Water-Soluble Star Brush Copolymer with Four Arms Composed of Poly(ethylene Oxide) as Backbone and Poly(acrylic Acid) as Side Chains

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ABSTRACT: A series of water-soluble star brush copolymers with four arms consisting of poly(ethylene oxide)-(PEO) as the backbone and poly(acrylic acid) as side chains with different grafting density were prepared by sequential anionic copolymerization and then atom transfer radical polymerization (ATRP). The anionic ring-opening copolymerization of ethylene oxide (EO) and ethoxyethyl glycidyl ether (EEGE) was carried out using pentaerythritol and diphenylmethylpotassium (DPMK) as co-initiator, and then ethoxyethyl groups of EEGE units of the copolymers obtained were removed by hydrolysis. The forming four-arm star copolymers of poly(ethylene oxide-*co*-glycidol) [poly(EO-*co*-Gly)]$_4$ was esterified by the reaction of pending hydroxyl groups of glycidol units of copolymers with 2-bromoisobutyryl bromide, and the resulting macroinitiators of poly(ethylene oxide-*co*-2-bromoisobutyryloxyglycidyl ether) [poly(EO-*co*-BiBGE)]$_4$ were used to initiate the polymerization of *t*-butyl acrylate by ATRP. Afterward, the *t*BA ester groups of [poly(EO-*co*-Gly)-g-P*t*BA]$_4$ were selectively hydrolyzed by trifluoroacetic acid to obtain the water-soluble [poly(EO-*co*-Gly)-g-PAA]$_4$. The final product and intermediates were characterized by SEC and NMR in details.

Introduction

Double-hydrophilic block copolymers are a new class of block copolymers composed of two or more different hydrophilic polymer segments.[1] What is interesting about these copolymers is that the segments of the copolymers have shown some special properties such as polarity transformation upon changing PH or temperature, interaction with metal ions, solid substrates, colloids, and biomolecules. The typical hydrophilic segments include poly(ethylene oxide)(PEO), poly(acrylic acid)(PAA), poly(vinyl pyridine), poly(*N*,*N*′-dimethyl aminoethyl methacrylate), poly(*N*-isopropylacrylamide), polypeptide, and RNA.[2−5] The block copolymers containing such segments have already found applications in reverse assembly,[5] stabilization of inorganic particles,[6] crystal growth modifiers,[7] drug carriers,[8] and gene therapies.[9]

Even though controlled radical polymerization techniques proved their value in deriving linear covalent arrangement of hydrophilic blocks,[10−14] the assembling of two hydrophilic segments in graft or starlike architecture still is a challenge and much attention has been devoted to it.[15,16] Interest in new structures consisting of hydrophilic segments is driven by the expectation that a well-controlled number of branching points can induce different properties as compared to their linear counterparts.

Densely grafted polymer, often referred to as molecular brush, is a kind of copolymer with intriguing structure and can be synthesized by "grafting onto", "grafting through", and "grafting from" methods.[17] More complex architectures using polymer brushes as building blocks, such as double-grafted brushes,[18] brush-coil block copolymers,[19] and star-shaped molecular brushes,[20−22] have also been obtained. It has to be pointed that the backbones of all these synthesized polymers are hydrophobic. Recently, the first synthesis of well-defined star graft copolymers with arms composed of hydrophilic PAA backbone and hydrophobic PMMA side chains by ATRP has been reported.[23]

However, the synthesis of double-hydrophilic star brush copolymer with arms consisting of hydrophilic PEO backbone and hydrophilic PAA side chains has never been reported in the literature due to the difficulty in preparation. PEO segments are not only hydrophilic but also nonionic and crystalline and can form the complex with monovalent metallic cations.[24] Branched PEO has shown potential applications in biomedical and pharmaceutical areas, and a lot of work has been done; the starlike and dendrimer-like PEOs[25] or starlike block copolymers containing poly(ethylene oxide) segments were synthesized.[26] PAA is a kind of weak polyelectrolyte in which the degree of ionization is governed by the pH and the ionic strength of the aqueous solution.[27] PAA is known to form an intermolecular complex with various nonionic proton-accepting polymers,[28] their derivatives, and cationic polyelectrolytes in aqueous and organic media. Numerous studies have also been devoted to the interaction of PAA with metal ions.[6,29] Copolymers with new structures containing PEO and PAA segments such as brush-coil block[30] and star-block[31] copolymers have been synthesized and used for crystallization modification of calcium carbonate. Preparation of water-soluble star brush copolymer composed of PEO and PAA is a challenge for synthesis technology and also important for further study of the relationship between polymer structure and its properties.

In the present work, we report the water-soluble star brush copolymers composed of a starlike PEO backbone and PAA side chains with different grafting density by combination of anionic ring-opening polymerization with ATRP.

Experimental Section

Materials. CuBr (98%, Acros) was purified by stirring overnight in acetic acid and filtered, then washed with ethanol and diethyl ether successively, and finally dried under vacuum. Pentaerythritol

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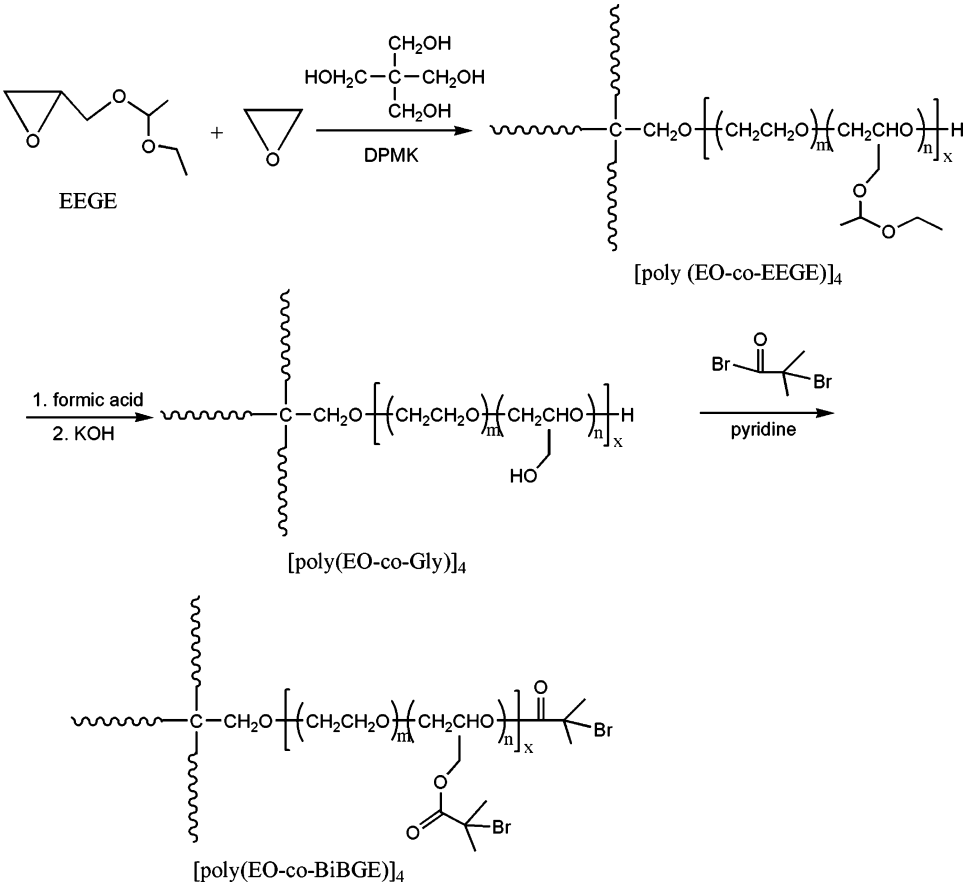
(Aldrich, 98%) was dried at 50 °C under vacuum. EO (98%, Sinopharm Chemical Reagent Co., Ltd (SCR)) was dried by calcium hydride for 48 h and then distilled under N_2 before use. THF (SCR, 99%) was refluxed over sodium wire and distilled from sodium naphthalenide solution. *tert*-Butyl acrylate (*t*BA, Aldrich 98%) and DMSO (SCR, 98%) was distilled over CaH_2 under reduced pressure just before use. Pyridine (SCR, 99.5%) was refluxed over sodium wire and distilled. 2-Bromoisobutyryl bromide (98%) and *N*,*N*′,*N*′,*N*′′-pentamethyldiethylenetriamine (PMDETA), were purchased from Aldrich and used as received. Ethoxyethyl glycidyl ether (EEGE) was prepared as described elsewhere[32] according to literature.[33] Diphenylmethylpotassium (DPMK) was prepared as described elsewhere.[32] Other reagents (SCR) were purified by common procedures.

Measurements. ^{1}H NMR spectra were obtained on a DMX 500 MHz spectrometer with tetramethylsilane (TMS) as the internal standard and $CDCl_3$ as the solvent, except for the final product [poly(EO-*co*-Gly)-g-PAA]$_4$, which was measured in D_2O. Size exclusion chromatography (SEC) was performed on an Agilent l100 with a G1310A pump, a G1362A refractive index detector, and a G1314A variable wavelength detector using tetrahydrofuran (THF) as eluent at 35 °C with an elution rate of 1.0 mL/min. One 5 μm PL gel column (500 Å, molecular range 500−2 × 10^4 g/mol) and two 5 μm PL gel mixed bed column (molecular range 200−3 × 10^6 g/mol) were calibrated by polystyrene standard samples. For [poly(EO-*co*-Gly)]$_4$, SEC was performed in 0.1 M $NaNO_3$ at 40 °C with an elution rate of 0.5 mL/min on the same instruments, except a G1315A diode-array detector was used to substitute for the G1314A variable wavelength detector. Three TSK-gel PW columns in series (bead size: 6, 13, 13 μm; pore size: 200 Å, greater than 1000 Å, less than 100−1000 Å; molecular range: 0−5 × 10^4, 5 × 10^4−8 × 10^6, (5−8) × 10^6 g/mol, respectively) were calibrated by PEO standard samples. The injection volume was 20 μL, and the concentration was 5 mg/mL. IR spectra were obtained on a Magna-550 Fourier transform infrared spectrometer. The ultrafiltration separator was purchased from the Shanghai Institute of Nuclear Research, Chinese Academy of Sciences, and the cutoff molecular weight of used poly(ether sulfone) membrane was 20 000 g/mol (calibrated by globular protein).

Synthesis of the Star Copolymers with Four Arms [Poly(EO-*co*-EEGE)]$_4$. The copolymerization was carried out in a stainless steel kettle. The typical synthesis of a four-arm star copolymers is described as follows: a 150 mL kettle was vacuumed at 80 °C for 24 h and cooled to room temperature and then to −20 °C. In the anhydrous pentaerythritol (0.134 g, 0.001mol) dissolved in 50 mL of mixed solvents of DMSO and THF (v/v: 3/2), a solution of DPMK in THF (1.6 mL, 0.5 M solution) was slowly introduced. The orange-red color of DPMK was changed to yellow when the alkoxides were formed. Afterward, the homogeneous initiator solution obtained was introduced into the cooled kettle by a syringe, then EEGE (10.41 g, 0.071mol) and EO (10.64 mL, 0.217mol) were added. After the solution was stirred at 60 °C for 48 h, the polymerization was terminated by adding of a few drops of acidified methanol. Then all the solvents were removed by reduced distillation. The crude product was dissolved in CH_2Cl_2, filtered, and dried over anhydrous $MgSO_4$. The yellowy viscous product [poly(EO-*co*-EEGE)]$_4$ was obtained in the yield of 85% after CH_2Cl_2 was removed. By changing the feed ratio of EEGE to EO in anionic copolymerization, the content of EEGE units in the star copolymers can be well controlled. The four-arm star homopolymer of EEGE [poly(EEGE)]$_4$ was also prepared using the similar method, except only EEGE was used.

Preparation of [Poly(EO-*co*-Gly)]$_4$ by Cleavage of the Ethoxyethyl Groups of [Poly(EO-*co*-EEGE)]$_4$. The hydrolysis procedure was carried out according to literature.[34] [Poly(EO-*co*-EEGE)]$_4$ ($M_{n(SEC)}$ = 13 900 g/mol, 9 g) was mixed with 100 mL of formic acid. The solution was stirred at room temperature for 30 min and then evaporated in vacuo at 50 °C to remove formic acid. The crude product was then dissolved in a mixture of dioxane (90 mL) and methanol (50 mL) and hydrolyzed by KOH aqueous solution (1 mol/L, 20 mL) under refluxing for 24 h and then neutralized with HCl aqueous solution (1 mol/L). After the solvents were removed

Scheme 1. Schematic Synthesis Route of Four-Arm Star Macroinitiator



under reduced pressure, the polymer was dissolved in water and purified by an ultrafiltration membrane. Then the filtered aqueous solution was concentrated to dryness, dissolved in CH_2Cl_2, and dried over anhydrous $MgSO_4$. The filtrate was distilled in vacuum to remove CH_2Cl_2 and dried in vacuo at 50 °C. The transparent viscous product [poly(EO-*co*-Gly)]$_4$ was obtained in a yield of 93%.

Preparation of Macroinitiator [Poly(EO-*co*-BiBGE)]$_4$. A 3 g sample of [poly(EO-*co*-Gly)]$_4$ ($M_{n(SEC)}$ = 7800 g/mol, 18.46 mmol hydroxyl groups) was dissolved in 100 mL of anhydrous degassed pyridine, then 3.4 mL (27.69 mmol) of 2-bromoisobutyryl bromide was added dropwise at 0 °C for 60 min under vigorous stirring. The mixture was stirred for 3 h at 0 °C, followed by stirring at room temperature for 24 h. After the insoluble salt was removed by filtration, pyridine was removed by azeotropic distillation with dry toluene. The residue was dissolved in CH_2Cl_2 and washed with KOH aqueous solution (1 mol/L), HCl aqueous solution (1 mol/L), and distilled water, respectively. After CH_2Cl_2 was removed by distillation in vacuum, the produced polymer dissolved in ethanol was purified by an ultrafiltration membrane to remove low-molecular-weight impurities. Then the ethanol was removed from the product by distillation, the remains were dried in vacuo at 50 °C, and the yellowy product with a yield of 85% was obtained.

Synthesis of Star Brush Copolymers with Four Arms by ATRP. In a typical process, 0.2100 g of the initiator [poly(EO-*co*-BiBGE)]$_4$ ($M_{n(SEC)}$ = 14 600 g/mol, 69 mmol of bromoisobutyryl groups), 4.97 mL of *t*BA, 50.2 mg of CuBr (0.35mmol), 0.0732 mL of PMDETA (0.35mmol), and 2.5 mL of acetone were charged in an ampule that was degassed by three freeze−pump−thaw cycles. Then the sealed ampule was immersed in an oil bath at 60 °C. After a certain time, the ampule was dipped into liquid nitrogen to stop the polymerization. The solution was diluted with acetone and passed through the neutral alumina column to remove the catalyst and then precipitated into methanol/water (v/v: 1/1). After filtration, the product was purified by dissolution/precipitation twice with acetone/methanol and water (v/v:1/1) and then dried at 40 °C in vacuo for 2 days.

Hydrolysis of the *tert*-Butyl Ester Groups on Side Chains. [Poly(EO-*co*-Gly)-g-P*t*BA]$_4$ was dissolved in CH_2Cl_2, and then a 5-fold molar excess of CF_3COOH (with respect to the amount of *t*-butyl groups in the side chains) was added. The reaction mixture was stirred at room temperature for 24 h. During the hydrolysis, the resulting brush with PAA side chains precipitated in CH_2Cl_2 gradually. The crude product was separated by filtration, washed with CH_2Cl_2, and then thoroughly dried by vacuum at 40 °C overnight.

Results and Discussion

Synthesis of Star Macroinitiators with Four Arms [Poly(EO-*co*-BiBGE)]$_4$. In Scheme 1, the procedure for the synthesis of starlike macroinitiators was described. The anionic ring-opening copolymerization of EO and EEGE was performed using DPMK as deprotonating agent, which could be easily reacted with hydroxyl groups to form alkoxides. To control the polymerization reasonably, it is important that only 20% of the hydroxyl groups of the pentaerythritol were activated, otherwise alkoxides would be precipitated.[26] A mixture of DMSO and THF (v/v: 3/2) was used as solvent for polymerization instead of THF because propagating alkoxides would be aggregated in pure THF.[25] Under such conditions, all of the four hydroxyl groups of pentaerythritol could efficiently initiate the copolymerization of EO and EEGE because of the rapid exchange of protons between dormant hydroxyls and propagating alkoxides, and all four arms grew at the same rate.[25]

It was found, however, that although efforts had been paid out to alleviate the side reaction during the polymerization, a small shoulder peak at large elution volume beside the main peak was still observed in the SEC curve, as shown in Figure 1.

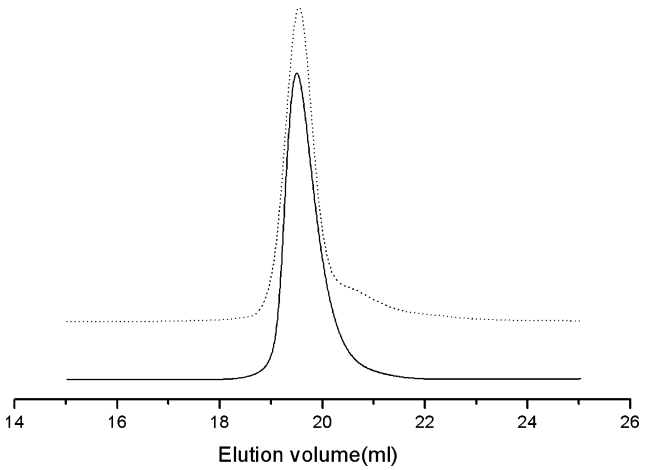


Figure 1. SEC traces of poly(EO-*co*-EEGE) four-arm star copolymer (entry 1 in Table 1) before (dot line) and after (solid line) purification by ultrafiltration membrane.

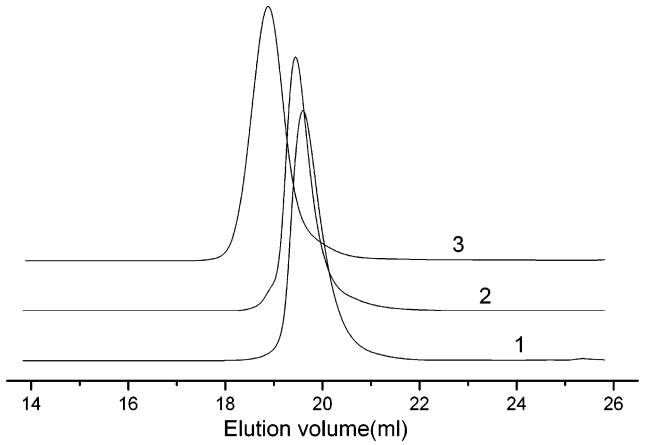


Figure 2. SEC traces of [poly(EO-*co*-EEGE)]$_4$ (1, 2, 3 were prepared as shown in Table 1) after purification by ultrafiltration membrane.

These low-molecular-weight byproducts may be attributed to the chain transfer of propagating alkoxides to DMSO resulting "dimsyl" carbanions ($CH_3(SO)CH_2^-$) to initiate the polymerization of EO and EEGE.[35,36] However, these byproducts can be easily removed by separation using an ultrafiltration membrane, as shown in Figure 1, and [poly(EO-*co*-EEGE)]$_4$ with a very narrow molecular weight distribution was obtained (Figure 2).

A typical ^{1}H NMR spectra of [poly(EO-*co*-EEGE)]$_4$ was shown in Figure 3A. The quadruplet at δ = 4.68−4.72 ppm was the methine protons of the ethoxyethyl groups in EEGE units; the protons of the two different methyl groups in the EEGE units appeared at δ = 1.29, 1.30 ppm as a doublet and at δ = 1.18−1.21 ppm as a triplet, respectively. The signal of the protons in main chain and methylene protons in lateral chains were in the range of δ = 3.46−3.75 ppm, and the methylene protons linked to the core were detected at 3.41 ppm.

The ratio of EEGE to EO in copolymers can be calculated from the following eq 1 on the basis of Figure 3A:

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

Here the R_T is the molar ratio of EEGE to EO in copolymers, A_c and A_{sum} are the peak area of methine protons (c) of the ethoxyethyl groups in EEGE units and sum of the protons in

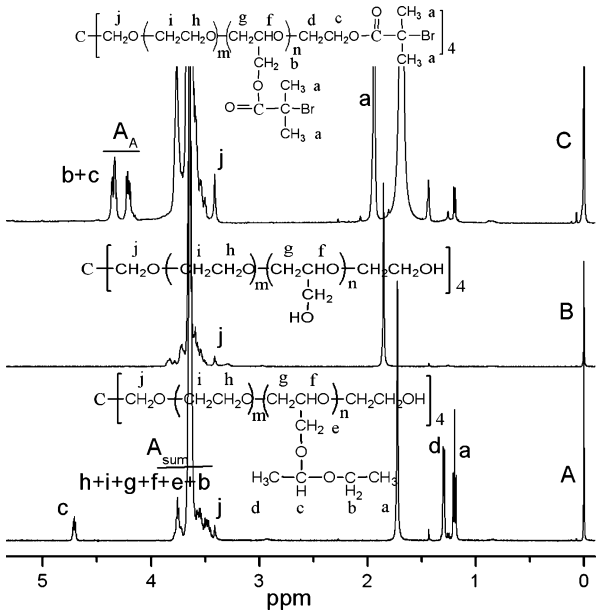


Figure 3. ^{1}H NMR spectra of four-arm star macroinitiator and its precursor in $CDCl_3$: (A) [poly(EO-*co*-EEGE)]$_4$ (entry 1 in Table 1), (B) [poly(EO-*co*-Gly)]$_4$) (entry 1 in Table 2), (C) [poly(EO-*co*-BiBGE)]$_4$ (entry 1 in Table 2).

Table 1. Data of the Four-Arm Star Backbone Polymers

sample	R_f[a]	R_T[b]	M_n[c]	M_w/M_n[c]	M_n[d]	N_{EEGE}[e]
1	1/10	1/12	12 500	1.09	11 076	16
2	1/3	1/2.9	13 900	1.06	12 282	44
3	1/0	1/0	18 500	1.12	17 020	114

[a] The feed ratio of EEGE to EO. [b] The molar ratio of EEGE to EO in four-arm star copolymer [poly(EO-*co*-EEGE)]$_4$ calculated from ^{1}H NMR on formula 1 in text. [c] Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) determined by SEC using PS as standard and THF as elution. [d] Number-average molecular weight (M_n) calculated from ^{1}H NMR on formula 2 in text. [e] The number of EEGE units in four-arm star [poly(EO-*co*-EEGE)]$_4$ calculated by the integration of protons from ^{1}H NMR.

main chain and methylene protons in lateral chains (h, i, g, f, e, and b), respectively. The R_T values of copolymers are close to the feed ratio, so the contents of EEGE unit in the main chain can be well controlled by changing the feed ratio of EO and EEGE, as shown in Table 1.

The number-average molecular weight (M_n) of the polymers was determined by NMR spectra on the basis of end group analysis using the following eq 2

$$M_n = \frac{8A_c}{A_j}(146 + 44/R_T) + 134 \qquad (2)$$

where A_j represents the peak areas of methylene protons (H_j) for the pentaerythritol core and A_c and R_T have the same meaning as eq 1.

To obtain the reactive hydroxyl groups on the [poly(EO-*co*-EEGE)]$_4$, the polymers were treated with formic acid first,[34] and formate was produced by the cleavage of the ethoxyethyl group. Then the polyformate was further saponified in the KOH dioxane/methanol mixture solution, and hydroxyl groups were recovered. Thus the [poly(EO-*co*-EEGE)]$_4$ was transformed to [poly(EO-*co*-Gly)]$_4$ with multipending hydroxyl groups.

The complete removal of the ethoxyethyl groups was confirmed by ^{1}H NMR analysis. The peaks at $\delta = 4.68-4.72$ ppm [$-$O$-$**CH**(CH$_3$)$-$O$-$] (c), at $\delta = 1.30, 1.29$ ppm [$-$OCH(**CH$_3$**)$-$O$-$] (d), and at $\delta = 1.18-1.21$ ppm ($-$O$-$CH$_2$**CH$_3$**) (a) assigned to the ethoxyethyl group of poly(EO-*co*-EEGE) in Figure 3A disappeared completely after hydrolysis, as shown in Figure 3B, so the [poly(EO-*co*-Gly)]$_4$ was really formed.

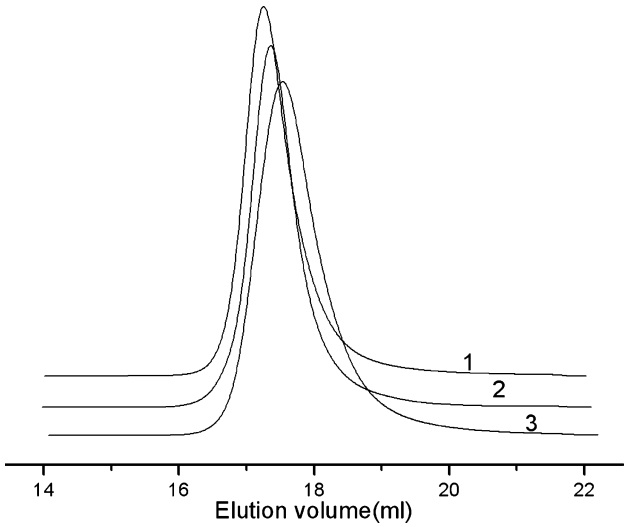


Figure 4. SEC traces of four-arm star [poly(EO-*co*-Gly)]$_4$ (1, 2, 3 were prepared as shown in Table 2).

Table 2. SEC and ^{1}H NMR Data of the Four-Arm Star Macroinitiators

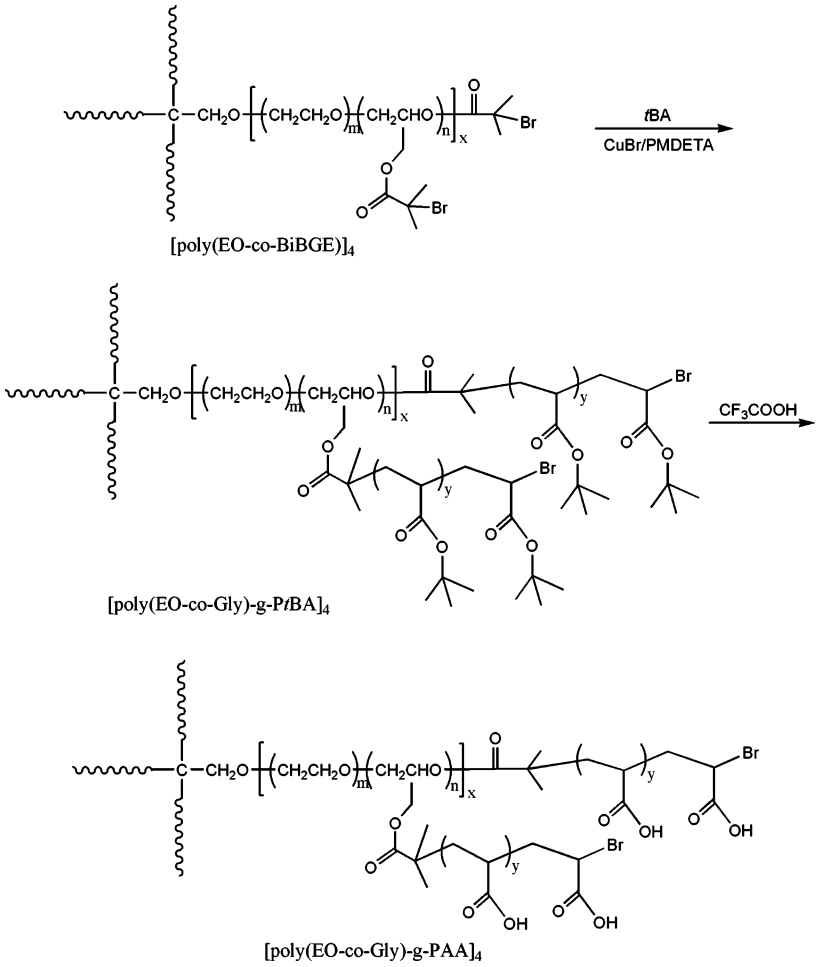
	[poly(EO-*co*-Gly)]$_4$		[Poly(EO-*co*-BiBGE)]$_4$		
sample[a]	M_n[b]	M_w/M_n[b]	M_n[c]	M_w/M_n[c]	$P_{n,NMR}$[d]
1	9400	1.15	13 600	1.11	20
2	7800	1.17	14 600	1.08	48
3	6500	1.19	18 800	1.12	115

[a] The samples 1, 2, 3 are coincident with the sample number in Table 1. [b] Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) determined by SEC, calibrated against PEO standards using 0.1 M $NaNO_3$ as elution. [c] Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) determined by SEC, calibrated against PS standards using THF as elution. [d] Number of initiator sites in four-arm star macroinitiators, calculated by comparing the integration of protons from ^{1}H NMR.

Figure 4 shows the SEC eluograms of [poly(EO-*co*-Gly)]$_4$. The monomodal curves indicated that there was no chain degradation during hydrolysis. However, the sharp difference between the molecular weight of [poly(EO-*co*-EEGE)]$_4$ and hydrolyzed [poly(EO-*co*-Gly)]$_4$ derived by SEC was found. For example, the former was about 13 900 g/mol and the latter was 7800 g/mol in the case of entry 2 (see Tables 1 and 2). This difference may be attributed to the different SEC measurement conditions. For [poly(EO-*co*-EEGE)]$_4$, the sample can be soluble in THF and insoluble in water, and the molecular weight was derived using PS as standard. For [poly(EO-*co*-Gly)]$_4$, however, it is soluble in water and insoluble in THF, so the molecular weight was obtained in water phase using PEO as standard. Nevertheless, as the following data shows, after esterification of hydroxyl groups of [poly(EO-*co*-Gly)]$_4$ with 2-bromoisobutyryl bromide, the molecular weight of the product derived by SEC using THF as eluent approximates that of [poly(EO-*co*-EEGE)]$_4$ (see Tables 1 and 2).

The hydroxyl groups of [poly(EO-*co*-Gly)]$_4$ were then esterified with 2-bromoisobutyryl bromide to obtain macroinitiators with narrow molecular weight distribution (Table 2), and the complete esterification of the hydroxyl groups of [poly(EO-*co*-Gly)]$_4$ was also confirmed by ^{1}H NMR (Figure 3C).

Scheme 2. Synthesis of Four-Arm Star Brush Copolymer [poly(EO-*co*-Gly)-g-PAA]$_4$



The hydroxyl group conversion can be calculated by the following formula:

$$E_T = \frac{\frac{A_A}{2}}{\frac{A_j}{8}(N_{EEGE} + 4)} \times 100\% \quad (3)$$

where E_T is the conversion efficiency of hydroxyl groups of [poly(EO-*co*-Gly)]$_4$, A_j and A_A represent the integral area of the methylene protons (H_j) for the pentaerythritol core (the peak at $\delta = 3.41$ ppm) and the integral area of the methylene protons (H_b, H_c) linked to the ester (the peaks at $\delta = 4.18-4.35$ ppm), respectively. N_{EEGE} is the number of EEGE units in [poly(EO-*co*-EEGE)]$_4$ measured by ^{1}H NMR (see Table 1).

The E_T values for all samples were nearly 100%, which suggested that hydroxyl groups were converted thoroughly into bromoisobutyryl completely. The FTIR spectra before and after esterification of [poly(EO-*co*-Gly)]$_4$ provided other evidence for complete esterification, the picks at 3473 cm^{-1} attributed to hydroxymethyl disappeared after esterification, and the new peaks at 1736 cm^{-1} attributed to the ester band appeared.

Synthesis of Star Brush Copolymers with Four Arms [Poly(EO-*co*-Gly)-g-P*t*BA]$_4$. The procedure for the synthesis water-soluble star brush copolymer based on poly(ethylene oxide) and poly(acrylic acid) using starlike macroinitiators was described in Scheme 2. The ATRP of *t*BA was carried out in acetone at 60 °C using the PMDETA/CuBr catalyst system. The conditions and results of ATRP by using three kinds of

Table 3. Experimental Conditions and Results of the Four-Arm Star Brush Copolymers

polymer[a]	[M]/[I]/[CuBr][b]	Time (h)	Conv (%)[c]	M_n[d]	M_w/M_n[d]	M_n[e]	N_{PtBA}[e]
A_1	50/1/1	6	29.7	37 200	1.19	51 744	14.9
A_2	50/1/1	10	45.0	49 600	1.23	73 760	23.5
B_1	50/1/0.5	4	10.1	21 000	1.15	43 587	4.7
B_2	50/1/0.5	8	19.4	34 600	1.21	76 290	9.8
B_3	50/1/1	5	14.3	26 000	1.16	58 346	7.1
C_1	30/1/1	6	87	139 000	1.22		
C_2	30/1/0.5	20	84.2	129 000	1.31	391 735	25

[a] Polymers A, B, C were prepared from [poly(EO-*co*-BiBGE)]$_4$ labeled as sample 1, 2, 3 in Table 2, respectively. [b] Molar ratio of monomer [M], initiating bromine groups [I], and [CuBr], the used mole amount of [PMDETA] was equal to [CuBr] in every polymerization. [c] Determined by gravimetric method. [d] Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) determined by SEC, calibrated against PS standards using THF as elution. [e] Number-average molecular weight (M_n) and the average number of *t*-butyl acrylate units in every side chain (N_{PtBA}) of the four-arm star brush copolymers, calculated from the ^{1}H NMR data.

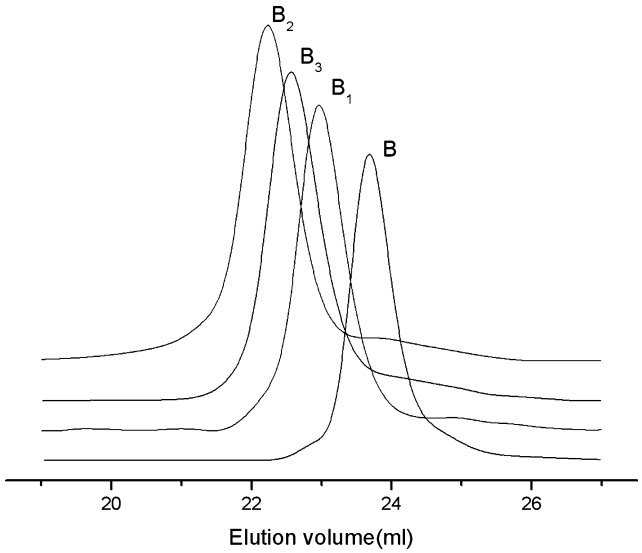


Figure 5. SEC traces of four-arm star brush copolymers and their precursor (from right to left : four-arm star macroinitiators [poly(EO-*co*-BiBGE)]$_4$ M_n = 14 600 and the corresponding four-arm star brush copolymers entries B_1, B_2, B_3 in Table 3).

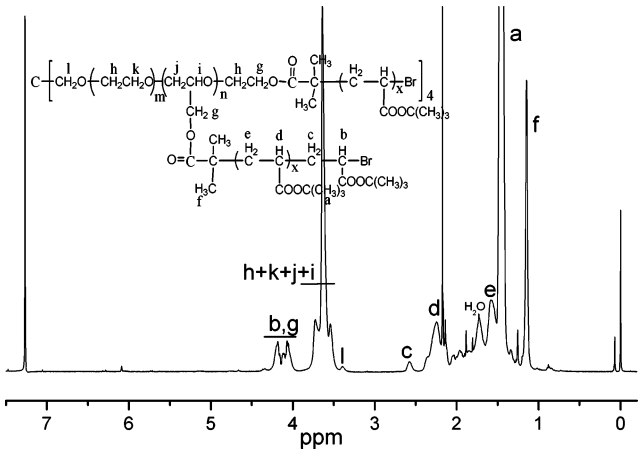


Figure 6. ^{1}H NMR spectra of four-arm star brush copolymer (entry B1 in Table 3) in $CDCl_3$.

[poly(EO-*co*-BiBGE)]$_4$ with different bromoisobutyryl group density as macroinitiator were presented in Table 3.

As shown in Table 3, the molecular weight distributions in all cases were low (M_w/M_n < 1.31), indicating the good control of polymerization in our system, and star brush copolymers with different grafting density of side chains can be obtained by using macroinitiators with varied contents of bromoisobutyryl groups. If the macroinitiator with low content of bromoisobutyryl groups (entry 1 in Table 2, one bromoisobutyryl groups in every 10 EO units) was used and the molar ratio of CuBr to bromoisobutyryl groups was 1:1, the molecular weight distribution of graft copolymer is rather narrow (1.23) and even the conversion of *t*-BA reached to 45%. However, when the homopolymer of EEGE, [poly(EEGE)]$_4$, was used for the preparation of macroinitiator, after hydrolysis and esterification (entry 3 in Table 2), each repeating unit of macroinitiator [PBiBGE]$_4$ has one bromoisobutyryl group. In this case, although the molar ratio of CuBr to bromoisobutyryl groups was still 1:1, after 6 h, the viscosity of the polymerization system is so high that further reaction is very difficult to conduct, but the molecular weight distribution remains narrow. When the ratio of CuBr and bromoisobutyryl groups decreased to 0.5:1 for [PBiBGE]$_4$ in

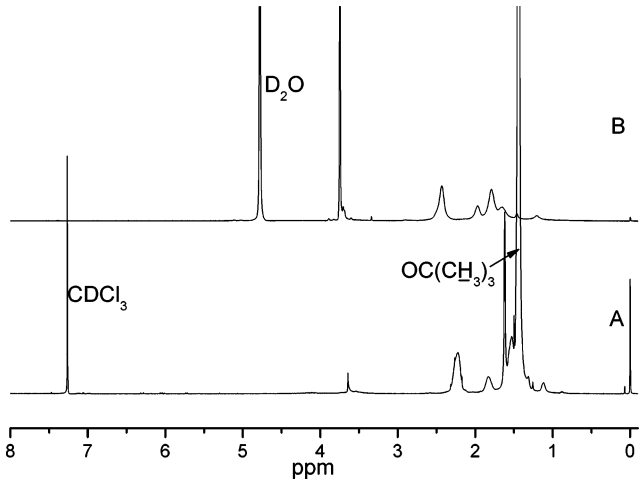


Figure 7. ^{1}H NMR spectra of four-arm star brush copolymer (A) [poly(EO-*co*-Gly)-g-P*t*BA]$_4$ (entry C2 in Table 3) in $CDCl_3$ and (B) the resulting [poly(EO-*co*-Gly)-g-PAA]$_4$ in D_2O.

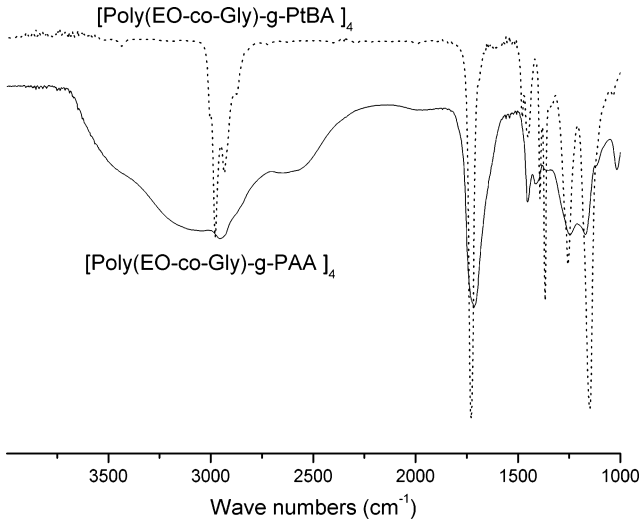


Figure 8. FT−IR (KBr) spectra of star brush copolymer [poly(EO-*co*-Gly)-g-P*t*BA]$_4$ and the result [poly(EO-*co*-Gly)-g-PAA]$_4$.

the same conditions, the polymerization could be conducted smoothly even when the conversion is higher than 80%. These results are consistent with the conclusion of a recent report[37] in the preparation of multiarm star polyglycerol-*block*-poly(*tert*-butyl acrylate).

Figure 5 shows the SEC traces of four-arm star brush copolymers B_1, B_2, and B_3 and their precursor. It revealed that, in our cases when the mole ratio of the CuBr to bromoisobutyryl groups is in the range of 0.5:1−1:1, the star brush copolymers with narrow molecular weight distribution were obtained no matter whether the polymerization time is long or short. We also noticed that, in all SEC measurements, the nice symmetric peaks for all copolymers were observed, it was confirmed that no interbrush coupling termination occurred, and the molecular weight distribution of the star molecular brushes as low as 1.15 demonstrates that the star molecular brushes have uniform molecular weights.

Figure 6 shows the ^{1}H NMR spectrum of the resultant polymer sample B_1 (see Table 3). The peaks at δ = 4.05−4.20 ppm were assigned to the methylene protons (H_g) linked to ester and end methine protons (−**CH**Br, H_b) at the ω end of the copolymer side chains. A characteristic strong peak at 1.45 ppm (peak *a*), corresponding to the methyl protons in the *t*-butyl

group ($-C(\mathbf{CH}_3)_3$), and the chemical shift at $\delta = 3.46-3.75$ ppm represent the protons of the PEO main chain. Thus the degree of polymerization of P*t*BA side chains can be obtained by eq 4:

$$N_{PtBA} = \frac{\frac{A_a}{9}}{\frac{A_f}{6}} \quad (4)$$

where N_{PtBA} is the average number of *t*-butyl acrylate units on each side chain (see Table 3), and A_a and A_f represent the integral area of the methyl protons in the *t*-butyl group of the grafted P*t*BA chains and the integral area of methyl protons at the α-end of the P*t*BA side chains, respectively.

The initiation efficiency in the synthesis of molecular brushes by atom transfer radical polymerization has been widely studied. Reports[38,39] have shown that not every initiating site in the backbone generated a side chain and incomplete initiation was always attributed to steric hindrance due to the high density of initiating centers. In our case, however, the density of initiating centers in the backbone is lower than that reported in the literature, so higher initiation efficiency is anticipated. The initiation efficiency of bromoisobutyryl for atom transfer radical polymerization could be estimated from the ^{1}H NMR spectrum by comparing the integral area of methyl protons for the bromoisobutyryl group (A_f) (its chemical shift is different in before and after initiating) and the peak area of the main chain in eq 5:

$$E_T = \frac{\left(\frac{4}{R_T} + 3\right) \times A_f \times N_{EEGE}}{6A_{sum} \times (N_{EEGE} + 4)} \times 100\% \quad (5)$$

E_T is the reaction efficiency of bromoisobutyryl for ATRP, A_{sum} represented the integral area of all protons of the PEO main chain (H_h, H_k, H_j, H_i), and R_T is the molar ratio of EEGE to EO in copolymer [poly(EO-*co*-EEGE)]$_4$ measured by ^{1}H NMR, and N_{EEGE} is the number of EEGE units in [poly(EO-*co*-EEGE)]$_4$ (see Table 1).

The calculated E_T value is as high as 96%, which indicates that nearly all the bromoisobutyryl groups took part in the polymerization, so the molecular weight of the brushes could be derived from N_{PtBA} and the mass of *t*-butyl acrylate on the assumption that all the initiator sites took part in the radical polymerization (see Table 3).

Hydrolysis of *t*-butyl Groups of the Poly(*t*-butyl acrylate) Side Chains. The *t*-butyl groups of [poly(EO-*co*-Gly)-g-P*t*BA]$_4$ could be hydrolyzed selectively by trifluoroacetic acid, and the process is selective and highly efficient,[30,40] and the resulting product [poly(EO-*co*-Gly)-g-PAA]$_4$ is water soluble. Figure 7 shows the ^{1}H NMR spectrum of the star brush copolymers before and after hydrolysis.

The complete disappearance of the characteristic strong peak at 1.44 ppm corresponding to the methyl protons of the *t*-butyl group demonstrates the successful hydrolysis of P*t*BA side chains. FT−IR analysis was used to support the presence of the acid groups.

As shown in Figure 8, the broad absorbance characteristic of a carboxylic acid group was seen at 2800−3600 cm^{-1} and the carbonyl stretch had shifted from 1726 to 1700 cm^{-1}.

Conclusions

A novel water-soluble star brush copolymer with four arms composed of poly(ethylene oxide) as backbone and poly(acrylic acid) as grafts using pentaerythritol as the core was successfully prepared by combination of the anionic copolymerization with the atom transfer radical polymerization. The synthesized star brush copolymers had narrow molecular weight distributions, and the grafting density of side chains can be well controlled though changing the feed ratio of monomers in anionic copolymerization.

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