Synthesis and Characterization of Well-Defined ABC 3-Miktoarm Star-Shaped Terpolymers Based on Poly(styrene), Poly(ethylene oxide), and Poly(ε-caprolactone) by Combination of the "Living" Anionic Polymerization with the Ring-Opening Polymerization

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ABSTRACT: A series of well-defined ABC 3-Miktoarm star-shaped terpolymers [Poly (styrene)-Poly(ethylene oxide)-Poly(ε-caprolactone)](PS-PEO-PCL) with different molecular weight was synthesized by combination of the "living" anionic polymerization with the ring-opening polymerization (ROP) using macro-initiator strategy. Firstly, the "living" poly(styryl)lithium (PS^-Li^+) species were capped by 1-ethoxyethyl glycidyl ether(EEGE) quantitatively and the PS-EEGE with an active and an ethoxyethyl-protected hydroxyl group at the same end was obtained. Then, using PS-EEGE and diphenylmethylpotassium (DPMK) as coinitiator, the diblock copolymers of $(PS\text{-}b\text{-}PEO)_p$ with the ethoxyethyl-protected hydroxyl group at the junction point were achieved by the ROP of EO and the subsequent termination with bromoethane. The diblock copolymers of $(PS\text{-}b\text{-}PEO)_d$ with the active hydroxyl group at the junction point were recovered via the cleavage of ethoxyethyl group on $(PS\text{-}b\text{-}PEO)_p$ by acidolysis and saponification successively. Finally, the copolymers $(PS\text{-}b\text{-}PEO)_d$ served as the macro-initiator for ROP of ε-CL in the presence of tin(II)-bis(2-ethylhexanoate)$(Sn(Oct)_2)$ and the star(PS-PEO-PCL) terpolymers were obtained. The target terpolymers and the intermediates were well characterized by ^{1}H-NMR, MALDI-TOF MS, FTIR, and SEC. © 2007 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 46: 1136–1150, 2008

Keywords: anionic polymerization; poly(ε-caprolactone); poly(ethylene oxide); polystyrene; ring-opening polymerization; star polymers

INTRODUCTION

The design and preparation of new well-defined block copolymers with different blocks in structure and polarity represented a molecular level architecture with monomeric building blocks. These model materials have facilitated the investigation of many polymer fields, such as the microphase separation,[1] the relationship of morphology and composition,[2] unperturbed dimensions,[3] and rheology.[4] Comparing with the comb-shaped,[5] block-grafted,[6] cyclic,[7] dendritic,[8] hyperbranched,[9] and symmetrical star-shaped[10] copolymers, increasing attention had been paid

to the asymmetric star-shaped terpolymers in the past a few decades because these terpolymers were composed by three different homopolymer arms connected at one central junction.[11] The investigation of ABC 3-Miktoarm star-shaped terpolymers on microdomain morphologies in bulk[12] and self-assembly behavior in solution[13] has preliminarily exhibited their potential applications in many fields and further evoked the warmth of researchers. Specially, in the theoretical investigations, various interesting morphologies had already been well envisioned using the simulation methods such as the Monte Carlo Simulations[14] and the real-space implementation of the Self-consistent Field Theory (SCFT).[15] However, the construction of ABC 3-Miktoarm star-shaped terpolymers with controlled and expected composition was still a challenge for the chemists because of the difficulty of synthesis and purification.

Until recently, the ABC 3-Miktoarm star-shaped terpolymers could be prepared by several limited strategies. Typically, Hadjichristidis et al. prepared the star poly(isoprene)-poly(styrene)-poly(butadiene)[16] and star poly(styrene)-poly(butadiene)-poly(methyl methacrylate)[17] by using methyl trichlorosilane as linking agent. Wei and Huang,[18] got the star poly(styrene)-poly(ethylene oxide)-poly(isoprene) copolymer by coupling the ω-end functionalized poly(styrene), poly(ethylene oxide), and poly(isoprene) with the core molecule lysine successively. Using the non-polymerizable macromonomers technique, Fujimoto et al. synthesized the star poly(styrene)-poly(*tert*-butyl methacrylate)-poly(dimethyl siloxane)[19] and star poly(styrene)-poly(butadiene)-poly (2-vinylpyridine)[20] by capping the "living" polymer species with the 1,1-diphenylethylene functionalized polymer and then initiating the polymerization of the third monomer by resulting the species. Lambert et al.[21] also developed the macro-initiator method by using the multifunctional compound to cap the "living" polymer species and then polymerizing other two monomers in turn by variation of functional groups, and the star poly(styrene)-poly(ethylene oxide)-poly(*tert*-butyl methacrylate)[22] was obtained. Pan et al. synthesized the star poly(tetrahydrofuran)-poly(1,3-dioxepane)-poly (styrene)[23] and star poly(styrene)-poly(methyl acrylate)-poly (*N*-isopropylacrylamide)[24] using the similar route. Recently, Zhao and coworker[25] synthesized star poly(ε-caprolactone)-poly(styrene)-poly (methyl methacrylate) by preparation of a compound

with three functional groups such as a hydroxyl group for ROP of ε-caprolactone, a bromide group for atom transfer radical polymerization (ATRP) of methyl methacrylate and a tetramethyl-piperidinyloxyl group for nitroxide-mediated radical polymerization (NMRP) of styrene. Tunca and coworker[26] synthesized the star poly(methyl methacrylate)-polystyrene-poly(*tert*-butyl acrylate) by combining the "click" chemistry and the multi-functional compound method.

Nevertheless, when the linking agent and macromonomers were used, the reaction efficiency was always a problem for both of them, the higher the molecular weight of the homopolymers, the lower the reaction efficiency. On the other hand, the design and synthesis of a capping molecule or an initiator with multi-functional groups for the different polymerization mechanism was not an easy thing because the different polymerization methods generally need different polymerization conditions.

In this contribution, a novel and universal route was suggested to synthesize the well-defined ABC 3-Miktoarm star(PS-PEO-PCL) terpolymers based on a versatile macro-initiator with a hydroxyl group and a protected hydroxyl group at the same end. The active or ethoxy-ethyl-protected hydroxyl group at PS-EEGE end might be transformed into the dithio group for reversible addition-fragmentation chain transfer polymerization (RAFT)[24,27] and the halide group for atom transfer radical polymerization (ATRP)[28] by simple variation of the end groups. Thus the multiple polymerization mechanism could be completed by this strategy and a variety of monomers could be used for preparation of the ABC 3-Miktoarm star-shaped terpolymers.

Herein, it was focused on the construction of a series of well-defined star(PS-PEO-PCL) terpolymers with different molecular weight by combination of the "living" anionic polymerization with the ring-opening polymerization successively.

EXPERIMENTAL

Materials

Styrene(St, >99.5%) was washed with 10% NaOH aqueous solution and then water three times successively, then dried over CaH$_2$ and distilled under reduced pressure. Ethylene oxide

(EO) was dried over CaH_2 for one week and then distilled, stored at -20 °C. ε-Caprolactone (ε-CL) (Aldrich, 99%), 1,1-Diphenylmethane (99%), and Glycidol (Aldrich, 96%) were dried over CaH_2 and distilled under reduced pressure. Tetrahydrofuran (THF, 99%) and pyridine (99.5%) were refluxed and distilled from sodium naphthalenide solution and sodium respectively. Ethyl vinyl ether (Aldrich, 98%), bromoethane, toluene, cyclohexane, and 1-butyl chloride were distilled from CaH_2 just before use. Dithranol (Aldrich, 99.0%), silver trifluoroacetate (Fluka, 99.99%) were used as received. All other reagents and solvents were purchased from Sinopharm Chemical Reagent, Ltd. (SCR) except for declaration and used as received.

Diphenylmethylpotassium (DPMK) solution was freshly prepared by the reaction of potassium naphthalenide with diphenylmethane in THF according to the literature,[29] and the concentration was 0.61mol/L. The tin(II)-bis(2-ethylhexanoate) $(Sn(Oct)_2)$ was dissolved in dried toluene and the concentration was 0.0787 mol/L. p-Nitrobenzoyl chloride (pNBC) was synthesized by the reaction of p-nitrobenzoic acid with thionyl chloride $(SOCl_2)$ according to the literature.[30] 1-Ethoxyethyl glycidyl ether (EEGE) was synthesized from glycidol and ethyl vinyl ether according to the literature[31] and distilled under reduced pressure.[32] n-Butyllithium (n-Bu$^-$Li$^+$) was prepared according to the literature[18] and analyzed by the double-titration method,[33] and the concentration was 1.57 mol/L.

Measurements

^{1}H-NMR spectra were obtained at a DMX500 MHz spectrometer with tetramethylsilane (TMS) as the internal standard and $CDCl_3$ as the solvent. 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 μm LP gel column (500 Å, molecular range 500 to 2×10^4 g/mol) and two 5 μm LP gel mixed bed column (molecular range 200 to 3×10^6 g/mol) were calibrated with polystyrene standard samples. The MALDI-TOF MS measurement was performed using a Perspective Biosystem Voyager-DE STR MALDI-TOF (matrix-assisted laser desorption/ionization time-of-flight) mass spectrometer (PE Applied Biosystems, Framingham, MA). The instrument was

equipped with a nitrogen laser emitting at 337 nm with a 3 ns pulse width and working in positive mode. Accelerating voltage, grid voltage, and delay time were optimized for each sample and all the spectra were recorded in reflectron mode. Matrix solution of dithranol (20 mg/mL), end-functionalized polymer (10 mg/mL), and cationizing salt of silver trifluoroacetate (10 mg/mL) in THF were mixed in the ratio of matrix: cationizing salt: polymer = 10:1:2, and 0.8 μL of mixed solution was deposited on the sample holder (well-plate). The mass scale was calibrated externally using polystyrene standards. Fourier transform infrared (FTIR) spectra were recorded on a Magna-550 FTIR instrument by casting film on a NaCl tablet.

Preparation of 1-Ethoxyethyl Glycidyl Ether-Functionalized Polystyrene (PS-EEGE)

The anionic polymerization of St was carried out according to the literature under the nitrogen (N_2) atmosphere,[18] typically, the St (10 mL), cyclohexane (120 mL), and THF (4 mL) were charged into a 500 mL dried ampoule under nitrogen atmosphere, then the n-Bu$^-$Li$^+$ solution (1.93 mL, 3.03 mmol) was injected by a syringe under magnetic stirring. The reaction was kept at room temperature for 8 h, then a mixture of EEGE (3.0 mL, 20.55 mmol) and THF (4 mL) was added promptly and the system was stirred for another 8 h before the termination by methanol. After the solvents was evaporated, the product was purified by dissolution/precipitation twice with THF/methanol and the obtained white powder of functionalized polystyrene (PS-EEGE) was dried under vacuum at 45 °C for 24 h to a constant weight of 9.02 g in a yield of 99.2%. ^{1}H-NMR ($CDCl_3$) δ ppm: 0.80 (m, C$\boldsymbol{H}_3$CH$_2$—), 1.13 (m, C$\boldsymbol{H}_3$CH$_2$O—), 1.22 (m, —CH(C$\boldsymbol{H}_3$)—), 1.26–2.01 (m, 3H, aliphatic main chain —C$\boldsymbol{H}_2$C— of PS chain), 3.09–3.43 (m, CH$_3$C$\boldsymbol{H}_2$O—, —CH(OH)C$\boldsymbol{H}_2$O—), 3.52 (m, —C$\boldsymbol{H}$(OH)—), 4.65–4.76 (m, —OC$\boldsymbol{H}$O—), 6.30–7.30 (m, 5H, aromatic —C$_6\boldsymbol{H}_5$ of PS chain). $M_{n(SEC)}$ = 2800 g/mol, PDI(polydispersity index) = 1.04, $M_{n(NMR)}$ = 2900 g/mol, $M_{n(MALDI\text{-}TOF\ MS)}$ = 2640.2.

According to the thin layer chromatography (TLC) results, the R_f value of functionalized PS-EEGE was 0.23 and the corresponding unfunctionalized PS was 1.00 when toluene was used as the developing agent.[34] Thus, the crude product could be purified by column chromatography

using silica gel (200–300 mesh) as filling material and toluene as the first eluent. After the front running of unfunctionalized PS was eluted, the eluent was gradually changed to pure THF to wash out the remaining functionalized PS-EEGE completely.

Preparation of Diblock Copolymers Poly(styrene)-*b*-Poly(ethylene oxide) with the Ethoxyethyl-Protected Hydroxyl Group at the Junction Point ((PS-*b*-PEO)$_p$)

Firstly, the dried PS-EEGE (3.91 g, 1.40 mmol, $M_{n(SEC)}$ = 2,800 g/mol) in 100 mL THF was added to a 250 mL dried ampoule, and the needed DPMK solution (2.9 mL,1.77 mmol) was introduced dropwise by a syringe under magnetic stirring. Then the ampoule was placed into an ice bath and the cold EO (7.2 mL, 6.26 g, 142.27 mmol) was added quickly, and the solution was heated to 50 °C and stirred for 96 h. After the reaction was completed, an additional DPMK solution (8 mL, 4.88 mmol) was injected into the system to guarantee the complete deprotonation of all hydroxyl groups, then terminated with excess bromoethane (5 mL, 7.31 g, 67.05 mmol). The obtained solution was stirred at 50 °C for another 24 h and the solvent was evaporated, subsequently, the salt was removed by filtration and the diblock copolymers of (PS-*b*-PEO)$_p$ were precipitated in cold petroleum ether (30–60 °C) slowly and dried under vacuum at 45 °C for 24 h till to a constant weight of 9.46 g (93.0% yield according the EO and PS-EEGE added; 93.2% conversion of EO according to the calculated M_n by ^{1}H-NMR and the theoretical M_n).

The white powder of (PS-*b*-PEO)$_p$ was purified by extraction with cyclohexane twice to remove the homoploymer PS, then precipitated into cold petroleum ether again and dried under vacuum. The product weighted 8.44 g (89.2% yields according the product before purification). ^{1}H-NMR (CDCl$_3$) δ ppm: 0.80 (m, C**H**$_3$CH$_2$—), 1.13 (m, C**H**$_3$CH$_2$O—), 1.22 (m, —CH(C**H**$_3$)—), 1.26–2.01 (m, 3H, aliphatic main chain —C**H**$_2$CH— of PS block), 2.72–3.53 (m, CH$_3$C**H**$_2$O—, —C**H**(O—)C**H**$_2$O—), 3.53–3.70 (m, 4H, —C**H**$_2$CH$_2$O— of PEO block), 4.65–4.76 (m, —OC**H**O—), 6.30–7.30 (m, 5H, aromatic —C$_6$**H**$_5$ of PS block). $M_{n(NMR)}$ = 7200 g/mol, PDI = 1.06.

To evaluate the blocking efficiency of PEO oxanionic species by bromoethane, the following two experiments was designed and completed. (1) The methoxy-poly(ethylene oxide) (mPEO)

was used as model polymer and the hydroxyl group at ω-end was blocked by bromoethane under the same conditions as that for (PS-*b*-PEO)$_p$. (2) In a 100 mL round-bottom flask, the dried (PS-*b*-PEO)$_p$ (1.00 g, 0.14 mmol, $M_{n(NMR)}$ = 7200 g/mol) in 30 mL anhydrous pyridine was introduced, then 0.6 mL pNBC solution (1.56 mol/L in THF) was added dropwise at 0 °C over a period of 1 h. The reaction was continued for 36 h at 0–5 °C, then 3.01 g K$_2$CO$_3$ was added and stirred for 4 h and the insoluble salt was removed by filtration. The product was purified by precipitation in cold petroleum ether and dried under vacuum at 45 °C for 24 h. The product weighted 0.76 g (76.0% yield).

Deprotection of Hydroxyl Group of Diblock Copolymers Poly(styrene)-*b*-Poly(ethylene oxide) at the Junction Point ((PS-*b*-PEO)$_d$)

The (PS-*b*-PEO)$_d$ copolymers with the active hydroxyl group at the junction point were obtained by the cleavage of ethoxyethyl group on (PS-*b*-PEO)$_p$ copolymers. Typically, the (PS-*b*-PEO)$_p$ copolymers (6.60 g, $M_{n(NMR)}$ = 7200 g/mol) were dissolved in 40 mL THF, then 80 mL formic acid was added. The solution was stirred at 35 °C for 5 h and then the formic acid and THF were removed completely under reduced pressure. After the dried residue was dissolved in 40 mL THF again, the KOH (2N) aqueous solution was added dropwise till pH 12.0, then the mixture was refluxed at 65 °C for 24 h and neutralized with HCl (6%) aqueous solution. The formed salts were filtrated, and the product were precipitated in cold petroleum ether and dried under vacuum at 45 °C for 24 h. The product weighted 6.29 g (95.3% yield according to (PS-*b*-PEO)$_p$ added). ^{1}H-NMR (CDCl$_3$) dppm: 0.80 (m, C**H**$_3$CH$_2$—), 1.13 (m, C**H**$_3$CH$_2$O—), 1.26–2.01 (m, 3H, aliphatic main chain —C**H**$_2$CH— of PS block), 2.85–3.53 (m, CH$_3$C**H**$_2$O—, —C**H**(C**H**$_2$OH)O—), 3.60–3.70 (m, 4H, —C**H**$_2$CH$_2$O— of PEO block), 6.30–7.30 (m, 5H, aromatic —C$_6$**H**$_5$ of PS block). $M_{n(NMR)}$ = 7100 g/mol, PDI = 1.06.

Preparation of the Star(poly(styrene)-poly(ethylene oxide)-Poly(ε-caprolactone)) Terpolymers (Star(PS-PEO-PCL)) and Linear Triblock Poly(styrene)-*b*-Poly(ethylene oxide)-*b*-Poly(ε-caprolactone) Copolymers (PS-*b*-PEO-*b*-PCL)

In an 100 mL ampoule, the dried (PS-*b*-PEO)$_d$ (1.39 g, 0.20 mmol, $M_{n(NMR)}$ = 7100 g/mol) in

5 mL dry toluene was added, and then 2.20 mL freshly distilled ε-CL (2.35g, 20.64 mmol) was introduced. The Sn(Oct)$_2$ solution (1.14 mL, 0.5 equiv with respect to the hydroxyl groups) was rapidly injected through a septum by a syringe when the solution was heated to 100 °C, and the polymerization was carried out for 36 h. After the copolymer species was terminated by methanol, the product was precipitated in cold petroleum ether and dried under vacuum at 45 °C for 24 h. The product weighted 3.02 g (80.7% yield according to (PS-b-PEO)$_d$ and ε-CL added). ^{1}H-NMR (CDCl$_3$) δ ppm: 0.80 (m, C$\boldsymbol{H}_3$CH$_2$—), 1.13 (m, C$\boldsymbol{H}_3$CH$_2$O—), 1.26–2.01 (m, 3H, aliphatic main chain —C$\boldsymbol{H}_2$CH— of PS arm), 2.20–2.41 (m, —C$\boldsymbol{H}_2$—CO—O— of PCL arm), 2.85–3.53 (m, CH$_3$C$\boldsymbol{H}_2$O—, —C$\boldsymbol{H}$O—), 3.60–3.70 (m, 4H, —C$\boldsymbol{H}_2$CH$_2$O— of PEO arm), 3.96–4.13 (m, 2H, —C$\boldsymbol{H}_2$—O—CO— of PCL arm) 6.30–7.30 (m, 5H, aromatic —C$_6\boldsymbol{H}_5$ of PS arm). $M_{n(NMR)} = 11,200$ g/mol, $M_{n(NMR)} = 16,600$ g/mol, PDI = 1.19. FTIR (cm^{-1}): 1735 (—COO—).

The linear triblock copolymers PS-b-PEO-b-PCL was also synthesized and used as the comparison with the star(PS-PEO-PCL) copolymers. Similar to the preparation procedure for star (PS-PEO-PCL), 1.41 g (0.20 mmol, $M_{n(NMR)}$ = 7200 g/mol) dried (PS-b-PEO)$_p$ (before the termination with bromoethane), 5 mL dry toluene, 2.20 mL freshly distilled ε-CL (2.35 g, 20.64 mmol) and 1.14 mL Sn(Oct)$_2$ solution was used. The polymerization was also carried out for 36 h under 100 °C, then precipitated in cold petroleum ether and dried under vacuum at 45 °C for 24 h. $M_{n(SEC)} = 15,400$ g/mol, $M_{n(NMR)} = 16,900$ g/mol, PDI = 1.19.

RESULTS AND DISCUSSION

Preparation and Characterization of the Macro-Initiator PS-EEGE

The quantitative reaction between polymeric organolithium and epoxides was always used to design the functionalized polymers because of the high aggregation degree of lithium alkoxides and their disability to initiate the further polymerization.[34a,b,35] In our work, the EEGE which had an oxirane ring and a protected hydroxyl group was designed to cap the "living" PS$^-$Li$^+$ in nonpolar cyclohexane with a small amount of THF (Scheme 1). The additional THF was used to decrease the average degree of aggregation at PS$^-$Li$^+$ chain ends[34b,35a] and promote the effi-

ciency of functionalization (E.F.) between PS$^-$Li$^+$ and EEGE. Obviously, once the EEGE was added, the characteristic red color of PS$^-$Li$^+$ should be turned into light yellow of alkoxides immediately, which proved that the capping reaction proceeded quickly.

After the polymerization was terminated by methanol, the product was purified by precipitating in methanol several times to remove the excess EEGE (EEGE could be dissolved in methanol very well and washed out from PS-EEGE completely). From the SEC results of PS-EEGE [Fig. 1(a, c)], the monomodal and low PDIs (<1.05) confirmed that the "living" anionic polymerization and the capping reaction were successful. However, in the case of PS-EEGE with molecular weigh $M_{n(SEC)}$ = 14,600 g/mol [Fig. 1(b)], there was a small peak corresponding to dimeric product although the PDI of major peak was low (1.04). The inset Figure was the expanded region for dimeric product. According to the report from Quirk and Chen,[35a] the dimeric product was observed when styrene oxide was used to cap PS$^-$Li$^+$ and explained as Electron-transfer Mechanism.[35e] However, in their previous work, they also showed that the dimeric product might be produced in the presence of oxygen or carbon dioxide.[35b,36] To clarify the mechanism in our experiment, the "living" PS$^-$Li$^+$ species were terminated by methanol in the presence of air (oxygen and carbon dioxide), and a small peak with dimeric product at shorter elution time was really found [Fig. 1(c')]. It was obvious that the existence of the dimeric product was mainly attributed to the trace oxygen or carbon dioxide which might be introduced during the addition of EEGE. Especially, the PS$^-$Li$^+$ species with the higher molecular weight was more sensitive to the air.

The functionalized polymer with defined structure could be well confirmed by MALDI-TOF MS.[37] Typically, the MALDI-TOF MS of PS-EEGE was shown in Figure 2, in which dithranol (matrix), silver trifluoroacetate (cationizing salt), and the reflecton mode were selected for PS.[38] The peak with the highest intensity at m/z = 2917.8 (a monoisoptic mass peak) was assigned to the EEGE-functionalized PS-EEGE [C$_4$H$_9$—(C$_8$H$_8$)$_{25}$—C$_7$H$_{15}$O$_3$.Ag$^+$ = 2917.8, cal. 2917.65 (calculated from the "Data Explorer TM software 4.0")], and the m/z spacing of 104.1 between the adjacent peaks was the mass of St monomer unit. The absence of molecular weight corresponding to the
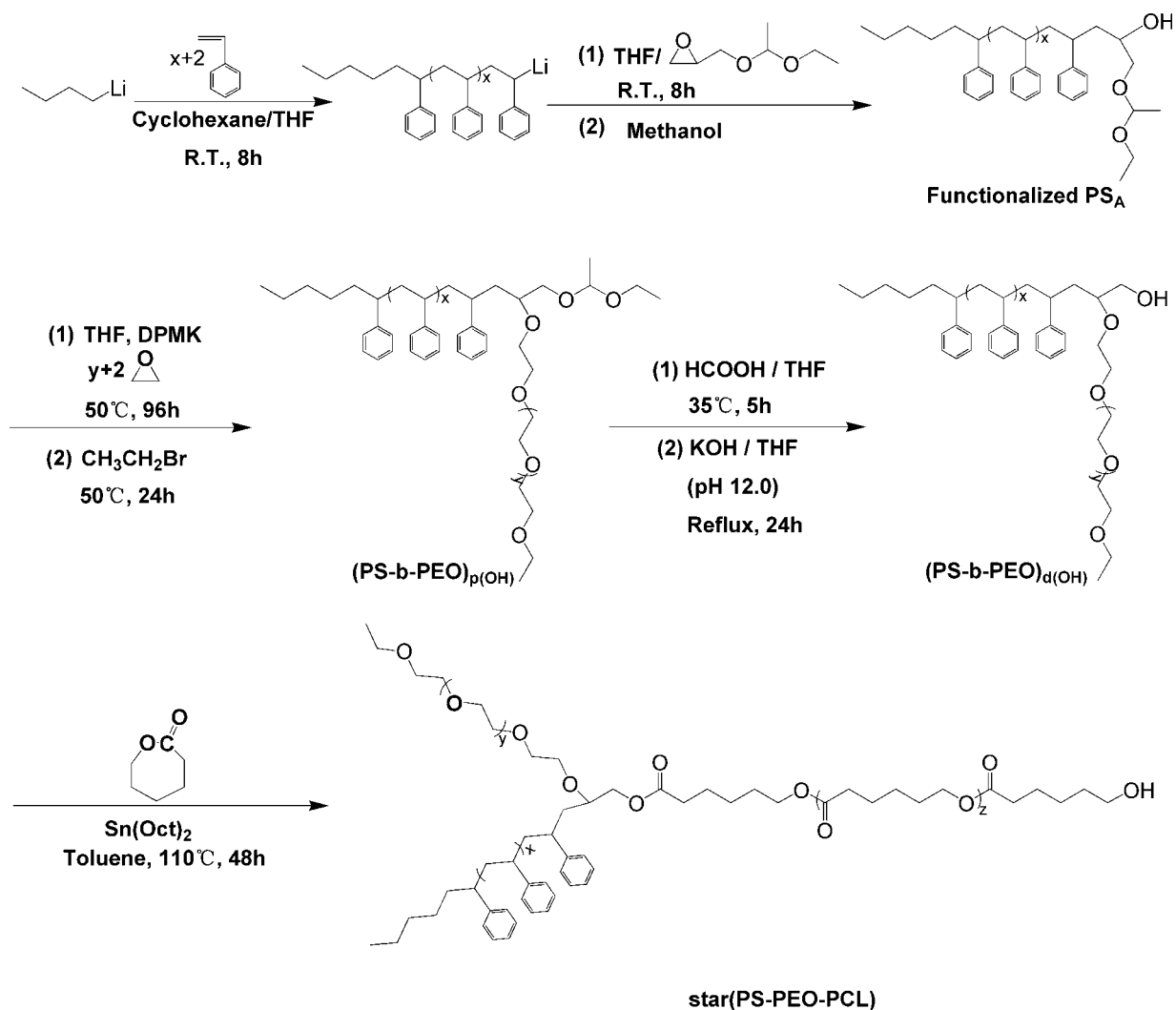
Scheme 1. Preparation of star(PS-PEO-PCL), diblock copolymers and macro-initiator PS-EEGE.

dimeric product in the MALDI-TOF MS was consistent well with the SEC results shown in Figure 1(a). When the mass spectrum was expanded, a series of minor peaks could be identified and the adjacent peaks were also separated by the mass of a St unit 104.1. According the capping reaction, it was presumed that this series of peaks was attributed to the unfunctionalized PS resulting from the trace impurities in EEGE. From the MALDI-TOF MS spectra, the number average molecular weight $M_{n(\text{MALDI-TOF MS})}$ of 2640.2 was also calculated, which was quite consistent with the values determined by SEC and ^{1}H-NMR.

To finely characterize the PS-EEGE, the crude material was purified by column chromatography according to the TLC results, then the

purified PS-EEGE, the crude PS-EEGE and their precursor of unfunctionalized PS were determined by MALDI-TOF MS (Fig. 3). Obviously, the m/z spacing of 104.1 between adjacent peaks in each spectrum was equal to the mass of St unit. When the spectra were expanded from m/z of 3010–3480, it was observed an increase of m/z 145.8 from peak $A_2[C_4H_9$—$(C_8H_8)_{29}$—$H.Ag^+ = 3186.0$Da, cal. $m/z = 3185.80]$ to peak $B_3[C_4H_9$—$(C_8H_8)_{29}$—$C_7H_{15}O_3.Ag^+ = 3331.8$, cal. $m/z = 3331.90]$, which was attributed to the mass of EEGE. Furthermore, there was a series of lower peaks B′ accompanied with the series B, and it was ascribed to the unfunctionalized PS chains. After the purification by column chromatography, the disappearance of series B′, and the unique
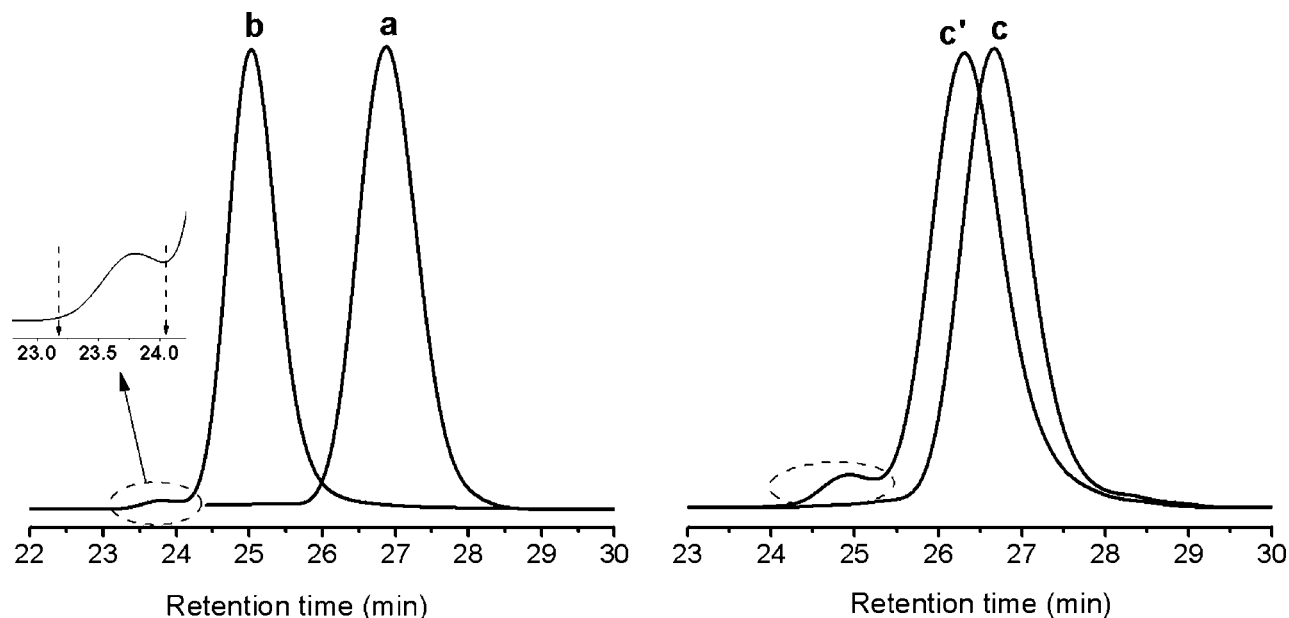
Figure 1. SEC curves of the functionalized PS-EEGE (a, $M_{\text{n(SEC)}}$ = 2500 g/mol; b, $M_{\text{n(SEC)}}$ = 14,600 g/mol; c, $M_{\text{n(SEC)}}$ = 3100 g/mol) and the precursor of unfunctionalized PS for PS-EEGE(c) (c′, $M_{\text{n(SEC)}}$ = 3500 g/mol).

series C confirmed the successful remove of the trace impurities.

The ^{1}H-NMR spectra of functionalized PS-EEGE and unfunctionalized PS($M_{\text{n(SEC)}}$ = 2800 g/mol) were shown in Figure 4. Besides the resonance signal at 0.80 ppm (a) attributed to α-methyl group protons (—C**H**$_3$) and the signal at 6.30–7.30 ppm (f) assigned to aromatic protons (—C$_6$**H**$_5$) on PS chain, the appearance of ω-ethoxyethyl group proton (—OC**H**(CH$_3$)O—) at 4.65–4.76 ppm (j) and ω-hydroxymethyl group

proton (—C**H**(OH)—) at 3.52 ppm (h) in Figure 4(B) proved the successful addition of EEGE to PS chain end. From the ^{1}H-NMR spectra, the number-average molecular weight of PS-EEGE and the efficiency of functionalization between EEGE and PS$^-$Li$^+$ could be determined by end group analysis using Formula (1) and (2) respectively (Fig. 4 and Table 1).

$$M_{\text{n(NMR)PS}} = \frac{3 \times 104 \times A_{\text{f}}}{5 \times A_{\text{a}}} + 57 + 147 \quad (1)$$

$$\text{E.F.} = \frac{3 \times A_{\text{j}}}{A_{\text{a}}} \times 100\% \quad (2)$$

Where A_{a}, A_{f}, and A_{j} were the integral area of the characteristic α-methyl group protons (—C**H**$_3$) at 0.80 ppm (a), the aromatic protons (—C$_6$**H**$_5$) at 6.30–7.30 ppm (f) and the ω-ethoxyethyl group proton (—OC**H**(CH$_3$)O—) at 4.65–4.76 ppm (j) on PS chain respectively. The value of 104 and 57 were the molecular weight of St monomer unit and the mass of residual butyl group (—C$_4$H$_9$) at α-end of PS-EEGE respectively, the value of 147 was the mass sum of ω-end cap molecule EEGE (C$_7$H$_{14}$O$_3$) and a proton (—H).

According to the literature,[34] the reaction between the PS$^-$Li$^+$ and 1-butene oxide, and propylene oxide in toluene was highly regioselective by formation of the secondary alcohol at
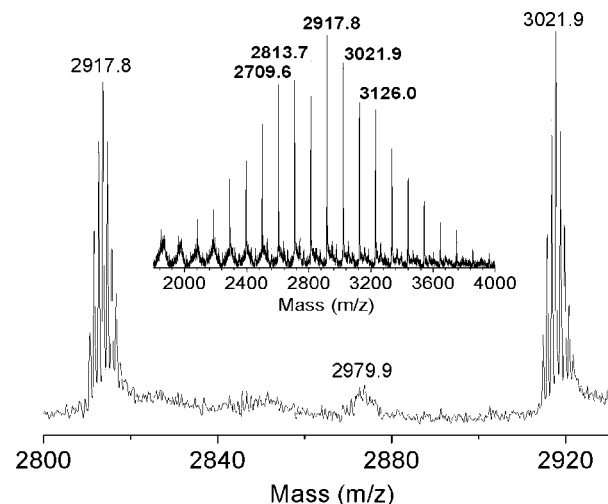

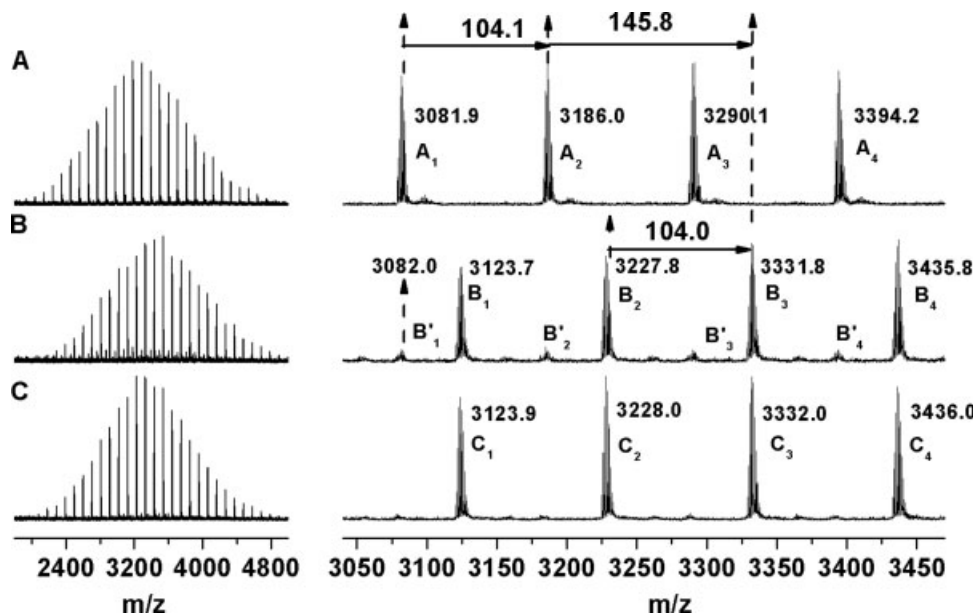**Figure 2.** The MALDI-TOF MS of PS-EEGE ($M_{\text{n(SEC)}}$ = 2800 g/mol, PDI = 1.04).

Figure 3. The MALDI-TOF MS of PS-EEGE (**B** and **C**, $M_{n(SEC)}$ = 3100 g/mol) and its precursor of unfunctionalized PS (**A**, $M_{n(SEC)}$ = 3500 g/mol).

the chain end predominantly, resulting from the attack of anions at the least hindered carbon because of the high steric effects of the methyl or ethyl group. While in the case of 3,4-epoxy-1-butene and styrene oxide,[35] there was almost not regioselective because the steric and electronic factors were affecting the regiochemistry simultaneously.
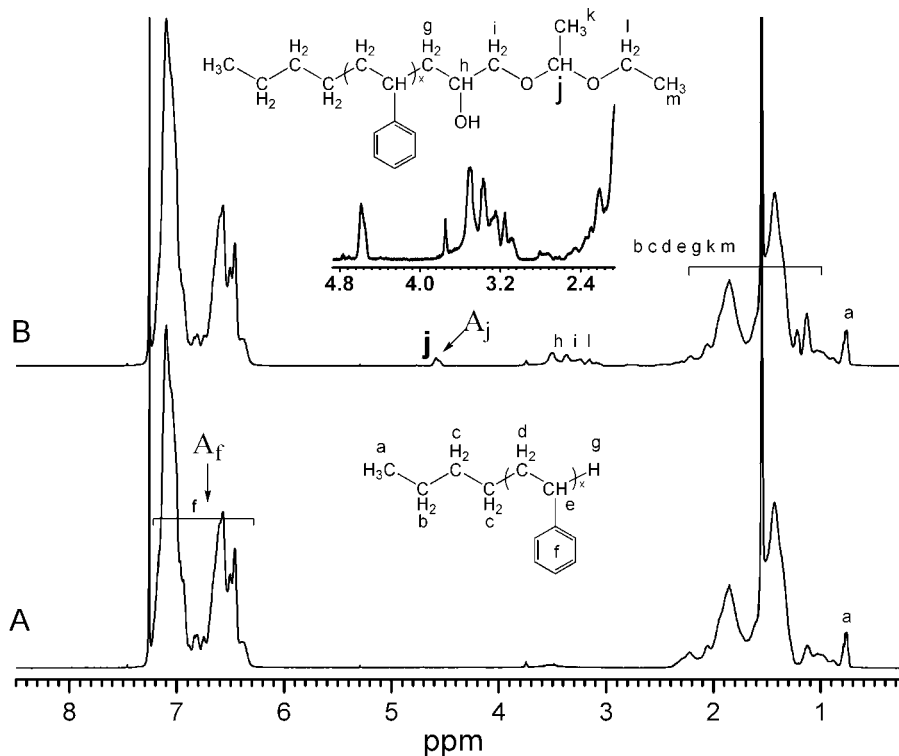
Figure 4. ^{1}H-NMR spectra (CDCl$_3$) of (**A**) PS-EEGE and (**B**) its precursor of the unfunctionalized PS.

Table 1. Polymerization Data of the Star(PS-PEO-PCL), Diblock Copolymers and Macro-Initiator PS-EEGE

	PS					PS-b-PEO				Star(PS-PEO-PCL)		
Polymer[a]	$M_{n(SEC)}$[b] (g/mol)	$N.$[c]	PDI[b]	$M_{n(NMR)}$[d] (g/mol)	E.F.[e] (%)	$M_{n(NMR)}$[f] (g/mol)	PDI[b]	$M_{n(NMR)}$[g] (g/mol)	$N.$[c]	$M_{n(NMR)}$[h] (g/mol)	$N.$[c]	PDI[b]
$S_{23}EO_{33}CL_{44}$	2500	24	1.04	2500	95.4	6200	1.09	6000	80	10,800	42	1.15
$S_{28}EO_{39}CL_{33}$										8900	25	1.12
$S_{13}EO_{19}CL_{68}$	2800	28	1.04	2900	94.2	7100	1.05	7000	93	22,100	132	1.18
$S_{17}EO_{26}CL_{57}$						7200	1.06	7100	95	16,600	83	1.16
$S_{21}EO_{38}CL_{41}$	7500	72	1.03	7500	92.1	21,100	1.04	21,000	307	35,300	125	1.12
$S_{13}EO_{18}CL_{69}$						18,500	1.03	18,300	245	59,100	358	1.28
$S_{28}EO_{34}CL_{38}$	14,600	138	1.04	14,400	96.0	32,300	1.06	32,300	409	51,900	171	1.22

[a] The subscripts represent the weight percent of each arm (S-styrene, EO-ethylene oxide, CL-ε-caprolactone).

[b] Determined by SEC-RI with THF as solvent using PS standards.

[c] $N.$ was the numbers of the monomer units of each arm.

[d] $M_{n(NMR)}$ of PS-EEGE (noted as $M_{n(NMR)PS}$) was determined by ^{1}H NMR in CDCl$_3$ by the end group analysis based on the integral area using the Formula (1) (see Fig. 4).

[e] E.F. (Efficiency of Functionalization) was determined by ^{1}H NMR in CDCl$_3$ using the Formula (2) (see Fig. 4).

[f] $M_{n(NMR)}$ of (PS-b-PEO)$_p$ (noted as $M_{n(NMR)(PS-b-PEO)p}$) was determined by ^{1}H NMR in CDCl$_3$ using the known $M_{n(NMR)PS}$ and $M_{n(SEC)}$ of PS-EEGE (noted as $M_{n(SEC)PS}$) according to the Formula (3) (see Fig. **7**).

[g] $M_{n(NMR)}$ of (PS-b-PEO)$_d$ (noted as $M_{n(NMR)(PS-b-PEO)d}$) was determined by ^{1}H NMR in CDCl$_3$ using the known $M_{n(NMR)PS}$ and $M_{n(SEC)PS}$ according to the Formula (4) (see Fig. 7).

[h] $M_{n(NMR)}$ of star(PS-PEO-PCL) (noted as $M_{n(NMR)star(PS-PEO-PCL)}$) was determined by ^{1}H NMR in CDCl$_3$ using the known $M_{n(SEC)PS}$ and $M_{n(NMR)(PS-b-PEO)d}$ according to the Formula (5) (see Fig. 10).

In our work, the epoxide with a substituted ethoxyethyl group was used as the functionalization agent to cap the polystyrene anions. In the ^{1}H-NMR of the functionalized PS-EEGE [Fig. 4(B)], the peaks at 2.75 ppm attributed to the methine proton (—C**H**CH$_2$OH) was detected, which showed that the addition of PS$^-$Li$^+$ to the most hindered carbon also occurred. By calculating the integral area of ω-ethoxyethyl group proton (—OC**H**(CH$_3$)O—) at 4.65–4.76 ppm and the one of methine proton (—C**H**CH$_2$OH) at 2.75 ppm, it was confirmed that the product con- tained 15.3 mol % of PS-EEGE resulting from addition to the most hindered carbon and 84.7 mol % resulting from the least hindered carbon.

Comprehensively, all the results of ^{1}H-NMR, SEC, and MALDI-TOF MS well confirmed that the capping reaction of PS$^-$Li$^+$ species with EEGE was successful.

Preparation and Characterization of (PS-b-PEO)$_p$ Copolymers

The diblock copolymers of (PS-b-PEO)$_p$ with the ethoxyethyl-protected hydroxyl group at the junction point were prepared by ROP of EO using PS-EEGE as macro-initiator and DPMK as deprotonated agent (Scheme 1). It was well known that the exchange rate of protons between hydroxyl groups and alkoxides was much faster than that of

the propagation, and usually, 20 mol % of the hydroxyl groups were deprotonated by DPMK when small molecular weight initiator was used.[39] However, in the case of the macro-initiator star (PS(OH))$_3$, 60–80 mol % of the hydroxyl groups was deprotonated.[29,40] In our system, when the DPMK solution with the R (R was defined as the molar ratio of DPMK to the hydroxyl groups, namely R = (mol$_{DPMK}$/mol$_{-OH}$) $\times$ 100%) of 80% was used, most of the macro-initiator PS-EEGE was left after the ROP of EO (Fig. 5b$_{11}$). And even if the R value exceeded 100%, the macro-initiator PS-EEGE was still deprotonated partially and there were always some PS homopolymer left (Fig. 5b$_{12}$ and b$_{21}$). Thus, we presumed that the consumption of DPMK solution with the high R value (exceeded the expected the stoichiometry) was largely because of the existence of the impurities in PS-EEGE.

To well control the addition of DPMK solution and the complete initiation of PS-EEGE, the macro-initiator was precipitated five (or more) times by methanol and then the content of DPMK was well controlled and the hydroxyl groups were almost completely deprotonated with the R of 100%, and the ROP of EO was also well controlled and there was almost no PS homopolymer left.

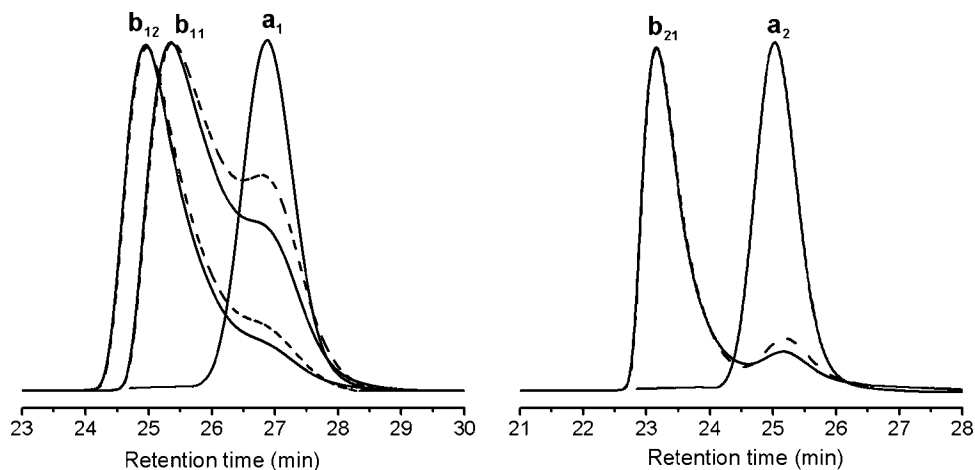As described earlier, sometimes, there was homopolymer PS accompanied in the product

Figure 5. SEC curves of crude $(PS\text{-}b\text{-}PEO)_p$ block copolymers(b_{11}, b_{12}, b_{21}) before the termination with bromoethane and their corresponding precursors of PS-EEGE (a_1, $M_{n(SEC)}$ = 2800 g/mol; a_2, $M_{n(SEC)}$ = 7500 g/mol) (SEC-RI Signal, solid line; SEC-UV Signal, dash line).

and the former could be removed easily from the $(PS\text{-}b\text{-}PEO)_p$ diblock copolymer by extraction with cyclohexane.[41] The SEC results of the purified $(PS\text{-}b\text{-}EPO)_p$ copolymers in Figure 6(**b**, $M_{n(NMR)(PS\text{-}b\text{-}PEO)p}$ = 21,100 g/mol) showed a monomodal curve, which meant that the PS homopolymer had been extracted by cyclohexane completely. The superimposable curves achieved by RI and UV (at 254 nm) detector further confirmed that no PEO homopolymer occurred in our conditions (the PEO homopolymer had no absorbance at 254 nm, so RI and UV were used simultaneously.). The low PDIs (<1.10) of $(PS\text{-}b\text{-}PEO)_p$ copolymers proved that the ROP of EO initiated by coinitiation system of PS-EEGE and DPMK was well controlled. On the other hand, the asymmetrical SEC traces with a tail at longer elution time were always detected due to the strong adsorption of PEO segment by the column in THF solvent (THF was not a good solvent for PEO segment), and the similar phenomenon was also reported by other groups.[42] Although the tail was overlapped with the initial PS-EEGE region, but the absence of a shoulder peak further proved that there was not any PS homoplomer coexisted in PS-b-PEO.

Figure 7(C) showed the ^{1}H-NMR spectrum of purified $(PS\text{-}b\text{-}PEO)_p$ copolymers ($M_{n(NMR)}$ = 7200 g/mol), besides the resonance signal at 6.30–7.30 ppm(f) for aromatic protons ($-C_6\boldsymbol{H}_5$) on PS block, the appearance of resonance signal at 3.53–3.70 ppm(n) for methylene group protons ($-C\boldsymbol{H}_2CH_2O$) on PEO block confirmed the successful polymerization of EO, and the signal

at 4.65–4.76 ppm(j) proved that the ethoxyethyl group proton ($-OC\boldsymbol{H}(CH_3)O-$) was still at the junction point after ROP of EO. The molecular weight of $(PS\text{-}b\text{-}PEO)_p$ determined by SEC using THF as eluent was unreliable because the PS-b-PEO might aggregated into micellar structures by self-association in THF.[42c,43] Alternatively, the most reliable method to determine the actual molar mass of $(PS\text{-}b\text{-}PEO)_p$ copolymers was the ^{1}H-NMR. To avoid the formation of micelles in a selective solvent,[44] the ^{1}H-NMR measurement was carried out in $CDCl_3$, which was a good solvent for both PEO and PS blocks. The molecular weight of $(PS\text{-}b\text{-}PEO)_p$ ($M_{n(NMR)(PS\text{-}b\text{-}PEO)p}$) was determined according to the already known
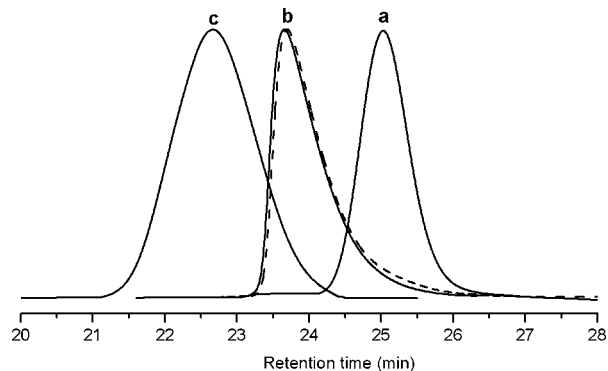

Figure 6. SEC curves of star(PS-PEO-PCL) (c) and its corresponding precursors of PS-EEGE (a) and (PS-b-PEO)$_p$ (b). (Polymer $S_{21}EO_{38}CL_{41}$: a, $M_{n(SEC)}$ = 7500 g/mol; b, $M_{n(NMR)}$ = 21,100 g/mol; c, $M_{n(NMR)}$ = 35,300 g/mol. solid line : SEC-RI signal; dash line: SEC-UV signal).
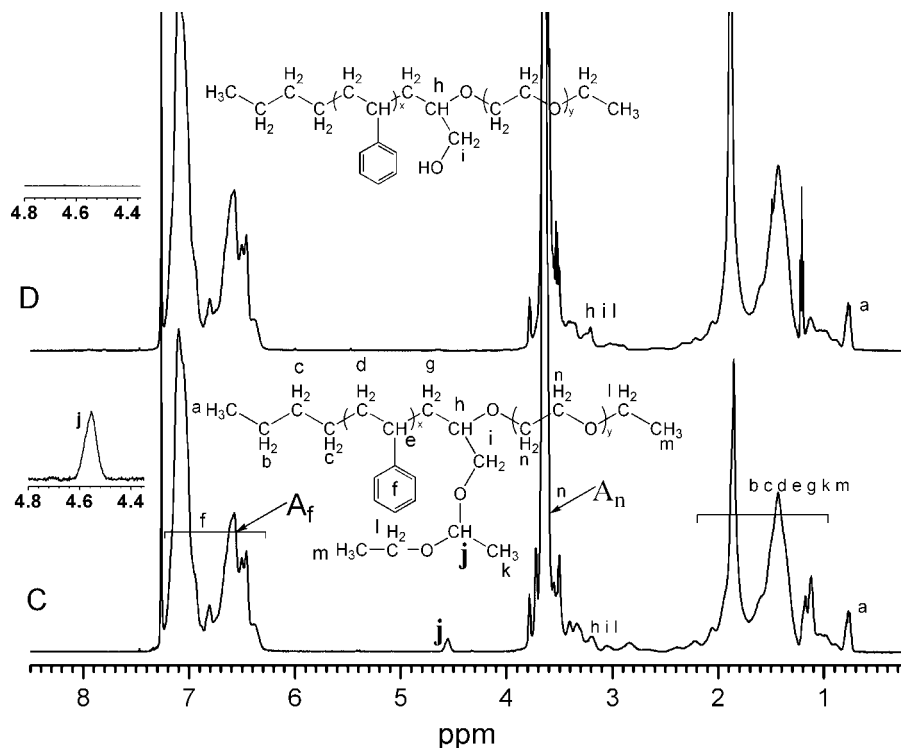
Figure 7. ^{1}H-NMR spectra (CDCl$_3$) of (**C**) (PS-*b*-PEO)$_p$ and (**D**) (PS-*b*-PEO)$_d$ copolymer.

$M_{n(SEC)PS}$ and $M_{n(NMR)PS}$ of PS-EEGE using Formula (3) [Fig. 7 and Table 1].

$$M_{n(NMR)(PS\text{-}b\text{-}PEO)p} = \frac{5 \times A_n \times M_{n(SEC)PS}}{4 \times 104 \times A_f} \times 44 + M_{n(NMR)PS} + 28 \quad (3)$$

Here, A_n was the integral area of the peak at 3.53–3.70 ppm(n) for methylene group protons ($-C\boldsymbol{H}_2CH_2O$) on PEO block, the value 44 was the molecular weight of EO monomer unit, and the value 28 was the mass difference between the ethyl group ($-C_2H_5$) and a proton ($-H$). Others were the same as defined before.

After the polymerization of EO initiated by PS-EEGE, the "living" PEO species were blocked by bromoethane. The high blocking efficiency was necessary for the next ROP of ε-CL, otherwise the unterminated PEO species would initiate the polymerization of ε-CL continuously. From the ^{1}H-NMR spectrum of (PS-*b*-PEO)$_p$ in Figure 7(C), it was difficult to detect the existence or content of ethyl group protons at the end of diblock copolymers because of the overlapping of ethyl group protons with other protons. To resolve this problem, two methods were suggested: (1) monomethoxy-blocked PEO (mPEO)

was used as the model polymer, on which the hydroxyl group was blocked by bromoethane in the same conditions as the (PS-*b*-PEO)$_p$ copolymers used (using DPMK as deprotonation agent for hydroxyl groups). From the MALDI-TOF MS spectra (Fig. 8), it was observed that there was an increase of m/z 27.9 from the peak [CH$_3$O—(C$_2$H$_4$O)$_{175}$—H.Na = 7720.1, cal. m/z = 7719.9] in series A to the peak [CH$_3$O—(C$_2$H$_4$O)$_{175}$—H.Na = 7748.1, cal. m/z = 7748.0] in series B. The value of 27.9 corresponding to the mass difference between the ethyl group
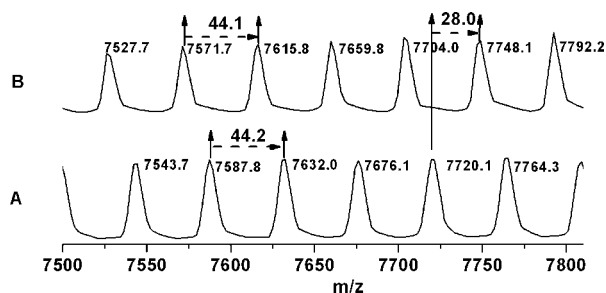

Figure 8. The MALDI-TOF MS of model mPEO (**A**) before the termination and (**B**) after the termination with bromoethane. ($M_{n(SEC)}$ = 7800 g/mol, PDI = 1.10).
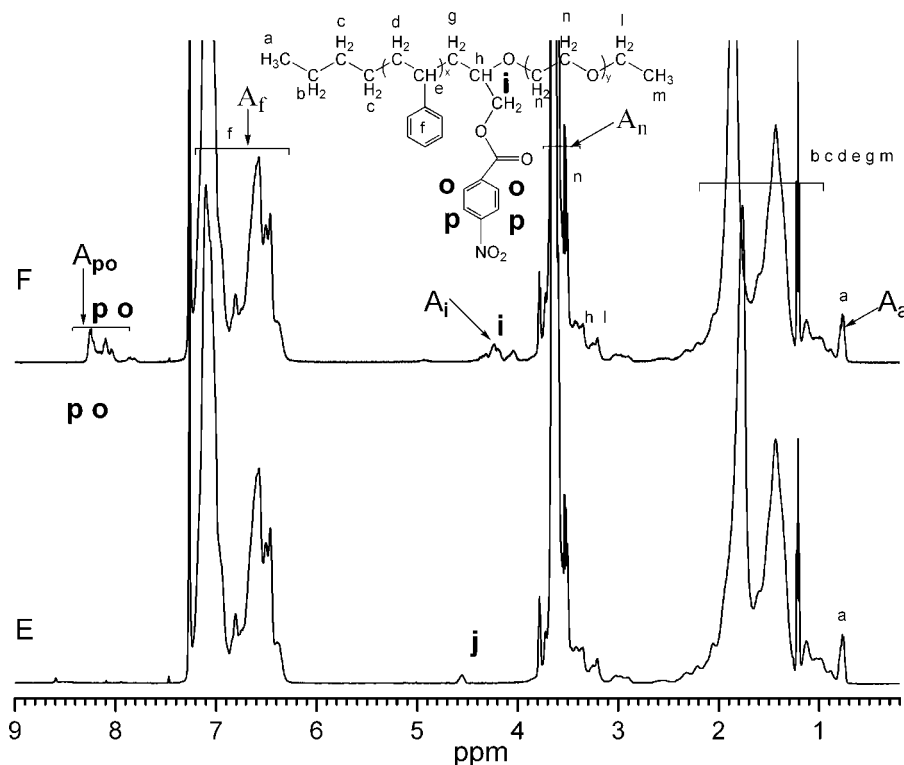
Figure 9. ^{1}H-NMR spectra(CDCl$_3$) of (**E**) product of (PS-b-PEO)$_p$ with pNBC and (**F**) product of (PS-b-PEO)$_d$ with pNBC copolymer.

(—C$_2$H$_5$) and a proton, and the regular m/z shift well confirmed that the hydroxyl groups at PEO end were completely blocked by bromo-ethane under the experimental conditions. (2) The p-Nitrobenzoyl chloride (pNBC) was also used to probe the reaction efficiency of hydroxyl group at the end of (PS-b-PEO)$_p$. If there were some unblocked species, the (PS-b-PEO)$_p$ should react with pNBC in pyridine and the obtained product could be detected and evaluated by ^{1}H-NMR spectrum [Fig. 9(E)]. However, the ^{1}H-NMR (the sample was scanned for 128 times, and the sensitivity of the instrument was: 0.1% ethylbenzene; NS = 1, LB = 1; S/N = 300:1) spectrum of the reacted product was almost the same as the one shown in Figure 7(C) and not any signal for the protons of —C$_6$H$_4$—NO$_2$ or —CH_2—COO— were detected. As the compari-son, the pNBC was also reacted with (PS-b-PEO)$_d$ and ^{1}H-NMR spectrum of the product was shown in Figure 9(F), in which the reso-nance signal at 8.00-8.42 ppm (o, p) attributed to the aromatic protons (—C$_6$H$_4$—NO$_2$) of pNBC and the signal at 3.98-4.28 ppm (i) for the methy-lene group protons (—CH_2COO—) connected with the ester bond were detected. Obviously,

the nonexistence of the resonance signal [Fig. 9(E)] for —C$_6$H$_4$—NO$_2$ further confirmed the complete reaction between the hydroxyl groups (on (PS-b-PEO)$_p$) and bromoethane. Thus, it could be reliably concluded that all the PEO oxanionic species were blocked by bromoethane.

Preparation and Characterization of (PS-b-PEO)$_d$ Copolymers

After the hydroxyl groups at the diblock copoly-mer end was completely deactivated, the (PS-b-PEO)$_d$ copolymers were obtained by the cleavage of ethoxyethyl group (—OCH(CH$_3$)OC$_2$H$_5$) at the junction point of (PS-b-PEO)$_p$ copolymers. Figure 7(D) indicated the ^{1}H-NMR spectrum of (PS-b-PEO)$_d$ copolymers ($M_{n(NMR)}$ = 7100 g/mol) and it was observed that the resonance signal of ethoxyethyl group proton (—OCH(CH$_3$)O—) at 4.65–4.76 ppm (j) disappeared completely, which confirmed that the ethoxyethyl group could be removed completely by the successive acidolysis and saponification procedure. The molecular weight of (PS-b-PEO)$_d$ ($M_{n(NMR)(PS-b-PEO)d}$) was also determined by ^{1}H-NMR spectrum using Formula (4) [Fig. 7 and Table 1].
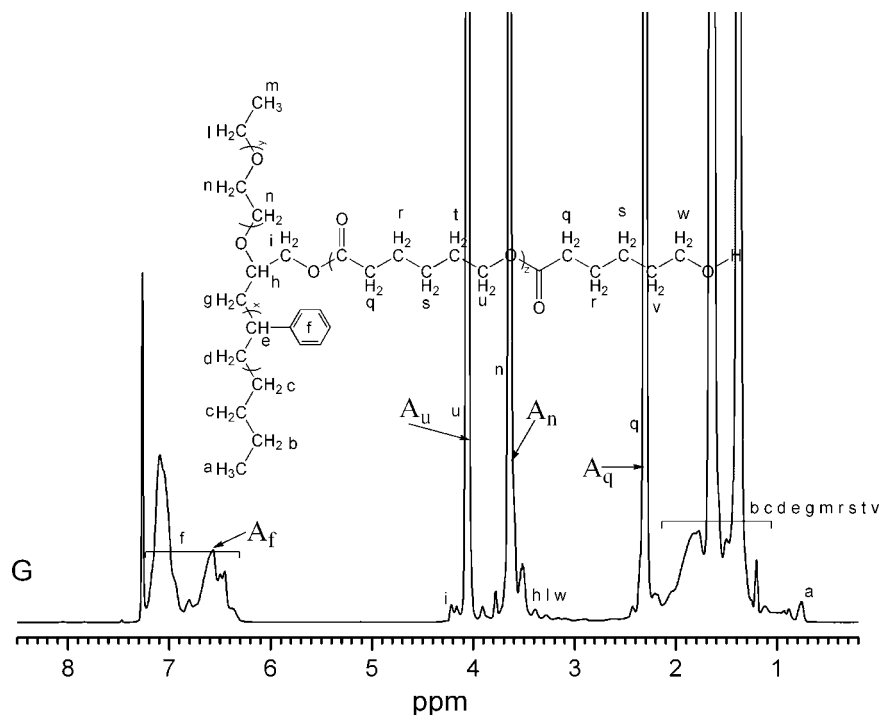
Figure 10. ^{1}H-NMR spectrum(CDCl$_3$) of (**G**) star(PS-PEO-PCL) terpolymer.

$$M_{n(NMR)(PS\text{-}b\text{-}PEO)d} = \frac{5 \times A_n \times M_{n(SEC)PS}}{4 \times 104 \times A_f} \times 44$$
$$+ M_{n(NMR)PS} + 28 - 72 \quad (4)$$

where the value 72 was the mass difference between ethoxyethyl group ($-OCH(CH_3)OC_2H_5$) and a proton ($-H$), others were the same as defined before.

The value of $M_{n(NMR)(PS\text{-}b\text{-}PEO)d}$ was close to its corresponding $M_{n(NMR)(PS\text{-}b\text{-}PEO)p}$, which confirmed that no degradation occurred on PEO chain during the acidolysis in formic acid/THF and saponification in KOH solution of water/THF (pH = 12.0) successively.

Preparation and Characterization of the Star(PS-PEO-PCL) Terpolymers

Once the hydroxyl groups at (PS-b-PEO)$_p$ end were completely blocked and deactivated, only the hydroxyl groups recovered at the junction point could initiate the ROP of ε-CL. The third arm of PCL was prepared by ROP of ε-CL using (PS-b-PEO)$_d$ as macro-initiator and Sn(Oct)$_2$ as catalyst (Scheme 1). It had been reported that the Sn(Oct)$_2$ could react fast with hydroxyl groups to form tin(II) alkoxide initiating species reversibly. Thus, the hydroxyl group was not

only an initiator but also a chain transfer agent at a given ratio of [ROH]/[Sn(Oct)$_2$] higher than 2.0.[45]

The SEC results of star(PS-PEO-PCL) terpolymers were shown in Figure 6(c, $M_{n(NMR)} = 35,300$ g/mol) and the actual molecular weight was determined by ^{1}H-NMR spectrum. Figure 10(G) showed the ^{1}H-NMR spectrum of star(PS-PEO-PCL) terpolymers, besides the characteristic signal at 6.30–7.30 ppm (f) for aromatic protons ($-C_6H_5$) on PS arm and that at 3.43–3.83 ppm (n) for methylene group protons ($-CH_2CH_2O-$) on PEO arm, the appearance of the resonance signal at 2.20–2.41 ppm (o) and 3.96–4.13 ppm (s) for methylene group protons on PCL arm confirmed that the synthesis of the star(PS-PEO-PCL) was successful. The molecular weight of star (PS-PEO-PCL) $M_{n(NMR)star(PS\text{-}PEO\text{-}PCL)}$ were determined using Formula (5). [Fig. 10 and Table 1].

$$M_{n(NMR)star(PS\text{-}PEO\text{-}PCL)} = \frac{5 \times A_s \times M_{n(SEC)PS}}{2 \times 104 \times A_f} \times 114$$
$$+ M_{n(NMR)(PS\text{-}b\text{-}PEO)d} \quad (5)$$

Here, A_s was the integral area for methylene group protons at 3.96–4.13 ppm (s), the value 114 was the molecular weight of ε-CL monomer
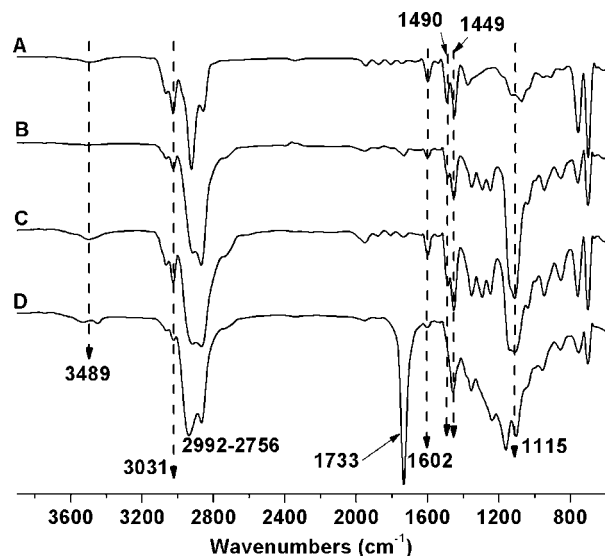
Figure 11. FTIR spectra of (film on NaCl crystal): (**A**) PS-EEGE; (**B**) (PS-*b*-PEO)$_p$ copolymer; (**C**) (PS-*b*-PEO)$_d$ copolymer; (**D**) star(PS-PEO-PCL) terpolymer.

unit and others were the same as defined before.

To find the direct evidence that we actually prepared the ABC 3-Miktoarm star(PS-PEO-PCL) terpolyemrs rather than the linear ABC triblock copolymers PS-*b*-PEO-*b*-PCL, a series of well-defined linear triblock copolymers PS-*b*-PEO-*b*-PCL with the similar molecular weight of star copolymer was synthesized by successive polymerization using the diblock copolymer PS-*b*-PEO as initiator. However, only the difference of SEC between them was found due to different hydrodynamic volume[46] originating from their structure respectively, the star-shaped terpolymers had a shorter elution time than the corresponding linear triblock copolymer in SEC curves. On the other hand, according to the literature,[12,13a,15,47] the distinct microdomain morphologies between the linear triblock copolymers and star-shaped terpolymers could also be observed due to their different topological structure. The detailed work about this part is undergoing and would be discussed elsewhere.

The structure of targeted star terpolymers and intermediates were further verified by FTIR spectra and the Figure 11 showed the FT-IR spectra of PS-EEGE (**A**), (PS-*b*-PEO)$_p$ (**B**), (PS-*b*-PEO)$_d$ (**C**), and star(PS-PEO-PCL) (**D**) respectively. A multipeak at 3031 (benzene ring = C—H), 1602, 1490, 1449 cm^{-1} (benzene bend vibration) and a strong band at 2992–2756 cm^{-1} for the methylene group (—CH$_2$CH—) attrib-

uted to PS were detected in all four spectra (**A**, **B**, **C**, **D**), which confirmed the existence of PS chains. The strong band at 1115 cm^{-1} was attributed to the ether linkage (—C—O—C—) on PEO chains (**B**, **C**, **D**), and the peak at 1733 cm^{-1} was attributed to the characteristic ester linkage (—COO—) on PCL chains (**D**). The peak at 3489 cm^{-1} corresponding to the hydroxyl groups on (co)polymer was also detectable in **A**, **C**, and **D** spectra, while no such peak in B spectrum was found. Thus, the FTIR spectra were consistent well with the (co)polymer structure.

CONCLUSIONS

The ABC 3-Miktoarm star-shaped terpolymers of star(PS-PEO-PCL) were prepared successfully by combination of the "living" anionic polymerization with the ROP mechanism using the macro-initiator technique successfully. Particularly, the protected glycidol with potential multifunctional groups was used as the cap molecule. The polymerization could be controlled smoothly by the variation of the functional groups and each arm length of the star terpolymers could be tuned elaborately.

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