One-Pot, Three-Step Synthesis of Amphiphilic Comblike Copolymers with Hydrophilic Backbone and Hydrophobic Side Chains

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ABSTRACT: A well-defined amphiphilic comblike copolymer consisting of a hydrophilic poly(methacrylic acid) backbone and polystyrene [poly(St)] side chains was prepared by a one-pot, three-step successive method. First, the anionic copolymerization of two functional monomers, namely, 1-(ethoxy)ethyl methacrylate (EEMA) and a small amount of glycidyl methacrylate (GMA), was carried out in THF, using 1,1-diphenylhexyllithium (DPHL) as the initiator, in the presence of LiCl ($[\mathrm{LiCl}]/[\mathrm{DPHL}]_0 = 1$), at −40 °C. The copolymer poly(EEMA-*co*-GMA) thus obtained possessed a controlled molecular weight and composition as well as a narrow molecular weight distribution ($M_w/M_n = 1.09-1.13$). Without termination and copolymer separation, an anionic living poly(St) solution was introduced into the above system at −40 °C. The coupling reaction (second step) between the epoxy groups of poly(EEMA-*co*-GMA) and the living sites of poly(St)s occurred rapidly, generating a comblike copolymer with a poly(EEMA-*co*-GMA) backbone and poly(St) side chains. This copolymer was free of its precursors, and its molecular weight distribution was narrow ($M_w/M_n = 1.14-1.21$). In addition, the lengths of both the backbone and side chains, hence the total molecular weight of the copolymer, could be controlled. In the final step, the excess of unreacted epoxy groups in the backbone was reacted with DPHL or sodium ethoxide, and this was followed by the hydrolysis of EEMA units under acidic conditions. This procedure changed the EEMA units to methacrylic acid units by eliminating the protecting 1-(ethoxy)ethyl groups, and an amphiphilic comblike copolymer was thus obtained.

Introduction

A number of well-defined amphiphilic block copolymers have been prepared by the living anionic polymerization technique.[1] Usually, two monomers were first polymerized sequentially to obtain a block copolymer. This was followed by hydrolysis which changed one block to hydrophilic, while keeping the other one hydrophobic.[2] Compared to this relatively simple procedure, the synthetic methodology of well-defined amphiphilic graft or comblike copolymers is much more difficult, and for this reason, these kinds of copolymers were seldom prepared.

The present paper will focus on the preparation of a well-defined amphiphilic comblike copolymer with a hydrophilic backbone and hydrophobic side chains, based on two functional monomers, namely, 1-(ethoxy)ethyl methacrylate (EEMA) and glycidyl methacrylate (GMA). In previous papers,[3] the living anionic homopolymerization of EEMA and its block copolymerization with methyl methacrylate (MMA) or St has been investigated. It was found that the 1-(ethoxy)ethyl group could be easily eliminated by hydrolysis after (co)polymerization, thus generating well-defined hydrophilic poly(methacrylic acid) [poly(MAA)] or amphiphilic block copolymers. On the other hand, the bifunctional monomer GMA could be anionically polymerized, but its epoxy group, which remained unreacted,[4] could be further used for the coupling reaction with anionic living polymers.[5] Combining the advantages of the above two monomers, a three-step successive route to well-defined amphiphilic comblike copolymers was developed.

As shown in Scheme 1, in the first step, the anionic copolymerization of EEMA with a small amount of GMA was carried out to generate a living copolymer, poly(EEMA-*co*-GMA) (1 in Scheme 1). Without termination and polymer separation, an anionic living polystyrene [poly(St)] solution was introduced into the above system. During this second step, a coupling reaction between the epoxy groups of the GMA units and the living sites of poly(St) occurred, generating a comblike copolymer (2 in Scheme 1) with a poly(EEMA-*co*-GMA) backbone and poly(St) side chains. In the final step, the 1-(ethoxy)ethyl protecting groups of EEMA units of the backbone were eliminated by adding a small amount of acid to the system after the coupling reaction. The three steps could be carried out in a single pot, and an amphiphilic comblike copolymer (3 in Scheme 1) consisting of a hydrophilic poly(MAA) backbone and hydrophobic poly(St) side chains could be obtained.

Experimental Section

Materials. Tetrahydrofuran (THF) was dried with CaH_2 under reflux for more than 24 h, distilled, and distilled again from a solution of 1,1-diphenylhexyllithium (DPHL) just before use. Toluene was washed with concentrated sulfuric acid and then with water, dried over $MgSO_4$, distilled over CaH_2, and distilled again from a DPHL solution before use. Hexane was first dried and distilled over CaH_2 and then distilled from a solution of *n*-BuLi. 1-(Ethoxy)ethyl methacrylate (EEMA) was prepared through the reaction of methacrylic acid (MAA; Aldrich, 99%) and ethyl vinyl ether (Aldrich, 99%).[3a] Prior to polymerization, this monomer was purified by distillation twice over CaH_2 under reduced pressure. Glycidyl methacrylate (GMA, Aldrich, 97%) was dried over CaH_2 with magnetic stirring under reduced pressure for more than 24 h and vacuum distilled slowly, and the middle fraction (about half volume) was recovered and distilled twice over CaH_2. Styrene (St; 99%, Aldrich) was washed with 10% aqueous NaOH solution and then with water, dried overnight with $MgSO_4$, distilled over CaH_2, and finally distilled in the presence of phenylmagnesium chloride just before use. 1,1-Diphenyleth-

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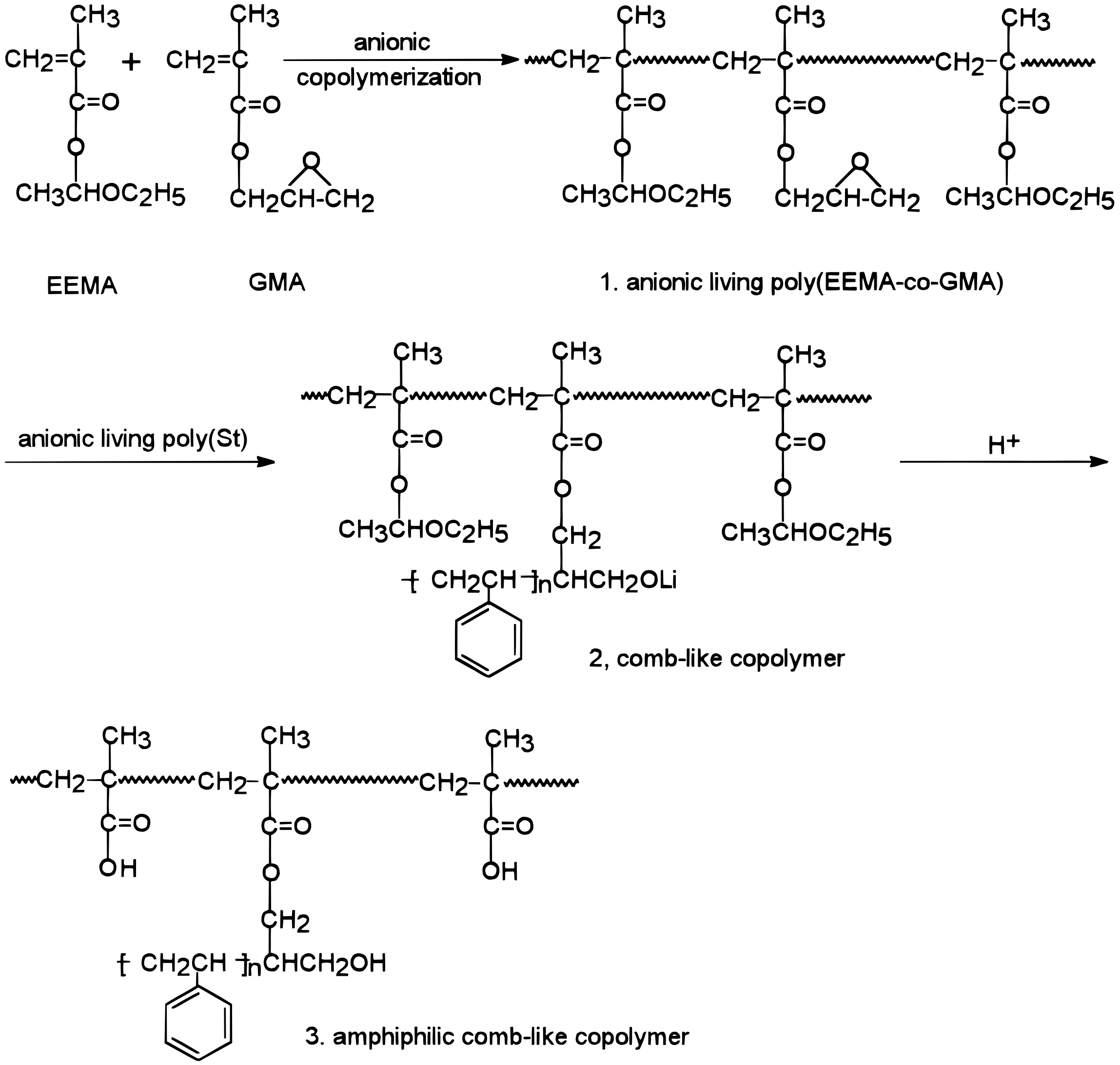
Scheme 1



ylene (DPE; Aldrich, 97%) was distilled over CaH_2 and then distilled in the presence of DPHL under reduced pressure. Lithium chloride (Aldrich, 99.99%) was dried at 120 °C for 24 h and dissolved in THF.[6] *n*-BuLi (Aldrich, 1.6 M solution in hexane) was diluted with purified hexane. Sodium ethoxide (Aldrich, 21 wt % in ethanol) and benzoic anhydride (Aldrich, 90%) were used as received.

Preparation of a THF Solution of the Living Backbone Copolymer Poly(EEMA-*co*-GMA) by the Anionic Copolymerization of EEMA and GMA. All polymerizations, namely the copolymerization of EEMA and GMA and the homopolymerization of St, were carried out in a round-bottom glass flask under an overpressure of argon with magnetic stirring. The anionic copolymerization of EEMA and GMA was performed in THF, at −40 °C, in the presence of LiCl[6] ($[LiCl]/[DPHL]_0 = 1$). After THF, DPE, and a THF solution of LiCl were added with dry syringes, the flask was cooled to −40 °C, and *n*-BuLi (in hexane) was added. The deep red color of DPHL appeared at once, and the reaction between *n*-BuLi and DPE was allowed to continue for 15 min. The polymerization reaction was induced by the addition of a prechilled mixture of EEMA and GMA to the above system, and the reaction was allowed to last 1.5 h. Without termination and polymer separation, this THF solution was directly used in the next coupling step with living poly(St).

Preparation of the Living Poly(St) Solution by the Anionic Polymerization of St. The anionic polymerization of St was carried out using *n*-BuLi as initiator, in a mixture of toluene and THF (2:1 by volume), at −40 °C. After toluene, THF, and a hexane solution of *n*-BuLi were introduced into a flask kept at −40 °C, the polymerization was started by adding prechilled monomer to the above system. About 1 h later, this solution was directly employed in the next coupling reaction step.

Synthesis of the Comblike Copolymer Poly[(EEMA-*co*-GMA)-*g*-St] by the Coupling Reaction between the Epoxy Group of Poly(EEMA-*co*-GMA) and the Living Site of Poly(St). The coupling reaction was carried out with vigorous magnetic stirring, at −40 °C. While the copolymerization of EEMA and GMA was proceeding, an anionic living poly(St) solution was simultaneously prepared. The latter solution was transferred into the THF solution of poly(EEMA-*co*-GMA). Although the coupling reaction occurred rapidly, it was still allowed to last 1 h at −40 °C to ensure complete conversion. Then, the system was quenched by adding a small amount of methanol (ca. 1 mL). About half of the polymerization solution was poured into methanol to precipitate the polymer. The polymer was reprecipitated by pouring its THF solution into methanol, washed with methanol, and vacuum-dried overnight at 40 °C. The remaining part of the polymerization solution was subjected to the next step, the hydrolysis reaction.

Elimination of 1-(Ethoxy)ethyl Groups of EEMA Units of the Backbone. To destroy the unreacted epoxy groups, one of the following two methods was employed. (i) After the coupling reaction and before adding the aqueous HCl solution, the unreacted epoxy groups of the backbone were reacted with DPHL at −40 °C by the dropwise addition of a THF solution of DPHL until the red color of DPHL could be maintained. (ii) After the coupling reaction, the temperature was raised to 25 °C, sodium ethoxide (21 wt % in ethanol) was added, and the stirring was continued for more than 5 h. After the treatment by any of the above two methods, 1.0 M HCl aqueous solution was dropwise added until pH ≤ 1, and the reaction was allowed to last 1.5 h. The hydrolyzed polymer was precipitated into hexane, washed with ethanol and then with water, immersed in water for more than 5 h, and finally vacuum-dried at 40 °C for 24 h.

Reprotection of the Hydrolyzed Copolymer. To verify by GPC whether cross-linking occurred during hydrolysis, the hydrolysate was reprotected by the reaction of the formed carboxyl groups with benzoic anhydride. For instance, 1.0 g of hydrolyzed CLP-3 (Table 3) was dissolved in 20 mL of THF, to which 2.5 g of benzoic anhydride was added, and the reaction was allowed to last 24 h. Then, the polymer was precipitated into methanol, washed with methanol, and vacuum-dried overnight.

Measurements. ^{1}H NMR spectra were recorded in $CDCl_3$ or THF-d_8 on an INOVA-500 spectrometer. M_n and M_w/M_n of the copolymer were determined by gel permeation chromatography (GPC) on the basis of a polystyrene calibration curve and by vapor pressure osmometry (VPO). The VPO measurements were performed in toluene at 45 °C, using an UIC SA 070 vapor pressure osmometer. The GPC measurements were carried out using THF as solvent, at 30 °C, with a 1.0 mL/min flow rate and a 1.0 cm/min chart speed. Three polystyrene gel columns (Waters, 7.8 × 300 mm; one HR 5E, part no. 44228; one Linear, part no. 10681; and one HR 4E, part no. 44240) were used, which were connected to a Waters 515 precision pump.

Results and Discussion

Preparation of the Living Backbone Copolymer, Poly(EEMA-*co*-GMA), by the Anionic Copolymerization of EEMA and GMA. The backbone copolymer, poly(EEMA-*co*-GMA), which will be used in a subsequent coupling reaction, should possess the following characteristics: (i) It should have a controlled molecular weight and composition as well as a narrow molecular weight distribution (MWD), to allow the control of the molecular weight of the final comblike copolymer. (ii) The monomer conversions of both EEMA and GMA must be quantitative; otherwise, the monomer which is not incorporated into the polymer chain might react with the anionic living poly(St). If this would happen, the grafting reaction would be incomplete, and a pure comblike copolymer would not be obtained. (iii) The GMA units, which provide the grafting sites, should be distributed randomly along the polymer chain.

It has been reported that when the anionic polymerization of GMA was carried out in a polar solvent (THF), the suitable temperature should be between −50 and −40 °C.[4] At higher temperatures, side reactions might occur, and at very low temperatures, the solubility of the living polymer formed would be poor. Fortunately, the best conditions for the living anionic polymerization of EEMA coincide with those of GMA. We have found that the living anionic polymerization of EEMA can proceed smoothly using the bulky DPHL as initiator, in THF, in the presence of LiCl ($[LiCl]/[DPHL]_0 = 1$), at −40 °C.[3] Therefore, the copolymerization of EEMA and GMA was carried out under the above conditions.

As shown in Table 1, the monomer conversions of both EEMA and GMA were 100% in each case, the determined molecular weight was in agreement with that calculated, and the MWD was narrow ($M_w/M_n = 1.09-1.13$). In addition, by changing the feed amounts of the initiator and the monomers, copolymers with different molecular weights could be prepared. As shown later in Figure 2A-b, the GPC chromatogram of the obtained polymer exhibited a single, symmetrical peak. The above results indicate that as their homopolymerizations, the anionic copolymerization of EEMA and GMA proceeded smoothly under the above conditions.

Because the GMA unit just provides the grafting site, its amount in the polymer chain was selected to be only 10 wt % compared to that of EEMA units (BCP-1 to 4 in Table 1). However, to investigate the composition and

Table 1. Preparation of the Backbone Copolymer (BCP) by the Anionic Copolymerization of EEMA and GMA[a]

no.	$[DPHL]_0$,[b] mM	$[EEMA]_0$, M	$[GMA]_0$, M	$10^{-3}M_n$ calcd	$10^{-3}M_n$ obsd[c]	M_w/M_n [c]
BCP-1	20.0	0.63	0.071	5.74	5.67	1.10
BCP-2	18.3	0.63	0.071	6.24	6.13	1.09
BCP-3	12.5	0.63	0.083	9.24	9.37	1.10
BCP-4	8.0	0.63	0.083	14.2	14.1	1.11
BCP-5	11.0	0.21	0.23	6.24	6.35	1.13

[a] The copolymerization was carried out in THF, in the presence of LiCl ($[LiCl]/[DPHL]_0 = 1$), at −40 °C, for 90 min. The monomer conversion was 100% in each case. [b] The initiator DPHL was prepared in situ before the monomer addition by reacting n-BuLi with excess of DPE ($[DPE]/[n\text{-BuLi}]_0 = 1.2$), at −40 °C, for about 15 min. [c] Determined by GPC.

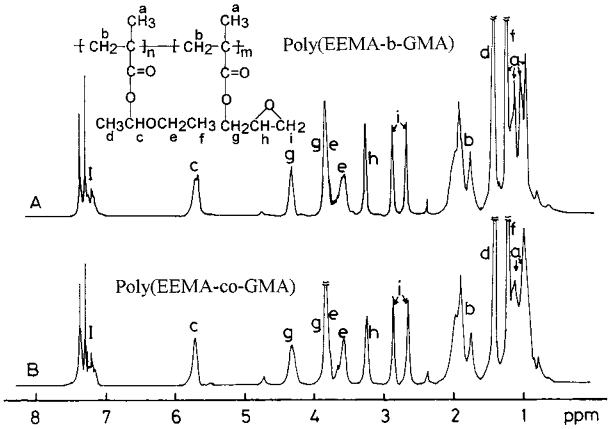


Figure 1. ^{1}H NMR spectra (in $CDCl_3$) of the block (A) and random (B) copolymers of EEMA and GMA. (A) $M_n = 6140$, $M_w/M_n = 1.17$, $W_{EEMA}/W_{GMA} = 53/47$. (B) (BCP-5 in Table 1) $M_n = 6350$, $M_w/M_n = 1.13$, $W_{EEMA}/W_{GMA} = 52/48$. Peak I: phenyl groups of the initiator DPHL.

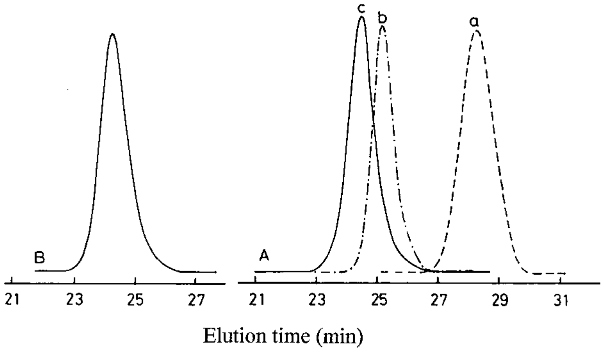


Figure 2. (A) GPC traces of a comblike copolymer, poly-[(EEMA-*co*-GMA)-*g*-St], and its precursors: (a) living poly(St) (side chain; PS-5 in Table 2, $M_n = 1490$, $M_w/M_n = 1.17$); (b) poly(EEMA-*co*-GMA) (backbone; BCP-4 in Table 1, M_n = 14 100, $M_w/M_n = 1.11$); (c) comblike copolymer (CLP-5 in Table 3, M_n = 22 600, $M_w/M_n = 1.15$) prepared via the coupling reaction of (a) and (b). (B) GPC trace of the reprotected product of hydrolyzed CLP-5 (M_n = 23 900, $M_w/M_n = 1.17$).

Table 2. Preparation of the Living Side Chain Polymer (PS) by the Anionic Polymerization of St[a]

no.	[n-BuLi]$_0$, mM	[St]$_0$, M	M_n calcd	M_n obsd[b]	M_w/M_n [b]
PS-1	52.0	0.769	1600	1680	1.17
PS-2	64.0	0.923	2060	1980	1.17
PS-3	52.0	0.769	1600	1620	1.16
PS-4	32.0	0.769	2560	2660	1.14
PS-5	71.5	0.962	1460	1490	1.17
PS-6	39.6	0.692	1880	1960	1.17

[a] The anionic polymerization was carried out in a mixture of toluene and THF (2:1 by volume), at −40 °C, for 1 h. The monomer conversion was 100% in all cases. [b] Determined by GPC.

the chain structure by NMR, a copolymer (BCP-5 in Table 1) with the same weight amounts of EEMA and GMA was also prepared. As shown in Figure 1B, the absorptions corresponding to both EEMA and GMA units are present quantitatively. The weight ratio of the two units calculated from the peak intensities is $W_{EEMA}/W_{GMA} = 52/48$, which is consistent with the feed amount ratio ($W_{EEMA}/W_{GMA} = 50/50$). In addition, the absorption due to the α-methyl (peak a in Figure 1B) only splits into two peaks. It has been reported that the random copolymer of GMA and methyl methacrylate (MMA) exhibits such a behavior.[4b] For comparison, a block copolymer of EEMA and GMA was also prepared under the same conditions as BCP-5, employing, however, a sequential monomer addition of EEMA and GMA. As illustrated in Figure 1A, the absorption of the α-methyl (peak a) splits into four peaks, which is consistent with the ^{1}H NMR results of the block copolymer of GMA and MMA.[4b] The above results imply that the GMA units of poly(EEMA-*co*-GMA) prepared in the present paper are distributed randomly along the polymer chain.

Preparation of the Comblike Copolymer, Poly[(EEMA-*co*-GMA)-*g*-St], via the Coupling Reaction of Poly(EEMA-*co*-GMA) and the Anionic Living Poly(St). Upon the copolymerization of EEMA and GMA, without termination and polymer separation, the THF solution of the living poly(EEMA-*co*-GMA) was directly used in the next step coupling reaction. In this way, the tedious polymer separation and purification were avoided, and no impurity was introduced into the reaction system.

While the copolymerization of EEMA and GMA was proceeding, a living poly(St) solution was also prepared. The anionic polymerization of St was carried out using *n*-BuLi as initiator, in a mixture of toluene and THF (2:1 by volume), at −40 °C, for 1 h. As shown in Table 2, the living polymer of St also possessed a controlled molecular weight and a narrow MWD ($M_w/M_n = 1.14-1.17$).

The coupling reaction between the epoxy groups of living poly(EEMA-*co*-GMA) and the living sites of poly(St) was carried out with vigorous magnetic stirring, at −40 °C. As soon as the living poly(St) solution was introduced into the THF solution of poly(EEMA-*co*-GMA), the red color of the living poly(St) disappeared, and the viscosity of the system increased, indicating that the coupling reaction took place instantaneously. As shown in Figure 2A, the GPC peaks corresponding to the living poly(St) (peak a, $M_n = 1490$, $M_w/M_n = 1.17$) and the living poly(EEMA-*co*-GMA) (peak b, $M_n = 14\,100$, $M_w/M_n = 1.11$) disappeared completely, and a new peak due to the formation of the comblike copolymer emerged (peak c, $M_n = 22\,600$, $M_w/M_n = 1.15$; see CLP-5 in Table 3). Obviously, this copolymer is free of its precursors. Its ^{1}H NMR spectrum is presented in Figure 3A. The absorptions corresponding to GMA units could be hardly detected, because only a small amount of GMA was used in the preparation of the backbone copolymer (see Table 1). However, the peaks due to the EEMA units (a, b, c, d, e, and f) in the backbone and poly(St) side chains (g, h, and i) are present quantitatively. The combination of GPC and ^{1}H NMR measurements indicates that a pure comblike copolymer consisting of a poly(EEMA) backbone and poly(St) side chains was obtained. Because the backbone and the side chain polymers were prepared separately, their chain lengths, hence the molecular weight of the final comblike copolymer, could be controlled.

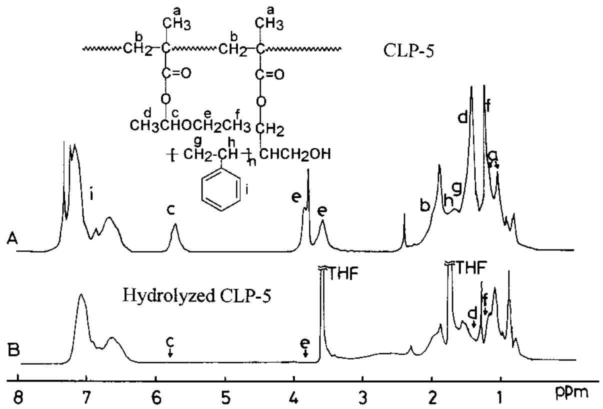


Figure 3. ^{1}H NMR spectra of CLP-5 (A; in $CDCl_3$, see Table 3) and its hydrolysate (B; in THF-d_8).

It has been reported that the carbonyl groups of poly(MMA) can react with the anionic living poly(St) or poly(α-methyl styrene) to form a graft copolymer, although the coupling reaction hardly proceeded quantitatively, and a fraction of the living polymer remained unreacted.[7] The backbone polymer, poly(EEMA-*co*-GMA), employed in the present paper, contains not only epoxy groups in GMA units but also carbonyl groups in both EEMA and GMA units. For this reason, it was necessary to identify the positions where the coupling reaction took place.

A THF solution of homopoly(EEMA) was prepared by the anionic homopolymerizarion of EEMA, which was carried out using DPHL as initiator ([DPHL]$_0$ = 11.3 mM, [EEMA]$_0$ = 0.669 M), in the presence of LiCl ([LiCl] = 11.6 mM), in THF, at −40 °C, for 1 h. The resulting polymer possessed a controlled molecular weight and a narrow MWD ($M_n = 9630$, $M_w/M_n = 1.08$). As shown in Figure 4B, its GPC chromatogram exhibited a sharp, symmetrical peak. Without quenching, a living poly(St) solution (Figure 4A; see PS-6 in Table 2) was introduced into the above system, and the stirring was continued for 1 h at −40 °C. The red color of the living poly(St) remained during the whole process until a small amount of methanol was added. The GPC chromatogram did not show any shift (Figure 4C), and a mixture of poly(EEMA) and poly(St) was recovered. This experiment excluded the possibility of a reaction between the carbonyl group and the living poly(St). Because of the low temperature (−40 °C), such a reaction could hardly occur. Consequently, only the GMA units of poly(EEMA-*co*-GMA) have acted as coupling sites.

Preparation of Amphiphilic Comblike Copolymer via the Elimination of 1-(Ethoxy)ethyl Groups in the Backbone Polymer. We found previously[3] that

Table 3. Preparation of the Comblike Copolymer (CLP) by the Coupling Reaction of Poly(EEMA-*co*-GMA) and the Anionic Living Poly(St)[a]

no.	backbone[b]	mmol$_{\text{epoxy}}$ [c]	PSt/mmol[d]	N[e]	$10^{-4}M_n$ calcd	$10^{-4}M_n$ VPO[f]	$10^{-4}M_n$ GPC[g]	M_w/M_n [g]
CLP-1	BCP-1	1.41	PS-1/1.30	3.3	1.12	1.08	1.14	1.21
CLP-2	BCP-2	1.41	PS-2/1.20	3.3	1.27	1.31	1.23	1.19
CLP-3	BCP-3	1.65	PS-3/1.30	5.2	1.78	1.82	1.75	1.14
CLP-4	BCP-3	1.65	PS-4/0.80	3.2	1.79	1.86	1.81	1.20
CLP-5	BCP-4	3.30	PS-5/2.93	9.2	2.78	2.65	2.26	1.15

[a] The coupling reaction was carried out at −40 °C, by introducing a living poly(St) solution into a THF solution of poly(EEMA-*co*-GMA). The stirring was continued for 1.0 h. [b] See Table 1. [c] Molar amount of GMA units in poly(EEMA-*co*-GMA). [d] See Table 2. [e] Calculated graft number. [f] Determined by VPO. [g] Determined by GPC.

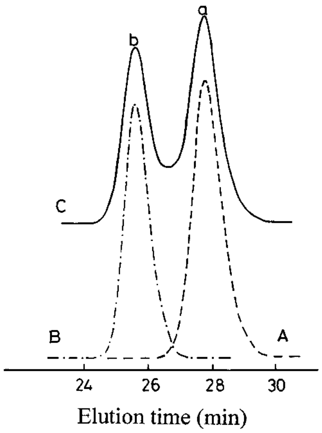


Figure 4. Demonstration by GPC of the coupling position: (A) living poly(St), $M_n = 1960$, $M_w/M_n = 1.17$ (PS-6 in Table 2); (B) living homopoly(EEMA) ($M_n = 9630$, $M_w/M_n = 1.08$) prepared using DPHL as the initiator ($[\text{DPHL}]_0 = 11.3$ mM, $[\text{EEMA}]_0 = 0.669$ M), in the presence of LiCl ([LiCl] = 11.6 mM), in THF, at −40 °C, for 1 h; (C) the product obtained after mixing (A) and (B) for 1 h.

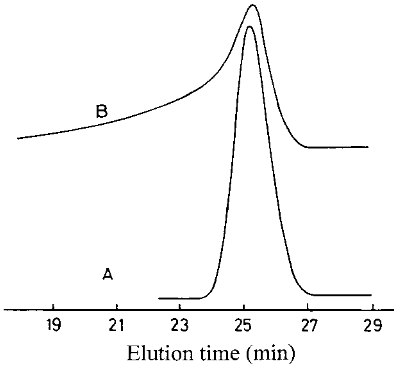


Figure 5. GPC traces of CLP-2 (A, $M_n = 12\,300$, $M_w/M_n = 1.19$, see Table 3) and the reprotected product of its hydrolysate (B, $M_n = 19\,100$, $M_w/M_n = 1.62$).

the 1-(ethoxy)ethyl groups could be easily eliminated from the homopolymer of EEMA and its block copolymer with MMA or St. For instance, 3.0 mL of HCl aqueous solution (5.0 M) was added to a 30 mL of THF solution containing 3.0 g of poly(EEMA). After 2 min, 1-(ethoxy)ethyl groups could be removed completely. However, the elimination of the same protecting groups from the comblike copolymer prepared in the present paper could not be so easily achieved, because of side reactions.

The hydrolysis of CLP-2 (peak A in Figure 5, $M_n = 12\,300$, $M_w/M_n = 1.19$; see Table 3) was carried out as follows. After the coupling reaction, 2.0 mL of aqueous HCl (5.0 M) solution was added to 20 mL of polymerization solution, and the reaction was allowed to last 30 min. For the GPC measurement, the hydrolysate was reacted with benzoic anhydride (see the Experimental Section). This reprotected polymer was subjected to a GPC measurement. As shown in Figure 5B, the GPC chromatogram exhibited a heavy tailing in the high molecular weight region, which was obviously caused by the cross-linking during the hydrolysis process.

To ensure complete coupling, the molar amount of the living poly(St) was less than that of the epoxy groups (Table 3). Therefore, the unreacted epoxy groups could react with the carboxyl groups formed during hydrolysis, resulting in cross-linking. On the other hand, the hydroxyl groups formed via the coupling reaction (see Scheme 1) could also have reacted with the carboxyl groups. As well-known, such a reaction, even between small molecules, such as acetic acid and ethanol, can proceed only at high temperatures and only if the resulting water is removed continuously. The hydrolysis in the present paper was carried out at room temperature by using an aqueous solution of HCl. Therefore, the above side reaction could hardly have occurred. However, the reaction between the epoxy and the carboxyl groups can easily take place, and this reaction must be avoided. The method used for this purpose was to open the epoxy rings after the coupling reaction and before the elimination of the 1-(ethoxy)ethyl groups. One of the following two reactions could be employed. (i) After the coupling reaction, a THF solution of DPHL was dropwise added to the system at −40 °C until the red color of DPHL could be maintained. This reaction was completed instantaneously. (ii) Instead of DPHL, an excess of sodium ethoxide was introduced into the system, and the stirring was continued for more than 5 h at room temperature. After the treatment via any of the above two methods, the hydrolysis was carried out, and the polymer thus obtained was washed carefully with ethanol and water and then was immersed in water for more than 5 h to remove the hydrochloric acid completely. For instance, CLP-5 (Table 3) was treated with sodium ethoxide, and its hydroxylate was reprotected with benzoic anhydride. As illustrated in Figure 2B, the GPC chromatogram of the polymer thus obtained exhibited a single, sharp peak, and its MWD ($M_n = 23\,900$, $M_w/M_n = 1.17$) was as narrow as that of its precursor (Figure 2A-c, $M_n = 22\,600$, $M_w/M_n = 1.15$). This means that, upon the above precautions, no cross-linking occurred and that the hydrolysis has not detached the pending poly(St) side chains.

Figure 3B depicts a ^{1}H NMR spectrum of the hydrolyzed comblike copolymer (CLP-5 in Table 3). Compared to its precursor (Figure 3A), peaks c, d, e, and f corresponding to the 1-(ethoxy)ethyl group disappeared completely, indicating that the EEMA units of the backbone were changed to the hydrophilic MAA units. As shown in Table 4, the copolymer CLP-5 exhibited

Table 4. Solubilities of the Comblike Copolymers (CLP-5) before and after Hydrolysis[a]

	hexane	$CHCl_3$	Bz	dioxane	THF	DMF	acetone	CH_3OH	C_2H_5OH	H_2O
before	I	S	S	D	S	S	D	I	I	I
after	I	I	W	S	S	S	S	W	W	I

[a] The experiment was carried out at room temperature (23 °C). The amounts of polymer and the solvent were 0.03 g and 1.0 mL, respectively. S = soluble; D = dissolved slowly; W = wetting; I = insoluble.

different solubilities before and after hydrolysis. The former copolymer was soluble in chloroform, benzene, 1,4-dioxane, THF, DMF, and acetone, but insoluble in methanol and ethanol. However, its hydrolysate was insoluble in chloroform, was wetted by both benzene and alcohol, and was soluble in 1,4-dioxane, THF, DMF, and acetone. The other copolymers exhibited similar behaviors.

Conclusion

Using 1,1-diphenylhexyllithium (DPHL) as initiator, in the presence of LiCl ($[LiCl]/[DPHL]_0 = 1$), in THF, at −40 °C, the anionic copolymerization of 1-(ethoxy)ethyl methacrylate (EEMA) with a small amount of glycidyl methacrylate (GMA) could proceed smoothly, and a copolymer, poly(EEMA-*co*-GMA), with a controlled molecular weight and composition as well as a narrow molecular weight distribution ($M_w/M_n = 1.09-1.13$) could be obtained. Without quenching, the coupling reaction of the epoxy groups of the above copolymer with the living sites of the anionic living polystyrene [poly(St)] generated a well-defined comblike copolymer consisting of a poly(EEMA-*co*-GMA) backbone and poly(St) side chains. Subsequently, the excess epoxy groups of the backbone were reacted with either DPHL or sodium ethoxide, and this was followed by the elimination of 1-(ethoxy)ethyl groups of the backbone under acidic conditions. The above one-pot, three-step successive procedure generated an amphiphilic comblike copolymer with a hydrophilic poly(methacrylic acid) backbone and hydrophobic poly(St) side chains.

References and Notes

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