

# A New Strategy for Preparation of Graft Copolymers via “Graft onto” by Atom Transfer Nitroxide Radical Coupling Chemistry: Preparation of Poly(4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl-co-ethylene oxide)-graft-polystyrene and Poly(*tert*-butyl acrylate)

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Received December 17, 2007; Revised Manuscript Received January 25, 2008

**ABSTRACT:** A series of graft copolymers poly(4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl-co-ethylene oxide)-graft-polystyrene or poly(*tert*-butyl acrylate) [poly(GTEMPO-co-EO)-*g*-PS/PtBA] were synthesized by atom transfer nitroxide radical coupling (ATNRC) chemistry. Linear precursor copolymers with multipending 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) groups [poly(GTEMPO-co-EO)] were prepared first by anionic ring-opening copolymerization of 4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (GTEMPO) and ethylene oxide (EO), and then polystyrene (PS) and poly(*tert*-butyl acrylate) (PtBA) with bromide end group were obtained by atom transfer radical polymerization (ATRP) using ethyl 2-bromoisobutyrate (EBiB) as the initiator and CuBr/*N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA) as catalyst. When the linear precursor copolymer poly(GTEMPO-co-EO) was mixed with PS or PtBA chains and heated to 90 °C in the presence of CuBr/PMDETA, the formed secondary carbon radicals at the PS or PtBA chain ends were quickly trapped by the nitroxide radicals on poly(GTEMPO-co-EO) main chain to form graft copolymer in which the alkoxyamines were at the conjunction points. The efficiency of coupling reaction was in the range of 90.2–95.9% for PS and 82.3–88.4% for PtBA when their number average of molecular weight  $M_n$  was in the range of 1500–7800 g/mol and ratio of GTEMPO/EO in copolymer was 1:21.

## Introduction

In the past decades, considerable efforts had been expended to develop different polymerization technologies, such as living anionic polymerization,<sup>1</sup> group transfer polymerization (GTP),<sup>2,3</sup> and “living”/controlled radical polymerization (CRP),<sup>4</sup> which displayed the essential characteristics of controlled polymerization. By using the CRP method, not only the polymers with predetermined number average of molecular weight  $M_n$  and low polydispersity indices (PDI) can be prepared but also a number of polymers with complicated structures which were difficult to obtain before can also be prepared.<sup>5,6</sup> The most popular used CRP methods are nitroxide-mediated polymerization (NMP),<sup>7,8</sup> reversible addition–fragmentation chain transfer (RAFT),<sup>9,10</sup> polymerization, and atom transfer radical polymerization (ATRP).<sup>11–14</sup> Especially, the polymers with halogen-containing ends prepared by ATRP had attracted much attention because of the easy transformations of terminal halogen atoms to other functional groups by chemical modification. For example, a polymer with halogen end group can be efficiently substituted by an azide anion via nucleophilic reaction, and then the latter could be reacted further with alkyne in the presence of metal catalyst to form a substituted triazoles ring. It was termed “click” chemistry.<sup>15</sup>

“Click” reactions had been successfully used in polymer and materials chemistry,<sup>16</sup> such as the preparations of well-defined linear<sup>17</sup> or star polymers,<sup>18</sup> cyclic polymers,<sup>19</sup> graft copolymers,<sup>20</sup> dendrimers,<sup>21</sup> and other applications.<sup>22–26</sup> However, the polymer with azide group is 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. Obviously, 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 reactive functional groups than azide.

Matyjaszewski reported that the macroradicals generated in situ by an atom transfer radical equilibrium in ATRP would take part in bimolecular termination reactions in the presence of a reducing agent.<sup>27–29</sup> This process was termed atom transfer radical coupling (ATRC) reaction, and the hydroxy-telechelic polystyrene (OH–PS–OH) and poly(methyl acrylate) (OH–PMA–OH) were obtained.<sup>30</sup>

We think that if the radical scavengers as TEMPO or TEMPO derivatives existed, bimolecular termination generated by the macroradicals in ATRP would not have happened, and the radicals might be trapped by nitroxide radicals instantly. On the basis of this idea, it is suggested by us if a polymer containing-TEMPO groups is mixed with another containing-halide polymer in the presence of CuBr/PMDETA, the coupling reactions between TEMPOs and radicals would be realized in high efficiency (Scheme 1).

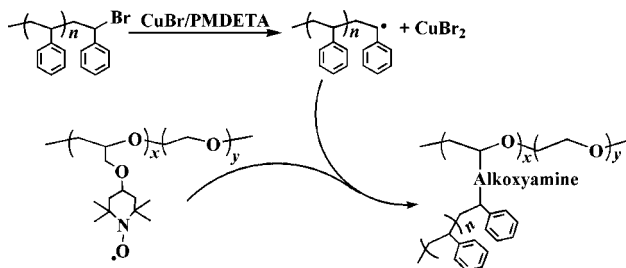
Herein, we report this coupling strategy; the graft copolymers poly(GTEMPO-co-EO)-*g*-PS (or PtBA) are effectively prepared by this method. In the reaction, the secondary carbon radicals of PS and PtBA at the chain ends formed by atom transfer using the CuBr as reductant are instantly trapped by the nitroxide radicals of the TEMPO groups on main chains, so this coupling reactions is termed atom transfer nitroxide radical coupling (ATNRC) chemistry.

## Experimental Section

**Materials.** Ethylene oxide (EO; Sinopharm Chemical Reagent) (SCR) was dried by CaH<sub>2</sub> for 48 h and distilled under N<sub>2</sub> before use. Styrene (St; 99.5%) purchased from SCR was washed with a 15% NaOH aqueous solution and water successively, dried over anhydrous MgSO<sub>4</sub>, further dried over CaH<sub>2</sub>, and then distilled under reduced pressure twice before use. *tert*-Butyl acrylate (*t*BA; 99%; SCR) was dried over CaH<sub>2</sub> 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. *N,N,N',N',N''*-Pentamethyldiethylenetriamine (PMDETA)

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**Scheme 1. Synthetic Mechanism for Poly(GTEMPO-*co*-EO)-*g*-PS by Atom Transfer Nitroxide Radical Coupling Chemistry**



and ethyl 2-bromoisobutyrate (EBiB) were purchased from Aldrich and used without further purification. 2-(2-Methoxyethoxy)ethanol (99%), tetrahydrofuran (THF; 99%), toluene (99%), and other reagents were all purchased from SCR and purified by standard methods before use. 4-Glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (GTEMPO) was synthesized according to our previous work<sup>8</sup> and distilled under a reduced pressure; the fraction at 130 °C/80 Pa was collected and recrystallized in hexane at 2 °C twice (mp 38–39 °C). <sup>1</sup>H NMR (500 MHz, sol.: CD<sub>3</sub>OD, 25 °C, tetramethylsilane as internal standard, in the presence of calculated amounts of HCOONH<sub>4</sub> and Pd/C;  $\delta$ , ppm): 1.18, 1.45, 1.93, and 3.40–3.49 (complex, 17H,  $-CH_3$ ,  $-CH_2-$  and  $-CH-$  of the TEMPO group); 2.60–2.79 (m, 2H,  $-OCH_2CH(CH_2)-$  of the glycidyl ring), 3.31 (m, 1H,  $-OCH_2CH(CH_2)-$  of the glycidyl ring), 3.62–3.87 (m, 2H,  $-OCH_2CH(CH_2)-$  of the glycidyl ring), 8.53 ( $-OOCH$  of HCOONH<sub>4</sub>). Gas chromatography: 99%. Mass spectrometry (70 eV)  $m/z$  (%): 228 [M<sup>+</sup>], 172 [C<sub>9</sub>H<sub>19</sub>NO<sub>2</sub>]<sup>+</sup>, 57 [C<sub>3</sub>H<sub>5</sub>O]<sup>+</sup>. Elem Anal. Calcd for C<sub>12</sub>H<sub>22</sub>NO<sub>3</sub> (228.16): C, 63.13%; H, 9.71%; N, 6.13%. Found: C, 63.02%; H, 9.91%; N, 6.03%.

#### Synthesis of Precursor Copolymers Poly(GTEMPO-*co*-EO).

The initiator was synthesized as follows: To a 150 mL, three-necked flask, 100 mL of dry THF and 6.0 mL (0.05 mol) of 2-(2-methoxyethoxy)ethanol were added, and then 2.1 g (0.054 mol) of potassium with fresh surface was introduced under a 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 using 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 (6.6 mL, 2.8 mmol) in 50 mL of THF, GTEMPO (4.6 g, 0.02 mol), and EO (20 mL, 0.4 mol) 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 of deionized water and extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. Combined CH<sub>2</sub>Cl<sub>2</sub> was dried over anhydrous MgSO<sub>4</sub>, then the solvents were removed by reduced distillation, and the precursor copolymer poly(GTEMPO-*co*-EO) was obtained in a yield of 96%. A series of copolymers with various compositions of GTEMPO to EO were synthesized in the same way. As the contents of GTEMPO in the copolymers were varied, solid or gumlike products with dark red color were obtained. <sup>1</sup>H NMR (CD<sub>3</sub>OD), in the presence of calculated amounts of HCOONH<sub>4</sub> and Pd/C,  $\delta$  (ppm): 1.18, 1.43, and 1.91 (complex, 16H,  $-CH_3$  and  $-CH_2-$  of the GTEMPO group), 3.37 (s, 3H, CH<sub>3</sub>O- of the methoxyl group), 3.53–3.78 (m, 10H,  $-CH-$ ,  $-OCH_2CH(CH_2)-$  of the GTEMPO group and  $-OCH_2CH_2-$  of PEO), 8.53 ( $-OOCH$  of HCOONH<sub>4</sub>); SEC,  $M_n$ : 8400 g/mol,  $M_w/M_n$ : 1.08.

**Synthesis of Halogen-Containing Polystyrene (PS-Br) by ATRP.** The mixture of St (26.4 mL, 230 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 ampule and degassed by three freeze–pump–thaw cycles. The ampule was immersed in oil bath at 90 °C for 2.5 h, then taken from the oil bath, and dipped in liquid nitrogen to stop the polymerization. The products were diluted with THF, and the solution was passed through a column chro-

matograph filled with neutral alumina to remove the copper complex before the polymer was precipitated in cold CH<sub>3</sub>OH. The precipitate was collected and purified by dissolution/precipitation with THF/cold CH<sub>3</sub>OH twice and then dried at 40 °C in vacuo. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 0.70–0.99 (m, 9H,  $-C(CH_3)_2-PS$ , CH<sub>3</sub>CH<sub>2</sub>O-), 1.20–2.25 (m, 3H,  $-CH_2CH-$  of PS), 3.44–3.63 (m, 2H, CH<sub>3</sub>CH<sub>2</sub>O-), 4.41–4.52 (m, 1H,  $-CH(Ph)-Br$ ), 6.30–7.30 (m, 5H, C<sub>6</sub>H<sub>5</sub> of PS); SEC,  $M_n$ : 1500 g/mol,  $M_w/M_n$ : 1.10.

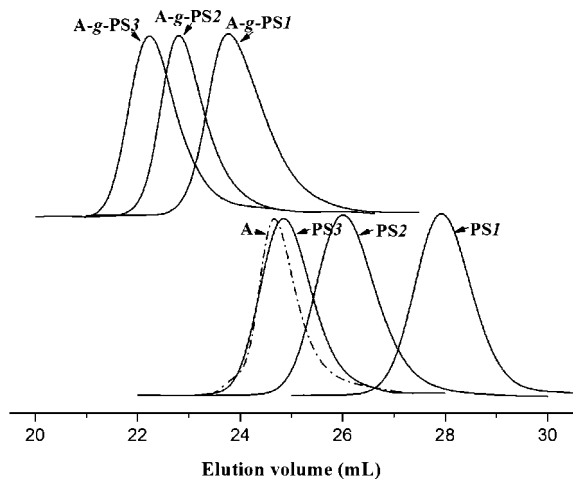
**Synthesis of Halogen-Containing Poly(*tert*-butyl acrylate) (PtBA-Br) by ATRP.** To a 50 mL ampule, EBiB (0.15 mL, 1 mmol), CuBr (0.144 g, 1 mmol), PMDETA (0.2 mL, 1 mmol), and tBA (7.3 mL, 50 mmol) in 10 mL of acetone were charged, and then it was vacuumed by three freeze–thaw cycles in liquid nitrogen, sealed, and immersed in oil bath at 60 °C. The reaction was stopped by dipping the ampule in liquid nitrogen. Crude products were diluted with THF, and the solution was filtered through a column chromatograph filled with neutral alumina to remove the copper complex. The polymer was precipitated in CH<sub>3</sub>OH/H<sub>2</sub>O (v/v = 1/1) to obtain pure PtBA. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 1.13 (s, 6H,  $-C(CH_3)_2-PtBA$ ), 1.20–2.29 (m, 15H, CH<sub>3</sub>CH<sub>2</sub>O-,  $-CH_2CH-$ , and  $-C(CH_3)_3$  of PtBA), 4.05–4.15 (m, 3H, CH<sub>3</sub>CH<sub>2</sub>O- and  $-CH-Br$ ); SEC,  $M_n$ : 1800 g/mol,  $M_w/M_n$ : 1.12.

#### Coupling Reactions between PS-Br (PtBA-Br) and TEMPO

**Groups on Poly(GTEMPO-*co*-EO) Main Chain.** The coupling reaction was carried out using the following procedure: An ampule charged with precursor copolymer poly(GTEMPO-*co*-EO) ( $M_n$ : 8400 g/mol,  $R_G$ : 1/21.8, here  $R_G$  was the molar ratio of GTEMPO to EO in copolymer; 0.1 g, 0.012 mmol), PS-Br ( $M_n$ : 4000 g/mol; 0.4 g, 0.1 mmol; [TEMPO]/[PS-Br] = 1/1.2), CuBr (0.014 g, 0.1 mmol), PMDETA (0.018 mL, 0.1 mmol), and toluene (5 mL) was degassed by three freeze–pump–thaw cycles. It was placed in an oil bath at 90 °C for 24 h and then immersed in liquid nitrogen. Crude products were diluted with THF, and the solution was passed through a column chromatograph filled with neutral alumina to remove the copper complex and then precipitated into CH<sub>3</sub>OH. The products were diluted with cyclohexane at 40 °C under magnetic stirring. When the solution was cooled to 0 °C, it was turbid, and the final products were precipitated as a white gel, while the excess PS was still in the solution. After centrifuging, the white gel was collected and dried at 35 °C in vacuo. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 0.70–1.18 (m, 21H,  $-CH_3$  of GTEMPO group,  $-C(CH_3)_2-PS$  and CH<sub>3</sub>CH<sub>2</sub>O-), 1.20–2.20 (m, 3H,  $-CH_2CH-$  of PS), 3.38 (s, 3H, CH<sub>3</sub>O- of PEO), 3.53–3.78 (m, 10H,  $-CH-$ ,  $-OCH_2CH(CH_2)-$  of GTEMPO group and  $-OCH_2CH_2-$  of PEO), 6.30–7.30 (m, 5H, C<sub>6</sub>H<sub>5</sub> of PS); SEC,  $M_n$ : 23 200 g/mol,  $M_w/M_n$ : 1.09.

The reaction between poly(GTEMPO-*co*-EO) and PtBA-Br was carried out as follows. A 50 mL ampule charged with precursor copolymer poly(GTEMPO-*co*-EO) ( $M_n$ : 8400 g/mol,  $R_G$ : 1/21.8; 0.22 g, 0.026 mmol), PtBA-Br ( $M_n$ : 4900 g/mol; 0.94 g, 0.19 mmol; [TEMPO]/[PtBA-Br] = 1/1.2), CuBr (0.027 g, 0.19 mmol), PMDETA (0.034 mL, 0.19 mmol), and toluene (10 mL) was degassed by three freeze–pump–thaw cycles. Then the ampule was immersed in an oil bath at 90 °C and heated for 24 h. The reaction was stopped by placing the ampule in liquid nitrogen. Crude products were diluted with THF, and the solution was filtered through a column filled with neutral alumina to remove the copper complex. The purification of the obtained products was performed by dissolution of the products in CH<sub>3</sub>OH and then separating by an ultrafiltration membrane separator. The separated CH<sub>3</sub>OH solution was concentrated and precipitated into CH<sub>3</sub>OH/H<sub>2</sub>O (v/v = 1/1). After filtrating, the products were collected and then dried at 35 °C in vacuo. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 1.13 (s, 6H,  $-C(CH_3)_2-PtBA$ ), 1.20–2.29 (m, 15H, CH<sub>3</sub>CH<sub>2</sub>O-,  $-CH_2CH-$ , and  $-C(CH_3)_3$  of PtBA), 3.38 (s, 3H, CH<sub>3</sub>O- of PEO), 3.53–3.78 (m, 10H,  $-CH-$ ,  $-OCH_2CH(CH_2)-$  of the GTEMPO group, and  $-OCH_2CH_2-$  of PEO), 4.05–4.15 (m, 2H, CH<sub>3</sub>CH<sub>2</sub>O-); SEC,  $M_n$ : 17 800 g/mol,  $M_w/M_n$ : 1.07.

**Measurements.** The ultrafiltration membrane separator was purchased from Shanghai Institute of Applied Physics, Chinese Academy of Science; the cutoff molecular weight of used poly(ether sulfone) film was  $M_{w,cutoff} = 6000$  g/mol (calibrated by globin). Size exclusion chromatography (SEC) was performed at 35 °C in tetrahydrofuran



**Figure 1.** SEC traces of the halogen-containing homopolymers PS-Br (PS1 to PS3), linear precursor copolymers A, and their coupling products A-g-PS (A-g-PS1 to A-g-PS3). (The precursor copolymer A poly(GTEMPO-co-EO) is depicted as the dash-dot trace.)

(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  $10^4$ ) and a Waters 410 refractive index detector; monodistributed PS (molecular weight in the range of 580–3 390 000 g/mol) was used as the calibration standard.  $^1\text{H}$  NMR spectra were recorded at room temperature by a Bruker (500 MHz) spectrometer using tetramethylsilane as the internal standard and  $\text{CDCl}_3$  as the solvent, except for the monomer GTEMPO and the precursor copolymer poly(GTEMPO-co-EO); the latter were determined in deuterated methanol in the presence of stoichiometric ammonium formate ( $\text{HCOONH}_4$ ) and the catalyst palladium on carbon (Pd/C). 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 the samples were heated at  $10^\circ\text{C}/\text{min}$  heating rate from  $-70$  to  $140^\circ\text{C}$  for the first scan, then cooled at  $-10^\circ\text{C}/\text{min}$  to  $-70^\circ\text{C}$ , and immediately heated a second time. 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  $\text{CH}_2\text{Cl}_2$ . The conversions were determined by a gravimetric method. 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  $30\text{ m} \times 0.25\text{ mm}$  (i.d.) with a  $0.25\text{ }\mu\text{m}$  film thickness (DB-5, Restek). The GC/MS parameters were as follows: the ion source temperature was  $200^\circ\text{C}$ , the carrier gas was helium, the column flow was 1 mL/min, the temperature program was  $100\text{--}200^\circ\text{C}$  at  $15^\circ\text{C}/\text{min}$ , and splitless injection was used at  $250^\circ\text{C}$ . Ionization was achieved at  $70\text{ eV}$ .

## Results and Discussion

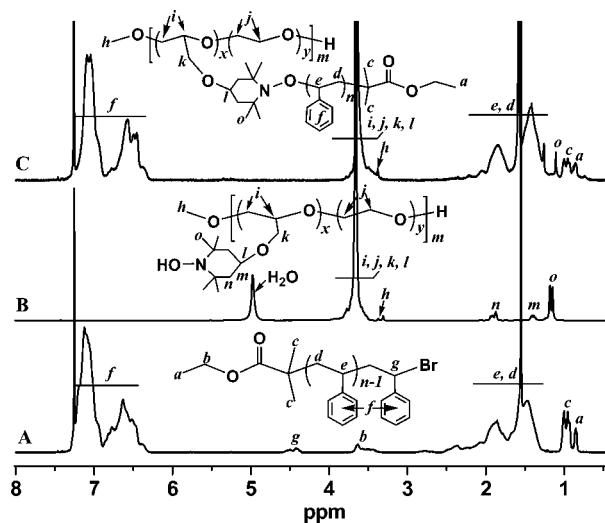
**Synthesis and Characterization of Precursor Copolymer Poly(GTEMPO-co-EO).** The monomer GTEMPO was synthesized as reported,<sup>8</sup> in which HTEMPO was reacted directly with epichlorohydrin using tetrabutylammonium hydrogen sulfate (TBAHS) as phase-transfer catalyst, and then it was copolymerized with EO by anionic ring-opening polymerization using potassium 2-(2-methoxyethoxy) ethoxide as initiator at  $40^\circ\text{C}$ . Curve A in Figure 1 was the SEC of the linear copolymer A ( $M_n$ : 8400 g/mol); the dash-dot trace showed the low  $M_w/M_n$  (1.08) and a nice Gaussian distribution. All the data of the three linear copolymers are presented in Table 1.

Because of the paramagnetism of the pending TEMPO radicals, the  $^1\text{H}$  NMR was carried out in deuterated methanol in the presence of stoichiometric  $\text{HCOONH}_4$  and catalytic Pd/

**Table 1.** Characterization of the Synthetic Precursor Copolymers Poly(GTEMPO-co-EO)

sample	$R_i^a$	$R_G^b$	$M_n^c$ (g/mol)	$M_w/M_n^c$	$N_{\text{TEMPO}}^d$	yield (%) <sup>e</sup>
A	1/20	1/21.8	8400	1.08	7.1	96
B	1/20	1/21.0	6100	1.12	5.3	97
C	1/5	1/5.4	6000	1.10	12.9	94

<sup>a</sup> Feed ratio of GTEMPO to EO. <sup>b</sup> Observed molar ratio of GTEMPO to EO, measured by  $^1\text{H}$  NMR. <sup>c</sup> Measured by SEC in THF with linear PS as standard. <sup>d</sup> Number-average of TEMPO groups on each poly(GTEMPO-co-EO) chain was calculated from  $^1\text{H}$  NMR data. <sup>e</sup> The yields of copolymers poly(GTEMPO-co-EO) were determined by the gravimetric method.



**Figure 2.**  $^1\text{H}$  NMR spectra of (A) PS1 (Table 2;  $M_n$ : 1500 g/mol; solvent:  $\text{CDCl}_3$ ), (B) poly(GTEMPO-co-EO) A (Table 1;  $M_n$ : 8400 g/mol; solvent:  $\text{CD}_3\text{OD}$ ), and (C) coupling product A-g-PS1 (Table 3;  $M_n$ : 16 900 g/mol; solvent:  $\text{CDCl}_3$ ).

**Table 2.** Characterization of the Synthetic Homopolymers PS-Br and PtBA-Br

sample	$M_n^a$ (g/mol)	$M_w/M_n^a$	$M_n^b$ (g/mol)	DP <sup>c</sup>
PS1	1500	1.10	1700	14.8
PS2	4000	1.08	4200	38.8
PS3	7800	1.09	7700	72.0
PtBA1	1800	1.12	1800	13.1
PtBA2	4900	1.08	5400	40.6

<sup>a</sup> Measured by SEC in THF using PS as standard. <sup>b</sup> Calculated from the  $^1\text{H}$  NMR data,  $M_{n,\text{NMR}} = \text{MW} \times \text{DP} + 195$ , where MW represents the molecular weight of the monomers. <sup>c</sup> Average degree of polymerization of St or tBA, calculated from the  $^1\text{H}$  NMR data.

C; the TEMPO radicals on the copolymers were reduced to corresponding oximes, and clear  $^1\text{H}$  NMR spectra were then performed (see Figure 2).

The  $^1\text{H}$  NMR spectrum of the copolymer A is shown in Figure 2B; the methine or methylene resonances for the  $-\text{CH}-$  group ("l"),  $-\text{OCH}_2\text{CH}(\text{CH}_2)-$  group ("i, k") of GTEMPO, and the  $-\text{OCH}_2\text{CH}_2-$  group ("j") of PEO appeared in the region 3.53–3.78 ppm. In addition, the methyl ("o") resonance was at 1.18 ppm and methylene ("m, n") resonances were at 1.43 and 1.91 ppm for GTEMPO.<sup>31</sup> The methoxyl resonance for the unique  $\text{CH}_3\text{O}-$  group ("h") at the chain end of the copolymers was also observed at 3.37 ppm. Thus, the copolymer composition could be calculated by the formula

$$R_G = \frac{2A_o}{6A_{3.5-3.8} - 3A_o} \quad (1)$$

Here  $R_G$  represents molar ratio of GTEMPO to EO in linear copolymers poly(GTEMPO-co-EO),  $A_o$  is the integral area of the protons on the methyl groups of GTEMPO at 1.18 ppm, and  $A_{3.5-3.8}$  are the integral areas of all the methine or methylene

Table 3. Data of the Coupling Reaction between Poly(GTEMPO-co-EO) and PS-Br(PrBA)

ATNRC			time (h)	$M_n^a$ (g/mol)	$M_w/M_n^a$	$M_n^b$ (g/mol)	EF <sup>c</sup> (%)
poly(GTEMPO-co-EO)	homopolymers						
A	PS1	A-g-PS1	24	16 900	1.13	19 600	95.9
	PS2	A-g-PS2	24	23 200	1.09	35 700	92.7
	PS3	A-g-PS3	24	30 200	1.16	57 000	90.2
B	PS2	B-g-PS2	24	15 700	1.14	27 200	95.8
	PS3	B-g-PS3	24	22 500	1.12	42 700	90.5
C	PS2	C-g-PS2	24	25 700	1.16	49 800	81.6
	PS3	<sup>1</sup> C-g-PS3	24	30 600	1.14	57 900	52.8
	PS3	<sup>2</sup> C-g-PS3	48	53 400	1.08	70 500	65.7
A	PrBA1	A-g-PrBA1	24	10 000	1.08	24 300	88.4
	PrBA2	A-g-PrBA2	24	17 800	1.07	46 100	82.3

<sup>a</sup> Measured by SEC in THF with RI detector, calibration with linear PS as standard. <sup>b</sup> Calculated from the <sup>1</sup>H NMR data. <sup>c</sup> Coupling efficiency of ATNRC, calculated from <sup>1</sup>H NMR data.

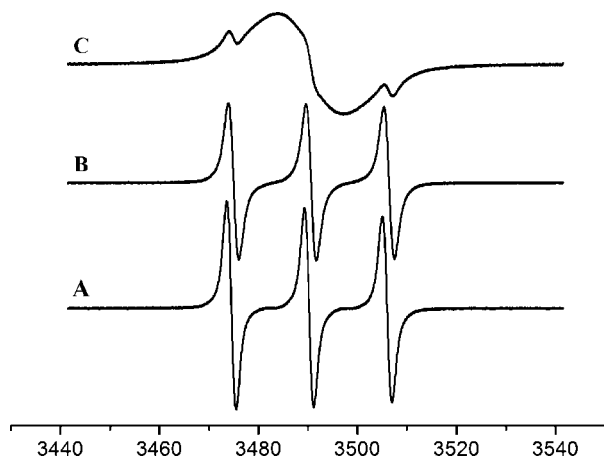


Figure 3. ESR spectra of GTEMPO (A) and copolymers poly(GTEMPO-co-EO) (Table 1) with different compositions (B) GTEMPO/EO = 1/21.8 and (C) GTEMPO/EO = 1/5.4.

group protons at 3.53–3.78 ppm. The  $R_G$  value is very close to the feed ratio of GTEMPO to EO, as shown in Table 1. The data of other precursor copolymers B and C with different contents of GTEMPOs are also displayed in Table 1.

The ESR spectra of GTEMPO and its copolymers are shown in Figure 3. According to previous reports, GTEMPO, like all other monomeric nitroxyls, also gave a clean triplet with equal intensity<sup>32</sup> (Figure 3A). On the contrary, the ESR spectra of the poly(GTEMPO-co-EO) copolymers with multiradicals showed different behavior. Figures 3B and C were the corresponding spectra of poly(GTEMPO-co-EO) obtained at different monomer feed ratios (GTEMPO/EO = 1/20 and 1/5; Table 1). With increasing GTEMPO radical content, the characteristic triplet signal became broader and even close to the singlet when the feed ratio of GTEMPO to EO was 1/5. Generally, the causes for this broadening and change to the singlet were considered to be spin–spin coupling between the radicals. To avoid the high radical concentration leading to intermolecular spin–spin coupling, solution C was diluted, and its concentration was about a tenth of those of solutions A and B. However, the ESR signals did not markedly change. Therefore, the gradual broadening of the ESR spectra should be attributed to the intramolecular spin–spin coupling. That is, as the TEMPO radical density along the polymer chains increased, the possibility of spin–spin interaction was unavoidable, although the polymer concentration was as low as  $10^{-6}$  M. Consequently, the transition time of spins from the excited state to the ground state was reduced significantly, and the width of the triplet to a singlet was broadened.

**Synthesis and Characterization of PS-Br and PrBA-Br.** PS-Br and PrBA-Br were synthesized by typical ATRP using EBiB as initiator and CuBr/PMDETA as catalyst. The reaction

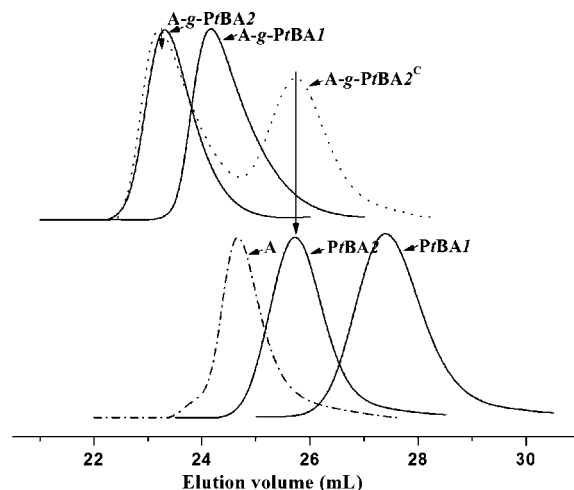


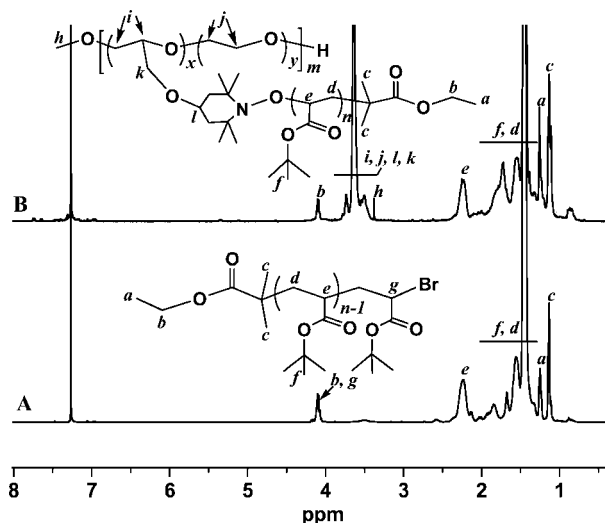
Figure 4. SEC traces of the homopolymers PrBA (PrBA1, PrBA2) and their coupling products A-g-PrBA (A-g-PrBA1 and A-g-PrBA2). (The precursor copolymer A [poly(GTEMPO-co-EO)] is illustrated as dash-dot trace, and the dot trace A-g-PrBA2<sup>c</sup> describes crude products of A-g-PrBA2 without further purification.)

was stopped at low conversion (<30%) to ensure a high degree of bromines at chain ends.<sup>33</sup> By controlling the reaction time, a series of PS-Br or PrBA-Br with different  $M_n$  were obtained. The SEC traces of these PS-Br or PrBA-Br are illustrated in Figure 1 (PS1 to PS3) and Figure 4 (PrBA1, PrBA2). All the details are listed in Table 2, in which all traces of PS-Br and PrBA-Br were accorded with a Gaussian distribution and the  $M_w/M_n$  for them were less than 1.12.

Figure 2A shows the <sup>1</sup>H NMR spectrum of PS1. There were two main regions. The resonances for the methylene and methine groups (“e, d”) of PS occur at 1.20–2.20 ppm, and the resonances for the aromatic protons (“f”) of PS occur in the region 6.30–7.30 ppm. In addition, the methine resonance for the unique –CH(Ph)–Br functional group (“g”) was observed at 4.40 ppm. The methyl and methylene resonances for the CH<sub>3</sub>CH<sub>2</sub>O– (“a”), –C(CH<sub>3</sub>)<sub>2</sub>– (“c”), and CH<sub>3</sub>CH<sub>2</sub>O– (“b”) groups from EBiB occur at 0.84, 0.92–1.10, and 3.44–3.63 ppm, respectively. The average degree of polymerization (DP) was analyzed with the formula

$$DP_{St} = \frac{9A_{6.3-7.3}}{5(A_a + A_c)} \quad (2)$$

Here  $DP_{St}$  represents the average degree of polymerization of styrene by <sup>1</sup>H NMR spectra.  $A_a$  and  $A_c$  are the integral areas of the protons of methyl groups (CH<sub>3</sub>CH<sub>2</sub>O– and –C(CH<sub>3</sub>)<sub>2</sub>–), respectively.  $A_{6.3-7.3}$  is the integral area of the aromatic protons of PS. The  $DP_{St}$  values of resultant polymers PS1, PS2, and PS3 are 14.8, 38.8, and 72.0, respectively, which are nearly the same as we obtained by SEC (Table 2).



**Figure 5.**  $^1\text{H}$  NMR spectra of (A) PtBA1 (Table 2;  $M_n$ : 1800 g/mol; solvent:  $\text{CDCl}_3$ ) and (B) coupling products A-g-PtBA1 (Table 3;  $M_n$ : 10 000 g/mol; solvent:  $\text{CDCl}_3$ ).

The SEC traces of synthesized PtBA-Br are shown in Figure 4. It was observed that the SEC traces of PtBA-Br were accorded with a Gaussian distribution, and the  $M_w/M_n$  were less than 1.2. Figure 5A shows the  $^1\text{H}$  NMR spectrum of PtBA1, in which two main regions can be seen. The methyl resonances for the  $-\text{C}(\text{CH}_3)_2-$  group ("c") from EBiB occur at 1.13 ppm. The methyl resonance for the  $\text{CH}_3\text{CH}_2\text{O}-$  group ("a") from EBiB and the resonances for the methyl or methylene groups ("f, d") of PtBA occur at 1.20–1.90 ppm. The resonance for the methine protons ("e") of PtBA occur in the region 2.10–2.29 ppm. In addition, the methine resonance for the unique  $-\text{CH}-\text{Br}$  ("g") functional group and the methylene resonances for the  $\text{CH}_3\text{CH}_2\text{O}-$  group ("b") from EBiB are observed at 4.05–4.15 ppm. Thus, the DP of PtBA-Br was derived from the  $^1\text{H}$  NMR spectrum using the formula

$$\text{DP}_{\text{PtBA}} = \frac{3A_e}{A_{b+g}} \quad (3)$$

Here,  $\text{DP}_{\text{PtBA}}$  is the average degree of polymerization of tBA.  $A_e$  is the integral area of the methine group ( $-\text{CH}_2\text{CH}-$ ) proton of PtBA at 2.10–2.29 ppm.  $A_{b+g}$  is the sum of the integral areas of the protons on  $\text{CH}_3\text{CH}_2\text{O}-$  group and the unique  $-\text{CH}-\text{Br}$  functional group (4.05–4.15 ppm). The results are presented in Table 2. As is well-known, the structure of PtBA is quite different from the PS standard; when the  $\text{DP}_{\text{PtBA}}$  with high molecular weight (PtBA2 in Table 2) was measured, the actual  $M_n$  of PtBA would deviate from the value by SEC.

**Coupling Reaction between PS-Br or PtBA-Br and TEMPO Groups on Poly(GTEMPO-co-EO).** The whole coupling process using PS-Br as sample is described in Scheme 1. In the coupling reaction, the used PS-Br or PtBA-Br was slightly excessive, the molar ratio of PS-Br and PtBA-Br to TEMPO groups on copolymers was about 1.2/1. The excessive PS-Br could be easily removed from the mixture by extraction with cyclohexane<sup>34,35</sup> after the coupling reaction was carried out. The SEC traces of A-g-PS series are depicted in Figure 1 and Table 3 (A-g-PS1, A-g-PS2, and A-g-PS3).

The A-g-PtBA series were also prepared under the same conditions, and the SEC traces of A-g-PtBA series are shown in Figure 4. The dot trace named A-g-PtBA2<sup>C</sup> represented crude products without further purification. It can be observed that there were two peaks corresponding to final graft products and excessive PtBA-Br; the latter could be removed from the final

products by the ultrafiltration membrane separator. The pure products are illustrated in Figure 4 named A-g-PtBA2.

When the mixture of PS-Br or PtBA-Br and poly(GTEMPO-co-EO) with TEMPO groups was heated to 90 °C in the presence of CuBr/PMDETA, the bromine atoms at PS-Br and PtBA-Br chain ends serving as oxidant were reduced to bromine anions, and then secondary carbon radicals of PS or PtBA were formed; CuBr was served as reductant, the  $\text{Cu}^{1+}$  was oxygenated to  $\text{Cu}^{2+}$ , and the  $\text{CuBr}_2$  was formed. The macroradicals of PS or PtBA were quickly trapped by the nitroxide radicals of TEMPO groups on poly(GTEMPO-co-EO) to form the alkoxyamines shown in Scheme 1.<sup>36,37</sup>

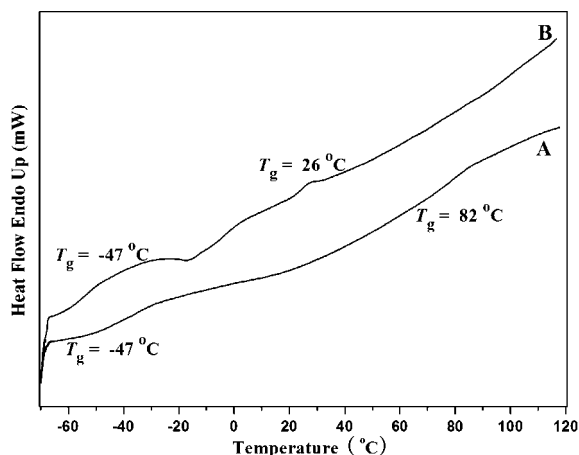
This process was irreversible in our experimental conditions which was quite different from ATRC. In the typical ATRC chemistry, the coupling reactions occurred between macroradicals, which generated after bromine atoms broken off from PS-Br. While, in the presence of nitroxide radicals with low concentration, the gradually generating macroradicals would instantly trapped by nitroxide radicals to form alkoxyamines.<sup>36</sup> SEC (Figures 1 and 4) results revealed that there were only two peaks corresponding to the A-g-PS and linear PS-Br, A-g-PtBA and linear PtBA; no traces of bimolecular termination products PS-PS or PtBA-PtBA were detected. Obviously, the coupling reaction between nitroxide radicals and macroradicals was more efficient than the bimolecular termination.

Figure 2C shows the  $^1\text{H}$  NMR spectrum of A-g-PS1. Compared with Figure 2A of the PS-Br, the original resonance observed in the region 4.4–4.6 ppm for methine protons of  $-\text{CH}(\text{Ph})-\text{Br}$  functional group disappeared; they moved to the upfield after the bromine atoms were broken off from PS chain. The resonances for aromatic ring of PS at 6.30–7.30 ppm and for methine or methylene groups of main chains at 3.53–3.78 ppm were observed. Figure 5B shows the  $^1\text{H}$  NMR spectrum of A-g-PtBA1. Compared with Figure 5A, the intensity of original resonance occurred at 4.05–4.15 for the methine protons of the  $-\text{CH}-\text{Br}$  functional group ("g") and methylene protons on the  $\text{CH}_3\text{CH}_2\text{O}-$  group ("b") was reduced (the original integral area for the methine group of PtBA ("A<sub>e</sub>") was used as standard) because the methine protons of  $-\text{CH}-\text{Br}$  functional group moved to the upfield after the bromine atoms were broken off from PtBA chain. The resonances for methine or methylene groups ("j") of PEO at 3.53–3.78 ppm were also observed. Thus, it could reliably concluded that the coupling reaction was successfully carried out.

The coupling efficiency between pending-TEMPO groups on poly(GTEMPO-co-EO) and halogen-containing polymer PS-Br can be calculated by the formula

$$\text{EF} (\%) = \frac{A_{6.3-7.3}(4R_G + 6)}{5\text{DP}_{\text{St}}A_{3.5-3.8}} \times 100\% \quad (4)$$

Here  $R_G$ ,  $\text{DP}_{\text{St}}$ ,  $A_{6.3-7.3}$ , and  $A_{3.5-3.8}$  represent the same meaning as mentioned above.  $(4R_G + 6)$  refers to the sum of protons on every (GTEMPO-co-EO)<sub>21</sub> unit [or (GTEMPO-co-EO)<sub>5.4</sub>]. The calculated EF (%) for all samples are listed in Table 3. Compared with the EF (%) of A-g-PS series, it was found that for the same poly(GTEMPO-co-EO) the EF (%) decreased with the increasing of the  $M_n$  of PS; for the same PS-Br, EF (%) decreased with the increasing of GTEMPO contents in copolymers. Copolymers A and B were designed with the same composition (GTEMPO/EO = 1/21) and different molecular weight. However, the EF (%) for both of them were more than 90%. It seemed that in these cases the  $M_n$  of poly(GTEMPO-co-EO) showed little influence on the coupling efficiency than that of PS-Br. The copolymer C was designed to have the similar  $M_n$ , while different composition (GTEMPO/EO = 1/5.4) comparing with copolymer B (GTEMPO/EO = 1/21). The EF (%) of C-g-PS was 81.6% for C-g-PS2, 52.8% for <sup>1</sup>C-g-PS3



**Figure 6.** DSC thermograms of (A) A-g-PS2 and (B) A-g-PtBA1 graft copolymers.

(reacted for 24 h), and 65.7% for <sup>2</sup>C-g-PS3 (reacted for 48 h). Comparing with A-g-PS and B-g-PS, the coupling efficiency of C-g-PS decreased acutely. The inability of all TEMPO groups on the poly(GTEMPO-co-EO) to participate in the ATNRC reaction can be attributed to steric hindrance, which was increased with the number of attached grafted chains. The results presented here were in accordance with recent report; the moderate efficiency of click grafting of PEO chains onto azide functionalized poly(methyl methacrylate) backbones was observed.<sup>20</sup> Therefore, it was reasonable to postulate that the coupling reaction efficiency in the “graft onto” method was intensively influenced by steric hindrance whether ATNRC or click chemistry.

The EF (%) of A-g-PtBA series could also be determined from the <sup>1</sup>H NMR spectra by the formula

$$\text{EF (\%)} = \frac{A_e(4R_G + 6)}{\text{DP}_{tBA}A_{3.5-3.8}} \times 100\% \quad (5)$$

Here  $R_G$ ,  $A_{3.5-3.8}$ ,  $A_e$ , and  $\text{DP}_{tBA}$  represent the same meaning as mentioned above. The calculated results are shown in Table 3. The values were lower (<90%) than that of A-g-PS series. The  $M_n$  of the graft copolymers could be calculated from <sup>1</sup>H NMR data by the formula

$$M_n = [(44 \times R_G + 228) + (\text{MW} \times \text{DP} + 115) \times \text{EF (\%)}] \times N_{\text{TEMPO}} + 120 \quad (6)$$

Here MW is the molecular weight of monomer St or tBA, and other parameters have the same meaning as mentioned above. In all cases, the  $M_n$  derived from <sup>1</sup>H NMR was much higher than that from SEC; it can attributed to the smaller hydrodynamic volumes of the graft copolymers than that of the PS standard.

The glass transition temperatures ( $T_g$ ) of the graft copolymers were determined by DSC as shown in Figure 6. For graft copolymer A-g-PS2 (Figure 6A), two  $T_g$ s at  $-47$  and  $82$  °C were observed. The first transition was similar with the PEO segment ( $T_g$  for PEO homopolymer:  $-60$  °C), while the second transition was similar to PS segment ( $T_g$  for PS homopolymer:  $90$  °C).<sup>38</sup> Figure 6B also exhibits two  $T_g$ s for graft copolymer A-g-PtBA1. The first  $T_g$  for the PEO segment was also observed at  $-47$  °C, and the second  $T_g$  for the PtBA segment was at  $26$  °C, which is lower than the expected  $T_g$  for PtBA precursor ( $45$  °C).<sup>38</sup> These results may attribute to the interaction between different segments. In the case of A-g-PS3 with higher molecular weight of PS, the  $T_g$  for PEO segment cannot be observed, while the  $T_g$  for PS segments was increased to  $88$  °C. In this case, the relative longer PS segment of PS3 ( $M_n$ :  $7800$  g/mol) may exert

a greater effect on the copolymer. Clearly, the DSC investigation provided another evidence for the successful synthesis of the graft copolymers by ATNRC method.

## Conclusion

By means of the high coupling efficiency between bromine and TEMPO groups attached on the different polymer chains in the presence of CuBr, graft copolymers of poly(GTEMPO-co-EO) as the backbones and PS or PtBA as side chains were successfully synthesized via the ATNRC method. The coupling reaction was influenced by the density of graft GTEMPO groups on poly(GTEMPO-co-EO) and molecular weight of grafted chains. This approach affords another choice for preparation of the polymers with different compositions and well-defined structures.

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

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MA7028117