Synthesis of a Novel Graft Copolymer with Hyperbranched Poly(glycerol) as Core and ''Y''-Shaped Polystyrene-*b*-Poly(ethylene oxide)$_2$ as Side Chains

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ABSTRACT: The graft copolymers composed of "Y"-shaped polystyrene-*b*-poly(ethylene oxide)$_2$ (PS-*b*-PEO$_2$) as side chains and hyperbranched poly(glycerol) (HPG) as core were synthesized by a combination of "click" chemistry and atom transfer radical polymerization (ATRP) via "graft from" and "graft onto" strategies. Firstly, macroinitiators HPG-Br were obtained by esterification of hydroxyl groups on HPG with bromoisobutyryl bromide, and then by "graft from" strategy, graft copolymers HPG-*g*-(PS-Br) were synthesized by ATRP of St and further HPG-*g*-(PS-N$_3$) were prepared by azidation with NaN$_3$. Then, the precursors (Bz-PEO)$_2$-alkyne with a single alkyne group at the junction point and an inert benzyl group at each end was synthesized by sequentially ring-opening polymerization (ROP) of EO using 3-[(1-ethoxyethyl)-ethoxyethyl]-1,2-propanediol (EEPD) and diphenylmethylpotassium (DPMK) as coinitiator, termination of living polymeric species by benzyl bromide, recovery of protected hydroxyl groups by HCl and modification by propargyl bromide. Finally, the "click" chemistry was conducted between HPG-*g*-(PS-N$_3$) and (Bz-PEO)$_2$-alkyne in the presence of *N,N,N′,N′,N″*-pentamethyl diethylenetriamine (PMDETA)/CuBr system by "graft onto" strategy, and the graft copolymers were characterized by SEC, ^{1}H NMR and FTIR in details. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 5856–5864, 2010

KEYWORDS: atom transfer radical polymerization (ATRP); "Click" chemistry; graft copolymers; hyperbranched poly(glycerol) (HPG); ring-opening polymerization (ROP)

INTRODUCTION In recent years, the graft copolymers with different compositions have drew much attention of polymer chemists. The graft copolymers may exhibit some unique chemical and/or physical properties because of their peculiar structures. Depending upon the used substrates, the graft copolymers can be divided into 1D,[1] 2D,[2] and 3D,[3] which correspond to side chains grafted on linear polymers, planar surfaces and spherical particles, respectively. Generally, three strategies were used for the preparation of the these copolymers:[4] "grafting onto,"[5] "grafting from,"[6] and "grafting through."[7]

The hyperbranched polymers prepared by one step from AB$_2$ type molecules were widely used to prepare the 3D graft copolymers. Among them, hyperbranched poly(glycerol) (HPG) with narrow polydispersity index (PDI), which was obtained via ring-opening polymerization (ROP) under slow addition of the monomer,[8] was one of the most promising cores for 3D graft copolymers. They showed some interesting properties in solid state or in solution[9] and enable potential applications, including drug carriers,[10] nanotechnology,[11] and supermolecular science.[12] The 3D graft copolymers with mixed or block side chains have been reported by many groups,[13] for example, Tunca synthesized (P*t*BA)$_k$-(PMMA)$_n$-(PS)$_m$-polyDVB and (PEG)$_p$-(PMMA)$_n$-(PS)$_m$-polyDVB,[14–16] using polyDVB as core and block copolymer as side chains. However, only few publications reported the graft copolymers with branched side chains (such as the "V"-shaped, "Y"-shaped or star-shaped).[17,18] Thus, finding a versatile protocol to prepare the graft copolymers with defined compositions and structures of side chains would still be a very interesting work.

In the past decades, several "living" polymerization mechanisms including anionic polymerization,[19] ROP, reverse addition-fragmentation chain transfer polymerization (RAFT),[20] nitroxide-mediated radical polymerization (NMRP),[21] single electron transfer "living" radical polymerization (SET-LRP),[22] and atom transfer radical polymerization (ATRP)[23] had been developed, which provide some convenient routes for polymer scientists to synthesize copolymers with well-defined structures. It was also possible to make topological tailoring on polymer by the further reactions with some functional compounds or modification of the end groups.[24] Typically, the "click" chemistry were widely explored and used in polymer science because of its high efficiency and tolerance of oxygen and water during the past few years.[25]

Additional Supporting Information may be found in the online version of this article. Correspondence to: J. Huang (E-mail: jlhuang@fudan.edu.cn)
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In this article, by combination of ROP and ATRP mechanisms with "click" chemistry, a new strategy for synthesis of some graft copolymers with "Y"-shaped side chains of polystyrene-*b*-poly(ethylene oxide)$_2$ (PS-*b*-PEO$_2$) was described.

EXPERIMENTAL

Materials

Ethylene oxide (EO) was dried over CaH_2 for 1 week and distilled, stored at −20 °C before use. Styrene (St. Aldrich, 98%) was washed with 10% NaOH aqueous solution followed by water three times successively, dried over anhydrous $MgSO_4$, further dried over CaH_2 and distilled under reduced pressure. Tetrahydrofuran (THF, 99%) and pyridine (99.5%) purchased from Sinopharm Chemical Reagent (SCR) were refluxed over sodium wire, then distilled from sodium naphthalenide and sodium wire solution, respectively. Cuprous bromide (CuBr, Acros, 98%) was purified by stirring overnight in acetic acid and filtered, then washed with ethanol and diethyl ether successively, and finally dried under vacuum. Benzyl bromide (>99%), propargyl bromide (>99%), toluene (99%), *N,N*-dimethyl formamide (DMF, 99%) and dichloromethane (CH_2Cl_2) were dried by CaH_2 and distilled just before use. 1,1,1-Tris(hydroxymethyl)propane, 2-bromoisobutyryl bromide (98%), 2,2'-bipyridyl(bpy) and *N,N,N′,N″,N″*-pentamethyl diethylenetriamine (PMDETA, 99%) were purchased from Aldrich and used as received. All other regents and solvents were purchased from SCR and used as received except declaration.

Diphenylmethylpotassium (DPMK) solution was freshly prepared by the reaction of potassium naphthalenide with diphenylmethane in THF according the literature,[26] and the concentration was 0.75 mol/L. Ethoxyethyl glycidyl ether (EEGE) was synthesized from glycidol and ethyl vinyl ether according to Fitton et al.[27] and distilled under reduced pressure (b.p. 152-154 °C), and the purity exceeded 99.6 GC%.[28] Silica gel plates (GF254, purchased from Yantai Jiangyou Silica Gel Development, China) were used for thin-layer chromatographic (TLC) analysis.

Measurements

The number average molecular weight (M_n) and PDI were measured by size-exclusion chromatography (SEC). For the HPG and PEO, SEC was performed in a 0.1 M $NaNO_3$ aqueous solution at 40 °C with an elution rate of 0.5 mL/min on an Agilent 1100 with a G1310A pump, a G1362A refractive index detector, and a G1315A diodearray detector, and PEO standard samples were used for calibration. SEC traces of the rest of the polymers were performed in THF at 35 °C with an elution rate of 1.0 mL/min on an Agilent 1100 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 with polystyrene standard samples. ^{1}H NMR and ^{13}C NMR spectra were obtained on a DMX 500 MHz spectrometer using tetramethylsilane (TMS) as the internal standard and $CDCl_3$ or CD_3OD as the solvents. Fourier transform infrared (FTIR) spectra were recorded on a Magna 550 FTIR instrument, the polymer samples were dissolved in dry dichloromethane or methanol and then cast onto a NaCl disk to form the film by the evaporation of the solvent under infrared lamp. The ultrafiltration separator was purchased from the Shanghai Institute of Nuclear Research, Chinese Academy of Science, and the cutoff molecular weight of the poly(ether sulfone) membrane was 10,000 g/mol (calibrated by globular protein).

Synthesis of Hyperbranched Polyglycerol (HPG) and Macroinitiator HPG-Br

The synthesis procedure of hyperbranched polyglycerol (HPG) was accorded to a previous work by a ring-opening polymerizaion(ROP) mechanism(see Supporting Information),[8(a),29] and two samples with different molecular weight (HPG, $M_{n(SEC)}$ = 1900 g/mol, PDI = 1.25, $M_{n(NMR)}$ = 15,200 g/mol, 200 hydroxyl groups and $M_{n(SEC)}$ = 6700 g/mol, M_n = 30,000 g/mol, PDI = 1.24, 400 hydroxyl groups) was synthesized.

The macroinitiator HPG-Br was synthesized by esterification of HPG with 2-bromoisobutyryl bromide. Typically, HPG (3.00 g, $M_{n(NMR)}$ = 30,000 g/mol, 40 mmol hydroxyl groups) was dried by azeotropic distillation with toluene and then dissolved in 100 mL of anhydrous pyridine, to which 6.20 mL (50 mmol) of 2-bromoisobutyryl bromide was added dropwise at 0 °C over 30 min under vigorous stirring. After the reaction was allowed to proceed for 48 h, a large part of pyridine was distilled under reduced pressure first and then azotropically distilled with toluene, and the residue was washed with cyclohexane and water for three times, respectively. After removal of the water, viscous HPG-Br(3) with a pale yellow color was obtained.

^{1}H NMR ($CDCl_3$) δ (ppm): 1.95 (s, —C(C***H*****$_3$**)$_2$Br), 3.40–4.00 (m, C***H***, C***H*****$_2$** of HPG), 4.16, 4.33, 4.50, 5.12, 5.24 (m,—COOC***H*****$_2$**—, —COOC***H***—).

FTIR (cm^{-1}): 1075 (—C—O—C—), 1730 (—COO—).

Synthesis of Graft Copolymer HPG-*g*-(PS-Br) and HPG-*g*-(PS-N$_3$)

The synthesis of graft copolymers with PS side chains was completed as the following. Typically, HPG-Br(3) (0.198 g, 0.884 mmol Br groups), CuBr (0.129 g, 0.884 mmol), bpy (0.132 g, 0.884 mmol) and St (30 mL, 0.262 mol) were added into a 100 mL ampoule. The system were vacuumed by three freeze-thaw cycles at the temperature of liquid nitrogen, then sealed and placed in an oil bath at 90 °C. After 2 h, the ampoule was taken out from the oil bath and the polymerized products was diluted by THF and passed through the activated neutral alumina column to remove the copper salts, then the colorless solution was concentrated and purified thrice by dissolving/precipitation with THF/methanol, and white powder HPG-*g*-(PS-Br)(3) was obtained.

^{1}H NMR ($CDCl_3$) δ (ppm): 0.70–0.95 (s, —C(C***H*****$_3$**)$_2$—), 1.20–2.20 (m, —C***H*****$_2$**C***H***— of PS), 2.80–4.05 (m, C***H***, C***H*****$_2$** of HPG), 4.35–4.65 (d, CH_2—C***H***(Ph)—Br), 6.30–7.30 (m, —C$_6$***H*****$_5$** of PS).

FTIR (cm^{-1}): 1075 (—COC—), 1453, 1496, 1585, 1603 (—C=C— (aromatic ring)) 1730 (—COO—), 3050–3190 (—CH of aromatic ring). SEC (THF): M_n = 90,000 g/mol, PDI = 1.12.

To obtain the accurate information of graft copolymers, the PS side chains were cleaved by hydrolysis. Typically, HPG-*g*-(PS-Br)(3) (0.520 g) was dissolved in 50 mL of THF, and 10 mL KOH solution (1 M in methanol) was added. The mixture was refluxed for 48 h, and then evaporated to dryness. The remains were dissolved in CH_2Cl_2 and centrifuged, the filtered solution was concentrated and purified by dissolution/precipitation with methanol/water, and the cleaved PS homopolymer was dried at 50 °C *in vacuo* for 24 h. SEC (THF): M_n = 4500 g/mol, PDI = 1.20.

Then, the HPG-*g*-(PS-Br)(3) (3.60 g, 1.20 mmol) was dissolved in DMF (15 mL), and sodium azide (0.390 g, 6.00 mmol) was added to the solution. After the reaction mixture was stirred 24 h at room temperature, a large part of DMF was distilled under reduced pressure first, and dichloromethane (25.0 mL) was added into the mixture and washed three times with distilled water. The organic layer was dried with anhydrous $MgSO_4$, and the solvent was removed by vacuum. And the product was collected and dried at 40 °C *in vacuo* for 4 h. FTIR (cm^{-1}): 2100 cm^{-1} ($—N_3$ stretching vibration).

Synthesis of Precursor Poly(Ethylene oxide)$]_2$ with a Protected Hydroxyl Group at the Junction Point ((Bz-PEO)$_2$-EE)

Firstly, the initiator 3-[(1'-ethoxyethyl)-ethoxyethyl]-1,2-propanediol (EEPD) was synthesized by ring-opening of 1-ethoxyethyl glycidyl ether (EEGE). In a 250 mL three-neck flask, 100 mL THF and 10 mL KOH solution (1 M in water) were added, and the mixture was heated to 70 °C. Then, the solution of 10 mL EEGE in 50 mL THF was added dropwise into the mixture under vigorous stirring and the mixture was continuously stirred for 36 h. After evaporation to dryness, the residue was neutralized by HCl(2M) and dissolved in CH_2Cl_2 and centrifuged. The filtered solution was concentrated and purified by silica gel column chromatography using mixed solvents of CH_2Cl_2/THF (from 19/1 to 1/19 v/v) as eluent. The obtained solvents were removed under reduced pressure, and the viscous and pale yellow color product EEPD was obtained and dried at 45 °C *in vacuo* for 12 h.

^{1}H NMR (CD_3OD) δ (ppm): 1.11 (t, C***H*$_3$**CH_2O—), 1.18 (d, C***H*$_3$**CH—), 3.25–3.67 (m, —C***H*$_2$**OH, —C***H***—OH, —CHC***H*$_2$**O—, —C**H**$_2$$CH_3$), 4.65 (m, —OC***H***$(CH_3)$O—).

Then, the ROP of EO proceeded by using EEPD as initiator. In a reaction kettle, EEPD (1.64 g, 10 mmol) dried by azeotropic distillation with dry toluene was dissolved in 80 mL THF and 20 mL DMSO under dry nitrogen atmosphere, and DPMK solution(6.56 mL, 0.75 M in THF) was added. Afterward, 40 mL EO (35.2 g, 0.8 mol) was introduced, and the vessel was heated to 40 °C under stirring for 72 h. The reaction was terminated by few drops of acidified methanol, and the crude product (HO-PEO)$_2$-EE with a protected hydroxyl group at the junction point and an active hydroxyl group at each end was purified by precipitation in cold ethyl ether twice and dried at 45 °C *in vacuo* for 12 h. SEC (H_2O): M_n = 3400 g/mol , PDI = 1.12.

^{1}H NMR ($CDCl_3$) δ (ppm): 1.18 (t, C***H*$_3$**CH_2O—), 1.28 (d, C***H*$_3$**CH—), 3.25–4.67 (m, —C***H*$_2$**OH, —C***H***—OH, —CHC***H*$_2$**O—, —C**H**$_2$$CH_3$ and —C***H*$_2$**C***H*$_2$**O— of PEO), 4.65 (m, —OC***H***-(CH_3)O—).

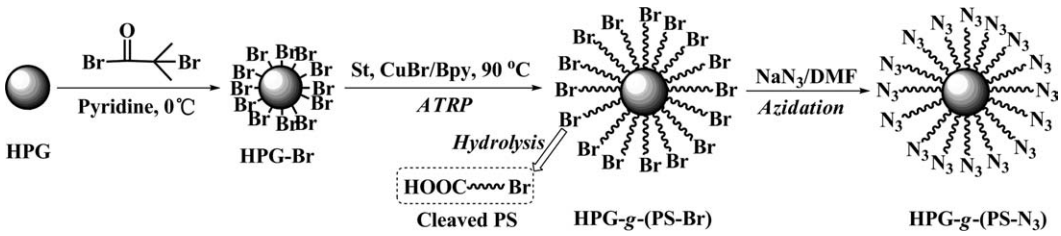
Finally, in THF/NaH system, the terminal hydroxyl groups were capped by benzyl bromide. (HO-PEO)$_2$-EE (20 g, 5.88 mmol, $M_{n(H2O)}$ = 3400 g/mol) was dried by azeotropic distillation with dry toluene and then dissolved in 200 mL THF, and NaH(2.83 g, 0.118 mol) was added in batches. After the mixture was stirred at room temperature for 12 h, benzyl bromide (13.8 mL, 0.118 mol) was added dropwise in the solution and the mixture was stirred at 35 °C for 24 h. The mixture was evaporated and again dissolved in 100 mL CH_2Cl_2. After centrifugation, the organic layer was washed with deionized water (50 mL × 2), and (Bz-PEO)$_2$-EE with a protected hydroxyl group at the junction point and an inert benzyl group at each end was obtained by precipitation in cold ethyl ether twice and dried at 40 °C *in vacuo* for 12 h.

^{1}H NMR ($CDCl_3$) δ (ppm): 1.18 (t, C***H*$_3$**CH_2O—), 1.28 (d, C***H*$_3$**CH—), 3.25–3.67 (m, —C***H*$_2$**OH, —C***H***—OH, —CHC***H*$_2$**O—, —C**H**$_2$$CH_3$ and —C***H*$_2$**C***H*$_2$**O— of PEO), 4.56 (s, —C***H*$_2$**—C_6H_5), 4.65 (m, —OC***H***(CH_3)O—), 7.26-7.35 (m, —CH_2—C_6***H*$_5$**).

Synthesis of Precursor [Poly(Ethylene oxide)$]_2$ with an Alkyne Group at the Junction Point ((Bz-PEO)$_2$-alkyne)

Firstly, the precursor (Bz-PEO)$_2$-EE was hydrolyzed for (Bz-PEO)$_2$-OH with an active hydroxyl group at the junction point. Typically, a mixture of (Bz-PEO)$_2$-EE (12 g, 3.53 mmol), anhydrous methanol (15mL) and concentrated hydrochloric acid (15 mL) was stirred at room temperature for 2 h. The pH value of the solution was adjusted to 7.0 by KOH aqueous solution (1 M). The product was extracted with dichloromethane (200 mL × 2), the organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The product (Bz-PEO)$_2$-OH was obtained by precipitation in cold ethyl ether twice and dried at 40 °C *in vacuo* for 12 h.

Then, the precursor [poly(ethylene oxide)$]_2$ with an alkyne group at the junction point (Bz-PEO)$_2$-alkyne was obtained by modification of (Bz-PEO)$_2$-OH with propargyl bromide. (Bz-PEO)$_2$-OH (8.0 g, 2.35 mmol) was dried by azeotropic distillation with dry toluene and then dissolved in 200 mL THF, in which NaH (1.13 g, 47.1 mmol) was added into batches. The mixture was stirred at room temperature for 12 h, propargyl bromide (5.50 mL, 47.0 mmol) was then added dropwise in the solution and stirred at 35 °C for 24 h. After the mixture was evaporated under reduced pressure, the residue was dissolved in 100 mL CH_2Cl_2 and centrifuged, the organic layer was washed with deionized water (50 mL × 2). Then the product (Bz-PEO)$_2$-alkyne was obtained by precipitation in cold ethyl ether twice and dried at 45 °C *in vacuo* for 12 h.



SCHEME 1 Synthetic procedure of graft copolymers HPG-*g*-(PS-N_3).

^{1}H NMR ($CDCl_3$) δ (ppm): 2.50 (s, —C≡C***H***), 4.20 (s, —OC***H***$_2$C≡CH), 3.45–4.00 (m, —C***H***$_2$C***H***$_2$O— of PEO), 4.56 (s, —C***H***$_2$—C_6H_5), 7.26-7.35 (m, —CH_2—C_6***H***$_5$).

Synthesis of Graft Copolymers HPG-*g*-(PS-*b*-PEO_2) by Click Chemistry

In a 50 mL ampoule, HPG-*g*-(PS-N_3)(3) (0.211 g, 0.000112 mmol, 0.0448 mmol), (Bz-PEO)$_2$-alkyne (0.175 g, 0.0513 mmol), CuBr (0.0760 g, 0.528 mmol), and PMDETA (0.107 mL, 0.528 mmol) were charged, the mixture was then vacuumed by three freeze-thaw cycles and purged with N_2, heated to 80 °C for 48 h. After the evaporation of DMF, the reaction mixture was diluted with CH_2Cl_2 and passed through an activated basic alumina column to remove the copper salts. The crude product was diluted with methanol and the remaining (Bz-PEO)$_2$-alkyne was removed by ultra filtration membrane. The final product HPG-*g*-(PS-*b*-PEO_2)(3) was concentrated and dried *in vacuo* at 40 °C for 12 h.

^{1}H NMR ($CDCl_3$) δ (ppm): 0.70–0.90 (s, —C(C***H***$_3$)$_2$—PS), 1.25–2.10 (m, —C***H***$_2$C***H***— of PS), 3.40–4.00 (m, —C***H***$_2$C***H***$_2$O— of PEO), 6.50–7.30 (m, —C_6***H***$_5$ of PS). SEC (THF): M_n =4,800 g/mol, PDI =1.17.

FTIR (cm^{-1}): 1120 (—C—O—C—), 1453, 1496, 1585, 1600 [—C=C— (aromatic ring)].

To obtain the accurate molecular weight of HPG-*g*-(PS-*b*-PEO_2), the "Y"-shaped side chains of PS-*b*-PEO_2 were cleaved from the main chain by hydrolysis method. Typically, HPG-*g*-(PS-*b*-PEO_2)(3) (0.323 g) was dissolved in 50 mL of THF, and 10 mL KOH solution (1 M in methanol) was added. The mixture was refluxed for 48 h and evaporated to dryness. The remains were dissolved in methanol and ultra filtrated. The cleaved copolymer PS-*b*-PEO_2 was dried *in vacuo* at 40 °C for 12 h.

1H NMR (CDCl3) δ (ppm): 0.70–0.90 (s, —C(CH3)2—PS), 1.25–2.20 (m, —CH2CH— of PS), 3.40–4.00 (m, —CH2CH2O— of PEO), 6.50–7.30 (m, —C6H5 of PS). SEC (THF): M_n = 7,200 g/mol, PDI = 1.20.

RESULTS AND DISCUSSION

Synthesis and Characterization of Graft Copolymers HPG-*g*-(PS-N_3)

The graft copolymer HPG-*g*-(PS-N_3) was obtained by azidation of HPG-*g*-(PS-Br), which was synthesized by ATRP of St monomer using HPG-Br as macroinitiator. And the macroinitiator was firstly obtained by esterification of hydroxyl groups on HPG (Scheme 1).

According to previously published references,[8(a),29] HPG samples were prepared by ROP of glycerol using tris(hydroxymethyl)propane as initiator. Figure 1 showed the SEC curves of HPG, which showed unimodal peaks and low PDIs. However, the hyperbranched polymers often exhibit special assembly behavior in solutions due to their special structure, which always lead to erroneous molecular weight characterization in SEC measurement. According to the ^{13}C NMR spectrum (Supporting Information Fig. S1), the accurate molecular weight (M_n) and numbers of hydroxyl groups (N_{OH}) on each molecule were obtained (see Supporting Information). Two HPG samples with 200 and 400 hydroxyl groups were listed in Table 1, and the M_n were 15,200 and 30,000 g/mol, respectively.

Subsequently, the hydroxyl groups on HPG were esterified by 2-bromoisobutyrylbromide to generate macroinitiators HPG-Br for ATRP mechanism. From Figure 2(A), the resonance signal for methylene and methine protons (—C***H***$_2$OH, —C***H***(—)OH) on HPG were ascribed at 3.40–4.00 ppm, and the resonance signal for methyl protons (—CH_2C***H***$_3$) were ascribed at 0.92 ppm, respectively. Figure 2(B) was the ^{1}H NMR spectrum of HPG—Br. Comparing with Figure 2(A), the five resonance signals were observed in the range of 4.1–5.3 ppm in, which was ascribed to the protons of the methylene and methine protons (—C***H***$_2$OO—, —C***H***(—)OO—) linked to ester bond. The appearance of the resonance signal at 1.95 ppm for the protons of the methyl groups (—CC***H***$_3$) close to Br atom were also proved the successful esterification. According to ^{1}H NMR spectrum of HPG—Br, the Br numbers could be calculated using Formula 1:

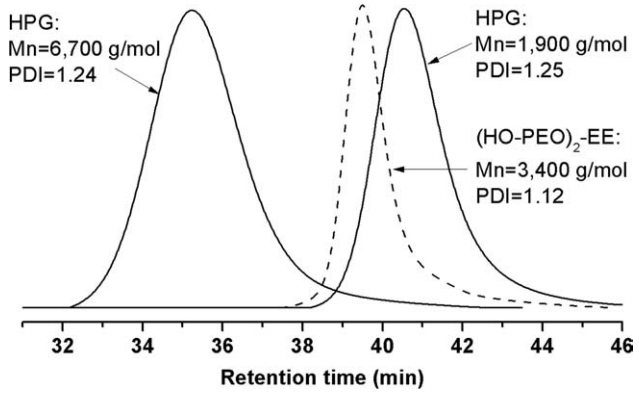


FIGURE 1 The SEC curves of HPG and (HO-PEO)$_2$-EE (in H_2O).

TABLE 1 The Data of HPG and Macroinitiator HPG-Br Characterized by SEC and ^{1}H NMR Measurement

	HPG				HPG-Br		
Entry	M_n (g/mol)[a]	PDI[a]	M_n ($\times 10^4$ g/mol)[b]	N_{OH}[b]	N_{Br}[c]	Br (%)[c]	M_n ($\times 10^4$ g/mol)[c]
HPG-Br(1)	1900	1.25	1.52	200	70	35.0	2.54
HPG-Br(2)	6700	1.24	3.00	400	210	52.5	6.15
HPG-Br(3)	6700	1.24	3.00	400	400	100	8.96

[a] M_n and PDI of HPG was measured by SEC using PEO as standard, performed in 0.1 M $NaNO_3$ aqueous solution.
[b] Molecular weight (M_n) and the number of hydroxyl groups (N_{OH}) on HPG were measured by ^{13}C NMR (see Supporting Information).
[c] The M_n, number (N_{Br}) and percentage (Br%) of Br on HPG-Br were measured by ^{1}H NMR.

$$N_{Br} = \frac{A_{1.95}/6}{A_{3.4-5.3}/5} \times N_{OH} \quad (1)$$

where $A_{1.95}$ and $A_{3.4-5.3}$ were the integral areas of the resonance signal at 1.95 ppm and that at 3.4–5.3 ppm, respectively, and the results were listed in Table 1.

Using HPG-Br as macroinitiator, the ATRP of St proceeded in the presence of CuBr/Bpy. Figure 3 shows the SEC curve of HPG-*g*-(PS-Br), the M_n of the graft copolymers was smaller than the values theoretically predicted due to the smaller hydrodynamic volume of the star polymers than that of the linear chains, so the M_n of HPG-*g*-(PS—Br) obtained from SEC was unreliable. Similarly, because the methine and methylene protons of HPG core showed a weak and broad peak in ^{1}H NMR spectrum due to the wrapping by outer PS chains, the M_n calculated from ^{1}H NMR results [Fig. 4(A)] was also not accurate. So the cleavage of the PS side chains was used for the characterization of the real M_n of the graft copolymers, and the M_n could be obtained by Formula 2:

$$M_{n(\text{cal., HPG-}g\text{-(PS-Br)})} = M_{n(\text{SEC, cleaved PS})} \times N_{Br} + M_{n(\text{NMR, HPG-}g\text{-Br})} \quad (2)$$

where N_{Br} was defined as before, and the M_n data of HPG-*g*-(PS-Br) were summarized in Table 2. Finally, according to reference,[30] the Br groups at terminal end of PS chain were easily transformed into azide groups (N_3) by a nucleophilic substitution reaction with NaN_3 in DMF at room temperature.

Figure 5 also showed the FTIR spectra of HPG and HPG-Br. Comparing with Figure 5(A), the appearance of a characteristic absorption of ester group at 1730 cm^{-1} and the decrease of intensity for the characteristic bands of the hydroxyl groups at 3200–3500 cm^{-1} in Figure 5(B,C) supported the successful synthesis of HPG-Br. For graft copolymer HPG-(PS-Br) [Fig. 6(A)], the appearance of the characteristic bands of PS blocks C=C aromatic stretching at 1450–1600 cm^{-1}, C—H aromatic stretching at 3050–3200 cm^{-1} indicated the successful polymerization of St monomer. After the Br groups was reacted with NaN_3, the peak ascribed to —N_3 (2100 cm^{-1}) was also observed from the FTIR [Fig. 6(B)].

Synthesis and Characterization of Precursor (Bz-PEO)$_2$-alkyne

To obtain the "V"-shaped precursor (Bz-PEO)$_2$-alkyne with an active hydroxyl group at the junction point and a phenyl

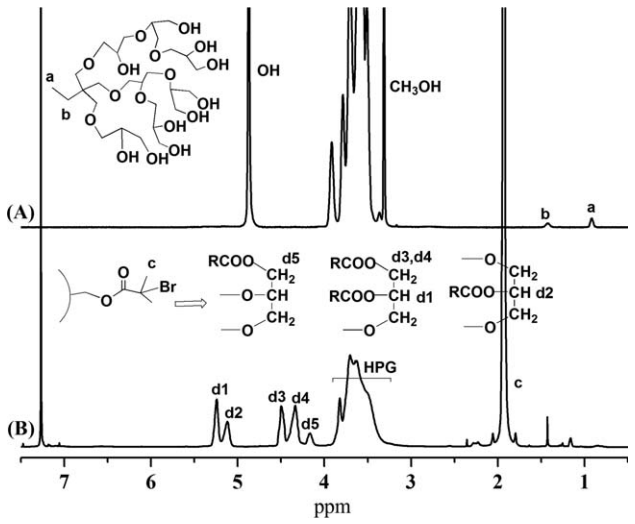


FIGURE 2 The ^{1}H NMR spectra of (A): HPG (in CD_3OD) and (B): HPG-Br (in $CDCl_3$).

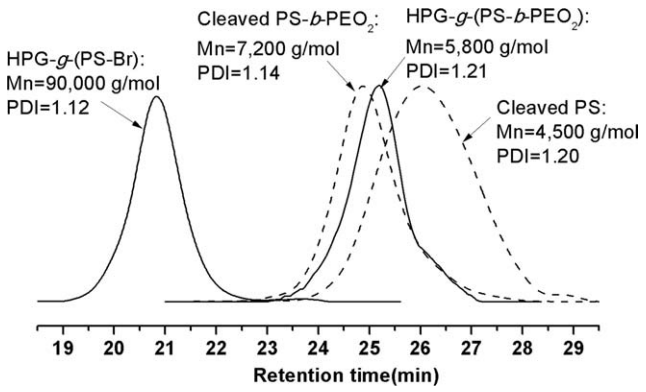


FIGURE 3 The SEC curves of HPG-*g*-(PS-Br), cleaved PS, HPG-*g*-(PS-*b*-PEO$_2$) and cleaved PS-*b*-PEO$_2$.

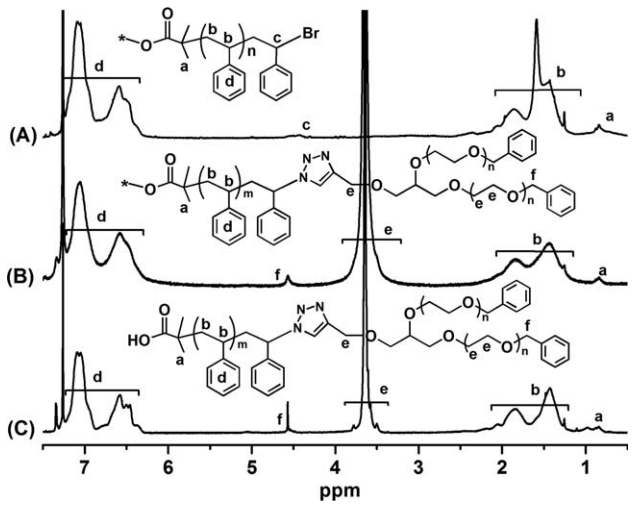


FIGURE 4 The ^{1}H NMR spectra of (A): HPG-*g*-(PS-Br), (B): HPG-*g*-(PS-*b*-PEO_2) and (C): cleaved PS-*b*-PEO_2 side chains (in $CDCl_3$).

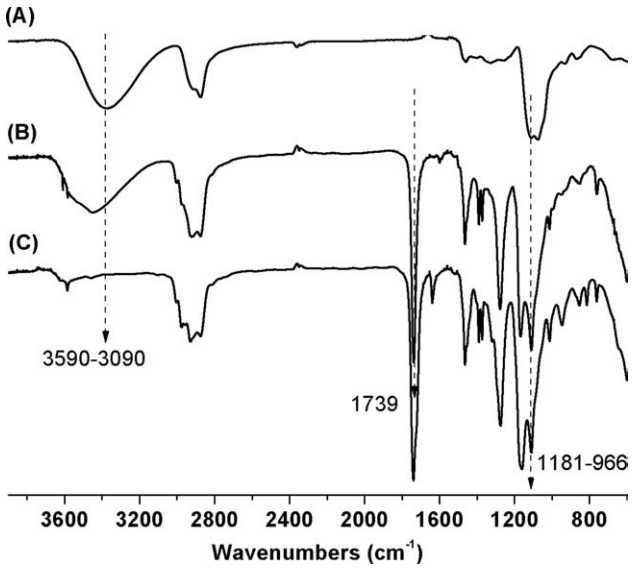


FIGURE 5 The FTIR spectra of (A): HPG, (B): HPG-Br (contained 70 Br on each macromolecule) and (C): HPG-Br (contained 400 Br on each macromolecule).

groups at each terminal end, a novel initiator EEPD was synthesized by ring-opening of EEGE in the presence of KOH and then acidified. The EEGE could be obtained by reaction of glycidol with ethyl vinyl ether,[27] the formed protected group was stable in basic conditions and would not interfere the following ROP of EO. Furthermore, the hydroxyl group can be easily hydrolyzed and recovered in acid solution. After the epoxy group of EEGE was opened by KOH, the crude product was purified by gradient eluent of CH_2Cl_2/THF (from 19/1 to 1/19 v/v).

Using EEPD as initiator, DPMK as protonation agent, the $(HO\text{-}PEO)_2$-EE with a protected hydroxyl groups at the junction point was obtained by ROP of EO (Scheme 2). Figure 1 showed the SEC result of the obtained polymer with a unimodal peak and narrow PDI of less than 1.15, which indicated the successful polymerization of EO. Figure 7(A) showed the ^{1}H NMR spectrum of $(HO\text{-}PEO)_2$-EE. The apparent resonance at 4.65 ppm ascribed to methine proton from EEPD (—OC***H***(CH_3)O—) and 3.40–4.00 ppm ascribed to methylene protons (—C***H***$_2$C***H***$_2$O—) from PEO_2 main chain also proved the successful polymerization of EO.

To transform the protected hydroxyl group at the junction point into alkyne group, the active hydroxyl group at each terminal end of $(HO\text{-}PEO)_2$-EE must be modified as an inert group firstly. Herein, benzyl bromide was used as the end-capping reagent in the presence of NaH, and Figure 7(B) was the ^{1}H NMR spectrum of the benzyl group capped product $(Bz\text{-}PEO)_2$-EE. After the end-capping reaction, the characteristic resonance signal for phenyl group protons (—C_6***H***$_5$—) and methylene group protons (—C***H***$_2$—) on $(Bz\text{-}PEO)_2$-EE were observed at 7.26–7.35 ppm and 4.56 ppm, respectively. The efficiency of end-capping can be calculated by Formula 3:

$$\mathrm{Eff.}_{(\mathrm{benzyl})} = \frac{A_{4.56}}{4A_{4.65}} \times 100\% \qquad (3)$$

where $A_{4.65}$ and $A_{4.56}$ represented the integral areas of resonance signals at 4.65 and 4.56 ppm, respectively, and the efficiency of 98.4% was obtained.

TABLE 2 The Data of HPG-*g*-(PS-Br) Characterized by SEC and ^{1}H NMR Measurement

	HPG-*g*-(PS-Br)				Cleaved PS	
Entry	Conv. (St) (%)	M_n ($\times 10^4$ g/mol)[a]	PDI[a]	M_n ($\times 10^5$ g/mol)[b]	M_n (g/mol)[a]	PDI[a]
HPG-*g*-(PS-Br)(1)[c]	13.9	3.7	1.18	2.28	2900	1.20
HPG-*g*-(PS-Br)(2)[c]	18.2	7.8	1.14	10.69	4800	1.18
HPG-*g*-(PS-Br)(3)[c]	20.9	9.0	1.12	18.89	4500	1.20

[a] The M_n and PDI of HPG-*g*-(PS-Br) or cleaved PS were measured by SEC using PS as standard.
[b] The M_n of HPG-*g*-(PS-Br) was measured by ^{1}H NMR and calculated by Formula 4.
[c] Graft copolymer HPG-*g*-(PS-Br)(1), (2) and (3) were prepared using HPG-*g*-Br(1), (2) and (3) as initiator, respectively.

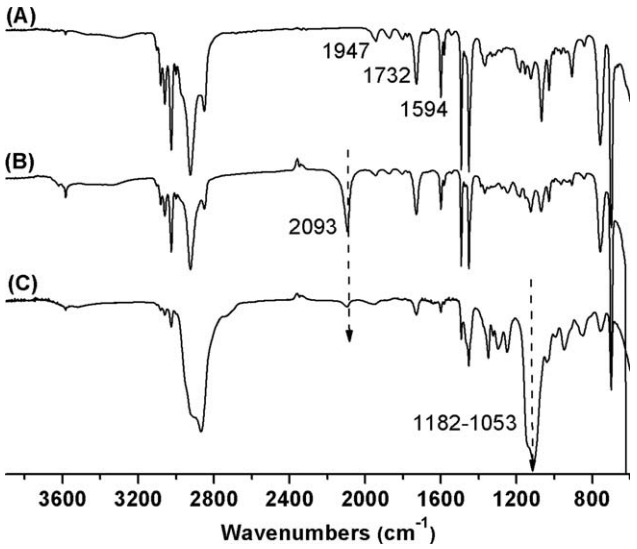


FIGURE 6 The FTIR spectra of (A): HPG-*g*-(PS-Br), (B): HPG-*g*-(PS-N_3) and (C): HPG-*g*-(PS-*b*-PEO_2).

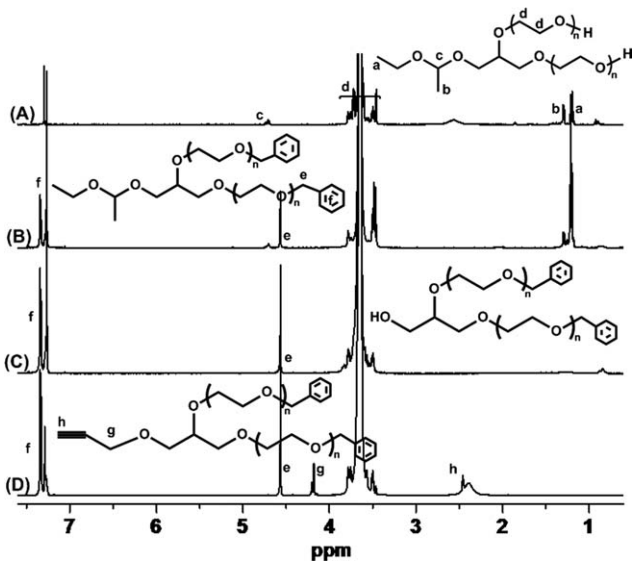


FIGURE 7 The ^{1}H NMR spectra of (A): $(HO\text{-}PEO)_2$-EE, (B): $(Bz\text{-}PEO)_2$-EE, (C): $(Bz\text{-}PEO)_2$-OH, and (D): $(Bz\text{-}PEO)_2$-alkyne (in $CDCl_3$).

The hydrolysis of protected group at the junction point of $(Bz\text{-}PEO)_2$-EE was carried out in acid condition. Figure 7(C) showed the ^{1}H NMR spectrum of formed $(Bz\text{-}PEO)_2$—OH. Comparing with Figure 7(B), the resonance signals ascribed to proton (—OC***H***(CH_3)O—) at 4.65 ppm and methyl groups protons (—C***H***$_3$) at 1.18-1.28 ppm was disappeared completely after hydrolysis.

Finally, the alkyne group was introduced by nucleophilic substitution reaction of hydroxyl with propargyl bromide in the presence of NaH for $(Bz\text{-}PEO)_2$-alkyne. The product was well characterized by ^{1}H NMR in detail [Fig. 7(D)]. The apparent resonance signal at 4.20 ppm ascribed to the methylene group protons (—C***H***$_2$C=CH) close to alkyne group proved the successful modification of the active hydroxyl. And the efficiency of the modification could be calculated by Formula 4:

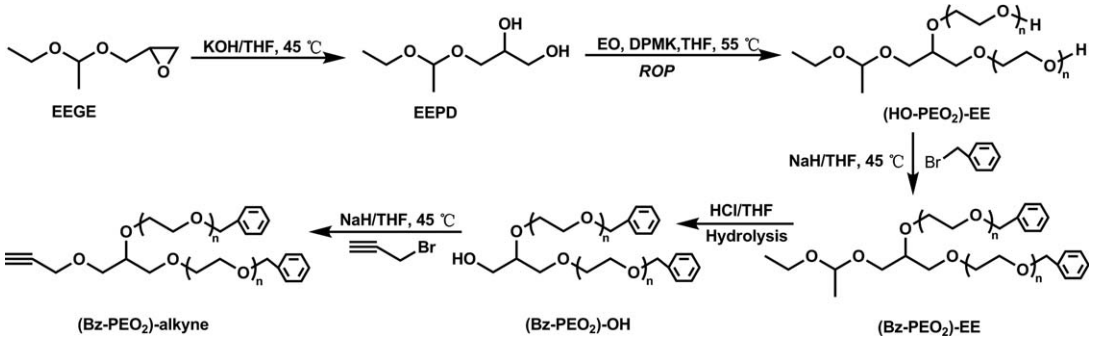
$$\mathrm{Eff}_{\cdot\mathrm{alkyne}} = \frac{2A_{4.20}}{A_{4.56}} \times \mathrm{Eff}_{\cdot\mathrm{benzyl}} \times 100\% \qquad (4)$$

where $A_{4.20}$ and $A_{4.56}$ represented the integral area of resonance signals at 4.20 and 4.56 ppm, respectively, and the efficiency of modification was 95.0%.

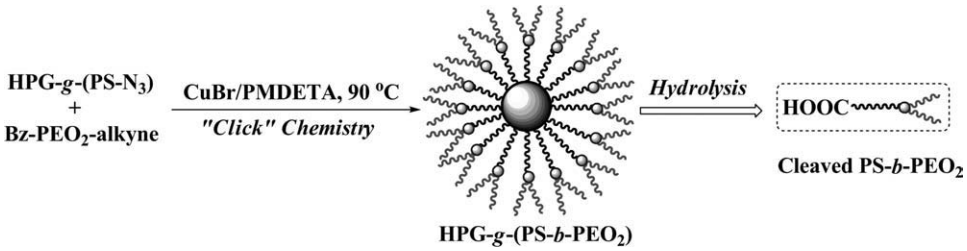
Synthesis and Characterization of Graft Copolymers HPG-*g*-(PS-*b*-PEO_2)

Graft copolymer HPG-*g*-(PS-*b*-PEO_2) was synthesized by "click" reaction between HPG-*g*-(PS-N_3) and $(Bz\text{-}PEO)_2$-alkyne via "graft onto" strategy in the presence of CuBr/PMDETA using DMF as solvent at 80 °C. In all cases, 20% excessive of $(Bz\text{-}PEO)_2$-alkyne was used to make sure the high efficiency of "click" chemistry (Scheme 3). After complete removal of copper salts by basic alumina column, the crude product was purified by ultra filtration membrane using methanol as solvent.

Figure 3 showed the SEC curve of HPG-*g*-(PS-*b*-PEO_2). Comparing with the their precursor of HPG-*g*-(PS-*b*-Br), an apparent shift of the peak HPG-*g*-(PS-*b*-PEO_2) to higher elution time was observed. This behavior could be attributed to the larger hydrodynamic volume of amphiphilic graft copolymer HPG-*g*-(PS-*b*-PEO_2) than copolymer HPG-*g*-(PS-Br) in THF. The result presented here was in agreement with recent references.[31,32]



SCHEME 2 Synthesis procedure of "V"-shaped precursor $(Bz\text{-}PEO)_2$-alkyne.



SCHEME 3 Synthesis procedure of graft copolymer HPG-*g*-(PS-*b*-PEO_2).

To further verify the structure of the graft copolymers, ^{1}H NMR and FTIR analyses were utilized. Figure 4(B) was the ^{1}H NMR spectrum of HPG-*g*-(PS-*b*-PEO_2). The resonance at 3.40–4.00 ppm ascribed to methylene group protons (—C***H***$_2$C***H***$_2$O—) on PEO main chains could be observed, and the resonance signals of phenyl groups (—C_6***H***$_5$) and methylene or methine groups (—C***H***C***H***$_2$—) on PS occurred in the region of 6.50–7.30 ppm and 1.25–2.10 ppm, respectively. FTIR spectrum also proved the success of "click" chemistry, comparing with Figure 6(A), the broad band at 1120 cm^{-1} ascribed to the C—O—C stretching on PEO was appeared in Figure 6(C).

To calculate the efficiency of "click" reaction, the cleavage method was also employed to hydrolyze the ester bond on graft copolymer using KOH in THF/CH_3OH, and the crude product was purified by ultra filtration membrane to remove the HPG core. Figure 3 showed the SEC curve of cleaved PS-*b*-PEO_2 from HPG-*g*-(PS-*b*-PEO_2). Comparing with the cleaved PS side chains from HPG-*g*-(PS-Br), an apparent shift of the peak toward lower elution time was observed, which proved the successful occurrence of "click" chemistry. The efficiency of "click" reaction could be calculated by the ^{1}H NMR analysis [Fig. 4(C)] using Formula 5:

$$\mathrm{Eff}_{\cdot\mathrm{Click}} = \frac{A_{3.40-4.00}}{A_{6.50-7.30}} \times \frac{5M_{n(PS)}/104}{4M_{n(PEO)}/44} \times 100\% \qquad (5)$$

where $A_{6.50-7.30}$ and $A_{3.40-4.00}$ were the integral areas of the phenyl ring protons on PS and methylene group protons on PEO, respectively. $M_{n(PS)}$ and $M_{n(PEO)}$ were the M_n of PS and PEO obtained by SEC. The values of 104 and 44 were the molecular weight of the styrene and EO monomers, respectively. And the data of efficiency were listed in Table 3.

Based on the efficiency ($\mathrm{Eff}_{\cdot(\mathrm{click})}$) of "click" reaction, the M_n of HPG-*g*-(PS-*b*-PEO_2) could be calculated by Formula 6.

$$M_{n(\text{HPG-g-(PS-b-PEO}_2))} = M_{n(\text{HPG-g-(PS-Br)})} + N_{PS} \times M_{n((\text{Bz-PEO})_2\text{-alkyne})} \times \mathrm{Eff}_{\cdot\mathrm{Click}} \qquad (6)$$

where N_{PS} was the number of PS chains on HPG-*g*-(PS-Br) and $M_{n((Bz\text{-}PEO)2\text{-}alkyne)}$ was obtained by SEC. From Table 3, it was found that the application of "click" reaction in the synthesis of graft copolymers could provide a satisfactory efficiency (>75%).

CONCLUSIONS

A novel graft copolymer HPG-*g*-(PS-*b*-PEO_2) with "Y"-shaped side chains PS-*b*-PEO_2 was synthesized by combining "graft from" with "graft onto" methods, as well as the "click" chemistry. The results showed that the efficiency of "click" chemistry was quite acceptable even if the density of side chains on HPG was rather high. The structure of target copolymers and intermediates were well characterized by ^{1}H NMR, SEC, and FTIR. It was believed that this work provided a new way to prepare the graft copolymer with complex structure.

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TABLE 3 The Data of HPG-*g*-(PS-*b*-PEO_2) Characterized by SEC and ^{1}H NMR Measurement

	HPG-*g*-(PS-*b*-PEO_2)			Cleaved PS-*b*-PEO_2		
Entry	M_n (g/mol)[a]	PDI[a]	M_n ($\times 10^5$ g/mol)[b]	$M_{n(PS\text{-}PEO2)}$[a]	PDI[a]	Eff. (%)[c]
HPG-*g*-(PS-*b*-PEO_2)(1)[d]	7800	1.29	4.08	6300	1.18	89.4
HPG-*g*-(PS-*b*-PEO_2)(2)[d]	5100	1.31	16.75	8200	1.20	85.2
HPG-*g*-(PS-*b*-PEO_2)(3)[d]	4600	1.25	29.49	7200	1.14	78.5

[a] The M_n and PDI of HPG-*g*-(PS-*b*-PEO_2) and PS-*b*-PEO_2 were measured by SEC using PS as standard in THF elution.
[b] The M_n of HPG-*g*-(PS-*b*-PEO_2) was calculated by ^{1}H NMR using Formula 8.
[c] The efficiency of "Click" reaction was measured by ^{1}H NMR using Formula 7.
[d] The HPG-*g*-(PS-*b*-PEO_2)(1), (2), and (3) were prepared using HPG-*g*-(PS-Br) (1), (2), and (3) as precursors, respectively.

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