Synthesis of Amphiphilic A_2B Star-shaped Copolymers of Polystyrene-*b*-[Poly(ethylene oxide)]$_2$ via Atom Transfer Nitroxide Radical Coupling

Kun Huang, Jian Huang, Mugang Pan, Guowei Wang, Junlian Huang

Department of Macromolecular Science, State Key Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai 200433, China
Correspondence to: G. Wang (E-mail: gwwang@fudan.edu.cn)

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ABSTRACT: The amphiphilic A_2B star-shaped copolymers of polystyrene-*b*-[poly(ethylene oxide)]$_2$ (PS-*b*-PEO$_2$) were synthesized via the combination of atom transfer nitroxide radical coupling (ATNRC) with ring-opening polymerization (ROP) and atom transfer radical polymerization (ATRP) mechanisms. First, a novel V-shaped 2,2,6,6-tetramethylpiperidine-1-oxyl-PEO$_2$ (TEMPO-PEO$_2$) with a TEMPO group at middle chain was obtained by ROP of ethylene oxdie monomers using 4-(2,3-dihydroxypropoxy)-TEMPO and diphenylmethyl potassium as coinitiator. Then, the linear PS with a bromine end group (PS-Br) was obtained by ATRP of styrene monomers using ethyl 2-bromoisobutyrate as initiator. Finally, the copolymers of PS-*b*-PEO$_2$ were obtained by ATNRC between the TEMPO and bromide groups on TEMPO-PEO$_2$ and PS-Br, respectively. The structures of target copolymers and their precursors were all well-defined by gel permeation chromatographic and nuclear magnetic resonance (^{1}H NMR). © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 2635–2640, 2012

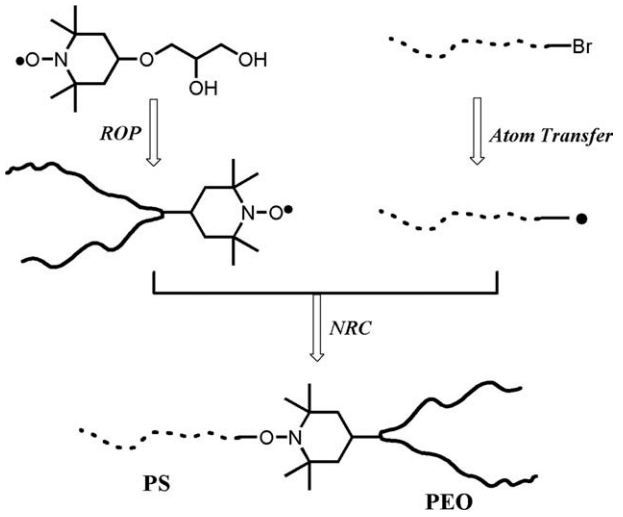
KEYWORDS: atom transfer nitroxide radical coupling; atom transfer radical polymerization; A_2B star-shaped copolymers; polystyrene; poly(ethylene oxide) (PEO); ring-opening polymerization

INTRODUCTION Among miktoarm star-shaped copolymers, the ones having poly(ethylene oxide) (PEO) segments were preferred for its chemical stability, water solubility, nontoxicity, and resistance to recognition by the immune system,[1] which exhibited a vast perspective in bio-therapeutic area. Not only the nonlinear architecture but also their unique physical properties differred from the linear analogous, such as crystalline,[2] microphase morphologies,[3,4] micellar behaviors,[5,6] increased the desire to assess their value in biomedical fields.

The synthetic methodologies for these star-shaped copolymers mainly contained living anionic polymerization using the derivatives of 1,1-diphenylethylene or chlorosilane as conjugating agent,[1(a,c),4] which always required rigorous conditions without moiety and oxygen. Recently, the living radical polymerization has become a powerful tool in macromolecular designing,[7] and the widely used mechanisms were atom transfer radical polymerization (ATRP),[8,9] single-electron transfer living radical polymerization,[10] reversible addition-fragmentation chain transfer,[11,12] and nitroxide mediated radical polymerization,[13] and so forth. Comparing with the direct synthetic strategies using one or more polymerization mechanisms, the high efficient coupling methods such as click chemistry,[14] acetylenic coupling,[15] nitroxide radical coupling (NRC)[16] for instance, had also been involved into the polymeric architecture construction. Especially, to obtain various of miktoarm star-shaped polymers contained PEO segment, the combination of ring-opening polymerization (ROP)[17,18] with above polymerization mechanisms and coupling methods might be the best choice.[1(a–c)]

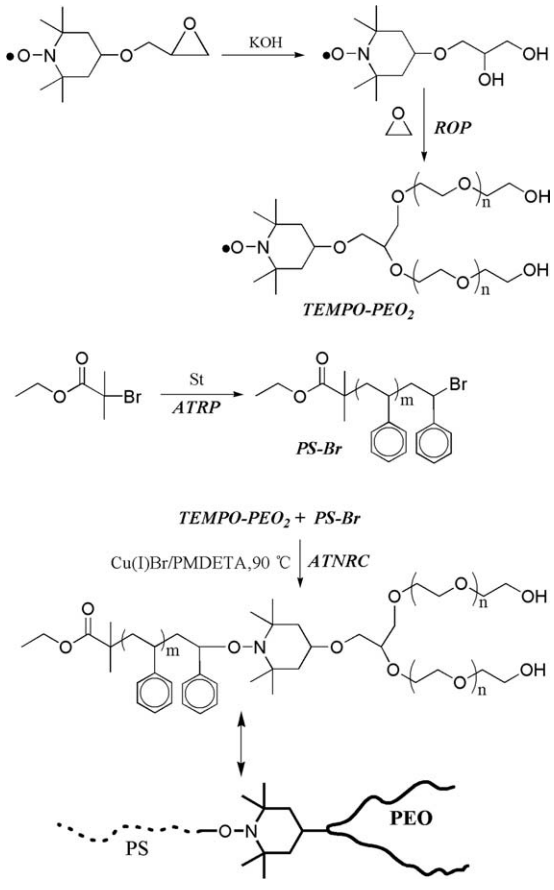
Among the coupling reactions, the NRC reaction was one of the energetic methods to polymeric architecture construction with high efficiency.[16,19] Fu et al. first introduced atom transfer NRC (ATNRC) into polymer chemistry by preparation of graft copolymer poly(4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl-*co*-ethylene oxide)-*graft*-polystyrene and poly(*tert*-butyl acrylate) [Poly(GTEMPO-*co*-EO)-*g*-PS/P*t*BA],[16(a)] in this case, TEMPO group could capture the radicals produced by polymer chains with halogen atoms efficiently. In the later works, the NRC reaction was further developed by our group[16(b,c),20] and Monteiro's group[16(d),21] for copolymers with various architecture such as the diblock, star-shape, comb-shape, and dendrimer like.

Till now, some A_2B star-shaped copolymers had been realized by combination of living anionic polymerization, ROP, ATRP with click chemistry and other coupling methods.[4,22]



SCHEME 1 The synthetic illustration of A_2B star-shaped copolymers of PS-*b*-PEO_2.

However, the NRC reaction had not been expanded for synthesizing copolymers with A_2B star-shaped copolymers. In our previous work, the NRC reaction between a linear PS-bromide (PS-Br) and a linear TEMPO-poly(ethylene oxide) (TEMPO-PEO) was used as a model reaction to study the effect of temperature, composition of catalysts and structures connected to bromide group on the efficiency of NRC, and the effect of steric hindrance on NRC reaction was less considered.[20(e,f)] Herein, as a continuous work on NRC reaction, the reaction between the linear PS-Br and a hindered TEMPO-[poly(ethylene oxide)]$_2$ (TEMPO-PEO_2) was proceeded for a novel A_2B star-shaped copolymers PS-*b*-PEO_2 via the combination of ATNRC with ROP and ATRP mechanisms (Scheme 1). The structures of target PS-*b*-PEO_2 and their precursors were all well-defined by gel permeation chromatographic (GPC) and nuclear magnetic resonance (^{1}H NMR).



SCHEME 2 The synthetic procedure of amphiphilic A_2B star-shaped copolymers of PS-*b*-PEO_2.

RESULTS AND DISCUSSION

The amphiphilic A_2B star-shaped copolymers of PS-*b*-PEO_2 were synthesized via the combination of ATNRC with ROP and ATRP mechanisms, and three steps were involved (Scheme 2): (1) the precursor of V-shaped TEMPO-PEO_2 with a TEMPO group at middle chain was synthesized by ROP of EO monomers using 4-(2,3-dihydroxypropoxy)-TEMPO (DHP-TEMPO) and diphenylmethyl potassium (DPMK) as coinitiator; (2) the precursor of linear PS-Br with a bromine end group was synthesized by ATRP of styrene (St) monomers using ethyl 2-bromoisobutyrate (EBiB) as initiator; (3) the target PS-*b*-PEO_2 were synthesized by ATNRC between the TEMPO and bromide groups on TEMPO-PEO_2 and PS-Br, respectively.

Synthesis and Characterization of TEMPO-PEO_2

The small molecular weight compound with two active hydroxyl groups and one TEMPO group (DHP-TEMPO) was synthesized via ring-opening of epoxide on GTEMPO, and the base KOH was used as catalyst. Subsequently, the precursor of TEMPO-PEO_2 was prepared via ROP of EO monomers in tetrahydrofuran (THF) using DMPK and DHP-TEMPO as coinitiator at 60 °C. The GPC curve of TEMPO-PEO_2 was shown in Figure 1, the molecular weight was 4600 g/mol and the PDI was 1.10.

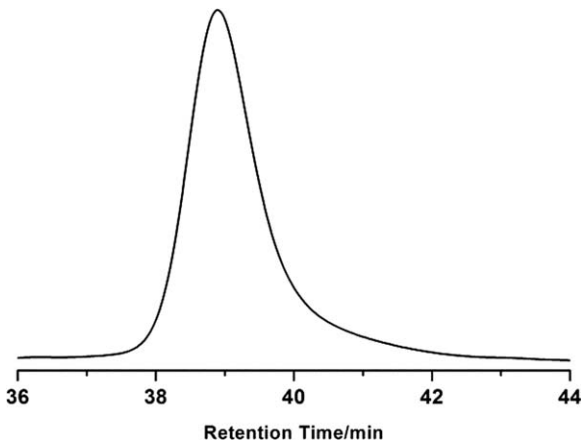


FIGURE 1 GPC curve of TEMPO-PEO_2 ($M_{n,GPC}$ = 4600 g/mol) (using 0.1 M $NaNO_3$ aqueous solution as eluent).

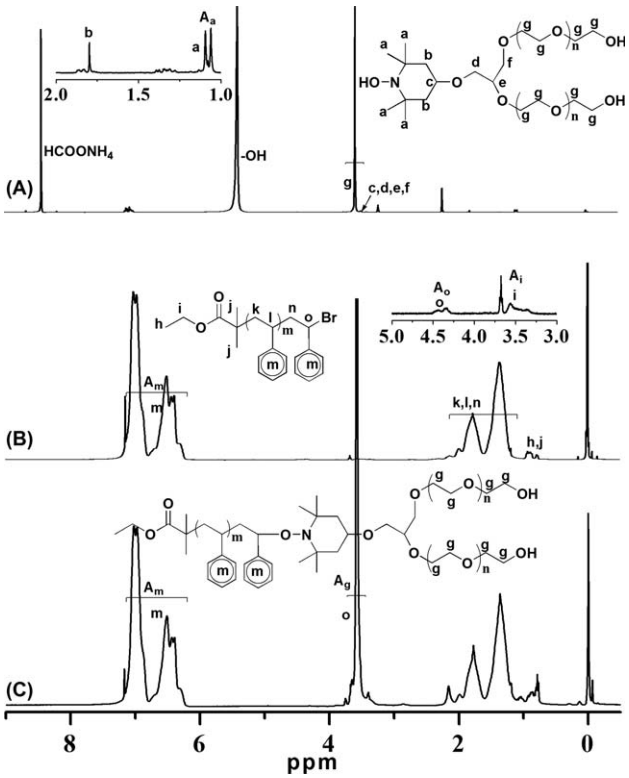


FIGURE 2 ^{1}H NMR spectra of (A) TEMPO-PEO_2; (B) PS_C-Br ($M_{n,GPC}$ = 10,000 g/mol); (C) PS_C-*b*-PEO_2 ($M_{n,GPC}$ = 18,300 g/mol).

The ^{1}H NMR resonance signal at 1.03–1.17 ppm was attributed to methyl protons (—C$\boldsymbol{H}_3$) on TEMPO group and that at 3.25–3.78 ppm was attributed to methylene protons (—C$\boldsymbol{H}_2$C$\boldsymbol{H}_2$O—) on PEO main chain [Fig. 2(A)]. The $M_{n,NMR}$ of TEMPO-PEO_2 ($M_{n,NMR,(TEMPO\text{-}PEO2)}$) was calculated by using eq 1:

$$M_{n,NMR,(TEMPO\text{-}PEO_2)} = \frac{A_g/4}{A_a/12} \times 44 + 247 \quad (1)$$

where, A_a and A_g represent the integral areas of resonance signal at 1.03–1.17 ppm (—C$\boldsymbol{H}_3$ on TEMPO group) and that at 3.25–3.78 ppm (—C$\boldsymbol{H}_2$C$\boldsymbol{H}_2$O— on PEO main chain), respectively. The value of 44 was the molecular weight of EO monomer, and 247 was the molecular weight of initiator DHP-TEMPO. The calculated $M_{n,NMR,(TEMPO\text{-}PEO2)}$ was 4800 g/mol, which was fit well with the molecular weight detected by GPC.

TABLE 1 The Data of Precursors PS-Br

Sample	$M_{n,GPC}$[a] (g/mol)	$M_{n,NMR}$[b] (g/mol)	PDI[a]	R.F.[c] (%)
PS_A-Br	2100	2500	1.13	84.67
PS_B-Br	6700	6600	1.05	94.24
PS_C-Br	10,100	9100	1.04	86.46

[a] Measured by GPC in THF, calibrated with linear PS standard.
[b] Calculated by using eq 3 according to ^{1}H NMR spectra.
[c] The retention of functional bromine (R.F.) at PS end was calculated by using eq 2.

Synthesis and Characterization of PS-Br

The precursor of PS-Br was synthesized by ATRP of St monomers using EBiB as initiator. By changing the polymerization time, a series of PS-Br with different M_n were prepared (Table 1). Figure 3(B) showed the GPC curves of PS-Br, which had symmetric peaks and low PDIs.

Figure 2(B) was ^{1}H NMR spectrum of PS-Br, the resonance signals at 7.39–6.24 ppm were attributed to the phenyl protons (—$C_6\boldsymbol{H}_5$) on PS main chain, the resonance signals at 1.08–0.90 and 0.90–0.76 ppm were attributed to the methyl protons (—C(C$\boldsymbol{H}_3$)$_2$— and C$\boldsymbol{H}_3$CH_2—) on initiator EBiB, and the resonance signals at 4.60–4.33 ppm and 3.72–3.32 ppm were attributed to methine proton (—C$\boldsymbol{H}$(Ph)-Br) connected to bromine group at PS end and methylene protons (CH_3C$\boldsymbol{H}_2$OCO—), respectively. The retention of functional bromine (R.F.) at PS end was calculated by using eq 2:

$$\text{R.F.} = \frac{A_o}{A_i/2} \times 100\% \quad (2)$$

where, A_o and A_i were the integral areas of resonance signals at 4.60–4.33 ppm (—C$\boldsymbol{H}$(Ph)-Br at PS end) and that at 3.72–3.32 ppm (CH_3C$\boldsymbol{H}_2$OCO— on initiator EBiB), respectively. The obtained R.F.s of PS-Br were lower than 100% (Table 1), which meant that a minor part of bromine groups were lost in polymerization or purified procedure. And the $M_{n,NMR}$ of PS-Br ($M_{n,NMR,(PS\text{-}Br)}$) was calculated by using eq 3:

$$M_{n,NMR,(PS\text{-}Br)} = \frac{A_m/5}{A_i/2} \times 104 + 195 \quad (3)$$

where, A_m was the integral area of resonance signals at 7.39–6.24 ppm (—$C_6\boldsymbol{H}_5$). The value of 104 was the molecular weight of St monomer, and 195 was the molecular weight of initiator EBiB. The others were the same as defined before, and all results were listed in Table 1.

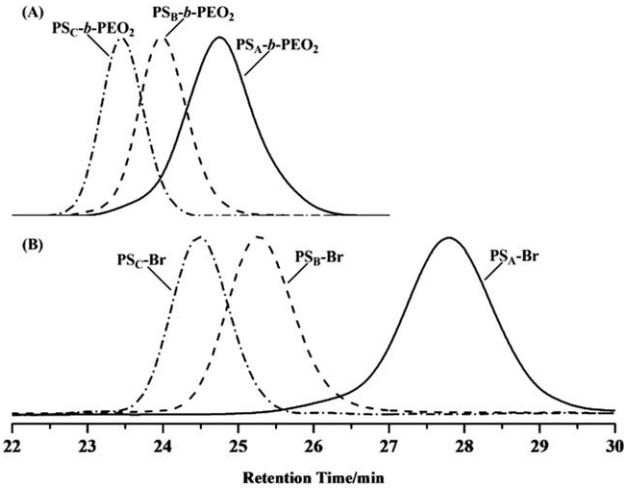


FIGURE 3 GPC curves of precursors: PS_A-Br ($M_{n,GPC}$ = 2100 g/mol), PS_B-Br ($M_{n,GPC}$ = 6700 g/mol), PS_C-Br ($M_{n,GPC}$ = 10,100 g/mol) and amphiphilic PS-*b*-PEO_2 star-shaped copolymers: PS_A-*b*-PEO_2 ($M_{n,GPC}$ = 8100 g/mol), PS_B-*b*-PEO_2 ($M_{n,GPC}$ = 13,400 g/mol), PS_C-*b*-PEO_2 ($M_{n,GPC}$ = 18,300 g/mol) (using THF as eluent).

Synthesis and Characterization of A_2B Star-Shaped Copolymers of PS-*b*-PEO_2

Based on the ATNRC method reported recently by our group, the amphiphilic A_2B star-shaped copolymers of PS-*b*-PEO_2 were synthesized by ATNRC reaction between the TEMPO and bromide groups on V-shaped TEMPO-PEO_2 and linear PS-Br, respectively. In previus work,[20(e,f)] the molar ratio of PS-Br to TEMPO-PEO was 1:1 for the diblock of PS-*b*-PEO and the efficiency of ATNRC almost reached to 95%. In this work, to consumed the precursor of TEMPO-PEO_2 completely and simplify the subsequent purification procedure, the excess of PS-Br precursor (2.0 equiv.) was fed in ATNRC reaction. After ATNRC reaction, the remained homopolymer of PS-Br was washed by mixture solvents of THF/petroleum ether according to the different solubility of PEO and PS segments in this solvent.

The GPC curves of PS-*b*-PEO_2 after purification with THF/petroleum ether were shown in Figure 3(A). The monomodal peaks and low PDIs showed that the TEMPO-PEO_2 had been consumed completely in ATNRC reaction, and the efficiency of ATNRC was almost 100% (based on the fed TEMPO-PEO_2). Figure 2(C) was the ^{1}H NMR spectrum of PS-*b*-PEO_2, the characteristic resonance signals of ethylene protons (—C$\boldsymbol{H}_2$C$\boldsymbol{H}_2$O—) on PEO main chain and phenyl protons (—$C_6\boldsymbol{H}_5$) on PS main chain were attributed at 3.25–3.78 and 6.16–7.51 ppm, respectively. The $M_{n,NMR}$ of PS-*b*-PEO_2 ($M_{n,NMR,(PS\text{-}b\text{-}PEO2)}$) was calculated by using eq 4:

$$M_{n,NMR,(PS\text{-}b\text{-}PEO_2)} = \frac{A_o/4}{\frac{A_m}{\left(M_{n,NMR,(PS\text{-}Br)}/104\right)\times 5}} \times 44 + M_{n,NMR,(PS\text{-}Br)} \quad (4)$$

where, A_m, A_o, the values of 44, 104, and $M_{n,NMR,(PS\text{-}Br)}$ were all the same as defined before. The calculated $M_{n,NMR,(TEMPO\text{-}PEO2)}$ were all closed to the theoretical molecular weight calculated by using eq 5:

$$M_{n,theo,(PS\text{-}b\text{-}PEO_2)} = M_{n,NMR,(TEMPO\text{-}PEO)} + M_{n,NMR,(PS\text{-}Br)} \quad (5)$$

These results further strongly proved that the efficiency of ATNRC was almost 100% and the A_2B star-shaped copolymers PS-*b*-PEO_2 were successfully obtained.

EXPERIMENTAL

Materials

St [99%, Sinopharm Chemical Reagent (SCR)] was washed with 10% NaOH aqueous solution followed by water three times, dried over anhydrous $MgSO_4$, further dried over CaH_2, and distilled under reduced pressure. EO [98%, SCR] was dried by CaH_2 for 48 h and then distilled under N_2 before use. THF (>99%, SCR) were refluxed and distilled from sodium naphthalenide solution. Dimethyl sulfoxide (DMSO, >99%, SCR) was dried over CaH_2 and distilled under reduced pressure. Copper(I) bromide [Cu(I)Br, 95%, SCR] was stirred overnight in acetic acid, filtered, washed with ethanol and ethyl ether successively, and dried in vacuum. EBiB, (98%) and *N*,*N*,*N*′,*N*″,*N*″-pentamethyl-diethylenetriamine (PMDETA, 99%) were purchased from Aldrich and used as received. Other reagents were all purchased from SCR and purified by standard method before use. DPMK solution was freshly prepared according to the literature,[23] and the concentration was 0.75 mol/L. GTEMPO was synthesized according to our previous work and purified by recrystallization from hexane.[24]

TABLE 2 The Data of A_2B Star-Shaped Copolymers PS-*b*-PEO_2

Sample	$M_{n,GPC}$[a] (g/mol)	$M_{n,NMR}$[b] (g/mol)	PDI[a]	$M_{n,theo.}$[c] (g/mol)
PS_A-*b*-PEO_2	8100	7300	1.07	7300
PS_B-*b*-PEO_2	13,400	11,800	1.03	11,400
PS_C-*b*-PEO_2	18,300	13,300	1.03	13,900

[a] Measured by GPC in THF, calibrated with linear PS standard.
[b] Calculated by using eq 4 according to ^{1}H NMR spectra.
[c] Calculated by using eq 5.

Measurements

GPC analysis of PEO was performed in 0.1 M $NaNO_3$ aqueous solution at 40 °C with an elution rate of 0.5 mL/min on an Agilent 1100 equipped with a G1310A pump, a G1362A refractive index detector, and a G1315A diode-array detector. Three TSK-gel PW columns in series [bead size: 6, 13, and 13 μm; pore size: 200, >1000, and <100–1000 Å; molecular range: 0–5 × 10^4, 5 × 10^4–8 × 10^6, and (5–8) × 10^6 g/mol respectively] were calibrated with PEO standard samples. GPC analysis of the rest polymers were performed in THF at 35 °C with an elution rate of 1.0 mL/min on an Agilent 1100 equipped with a G1310A pump, a G1362A refractive index detector, and a G1314A variable wavelength detector. One 5 μm LP gel column (500 Å, molecular range 500–2 × 10^4 g/mol) and two 5 μm LP gel mixed bed column (molecular range 200–3×10^6 g/mol) were calibrated by PS standard samples. The injection volume was 20 μL, and the concentration was 5 mg/mL. ^{1}H NMR spectra were recorded at room temperature by a Bruker (500 MHz) spectrometer using tetramethylsilane as the internal standard and $CDCl_3$ as the solvent, except for initiator DHP-TEMPO and TEMPO-$(PEO)_2$ which were measured in CD_3OD in the presence of $HCOONH_4$ and Pd/C. 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.

Preparation of DHP-TEMPO

The compound with two active hydroxyl groups and one TEMPO group (DHP-TEMPO) was prepared via ring-opening of epoxide on GTEMPO under base condition (KOH). In a 500 mL round flask, KOH (10.0 g) and water (150 mL) was added, and the solution was heated to 80 °C. Then, GTEMPO (6.0 g, 26.3 mmol) dissolved in H_2O (80 mL) and THF (30 mL) was added dropwise into the flask under vigorous stirring. After the addition of GTEMPO, the mixture solution was stirred for another 48 h. The crude product was neutralized by hydrochloric acid (2 M), evaporated under reduced pressure to remove THF solvent, and extracted with CH_2Cl_2 to

remove the formed salts. Finally, the product was purified by gradient eluting with silica gel by CH_2Cl_2 and THF.

^{1}H NMR (CD_3OD, in the presence of calculated amounts of $HCOONH_4$ and Pd/C), δ (ppm): 0.95–1.13 (d, J = 11.2Hz, 12H, C***H***$_3$— of TEMPO group), 1.26–1.41, 1.82–1.92 (m, 4H, —C***H***$_2$— of TEMPO group), 3.33–3.69 (m, 6H, —C***H***— of TEMPO group, —OC***H***$_2$C***H***(OH)C***H***$_2$OH), 5.38–5.91 (s, 3H, —O***H*** of DHP-TEMPO).

Preparation of V-Shaped 2,2,6,6-Tetramethyl piperidine-1-oxyl-PEO$_2$ with a TEMPO Group at Middle Chain (TEMPO-PEO$_2$) by ROP Mechanism

The precursor of TEMPO-PEO_2 was prepared by ROP of EO monomers in THF using DHP-TEMPO and DPMK as coinitiator. Typically, DHP-TEMPO (2.47 g, 10 mmol) dried by azeotropic distillation with toluene was dissolved in 80 mL THF and 20 mL DMSO, and DPMK (6.67 mL, 5 mmol) was added dropwise. Then, the initiator solution and EO monomers (56 mL, 1.1 mol) were introduced into a stainless steel kettle with syringe successively, and the kettle was heated to 50 °C in oil bath for 72 h. After the reaction was terminated with 5 mL methanol, THF was evaporated under reduced pressure. The crude product was extracted with CH_2Cl_2/H_2O, dried with $MgSO_4$ and precipitated into diethyl ether for three times. The obtained TEMPO-PEO_2 was dried at 45 °C in vacuum to a constant weight. ($M_{n,GPC}$ = 4600 g/mol, M_w/M_n = 1.10; $M_{n,NMR}$ = 4800 g/mol).

^{1}H NMR (CD_3OD, in the presence of calculated amount of $HCOONH_4$ and Pd/C), δ (ppm): 1.03–1.17 (d, C***H***$_3$ of TEMPO group), 1.26–1.42, 1.74–1.90 (m, —C***H***$_2$—, protons of methylene of TEMPO group), 3.35–3.78 (m, —CH_2C***H***CH_2—, methenyl proton of TEMPO group; —OCH_2C***H***CH_2— of initiator DHP-TEMPO and —OC***H***$_2$C***H***$_2$—, repeating unit of PEO).

Preparation of Linear PS with Bromine End Group (PS-Br) by ATRP Mechanism

The precursor of linear PS-Br was prepared by ATRP of St monomers using EBiB as initiator and Cu(I)Br /PMDETA as catalyst. Typically, EBiB (0.09 mL, 0.625 mmol), Cu(I)Br (0.0905 g, 0.625 mmol), PMDETA (0.15 mL, 0.625 mmol), and St monomers (30 mL, 262 mmol) were added into a 150 ml ampule. The reaction mixture was degassed by three freeze-pump-thaw cycles and purged with nitrogen, and the ampule was immerged into oil bath at 90 °C for 6 h. After the polymerization was stopped by dipping into liquid nitrogen, the crude product was diluted with THF and passed through a column chromatograph filled with neutral alumina to remove the copper complex, and precipitated into methanol. The precipitate was collected and dried at 35 °C in vacuum to a constant weight. ($M_{n,GPC}$ = 10,100 g/mol, M_w/M_n = 1.04). A series of PS-Br with different M_n were prepared (Table 2) by changing the polymerization time. ^{1}H NMR ($CDCl_3$), δ (ppm): 7.25–6.32 (phenyl protons of PS), 4.64–4.39 (—C***H***(Ph)-Br, end group of PS), 3.75–3.34 (CH_3C***H***$_2$— of initiator EBiB), 2.96—1.10 (—C***H***$_2$C***H***(Ph)—, repeating unit of PS), 1.10–0.95 (—C(C***H***$_3$)$_2$— of residual on EBiB, 0.93–0.85 (C***H***$_3$$CH_2$- of residual on EBiB).

Synthesis of Amphiphilic A$_2$B Star-Shaped Copolymers of PS-*b*-PEO$_2$ by ATNRC Reaction

The amphiphilic A_2B star-shaped copolymers of PS-*b*-PEO_2 were synthesized via the ATNRC between TEMPO and bromide groups on V-shaped TEMPO-PEO_2 and linear PS-Br, respectively. Typically, TEMPO-PEO_2 (0.3041 g, 0.07 mmol) and PS-Br (0.2385 g, 0.11 mol) were dissolved in DMF (10.0 mL) in a 100 mL ampule, then Cu(I)Br (0.0167 g, 0.11 mmol), Cu (0.0359 g, 0.56 mmol) and PMDETA (0.14 mL, 0.67 mmol) were added. The reaction mixture was degassed by three freeze–pump–thaw cycles and purged with N_2, immersed into oil bath at 90 °C for 24 h, and then, immersed into liquid nitrogen to stop the coupling reaction. The crude product was extracted with CH_2Cl_2/H_2O to remove the copper complex. The unreacted PS-Br was washed by mixture solvents of THF/petroleum ether. Finally, the product was precipitated into petroleum ether and the obtained powder was dried at 45 °C in vacuum. ($M_{n,GPC}$ = 18,300 g/mol, M_w/M_n = 1.02; $M_{n,NMR}$ = 13,300 g/mol).

^{1}H NMR ($CDCl_3$), δ (ppm): 0.67–2.60 (m, C***H***$_3$$H_2O$—, —C(C***H***$_3$)$_2$— of PS block; —C***H***$_2$C***H***(Ph) —, repeating unit of PS); 3.31–4.02 (m, methylene and methine protons of PEO block), 6.26–7.38 (m, phenyl protons of repeating unit of PS block).

CONCLUSION

In summary, a novel amphiphilic A_2B star-shaped copolymers of PS-*b*-PEO_2 were successfully synthesized via the combination of ATNRC with ROP and ATRP mechanisms. By tuning the molecular weight of the precursors, a series of samples were obtained, which showed the versatility of this method in construction of copolymers with complicated structures.

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