ABSTRACT: A well-defined amphiphilic copolymer brush with poly(ethylene oxide) as the main chain and polystyrene as the side chain was successfully prepared by a combination of anionic polymerization and atom transfer radical polymerization (ATRP). The glycidol was first protected by ethyl vinyl ether to form 2,3-epoxypropyl-1-ethoxyethyl ether and then copolymerized with ethylene oxide by the initiation of a mixture of diphenylmethylpotassium and triethylene glycol to give the well-defined polymer poly(ethylene oxide-co-2,3-epoxypropyl-1-ethoxyethyl ether); the latter was hydrolyzed under acidic conditions, and then the recovered copolymer of ethylene oxide and glycidol [poly(ethylene oxide-co-glycidol)] with multiple pending hydroxymethyl groups was esterified with 2-bromoisobutyryl bromide to produce the macro-ATRP initiator [poly(EO-co-Gly)]_{ATRP}. The latter was used to initiate the polymerization of styrene to form the amphiphilic copolymer brushes. The object products and intermediates were characterized with $^1$H NMR, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry, Fourier transform infrared, and size exclusion chromatography in detail. In all cases, the molecular weight distribution of the copolymer brushes was rather narrow (weight-average molecular weight/number-average molecular weight $<1.2$), and the linear dependence of $\ln[M_0]/[M]$ (where $M_0$ is the initial monomer concentration and $M$ is the monomer concentration at a certain time) on time demonstrated that the styrene polymerization was well controlled. This method has universal significance for the preparation of copolymer brushes with hydrophilic poly(ethylene oxide) as the main chain.

Keywords: amphiphiles; anionic polymerization; atom transfer radical polymerization (ATRP); 2,3-epoxypropyl-1-ethoxyethyl ether; poly(ethylene oxide); polystyrene

INTRODUCTION

In recent years, amphiphilic copolymer brushes (or molecular bottlebrushes) have received considerable attention because of their unique chemical and physical properties as well as their potential applications in additives, drugs and biomaterials, nanotechnology, polymer-hybrid nanocomposites, and supramolecular science. Generally, there are three methods of preparing amphiphilic copolymer brushes:

1. Grafting-through: Macromonomers are synthesized first and then homopolymerized or copolymerized with other monomers.
2. Grafting-onto: First, the backbone with reactive sites and side chains with functional end groups are prepared separately, and then the copolymers are formed via a coupling reaction between them.
3. Grafting-from: The side chains are grown from the polymeric backbone pending initiating groups; the easy purification of the resulting polymer brushes is the peculiarity of this method.

In addition, noncovalent interactions, such as hydrogen bonding,\(^8\) ionic interactions,\(^9,10\) and coordination bonding\(^11\) have also been used to form copolymer brushes.

Recently, graft copolymers containing poly (ethylene oxide) (PEO) segments were reviewed by Xie and Xie\(^12\) and Borner and Matyjaszewski,\(^13\) and almost all the pendent grafted chains were PEO. Amphiphilic polymer brushes with PEO as the main chain, however, have hardly been reported in past publications because of the difficulty of the synthesis. Xie and Sun\(^14\) prepared poly(ethylene oxide)-graft-polystyrene (PEO-g-PS) through the copolymerization of ethylene oxide (EO) and polystyrene (PS) macromer terminated by epichlorohydrin in toluene with \(i\)-Bu\(_3\)Al–\(\cdot\)H\(_2\)O–H\(_3\)PO\(_4\)–DMA (where DMA is dimethyl aniline) as the catalyst. However, this method shows some weak points for the preparation of copolymer brushes with PEO as the backbone:

1. The capped efficiency of epichlorohydrin is only about 35% of the total PS.
2. The complex quaternary catalyst \((i\)-Bu\(_3\)Al–\(\cdot\)H\(_2\)O–H\(_3\)PO\(_4\)–DMA catalyst\) must be used in the synthesis, and the grafting efficiency is dependent on the quantity of the catalyst used and the molecular weight of the macromer. It decreases with an increase in the molecular weight of the macromer.
3. The excessive catalyst must be removed after polymerization.

In this presentation, an efficient method is introduced to synthesize well-defined amphiphilic copolymer brushes with PEO as the main chain and PS as the side chains. In the reaction, glycaldol (Gly) that is protected \((2,3\text{-epoxypropyl}-1\text{-ethoxyethyl ether (EPEE)) is co} \text{polymerized with EO by an anionic mechanism f} \text{irst, and then the recovered hydroxyethyl groups from the deprotection of the EPEE units of the copolymer under acidic conditions are further reacted with 2-bromoisobutyl bromide. The resulting macro-ATRP initiator (where ATRP is atom transfer radical polymerization) is used to initiate the graft polymerization of styrene (St).\)

### EXPERIMENTAL

**Materials**

Gly (technical-grade) was purchased from Acros, dried over calcium hydride for 48 h, and then distilled under reduced pressure just before use. 2-Bromoisobutyl bromide (98%) and 2,2′-bipyridyl (bpz; >99%) and \(p\)-toluene sulfonic acid (TsOH; >98%), ethyl vinyl ether (98%), and pyridine (99.5%) were purchased from Aldrich and Sinopharm Chemical Reagent Co., Ltd., respectively, and used as received. CuBr (95%) was stirred overnight in acetic acid, filtered, washed with ethanol and diethyl ether successively, and dried *in vacuo*. St (99.5%) was washed with a 10% NaOH aqueous solution and water successively, dried over anhydrous MgSO\(_4\), further dried over CaH\(_2\), and distilled under reduced pressure. Triethylene glycol (TEG) was distilled from CaH\(_2\) under reduced pressure, and the fraction at 134 °C/90 Pa was collected. 1,1-Diphenylmethane (99%) was also distilled from CaH\(_2\) under reduced pressure, and the fraction at 105 °C/80 Pa was collected. Tetrahydrofuran (THF; 99%) was refluxed over sodium wire and distilled from a sodium naphthalene solution. EO (Sinopharm Chemical Reagent; 98%) was dried by CaH\(_2\) for 48 h and then distilled under N\(_2\) before use. All other reagents were purified by common purification procedures.

**Measurements**

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was performed with a Bruker Reflex II MALDI-TOF mass spectrometer equipped with a nitrogen laser delivering 3-ns laser pulses at 337 nm; \(z\)-cyano-4-hydroxycinnamic acid was used as the matrix. \(^1\)H NMR spectra were obtained on a DMX 500-MHz spectrometer with tetramethylsilane as the internal standard and CDCl\(_3\) as the solvent. Size exclusion chromatography (SEC) was performed on an Agilent 1100 with a G1310A pump, a G1362A refractive-index detector, and a G1314A variable-wavelength detector with THF as the eluent at 35 °C at an elution rate of 1.0 mL/min. One 5-μm LP gel column (500 Å, molecular range = 500 to 2 × 10\(^5\) g/mol) and two 5-μm LP gel mixed-bed columns (molecular range = 200 to 3 × 10\(^6\) g/mol) were calibrated with PS standard samples. For poly(EO-g-Gly), SEC was performed in distilled water at 40 °C with an elution rate of 0.5 mL/min on the same instrument, except that a G1315A diode-array detector was used in...
Three TSKgel PW columns in series (with bead sizes of 6, 13, and 13 μm, pore sizes of 200 Å, greater than 1000 Å, and less than 100–1000 Å, and molecular ranges of 0 to $5 \times 10^4$, 5 × $10^4$ to $8 \times 10^6$, and (5–8) × $10^6$ g/mol, respectively) were calibrated with 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 (FTIR) spectrometer. Gas chromatography/mass spectrometry analysis (GC/MS) of monomer EPEE was carried out with a Finnigan Voyager system with mass-selective detection operating in electronic ionization. The silica capillary column was 30 m × 0.25 mm (i.d.) with a 0.25-μm film thickness (DB-5 Restek). The GC/MS parameters were as follows: the ion source temperature was 200 °C, the carrier gas was helium, the column flow was 1 mL/min, the temperature program was from 100 to 200 °C at 15 °C/min, splitless injection was performed at 250 °C, and ionization was achieved at 70 eV. An ultrafiltration separator was purchased from the Shanghai Institute of Nuclear Research (Chinese Academy of Science); the cutoff molecular weight of the poly(ether sulfone) film was 2000 (calibrated with a global protein). The conversions were determined by a gravimetric method.

Synthesis of Gly with an Acetal Protecting Group (EPEE)

Gly was protected with ethyl vinyl ether according to a previously described procedure, as Scheme 1 shows. Typically, the operation was carried out in a 250-mL three-necked flask with a magnetic stirrer; 1.25 g of TsOH was added in a batch to 50 g (0.675 mol) of Gly in 200 mL of an ethyl vinyl ether solution, the temperature was kept below 40 °C, and 100 mL of a saturated NaHCO₃ aqueous solution was added after the mixture was stirred for 3 h. The organic layer was separated and dried with MgSO₄. After filtration, the ethyl vinyl ether was evaporated, the remainder was distilled under reduced pressure, and the fraction at 51 °C/80 Pa was collected. The product (bp = 152–154 °C) was a colorless liquid and weighed 80.3 g with a yield of 84%.

**Synthesis of EPEE.**

**Scheme 1.**

Anionic Copolymerization of EPEE with EO

The copolymerization of EPEE with EO is described in Scheme 2. Diphenylmethylpotassium (DPMK) was prepared according to the literature. To a 150-mL, three-necked flask, 100 mL of dry THF and 7.7 (0.06 mol) of naphthalene were added, and then 2.34 g (0.06 mol) of potassium with a fresh surface was added under a nitrogen atmosphere; after 4 h of stirring, 11.1 g (0.066 mol)
of diphenylmethane was introduced with a syringe, and the system was refluxed at 80 °C for 24 h and titrated with 0.1 M HCl after filtration. The concentration of DPMK was 0.57 M.

The copolymerization was carried out in a kettle. A typical procedure was as follows. A 150-mL kettle was vacuumed at 80 °C for 2 h and cooled to room temperature and then to −20 °C. A given volume of an initiator solution (TEG (0.67 mL, 0.005 mol) with DPMK (3.5 mL, 0.002 mol) in 50 mL of THF), EPEE (16.0 g, 0.11 mol), and EO (44.0 g, 1.0 mol) were introduced successively into the kettle under magnetic stirring. Subsequently, it was heated to 60 °C under stirring for 48 h. The reaction was terminated by the addition of a few drops of acidified methanol. After all the solvents were removed by reduced distillation, the crude product was dissolved in CH₂Cl₂, dried over anhydrous MgSO₄, and filtered. A yellow, viscous, waxlike product (poly(ethylene oxide-co-2,3-epoxypropyl-1-ethoxyethyl ether) [poly(EO-co-EPEE)]) was obtained in a yield of 94% after CH₂Cl₂ was removed.

Hydrolysis of the EPEE Units of the Copolymers

The hydrolysis of the EPEE units of the copolymers could occur in two steps, as Scheme 3 shows. First, 10.0 g of poly(EO-co-EPEE) [number-average molecular weight (Mₐ) = 12,700; 0.855 mmol] was mixed with 160 mL of formic acid (0.266 mol), the solution was stirred at 20 °C for 30 min and then poured into methanol, and the precipitate was separated and dried in vacuo at 50 °C. Second, the dried product was then dissolved in a mixture of dioxane (100 mL) and methanol (50 mL), hydrolyzed with a KOH methanol solution (1 N, 27 mL) under refluxing for 24 h, and then neutralized with 5% HCl. After the solvents were removed under reduced pressure, the polymer was dissolved in water and purified by an ultrafiltration membrane separator; the filtered aqueous solution was concentrated to dryness, dissolved in CH₂Cl₂, dried over anhydrous MgSO₄, and filtered. The filtrate was distilled in vacuo to remove CH₂Cl₂ and dried in vacuo at 50 °C. The pale yellow product, poly(ethylene oxide-co-glycidol) [poly(EO-co-Gly)], was obtained in a yield of 93%.

Esterification of Poly(EO-co-Gly) with 2-Bromoisobutyryl Bromide

The esterification of hydroxymethyl groups on Gly units of poly(EO-co-Gly) with 2-bromoisobutyryl bromide occurred as Scheme 4 shows. A typical example can be described as follows. Poly(EO-co-Gly) (26.5 g, 0.49 mmol; Mₐ = 10,200; 12.8 mmol of hydroxyl methyl) was dissolved in 100 mL of anhydrous pyridine under bubbling dry nitrogen; 2.4 mL (19.2 mmol, 1.5 equiv) of 2-bromoisobutyryl bromide was added dropwise at 0 °C over 20 min under vigorous stirring. The initial yellow color disappeared

Scheme 3. Deprotection of EPEE units of the copolymers.

Scheme 4. Esterification of poly(EO-co-Gly) with 2-bromoisobutyryl bromide.
immediately, and pyridinium bromide with a reddish-brown color precipitated and then was continuously stirred for another 15 min. The reaction process was monitored with IR (KBr, ester band at 1736 cm\(^{-1}\)). After that, 10 g (72.2 mmol) of K\(_2\)CO\(_3\) was added to the system at room temperature, and the pyridine was removed by azeotropic distillation with dry toluene (6 × 40 mL). The residue was dissolved in water and separated by an ultrafiltration membrane separator. The aqueous solution was concentrated to dryness and dissolved in CH\(_2\)Cl\(_2\), dried over anhydrous MgSO\(_4\), and then filtered; CH\(_2\)Cl\(_2\) of the filtrate was removed by distillation \(\text{in vacuo}\), and the remains were dried \(\text{in vacuo}\) at 50 °C. A yellowy product with a yield of 95% was obtained.

**Grafted Polymerization of St**

The grafted polymerization of St was carried out with poly(EO-co-Gly) with pending bromoisobutyryl groups \([(\text{poly(EO-co-Gly)})_{\text{ATRP}}]\) as the macro-initiator, as shown in Scheme 5. Ampules charged with CuBr (27.6 mg, 0.192 mmol), bpy (30.0 mg, 0.192 mmol), poly(EO-co-Gly)\(_{\text{ATRP}}\) (\(M_n = 13,800\); 0.101 g, 0.0074 mmol), and St (3.1 mL, 28.8 mmol) were vacuumed by three freeze–thaw cycles at the temperature of liquid nitrogen and then sealed and placed in an oil bath at 90 °C. The ampules were taken from the oil bath and dipped in liquid nitrogen at different times to stop the polymerization. The polymerized products were diluted with CH\(_2\)Cl\(_2\) and precipitated in cold methanol. After filtration, the products were purified by dissolution/precipitation with CH\(_2\)Cl\(_2\)/cold methanol twice and then dried at 35 °C \(\text{in vacuo}\).

**Hydrolysis of PEO-g-PS**

The grafted PS chains were hydrolyzed under a basic condition: \(0.2 \text{ g of PEO-g-PS} \left[\left(\text{weight-average molecular weight/number-average molecular weight (} M_w/M_n = 1.13\right)\right]\) was dissolved in 50 mL of THF, 10 mL of a 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\(_2\)Cl\(_2\) and then precipitated into acidified methanol; the products were purified twice by dissolution/precipitation with CH\(_2\)Cl\(_2\)/methanol and then dried at 50 °C.

**RESULTS AND DISCUSSION**

**Characterization of Parent Copolymer Poly(EO-co-EPEE) and Hydrolysis of EPEE Units**

In the anionic copolymerization of EO and Gly, Gly should be protected because of the exchange
reaction between the hydroxyl group of Gly and DPMK, so the side reaction should be unavoidable. Gly is protected by ethyl vinyl ether first and then copolymerized with EO with a mixture solution of TEG and 20% DPMK as the initiator; a linear \( \alpha \)-hydroxyl-\( \alpha \)-hydroxyl poly(EO-co-EPEE) is formed. A series of parent copolymers with different contents of EPEE and different molecular weight were prepared by the variation of the monomer feed ratio and initiator volume, as Table 1 and Figure 1 indicate, from which it can be observed that in all cases the molecular weight distribution is much narrower, and with an increase in EPEE in the monomer feed ratio, the content of EPEE in the copolymer is also increased. Figure 2(A) is a typical \(^1\)H NMR spectrum of copolymer poly(EO-co-EPEE); the quadrilets at \( \delta = 4.63-4.75 \) are ascribed to the methyl protons (H\(_a\)) of the EPEE moiety, the doublets at \( \delta = 1.30 \) and 1.29 and the triplet at \( \delta = 1.21, 1.19, \) and 1.18 are ascribed to the methyl protons of the EPEE moiety (H\(_b\) and H\(_c\)), and the chemical shift at \( \delta = 3.53-3.80 \) is assigned to protons of the main chain (H\(_f\), H\(_g\), H\(_h\), and H\(_i\)) and protons of the lateral chains (H\(_e\) and H\(_o\)). The copolymer composition can be

Table 1. Data for Parent Copolymer Poly(EO-co-EPEE)

<table>
<thead>
<tr>
<th>Sample</th>
<th>( R_f^b )</th>
<th>( R_T^c )</th>
<th>( M_n^d )</th>
<th>( M_w/M_n^e )</th>
<th>( M_n^f )</th>
<th>( M_w/M_n^g )</th>
<th>( N_{EPEE}^h )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1/9</td>
<td>1/8.4</td>
<td>12,700</td>
<td>1.06</td>
<td>11,600</td>
<td>1.01</td>
<td>24</td>
</tr>
<tr>
<td>B</td>
<td>1/9</td>
<td>1/9.5</td>
<td>6,400</td>
<td>1.08</td>
<td>6,210</td>
<td>1.05</td>
<td>13</td>
</tr>
<tr>
<td>C</td>
<td>1/5</td>
<td>1/5.3</td>
<td>5,640</td>
<td>1.05</td>
<td>5,340</td>
<td>1.04</td>
<td>17</td>
</tr>
</tbody>
</table>

\(^a\) The molecular weight of poly(EO-co-EPEE) was determined with the following formula: \( M_n = W_{EO} + W_{EPEE} + W_{TEG}/N_{TEG} \), where \( W_{EO}, W_{EPEE}, \) and \( W_{TEG} \) are the weights of EO, EPEE, and TEG, respectively, and \( N_{TEG} \) is the moles of TEG. The reaction was conducted at 60 °C.

\(^b\) Feed ratio of EPEE to EO.

\(^c\) Molar ratio of EPEE to EO in poly(EO-co-EPEE) as measured by \(^1\)H NMR.

\(^d\) Number-average molecular weight determined by SEC calibrated against PS standards.

\(^e\) Polydispersity determined by SEC.

\(^f\) Number-average molecular weight determined by MALDI-TOF mass spectrometry.

\(^g\) Polydispersity determined by MALDI-TOF mass spectrometry.

\(^h\) Number of EPEE units in poly(EO-co-EPEE) calculated with the following formula: \( N_{EPEE} = M_n/(146 + 44/R_T) \).

Figure 1. SEC traces of poly(EO-co-EPEE) (see Table 1 for the preparation of A–C).
readily obtained with the following formula based on the $^1$H NMR spectrum:

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

where $R_T$ is the molar ratio of EPEE to EO in the copolymers and $A_{sum}$ and $A_a$ represent the peak area sum of protons c, e, f, g, h, and i and the peak areas of the methine protons of the EPEE moiety, respectively. The $R_T$ values of copolymers A, B, and C are 1/8.4, 1/9.5, and 1/5.3, respectively, which are nearly equivalent to the monomer feed ratios of EPEE to EO.

The protecting group acetal of EPEE units in poly(EO-co-EPEE) can be cleaved by formic acid, and then hydroxymethyl is recovered after saponification, as Schemes 3 and 4 show. Table 2 lists the data for the hydrolyzed products of the poly(EO-co-EPEE) samples, from which it can be observed that the molecular weight and molecular weight distribution before and after hydrolysis do not change obviously if the mass variation of EPEE before and after hydrolysis is considered. This means that the main chain of the copolymer is not cleaved, and the hydrolysis is successful. Figure 2(B) is the $^1$H NMR spectrum of hydrolyzed product poly(EO-co-Gly). In comparison with Figure 2(A), the peaks at $\delta = 4.71$ [−O−CH(CH$_3$)−O−], 1.33 [−OCH(CH$_3$)−O−], and 1.19 (−O−CH$_3$), attributed to EPEE units of

![Figure 2. $^1$H NMR spectra of (A) poly(EO-co-EPEE) (A: $M_n = 1.27 \times 10^4$; solvent = CDCl$_3$), (B) poly(EO-co-Gly) (A: $M_n = 1.02 \times 10^4$; solvent = CDCl$_3$), and (C) poly (EO-co-Gly)$_{ATRP}$ (A: $M_n = 1.38 \times 10^4$; solvent = CDCl$_3$).](image_url)
poly(EO-co-EPEE), disappear, and the hydrolysis of poly(EO-co-EPEE) is complete. The FTIR spectra before [Fig. 3(A)] and after the hydrolysis [Fig. 3(B)] of poly(EO-co-EPEE) provide more evidence for complete hydrolysis; the peak at 1379 cm⁻¹, attributed to the acetal group in Figure 3(A), disappears, and new peaks at 3473 cm⁻¹ in Figure 3(B), attributed to the recovered hydroxymethyl groups, appear.

Graft Polymerization of St with Poly(EO-co-Gly)_{ATRP} as the Initiator

Poly(EO-co-Gly) can be regarded as PEO with pendant multiple hydroxyl methyl groups, and the hydroxyl methyl groups can be easily reacted with 2-bromoisobutyryl bromide to form the macro-ATRP initiator poly(EO-co-Gly)_{ATRP}. Figure 2(C) is a typical ¹H NMR spectrum of poly(EO-co-Gly) with pendant multiple bromoisobutyryl groups [poly(EO-co-Gly)_{ATRP}]. The he hydroxyl group conversion can be calculated with the following formula:

\[ E_T = \frac{2A_{\text{sum}}}{\left(\frac{4}{R_T} + 3\right) \times A_A} \times 100\% \]  

(2)

where \( E_T \) is the conversion efficiency of hydroxyl groups of poly(EO-co-Gly); \( A_{\text{sum}} \) and \( A_A \) represent the integral area of the protons of the PEO main chain (the peaks at \( \delta = 3.35–3.90 \)) and the integral area of the methylene protons (\( H_c \) and \( H_j \)) linked to the ester (the peaks at \( \delta = 4.13–4.42 \)), respectively; and \( R_T \) is the molar ratio of EPEE to EO in copolymer poly(EO-co-EPEE) measured by ¹H NMR (see Table 1). The \( E_T \) values for the two samples are nearly 100%, and this suggests that hydroxyl groups are converted to bromoisobutyryl completely. The FTIR spectra before and after the esterification of poly(EO-co-Gly) provide more evidence for complete esterification; the peak at 3473 cm⁻¹, attributed to hydroxymethyl groups in Figure 3(B), disappears, and a new peak at 1736 cm⁻¹ in Figure 3(C), attributed to an ester band, appears.

Table 3 presents the results of ATRP with two kinds of poly(EO-co-Gly)_{ATRP} with different molecular weights as macroinitiators. The obtained

<table>
<thead>
<tr>
<th>Initiator</th>
<th>Entry</th>
<th>Time (h)</th>
<th>Conversion (%)(^a)</th>
<th>( M_n ) (×10⁴)(^b)</th>
<th>( M_w/M_n ) (^c)</th>
<th>( N_{PS} ) (^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>A₁</td>
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<td>4.3</td>
<td>2.81</td>
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<td></td>
<td>A₂</td>
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<td>3.63</td>
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<tr>
<td></td>
<td>A₃</td>
<td>2</td>
<td>17.8</td>
<td>4.44</td>
<td>1.16</td>
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<td></td>
<td>A₄</td>
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<td></td>
<td>A₆</td>
<td>12</td>
<td>62</td>
<td>8.18</td>
<td>1.34</td>
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<tr>
<td>B</td>
<td>B₁</td>
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<td>1.47</td>
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<tr>
<td></td>
<td>B₂</td>
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<td>1.12</td>
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<tr>
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<td>B₄</td>
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<tr>
<td></td>
<td>B₅</td>
<td>4</td>
<td>23.4</td>
<td>2.74</td>
<td>1.17</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Determined by a gravimetric method.
\(^b\) Number-average molecular weight determined by SEC calibrated against PS standards.
\(^c\) Polydispersity determined by SEC.
\(^d\) Average number of St on the grafting chain of the final copolymers calculated from the ¹H NMR data with eq 3.
copolymer brushes with PEO as the main chain and PS as the side chains show monomodal SEC eluograms (Fig. 4); the molecular weight of the graft copolymer increases with the polymerization time, and the molecular weight distributions in all cases are low (polydispersity index < 1.2).

However, when the hydroxyl methyl groups of poly(EO-co-Gly) are reacted with 2-bromoisobutyryl bromide, a small part of the main chain might break (<4%), although pyridine is used as a solvent; the molecular weight of this part of the copolymer is about 7000 Da [Fig. 4(A)]. Nevertheless, it does not affect the following ATRP process, as Table 3 shows; except for A6, the molecular weight distribution for all cases is still in a narrow range (<1.2). When the polymerization time is prolonged, for example, to 12 h, as Figure 4(A5, A6) shows, some shoulder peaks with a high molecular weight of 16,000 can be observed from the gel permeation chromatography curves; a side reaction via the irreversible coupling of the growing radicals between different graft copolymers may exist under these conditions. However, all the polymers are still completely soluble, and no insoluble copolymers have been detected even at high conversions. This means that in our system no crosslinking between grafts appears; this is in agreement with previous observations by Gnanou et al.20

**Figure 4.** SEC traces of graft copolymer PEO-g-PS. Sample A is the parent copolymer; the polymerization times for the rest are 0.5 h for A1, 1 h for A2, 2 h for A3, 3 h for A4, 4 h for A5, and 12 h for A6.

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However, when the hydroxyl methyl groups of poly(EO-co-Gly) are reacted with 2-bromoisobutyryl bromide, a small part of the main chain might break (<4%), although pyridine is used as a solvent; the molecular weight of this part of the copolymer is about 7000 Da [Fig. 4(A)]. Nevertheless, it does not affect the following ATRP process, as Table 3 shows; except for A6, the molecular weight distribution for all cases is still in a narrow range (<1.2). When the polymerization time is prolonged, for example, to 12 h, as Figure 4(A5, A6) shows, some shoulder peaks with a high molecular weight of 16,000 can be observed from the gel permeation chromatography curves; a side reaction via the irreversible coupling of the growing radicals between different graft copolymers may exist under these conditions. However, all the polymers are still completely soluble, and no insoluble copolymers have been detected even at high conversions. This means that in our system no crosslinking between grafts appears; this is in agreement with previous observations by Gnanou et al.20

**Figure 5.** $^1$H NMR spectrum of PEO-g-PS (A5: $M_n = 5.76 \times 10^4$, $M_w/M_n = 1.13$; solvent = CDCl$_3$).

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Figure 5 shows the $^1$H NMR spectrum of polymer sample A$_5$ (see Table 3). The peaks at $\delta = 4.28$–4.65 ppm are assigned to the methylene protons (H$_a$) linked to ester and end methine protons (H$_c$) at the end of the copolymer side chains; the chemical shift at $\delta = 6.33$–7.31 ppm is assigned to the protons of phenyl rings of PS chains, and the chemical shift at $\delta = 3.41$–3.86 ppm is assigned to the protons of the PEO main chain. Thus, the molecular weight of PS side chains and the initiation efficiency can be obtained with eqs 3 and 4:

\[
N_{PS} = \frac{\left(\frac{4}{R_T} + 3\right) A_A}{5 A_{sum}} \times N_{EPEE} \quad (3)
\]

\[
E_T = \frac{\left(\frac{4}{R_T} + 3\right) A_A \times N_{EPEE} \times M_{St}}{5 A_{sum} \times M_{n,PS} \times (N_{EPEE} + 2)} \times 100\% \quad (4)
\]

where $N_{PS}$ is the average number of St on each PS side (see Table 3); $E_T$ is the reaction efficiency of bromoisobutryl for ATRP; $A_A$ and $A_{sum}$ represent the integral area of phenyl protons on the grafted PS chains and the integral area of all protons of the PEO main chain, respectively; $R_T$ is the molar ratio of EPEE to EO in poly(EO-co-EPEE) measured by $^1$H NMR; and $N_{EPEE}$ is the number of EPEE units in poly(EO-co-EPEE) (see Table 1). The calculated $E_T$ value is 98.1%, and the molecular weight of side PS chains can be derived from $N_{PS}$ and mass of St; the value is 2964 g/mol for sample PEO-g-PS$_{A5}$. This suggests that nearly all the 2-bromoisobutyryl groups take part in the radical polymerization.

**Controllability of the Grafting Copolymerization of St**

The polymerization kinetics of St initiated by poly(EO-co-Gly)$_{ATRP}$ have also been investigated. Figure 6 shows a linear dependence of $\ln[M_0]/[M]$ (where $M_0$ is the initial St concentration and $[M]$ is...
the St concentration at a certain time) on time, and this means that in our system the radical concentration is stable during the polymerization and that the rate is mainly dependent on the concentration of the monomer. Figure 7 displays the linear relationship of the St conversion with $M_n$ and $M_w/M_n$, which $M_n$ is proportional to the conversion; in all cases, the molecular weight distributions are below 1.2.

Hydrolysis of the PS Side Chain

As is well known, the molecular weight of a graft copolymer obtained by SEC is apparent and unreliable because of the sharp difference in the hydrodynamic volumes of the graft copolymer and linear PS standard. The detachment of the PS side chains from the poly(EO-co-Gly) backbone by hydrolysis of the ester group under basic conditions and the subsequent measurement of the molecular weight of the free PS side chains can give real information about grafted PS chains. Figure 8 shows the SEC traces of the starting copolymer and the detached PS chains; a monomodal peak with a narrow distribution ($M_w/M_n = 1.18$) can be observed for the detached PS. Its molecular weight is $M_n = 3020$ g/mol, which is approximately the same as the value of 2964 g/mol derived by $^1$H NMR. Thus, it can be concluded that the ATRP of St initiated by poly(EO-co-Gly)$_{\text{ATRP}}$ is well controlled.

CONCLUSIONS

A universal method is suggested for the preparation of well-defined amphiphilic copolymer brushes with PEO as the main chains and PS as the side chain by a combination of anionic polymerization and ATRP. Protected Gly is copolymerized with EO first, and then the hydroxymethyl groups on the copolymer are recovered by hydrolysis and further esterified by 2-bromoisobutyryl bromide; the resultant macro-ATRP initiator [poly(EO-co-Gly)$_{\text{ATRP}}$] is used to initiate the polymerization of St. In all cases, the molecular weight distribution of the copolymer brushes is rather narrow ($M_w/M_n < 1.2$), and the linear dependence of $\ln[M_0]/[M]$ on time demonstrates that the St polymerization is well controlled.

REFERENCES AND NOTES