.72/0.58	0.81
B1	1/0.45/0.45	2	13,700	1.08	14,700	0.25/0.10	0.56/0.22	0.40
B2	1/0.45/0.45	4	14,400	1.09	19,200	0.31/0.21	0.69/0.47	0.68
B3	1/0.45/0.45	8	15,400	1.08	23,700	0.37/0.32	0.82/0.71	0.86
B4	1/0.45/0.45	12	16,400	1.08	25,400	0.41/0.35	0.91/0.78	0.85
B5	1/0.45/0.45	24	16,600	1.09	25,700	0.41/0.36	0.91/0.80	0.87

[a] The ratio of initial concentration of TEMPO groups to PS*2* and P*t*BA*2*.
[b] Measured by SEC in THF with RI detector, calibration with linear PS as standard.
[c] Calculated from the ^{1}H NMR data.
[d] Grafting ratio of PS and P*t*BA on main chain, calculated from ^{1}H NMR data.
[e] The x_{PS} and x_{PtBA} were defined as follow: $X_{PS} = \frac{[TEMPO]_0 \times G_{PS}}{[PS]_0}$; $X_{PtBA} = \frac{[TEMPO]_0 \times G_{PtBA}}{[PtBA]_0}$
[f] The y was defined as $y = \frac{G_{PtBA}}{G_{PS}}$.

amounts of PS, P*t*BA and precursor copolymer A in an ampoule with toluene as solvent. When the system was heated at 90 °C in the presence of CuBr/PMDETA, the bromine atoms of PS-Br and P*t*BA-Br would break off from the chain ends and serve as oxidant. They were reduced to bromine anions, and secondary carbon radicals of PS or P*t*BA were generated. CuBr was served as reductant, the Cu^{1+} was oxygenated to Cu^{2+}, and the $CuBr_2$ was formed. This process was reversible in typical ATRP, however it was irreversible in our experimental conditions because the macroradicals of PS and P*t*BA were quickly trapped by the nitroxide radicals of TEMPO groups on poly (GTEMPO-*co*-EO) to form the alkoxyamines shown in Scheme 1.

The crude products could be easily purified by extraction with CH_3OH and cyclohexane, respectively, to remove the unreacted P*t*BA-Br and PS-Br.[25] Figure 1 showed the SEC traces of PS-Br (PS2, M_n: 4000 g/mol), P*t*BA-Br (P*t*BA*2*, M_n: 4900 g/mol), copolymer poly(GTEMPO-*co*-EO) A (M_n: 6100 g/mol), heterograft copolymer poly (GTEMPO-*co*-EO)-*g*-PS/P*t*BA (A2, M_n: 24,900 g/mol) and its precursor crude products ($A2^C$) (it was purified by extraction with CH_3OH), all the curves showed the nice Gaussian distribution and low M_w/M_n except $A2^C$. It presented two peaks representing heterograft copolymer and unreacted PS, respectively. Moreover, no observable homo-coupling products at the higher elution time could be found. That means in our system no detectable coupling reaction between macroradicals formed from PS-Br or P*t*BA-Br occurred. Then the left PS could be removed successfully by the extraction with cyclohexane. All the data of heterograft copolymers obtained from copolymer A (poly(GTEMPO-*co*-EO) A) were presented in Table 3 as A1–A3, and from copolymer B were showed in Tables 3 and 4 as B1–B8.

Figure 4(B) showed the ^{1}H NMR spectrum of heterograft copolymer A2, in which three main regions can be observed. The typical methine group protons (—$CH_2C\boldsymbol{H}$—) of P*t*BA at 2.22 ppm ("f"), the aromatic ring (—$C_6\boldsymbol{H_5}$—) of PS at 6.30–7.30 ppm ("j") and the methine or methylene group protons of poly(GTEMPO-*co*-EO) at 3.53–3.78 ppm were detected. Comparing with ^{1}H NMR spectrum Figure 2(A), the characteristic resonance signal in the region 4.4–4.6 ppm for methine group proton (—C$\boldsymbol{H}$(Ph) —Br) disappeared. The signal of methine group proton (—C$\boldsymbol{H}$—Br) at 4.05–4.15 ppm [Fig. 2(B)], which was overlapped by the proton signal of C$\boldsymbol{H_2}$ from initiator EBiB, was weakened after the coupling reaction. These results suggested the bromine atoms had broken off from chain ends and coupling reaction was carried out.

The FTIR spectrum of heterograft copolymer A3 was shown in Figure 3(B), the characteristic bands of PS segments C=$C_{aromatic}$ stretching at 1450–1601 cm^{-1}, C—$H_{aromatic}$ stretching at 2950–3100 cm^{-1} and the characteristic bands of P*t*BA segments C=O stretching at 1726 cm^{-1} could easily be observed.

Table 4. Characterization of Heterograft Copolymers with Same Feed Ratio

	Feed[a] (%)				Ratio (%)		
Exp.	$[TEMPO]_0/[PS]_0/[PtBA]_0$ 1/0.45/0.45	M_n[b] (g/mol)	M_w/M_n[b]	$M_{n\ NMR}$[c] (g/mol)	G_{PS}/G_{PtBA}[d]	x_{PS}/x_{PtBA}[e]	y[f]
A2	A/PS*2*/P*t*BA2	24,900	1.09	47,600	0.38/0.30	0.84/0.67	0.79
B5	B/PS*2*/P*t*BA2	16,600	1.09	25,700	0.41/0.36	0.91/0.80	0.87
B6	B/PS*2*/P*t*BA1	13,500	1.10	20,900	0.40/0.40	0.89/0.89	1.0
B7	B/PS*1*/P*t*BA2	15,700	1.08	21,200	0.42/0.35	0.93/0.79	0.85
B8	B/PS*1*/P*t*BA1	12,200	1.09	16,900	0.42/0.40	0.93/0.89	0.95

[a] The ratio of initial concentration of TEMPO groups to PS*2* and P*t*BA*2*.
[b] Measured by SEC in THF with RI detector, calibration with linear PS as standard.
[c] Calculated from the ^{1}H NMR data.
[d] Grafting ratio of PS and P*t*BA on main chain, calculated from ^{1}H NMR data.
[e] The x_{PS} and x_{PtBA} were defined as follow: $X_{PS} = \frac{[TEMPO]_0 \times G_{PS}}{[PS]_0}$; $X_{PtBA} = \frac{[TEMPO]_0 \times G_{PtBA}}{[PtBA]_0}$.
[f] The y was defined as $y = \frac{G_{PtBA}}{G_{PS}}$.

Figure 5 showed the DSC determination of the heterograft copolymer A3. Two T_gs at 40 and 72 °C were observed. The first transition was similar to the P*t*BA segment, and the second transition was similar to PS segment.[26] While, the T_g of PEO segment on poly(GTEMPO-*co*-EO) was not observed because of the high copolymerization density of GTEMPOs on copolymer A (R_G: 1/5.4). These results suggested that the coupling reaction was accomplished and the heterograft copolymer was synthesized successfully.

The M_n of the heterograft copolymers can be calculated from ^{1}H NMR data by eq 4

$$M_{nNMR} = [(44 \times R_G + 228) + M_{nPS} \times G_{PS} + M_{nPtBA} \times G_{PtBA}] \times N_{TEMPO} + 120 \quad (4)$$

Here $M_{n\ PS}$ and $M_{n\ PtBA}$ were the molecular weights of PS and P*t*BA, obtained from ^{1}H NMR (Table S1 in supporting information). N_{TEMPO} referred to number-average of TEMPOs on poly (GTEMPO-*co*-EO) chain, calculated from ^{1}H NMR (12.9 for A and 5.3 for B, see Table 2). In all cases, the M_n derived from ^{1}H NMR were much higher than that from SEC, it may attribute to the different hydrodynamic volumes of the heterograft copolymers from the linear PS standard. So the data from ^{1}H NMR were preferable.

Effect of Side Chains Structure on the Grafted Efficiency

To confirm the effect of composition and structure of heterograft copolymers on the grafting efficiency, two parameters G_{PS} and G_{PtBA} were introduced to represent the grafting ratio of PS and P*t*BA segments onto poly(GTEMPO-*co*-EO) main chains. They can be calculated from ^{1}H NMR data by the following eqs 5 and 6:

$$G_{PS} = \frac{A_{6.3-7.3}(4R_G + 6)}{5DP_{St}A_{3.5-3.8}} \times 100\% \quad (5)$$

$$G_{PtBA} = \frac{A_f(4R_G + 6)}{DP_{tBA}A_{3.5-3.8}} \times 100\% \quad (6)$$

in which, R_G, DP_{St}, and DP_{PtBA} represented the same meanings mentioned above. $A_{6.3-7.3}$, A_f, $A_{3.5-3.8}$ referred to the integral areas of the

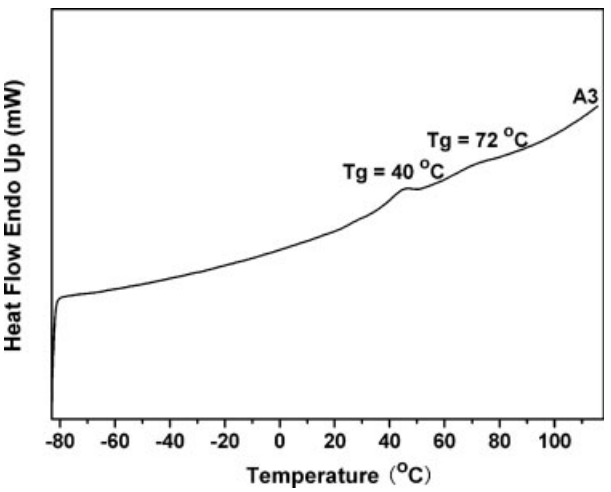


Figure 5. DSC thermogram of heterograft copolymer A3 at heating rate of 10 °C/min under nitrogen. The glass transition (T_g) were calculated as a midpoint of thermograms.

aromatic protons of PS, methine group proton of P*t*BA and the methine or methylene group protons of poly(GTEMPO-*co*-EO) at 3.53–3.78 ppm, respectively. The results for all heterograft copolymers were listed in Tables 3 and 4. The parameters x_{PS} and x_{PtBA} were introduced, which were equaled to the conversion of homopolymers (PS-Br/P*t*BA-Br) participating in ATNRC reaction.

Under similar ATNRC conditions, all the values of G_{PtBA} and x_{PtBA} were much smaller than G_{PS} and x_{PS}, that means the concentration of P*t*BA macroradicals were much lower than that of PS macroradicals in the same conditons,[27] because the phenyl group can stabilize radicals more strongly than $COOC_4H_9$ group.[28] With the increasing of feed molar ratio of homopolymers, the values of x_{PS} and x_{PtBA} reduced gradually for the steric hindrance. This was also confirmed by Matyjaszewski et al.[16] who reported the moderate grafting efficiency of PEO chains onto poly(methyl methacrylate) backbones by "click" chemistry.

Effect of GTEMPO Contents on Main Chains and M_n of PS-Br and P*t*BA-Br on Grafted Efficiency

To explore the effect of GTEMPO contents of main chains and M_n of PS and P*t*BA on the grafting efficiency, five heterograft copolymers (A*2*, B5–B8) were prepared (Table 2) under similar conditions (90 °C, 24 h), with same feed ratio of $[TEMPO]_0/[PS]_0/[PtBA]_0$ (1/0.45/0.45), but different density of GTEMPOs (R_G: 1/5.4 for A; R_G: 1/22 for B) and different M_n of PS and P*t*BA.

Since the lower density of GTEMPOs on copolymer B than copolymer A, when comparing A2 with B5, the later showed higher G_{PS}, G_{PtBA}, and x_{PS}, x_{PtBA} than the former. Moreover, the values of B6–B8 were all higher than A2. The comparison of B5 to B8 presented the relative G_{PS}, G_{PtBA}, and x_{PS}, x_{PtBA} versus M_n of side chains. When PS1 (2100 g/mol) was used in the coupling reaction, the G_{PS} was $\sim$ 42% and the x_{PS} was more than 93% (for B7 and B8); when PS2 (4000 g/mol) was used (for B5 and B6), both the G_{PS} and x_{PS} were reduced slightly. In the case of P*t*BA, the x_{PtBA} reduced more rapidly. For example, as the increasing of M_n from 2000 g/mol (B8) to 4900 g/mol (B7), the x_{PtBA} reduced from 88 to 79%. Thus it can be concluded that the G_{PS}, G_{PtBA}, and x_{PS}, x_{PtBA} values decreased with the increasing M_n both of PS and P*t*BA. However, there was a special case as B6 showed, when P*t*BA1 (2000 g/mol) and PS*2* (4000 g/mol) were used, the ratio of x_{PtBA} to x_{PS} (y) was up to 100%. In this case, the higher M_n of PS2 exhibited more steric hindrance, which reduced the activity of PS macroradicals in coupling reaction, so the latter's activity is approximate with the P*t*BA macroradicals. Therefore, it was reasonable to postulate that the grafting ratio and the conversion of homopolymers were intensively influenced by the density of GTEMPOs and the M_n of PS and P*t*BA.

Effect of Reaction Time on the Activity of Macroradicals

To investigate the relationship between reaction time and activity of macroradicals, five ampoules charged with same amounts of (co)polymers were reacted for 2, 4, 8, 12, and 24 h respectively, then the products were purified and characterized by ^{1}H NMR and SEC, the results were listed in Table 3 as B1–B5. Figure 6 showed the relationship plot of M_n and compositions versus reaction time, in which, the white square symbols represented M_n calculated by ^{1}H NMR spectra, and the black symbols represented y.

It can be observed that the M_n and y values increased with the increasing of reaction time during the starting 12 h, then, the variation was turned to stable. It indicated the ATNRC reaction can be efficiently completed over 12 h. The smaller y value of B1 (40%; reaction time: 2 h) suggested that the PS-Br can transfer to macroradicals and participate in ATNRC reaction more rapidly than P*t*BA-Br at the beginning time, and then, with the increasing of time, the y value increased to 87%. That means most P*t*BA-Br can

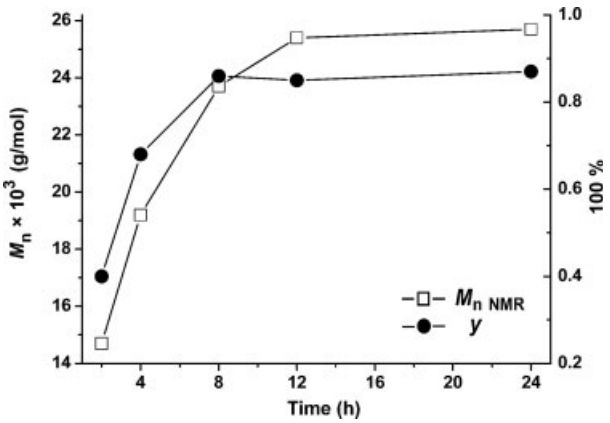


Figure 6. M_n and y versus reaction time in the ATNRC reaction for preparation of heterograft copolymers. (The white square symbols represent $M_{n\ NMR}$, and the black dot symbols represent y.)

transfer to macroradicals and complete ATNRC reaction at least over 8 h (B3, *y*: 86%).

CONCLUSIONS

Well-defined poly(GTEMPO-*co*-EO)-*g*-PS/P*t*BA heterograft copolymers were prepared in one-pot by ATNRC reaction via "graft onto." The density of GTEMPOs on precursor copolymer poly (GTEMPO-*co*-EO), the structure of macroradicals, molecular weights of side chains PS-Br and P*t*BA-Br can exert great effect on the coupling efficiency. The PS radicals are more reactive than that of P*t*BA in the coupling reaction. This approach can afford a useful strategy for synthesis of heterograft copolymers with various compositions and well-defined structures.

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