

# Investigation of Nitroxide Radical Coupling Reaction in Wide Temperature Range and Different Catalyst System

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**ABSTRACT:** The effect of temperature, catalyst system, and the structure of bromine connected groups on the nitroxide radical coupling (NRC) reaction is investigated in details. A series of polymers with different bromine connected groups as poly (*tert*-butyl acrylate) (PtBA-Br), polystyrene (PS-Br), and poly (methyl methacrylate) (PMMA-Br) are prepared by atom transfer radical polymerization first, then the bromine-containing polymers were coupled with 2,2,6,6-tetramethylpiperidiny-1-oxy-containing poly( $\epsilon$ -caprolactone) (PCL-TEMPO) in different catalyst systems as CuBr/PMDETA, Cu<sup>0</sup>/PMDETA and CuBr/Cu<sup>0</sup>/PMDETA in the temperature range from 90 °C to 25 °C. The result shows that the catalyst system of CuBr/Cu<sup>0</sup>/PMDETA is the best one for NRC reaction, in which the NRC reaction could be con-

ducted in high efficiency in the wide temperature range from room temperature to high temperature. The efficiency of NRC reaction between PtBA-Br and PCL-TEMPO is more than 85% in the temperature range from 25 to 75 °C, the efficiency between PS-Br and PCL-TEMPO is more than 90% from 25 to 90 °C, and the efficiency between PMMA-Br and PCL-TEMPO is more than 90% only at the room temperature. The effect of bromine connected groups on the NRC reaction is discussed. © 2010 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 48: 2991–2999, 2010

**KEYWORDS:** atom transfer radical polymerization (ATRP); block copolymers; nitroxide radical coupling; polystyrene; single electron transfer living radical coupling

**INTRODUCTION** Molecular design of the copolymers with complex structures is a very interesting research field. Always, applying coupling reaction of polymers with preformed functional groups has been proved to be an effective strategy to synthesize these kinds of copolymers with well-defined architectures and well monodispersity.<sup>1,2</sup> Click chemistry is one of the most widely used coupling reaction for its quantitative yields, high tolerance of functional groups, and insensitivity to solvents.<sup>3–7</sup> However, the polymers with azide group used in click chemistry are difficult to be preserved due to their photosensitivity and thermal instability. Moreover, the Glaser coupling reaction<sup>8,9</sup> of alkyne with alkyne group may also happen in some cases in the click reaction. Nowadays, the Diels–Alder reaction [4 + 2] system also has attracted considerable attention. The great potential of this coupling reaction has been quickly recognized in polymer synthesis and material science.<sup>10–13</sup> However, the maleimide and anthracene end groups generally require multistep synthesis and purification. Recently, our group find that the macroradicals, generated after the leaving of Br group in the presence of metal catalyst and conjugates, could be instantly captured by the 2,2,6,6-tetramethylpiperidiny-1-oxy (TEMPO) group in another polymer chain by formation of alkoxyamine linkage with high efficiency. The generation of the macroradicals is the key step for this coupling reaction. In the previous

work, we have found two strategies to generate the macroradicals: one is using CuBr and *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) as catalyst to generate macroradicals under a relatively high temperature (80–90 °C) by the mechanism of atom transfer radical polymerization (ATRP),<sup>14–17</sup> and this kind of coupling reaction was termed as Atom Transfer Nitroxide Radical Coupling (ATNRC)<sup>18–24</sup> reaction; the other is applying Cu<sup>0</sup>/PMDETA as catalyst system to generate macroradicals under ambient temperature (25 ± 5 °C) by the mechanism of single electron transfer living radical polymerization (SET-LRP),<sup>25–30</sup> hence this kind coupling reaction was termed as single-electron-transfer nitroxide-radical-coupling (SETNRC)<sup>31</sup> reaction. Both the ATNRC and SETNRC were referred as nitroxide radical coupling (NRC) reaction.

It was confirmed that in NRC reaction, both of ATNRC and SETNRC reaction are effective and the coupling efficiency is more than 85%, no matter at high temperature (80–90 °C)<sup>18–23</sup> or ambient temperature.<sup>31</sup>

However, the previous NRC work was only focused on the limited systems and reaction conditions. To enlarge the application field of NRC, looking for an optimal reaction condition is necessary. Thus, the effect of the reaction temperature, the structure of bromine connected groups, and catalyst

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system on the NRC reaction are investigated in this presentation in details.

## EXPERIMENTAL

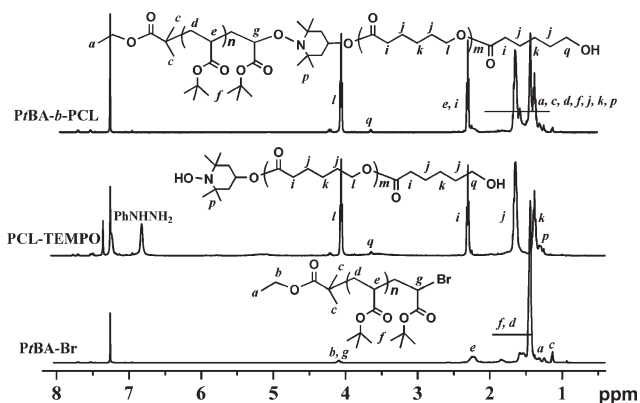
### Materials

*tert*-butyl acrylate (*t*BA, 99%, SCR),  $\epsilon$ -caprolactone (CL, 99%, SCR), and methyl methacrylate (MMA, 99%, SCR) were dried by CaH<sub>2</sub> for 48 h and distilled before use. Styrene (St, 99.5%) purchased from SCR was washed with a 15% NaOH aqueous solution and water successively for three times, respectively, dried over anhydrous MgSO<sub>4</sub>, further dried over CaH<sub>2</sub>, then distilled under reduced pressure twice before use. 4-Hydroxyl-TEMPO (HTEMPO) prepared according to the literature<sup>32</sup> was purified by recrystallization with hexane. CuBr (95%, SCR) was stirred overnight in acetic acid, filtered, washed with ethanol and diethyl ether successively, and dried *in vacuo*. *N,N,N',N'*-pentamethyldiethylenetriamine (PMDETA, 99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 97%) and ethyl 2-bromoisobutyrate (EBiB, 98%) were purchased from Aldrich and used without further purification. Acetone (99%), tetrahydrofuran (THF, 99%), toluene (99%), *N,N*-dimethyl formamide (DMF, 99%), and other reagents were all purchased from SCR and purified by standard method before use.

### Synthesis of TEMPO End-Functionalized PCL (PCL-TEMPO)

2,2,6,6-tetramethylpiperidinyl-1-oxy-containing poly( $\epsilon$ -caprolactone) (PCL-TEMPO) was prepared by ROP of  $\epsilon$ -CL in toluene solution using stannous octoate Sn(Oct)<sub>2</sub> as catalyst and HTEMPO as initiator. The dried HTEMPO (0.19 g, 1.10 mmol) by azeotropic distillation with dry toluene was dissolved in 3.5 mL toluene, to which  $\epsilon$ -CL (3.40 mL, 32 mmol) was added. Then a given amount of the catalyst ([Sn(Oct)<sub>2</sub>]/[OH] = 0.15) was injected under nitrogen by a syringe. The reaction was allowed to proceed at 100 °C for 24 h. After cooling to room temperature, the products were dissolved in THF and precipitated into an excess amount of methanol. The precipitate was isolated by filtration and dried at room temperature in a vacuum oven for 4 h. Characterization: [M]<sub>0</sub>/[I]<sub>0</sub> = 29, conversion = 90%, the number-average molecular weight from <sup>1</sup>H NMR ( $M_{n,NMR}$ ) = 3000 g/mol, number-average molecular weight from GPC ( $M_{n,GPC}$ ) = 6300 g/mol (relative to linear PS); the calibrated molecular weight of  $M_{n,GPC}$  ( $M_{n,cal}$ ) = 3100 g/mol; polydispersity index (PDI) = 1.13.

<sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 4.12–4.02 [–(CO)–CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O, the fifth methylene group connected to carbonyl, repeating unit of PCL], 3.70–3.62 [–(CO)–CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH, end group of PCL], 2.35–2.24 [–(CO)–CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O, the first methylene group connected to carbonyl, repeating unit of PCL], 1.72–1.56 [–(CO)–CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O, the second and fourth methylene groups connected to carbonyl, repeating unit of PCL], 1.42–1.33 [–(CO)–CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O, the third methylene group connected to carbonyl, repeating unit of PCL], 1.28–1.17 (CH<sub>3</sub>, methyl protons of TEMPO).



**FIGURE 1** <sup>1</sup>H NMR spectra of PtBA-*b*-PCL (using CuBr/Cu<sup>0</sup>/PMDETA as catalyst system at 25 °C) and the corresponding precursors PtBA-Br and PCL-TEMPO1 in CDCl<sub>3</sub>.

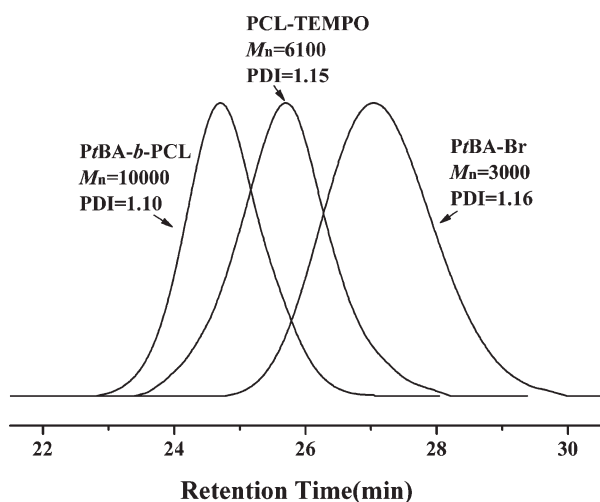
### Synthesis of PtBA with Bromine End Group (PtBA-Br)

Poly(*tert*-butyl acrylate) (PtBA-Br) was prepared by ATRP of *t*BA in acetone, using EBiB as initiator and CuBr/PMDETA as catalyst. EBiB (0.29 mL, 2.0 mmol), CuBr (0.22 g, 1.5 mmol), PMDETA (0.32 mL, 1.5 mmol), and *t*BA (18 mL, 126 mmol) were dissolved in acetone (18 mL). The reaction mixture was degassed by three freeze-pump-thaw cycles and left under nitrogen. The ampoule was immersed in oil bath at 60 °C for 4.5 h, then taken from the oil bath and dipped in liquid nitrogen to stop the polymerization. The products were diluted with THF, passed through a neutral alumina column to remove the copper complex, and precipitated in cold mixture solution of methanol and H<sub>2</sub>O (1/1 v/v). The precipitate was collected and dried at 40 °C in vacuum oven for 4 h. Characterization: [M]<sub>0</sub>/[I]<sub>0</sub> = 63; conversion = 24%;  $M_{n,NMR}$  = 2000 g/mol (Fig. 1);  $M_{n,GPC}$  = 3000 g/mol (relative to linear PS standard); PDI = 1.16 (Fig. 2).

<sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 4.13–4.07 (CH<sub>3</sub>CH<sub>2</sub>O of initiator EBiB and CH<sub>2</sub>CH–Br, end group of PtBA), 2.56–2.06 (CH<sub>2</sub>CH, repeating unit of PtBA), 2.05–1.30 (CH<sub>2</sub>CH and –(CO)–OC(CH<sub>3</sub>)<sub>3</sub>, repeating units of PtBA), 1.27–1.20 (CH<sub>3</sub>CH<sub>2</sub>O of initiator EBiB), 1.16–1.07 [–(CO)–C(CH<sub>3</sub>)<sub>2</sub> of initiator EBiB].

### NRC Reaction Between PtBA-Br and PCL-TEMPO

In three series of dry ampoules (each one has five ampoules for five different temperature), PtBA-Br (0.16 g, 0.080 mmol,  $M_{n,NMR}$ : 2000, PDI: 1.16) and PCL-TEMPO (0.20 g, 0.067 mmol,  $M_{n,NMR}$ : 3000, PDI: 1.13) dissolved in DMF (10 mL) were added, then Cu<sup>0</sup>/PMDETA [Cu<sup>0</sup> (0.025g, 0.40 mmol) and PMDETA (0.083 mL, 0.40 mmol)] for the first series, CuBr/PMDETA [CuBr (0.060g, 0.40 mmol) and PMDETA (0.083 mL, 0.40 mmol)] for second series and CuBr/Cu<sup>0</sup>/PMDETA [CuBr (0.012g, 0.080 mmol), Cu<sup>0</sup> (0.025g, 0.40 mmol) and PMDETA (0.018 mL, 0.080 mmol)] for the third series, are added, respectively. The reaction mixture was degassed by three freeze-pump-thaw cycles and left under nitrogen. The ampoules were immersed in oil bath at 90 °C, 75 °C, 60 °C, 45 °C, and 25 °C for 24 h, respectively, then taken out from the oil bath and dipped in liquid nitrogen to stop the reaction. The products were diluted with THF and



**FIGURE 2** Gel permeation chromatography (GPC) curves of the PtBA-*b*-PCL copolymer (using CuBr/Cu<sup>0</sup>/PMDETA as catalyst system at 25 °C) and corresponding precursors PtBA-Br and PCL-TEMPO1.

solution was passed through alumina column to remove copper salt, precipitated into cold methanol twice and dried in vacuum oven at 40 °C for 4 h. The PtBA-*block*-PCL (PtBA-*b*-PCL) diblock copolymer was obtained.

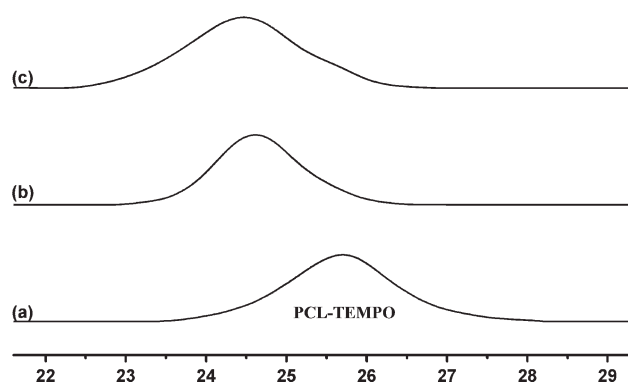
<sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 4.18–3.94 [–(CO)–CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O, the fifth methylene group connected to carbonyl, repeating unit of PCL], 3.70–3.62 [–(CO)–CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH, end group of PCL], 2.54–2.09 [CH<sub>2</sub>CH, repeating unit of PtBA and –(CO)–CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O, the first methylene group connected to carbonyl, repeating unit of PCL] (Fig. 1).

#### Contrast Experiments Between PtBA-Br and PCL-TEMPO in MeCN

In two series of dry ampoules, PtBA-Br (0.16 g, 0.080 mmol,  $M_{n,NMR}$ : 2000, PDI: 1.16) and PCL-TEMPO (0.20 g, 0.067 mmol,  $M_{n,NMR}$ : 3000, PDI: 1.13) dissolved in MeCN (20 mL) were added, then Cu<sup>0</sup>/PMDETA [Cu<sup>0</sup> (0.025g, 0.40 mmol) and PMDETA (0.083 mL, 0.40 mmol)] for the first series, CuBr/PMDETA [CuBr (0.060g, 0.40 mmol) and PMDETA (0.083 mL, 0.40 mmol)] for second series were added, respectively. The reaction mixture was degassed by three freeze-pump-thaw cycles and left under nitrogen. The ampoules were immersed in oil bath at 25 °C for 24 h, respectively, then taken out from the oil bath and dipped in liquid nitrogen to stop the reaction. The products were diluted with THF and solution was passed through alumina column to remove copper salt, precipitated into cold methanol twice, and dried in vacuum oven at 40 °C for 4 h (Fig. 3).

#### Synthesis of PS with Bromine End Group (PS-Br)

Bromine connected with polystyrene (PS-Br) was prepared by ATRP of St using EBiB as initiator and CuBr/PMDETA as catalyst. EBiB (0.15 mL, 1 mmol), CuBr (0.14 g, 1 mmol), PMDETA (0.21 mL, 1 mmol), St (20 mL, 175 mmol), and toluene (20 mL) were added to a dry ampoule. The reaction mixture was degassed by three freeze-pump-thaw cycles and



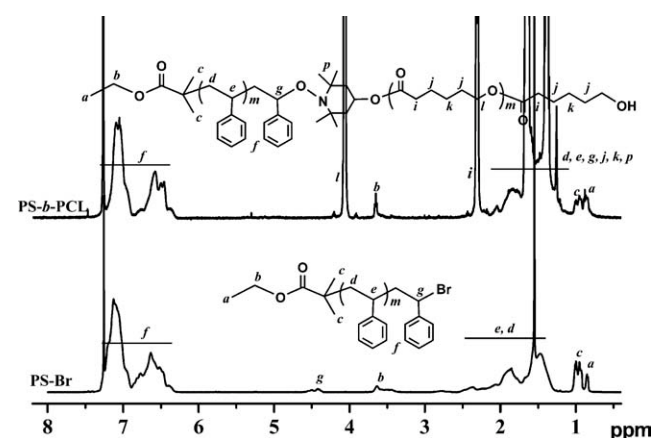
**FIGURE 3** Gel permeation chromatography (GPC) curves of (a) precursor PCL-TEMPO and (b) PtBA-*block*-PCL (PtBA-*b*-PCL) obtained in the system of Cu<sup>0</sup>/PMDETA in MeCN at 25 °C, and (c) PtBA-*block*-PCL (PtBA-*b*-PCL) obtained in the system of CuBr/PMDETA in MeCN at 25 °C.

purged with nitrogen. The ampoule was immersed in oil bath at 90 °C for 4 h, then taken from the oil bath and dipped in liquid nitrogen to stop the polymerization. The products were diluted with THF, passed through a neutral alumina column to remove the copper salt, and precipitated in cold methanol, and then dried at 40 °C in vacuum oven for 4 h. Characterization:  $[M]_0/[I]_0 = 175$ ; conversion = 28%;  $M_{n,NMR} = 5100$  (Fig. 4);  $M_{n,GPC} = 5000$  (relative to linear PS standard); PDI = 1.08 (Fig. 5).

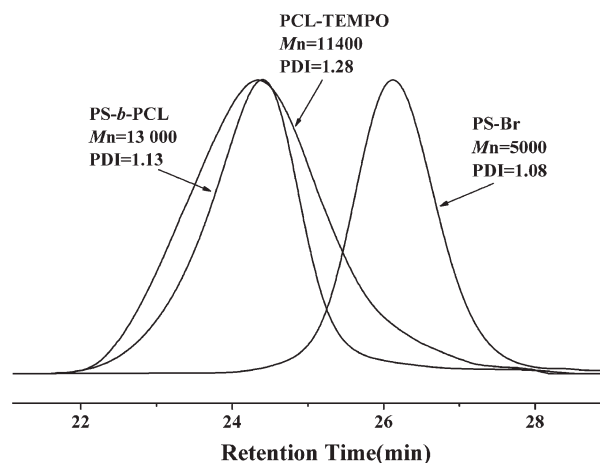
<sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 7.23–6.30 (phenyl protons of PS), 4.50–4.42 (CH(Ph)-Br, end group of PS), 3.63–3.42 (CH<sub>3</sub>CH<sub>2</sub>O of initiator EBiB), 2.24–1.20 (CH<sub>2</sub>CH(Ph), repeating unit of PS), 0.99–0.80 (CH<sub>3</sub>CH<sub>2</sub>O and C(CH<sub>3</sub>)<sub>2</sub> of initiator EBiB).

#### NRC Reaction Between PS-Br and PCL-TEMPO

In a series of dry ampoules (each one has five ampoules for five different temperature), PS-Br (0.25 g, 0.050 mmol,  $M_{n,NMR}$ : 5100, PDI: 1.08) and PCL-TEMPO (0.25 g, 0.042 mmol,  $M_{n,NMR}$ : 6000, PDI: 1.28) were dissolved in DMF (10 mL). CuBr (0.0070 g, 0.050 mmol), Cu (0.016g, 0.25 mmol), and



**FIGURE 4** <sup>1</sup>H NMR spectra of PS-*block*-PCL (PS-*b*-PCL) (using CuBr/Cu<sup>0</sup>/PMDETA as catalyst system at 25 °C) and the corresponding precursor PS-Br in CDCl<sub>3</sub>.



**FIGURE 5** Gel permeation chromatography (GPC) curves of PS-*block*-PCL (PS-*b*-PCL) copolymer (using the catalyst system of CuBr/Cu<sup>0</sup>/PMDETA at 25 °C) and the corresponding precursor.

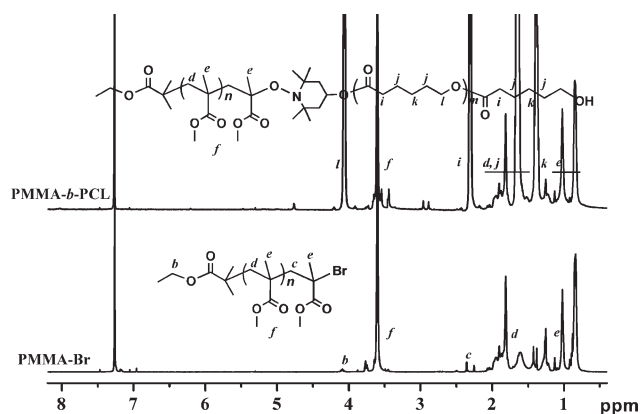
PMDETA (0.010 mL, 0.050 mmol) were added, and the reaction mixture was degassed by three freeze-pump-thaw cycles and left under nitrogen. The ampoules were immersed in oil bath at 90 °C, 75 °C, 60 °C, 45 °C, and 25 °C for 24 h, respectively. Then taken from the oil bath and dipped in liquid nitrogen to stop the reaction. The products were diluted with THF and solution was passed through alumina column to remove copper salt, precipitated into cold cyclohexane twice and dried in vacuum oven at 40 °C for 4 h. The PS-*b*-PCL diblock copolymer was obtained.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 7.23–6.30 (phenyl protons of PS), 4.16–3.97 [–(CO)–CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O, the fifth methylene group connected to carbonyl, repeating unit of PCL], 3.68–3.46 (CH<sub>3</sub>CH<sub>2</sub>O of initiator EBiB) (Fig. 4).

#### Synthesis of PMMA with Bromine End Group (PMMA-Br)

Bromine connected with poly(methyl methacrylate) (PMMA-Br) was prepared by ATRP of St using EBiB as initiator and CuCl/HMTETA as catalyst. EBiB (0.15 mL, 1 mmol), CuCl (0.05 g, 0.5 mmol), HMTETA (0.14 mL, 0.5 mmol), MMA (15 mL, 142 mmol), and ethanol (15 mL) were added to a dry ampoule. The reaction mixture was degassed by three freeze-pump-thaw cycles and purged with nitrogen. The ampoule was immersed in oil bath at 45 °C for 1 h, then taken from the oil bath and dipped in liquid nitrogen to stop the polymerization. The products were diluted with THF, passed through a neutral alumina column to remove the copper salt, precipitated in cold *n*-heptane, and dried at 25 °C in vacuum oven for 4 h. Characterization: [M]<sub>0</sub>/[I]<sub>0</sub> = 142; conversion = 25%; *M*<sub>n,NMR</sub> = 3500 (Fig. 6); *M*<sub>n,GPC</sub> = 5500 (relative to linear PS standard); PDI = 1.19 (Fig. 7).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 4.20–4.07 (CH<sub>3</sub>CH<sub>2</sub>O of initiator EBiB), 3.87–3.50 (–COOCH<sub>3</sub>, repeating unit of PMMA), 2.40–2.28 (CH<sub>2</sub>C(CH<sub>3</sub>)(C=O–OCH<sub>3</sub>)-Br, end group of PMMA), 2.10–1.50 (–CH<sub>2</sub>C–, repeating unit of PMMA), 1.48–1.35 (CH<sub>3</sub>CH<sub>2</sub>–, end group of PMMA), 1.34–1.19 (–CCH<sub>3</sub>, end group of PMMA), 1.15–0.75 (CH<sub>3</sub>–C–, repeating unit of PMMA).

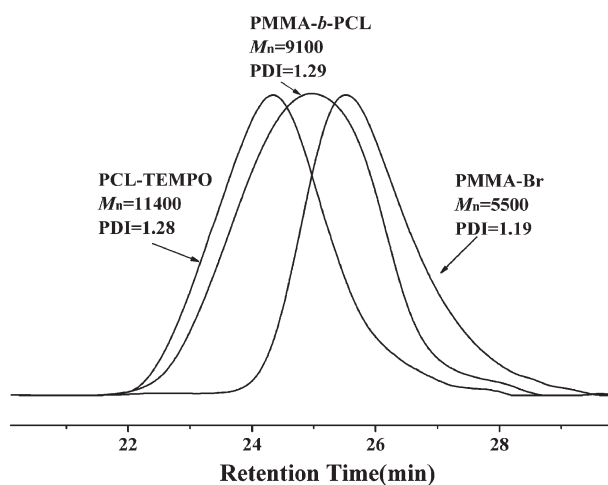


**FIGURE 6** <sup>1</sup>H NMR spectra of PMMA-*block*-PCL (PMMA-*b*-PCL) (using the catalyst system of CuBr/Cu<sup>0</sup>/PMDETA at 25 °C) and the corresponding precursor PMMA-Br.

#### NRC Reaction Between PMMA-Br and PCL-TEMPO

In a series of dry ampoules (each one has five ampoules for five different temperature), PMMA-Br (0.14 g, 0.040 mmol, *M*<sub>n,NMR</sub>: 3500, PDI: 1.18) and PCL-TEMPO (0.20 g, 0.033 mmol, *M*<sub>n,NMR</sub>: 6000, PDI: 1.28) were dissolved in DMF (10 mL). CuBr (0.0060g, 0.040 mmol), Cu (0.013g, 0.20 mmol), and PMDETA (0.010 mL, 0.040 mmol) were added, and the reaction mixture was degassed by three freeze-pump-thaw cycles and left under nitrogen. The ampoules were immersed in oil bath at 90 °C, 75 °C, 60 °C, 45 °C, and 25 °C for 24 h, respectively. Then taken from the oil bath and dipped in liquid nitrogen to stop the reaction. The products were diluted with THF and solution was passed through alumina column to remove copper salt, precipitated into cold methanol twice, and dried in vacuum oven at 40 °C for 4 h. The PMMA-*b*-PCL diblock copolymer was obtained.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 4.16–3.97 [–(CO)–CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O, the fifth methylene group connected to carbonyl, repeating



**FIGURE 7** Gel permeation chromatography (GPC) curves of PMMA-*block*-PCL (PMMA-*b*-PCL) copolymer (using the catalyst system of CuBr/Cu<sup>0</sup>/PMDETA at 25 °C) and the corresponding precursor.

unit of PCL], 3.70–3.55 ( $-\text{COOCH}_3$ , repeating unit of PMMA), 2.37–2.21 [ $-(\text{CO})-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$ , the first methylene group connected to carbonyl, repeating unit of PCL], 2.10–1.49 [ $-\text{CH}_2\text{C}-$  and  $-(\text{CO})-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$ , repeating unit of PMMA and the second together with fourth methylene group connected to carbonyl, repeating unit of PCL, respectively], 1.48–1.35 [ $-(\text{CO})-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$ , the third methylene group connected to carbonyl, repeating unit of PCL], 1.18–0.75 ( $-\text{CH}_3$ , repeating unit of PMMA) (Fig. 6).

#### NRC Reaction Between PMMA-Br and HTEMPO

PMMA-Br (0.14 g, 0.040 mmol,  $M_{n,\text{NMR}}$ : 3500, PDI: 1.18) and HTEMPO (0.007 g, 0.040 mmol) were dissolved in DMF (10 mL) in a dry ampoule. CuBr (0.0060g, 0.040 mmol), Cu (0.013 g, 0.20 mmol), and PMDETA (0.010 mL, 0.040 mmol) were added, and the reaction mixture was degassed by three freeze-pump-thaw cycles and left under nitrogen. The ampoule was immersed in oil bath at 45 °C for 24 h, respectively. Then taken from the oil bath and dipped in liquid nitrogen to stop the reaction. The products were diluted with THF and solution was passed through alumina column to remove copper salt, precipitated into methanol and  $\text{H}_2\text{O}$  (1/1 v/v) twice and dried in vacuum oven at 40 °C for 4 h.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 6.20 and 5.50 [ $\text{C}=\text{CH}_2$ , end group of PMMA], 4.28–4.18 ( $\text{CH}-\text{OH}$  of TEMPO group), 4.13–4.07 ( $\text{CH}_3\text{CH}_2\text{O}$  of initiator EBiB), 3.87–3.50 ( $-\text{COOCH}_3$ , repeating unit of PMMA), 2.54–2.45 ( $\text{PMMA}-\text{CH}_2-$ , end group of PMMA), 2.10–1.50 ( $-\text{CH}_2\text{C}-$ , repeating unit of PMMA), 1.48–1.35 ( $\text{CH}_3\text{CH}_2-$ , end group of PMMA), 1.34–1.19 ( $-\text{CCH}_3$ , end group of PMMA), 1.15–0.75 ( $\text{CH}_3-\text{C}-$ , repeating unit of PMMA) (Fig. 8).

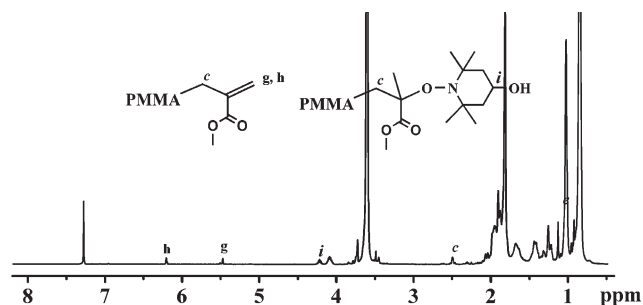
#### Measurements

Gel permeation chromatography (GPC) was performed on an Agilent 100 with a G1310A pump, a G1362A refractive-index detector, and a G1314A variable-wavelength detector with tetrahydrofuran (THF) as the eluent at a flow rate of 1.0 mL/min at 35 °C. One 5  $\mu\text{m}$  LP gel column (500 E, molecular range 500 to  $2 \times 10^4$  g/mol) and two 5  $\mu\text{m}$  LP gel mixed bed column (molecular range 200 to  $3 \times 10^6$  g/mol) were used. Polystyrene standards were used for calibration.  $^1\text{H}$  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. All of the samples were scanned for 128 times, and the sensitivity of the instrument was: 0.1% ethylbenzene; NS = 1, LB = 1; S/N = 300:1.

## RESULTS AND DISCUSSION

#### Synthesis of Precursors with Functional Groups

The precursors of bromine-containing polymers, as PtBA-Br, PS-Br, and PMMA-Br were prepared by ATRP with predetermined  $M_n$  and low PDI. The reactions were terminated at low conversion (<30%) to ensure a high degree of bromines at end chains.<sup>33,34</sup> By means of the NMR spectra, the end groups of bromine in PtBA-Br, PS-Br, and PMMA-Br were supported



**FIGURE 8**  $^1\text{H}$  NMR spectrum of the crude sample of NRC reaction between PMMA-Br and HTEMPO [at 45 °C in the catalyst system of CuBr/Cu<sup>0</sup>/PMDETA and precipitated in methanol and  $\text{H}_2\text{O}$  (1/1 v/v)] in  $\text{CDCl}_3$ .

by the appearance of signals at 4.13–4.07 ( $\text{CH}_2\text{CH}-\text{Br}$ , end group of PtBA, Fig. 1), 4.50–4.42 ( $\text{CH}(\text{Ph})-\text{Br}$ , end group of PS, Fig. 4) and 2.40–2.28 ( $\text{CH}_2\text{C}(\text{CH}_3)$  ( $\text{C}=\text{O}-\text{OCH}_3$ )-Br, end group of PMMA, Fig. 6), respectively.  $^1\text{H}$  NMR spectra of the initiator group in polymers displayed characteristic signals of 4.13–4.07 ( $\text{CH}_3\text{CH}_2\text{O}$  of initiator EBiB in PtBA-Br, Fig. 1), 3.63–3.42 ( $\text{CH}_3\text{CH}_2\text{O}-$  of initiator EBiB in PS-Br, Fig. 4) and 4.20–4.07 ( $\text{CH}_3\text{CH}_2\text{O}-$  of initiator EBiB in PMMA-Br, Fig. 6), respectively. The  $M_{n,\text{NMR}}$  of PtBA-Br was determined by comparing the integrals of  $-\text{CH}_2\text{CH}-$  of PtBA at 2.56–2.06 ppm with that of  $\text{CH}_3\text{CH}_2\text{O}-$  and  $-\text{CH}_2\text{CH}-\text{Br}$  (end group of PtBA) at 4.13–4.07 ppm (Fig. 1), using the following equation:

$$M_{n,\text{NMR}} = \frac{3A_{2.56-2.06}}{A_{4.13-4.07}} \times 128 + 195 \quad (1)$$

here  $A_{2.56-2.06}$  represented the integral area of the  $-\text{CH}_2\text{CH}-$  proton on PtBA repeating unit;  $A_{4.13-4.07}$  represented the integral areas of the  $\text{CH}_3\text{CH}_2\text{O}-$  and  $\text{CH}_2\text{CH}-\text{Br}$  protons on PtBA end group; the value 128 and 195 were the molecular weight of PtBA repeating unit and the initiator EBiB, respectively. Because the superposition of the  $\text{CH}_3\text{CH}_2\text{O}$  and  $\text{CH}_2\text{CH}-\text{Br}$ , it is hard to calculate the bromine end functionality in PtBA-Br. To resolve this problem, azide terminated PtBA (PtBA- $\text{N}_3$ ) was obtained by the reaction of PtBA-Br with  $\text{NaN}_3$  according to the literature.<sup>21</sup> In the  $^1\text{H}$  NMR spectrum of the PtBA- $\text{N}_3$ ,  $\text{CH}_2\text{CH}-$  was shifted from 4.13–4.07 to 3.81–3.61, and  $\text{CH}_3\text{CH}_2\text{O}$  remained at 4.13–4.07. Thus, the bromine end functionality could be expressed approximately by the  $\text{N}_3$  end functionality as 95%, which was determined by comparing the integrals of  $\text{CH}_2\text{CH}-\text{N}_3$  at 3.81–3.61 ppm with that of  $\text{CH}_3\text{CH}_2\text{O}$  at 4.13–4.07 ppm, using the following equation:

$$\text{Functionality} = \frac{2A_{3.81-3.61}}{A_{4.13-4.07}} \times 100\% \quad (2)$$

here  $A_{3.81-3.61}$  represented the integral area of the  $\text{CH}_2\text{CH}-\text{N}_3$  proton on PtBA end group.

The  $M_{n,\text{NMR}}$  of PS-Br was determined by comparing the integrals of phenyl protons of PS at 7.23–6.30 ppm with that of  $\text{CH}_3\text{CH}_2\text{O}$  (end group of PS) at 3.63–3.42 ppm (Fig. 4), using the following equation:

**TABLE 1** Characterization of the Synthetic Precursors

Precursors	$M_{n, \text{GPC}}^a$ (g/mol)	$M_{n, \text{NMR}}^b$ (g/mol)	PDI <sup>a</sup>	Functionality <sup>c</sup>
PtBA-Br	3,000	2,000	1.16	95%
PS-Br	5,000	5,100	1.08	97%
PMMA-Br	5,500	3,500	1.19	97%
PCL-TEMPO 1	6,300	3,000	1.13	–
PCL-TEMPO 2	11,400	6,000	1.28	–

<sup>a</sup> Measured by GPC in THF, calibration with linear PS as standard.

<sup>b</sup>  $M_{n, \text{NMR}}$  measured by <sup>1</sup>H NMR spectra.

<sup>c</sup> The bromine end functionality, measured by <sup>1</sup>H NMR spectra.

$$M_{n, \text{NMR}} = \frac{2A_{7.23-6.30}}{5A_{3.63-3.42}} \times 104 + 195 \quad (3)$$

here  $A_{7.23-6.30}$  represented the integral area of the phenyl protons on PS repeating unit;  $A_{3.63-3.42}$  represented the integral area of the  $\text{CH}_3\text{CH}_2\text{O}$  protons on PS end group; the value 104 was the molecular weight of PS repeating unit. The bromine end functionality was 97%, which was determined by comparing the integrals of  $\text{CH}(\text{Ph})\text{-Br}$  at 4.50–4.42 ppm with that of  $\text{CH}_3\text{CH}_2\text{O}$  at 3.63–3.42 ppm, using the following equation:

$$\text{Functionality} = \frac{2A_{4.50-4.42}}{A_{3.63-3.42}} \times 100\% \quad (4)$$

here  $A_{4.50-4.42}$  represented the integral area of the  $\text{CH}(\text{Ph})\text{-Br}$  proton on PS end group.

The  $M_{n, \text{NMR}}$  of PMMA-Br was determined by comparing the integrals of  $-\text{COOCH}_3$  of PMMA at 3.87–3.50 ppm with that of  $\text{CH}_3\text{CH}_2\text{O}$  (end group of PMMA) at 4.20–4.07 ppm (Fig. 6), using the following equation:

$$M_{n, \text{NMR}} = \frac{2A_{3.87-3.50}}{3A_{4.20-4.07}} \times 100 + 195 \quad (5)$$

here  $A_{3.87-3.50}$  represented the integral area of the  $-\text{COOCH}_3$  protons on PMMA repeating unit;  $A_{4.20-4.07}$  represented the integral area of the  $\text{CH}_3\text{CH}_2\text{O}$  protons on PMMA end group; the value 100 was the molecular weight of PMMA repeating unit. The bromine end functionality of PMMA-Br was 97%, which was determined by comparing the integrals of  $\text{CH}_2\text{C}(\text{CH}_3)(\text{C}=\text{O}-\text{OCH}_3)\text{-Br}$  at 2.40–2.28 ppm with that of  $\text{CH}_3\text{CH}_2\text{O}$  at 4.20–4.07 ppm, using the following equation:

$$\text{Functionality} = \frac{A_{2.40-2.28}}{A_{4.20-4.07}} \times 100\% \quad (6)$$

here  $A_{2.40-2.28}$  represented the integral area of the  $\text{CH}_2\text{C}(\text{CH}_3)(\text{C}=\text{O}-\text{OCH}_3)\text{-Br}$  protons on PMMA end group.

All of the data for PtBA-Br, PS-Br, and PMMA-Br are listed in Table 1

The TEMPO-containing polymers PCL-TEMPO were prepared by ROP of  $\epsilon\text{-CL}$  in toluene using  $\text{Sn}(\text{Oct})_2$  as catalyst and HTEMPO as initiator at 100 °C. TEMPO end group displays

characteristic signal of  $\text{CH}_3$  (methyl protons of TEMPO) at 1.28–1.17 ppm in <sup>1</sup>H NMR spectrum (Fig. 1). The  $M_{n, \text{NMR}}$  of the two kinds of PCL-TEMPO (PCL-TEMPO 1 and PCL-TEMPO 2) were 3000 and 6000 g/mol respectively, which were determined by the ratio of the integrated signals at 2.35–2.24 [-(CO)- $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$ , the first methylene group connected to carbonyl, repeating unit of PCL] to 1.28–1.17 ppm ( $\text{CH}_3$ , methyl protons of TEMPO), using the following equation.

$$M_{n, \text{NMR}} = \frac{12A_{2.35-2.24}}{2A_{1.28-1.17}} \times 114 + 172 \quad (7)$$

here  $A_{2.35-2.24}$  represented the integral area of the -(CO)- $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$  protons on PCL repeating unit;  $A_{1.28-1.17}$  represented the integral area of the  $\text{CH}_3$  protons on PCL end group, the value 114 and 172 were the molecular weight of the PCL repeating unit and the initiator HTEMPO, respectively. The  $M_n$  obtained by GPC is not correct because of structure difference of PCL with PS standard. The calibrated value  $M_{n, \text{cal}}$  could be derived by a formula:<sup>35,36</sup>  $M_{n, \text{cal}} = 0.259 \times M_{n, \text{GPC}}^{1.073}$ , the values are 3100 and 6300 g/mol, respectively, which is almost consistent with the  $M_{n, \text{NMR}}$  of PCL-TEMPO.

#### NRC Reaction Between PtBA-Br and PCL-TEMPO

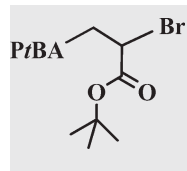
To explore the effect of reaction conditions on NRC, a series of experiments are accomplished by the coupling reaction between containing-bromine end group polymers and TEMPO-PCL using three different catalyst systems in the temperature range from 90 °C to 25 °C. In the NRC reaction between PtBA-Br and PCL-TEMPO, after removed the copper salt, the crude product was purified by dissolution/precipitation with THF/methanol twice, because the excessive PtBA-Br could be dissolved in methanol, but PtBA-*b*-PCL can not. <sup>1</sup>H NMR spectrum of PtBA-*b*-PCL showed the characteristic peaks of  $\text{CH}_2\text{CH}$  (repeating unit of PtBA) at 2.54–2.09 and -(CO)- $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$  (repeating unit of PCL) at 4.18–3.94 ppm, respectively (Fig. 1). The GPC curves of the PtBA-*b*-PCL copolymer and corresponding precursors showed singlet and low PDI (Fig. 2). These results indicated that the NRC reaction was successful.

The coupling efficiency of the NRC reaction could be calculated by the integration for  $\text{CH}_2\text{CH}$  of PtBA against the -(CO)- $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$  of PCL (Fig. 1), using the following equation:

$$\text{E.F.} = \frac{(A_{2.54-2.09} - A_{4.18-3.94}) \times \frac{M_n(\text{PCL-TEMPO})}{114}}{\frac{A_{4.18-3.94}}{2} \times \frac{M_n(\text{PtBA-Br})}{128}} \quad (8)$$

here  $A_{2.54-2.09}$  represented the integral areas of  $\text{CH}_2\text{CH}$  group proton on PtBA segment and -(CO)- $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$  group protons on PCL segment;  $A_{4.18-3.94}$  represented the integral area of -(CO)- $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$  group protons on PCL segment; the value 114 and 128 were the molecular weights of repeating unit of PtBA and PCL segment, respectively. The coupling efficiency of the PtBA-*b*-PCL copolymer obtained in different conditions was listed in Table 2.

**TABLE 2** The Coupling Efficiency of NRC Reaction Between PtBA-Br and PCL-TEMPO in Different Catalyst System

$P_n-X^a$	$T^b$ (°C)	E.F. (Cu <sup>0</sup> ) <sup>c</sup>	E.F. (CuBr) <sup>d</sup>	E.F. (CuBr/Cu <sup>0</sup> ) <sup>e</sup>
	90	–	–	76%
	75	69%	81%	90%
	60	82%	82%	85%
	45	88%	89%	92%
	25	90%	90%	93%

<sup>a</sup> Bromine-containing polymer.<sup>b</sup> Reaction temperature.<sup>c</sup> The efficiency in the system of Cu<sup>0</sup>/PMDETA (mol ratio of [P<sub>n</sub>-X]:[PCL-TEMPO]:[Cu<sup>0</sup>]:[PMDETA] = 1.2:1:6:6).<sup>d</sup> The efficiency in the system of CuBr/PMDETA (mol ratio of [P<sub>n</sub>-X]:[PCL-TEMPO]:[CuBr]:[PMDETA] = 1.2:1:6:6).<sup>e</sup> The efficiency in the system of CuBr/Cu<sup>0</sup>/PMDETA (mol ratio of [P<sub>n</sub>-X]:[PCL-TEMPO]:[CuBr]:[Cu<sup>0</sup>]:[PMDETA] = 1.2:1:1.2:6:1.2).

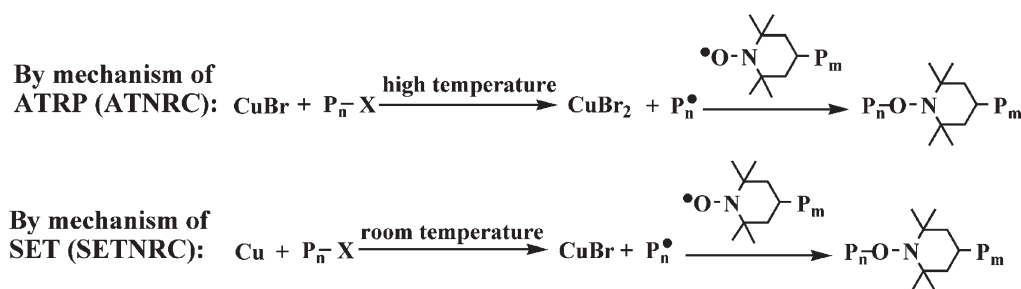
As we mentioned before, NRC reaction could be carried out by mechanism of ATRP and SET as Scheme 1 showed. In the process of SET, the bond of polymer dormant species (P<sub>n</sub>-X) is cleaved by the formation of radical anion intermediates via an outer-sphere single-electron-transfer process using Cu<sup>0</sup>/PMDETA as catalyst,<sup>37</sup> in this case, the dissociation energy of P<sub>n</sub>-X bond is very low and did not show obvious dependence on the structure of the halogen connected group; while in ATRP, the radical is generated by the dissociation of P<sub>n</sub>-X bond through the homolytic atom (X) transfer from P<sub>n</sub>-X to the copper catalyst via an inner-sphere atom sphere process using CuBr/PMDETA as catalyst, which requires high energy.<sup>37</sup> In the catalyst system of Cu<sup>0</sup>/PMDETA, the coupling reaction was carried out by the mechanism of SET, the coupling efficiency at low temperature was higher than that at high temperature, and the highest efficiency was obtained at room temperature. This may attribute to that in the room temperature the energy was enough for the formation of macroradicals by the mechanism of SET.<sup>25</sup> With the temperature arising, the greatly excessive energy may result to a higher radical concentration which may lead to the side reaction.<sup>31,33</sup> In the system of CuBr/PMDETA, the coupling reaction showed that the efficiency was more than 80% in the temperature range from 75 °C to 25 °C. In this case, the system may be a mixed system due to the disproportionation of a part of the CuBr in DMF,<sup>27,38</sup> so both of CuBr and Cu<sup>0</sup> may coexist. It was hard to determine which

mechanism took place in the system, ATRP or SET. To resolve this problem, the contrast experiments were carried out at 25 °C, using MeCN as solvent to prevent CuBr disproportionating to Cu<sup>0</sup>. The GPC curves (Fig. 3) showed that in the system of CuBr/PMDETA using MeCN as solvent, the coupling was also successful as that in the system of Cu<sup>0</sup>/PMDETA. The coupling efficiency obtained by <sup>1</sup>H NMR spectrum was about 88%, almost the same as that in the system of Cu<sup>0</sup>/PMDETA (90%), which indicated that both of Cu<sup>0</sup> and CuBr are sufficiently reactive to mediate the coupling reaction by the mechanism of ATRP and SET at room temperature for PtBA-Br.

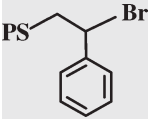
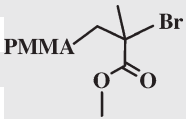
It is interesting that high efficiency (≥85%) within 75–25 °C was found in this system of CuBr/Cu<sup>0</sup>/PMDETA. Cu<sup>0</sup> in the system of CuBr/Cu<sup>0</sup>/PMDETA was acted not only as catalyst for the formation of macroradicals, but also as reducing agent to reduce the CuBr<sub>2</sub> to CuBr.<sup>20,39</sup> Therefore, Cu<sup>0</sup> was consumed severely in the reaction. To make sure that the Cu<sup>0</sup> were sufficient for the whole reaction, excessive Cu<sup>0</sup> with respect to CuBr was used. In the initial stage of this research, the different ratio of CuBr to Cu<sup>0</sup> at 1:0, 1:5, and 1:10 were used for comparison of the coupling efficiency. The result indicated that the efficiency of 1:5 was better than 1:0, but no clear difference could be found for 1:5 and 1:10, so the ratio of CuBr to Cu<sup>0</sup> at 1:5 was used in our following experiments and high efficiency was obtained in the wide range of the temperature range. When the temperature continuously increased to 90 °C, the coupling efficiency decreased to 76% due to the cleavage of alkoxyamine bond at high temperature.<sup>39</sup> Based on above experiments, it was found that in NRC, CuBr/Cu<sup>0</sup>/PMDETA is the optimal catalyst system.

#### NRC Reaction Between PS-Br/PMMA-Br and PCL-TEMPO

As we reported previously, in the NRC, the PS-Br showed the higher coupling efficiency than PtBA-Br,<sup>18</sup> the structure of bromine connected groups at the end of polymer chains would affect the coupling efficiency of NRC. To confirm it, the NRC reaction of PS-Br and PMMA-Br with PCL-TEMPO was conducted, respectively, using CuBr/Cu<sup>0</sup>/PMDETA as catalyst system. In the NRC reaction of PS-Br with PCL-TEMPO, after removed the copper salt, the crude product was purified by dissolution/precipitation with THF/cyclohexane twice, to remove the excessive PS-Br. The GPC curve of the polymer (Fig. 5) after purification showed singlet and low PDI. There was no peak existed in the position belong to the unreacted PS-Br, which indicated that the unreacted

**SCHEME 1** The mechanism of NRC reaction.

**TABLE 3** The Coupling Efficiency of NRC Reaction with Different Bromine Connected Groups

$P_n\text{-X}^a$	$T$ ( $^{\circ}\text{C}$ ) <sup>b</sup>	E.F. (CuBr/Cu <sup>0</sup> ) <sup>c</sup>	$P_n\text{-X}$	$T$ ( $^{\circ}\text{C}$ )	E.F. (CuBr/Cu <sup>0</sup> ) <sup>d</sup>
	90	94%		90	12%
	75	91%		75	19%
	60	93%		60	20%
	45	93%		45	29%
	25	93%		25	91%

<sup>a</sup> Bromine-containing polymer.

<sup>b</sup> Reaction temperature.

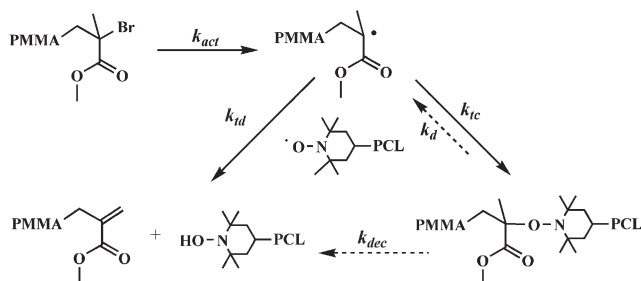
<sup>c</sup> The efficiency of ATNRC reaction between PS-Br and PCL-TEMPO in the system of CuBr/Cu<sup>0</sup>/PMDETA (mol ratio: [P<sub>n</sub>-X]: [PCL-TEMPO]: [CuBr]:[Cu<sup>0</sup>]:[PMDETA] = 1.2:1:1.2:6:1.2).

<sup>d</sup> The efficiency of ATNRC reaction between PMMA-Br and PCL-TEMPO in the system of CuBr/Cu<sup>0</sup>/PMDETA (mol ratio: [P<sub>n</sub>-X]: [PCL-TEMPO]: [CuBr]:[Cu<sup>0</sup>]:[PMDETA] = 1.2:1:1.2:6:1.2).

precursor PS-Br was removed completely after purification. However, Figure 5 did not show an apparent shift of chromatogram to lower elution time, compared with that of the precursor PCL-TEMPO. This phenomenon was unexpectedly. To confirm whether the polymer after purification was the PS-*b*-PCL copolymer or unreacted precursor PCL-TEMPO, <sup>1</sup>H NMR spectrum was used. A broad peak of phenyl protons at 7.23–6.30 ppm for PS segment disappeared indicated that the coupling reaction was successful (Fig. 4). The purified polymer was really PS-*b*-PCL copolymer. In the NRC reaction of PMMA-Br and PCL-TEMPO, Figure 7 also showed an unexpected shift of chromatogram for the purified polymer comparing with the precursor PCL-TEMPO, an apparent shift to higher elution time was observed for the PMMA-*b*-PCL copolymer. However, in NMR of PMMA-*b*-PCL, a related to 3.70–3.55 represented the integral area of the peaks for –COOCH<sub>3</sub> protons on PMMA segment (Fig. 6) confirmed that the NRC reaction was carried out. The unexpected GPC curves for PS-*b*-PCL and PMMA-*b*-PCL may be caused by their different hydrodynamic volume from polystyrenes standards. The similar phenomenon was also observed in the literatures.<sup>31,40</sup>

The coupling efficiency was calculated by the integration of phenyl protons of PS or –COOCH<sub>3</sub> protons of PMMA against the –(CO)–CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O of PCL respectively, using the equations (9) and (10):

$$\text{E.F.} = \frac{\left(\frac{A_{7.23-6.30}}{5}\right) \times \frac{M_n(\text{PCL-TEMPO})}{114}}{\frac{A_{4.16-3.97}}{2} \times \frac{M_n(\text{PS-Br})}{104}} \quad (9)$$


**SCHEME 2** The side reaction in NRC reaction for PMMA-Br.

here  $A_{7.23-6.30}$  represented the integral area of the peaks for phenyl protons on PS segment (Fig. 4);  $A_{4.16-3.97}$  represented the integral area of the peaks for –(CO)–CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O group protons on PCL segment; the value 104 was the molecular weight of repeating unit of PS segment.

$$\text{E.F.} = \frac{\left(\frac{A_{3.70-3.55}}{3}\right) \times \frac{M_n(\text{PCL-TEMPO})}{114}}{\frac{A_{4.16-3.97}}{2} \times \frac{M_n(\text{PMMA-Br})}{100}} \quad (10)$$

here  $A_{3.70-3.55}$  represented the integral area of the peaks for –COOCH<sub>3</sub> protons on PMMA segment (Fig. 6);  $A_{4.16-3.97}$  represented the integral area of the peaks for –(CO)–CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O group protons on PCL segment; the value 100 was the molecular weight of repeating unit of PMMA segment.

High efficiency ( $\geq 90\%$ ) was observed for the NRC reaction between PS-Br and PCL-TEMPO in the temperature range from 90  $^{\circ}\text{C}$  to 25  $^{\circ}\text{C}$ , the temperature did not show the obvious influence on the coupling efficiency for PS-Br (Table 3).

However, in the NRC reaction between PMMA-Br and PCL-TEMPO, the efficiency was decreased with the increasing of temperature (Table 3). This phenomenon may attribute to the side reaction<sup>39</sup> for PMMA-Br in NRC reaction (Scheme 2). The  $\beta$ -Hydrogen of methyl in PMMA is reactive, which may be captured by nitroxide radicals, leading to the formation of a terminal double bond in PMMA chain due to the disproportionation of chain radicals. This explanation could be verified by the NRC reaction between PMMA-Br and HTEMPO at 45  $^{\circ}\text{C}$ . Figure 8 recorded the <sup>1</sup>H NMR spectrum of the reaction product, remarkable characteristic signals of C=CH<sub>2</sub> appeared at 6.20 and 5.50 ppm indicating the side reaction of PMMA-Br at higher temperature, which leads to low efficiency. Therefore, it was concluded that only at the low temperature as 25  $^{\circ}\text{C}$ , the high NRC efficiency (91%) for PMMA-Br could be obtained.

## CONCLUSIONS

In summary, NRC reaction is an effective approach for preparation of copolymers with complicated structure and the catalyst system of CuBr/Cu<sup>0</sup>/PMDETA is the optimal one. NRC



reaction could be carried out in wide temperature range from room temperature to high temperature. A variety of halogen-containing polymers as polystyrene, poly(acrylate esters) and poly(methacrylate) can be coupled with TEMPO-containing polymer by NRC with high efficiency.

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