Preparation of Star Polymers of Hyperbranched Polyglycerol Core with Multiarms of PS-*b*-PtBA and PS-*b*-PAA

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ABSTRACT: Atom transfer radical polymerization (ATRP) was applied to synthesize a new kind of star polymers of hyperbranched polyglycerol (HPG) core with multiarms of PS-*b*-PtBA and PS-*b*-PAA by using the ''core first'' technique. The HPG core was obtained by anionic polymerization of glycerol first, and then the pendant hydroxyl groups of HPG were esterified with 2-bromoisobutyryl bromide to yield the HPG-*g*-Br, which was used as macroinitiator for ATRP of the first monomer (St) and then second monomer (tBA). After hydrolysis of the PtBA block, poly(acrylic acid) (PAA) side chains were formed. The final products and intermediates were characterized by GPC, NMR, and FTIR in detail. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 777–784, 2008

Key words: block copolymer; hyperbranched; star copolymer; polyglycerol; polystyrene; poly(*t*-butyl acrylate)

INTRODUCTION

Multiarm star polymers are the macromolecules with three-dimensional structure, in which a large number of linear arms with similar molecular weight (MW) and narrow polydispersity index (PDI) were emanated from a central core.[1–9] It attracts increasing interest because of its compact structure, which may lead to peculiar rheological properties.[10] In addition, end-functional multiarm star polymers possess unusually high functionality that permits further modification or crosslinking.[11] Generally, star polymers can be prepared by two different routes: the ''arm-first''[12–14] strategy, i.e., telechelic polymers are attached to a suitable core molecule; and the ''core-first''[15–17] strategy, i.e., a polyfunctional core is used as a multiple initiator for polymerization. Because of recent advances in radical polymerization and synthetic strategies, instead of living anionic/cationic polymerization, nowadays controlled radical polymerization techniques such as nitroxide-mediated radical polymerization,[18] atom transfer radical polymerization (ATRP),[19–23] and reversible addition-fragmentation chain transfer[24] polymerization are typically employed to synthesize multiarm star polymers with controlled structure and narrow PDI.

Dendrimers and hyperbranched polymers are attractive precursors of macroinitiators for the preparation of multiarm star polymers by the core-first strategy.[25–30] The hyperbranched polymers prepared by one step from AB_2 type molecules are more widely used because of the simple preparation procedure compared with dendrimers. Among them, hyperbranched polyglycerol (HPG) with narrow PDI, which is obtained via ring-opening multibranching polymerization under slow addition of the monomer,[31–33] is one of the most promising cores for multiarm star polymers.[34–45]

The HPG could be modified by attaching a suitable initiator moiety to the hydroxyl end groups. Up to now, many functional monomers are introduced onto the HPG core, including tBA, AA,[43] MA,[40] HEMA,[38] etc. But no block copolymer arms on the HPG core were reported because of the difficult of synthesis, purification, and characterization.

The self-assembly of block copolymers has attained considerable interest recently.[46] Amphiphilic block copolymers show highly interesting supramolecular associative behavior in selective solvents and this provides many unique properties to them.[46] Recent technological advancements have conjured the scope of the block copolymer micelles to a wide range of industrial and technological applications.[47] It is well demonstrated that the solution and bulk properties of the block copolymers spectacularly

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hinge on the chain architecture.[48] Star-shaped polymers possess specific three-dimensional structures, and so they could be expected to exhibit different morphological and physical properties from those of their linear polymer counterparts. As a result they have enabled potential applications.[49] Ternat et al. determined the capacity of H40-PCL-PtBA to encapsulate and disperse significant loadings of volatile hydrophobic molecules such as fragrances in water.[25] Mai et al. obtained hyperbranched multiarm PEHO-star-PPO and investigated its self-assembly behavior. The results indicate that the ill-defined PEHO-star-PPO molecules could aggregate into large spherical micelles with controlled sizes.[50] Very recently, Wang et al. prepared and evaluated a 16-arm amphiphilic star block copolymer based on a lipophilic PCL core and a water-soluble PEG shell as a drug carrier.[51]

One important challenge in the synthesis of star copolymers is to determine the MW of the side chains. Because the MW of stars estimated from gel permeation chromatography (GPC) using the linear polymer standards are smaller than the values theoretically predicted due to the smaller hydrodynamic volume of the star polymers than that of the linear chains, their MW obtained from GPC is unreliable. On the other hand, the cores are wrapped by the side chains, which causes the integration of proton peak area of core and part of side chains close to the core in NMR, called as partial immobilization,[52] and so the results are not very accurate. This deviation for the measurement of molecular weight is inevitable for the NMR analysis of star polymers.

In this article, the synthesis procedure of a new kind of star copolymer with multiarms of block copolymers HPG-*g*-(PS-*b*-PtBA) and HPG-*g*-(PS-*b*-PAA) were described, and the strategy for reliable determination of the MW of star copolymers were proposed by hydrolysis of the side chains from the core.

EXPERIMENTAL

Materials

1,1,1-Tris(hydroxymethyl)propane (TMP), glycidol, 2-bromoisobutyryl bromide, CuBr, 2,2′-bipyridyl (BPY), and *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA) were purchased from Aldrich (Steinheim, Germany), and used as received. Styrene (St) and *tert*-butyl acrylate (tBA) were dried with CaH_2 and distilled under reduced pressure before use. Tetrahydrofuran (THF) and pyridine were purchased from Sinopharm Chemical Reagent (SRC, Shanghai, China), and refluxed over sodium wire and distilled before use. Methanol (SRC) was refluxed over CaH_2 and distilled before use. Other reagents and solvents were purchased from SRC and used as received. Hyperbranched polyglycerol (HPG1: MW = 44,500 Da, PDI = 1.33, 600 hydroxyl groups; and HPG2: MW = 30,000 Da, PDI = 1.27, 400 hydroxyl groups) were synthesized according to Ref. 31. The number of hydroxyl groups could be calculated by the following equation: $N_{OH} = [MW_{(HPG)} - MW_{(TMP)}\ (134)]/MW_{(Glycerol)}\ (74)$.[31]

Measurements

The average MW and PDI were measured by GPC. For the HPG, 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 with a G1310 Å pump, a G1362 Å refractive index detector, and a G1315 Å diode-array detector, and PEO standard samples were used for calibration. GPC traces of the rest polymers were performed in THF at 35°C with an elution rate of 1.0 mL/min on an Agilent 1100 with a G1310 Å pump, a G1362 Å refractive index detector, and a G1314 Å 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 as the internal standard and $CDCl_3$, CD_3OD, DMSO-d_6 as the solvent. Fourier transform infrared (FTIR) spectra were recorded on 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.

Esterification of HPG with 2-bromoisobutyryl bromide

HPG2-*g*-(PS-*b*-PtBA)1 is exemplified for all synthesis section. 3.0 g (0.1 mmol) HPG2 (40 mmol hydroxyl groups) was dried by distillation with toluene, and then dissolved in 100 mL of anhydrous pyridine, to which 0.75 mL (6 mmol) of 2-bromoisobutyrylbromide was added dropwise at 0°C over 30 min under vigorous stirring and the reaction was kept overnight. A large part of pyridine was distilled under reduced pressure first, and then azeotropic distillation with toluene was performed; the residue was washed with cyclohexane three times and dialyzed against deionized water to ensure all the impurities were washed out. After removal of the water (vacuum, 50°C), transparent and viscous HPG-*g*-Br with a pale yellow was obtained. The percentage of esterification is 16.5%, which meant 66 hydroxyl groups on one HPG2 (400 hydroxyl groups) were esterified. ^{1}H-NMR (CD_3OD) δ (ppm): 0.92 (s, 3H, CH_3—CH_2— of TMP), 1.45 (s, 2H, CH_3—CH_2 of TMP), 1.96 (s, 6H, —$C(CH_3)_2$—Br), 3.40–4.00 (m, 5H, C*H*, CH_2 of HPG), 4.87 (s, OH); 4.24, 4.39, 4.53, 5.17, 5.28 (m, 4H,

Br—C(CH_3)$_2$—COO—CH_2—, Br—C(CH_3)$_2$—COO—CH—); FTIR (cm^{-1}): 1076 (—C—O—C—), 1731 (—COO—), 3200–3500 (—OH).

Synthesis of star polymer with multiarms (HPG-*g*-PS)

0.5 g (0.013 mmol, i.e., 0.8 mmol Br-atoms) HPG2-g-Br1, 0.11 g (0.8 mmol) CuBr, 0.12 g (0.8 mmol) BPY, and 30 mL (0.26 mol) of 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. After 5.5 h, the ampoule was quenched in liquid nitrogen and exposed to air, then the unreacted styrene was evaporated and the residue was diluted with $CHCl_3$, collected the upper solution after centrifuge, the product was precipitated thrice by dissolution/precipitation with methylene chloride/ethanol, a white powder HPG2-*g*-PS1 was obtained and dried *in vacuo* at 40°C for 24 h. ^{1}H-NMR ($CDCl_3$) δ (ppm): 0.70–0.95 (s, 6H, —C(CH_3)$_2$—PS), 1.20–2.20 (m, 3H, —CH_2CH— of PS), 2.80–4.05 (m, 5H, CH, CH_2 of HPG), 4.35–4.65 (d, 1H, CH_2—CH(Ph)—Br), 6.30–7.30 (m, 5H, —C_6H_5 of PS); FTIR (cm^{-1}): 1126 (—C—O—C—), 1452, 1492, 1583, 1601 (—C—C—aromatic ring)) 1731 (—COO— 3200–3500 (—OH); GPC: MW = 42,500 Da, PDI = 1.17.

Cleavage of HPG-*g*-PS

0.3 g HPG2-*g*-PS1 was dissolved in 50 mL of THF, to which 10 mL of KOH solution (1*M* in ethanol) was added, and the mixture was refluxed for 72 h. After evaporating to dryness, the polymer was dissolved in CH_2Cl_2 and by dissolution/precipitation with methylene chloride/ethanol, the PS homopolymer was dried at 50°C for 24 h. GPC: MW = 1800 Da, PDI = 1.23.

Synthesis of HPG-*g*-(PS-*b*-PtBA)

1.0 g (0.006 mmol, containing 0.4 mmol Br groups) HPG2-g-PS1, 0.055 g (0.4 mmol) CuBr, 0.08 mL (0.4 mmol) PMDETA, 8 mL tBA, and 2 mL toluene 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 80°C. After 24 h, the ampoule was quenched in liquid nitrogen and exposed to air, the reaction mixture was concentrated to 1/3 of its original volume, and then precipitated in mixed solution of ethanol and water (v/v = 1 : 1). The crude product HPG2-*g*-(PS-*b*-PtBA)1 was purified by dissolution/precipitation with methylene chloride/(ethanol:water = 1 : 1) twice and dried *in vacuo* at 40°C for 24 h. A yellow rubber-like powder was obtained. ^{1}H-NMR ($CDCl_3$) δ (ppm): 0.70–0.95 (m, 6H, —C(CH_3)$_2$—PS), 1.20–2.20 (m, 5H, —CH_2CH— of PS, —CH_2CH— of PtBA), 1.50 (s, 9H, —C(CH_3)$_3$), 2.22 (s, 1H, —CH_2—CH— of tBA), 2.80–4.05 (m, 5H, CH, CH_2 of HPG), 4.11 (s, 1H, CH_2—CH($COOC_4H_9$)—Br), 6.30–7.30 (m, 5H, —C_6H_5 of PS); FTIR (cm^{-1}): 1126 (—C—O—C—), 1451, 1478, 1494, 1598 (—C—C—(aromatic ring)) 1727 (—COO—), 3200–3500 (—OH); GPC: MW = 56,000 Da, PDI = 1.23.

Preparation of HPG-*g*-(PS-*b*-PAA)

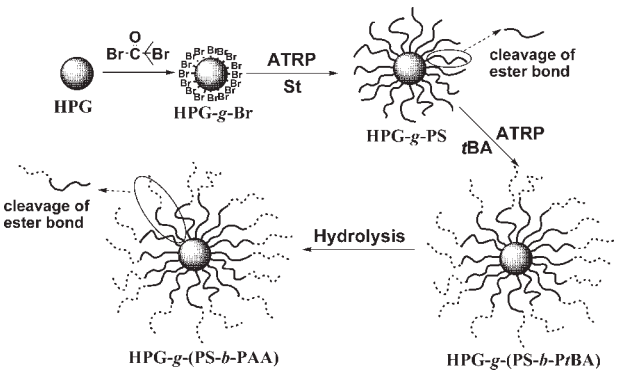
1.0 g HPG2-*g*-(PS-*b*-PtBA)1 and 3.8 mL (0.02 mol) trifluoroacetic acid (TFA) was dissolved in 50 mL CH_2Cl_2, and stirred for 36 h at room temperature. All volatiles were removed under reduced pressure, and the pale gray residue was dried at 40°C under vacuum for 24 h. ^{1}H-NMR (DMSO-d_6) δ (ppm): 0.70–0.95 (m, 6H, —C(CH_3)$_2$—PS), 1.20–2.20 (m, 5H, —CH_2CH— of PS, —CH_2CH— of PtBA), 2.22 (s, 1H, —CH_2—CH— of tBA), 2.80–5.00 (m, 6H, CH, CH_2 of HPG, CH_2—CH($COOC_4H_9$)—Br, H_2O), 6.30–7.30 (m, 5H, —C_6H_5 of PS); FTIR (cm^{-1}): 1126 (—C—O—C—), 1451, 1494, 1600 (—C—C—(aromatic ring)), 1715 (—COO—), 2400–3400 (—COOH).

Cleavage of HPG-*g*-(PS-*b*-PAA)

0.5 g of HPG2-*g*-(PS-*b*-PtBA)1 was dissolved in 30 mL of THF, 10 mL of KOH solution (1*M* in ethanol) was added, and the mixture was refluxed for 72 h, and then neutralized with 5% HCl and dialyzed against water. ^{1}H-NMR: $MW_{(PS\text{-}b\text{-}PAA)}$ = 3200 Da.

RESULTS AND DISCUSSION

The HPG-*g*-(PS-*b*-PtBA) and HPG-*g*-(PS-*b*-PAA) are a new kind of star polymers, and the whole preparation process is shown in Scheme 1.



Scheme 1 Synthetic procedure of HPG-*g*-(PS-*b*-PtBA) and HPG-*g*-(PS-*b*-PAA) blocked-arm star polymers and their cleavage by potassium hydroxide.

TABLE I
Preparation of HPG and HPG-*g*-Br

	HPG			HPG-*g*-Br		
Exp.	MW[a]	PDI[b]	N_{OH}[a]	N_{Br}[c]	Br (%)[c]	MW[c]
HPG1-*g*-Br1	44,500	1.33	600	60	10.0	53,500
HPG1-*g*-Br2	44,500	1.33	600	110	18.3	61,000
HPG2-*g*-Br1	30,000	1.27	400	66	16.5	40,000
HPG2-*g*-Br2	30,000	1.27	400	120	30.0	48,000
HPG2-*g*-Br3	30,000	1.27	400	210	52.5	61,500

[a] Molecular weight and the number of hydroxyl groups of HPG were measured by ^{13}C-NMR.
[b] Polydispersity of HPG was measured by GPC using PEO as standard, performed in 0.1*M* $NaNO_3$ aqueous solution.
[c] The number and the percentage of Br on one HPG-*g*-Br and the molecular weight of HPG-*g*-Br were measured by ^{1}H-NMR.

Esterification of HPG with 2-bromoisobutyryl bromide

In our work, hyperbranched polyglycerol samples HPG1 (MW = 44,500 Da, PDI = 1.33, 600 hydroxyl groups) and HPG2 (MW = 30,000 Da, PDI = 1.27, 400 hydroxyl groups) were synthesized by anionic polymerization of glycerol using trimethylolpropane (TMP) as initiator according to previously published references, and the molecular weight for them were derived from ^{13}C-NMR[31,32] (Table I). Then they were reacted with 2-bromoisobutyrylbromide to produce HPG-*g*-Br as macroinitiators. Five macroinitiators with average 60, 110 initiation sites for HPG1 and 66, 120, 210 initiation sites for HPG2 were prepared and shown in Table I.

Figure 1 is the ^{1}H-NMR spectra of HPG before and after reaction with 2-bromoisobutyrylbromide. Comparing with Figure 1(A) for the HPG scaffold, the five resonances observed in the range of 3.4–4.1 ppm for methylene and methine on HPG were moved to 4.1–5.5 ppm(d) in Figure 1(B), in which the methylene was linked to the ester bond, which meant esterification was carried out successfully. The appearance of the resonances at 1.95 ppm(c) for the protons of the methyl groups closed to Br atom also proved the successful reaction. Thus, Br number (N_{Br}) of HPG2-*g*-Br1 can be calculated by following two ways:

$$N_{Br} = \frac{\frac{A_c}{6}}{\frac{A_{3.1-4.4}}{5}} \times 400 \quad (1)$$

$$N_{Br} = \frac{A_{d1} + A_{d2} + \left[\frac{A_{d3}+A_{d4}}{2}\right] + \left(\frac{A_{d5}}{2}\right)}{\frac{A_{3.1-4.4}}{5}} \times 400 \quad (2)$$

where A_c and $A_{3.1-4.4}$ are the integral areas of the protons of the methyl groups close to Br atom at

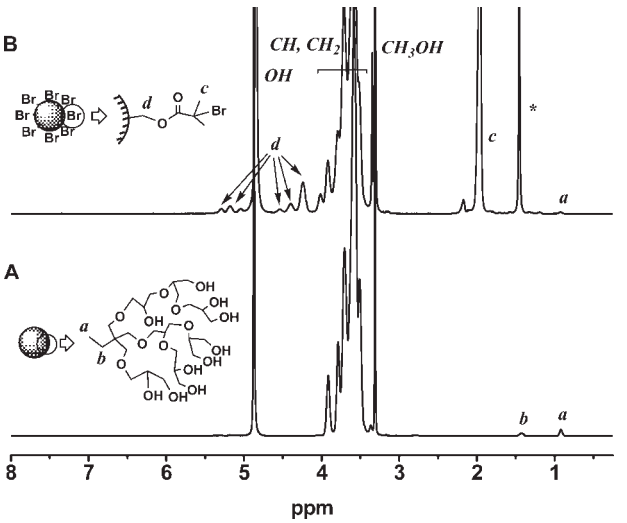


Figure 1 ^{1}H-NMR spectra of HPG (A) and HPG-*g*-Br (B).

1.95 ppm(c) and the HPG scaffold hydrogens at 3.4–4.1 ppm, respectively. A_{d1} to A_{d5} from high field to low field in the region 4.1–5.5 ppm(d) are due to methylene protons connected to the ester bond after esterification. Both results are coincident (see Table I), N_{Br} for HPG2-*g*-Br1 was 66 by formula (1) and 64 by formula (2).

In Figure 2, A and B are the FTIR spectra of HPG and HPG-*g*-Br. The appearance of a characteristic ester group at 1731 cm^{-1} supported the successful synthesis of HPG-*g*-Br. As it is well known the purity of the ATRP macroinitiators may exert great effect on the polymerization,[53] and there are two major impurities in the crude ATRP macroinitiators, small molecular ATRP initiators from 2-bromoisobutyrylbromide and pyridine salts from the pyridine solution. In our work, for the hydrophilic HPG1-*g*-Br1 and HPG2-*g*-Br1, cyclohexane was first used to wash away small molecular ATRP initiators, and then the pyridine salts could be removed by dialysis

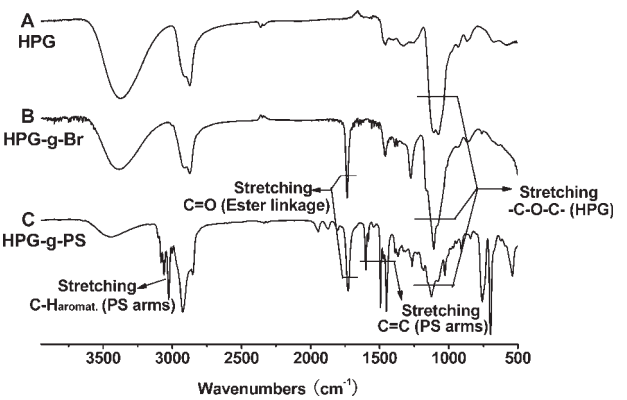


Figure 2 FTIR spectra of HPG (A), HPG-*g*-Br (B), and HPG-*g*-PS (C).

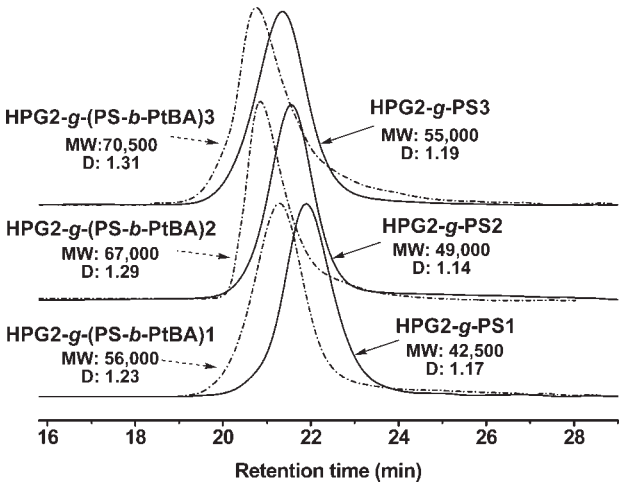


Figure 3 GPC curves of HPG-*g*-PS and HPG-*g*-PS/PtBA.

against water. For the hydrophobic HPG1-*g*-Br2, HPG2-*g*-Br2, and HPG2-*g*-Br3, the pyridine salts could be removed by simply washing with water. After purification, no trace of pyridine salts and small molecular ATRP initiators could be found by UV and ^{1}H-NMR spectra, respectively, and the purification was successful.

Synthesis of star copolymer HPG-*g*-PS by ATRP

ATRP of St using the HPG-based macroinitiator could only be conducted in limited conversions (<35%), because higher conversion may cause the gel formation.[53] This result was in agreement with previous observations by Gnanou and coworkers,[15] which was attributed to the coupling reactions between radicals. To suppress this process, in our work, the styrene monomer conversion was controlled below 20%. As shown in Figure 3 and Table II, the PDI in all cases were low (PDI < 1.26), indicating the good control of polymerization. In GPC measurements, the symmetric peaks for all polymers were observed, that means no coupling termination between different star copolymers occurred. The FTIR spectrum of HPG-*g*-PS is shown in Figure 2(C); the characteristic C=$C_{aromatic}$ stretching bands of PS block at 1450–1601 cm^{-1}, C—$H_{aromatic}$ stretching at 3020–3100 cm^{-1} confirmed the successful polymerization of St monomer. Comparing the ^{1}H-NMR spectra Figure 1(B) with Figure 4(A), after polymerization [Fig. 4(A)] the signals at 1.20–2.20 ppm(h) and 6.30–7.30 ppm(g) for St units appear; the peak at 1.94 ppm(c) for methyl groups close to Br atom is shifted to higher field (0.7–0.95 ppm) because of the change of carbon–bromine bond to carbon–carbon bond of the tertiary carbon; the appearance of the new peak at 4.35–4.65 ppm(f) is corresponding to the methine proton (CH_2—C*H*(Ph)—Br). These changes proved that the ATRP of St was successful, and all the initiating sites on HPG were served in ATRP, as no homopolymer of PS was found. This was also confirmed by Frey and coworkers in their previous work.[38,40]

Calculation of the MW of the star copolymer HPG-*g*-PS

As we know, the MW of stars, estimated from GPC using linear polystyrene as standards, were smaller than the values theoretically predicted due to the smaller hydrodynamic volume of the star polymers than that of the linear chains, and so the MW of HPG-*g*-PS obtained from GPC was unreliable. On the other hand, in the star polymers, the HPG cores were wrapped by the PS chains, and the methine and methylene protons from HPG core showed a weak and broad peak in ^{1}H-NMR spectrum due to the partial immobilization of the HPG in the star core, so the integration of proton peak area of HPG and part of PS chain close to the core in NMR was not very accurate, and this deviation for the measurement of molecular weight of star polymers is inevitable in the NMR analysis.[53] In our cases the PS side chains were detached from the HPG by basic hydrolysis of the ester group in KOH mixed solvents of THF and ethanol. The GPC measurement of

TABLE II
Preparation of HPG-*g*-PS

	HPG-*g*-PS							PS	
Exp.	N_{Br}	Conv. (%)	MW[a]	PDI[a]	MW (cal. 1)[b]	MW (cal. 2)[c]	MW (cal. 2)/MW	MW[a]	PDI[a]
HPG1-*g*-PS1	60	7.9	47,000	1.21	284,000	227,000	4.83	2900	1.20
HPG1-*g*-PS2	110	19.7	56,800	1.26	716,000	500,000	8.80	4000	1.19
HPG2-*g*-PS1	66	9.2	42,500	1.17	241,000	160,000	3.76	1800	1.23
HPG2-*g*-PS2	120	16.3	49,000	1.14	475,000	310,000	6.32	2200	1.16
HPG2-*g*-PS3	210	18.9	55,000	1.19	695,000	690,000	12.54	3000	1.31

[a] Molecular weight and PDI of HPG-*g*-PS and PS after cleavage measured by GPC using PS as standard and THF as eluent.
[b] Molecular weight of HPG-*g*-PS calculated by St monomer conversion using eq. (3).
[c] Molecular weight of HPG-*g*-PS calculated by the molecular weight of PS chains after cleavage using eq. (4).

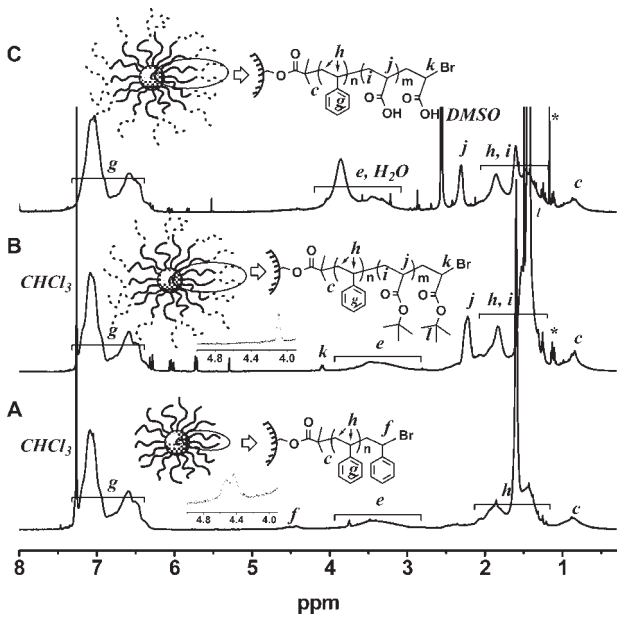


Figure 4 ^{1}H-NMR spectra of HPG-*g*-PS (A), HPG-*g*-(PS-*b*-PtBA) (B), and HPG-*g*-(PS-*b*-PAA) (C).

hydrolyzed PS is given in Table II; the narrow PDI of the detached PS side chains confirmed the well-controlled ATRP of styrene initiated by HPG-*g*-Br as well as the actual formation of a well-defined star copolymer HPG-*g*-PS. Thus the MW of HPG-*g*-PS could also be accurately derived from the MW of free PS chains. In this article, two methods were used to calculate the MW of HPG-*g*-PS, namely, it was derived by St monomer conversion (MW cal. 1) or by MW of detached PS chains from HPG-*g*-PS (MW cal. 2) (Table II).

$$\mathrm{MW(cal.1)} = \frac{\mathrm{St_{conv.}} \times 30 \times 0.909}{0.5} \times \mathrm{MW_{(HPG\text{-}g\text{-}Br)}} \quad (3)$$

$$\mathrm{MW(cal.2)} = \mathrm{MW_{(PS)}} \times N_{\mathrm{Br}} + \mathrm{MW_{(HPG\text{-}g\text{-}Br)}} \quad (4)$$

where in formula (3) (MW cal.1), $\mathrm{St_{conv.}}$ is the St conversion, 30 mL is the used St volume in ATRP, 0.909 is the density of St, 0.5 g is the used HPG-*g*-Br weight in ATRP for HPG-*g*-PS, and $\mathrm{MW_{(HPG\text{-}g\text{-}Br)}}$ is the MW of HPG-*g*-Br from ^{1}H-NMR. In eq. (4), $\mathrm{MW_{(PS)}}$ is the MW of PS after cleavage from HPG-*g*-PS by GPC, N_{Br} is the average number of Br groups on one HPG-*g*-Br molecule, and $\mathrm{MW_{(HPG\text{-}g\text{-}Br)}}$ is the MW of HPG-*g*-Br from ^{1}H-NMR. Both of the results were agreeable as shown in Table II.

The values of MW (cal. 2) were selected for the following reaction. It was found that the more arms of the star polymers, the higher the compact structure value [MW (cal. 2)/MW (GPC)].[52] Table II shows that the star polymer HPG2-*g*-PS3 with the most arms (arm number = 210) has the highest compact structure value 12.54, which means that HPG2-*g*-PS3 is more compact than any other samples.

Synthesis of star copolymer with multiarms of PS-*b*-PtBA [HPG-*g*-(PS-*b*-PtBA)]

Obviously, the terminal benzyl bromide on every PS chain can further initiate ATRP of the monomers, e.g., tBA, but the purification and characterization might be difficult. To suppress the coupling reactions between radicals, monomer (tBA) conversion in the chain extension polymerization was also controlled below 20%. As Figure 3 and Table III showed, the PDI in all cases were low (PDI < 1.35) indicating the good control of tBA polymerization in our system. In GPC measurements, we also did not detect any homopolymer of tBA. Figure 4(B) shows the ^{1}H-NMR spectrum of HPG-*g*-(PS-*b*-PtBA). The new peak at 2.22 ppm(p) corresponding to the methine proton on the main chain of tBA units appears besides the characteristic signals of HPG at 2.80–4.05 ppm(e) and St units at 6.30–7.30 ppm(g). Additionally, the appearance of methyl protons of PtBA at 1.50 ppm(q) could also be observed. Comparing with Figure 4(A), the peak (f) at 4.35–4.65 ppm attributed to the methine proton of (CH_2—C*H*(Ph)—Br) on HPG-*g*-PS disappears completely in Figure 4(B), and a new peak (k) at

TABLE III
Preparation of HPG-*g*-(PS-*b*-PtBA) and HPG-*g*-(PS-*b*-PAA)

Exp.	HPG-*g*-(PS-*b*-PtBA) N_{Br}	MW[a]	PDI[a]	MW (cal.)[b]	MW (cal.)/MW	MW (cal.)[c] of HPG-*g*-(PS-*b*-PAA)	MW[d] of PS-*b*-PAA
HPG1-*g*-(PS-*b*-PtBA(PAA))1	60	68,000	1.22	420,000	6.18	335,500	4700
HPG1-*g*-(PS-*b*-PtBA(PAA))2	110	76,400	1.35	1,050,000	13.74	809,000	6800
HPG2-*g*-(PS-*b*-PtBA(PAA))1	66	56,000	1.23	324,000	5.79	251,200	3200
HPG2-*g*-(PS-*b*-PtBA(PAA))2	120	67,000	1.29	696,000	10.39	528,000	4000
HPG2-*g*-(PS-*b*-PtBA(PAA))3	210	70,500	1.31	1,406,000	19.94	1,090,500	4900

[a] Molecular weight and PDI of HPG-*g*-(PS-*b*-PtBA) measured by GPC using PS as standard and THF as eluent.
[b] Molecular weight of HPG-*g*-(PS-*b*-PtBA) calculated by MW of free PS-*b*-PAA chain using eq. (5).
[c] Molecular weight of HPG-*g*-(PS-*b*-PAA) calculated by MW of free PS-*b*-PAA chain using eq. (6).
[d] Molecular weight of free PS-*b*-PAA chain measured by ^{1}H-NMR.

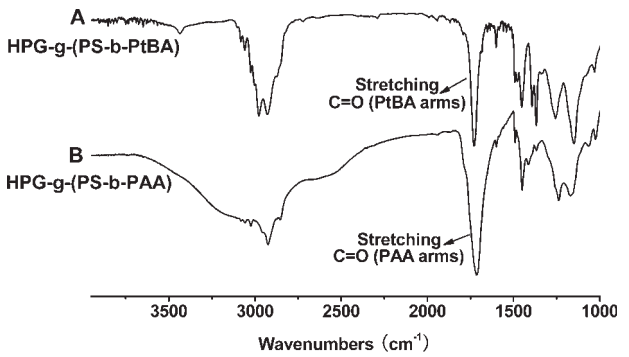


Figure 5 FTIR spectra of HPG-*g*-(PS-*b*-PtBA) (A) and HPG-*g*-(PS-*b*-PAA) (B).

4.11 ppm for the end methine protons (CH_2— C*H* ($COOC_4H_9$)—Br) at the ω-end of the block copolymer chains appears. This demonstrates the successful chain extension of the second monomer tBA. The FTIR spectrum of HPG-*g*-(PS-*b*-PtBA) is shown in Figure 5(A); a strong peak at 1727 cm^{-1} for C=O stretching band of PtBA arms was observed. It further confirmed that the chemical components of desired HPG-*g*-(PS-*b*-PtBA) were synthesized successfully.

Hydrolysis of *t*-butyl groups of HPG-*g*-(PS-*b*-PtBA)

The *t*-butyl groups of PtBA block could be hydrolyzed selectively by TFA to obtain the amphiphilic star polymer HPG-*g*-(PS-*b*-PAA), and the process is highly efficient. Figure 4(C) shows the ^{1}H-NMR spectrum of HPG-*g*-(PS-*b*-PAA). Compared with Figure 4(B), the peak strength at 1.50 ppm assigned to the methyl protons of tBA units which is overlapped with methylene protons of St units decreased, which means that the ester groups of tBA units were hydrolyzed successfully. FTIR analysis also supported the presence of the acid groups shown in Figure 5(A); the broad absorbance of carboxylic acid groups was observed at 2400–3400 cm^{-1} and the carbonyl stretch was shifted from 1727 cm^{-1} for ester bond of PtBA to 1715 cm^{-1} of carboxyl group of PAA. Thus it could be concluded that the *t*-butyl groups were hydrolyzed thoroughly in such condition.

Calculation of the MW of star copolymers

The MW of HPG-*g*-(PS-*b*-PtBA) and HPG-g-(PS-*b*-PAA) from GPC was deviated from their real values. So the same strategy as HPG-*g*-PS was used to confirm the real MW. The PS-*b*-PAA side chains were also hydrolyzed in KOH mixed solvents of THF and ethanol. By means of ^{1}H-NMR analysis, the MW of PS-*b*-PAA could be obtained by comparing the ratio of PS and PAA block, and then the MW of star polymers can be derived from the following equations:

$$\mathrm{MW}_{(\mathrm{HPG}\text{-}g\text{-}(\mathrm{PS}\text{-}b\text{-}\mathrm{PtBA}))} = \mathrm{MW}_{(\mathrm{HPG}\text{-}g\text{-}\mathrm{Br})} + N_{\mathrm{Br}} \times \left[\frac{128}{72} \times \left(\mathrm{MW}_{(\mathrm{PS}\text{-}b\text{-}\mathrm{PAA})} - \mathrm{MW}_{(\mathrm{PS})}\right) + \mathrm{MW}_{(\mathrm{PS})}\right] \quad (5)$$

$$\mathrm{MW}_{(\mathrm{HPG}\text{-}g\text{-}(\mathrm{PS}\text{-}b\text{-}\mathrm{PAA}))} = \mathrm{MW}_{(\mathrm{HPG}\text{-}g\text{-}\mathrm{Br})} + N_{\mathrm{Br}} \times \mathrm{MW}_{(\mathrm{PS}\text{-}b\text{-}\mathrm{PAA})} \quad (6)$$

where $\mathrm{MW}_{(\mathrm{HPG}\text{-}g\text{-}\mathrm{Br})}$ is the MW of HPG-*g*-Br from ^{1}H-NMR, $\mathrm{MW}_{(\mathrm{PS})}$ is the MW of PS after cleavage from HPG-*g*-PS by GPC, N_{Br} is the average number of Br groups on one HPG-*g*-Br molecule, and $\mathrm{MW}_{(\mathrm{PS}\text{-}b\text{-}\mathrm{PAA})}$ is the MW of free PS-*b*-PAA chain which is calculated by the ratio of PS and PAA block from ^{1}H-NMR.

For example, HPG2-*g*-(PS-*b*-PAA)1 is composed of a HPG-*g*-Br core of MW 40,000 Da and with 66 arms of PS-*b*-PAA side chains of MW 3200 Da, and so the total MW is 40,000 + 66 × 3200 = 251,200 (Da). The MW of PS-*b*-PtBA could be derived from $[(128/72) \times (\mathrm{MW}_{(\mathrm{PS}\text{-}b\text{-}\mathrm{PAA})} - \mathrm{MW}_{(\mathrm{PS})}) + \mathrm{MW}_{(\mathrm{PS})}]$, which is 4300 Da, and so the MW of HPG2-*g*-(PS-*b*-PtBA)1 is 40,000 + 66 × 4300 = 324,000 Da (Table III). We also noticed that the compact structure values MW (cal.)/MW (GPC) for HPG-*g*-(PS-*b*-PtBA) are larger than that of HPG-*g*-PS, and it seems the longer chains have the more compactable structures in star polymers.

CONCLUSIONS

The star polymers with hyperbranched polyglycerol core and polystyrene-*b*-poly(*t*-butyl acrylate) or polystyrene-*b*-poly(acrylic acid) block copolymer side chains were successfully synthesized by sequential ATRP using the ''core first'' method. In the whole preparation, no homopolymers of PS and P(tBA) were detected, and so the purification procedure is very simple. By detachment of PS and PS-*b*-PAA side chains from the HPG core, the reliable MW of star polymers could be obtained.

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