

# Preparation of H-Shaped ABCAB Terpolymers by Atom Transfer Radical Coupling

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**ABSTRACT:** H-shaped ABCAB terpolymers composed of polystyrene (PS) (A), poly(ethylene oxide) (PEO) (B), and poly(*tert*-butyl acrylate) (PtBA) (C) were prepared by atom transfer radical coupling reaction using ABC star terpolymers as precursors, CuBr and *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) as catalysts, and nanosize copper as the reducing agent. The synthesis of 3-miktoarm star terpolymer PS-PEO-(PtBA-Br) involved following steps: (1) the preparation of PS with an active and an ethoxyethyl-protected hydroxyl group at the same end; (2) the preparation of diblock copolymer PS-*b*-PEO with ethoxyethyl-protected group at the junction point through the ring-opening polymerization (ROP) of EO; (3) after de-protection of ethoxyethyl group and further modification of hydroxyl group, *t*BA was polymerized by atom transfer radical polymerization using PS-*b*-PEO with 2-bromoisobutyryl functional group as macroinitiator. The H-shaped terpolymer could be successfully formed by atom transfer radical coupling reaction in the presence of small quantity of styrene, CuBr/PMDETA, and Cu at 90 °C. The copolymers were characterized by SEC, <sup>1</sup>H NMR, and FTIR in detail. The optimized coupling temperature is 90 °C. © 2008 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 47: 59–68, 2009

**Keywords:** atom transfer radical coupling (ATRC) reaction; atom transfer radical polymerization (ATRP); H-shaped polymers; ring-opening polymerization; star polymers

## INTRODUCTION

During the last few years, various polymers with different compositions and complex structures were synthesized and tailored for some special properties, such as the comb-shaped,<sup>1</sup> star-shaped,<sup>2</sup> hyperbranched,<sup>3</sup> cyclic,<sup>4</sup> dendritic,<sup>5</sup> and H-shaped copolymers.<sup>6</sup> Of these diverse architectures, H-shaped polymer showed different morphologies and very interesting rheological properties of entangled polymer melts and solutions<sup>7–9</sup>

because of its unique structure. Therefore, much attention has been paid recently to the synthesis and investigation of H-shaped copolymers.

Generally, H-shaped copolymers have been prepared by anionic polymerization technique.<sup>10–14</sup> More recently, the development of controlled radical polymerization such as atom transfer radical polymerization<sup>15–17</sup> (ATRP), reversible addition fragmentation chain transfer polymerization<sup>18</sup> (RAFT), and nitroxide-mediated free radical polymerization<sup>19,20</sup> (NMP) has provided new routes for the synthesis of nonlinear polymers including H-shaped copolymer because more monomers can undergo the free radical polymerization. Gnanou and coworkers<sup>21</sup> prepared successfully H-shaped copolymer where poly(ethylene oxide) (PEO) and

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polystyrene (PS) represented the main chain and side chain [(PS)<sub>2</sub>-PEO-(PS)<sub>2</sub>] respectively, by combining ATRP and anionic polymerization. Subsequently, Pan and coworkers<sup>6,22</sup> reported the synthesis of H-shaped copolymer (PS)<sub>2</sub>-poly(ethylene glycol) (PEG)-(PS)<sub>2</sub> by single ATRP route and [poly(L-lactide)]<sub>2</sub>-PS-[poly(L-lactide)]<sub>2</sub> [(PLLA)<sub>2</sub>-PS-(PLLA)<sub>2</sub>] using ATRP and ring-opening polymerization (ROP). Zhang and coworkers<sup>23</sup> designed and synthesized an asymmetric H-shaped copolymer (PS)<sub>2</sub>-PEO-(poly(methyl methacrylate))<sub>2</sub> (PMMA)<sub>2</sub> via the combination of ATRP and anionic polymerization. More recently, Pan and coworkers<sup>24</sup> prepared heteroarm H-shaped terpolymer (PS)(PLLA)-PEG-(PS)(PLLA) in which PEG acted as the main chain and PS and PLLA as the side chains by the combination of RAFT and ROP.

Meanwhile, the appearance of click chemistry<sup>25</sup> created a novel way to construct polymer architecture, and it was extensively used in polymer chemistry.<sup>26</sup> Tunca and coworkers used click reaction strategies to synthesize heteroarm H-shaped copolymers including (PS) (poly(*tert*-butyl acrylate)) (PtBA)-PEG-(PtBA)(PS) and (PS) (PtBA)-Poly(propylene oxide) (PPO)-(PtBA)(PS) via Diel-Alder cycloaddition reaction,<sup>27</sup> and (PS)(PMMA)-PtBA-(PS)(PMMA), (PS)(PMMA)-PEG-(PS) (PMMA),<sup>28</sup> and ABCDE type quintopolymer<sup>29</sup> containing PtBA as the main chain and PS, poly( $\epsilon$ -caprolactone) (PCL), PMMA, and PEG as side chains via the copper-catalyzed azide-alkyne cycloaddition reaction.

Recently, atom transfer radical coupling (ATRC) has been demonstrated to be a highly efficient coupling reaction to afford a polystyrene dimmer.<sup>30–32</sup> In ATRC process, the concentration of macroradicals generated *in situ* by atom transfer radical equilibrium is maximized in the absence of monomers, whereas in the presence of a reducing agent,<sup>33</sup> this results in polymer termination. Thus, utilizing a functional ATRP macroinitiator with the halogen end group to produce the copolymer by coupling reaction in the presence of reducing agent is an alternative method to obtain the telechelic polymer<sup>34–36</sup> and the complex polymer.

Herein, we reported the synthesis of heteroarm H-shaped ABCAB terpolymers consisting of PtBA as the main chain and PS and PEO as the side chains, the ATRC reaction of the miktoarm star precursors (ABC) with bromine end group was carried out in the presence of the reducing agent successfully. The influence of the temperature on the coupling reaction was discussed.

## EXPERIMENTAL

### Materials

Styrene (St) was washed with 10% NaOH aqueous solution followed by water three times successively, dried over CaH<sub>2</sub>, and distilled under reduced pressure. Ethylene oxide (EO) was dried over CaH<sub>2</sub> and then distilled and stored at –20 °C before use. 1,1-Diphenylmethane (99%), benzyl bromide, and *tert*-butyl acrylate (*t*BA) were dried over CaH<sub>2</sub>, and then distilled under reduced pressure and stored at –20 °C before use. Toluene was dried over CaH<sub>2</sub> and distilled just before use. 2-bromoisobutyryl bromide (98%, Aldrich) and *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA, Aldrich) were used as received. Tetrahydrofuran (THF, 99%) and pyridine (99.5%) were refluxed over sodium naphthalenide solution and sodium wire, respectively, and distilled. CuBr (98%, Acros) was purified by stirring overnight in acetic acid and filtered, then washed with ethanol and diethyl ether successively, and finally dried *in vacuo*. Nanosize copper powder (~100 nm, Aldrich, 99.9+%) was used as received for the coupling reaction. All other reagents were purchased from Sinopharm Chemical Reagent (SCR) and used as received, unless otherwise noted. Diphenylmethylpotassium (DPMK) solution was freshly prepared according to the literature,<sup>37</sup> and the concentration was 0.61 mol/L.

### Measurements

Size-exclusion chromatography (SEC) was performed in THF at 35 °C with an elution rate of 1.0 mL/min on an Agilent1100 with a G1310A pump, a G1362A refractive index detector and a G1314A variable wavelength detector. One 5  $\mu$ m LP gel column (500 Å, molecular range 500–2  $\times$  10<sup>4</sup> g/mol) and two 5  $\mu$ m LP gel mixed bed column (molecular range 200–3  $\times$  10<sup>6</sup> g/mol) were calibrated by polystyrene standard samples. <sup>1</sup>H NMR spectra were obtained at a DMX500 MHz spectrometer with tetramethylsilane (TMS) as the internal standard and CDCl<sub>3</sub> as the solvent. Fourier transform infrared (FTIR) spectra were recorded on a Magna-550 FTIR spectrometer by casting film on a NaCl tablet. The ultra filtration separator was purchased from Shanghai Institute of Nuclear Research, Chinese Academy of Science, and the cut-off molecular weight of used poly(ether sulfone) membrane was calibrated by global protein.

### Synthesis of Functionalized $\alpha$ -Butyl- $\omega$ -hydroxyl, $\omega'$ -Ethoxyethyl-poly(styrene) (1)

The anionic polymerization of styrene was carried out under nitrogen atmosphere according to a reported procedure,<sup>38</sup> and the resulting functionalized polystyrene **1** was characterized as follows. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 0.80 (m, CH<sub>3</sub>CH<sub>2</sub>-), 1.13 (m, CH<sub>3</sub>CH<sub>2</sub>O-), 1.22 (m, -CH(CH<sub>3</sub>)-), 1.26–2.01 (m, 3H, aliphatic main chain -CH<sub>2</sub>CH- of PS), 3.09–3.43 (m, CH<sub>3</sub>CH<sub>2</sub>O-, -CH(OH)CH<sub>2</sub>O-), 3.52 (m, -CH(OH)-), 4.65–4.76 (m, -OCH(CH<sub>3</sub>)O-), 6.30–7.30 (m, 5H, aromatic -C<sub>6</sub>H<sub>5</sub> of PS chain).  $M_{n,SEC}$  = 3600 g/mol, PDI = 1.06;  $M_{n,NMR}$  = 3600 g/mol.

### Synthesis of Diblock Copolymer PS-*b*-PEO (2) with Ethoxyethyl-Protected Hydroxyl Group at the Junction Point

The diblock copolymer PS-*b*-PEO with ethoxyethyl-protected hydroxyl group at the junction point was prepared by the ring-opening polymerization of EO according to the literature<sup>38</sup> except using benzyl bromide to replace bromoethane for terminating the reaction. The characterization for PS-*b*-PEO **2** was shown as follows. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 0.80 (m, CH<sub>3</sub>CH<sub>2</sub>-), 1.13 (m, CH<sub>3</sub>CH<sub>2</sub>O-), 1.22 (m, -CH(CH<sub>3</sub>)-), 1.26–2.01 (m, 3H, aliphatic main chain -CH<sub>2</sub>CH- of PS), 3.05–3.43 (m, CH<sub>3</sub>CH<sub>2</sub>O-, -CH(O- )CH<sub>2</sub>O-), 3.50–3.70 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>O- of PEO block), 4.57 (s, C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>-O-), 4.65–4.76 (m, -OCH(CH<sub>3</sub>)O-), 6.30–7.30 (m, 5H, aromatic -C<sub>6</sub>H<sub>5</sub> of PS chain), 7.34 (s, C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>-O-).  $M_{n,SEC}$  = 8300 g/mol, PDI = 1.06;  $M_{n,NMR}$  = 8200 g/mol.

### Synthesis of Diblock Copolymer PS-*b*-PEO (3) with an Active Hydroxyl Group at the Junction Point

The diblock copolymer PS-*b*-PEO **2** (13.5 g, 1.65 mmol) was dissolved in a mixed solution of THF (50 mL) and formic acid (120 mL), stirred at 35 °C for 5 h, and then the formic acid and THF were evaporated off completely. After the residue was dissolved in THF (50 mL), the KOH (2 M) aqueous solution was added until the pH reached 12.0. Then, the mixture was refluxed for 24 h and neutralized with HCl aqueous solution. The product was obtained by removing the formed salts and precipitating in cold petroleum ether (60–90 °C), and then dried under vacuum at 40 °C until constant weight (12.9 g, yield: 95.6%). <sup>1</sup>H NMR (500

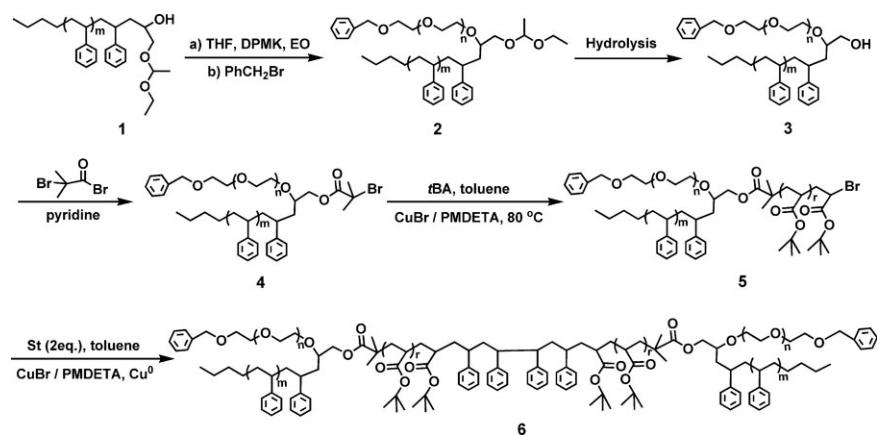
MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 0.80 (m, CH<sub>3</sub>CH<sub>2</sub>-), 1.26–2.01 (m, 3H, aliphatic main chain -CH<sub>2</sub>CH- of PS), 3.00–3.43 (m, -CH(CH<sub>2</sub>OH)O-), 3.50–3.70 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>O- of PEO block), 4.57 (s, C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>-O-), 6.30–7.30 (m, 5H, aromatic -C<sub>6</sub>H<sub>5</sub> of PS chain), 7.34 (s, C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>-O-).  $M_{n,NMR}$  = 8100 g/mol.

### Synthesis of Macroinitiator (PS-*b*-PEO)-Br (4)

The diblock copolymer PS-*b*-PEO **3** (5.6 g, 0.69 mmol) dried through azeotropic distillation with dry toluene was dissolved in anhydrous degassed pyridine (80 mL), then 2-bromoisobutyl bromide (2 mL, 16.2 mmol) was added dropwise at 0 °C for 30 min under vigorous stirring. The mixture was stirred for 3 h at 0 °C, followed by stirring at room temperature for 24 h. Pyridine was removed by azeotropic distillation with dry toluene. The residue was dissolved in ethanol and purified by an ultrafiltration membrane to remove low-molecular weight impurities. Then ethanol was removed from the product by distillation, the remains were dried *in vacuo* at 40 °C, and the yellow product was obtained (4.9 g, yield: 87.5%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 0.80 (m, CH<sub>3</sub>CH<sub>2</sub>-), 1.26–2.01 (m, 3H, aliphatic main chain -CH<sub>2</sub>CH- of PS), 1.94 (s, Br-C(CH<sub>3</sub>)<sub>2</sub>-COO-CH<sub>2</sub>-), 3.00–3.43 (m, -CH(CH<sub>2</sub>OOC)O-), 3.50–3.70 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>O- of PEO block), 4.32(d, Br-C(CH<sub>3</sub>)<sub>2</sub>-COO-CH<sub>2</sub>-), 4.57 (s, C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>-O-), 6.30–7.30 (m, 5H, aromatic -C<sub>6</sub>H<sub>5</sub> of PS chain), 7.34 (s, C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>-O-).  $M_{n,NMR}$  = 8300 g/mol.

### Synthesis of 3-Miktoarm Star Polymeric Precursor PS-PEO-(P*t*BA-Br) (5)

Macroinitiator (PS-*b*-PEO)-Br **4** (1.89 g, 0.23 mmol), CuBr (33.1 mg, 0.23 mmol), PMDETA (0.043 mL, 0.23 mmol), *t*BA (9 mL), and toluene (3 mL) were charged in an ampule and degassed by three freeze-pump-thaw cycles. Then the sealed ampule was immersed in an oil bath and stirred at 80 °C. After a certain time, the ampule was dipped into liquid nitrogen to stop the polymerization. The solution was diluted with THF and passed through the neutral alumina column to remove the copper salt, and then the polymer was recovered by precipitation in petroleum ether (60–90 °C) twice and dried under vacuum at 40 °C to constant weight. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 0.80–2.1 (m, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-, aliphatic main chain -CH<sub>2</sub>CH- of PS, -CH<sub>2</sub>CH- and



**Scheme 1.** Synthesis of H-shaped ABCAB terpolymers.

( $\text{CH}_3$ )<sub>3</sub>COOC— of PtBA), 2.12–2.4 (m,  $-\text{CH}_2\text{CH}-$  of PtBA), 3.00–3.43 (m,  $-\text{CH}(\text{CH}_2\text{OOC})\text{O}-$ ), 3.50–3.70 (m, 4H,  $-\text{CH}_2\text{CH}_2\text{O}-$  of PEO block), 4.18 (m,  $-\text{CH}_2\text{CH}-\text{Br}$ ), 4.57 (s,  $\text{C}_6\text{H}_5-\text{CH}_2-\text{O}-$ ), 6.30–7.30 (m, 5H, aromatic  $-\text{C}_6\text{H}_5$  of PS chain), 7.34 (s,  $\text{C}_6\text{H}_5-\text{CH}_2-\text{O}-$ ).  $M_{n,\text{SEC}} = 8500$  g/mol, PDI = 1.06; Conversion = 6.4%,  $M_{n,\text{NMR}} = 10,500$  g/mol.

#### Synthesis of H-Shaped ABCAB Terpolymer (6)

Star polymer PS-PEO-(PtBA-Br) **5** (0.6 g, 0.057 mmol) and CuBr (8.2 mg, 0.057 mmol) were placed in an ampule. Then the ampule was evacuated and backfilled with nitrogen, and toluene (2 mL) were added. When the polymer was completely dissolved, styrene (0.013 mL, 0.114 mmol), PMDETA (0.021 mL, 0.114 mmol), and nanosize copper powder (0.015 mg, 0.228 mmol) were introduced. After three freeze-pump-thaw cycles, the ampule was immersed in an 80 °C oil bath and stirred for 24 h. The ampule was cooled to the room temperature and diluted with THF, then passed through a column filled with neutral alumina. The product was purified by dissolution/precipitation in THF/petroleum ether (60–90 °C) twice and dried *in vacuo* at 40 °C to constant weight. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 0.80–2.1 (m,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$ , aliphatic main chain  $-\text{CH}_2\text{CH}-$  of PS,  $-\text{CH}_2\text{CH}-$  and ( $\text{CH}_3$ )<sub>3</sub>COOC— of PtBA), 2.12–2.4 (m,  $-\text{CH}_2\text{CH}-$  of PtBA), 3.00–3.43 (m,  $-\text{CH}(\text{CH}_2\text{OOC})\text{O}-$ ), 3.50–3.70 (m, 4H,  $-\text{CH}_2\text{CH}_2\text{O}-$  of PEO block), 4.57 (s,  $\text{C}_6\text{H}_5-\text{CH}_2-\text{O}-$ ), 6.30–7.30 (m, 5H, aromatic  $-\text{C}_6\text{H}_5$  of PS chain), 7.34 (s,  $\text{C}_6\text{H}_5-\text{CH}_2-\text{O}-$ ). In other experiments, only the reaction temperature

was varied to investigate the influence on the efficiency of the coupling reaction.

## RESULTS AND DISCUSSION

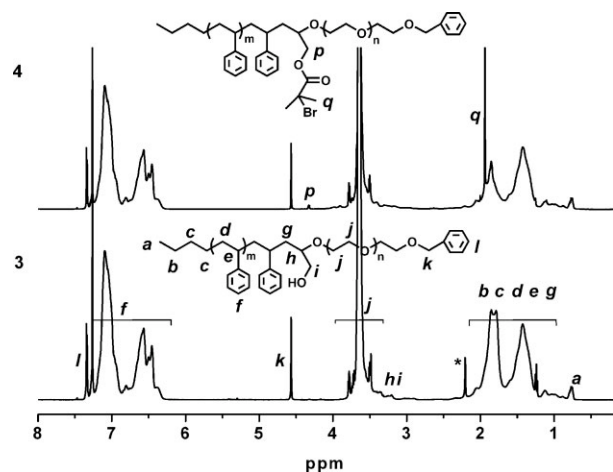
In the presentation, H-shaped ABCAB terpolymers composed of PS (A), PEO (B), and PtBA (C) were prepared according to the following strategy as Scheme 1 depicted.

#### Synthesis and Characterization of 3-Miktoarm Star Polymeric Precursor PS-PEO-(PtBA-Br)

In the previous work,<sup>39</sup> polystyrene with an active and a protected hydroxyl group at the same end was prepared by using EGE to cap poly(styryl) lithium. Here, the functionalized polystyrene **1** was used as macroinitiator for ring-opening polymerization of ethylene oxide in THF using DPMK as deprotonated agent and benzyl bromide as capping molecule, then the PS-*b*-PEO **2** with ethoxyethyl group at the junction point was obtained. Subsequently, the ethoxyethyl group was removed by acidolysis with formic acid and saponification with KOH solution, PS-*b*-PEO **3** with hydroxyl group at the junction point was produced.

Figure 1 (bottom) showed the <sup>1</sup>H NMR spectrum of diblock copolymer PS-*b*-PEO **3**.

Besides the resonance signal at 6.30–7.30 ppm attributed to aromatic protons of PS chain, the appearance of resonance signal at 3.50–3.70 ppm assigned to methylene protons of PEO chain confirmed the successful polymerization of EO, and the disappearance of signal at 4.65–4.76 ppm indicated that the ethoxyethyl group at the junction point was removed completely after hydrolysis. In



**Figure 1.**  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ ) of diblock copolymers PS-*b*-PEO **3** (bottom) and (PS-*b*-PEO)-Br **4** (top) (\* represents the impurity).

the process to prepare diblock copolymer PS-*b*-PEO **2**, benzyl bromide was used as capping molecule to terminate the living PEO species. When compared with the reported method<sup>40</sup> using bromoethane as capping molecule, it was more convenient to detect the blocking efficiency at PEO by using the chemical shift of benzyl group. From the  $^1\text{H}$  NMR spectrum of diblock copolymer PS-*b*-PEO **3** in Figure 1, the appearance of the signals at 4.57 ppm and 7.34 ppm due to the resonance of the methylene protons and aromatic protons of benzyl end group proved the successful nucleophilic substitution between PEO chain end and benzyl bromide, and the capping efficiency ( $E_{\text{capping}}$ ) was nearly 100% derived from the  $^1\text{H}$  NMR spectrum according to the following formula (1):

$$E_{\text{capping}} = \frac{A_k/2}{A_a/3} \times 100\% \quad (1)$$

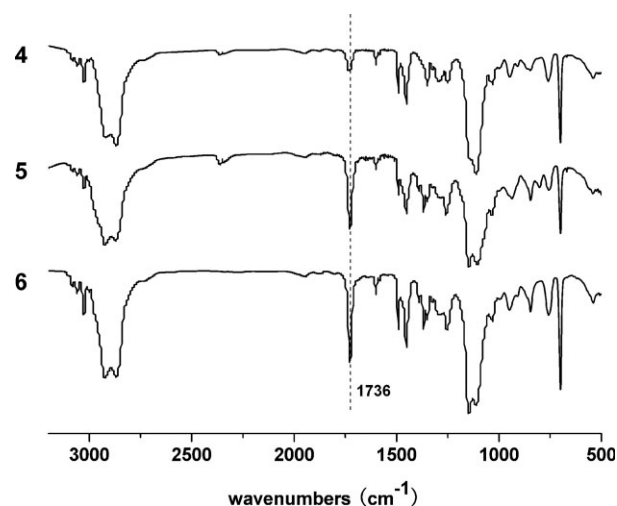
where  $A_k$  and  $A_a$  are the integral areas of methylene protons of benzyl group at 4.57 ppm and methyl protons of *n*-butyl end group at 0.8 ppm, respectively. As it is well known, the PS-*b*-PEO block copolymers might self-associate into the micellar structure in THF,<sup>21</sup> so the molecular weight of PS-*b*-PEO derived from SEC might be inaccurate. The reliable molecular weight of PS-*b*-PEO **3** was calculated by the formula (2) according to  $^1\text{H}$  NMR analysis.

$$M_{n,\text{NMR}}(\mathbf{3}) = \frac{5 \times A_j \times M_{n,\text{SEC}}(\mathbf{1})}{4 \times A_f \times 104} \times 44 + M_{n,\text{NMR}}(\mathbf{1}) + 90 - 72 \quad (2)$$

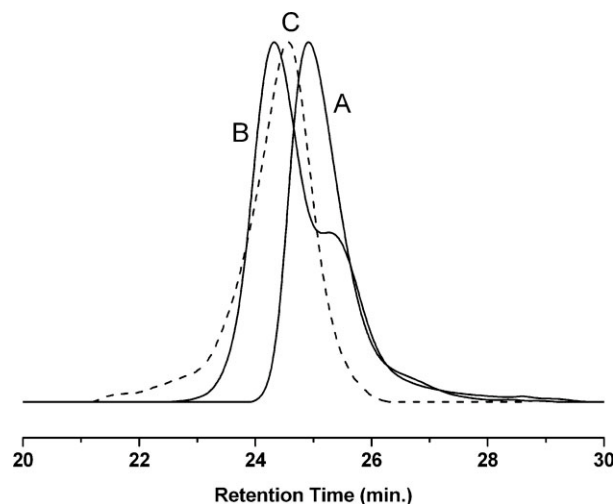
where  $A_j$  and  $A_f$  represent the integral area of methylene protons on PEO chain and aromatic protons on PS chain, respectively. Forty-four and 104 is the molecular weight of EO and St, and 90 is the difference between the mass of benzyl group and that of a proton. Seventy-two is the mass difference between the ethoxyethyl group and a proton.

Next, the diblock copolymer PS-*b*-PEO **3** with hydroxyl group at the junction point was reacted with 2-bromoisobutyryl bromide to yield the macroinitiator for ATRP of *t*BA. To guarantee the high efficiency of esterification, an excess of 2-bromoisobutyryl bromide was used. The resulting copolymer was characterized by  $^1\text{H}$  NMR as shown in Figure 1 (top). The appearance of the signals at 4.32 ppm for the methylene protons linked to the ester and 1.94 ppm for the methyl protons closed to Br atom provided the direct evidence for the successful esterification. Moreover, in the FTIR spectrum of copolymer (PS-*b*-PEO)-Br **4** (Fig. 2), the appearance of a characteristic stretching frequency of the ester bond at  $1736\text{ cm}^{-1}$  also gave the support to the occurrence of the reaction.

The obtained copolymer (PS-*b*-PEO)-Br **4** with bromide functionality was used as a macroinitiator in subsequent ATRP of *t*BA in the presence of CuBr/PMDETA at  $80\text{ }^\circ\text{C}$  to yield the 3-miktoarm star terpolymer PS-PEO-(*Pt*BA-Br) **5**. To preserve high halogen end functionality of the star precursors to suit the coupling reaction, the polymerization was stopped at low conversion.<sup>41</sup> Figure 3(A) showed the SEC trace of the star terpolymer, a



**Figure 2.** FTIR spectra of diblock copolymer (PS-*b*-PEO)-Br **4**, star terpolymer PS-PEO-(*Pt*BA-Br) **5**, and H-shaped terpolymer **6**.



**Figure 3.** SEC traces: (A) star terpolymer **5** (solid line), (B) the product of ATRC reaction at 90 °C (solid line), and (C) the pure H-shaped terpolymer (dash line).

unimodal symmetric peak confirmed that the ATRP of *t*BA was successful and no uninitiated (PS-*b*-PEO)-Br was remained. It also confirmed the aforementioned esterification was complete.  $^1\text{H}$  NMR spectrum for the star copolymer PS-PEO-(*Pt*BA-Br) **5** was shown in Figure 4 (bottom).

The new signals at 2.22 ppm corresponding to the resonance of the methine proton of *Pt*BA and 1.44 ppm for the methyl protons of *Pt*BA could be observed in addition to the characteristic signals of PS and PEO components. Moreover, the appearance of the signal at 4.18 ppm for the end methine proton linked to Br atom could also be observed. From  $^1\text{H}$  NMR spectrum, the halogen end functionality could be estimated by the following formula (3).

$$E_b = \frac{A_u}{A_k/2} \times 100\% \quad (3)$$

where  $E_b$  is the efficiency of bromine end functionality,  $A_u$  is the integral area of methine proton linked to Br atom at 4.18 ppm, and  $A_k$  has the same meaning as formula (1). The halogen end functionality of this star polymeric precursor was 95%. The reliable  $M_n$  of star terpolymer **5** was calculated by  $^1\text{H}$  NMR using the formula (4).

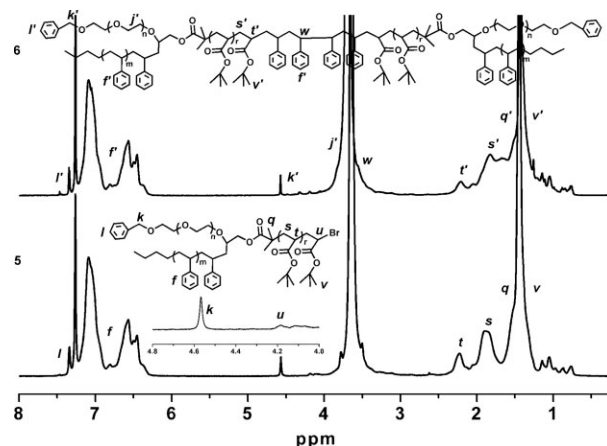
$$M_{n,\text{NMR}}(\mathbf{5}) = \frac{5 \times A_t \times M_{n,\text{SEC}}(\mathbf{1})}{A_f \times 104} \times 128 + M_{n,\text{NMR}}(\mathbf{3}) + 149 \quad (4)$$

where  $A_t$  represents the integral area of methine protons on *Pt*BA chain, 128 is the molecular weight of *t*BA, and 149 is the mass difference between 2-bromoisobutyryl group and a proton. The others have the same meaning as formula (2). In Figure 2, it was apparently observed the typical stretching frequency of ester bond in PS-PEO-(*Pt*BA-Br) **5** was strengthened when compared with that of (PS-*b*-PEO)-Br **4**.

### Synthesis of H-Shaped ABCAB Terpolymer

Previously, ATRC of poly(methyl acrylate) (PMA) has been reported.<sup>34</sup> In the ATRC reaction of PMA, a small amount of styrene was introduced to improve the extent of coupling. Now in this process, it was found that, the coupling efficiency is very low if the styrene is absent. Thus, the same approach<sup>34</sup> was applied to prepare H-shaped ABCAB terpolymer. In the coupling process, only limited units of styrene were inserted, thus the main chain in essentials are remained poly(*tert*-butyl acrylate).

Figure 3(B) showed the SEC traces of the resulting polymer for ATRC reaction at 90 °C. A clear shift to lower retention time indicated the formation of H-shaped terpolymer. Although there was a low molecular weight shoulder after the coupling reaction, the polydispersity index of the product was still narrow (PDI = 1.14). To determine whether bromine end group still existed in the minor uncoupled polymer, ATRC reaction of



**Figure 4.**  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ ) of star terpolymer PS-PEO-(*Pt*BA-Br) **5** (bottom) and H-shaped terpolymer **6** (top).

**Table 1.** The Characteristics of Star Polymeric Precursor and H-Shaped Terpolymer

Star Polymeric Precursor <b>5</b>				H-Shaped Terpolymer <b>6</b>				Coupling Efficiency <sup>a</sup>			
$M_{n,SEC}^b$	PDI <sup>b</sup>	$M_{n,NMR}^c$	Conv.	$M_{n,SEC}^b$	PDI <sup>b</sup>	$M_{n,NMR}^d$	$M_{n,theo}^e$	70 °C	80 °C	90 °C	100 °C
8500	1.06	10,500	6.4%	12,000	1.10	19,500	21,300	36%	53%	67%	60%

<sup>a</sup> Calculated from SEC trace with Gaussian function via peak splitting method.

<sup>b</sup> Determined by SEC calibrated against PS standards.

<sup>c</sup> Calculated from <sup>1</sup>H NMR spectrum of star polymeric precursor.

<sup>d</sup> Calculated from <sup>1</sup>H NMR spectrum of H-shaped terpolymer.

<sup>e</sup> Calculated by the formula (7) (in text).

the crude product was implemented again under the same condition. Consequently, the SEC traces of the resulting polymer for both cases were almost the same. It means that halogen end group was absent in the remained minor uncoupled polymer. The pure H-shaped terpolymer was obtained by collecting eluting solution with main component using SEC with preparative function. Figure 3(C) showed its SEC trace.

Figure 4 (top) presented <sup>1</sup>H NMR spectrum of H-shaped terpolymer. The absence of a peak at 4.18 ppm corresponding to the end methine proton linked to Br atom further confirmed the coupling reaction. The number of incorporated styrene could be calculated by the formula (5) according to <sup>1</sup>H NMR analysis.

$$N_{in-st} = \frac{2M_{n,SEC}(\mathbf{1})}{104} \times \left( \frac{A_t A_f}{A_t A_t'} - 1 \right) \quad (5)$$

in which  $A_t$  and  $A_t'$  are the integral area of methine protons on PtBA chain before and after coupling, and  $A_f$  and  $A_f'$  are the integral area of aromatic protons on PS chain before and after coupling.  $N_{in-st}$  is the number of incorporation styrene in H-shaped terpolymer. From the formula (5), the obtained  $N_{in-st}$  is 4.2. It means that for each 3-miktoarm star terpolymer, only two styrene monomers were inserted in the main chain during the coupling process, which was in agreement with the designed inserted amount of St. Thus the  $M_n$  and theoretical molecular weight of H-shaped polymer **6** could be determined by the following formula (6) and (7), respectively (Table 1).

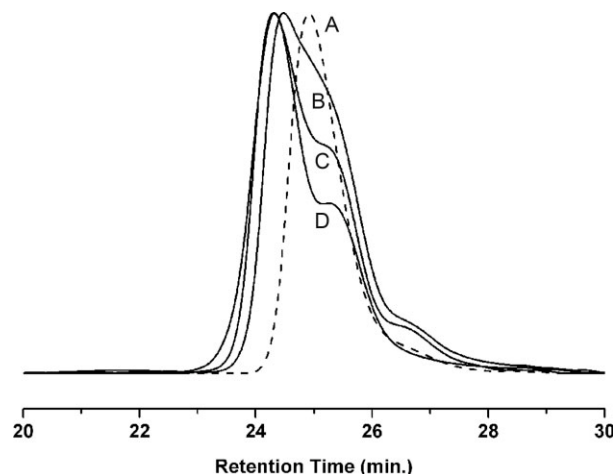
$$M_{n,NMR}(\mathbf{6}) = M_{n,NMR}(PS) + \frac{5 \times A_{j'} \times M_{n,NMR}(PS)}{4 \times A_f \times 104} \times 44 + \frac{5 \times A_{t'} \times M_{n,NMR}(PS)}{A_f \times 104} \times 128 \quad (6)$$

$$M_{n,theo}(\mathbf{6}) = M_{n,NMR}(\mathbf{5}) \times 2 + 104 \times 4 - 80 \times 2 \quad (7)$$

In formula (6),  $A_f$ ,  $A_{j'}$  and  $A_{t'}$  represent the integral area of aromatic protons on PS chain, methylene protons on PEO chain, and methine protons on PtBA chain of H-shaped terpolymer, respectively.  $M_{n,NMR}(PS)$  is the molecular weight of PS chain of H-shaped terpolymer including the inserted styrene units, which could be determined by the following formula (8).

$$M_{n,NMR}(PS) = \left( \frac{2 \times M_{n,SEC}(\mathbf{1})}{104} + N_{in-st} \right) \times 104 \quad (8)$$

In Table 1, there was an obvious discrepancy between the molecular weight of nonlinear terpolymers derived from SEC and that calculated by <sup>1</sup>H NMR, which could be ascribed to the compact conformation for the nonlinear terpolymers with complex structures. Generally, the hydrodynamic volume of nonlinear polymer is smaller than that of linear polymer with the same molecular weight. In addition, PEO chain may stay in the inner part in a compact form in THF,<sup>21</sup> so the molecular weight derived from SEC might be inaccurate and lower than that theoretically calculated. The reliable molecular weight could be obtained by calculation according to <sup>1</sup>H NMR analysis because CDCl<sub>3</sub> was a good solvent for PS, PEO, and PtBA chain of the terpolymers, and clear signals were observed from <sup>1</sup>H NMR spectra. This discrepancy also could be seen in other literatures.<sup>27,28,42</sup> In the FTIR spectra (Fig. 2), no clear difference could be detected for the



**Figure 5.** SEC traces: (A) star terpolymer **5** (dash line), (B) the product of ATRC reaction at 70 °C (solid line), (C) the product of ATRC reaction at 80 °C (solid line), and (D) the product of ATRC reaction at 90 °C (solid line).

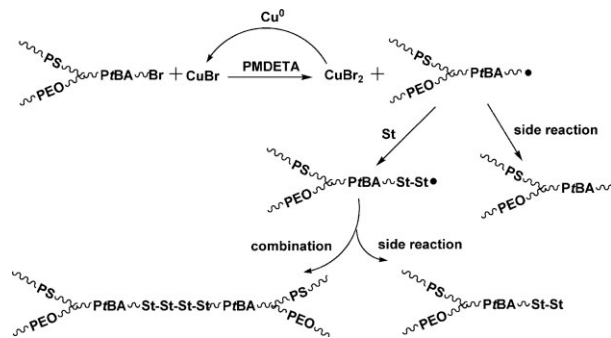
terpolymer **5** and **6** because they have the same polymer chains.

#### Influence of Temperature on the Coupling Efficiency

To optimize the coupling reaction conditions, the ATRC reactions were carried out at different temperature such as 70 °C, 80 °C, 90 °C, and 100 °C for 24 h, respectively, and all the SEC traces (Fig. 5) of the target H-shaped polymers exhibited a clear shift to lower retention time.

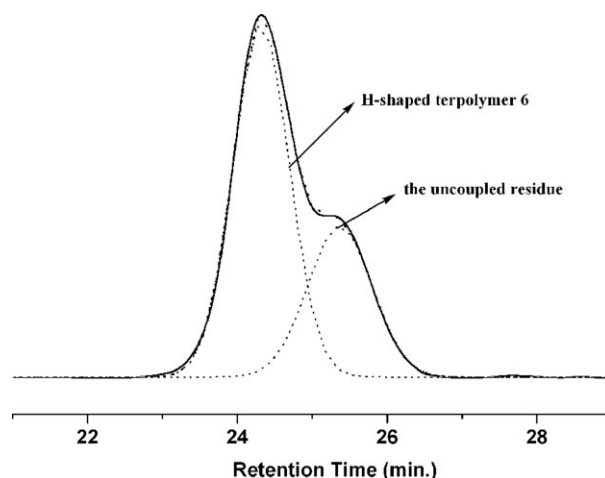
From the Figure 5, it was obviously observed that the coupling extent was improved with the increase of the reaction temperature from 70 °C to 90 °C. That is to say, the amount of the resulting H-shaped terpolymer was increased with the increase of the reaction temperature. As shown in Scheme 2, the polyacrylate macroradicals were generated *in situ* by an atom transfer radical process firstly, then they would react with a small amount of styrene monomer to yield styrene-terminated macroradicals, and simultaneously CuBr was produced continuously by the redox reaction between Cu and CuBr<sub>2</sub>; then the concentration of styrene-terminated macroradicals was maximized gradually to accelerate coupling.

With the increase of reaction temperature, the rate of forming polyacrylate macroradicals was speeded and then the rate of producing styrene-terminated macroradicals was increased. Meanwhile the deactivation reaction of the formed mac-



**Scheme 2.** The ATRC process of star terpolymer PS-PEO-(PtBA-Br).

roradicals was suppressed when an excessive amount of copper powder was present. As a result, the concentration of styrene-terminated macroradicals was increased with the increase of the reaction temperature, thus favoring the bimolecular termination. However, the coupling efficiency (Table 1) was decreased when the coupling reaction temperature was increased to 100 °C, which meant the side reactions such as disproportionation and elimination were enhanced in the process at higher temperature.<sup>43</sup> SEC results showed the proper reaction temperature for the coupling of this system was 90 °C. The efficiency of ATRC reaction could be calculated from SEC trace with Gaussian function via peak splitting method. Figure 6 showed the splitting of SEC traces of the H-shaped polymer **6** synthesized at 90 °C.



**Figure 6.** Peak splitting of SEC trace of the coupling product at 90 °C using Gaussian function.



The result indicated that the area ratio of H-shaped polymer **6** and star polymer was 0.67:0.33. In other words, 67% star polymeric precursors were coupled and 33% were not coupled. The moderate efficiency could be attributed to the large hindrance and long chain length<sup>30</sup> of the formed macroradicals and their side reactions during the bimolecular termination. As Table 1 showed the coupling efficiency at the other coupling temperature could also be derived using the same methods, 0.36:0.64 for 70 °C, 0.53:0.47 for 80 °C, and 0.60:0.40 for 100 °C, so the optimized coupling temperature is 90 °C. When compared with the recent literature<sup>29</sup> which reported the synthesis of H-shaped quintopolymer via click reaction strategy, its efficiency was only about 60%. Thus our stratagem provided feasible another approach to synthesize copolymer with complex structure. It was found that the molecular weight, chain structure, and composition of precursor copolymers would exert great effects on the coupling efficiency, and relative investigation is undergoing.

## CONCLUSIONS

H-shaped terpolymers containing PtBA as the main chain and PS and PEO as the side chains were successfully synthesized through ATRC reaction. The moderate coupling efficiency for the formation of H-shaped ABCAB terpolymer was obtained. The increase of the coupling temperature is favorable to improve the coupling efficiency, but the ideal reaction temperature is 90 °C.

## REFERENCES AND NOTES

- Zhang, H.; Ruckenstein, E. *Macromolecules* 2000, 33, 814–819.
- Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chem Rev* 2001, 101, 3747–3792.
- Gauthier, M.; Tichagwa, L.; Downey, J. S.; Gao, S. *Macromolecules* 1996, 29, 519–527.
- Laurent, B. A.; Grayson, S. M. *J Am Chem Soc* 2006, 128, 4238–4239.
- Teng, J.; Zubarev, E. R. *J Am Chem Soc* 2003, 125, 11840–11841.
- Li, Y.-G.; Shi, P.-J.; Pan, C.-Y. *Macromolecules* 2004, 37, 5190–5195.
- Heinrich, M.; Pyckhout-Hintzen, W.; Allgaier, J.; Richter, D.; Straube, E.; Read, D. J.; McLeish, T. C. B.; Groves, D. J.; Blackwell, R. J.; Wiedemann, A. *Macromolecules* 2002, 35, 6650–6664.
- Cong, Y.; Li, B.; Han, Y.; Li, Y.; Pan, C. *Macromolecules* 2005, 38, 9836–9846.
- Roovers, J. *Macromolecules* 1984, 17, 1196–1200.
- Roovers, J.; Toporowski, P. M. *Macromolecules* 1981, 14, 1174–1178.
- Hakiki, A.; Young, R. N.; McLeish, T. C. B. *Macromolecules* 1996, 29, 3639–3641.
- Perny, S.; Allgaier, J.; Cho, D.; Lee, W.; Chang, T. *Macromolecules* 2001, 34, 5408–5415.
- Iatrou, H.; Avgeropoulos, A.; Hadjichristidis, N. *Macromolecules* 1994, 27, 6232–6233.
- Christodoulou, S.; Driva, P.; Iatrou, H.; Hadjichristidis, N. *Macromolecules* 2008, 41, 2607–2615.
- Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* 1995, 28, 1721–1723.
- Wang, J.-S.; Matyjaszewski, K. *Macromolecules* 1995, 28, 7901–7910.
- Percec, V.; Barboiu, B. *Macromolecules* 1995, 28, 7970–7972.
- Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* 1998, 31, 5559–5562.
- George, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* 1993, 26, 2987–2988.
- Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem Rev* 2001, 101, 3661–3688.
- Angot, S.; Taton, D.; Gnanou, Y. *Macromolecules* 2000, 33, 5418–5426.
- Han, D.-H.; Pan, C.-Y. *J Polym Sci Part A: Polym Chem* 2006, 44, 2794–2801.
- Yu, X.; Shi, T.; Zhang, G.; An, L. *Polymer* 2006, 47, 1538–1546.
- Han, D.-H.; Pan, C.-Y. *J Polym Sci Part A: Polym Chem* 2007, 45, 789–799.
- Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew Chem Int Ed* 2001, 40, 2004–2021.
- Binder, W. H.; Sachsenhofer, R. *Macromol Rapid Commun* 2007, 28, 15–54.
- Durmaz, H.; Karatas, F.; Tunca, U.; Hizal, G. *J Polym Sci Part A: Polym Chem* 2006, 44, 3947–3957.
- Gungor, E.; Cote, G.; Erdogan, T.; Durmaz, H.; Demirel, A. L.; Hizal, G.; Tunca, U. *J Polym Sci Part A: Polym Chem* 2007, 45, 1055–1065.
- Gungor, E.; Durmaz, H.; Hizal, G.; Tunca, U. *J Polym Sci Part A: Polym Chem* 2008, 46, 4459–4468.
- Yoshikawa, C.; Goto, A.; Fukuda, T. *e-Polymers* 2002, 13, 1–12.
- Yurteri, S.; Cianga, I.; Yagci, Y. *Macromol Chem Phys* 2003, 204, 1771–1783.
- Otazagahine, B.; David, G.; Boutevin, B.; Robin, J. J.; Matyjaszewski, K. *Macromol Chem Phys* 2004, 205, 154–164.

33. Sarbu, T.; Lin, K.-Y.; Ell, J.; Siegwart, D. J.; Spanswick, J.; Matyjaszewski, K. *Macromolecules* 2004, 37, 3120–3127.
34. Sarbu, T.; Lin, K.-Y.; Spanswick, J.; Gil, R. R.; Siegwart, D. J.; Matyjaszewski, K. *Macromolecules* 2004, 37, 9694–9700.
35. Kopping, J. T.; Tolstyka, Z. P.; Maynard, H. D. *Macromolecules* 2007, 40, 8593–8599.
36. Tolstyka, Z. P.; Kopping, J. T.; Maynard, H. D. *Macromolecules* 2008, 41, 599–606.
37. Francis, R.; Taton, D.; Logan, J. L.; Masse, P.; Gnanou, Y.; Duran, R. S. *Macromolecules* 2003, 36, 8253–8259.
38. Wang, G.; Huang, J. *Macromol Rapid Commun* 2007, 28, 298–304.
39. Luo, X.; Wang, G.; Pang, X.; Huang, J. *Macromolecules* 2008, 41, 2315–2317.
40. Wang, G.; Huang, J. *J Polym Sci Part A: Polym Chem* 2008, 46, 1136–1150.
41. Lutz, J.-F.; Matyjaszewski, K. *J Polym Sci Part A: Polym Chem* 2005, 43, 897–910.
42. Li, H.; Riva, R.; Jérôme, R.; Lecomte, P. *Macromolecules* 2007, 40, 824–831.
43. Lutz, J.-F.; Matyjaszewski, K. *Macromol Chem Phys* 2002, 203, 1385–1395.