

# Synthesis of A Novel Kind of Amphiphilic Graft Copolymer with Miktoarm Star-shaped Side Chains

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## Supporting Information

### Experimental section

**Materials.** Styrene (St) was washed with 10% NaOH aqueous solution followed by water three times successively, dried over  $\text{CaH}_2$  and distilled under reduced pressure. Ethylene oxide (EO) was dried over  $\text{CaH}_2$  and then distilled, stored at  $-20\text{ }^\circ\text{C}$  before use. Glycidol (Acros) and 1,1-Diphenylmethane (99%) were dried over  $\text{CaH}_2$  and distilled under reduced pressure, stored at  $-20\text{ }^\circ\text{C}$  before use. Triethylene glycol (TEG) was distilled from  $\text{CaH}_2$  under reduced pressure, and the fraction at  $134\text{ }^\circ\text{C}$  /90 Pa was collected. Bromoethane, N,N-dimethylformamide (DMF), toluene, cyclohexane, 1-butyl chloride, ethyl vinyl ether (98%, Aldrich), propargyl bromide ( $\square$ 99%) were dried over  $\text{CaH}_2$  and distilled just before use. 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. Copper(I) bromide( $\text{CuBr}$ , 95%) was stirred overnight in acetic acid, filtered, washed with ethanol and diethyl ether successively, and dried in vacuo. Formic acid, sodium azide ( $\text{NaN}_3$ , >98%), potassium hydroxide

(KOH) were used as received. All other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. (SCR) and used as received, unless otherwise noted.

Diphenylmethylpotassium (DPMK) solution was freshly prepared according to the literature<sup>S1</sup>, the concentration was 0.61 mol/L. Ethoxyethyl glycidyl ether (EEGE) was synthesized from glycidol and ethyl vinyl ether according to Fitton et al.<sup>S2</sup>. *n*-Butyllithium (*n*-BuLi) with a concentration of 1.10 mol/L was prepared and analyzed according to the literature<sup>S3,S4</sup>.

**Instrumentation.** 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 5μm LP gel column (500 Å, molecular range 500–2×10<sup>4</sup> g/mol) and two 5 μm LP gel mixed bed column (molecular range 200–3×10<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 (FT-IR) spectra were recorded on a Magna-550 FT-IR spectrometer. 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.

**Preparation of Functionalized α-butyl-ω-hydroxyl, ω'-ethoxyethyl-Poly(styrene) (Polymer 1).** The anionic polymerization of styrene was carried out under nitrogen atmosphere. Typically, to a 500 ml dried ampoule, styrene (16.0 ml, 14.6 g, 140.4 mmol), cyclohexane (160 ml) and THF (4 ml) was charged under nitrogen atmosphere, then *n*-BuLi solution (7.8 ml, 8.6 mmol) was injected by a syringe under magnetic stirring. The reaction was kept at room temperature for 8 h, then the mixture of EEGE (8 ml, 54.8 mmol) and THF (8 ml) were added, and the system was stirred for another 8 h continuously before termination by methanol. The product was purified by dissolution/precipitation twice with THF/methanol, and the obtained functional polymer **1** was dried under vacuum at 40 °C for 12 h until constant weight (14.2 g, yield: 97.3%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 0.80 (**CH**<sub>3</sub>CH<sub>2</sub>–), 1.13 (**CH**<sub>3</sub>CH<sub>2</sub>O–),

1.22 ( $-\text{CH}(\text{CH}_3)-$ ), 1.26–2.01 (m, 3H, aliphatic main chain  $-\text{CH}_2\text{CH}-$  of PS), 3.09–3.43 (m,  $\text{CH}_3\text{CH}_2\text{O}-$ ,  $-\text{CH}(\text{OH})\text{CH}_2\text{O}-$ ), 3.52 ( $-\text{CH}(\text{OH})-$ ), 4.65–4.76 ( $-\text{OCH}(\text{CH}_3)\text{O}-$ ), 6.30–7.30 (m, 5H, aromatic  $-\text{C}_6\text{H}_5$  of PS chain),  $M_{n,\text{NMR}}=1800$  g/mol. SEC(THF):  $M_{n,\text{SEC}}=1700$  g/mol, PDI=1.06. FT-IR ( $\text{cm}^{-1}$ ): 1600, 1582, 1492, 1452 (aromatic  $-\text{C}-\text{C}-$ ), 3494 ( $-\text{O}-\text{H}$ ).

**Preparation of PS-*b*-PEO Block Copolymer with Ethoxyethyl-Protected Hydroxyl Group at the Junction Point (Copolymer 2).** The dried polymer **1** (14.2 g, 8.4 mmol,  $M_{n,\text{SEC}}=1700$  g/mol) in 150 mL THF was charged into a 250 mL dried ampoule, then the required amount of DPMK solution was added. After the addition of the cold EO (14 ml, 277.3 mmol), the solution was heated to 50 °C and stirred for 48 h. After completion of polymerization, an additional amount of DPMK solution (15 ml, 9.2 mmol) was injected into the mixture to guarantee complete protonation of all hydroxyl groups, then terminated with excess bromoethane (15 ml, 201.1 mmol). The crude powder of polymer **2** was purified by extraction with cyclohexane twice to remove the homopolymer PS, then precipitated in cold petroleum ether (30–60 °C) and dried under vacuum at 40 °C (25.0 g, yield: 94.7%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm: 0.80 ( $\text{CH}_3\text{CH}_2-$ ), 1.13 ( $\text{CH}_3\text{CH}_2\text{O}-$ ), 1.22 ( $-\text{CH}(\text{CH}_3)-$ ), 1.26–2.01 (m, 3H, aliphatic main chain  $-\text{CH}_2\text{CH}-$  of PS), 3.05–3.43 (m,  $\text{CH}_3\text{CH}_2\text{O}-$ ,  $-\text{CH}(\text{O}-)\text{CH}_2\text{O}-$ ), 3.50–3.70 (m, 4H,  $-\text{CH}_2\text{CH}_2\text{O}-$  of PEO block), 4.65–4.76 ( $-\text{OCH}(\text{CH}_3)\text{O}-$ ), 6.30–7.30 (m, 5H, aromatic  $-\text{C}_6\text{H}_5$  of PS chain),  $M_{n,\text{NMR}}=4200$  g/mol. SEC(THF):  $M_{n,\text{SEC}}=4600$  g/mol, PDI=1.06. FT-IR ( $\text{cm}^{-1}$ ): 1600, 1582, 1492, 1452 (aromatic  $-\text{C}-\text{C}-$ ), 1121 ( $-\text{C}-\text{O}-\text{C}-$ ).

**Preparation of Star (PS-PEO-PEEGE) (Copolymer 3).** Firstly, the hydroxyl group was recovered by the hydrolysis of ethoxyethyl group on polymer **2** according to the literature<sup>55</sup>. Typically, the (PS-*b*-PEO) polymer **2** (25.0 g) was dissolved in 50 mL THF and 120 mL formic acid, stirred at 35 °C for 5 h, and then the formic acid and THF were evaporated off completely. After the residue was dissolved in 50 mL THF, 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 (30–60 °C), and then dried under

vacuum at 40 °C until constant weight (23.9 g, yield: 95.6%). This hydrolysis was complete according to the disappearance of the resonance signals of the ethoxyethyl group protons in  $^1\text{H}$  NMR spectrum.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm: 0.80 ( $\text{CH}_3\text{CH}_2-$ ), 1.13 ( $\text{CH}_3\text{CH}_2\text{O}-$ ), 1.26–2.01 (m, 3H, aliphatic main chain  $-\text{CH}_2\text{CH}-$  of PS), 3.00–3.43 (m,  $-\text{CH}(\text{CH}_2\text{OH})\text{O}-$ ,  $\text{CH}_3\text{CH}_2\text{O}-$ ), 3.50–3.70 (m, 4H,  $-\text{CH}_2\text{CH}_2\text{O}-$  of PEO block), 6.30–7.30 (m, 5H, aromatic  $-\text{C}_6\text{H}_5$  of PS chain). Secondly, PS-*b*-PEO with an active hydroxyl group was used as macro-initiator for ROP of EEGE. To a 100 mL ampoule, the dried (PS-*b*-PEO) polymer with the hydroxyl group at the junction point (10.0 g, 2.4 mmol,  $M_{n,\text{NMR}}=4200$  g/mol) in 45 mL THF was charged, then the required amount of DPMK solution and EEGE monomer (6 ml, 41.1 mmol) were added, the solution was heated to 60 °C and stirred for 48 h. After termination with methanol and precipitation in cold petroleum ether (30–60 °C) twice, a light red product star (PS-PEO-PEEGE) copolymer **3** was obtained and dried under vacuum at 40 °C (15.4 g, yield: 96.3%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm: 0.80 ( $\text{CH}_3\text{CH}_2-$ ), 1.13 ( $\text{CH}_3\text{CH}_2\text{O}-$ ), 1.22 ( $-\text{CH}(\text{CH}_3)-$ ), 1.26–2.01 (m, 3H, aliphatic main chain  $-\text{CH}_2\text{CH}-$  of PS), 3.30–3.50 (m,  $\text{CH}_3\text{CH}_2\text{O}-$ ,  $-\text{CH}(\text{O}-)\text{CH}_2\text{O}-$ ,  $-\text{CHCH}_2\text{O}-$ ), 3.50–3.80 (m, 7H,  $-\text{CH}_2\text{CH}_2\text{O}-$  of PEO block and  $-\text{CH}_2\text{CHO}-$  of PEEGE block), 4.65–4.76 ( $-\text{OCH}(\text{CH}_3)\text{O}-$  of PEEGE block), 6.30–7.30 (m, 5H, aromatic  $-\text{C}_6\text{H}_5$  of PS chain).  $M_{n,\text{NMR}}=5900$  g/mol. SEC(THF):  $M_{n,\text{SEC}}=5100$  g/mol, PDI=1.07. FT-IR ( $\text{cm}^{-1}$ ): 1600, 1582, 1492, 1452 (aromatic  $-\text{C}-\text{C}-$ ), 1121( $-\text{C}-\text{O}-\text{C}-$ ), 3494 ( $-\text{O}-\text{H}$ ).

**Preparation of Star (PS-PEO-PEEGE) Copolymer with the Propargyl Group at the PEEGE Chain End (Copolymer 4).** To a 250 mL dried ampoule, 8.0 g dried polymer **3** ( $M_{n,\text{NMR}}=5900$  g/mol, 1.4 mmol) and 60 mL THF were added. Then the system was bubbled with  $\text{N}_2$  and DPMK solution was introduced until the solution color was turned to reddish-brown. After the ampoule was placed into ice bath, propargyl bromide (2.0 mL, 3.2 g, 26.9 mmol) was added dropwise during 2 h and the reaction was continued for 24 h at room temperature. The functionalized polymer **4** was obtained by separation of the formed salts and precipitation in cold petroleum ether (30–60 °C) twice, and dried under vacuum at 40 °C for 12 h until constant weight (7.7 g, yield: 96.3%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) (Figure S1)  $\delta$  ppm: 0.80 ( $\text{CH}_3\text{CH}_2-$ ), 1.13 ( $\text{CH}_3\text{CH}_2\text{O}-$ ), 1.22 ( $-\text{CH}(\text{CH}_3)-$ ), 1.26–2.01 (m, 3H, aliphatic main chain  $-\text{CH}_2\text{CH}-$

of PS), 2.43(–C≡CH), 3.30–3.50 (m, CH<sub>3</sub>CH<sub>2</sub>O–, –CH(O–)CH<sub>2</sub>O–, –CHCH<sub>2</sub>O–), 3.50–3.80 (m, 7H, –CH<sub>2</sub>CH<sub>2</sub>O– of PEO block and –CH<sub>2</sub>CHO– of PEEGE block), 4.35(–OCH<sub>2</sub>C≡CH), 4.65–4.76 (–OCH(CH<sub>3</sub>)O– of PEEGE block), 6.30–7.30 (m, 5H, aromatic –C<sub>6</sub>H<sub>5</sub> of PS chain). FT-IR (cm<sup>–1</sup>): 1600, 1582, 1492, 1452 (aromatic –C–C–), 1121(–C–O–C–), 3252(–C≡C–H) (Figure S4).

**Preparation of Poly(EO-*co*-EEGE) (Copolymer 5).** The copolymerization was carried out in the kettle, the typical procedure<sup>S6,S7</sup> was showed as follows: a 150 mL kettle was vacuumed at 80 °C for 24 h, and cooled to room temperature and then to –20 °C, given volume of initiator solution [triethylene glycol (0.67 mL, 5.0 mmol) mixed with DPMK (3.3 mL, 2.0 mmol) in 50 mL THF], EEGE (5.0 g, 34.2 mmol) and EO (44.0 g, 1.0 mol) were introduced successively into kettle under magnetic stirring. Subsequently, it was heated to 60 °C under stirring for 48 h. The reaction was terminated by a few drops of acidified methanol. Then all the solvents were removed by reduced distillation. The crude product was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, filtered and dried over anhydrous MgSO<sub>4</sub>. The copolymer **5** was obtained by precipitation in diethyl ether twice and dried in vacuo at room temperature (44.3 g, yield: 90.4%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 1.19 (t, CH<sub>3</sub>CH<sub>2</sub>O–), 1.29 (d, –CH(CH<sub>3</sub>)–), 3.50–3.80 (m, 11H, –CH<sub>2</sub>CH<sub>2</sub>O– of PEO block, –CH<sub>2</sub>CHO–, –CHCH<sub>2</sub>O– and –CH<sub>3</sub>CH<sub>2</sub>O– of PEEGE block), 4.65–4.75 (–OCH(CH<sub>3</sub>)O– of PEEGE block). SEC(H<sub>2</sub>O): M<sub>n,SEC</sub>=9300 g/mol, PDI=1.10. The composition of the copolymer could be obtained by the following formula based on <sup>1</sup>H NMR spectrum (Figure S2).

$$R_T = \frac{4A_a}{A_{sum} - 7A_a} \quad (1)$$

Where R<sub>T</sub> was the molar ratio of EEGE to EO in the copolymer **5**.

**Hydrolysis of the EEGE Units of the Copolymer 5 (Copolymer 6).** The hydrolysis process of the copolymer **5** was similar to that of ethoxyethyl group on PS-*b*-PEO copolymer **2**. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 3.50–3.80 (m, 9H, –CH<sub>2</sub>CH<sub>2</sub>O–, –CH<sub>2</sub>CHO– and –CHCH<sub>2</sub>OH), FT-IR (cm<sup>–1</sup>): 1121(–C–O–C–), 3500 (–O–H). SEC(H<sub>2</sub>O): M<sub>n,SEC</sub>=9600 g/mol, PDI=1.10.

**Preparation of the Copolymer 7 with Multiple Pending Bromide Groups.** A 6.0 g sample of copolymer **6** ( $M_{n,SEC}=9600$  g/mol, 5.6 mmol hydroxyl groups) was dissolved in 100 mL of anhydrous degassed pyridine, then 2.0 mL (16.2 mmol) of 2-bromoisobutyryl bromide 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. After the insoluble salt was removed by filtration, pyridine was removed by azeotropic distillation with dry toluene. The residue was dissolved in  $CH_2Cl_2$  and washed with KOH aqueous solution (1 mol/L), HCl aqueous solution (1 mol/L), and distilled water, respectively. After  $CH_2Cl_2$  was removed by distillation in vacuum, the produced polymer dissolved in ethanol was purified by an ultrafiltration membrane to remove low molecular-weight impurities. Then the ethanol was removed from the yellowy product by distillation, the remains were dried in vacuo at 40 °C (5.4 g, 90%).  $^1H$  NMR ( $CDCl_3$ )  $\delta$  ppm: 1.94 ( $-C(CH_3)_2Br$ ), 3.50–3.80 (m,  $-CH_2CH_2O-$ ,  $-CH_2CHO-$  and  $-CH_2CH_2OCO-$ ), 4.20 (t,  $-CH_2CH_2OCO-$ ), 4.36 (d,  $-CH_2CHOCO-$ ). FT-IR ( $cm^{-1}$ ): 1121( $-C-O-C-$ ), 1738 ( $-COO-$ ).

**Preparation of the Copolymer 8 with Multiple Pending Azide Groups.** The azidation of the pending bromide atoms of copolymer **7** was proceeded as follows: Typically, 1.0 g (0.93 mmol bromide atoms) copolymer **7** was dissolved in 15 mL of DMF, then  $NaN_3$  (0.61 g, 9.3 mmol) was added and stirred for 48 h at room temperature. After the remove of salts by centrifugation, the remaining DMF solution containing copolymer (1.0 g, 15 ml DMF) was collected and stored at  $-20$  °C for next coupling reaction. A small amount of DMF solution containing copolymer was purified by dialysis against water for 72 h to remove the salts and DMF solvent for  $^1H$  NMR and FT-IR characterization.  $^1H$  NMR ( $CDCl_3$ )  $\delta$  ppm: 1.47 ( $-C(CH_3)_2N_3$ ), 3.50–3.80 (m,  $-CH_2CH_2O-$ ,  $-CH_2CHO-$  and  $-CH_2CH_2OCO-$ ), 4.20 (t,  $-CH_2CH_2OCO-$ ), 4.36 (d,  $-CH_2CHOCO-$ ). FT-IR ( $cm^{-1}$ ): 1121( $-C-O-C-$ ), 1738 ( $-COO-$ ), 2108 ( $-N_3$ ). From the  $^1H$  NMR (Figure S3), the signal at 1.94 ppm typical of the  $-C(CH_3)_2Br$  protons disappeared completely, the signal at 1.47 ppm assigned to the  $-C(CH_3)_2N_3$  protons appeared after substitution of bromide by azide, which confirmed that the derivatization reaction was complete.

**Preparation of the Amphiphilic Graft Copolymer 9 with Star-like Side Chains.** Typically, into a 50 mL ampoule, 0.3 g copolymer **4** ( $5.1 \times 10^{-5}$  mol,  $M_{n,NMR-coolymer\ 3}=5900$  g/mol), 0.9 ml copolymer **8** ( $5.1 \times 10^{-5}$  mol azide units,  $M_{n,SEC-polymer\ 5}=9300$  g/mol), DMF (2 mL), CuBr (0.15 g,  $1.0 \times 10^{-3}$  mol), and PMDETA (0.19 ml,  $1.0 \times 10^{-3}$  mol) were charged. The reaction mixture was then vacuumed by three freeze-thaw cycles and purged with N<sub>2</sub>, and then heated to 80 °C for 48 h. After the evaporation of DMF, the reaction mixture was diluted with THF and passed through an activated neutral alumina column to remove the copper salts. The crude product was concentrated and dried in vacuo at 40 °C. The purification of **9** was carried out in ethanol by an ultrafiltration membrane. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 0.80 (CH<sub>3</sub>CH<sub>2</sub>–), 1.13 (CH<sub>3</sub>CH<sub>2</sub>O–), 1.22 (–CH(CH<sub>3</sub>)–), 1.26–2.01 (m, 3H, aliphatic main chain –CH<sub>2</sub>CH– of PS), 3.30–3.85 (m, –CH<sub>2</sub>CH<sub>2</sub>O–, CH<sub>3</sub>CH<sub>2</sub>O–, –CHCH<sub>2</sub>O–, –CH<sub>2</sub>CHO–, –CH(O–)CH<sub>2</sub>O–, –CH<sub>2</sub>CH<sub>2</sub>OCO–), 4.15 (–CH<sub>2</sub>CH<sub>2</sub>OCO–), 4.32 (–CHCH<sub>2</sub>OCO–), 4.65–4.76 (–OCH(CH<sub>3</sub>)O– of PEEGE block), 4.81 (s, 2H, –OCH<sub>2</sub>–(4-triazole)–), 6.30–7.30 (m, 5H, aromatic –C<sub>6</sub>H<sub>5</sub> of PS chain), 7.76 (s, 1H, –CH– of the triazole ring). SEC(THF):  $M_{n,SEC}=3300$  g/mol, PDI=1.04. FT-IR (cm<sup>–1</sup>): 1600, 1582, 1492, 1452 (aromatic –C–C–), 1121(–C–O–C–), 1633 (–C=C– of the triazole ring).

Table S1. Polymerization Data of Alkyne-terminated Star Copolymers and the Precursors

Exp.	PS				PS- <i>b</i> -PEO			Star PS-PEO-PEEGE			Star polymer
	<b>1</b>				<b>2</b>			<b>3</b>			<b>4</b>
	$M_{n,SEC}^a$ (g/mol)	PDI <sup>a</sup>	$M_{n,NMR}$ (g/mol)	E.F. <sup>b</sup> (%)	$M_{n,SEC}^a$ (g/mol)	PDI <sup>a</sup>	$M_{n,NMR}$ (g/mol)	$M_{n,SEC}^a$ (g/mol)	PDI <sup>a</sup>	$M_{n,NMR}$ (g/mol)	E.F. <sup>c</sup> (%)
A	1,700	1.06	1,800	95.1	4,600	1.06	4,200	5,100	1.07	5,900	>99
B	3,600	1.06	3,600	94.2	8,300	1.06	8,200	15,00	1.09	13,10	>99
								0		0	

<sup>a</sup> Determined by SEC using PS as standard and THF as eluent.

<sup>b</sup> E.F. was the efficiency of functionality, which was determined by <sup>1</sup>H NMR in CDCl<sub>3</sub> according to the previous work<sup>S8</sup>.

<sup>c</sup> E.F. was the efficiency of alkyne group functionality, which was determined by <sup>1</sup>H NMR in CDCl<sub>3</sub> (Figure S1).

**Table S2.** Polymerization Data of the Main Chain with Multiple Pending Azide groups and the Precursors

Exp.	Poly(EO- <i>co</i> -EEGE)					Poly(EO- <i>co</i> -Gly)		Main Chain-Br	Main Chain-N <sub>3</sub>
	<b>5</b>					<b>6</b>		<b>7</b>	<b>8</b>
	M <sub>n,SEC</sub> (g/mol)	PDI	R <sub>f</sub> <sup>c</sup>	R <sub>T</sub> <sup>d</sup>	N <sub>EEGE</sub> <sup>e</sup>	M <sub>n,SEC</sub> <sup>b</sup> (g/mol)	PDI <sup>b</sup>	E.F. <sup>f</sup> (%)	E.F. <sup>g</sup> (%)
A	9,300 <sup>b</sup>	1.10 <sup>b</sup>	1/29	1/29.44	6	9,600	1.10	100	100
B	10,000 <sup>a</sup>	1.07 <sup>a</sup>	1/15	1/16	12	6,000	1.09	100	100

<sup>a</sup> Determined by SEC using PS as standard and THF as solvent.

<sup>b</sup> Determined by SEC, calibrated against PEO standard using 0.1M NaNO<sub>3</sub> as eluent.

<sup>c</sup> The feed ratio of EEGE to EO.

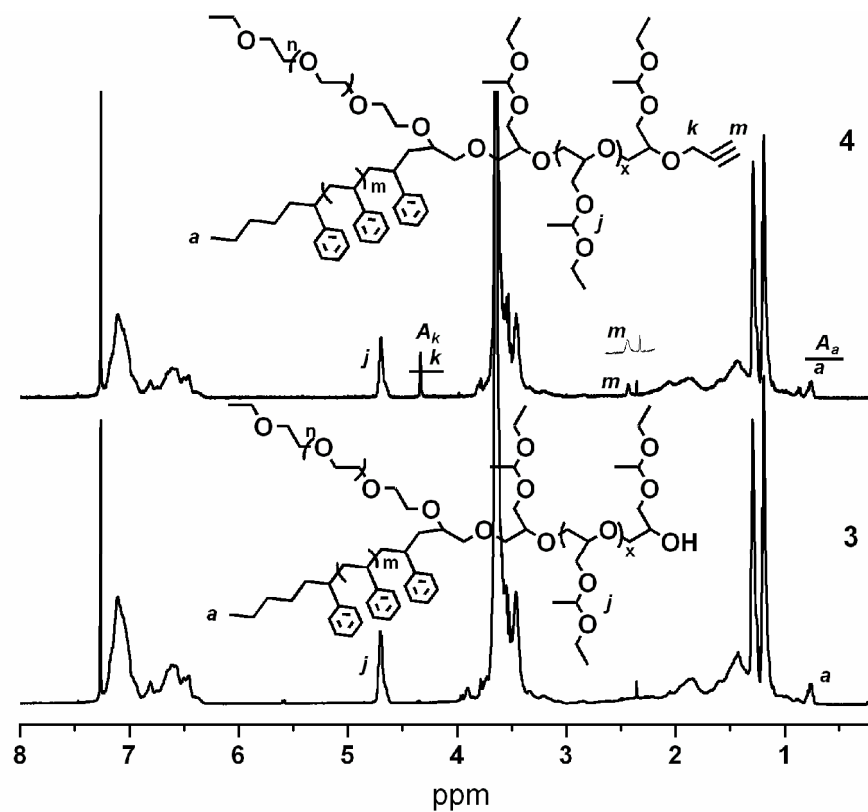
<sup>d</sup> The molar ratio of EEGE to EO in the copolymer poly(EO-*co*-EEGE) **5** calculated from <sup>1</sup>H NMR on the formula (1) in the text.

<sup>e</sup> The number of EEGE units in poly(EO-*co*-EEGE) **5**, calculated by the formula: N<sub>EEGE</sub>=M<sub>n,SEC</sub>/(146+44/R<sub>T</sub><sup>d</sup>).

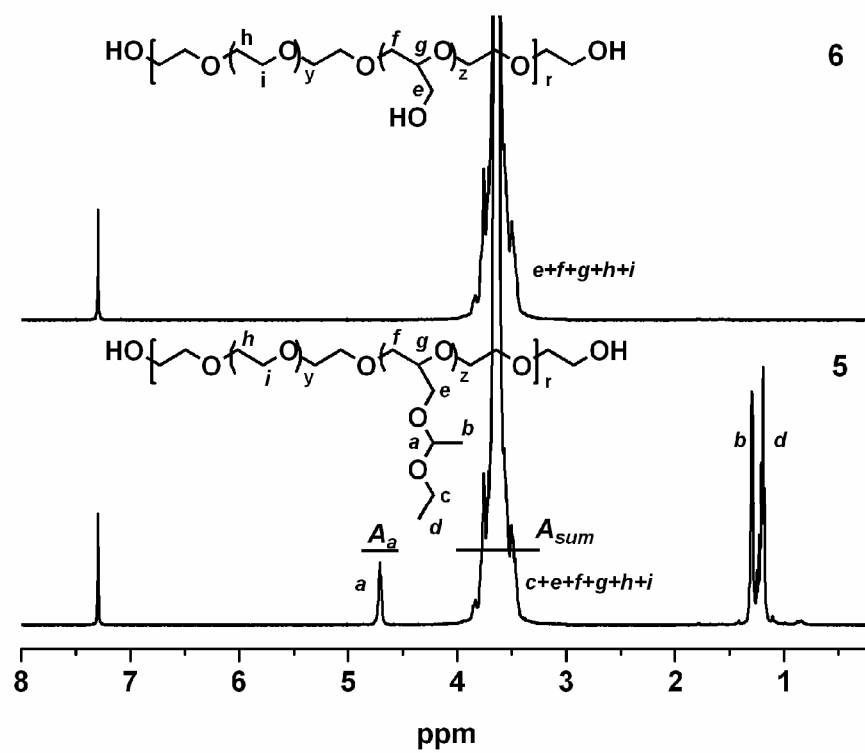
<sup>f</sup> E.F. was the esterification efficiency of the hydroxyl groups of poly(EO-*co*-Gly) **6**, calculated by the following formula: E.F.=[(4/R<sub>T</sub><sup>d</sup>+3)×N<sub>EEGE</sub>×A<sub>E</sub>]/[2(N<sub>EEGE</sub>+2)×A<sub>sum</sub>]×100% (Figure S3).

<sup>g</sup> E.F. was the azidation efficiency of the bromide atoms of copolymer **7**, which was determined by <sup>1</sup>H NMR analysis (Figure S3).

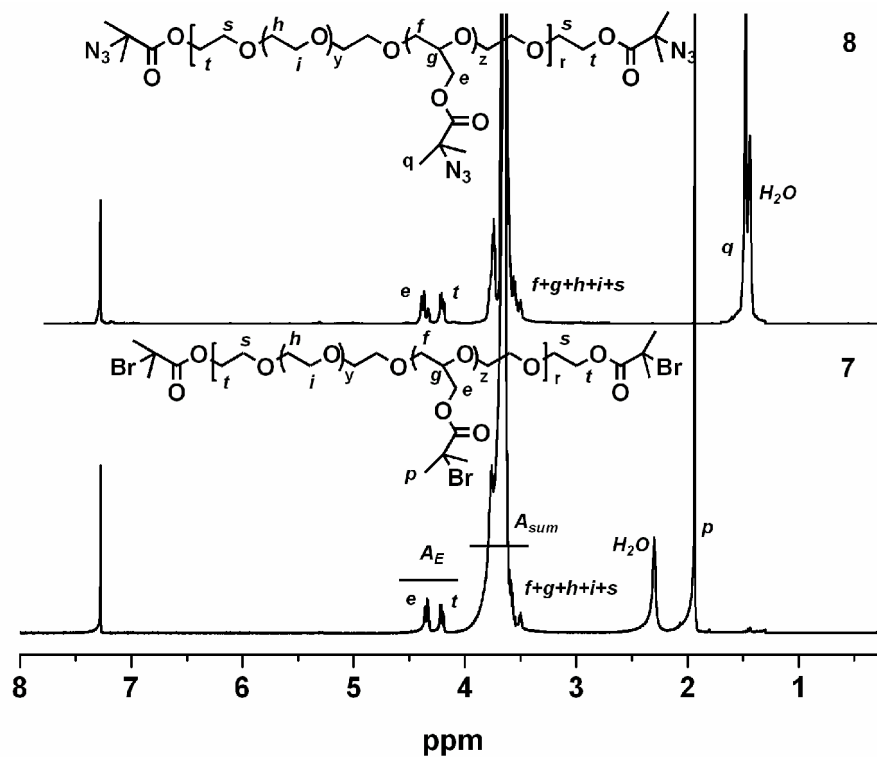




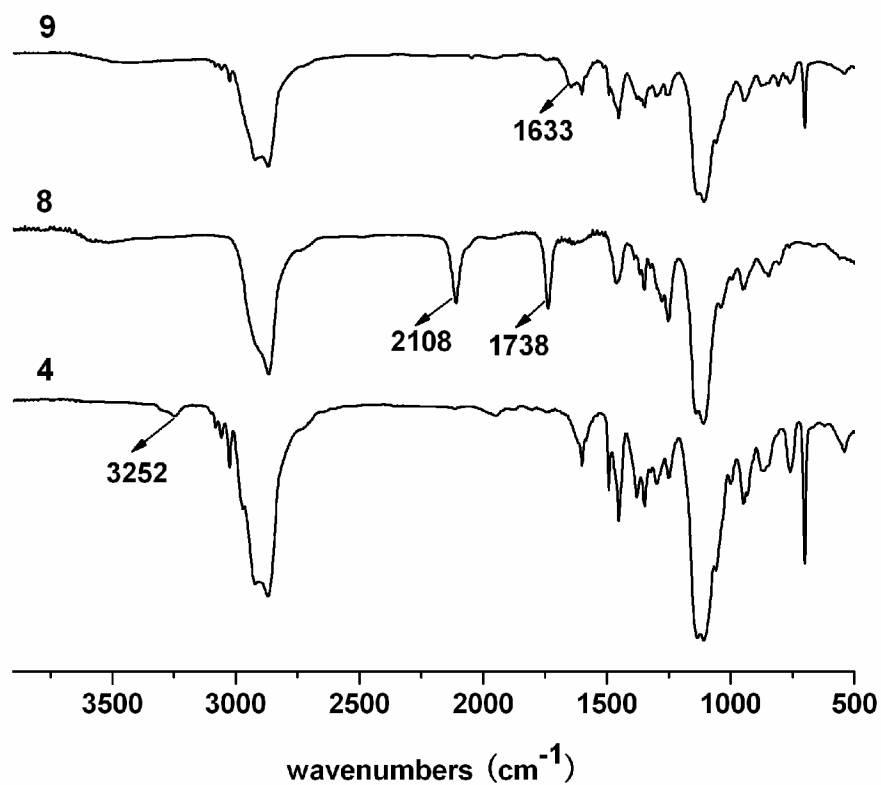
**Figure S1.**  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ ) of copolymer **3** and **4**.



**Figure S2.**  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ ) of copolymer **5** and **6**.



**Figure S3.**  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ ) of copolymer **7** and **8**.



**Figure S4.** FT-IR spectra of copolymer **4**, **8** and **9**.

## References

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