Preparation of Star Block Copolymers with Polystyrene-*block*-Poly(ethylene oxide) as Side Chains on Hyperbranched Polyglycerol Core by Combination of ATRP with Atom Transfer Nitroxide Radical Coupling Reaction

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ABSTRACT: The star block copolymers with polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) as side chains and hyperbranched polyglycerol (HPG) as core were synthesized by combination of atom transfer radical polymerization (ATRP) with the "atom transfer nitroxide radical coupling" ("ATNRC") reaction. The multiarm PS with bromide end groups originated from the HPG core (HPG-*g*-(PS-Br)$_n$) was synthesized by ATRP first, and the heterofunctional PEO with α-2,2,6,6-tetramethylpiperidinyl-1-oxy group and ω-hydroxyl group (TEMPO-PEO) was prepared by anionic polymerization separately using 4-hydroxyl-2,2,6,6-tetramethylpiperidinyl-1-oxy (HTEMPO) as parents compound. Then ATNRC reaction was conducted between the TEMPO groups in PEO and bromide groups in HPG-*g*-(PS-Br)$_n$ in the presence of CuBr and pentamethyldiethylenetriamine (PMDETA). The obtained star block copolymers and intermediates were characterized by gel permeation chromatography, nuclear magnetic resonance spectroscopy, fourier transform-infrared in detail. Those results showed that the efficiency of ATNRC in the preparation of multiarm star polymers was satisfactory (>90%) even if the density of coupling cites on HPG was high. © 2008 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 46: 6754–6761, 2008
Keywords: atom transfer nitroxide radical coupling reaction; ATRP; block copolymers; hyperbranched; star block copolymer; star polymers

INTRODUCTION

In recent years, controlled radical polymerization (CRP) techniques have developed rapidly for facile preparation of a variety of polymeric materials with predetermined molecular weight, low polydispersity, and high degree of chain end functionalization.[1] When compared with conventional living ionic polymerizations, CRP techniques possess the advantages that they are suited for the larger variety of applicable monomers and more tolerant experimental conditions. The most widely used CRP methods are nitroxide-mediated polymerization (NMP),[2,3] reversible addition-fragmentation chain transfer[4] polymerization, and atom transfer radical polymerization (ATRP).[5–7] Percec reported, recently, ultrafast synthesis of ultrahigh molar mass polymers by ATRP via single electron

Additional Supporting Information may be found in the online version of this article.

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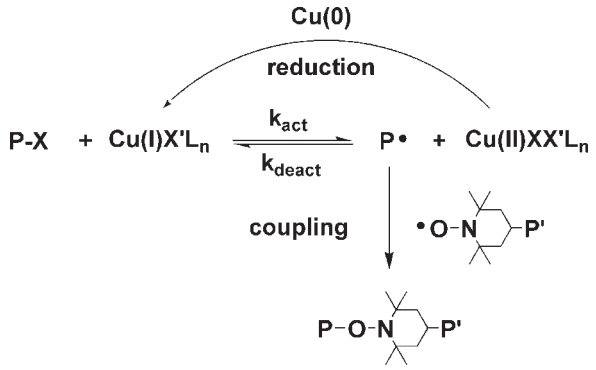
transfer could be performed.[8–10] In particular, the polymers with halogen-containing ends prepared by ATRP have attracted much attention due to the easy transformations of terminal halogen atoms to other functional groups by chemical modification. For example, the halogen end group in a polymer could be efficiently substituted by an azide anion via nucleophilic reaction and then transforms to a triazoles ring via further reaction with alkyne in the presence of metal catalyst, which was termed by Sharpless as "Click" chemistry.[11] Because of its quantitative yields, high tolerance of functional groups and insensitivity of the reaction to solvents,[12] "Click" chemistry has already gained extensive application in polymeric science and material, such as the synthesis of linear,[13,14] dendritic,[15,16] cyclic,[17] and star polymers.[18] It has also been utilized in functionalized surfaces,[19–21] sugars,[22] robe biological systems,[23,24] and synthesis of synthesize analogues of vitamin D.[25] The great potential of this coupling procedure for the construction of well-defined (functional) polymer architectures was quickly recognized and became the subject of intensive research.[26] The fact has shown that it was a wonderful route to use "Click" chemistry in synthesis of block copolymer.[27] However, the polymers with azide groups are difficult to be reserved because of their photosensitivity, shock sensitivity, and thermal instability.[28] Thus, special care should be taken in the operations of "Click" chemistry.

Recently, a new coupling reaction named as atom transfer nitroxide radical coupling (ATNRC) reaction was reported by our group.[29,30] In the presence of copper bromide (CuBr) and *N,N,N′,N″,N″*-penta-methyl diethylenetriamine (PMDETA), the terminal bromine group in polymer chain served as oxidant was reduced to bromine anion, whereas Cu^{1+} was oxidized to Cu^{2+}. Meanwhile, the secondary carbon radical was formed. The carbon-centered radical was immediately captured by the 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) radical in another polymer chain, forming an alkoxyamine between the two polymers, as shown in Scheme 1. When compared with azide group, TEMPO group is less sensitive to light, shock, and thermal changes, which makes the polymer materials stable.

In this article, the coupling efficiency of ATNRC in the preparation of multiarm star polymers was investigated. The selected two precursor polymers were multiarm PS with bromide end groups obtained by ATRP from the HPG core (HPG-*g*-(PS-Br)$_n$) and end functional PEO with



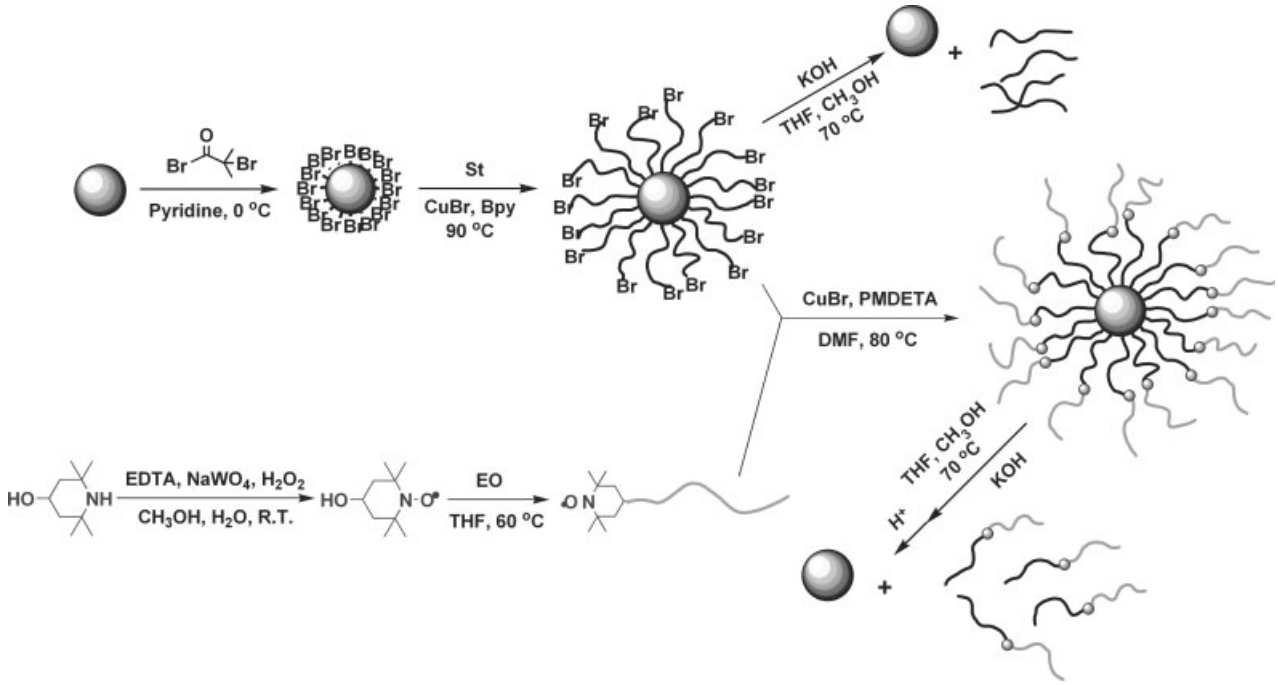
Scheme 1. The mechanism of the "ATNRC" reaction.

2,2,6,6-tetramethylpiperidinyl-1-oxy group and hydroxyl group (TEMPO-PEO) (Scheme 2).

EXPERIMENTAL

Materials

HPG (M_n = 30,000, PDI = 1.27) and 4-hydroxyl-2,2,6,6-tetramethylpiperidinyl-1-oxy (HTEMPO) (98.7%, determined by GC-MS analysis) were synthesized and purified according to the previous literature.[31,32] (See the details in the supporting information.) Styrene (St, >99.5%, Aldrich) was washed with 10% NaOH aqueous solution followed by water three times successively, dried over CaH_2, and distilled under reduced pressure. Ethylene oxide (EO) was purchased from Sinopharm Chemical Reagent (SCR), dried by calcium hydride for 1 week and then distilled, stored at −20 °C before use. 1,1,1-Tris(hydroxymethyl) propane (TMP), glycidol, 2-bromoisobutyryl bromide, Copper (I) bromide (CuBr), 2,2′-Bipyridyl (BPY) *N,N,N′,N″,N″*-penta-methyl diethylenetriamine (PMDETA) were purchased from Aldrich, used as received. Sodium azide (NaN_3) and potassium hydroxide (KOH) were purchased from SCR and used as received. *N,N*-dimethylformamide (DMF, SCR) was dried by CaH_2 and distilled just before use. Tetrahydrofuran (THF, 99%, SCR) and pyridine (99.5%, SCR) were refluxed and distilled from sodium naphthalenide solution and sodium wire, respectively. Diphenylmethyl potassium (DPMK) solution was freshly prepared by the reaction of potassium naphthalenide with diphenylmethane in THF according to the literature,[33] and the concentration was 0.61 mol/L. All the other regents and solvents were purchased from Sinopharm Chemical Reagent (SCR) and used as received except for declaration.



Scheme 2. Synthetic procedure of HPG-*g*-(PS-*b*-PEO)$_n$ star block copolymers and their cleavage by potassium hydroxide.

Esterification of HPG with 2-Bromoisobutyryl Bromide

HPG-*g*-polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO)$_{66}$ (66 means there are 66 arms of PS-*b*-PEO on HPG) is exemplified for all synthesis section. 3.0 g (0.1 mmol) HPG (40 mmol hydroxyl groups) was dried by azeotropic distillation with toluene, and then dissolved in 100 mL anhydrous pyridine, to which 0.75 mL (6 mmol) of 2-bromoisobutyrylbromide was added dropwise at 0 °C over 30 min under vigorous stirring. The reaction was completed overnight. A large part of pyridine was distilled under reduced pressure first, and then distilled with toluene; the residue was washed with cyclohexane three times and dialysed against deionized water to ensure that all the impurities were removed. After removal of the water (vacuum, 50 °C), transparent and viscous HPG-*g*-Br$_{66}$ with a pale yellow was obtained. The degree of esterification is 16.5%, which means 66 hydroxyl groups out of 400 hydroxyl groups on one HPG were esterified. ^{1}H NMR (CD_3OD) δ (ppm): 0.92 (s, 3H, C***H*****$_3$**—CH_2— of TMP), 1.45 (s, 2H, CH_3—C***H*****$_2$**— of TMP), 1.96 (s, 6H, —C(C***H*****$_3$)$_2$**—Br), 4.87 (s, OH); 4.24, 4.39, 4.53, 5.17, 5.28 (m, 4H, Br—C(CH_3)$_2$—COO—C***H*****$_2$**—, Br—C(CH_3)$_2$—COO—C***H***—); FTIR (cm^{-1}): 1076 (—C—O—C—), 1731 (—COO—), 3200–3500 (—OH). (See the details in the supporting information.)

Synthesis of Multi-Arm Star Polymer HPG-*g*-(PS-Br)$_n$

About 0.5 g (0.013 mmol, i.e., 0.8 mmol Br-atoms) HPG-*g*-Br$_{66}$, 0.11 g (0.8 mmol) CuBr, 0.12 g (0.8 mmol) BPY, and 30 mL (0.26 mol) styrene were placed in an ampoule and freeze-pump-thaw degassed three times. The polymerization was started by immersing the flask into an oil bath at 90 °C, and after 5.5 h, the ampoule was quenched in liquid nitrogen and then placed to air. The unreacted styrene was evaporated, the residue was diluted with $CHCl_3$, and the upper solution was collected after centrifuge and precipitated thrice by dissolution/precipitation with methylene chloride/ethanol. The obtained white powder HPG-*g*-(PS-Br)$_{66}$ was dried in vacuum at 40 °C for 24 h. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.70–0.95 (s, 6H, —C(C***H*****$_3$)$_2$**—PS), 1.20–2.20 (m, 3H, —C***H*****$_2$**CH— of PS), 2.80–4.05 (m, 5H, C***H***, C***H*****$_2$** of HPG), 4.35–4.65 (d, 1H, CH_2—C**H**(Ph)—Br), 6.30–7.30 (m, 5H, —C_6***H*****$_5$** of PS); FTIR (cm^{-1}): 1126 (—C—O—C—), 1452, 1492, 1583, 1601

(—C—C—(aromatic ring)) 1731 (—COO—), 3200–3500 (—OH); GPC: M_n = 42,500, PDI = 1.17.

Cleavage of HPG-*g*-(PS-Br)$_n$

0.3 g HPG-*g*-(PS-Br)$_{66}$ was dissolved in 50 mL of THF, to which 10 mL KOH solution (1 M in ethanol) was added, and the mixture was refluxed for 72 h. After evaporation to dryness, the polymer was dissolved in CH_2Cl_2 and purified by dissolution/precipitation with methylene chloride/ethanol, the PS homopolymer was dried at 50 °C for 24 h. GPC: M_n = 1800, PDI = 1.23.

Synthesis of End Functional Polymer TEMPO-PEO

In a reaction kettle, 1.52 g HTEMPO (8.8 mmol) dried by azeotropic distillation with dry toluene was dissolved in 40 mL THF and 40 mL DMSO under dry nitrogen atmosphere, and the required amount of DPMK solution was added. Afterwards, 40 mL EO (35.2 g, 0.8 mol) was introduced, and the vessel was kept at 60 °C under stirring for 72 h. The reaction was terminated by addition of a few drops of acidified methanol. The crude product was purified by dissolution/precipitation thrice with chloroform/ethyl ether, and the pink powder was obtained. ^{1}H NMR (CD_3OD, in the presence of calculated amount of ammonium formate and palladium-on-carbon) δ (ppm): 1.15–1.18 (s, 12H, —C***H***$_3$ of TEMPO group), 1.45 and 1.95 (d, 4H, —C***H$_2$***— of TEMPO group), 3.36–3.75 (m, 4H, —C***H$_2$***CH_2O— of PEO chain), 8.53 (***H***COO— of ammonium formate). GPC: M_n = 3200, PDI = 1.12.

Preparation of HPG-*g*-(PS-*b*-PEO)$_n$ by "ATNRC"

Typically, 0.25 g HPG-*g*-(PS-Br)$_{66}$ (1.5×10^{-3} mmol), 0.45 g TEMPO-PEO (0.14 mmol), DMF (10 mL), CuBr (267 mg, 1.8 mmol), and PMDETA (311 mg, 1.8 mmol) were charged in a 50 mL ampoule. The reaction mixture was vacuumed by three freeze-thaw cycles and then purged with N_2, kept at 80 °C for 48 h. After the evaporation of DMF, the mixture was diluted with THF and passed through an activated basic alumina column to remove the copper salts. The crude product was diluted with methanol and the remaining TEMPO-PEO was removed by ultra filtration membrane. The final product HPG-*g*-(PS-*b*-PEO)$_{66}$ was concentrated to dryness and then vacuumed at 45 °C for 12 h to reach a constant weight. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.70–0.95 (s, 6H, —C(C***H$_3$***)$_2$—PS), 1.20–2.20 (m, 3H, —C***H$_2$*** CH— of PS), 3.40–4.05 (m, 4H, —C***H$_2$***CH_2O— of PEO), 6.30–7.30 (m, 5H, —C_6***H$_5$*** of PS). M_n = 350,000. GPC: M_n = 47,000, PDI = 1.07.

Cleavage of HPG-*g*-(PS-*b*-PEO)$_n$

0.3 g of HPG-*g*-(PS-*b*-PEO)$_{66}$ was dissolved in 30-mL THF and mixed with 10-mL KOH solution (1 M in ethanol), the mixture was refluxed for 72 h. After evaporation to dryness, the polymer was dissolved in methanol and ultra filtrated. The pure block copolymer PS-*b*-PEO was dried at 50 °C for 24 h. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.70–0.95 (s, 6H, —C(C***H$_3$***)$_2$—PS), 1.20–2.20 (m, 3H, —C***H$_2$***CH— of PS), 3.40–4.05 (m, 4H, —C***H$_2$***CH_2O— of PEO), 6.30–7.30 (m, 5H, —C_6***H$_5$*** of PS). GPC: M_n = 7500, PDI = 1.11.

Measurements

The number average molecular weight and polydispersity index M_w/M_n were estimated by gel permeation chromatography (GPC). For the measurement of HPG and PEO, GPC was performed in 0.1 M $NaNO_3$ aqueous solution at 40 °C with an elution rate of 0.5 mL/min on an Agilent 1100 equipped with a G1310A pump, a G1362A refractive index detector, and a G1315A diode-array detector, and PEO standard samples were used for calibration. GPC traces of the rest polymers were performed in tetrahydrofuran (THF) at 35 °C with an elution rate of 1.0 mL/min on an Agilent 1100 equipped with a G1310A pump, a G1362A refractive index detector, and a G1314A variable wavelength detector, and polystyrene standard samples were used for calibration. ^{1}H NMR and ^{13}C NMR spectra were obtained by a DMX 500 MHz spectrometer using tetramethylsilane (TMS) as the internal standard and $CDCl_3$, CD_3OD as the solvent. All fourier transform infrared (FTIR) spectra were recorded using Magna 550 FTIR instrument. For sample preparation, the polymers were dissolved in dry dichloromethane or methanol and then cast onto a NaCl disk to form a film through the evaporation of the solvent under infrared lamp. The MALDI-TOF MS measurement was performed on a Perspective Biosystem Voyager-DE STR MALDI-TOF (matrix-assisted laser desorption/ionization time-of-flight) mass spectrometer (PE Applied Biosystems, Framingham, MA) equipped with a nitrogen laser emitting at 337 nm with a 3 ns pulse width and worked in negative mode. The spectra were recorded in

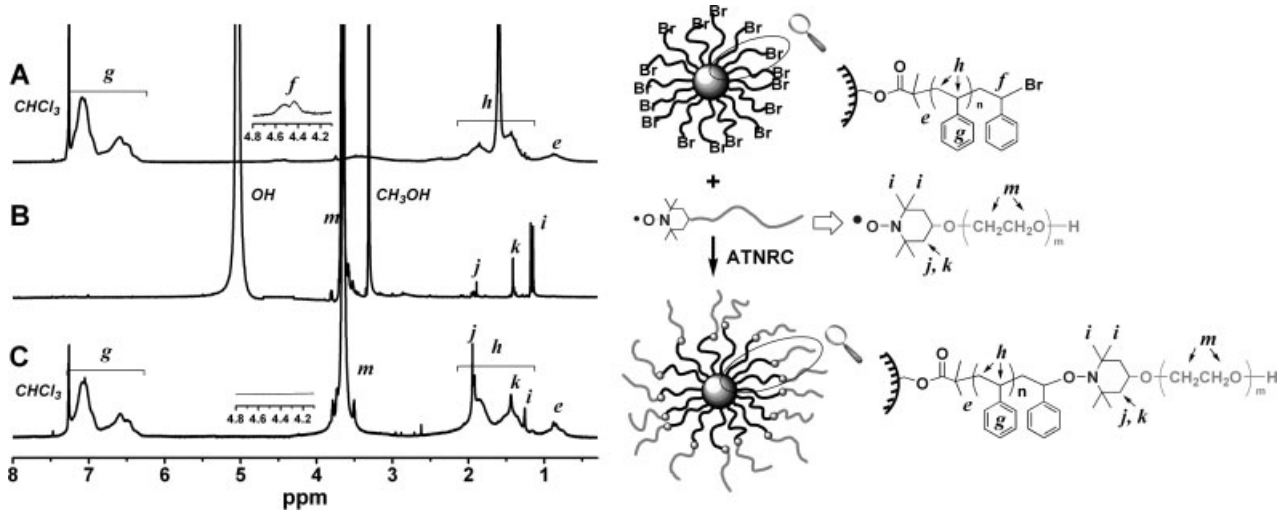


Figure 1. ^{1}H NMR spectra of HPG-*g*-(PS-Br)$_n$ (A), TEMPO-PEO (B) and HPG-*g*-(PS-*b*-PEO)$_n$ (C).

reflectron mode. 0.8 μL sample dope, which was prepared by mixing matrix solution of dithranol (20 mg/mL) and polymer (10 mg/mL) in the ratio of 5:1, was deposited on the sample holder (well-plate). An untrafliltration separator was purchased from the Shanghai Institure of Nuclear Research (Chinese Academy of Sciences), the cut-off molecular weight of the poly(ether sulfone) film was 50,000 g/mol (calibrated by global protein).

RESULTS AND DISCUSSION

Matyjaszewski reported that in ATRP the macroradicals generated *in situ* by an atom transfer radical equilibrium would take part in bimolecular termination reactions in the presence of a reducing agent.[34–37] It is supposed that if the radical scavengers such as TEMPO or TEMPO derivatives were existent in ATRP reaction, the macroradicals might be trapped by nitroxide radicals instantly and hereby the bimolecular termination between macroradicals could be avoided. Based on this idea, a polymer containing TEMPO group was mixed with another halide-containing polymer in the presence of CuBr/PMDETA. Upon heating, the terminal bromine group served as oxidant was reduced to bromine anion, whereas Cu^{1+} was oxidized to Cu^{2+} accordingly. Meanwhile, the secondary carbon radical was formed and immediately captured by the TEMPO radical in another polymer chain, forming an alkoxyamine between the two polymers. In ATNRC reaction, CuBr participated in the reaction as reactant, and the reaction is irreversible, which is quite different from the common ATRP.

Synthesis of Multi-Arm Star Polymer HPG-*g*-(PS-Br)$_n$

The multi-arm star polymer HPG-*g*-(PS-Br)$_n$ was prepared by ATRP of styrene using the HPG-based macroinitiator HPG-*g*-Br$_n$. The M_n of selected HPG was around 30,000 as determined by ^{13}C NMR, and the Br numbers of 66, 120, and 210. Polymerization was conducted for 5.5 h in the presence of CuBr and bipyridine (BPY) (see supporting information).

The ^{1}H NMR spectrum [Fig. 1(A)] indicated the successful synthesis of HPG-*g*-(PS-Br)$_n$ with signals appearing at 1.27–2.25 ppm (h), 6.27–7.22 ppm (g) for St units, and 0.7–1.0 ppm (e) for methyl groups close to ester bond. The peak at 4.35–4.65 ppm (f) was corresponding to the methine proton on (CH_2—C***H***(Ph)—Br).

It is well known that the M_n of star polymer, estimated by GPC with linear polystyrene standards, is smaller than the value predicted theoretically, which is due to the smaller hydrodynamic volume of the star chain than that of the linear chain. Thus the M_n of HPG-*g*-(PS-Br)$_n$ estimated by GPC was unreliable. Moreover, in the star polymer HPG-*g*-(PS-Br)$_n$, the HPG core was wrapped by the PS chains, so the integration of proton peak area of HPG and part of PS chain closed to the core in ^{1}H NMR was not very accurate. Thus the methine and methylene protons from HPG core showed a weak and broad peak in

Table 1. Data of HPG-*g*-(PS-*b*-PEO)$_n$

	HPG-*g*-(PS-Br)$_n$					HPG-*g*-(PS-*b*-PEO)$_n$			
Sample	N_{PS}[a]	M_n[b]	M_n[c]	PDI[c]	$M_{n(PS)}$[c]	M_n[d]	M_n[c]	PDI[c]	E.F. (%)[e]
HPG-*g*-(PS-*b*-PEO)$_{66}$	66	160,000	42,500	1.17	1,800	335,000	47,000	1.07	90
HPG-*g*-(PS-*b*-PEO)$_{120}$	120	310,000	49,000	1.14	2,200	653,000	53,000	1.14	94
HPG-*g*-(PS-*b*-PEO)$_{210}$	210	690,000	55,000	1.19	3,000	1,260,000	59,000	1.19	92

[a] The number of PS on one HPG-*g*-(PS-Br)$_n$.
[b] The molecular weight of HPG-*g*-(PS-Br)$_n$ was measured by ^{1}H NMR, using eq 1.
[c] The molecular weight and polydispersity of PS and HPG-*g*-(PS-*b*-PEO)$_n$ were measured by GPC using PS as standard, performed in THF solution.
[d] The molecular weight of HPG-*g*-(PS-*b*-PEO)$_n$ was calculated by eq 3.
[e] The Efficiency of "ATNRC" was measured by ^{1}H NMR, using eq 2.

^{1}H NMR spectrum due to the partial immobilization of the HPG in the star core, and this deviation in the measurement of molecular weight is inevitable for the ^{1}H NMR analysis of star polymers.[19] In this article, linear PS chains were cleaved from HPG-*g*-(PS-Br)$_n$, then the M_n of HPG-*g*-(PS-Br)$_n$ and the number of PS on HPG could be derived by following equation (eq 1) and

$$M_{n(\text{HPG-}g\text{-(PS-Br)}_n)} = M_{n(PS)} \times N_{Br} + M_{n(\text{HPG-}g\text{-Br}_n)} \quad (1)$$

where $M_{n(PS)}$ is the M_n of PS after cleavage from HPG-*g*-(PS-Br)$_n$ which could be obtained by GPC; N_{Br} is the number of Br groups on HPG-*g*-Br$_n$, and $M_{n(\text{HPG-}g\text{-Br}_n)}$ is the M_n of HPG-*g*-Br$_n$. All data were listed in Table 1.

Synthesis of PEO with TEMPO End Group (TEMPO-PEO)

TEMPO-PEO was prepared according to our previous work.[38] HTEMPO mixed with DPMK was used as coinitiation system for the polymerization of EO through ROP. The resulting polymer showed a unimodal trace with a narrow polydispersity index of 1.12 and molecular weight of 3200 g/mol.

Figure 1(B) shows a typical ^{1}H NMR spectrum of TEMPO-PEO, which was measured in the presence of calculated amount of ammonium formate and palladium-on-carbon due to the paramagnetism of nitroxide radicals. The resonances of the methylene protons in PEO repeating units could be observed in the region of 3.36–3.80 ppm (m). The signals at 1.15 ppm and 1.18 ppm (i) are attributed to the methyl in HTEMPO, and those at 1.45 (k) and 1.95 ppm (j) are attributed to methylene protons in HTEMPO.

Synthesis of HPG-*g*-(PS-*b*-PEO)$_n$

HPG-*g*-(PS-*b*-PEO)$_n$ was synthesized by ATNRC reaction between HPG-*g*-(PS-Br)$_n$ and TEMPO-PEO in the presence of CuBr/PMDETA using DMF as solvent at 80 °C. After complete removal of copper salts by basic alumina column, the crude product was purified by ultra filtration membrane using methanol as the solvent, which was an efficient method to remove the unreacted TEMPO-PEO and avoid the sample loss by the common operation of dissolution/precipitation.

Figure 2(C) shows the ^{1}H NMR spectrum of HPG-*g*-(PS-*b*-PEO)$_n$ which is featured by two main regions. The resonances of the methylene groups on PEO could be observed in 3.40–4.05 ppm, phenyl groups and methylene or methine groups on PS occur in the region of 6.30–7.30 ppm or 1.20–2.20 ppm. When compared with Figure 2(A), the signal at 4.35–4.65 ppm (f) attributed to the methine proton in (CH_2—C***H***(Ph)—Br) disappears completely after ATNRC reaction due to the

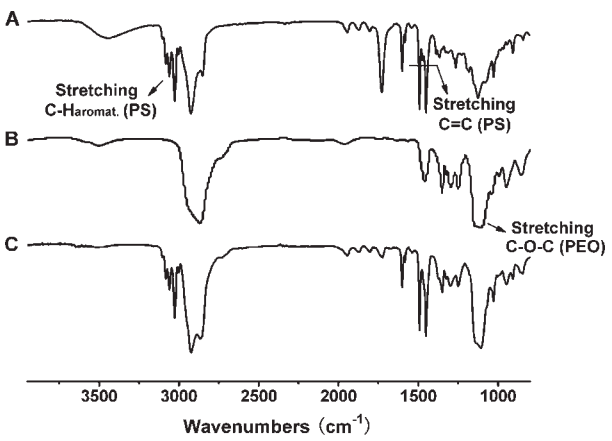


Figure 2. FTIR spectra of HPG-*g*-(PS-Br)$_n$ (A), TEMPO-PEO (B) and HPG-*g*-(PS-*b*-PEO)$_n$ (C).

change of carbon-bromide bond to carbon–oxygen bond after coupling, which confirmed the successful synthesis of star block copolymers.

The FTIR spectrum of HPG-*g*-(PS-*b*-PEO)$_n$ [Fig. 2(C)] seems to combines the features of Figure 2(A,B together), in which the bands in the region of 3020–3100 cm^{-1} and 1450–1601 cm^{-1} are due to C—H$_{aromat}$ and C=C$_{aromatic}$ in PS respectively, whereas band at 1121 cm^{-1} is ascribed to the C—O—C stretching in PEO.

The GPC curve of HPG-*g*-(PS-*b*-PEO)$_n$ [Fig. 3(D)] is unimodal with smaller retention time than HPG-*g*-(PS-Br)$_n$ [Fig. 3(C)], which was another evidence for successful ATNRC reaction.

The Efficiency of "ATNRC" Reaction

The efficiency of ATNRC (EF) was achieved by calculating the M_n of PS-*b*-PEO side chains cleaved from the HPG core.

As shown in Figure 3(B), a small shoulder at longer retention time (lower molecular weight region) is observed in the GPC curve of cleaved PS-*b*-PEO, which overlapped with the peak of cleaved PS from HPG-*g*-(PS-Br)$_n$ [Fig. 3(A)]. Therefore, we believe that it was the uncoupled PS chain, which did not participate in the ATNRC reaction.

The content of unreacted PS was confirmed by the ^{1}H NMR spectrum (Fig. 4) of cleaved PS-*b*-PEO using following equation (eq 2).

$$\mathrm{EF} = \frac{A_m}{A_g} \times \frac{\frac{M_{n(PS)} \times 5}{104}}{\frac{M_{n(PEO)} \times 4}{44}} \times 100\% \quad (2)$$

where A_m and A_g are the integral areas of the (—C$_6$***H*$_5$**—) protons on PS and (—C***H*$_2$**CH$_2$O—) protons on PEO, respectively; $M_{n(PS)}$ and $M_{n(PEO)}$ are the M_n of PS and PEO obtained by GPC; 104 and 44 are the molecular weight of the monomer styrene and ethylene oxide, respectively.

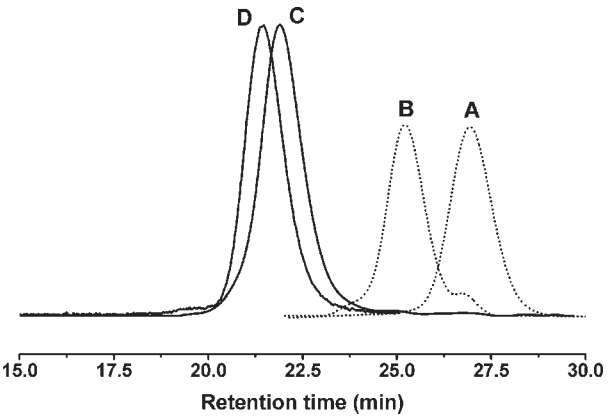


Figure 3. GPC curves of cleaved PS (A), cleaved PS-*b*-PEO (B), HPG-*g*-PS-Br$_n$ (C) and HPG-*g*-(PS-*b*-PEO)$_n$ (D).

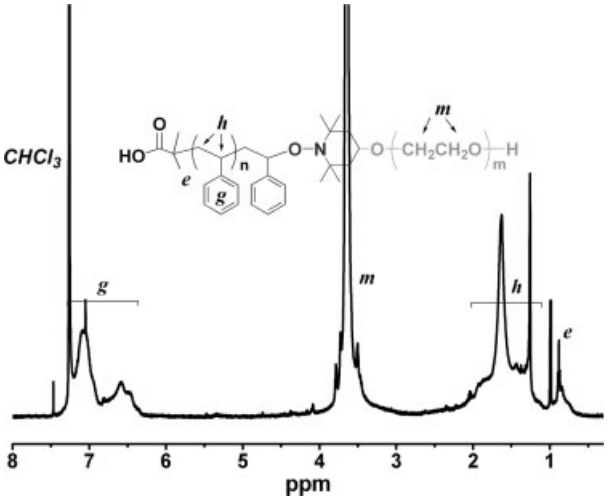


Figure 4. ^{1}H NMR spectrum of cleaved PS-*b*-PEO.

It was found that the application of ATNRC reaction in the synthesis of multi-arm star polymers could provide a satisfactory efficiency (>90%). To compare the efficiency with the linear one, linear PS sample was produced by the ATRP using a small molecule ethyl 2-bromoisobutylate as initiator; the M_n of linear PS was 2000 g/mol with the PDI 1.08. In the same conditions, the former was coupled with TEMPO-PEO of 3200 g/mol, the efficiency of the coupling reaction was 95%, which was slightly higher than that of multiarm PS.

Based on the efficiency of ATNRC reaction, the M_n of HPG-*g*-(PS-*b*-PEO)$_n$ can be calculated using the following equation (eq 3).

$$M_{n(\text{HPG-}g\text{-(PS-}b\text{-PEO)}_n)} = M_{n(\text{HPG-}g\text{-(PS-Br)}_n)} + N_{PS} \times M_{n(PEO)} \times \mathrm{EF} \quad (3)$$

where $M_{n(\text{HPG-}g\text{-(PS-Br)}_n)}$ is the M_n of HPG-*g*-(PS-Br)$_n$; N_{PS} is the number of PS chains on HPG-*g*-(PS-Br)$_n$; and $M_{n(PEO)}$ are the M_n of PEO obtained by GPC and EF is the efficiency of ATNRC reaction.

CONCLUSIONS

The star block copolymers with polystyrene-*block*-polyethylene oxide (PS-*b*-PEO) side chains and

hyperbranched polyglycerol (HPG) core were synthesized via combination of ATRP with the ATNRC reaction. The results showed that the efficiency of ATNRC was quite acceptable even if the density of coupling cites on HPG was rather high. It was believed that this modular approach would provide great potential for production of the polymers with varied compositions and well-defined structures.

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