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Graft, Block−Graft and Star-Shaped Copolymers by an in Situ Coupling Reaction

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ABSTRACT: A tetrahydrofuran (THF) solution of the living poly(glycidyl methacrylate) (poly(GMA)) was prepared by the living anionic polymerization of GMA, using 1,1-diphenylhexyllithium (DPHL) as initiator, in the presence of LiCl ($[\mathrm{LiCl}]/[\mathrm{DPHL}]_0 = 3$), at −45 °C. Upon introduction of a benzene solution of living polystyrene (poly(St)) into the above system at −30 °C, a very rapid coupling reaction between the epoxy groups of the living poly(GMA) and the propagating sites of the living poly(St) generated a graft copolymer containing a polar backbone and nonpolar side chains. When benzene solutions of living poly(St) and polyisoprene were sequentially transferred to the THF solution of living poly(GMA), a graft copolymer possessing two different nonpolar side chains was obtained. Further, a THF solution of the living block copolymer of methyl methacrylate (MMA) and GMA was prepared by the sequential anionic polymerization of the two monomers, at low temperatures. A block−graft copolymer having a poly(MMA-*b*-GMA) block backbone and poly(St) side chains was synthesized by reacting the living poly(St) with the epoxy groups of the above living block copolymer. In addition, when the poly(GMA) segment in poly(MMA-*b*-GMA) was short, a star-shaped copolymer containing a poly(MMA) arm and several poly(St) arms was obtained. GPC and ^{1}H NMR measurements indicated that all the above copolymers possess high purity, designed molecular architectures, controlled molecular weights and narrow molecular weight distributions ($M_w/M_n = 1.10-1.23$).

Introduction

The living polymerization techniques provide the possibility to synthesize well-defined graft copolymers.[1−3] Three approach routes have been suggested, namely the "grafting from", "grafting onto", and "grafting through" routes.[4] The first is based on the sequential polymerizations from the backbone to side chains, with the backbone acting as a macroinitiator for the latter step. In this manner, using a continuous transformation from anionic to cationic polymerization, several well-defined graft and block−graft copolymers, consisting of a polymethacrylate backbone and poly(alkyl vinyl ether) side chains have been recently prepared.[5] The present paper will focus on the preparation of well-defined graft, block−graft, and star-shaped copolymers by a "grafting onto" method. These copolymers contain both polar (polymethacrylate) and nonpolar (polystyrene or/and polyisoprene) components.

The "grafting onto" method by the anionic polymerization technique is based on a nucleophilic reaction of electrophilic groups attached to a backbone polymer (generally prepared by radical polymerization) and propagating sites of a living polymer. The electrophilic groups attached to the backbone can be esters,[6] chloro- or bromomethyls,[7] and dimethylvinylsilyls.[8] The coupling reaction between the epoxy groups and living anionic polymers was also employed in the preparation of a graft copolymer consisting of a polystyrene (poly(St)) backbone and poly(St) side chains, by reacting the living poly(St) with poly(*p*-vinylstyrene oxide) backbone or its styrene copolymer,[9] which was prepared by radical homo- or copolymerization. Generally, the backbone polymer had to be purified carefully by several reprecipitations and freeze-drying under high vacuum. However, even with such precautions, the impurities were not completely removed and usually caused the deactivation of a part of the living polymers. Because of the presence of the deactivated homopolymer, it was difficult to obtain pure graft copolymers.

Recently, the living anionic polymerization of the bifunctional glycidyl methacrylate (GMA) has been achieved by using a bulky initiator with low reactivity, in the presence or absence of LiCl, in a polar solvent, at a low temperature.[10−13] The C=C bonds of GMA were selectively polymerized, and the epoxy groups remained unreacted. In this manner, the functional poly(GMA) and its methyl methacrylate (MMA) copolymer with controlled molecular weights and narrow molecular weight distributions were obtained. This technique will be employed in what follows as a step in the preparation of model copolymers with complex molecular architectures. The scope of the present paper is to synthesize the following graft, block−graft, and star-shaped copolymers by in situ coupling reactions. (1) AB_x graft copolymer (**1** in Figure 1), consisting of a poly(GMA) backbone and poly(St) or polyisoprene (poly(Is)) side chains; (2) AB_xC_y graft copolymer (**2** in Figure 1), consisting of a poly(GMA) backbone and two different side chains, poly(St) and poly(Is); (3) DAB_x block−graft copolymer (**3** in Figure 1), consisting of a poly(MMA-*b*-GMA) block backbone and poly(St) side chains attached to the poly(GMA) segment of the backbone; (4) DaB_x star-shaped copolymer (**4** in Figure 1), consisting of a poly(MMA) arm and several poly(St) arms.

As shown in Scheme 1, a tetrahydrofuran (THF) solution of the living poly(GMA) (**1** in Scheme 1) and a benzene solution of the living poly(St) were separately prepared at the same time. Then, the coupling reaction between the epoxy groups of the living poly(GMA) and the propagating sites of the living poly(St) was carried out by introducing the solution of the latter into the

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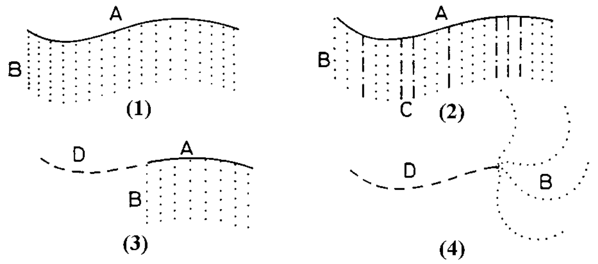
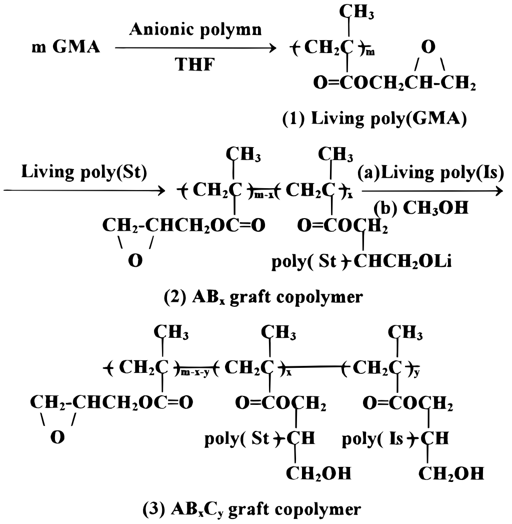
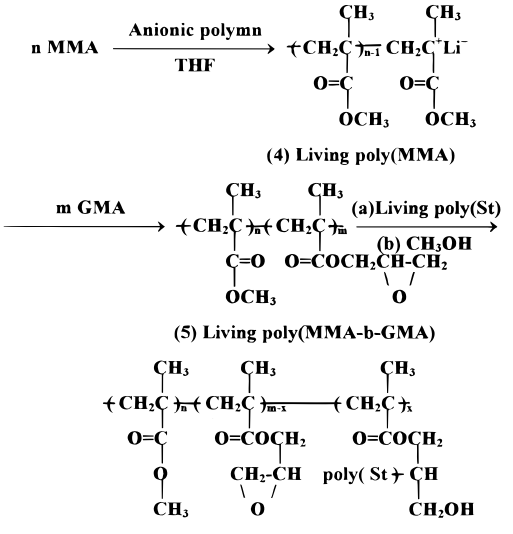


Figure 1. Schematic representation of four model copolymers prepared in the present paper. (1) AB_x graft copolymer; (2) AB_xC_y graft copolymer; (3) DAB_x block−graft copolymer; (4) DaB_x star-shaped copolymer. Components: A, poly(glycidyl methacrylate); B, polystyrene; C, polyisoprene; D, poly(methyl methacrylate); a, a short poly(glycidyl methacrylate) segment with a few repeating units.

Scheme 1



Scheme 2



former. Thus, an AB_x graft copolymer (**2** in Scheme 1) was prepared. Furthermore, when both the living poly(St) and poly(Is) solutions were sequentially introduced into the solution of living poly(GMA), an AB_xC_y graft copolymer could be produced (**3** in Scheme 1). The preparation routes of DAB_x block−graft and DaB_x star-shaped copolymers are presented in Scheme 2. A THF solution of the living block copolymer, poly(MMA-*b*-GMA) (**5** in Scheme 2), was first prepared by the sequential anionic polymerization of MMA and GMA in THF at low temperature; its reaction with living poly(St) generated a DAB_x graft copolymer (**6** in Scheme 2). If the polymerization degrees of MMA and St are large and that of GMA (m) is small, the poly(GMA) segment is very short and a DaB_x star-shaped copolymer could be obtained (**6** in Scheme 2).

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. Benzene was washed with concentrated sulfuric acid and then with water, dried over $MgSO_4$, distilled over CaH_2, and distilled from an *n*-BuLi solution before use. Hexane was first dried and distilled over CaH_2 and then distilled from a solution of *n*-BuLi. Methyl methacrylate (MMA, Aldrich, 99%) was washed with 10% aqueous sodium hydroxide solution and then with water, dried overnight with $MgSO_4$, distilled over CaH_2, and finally distilled in the presence of triisobutylaluminum[14] prior to polymerization. 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 prior to polymerization. Styrene (St, 99%, Aldrich) and isoprene (Is, 99%, Aldrich) were 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 benzylmagnesium chloride just before use. 1,1-Diphenylethylene (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.[15] *n*-BuLi (Aldrich, 1.6 M solution in hexane) was diluted with purified hexane.

Preparation of the THF Solutions of Living Poly(GMA) by the Anionic Polymerization of GMA and of Living Block Copolymer of MMA and GMA by the Sequential Anionic Polymerization of the Two Monomers. All polymerizations, namely homopolymerizations of GMA, St, and Is and the block copolymerization of MMA and GMA, were carried out in a round-bottom glass flask under an overpressure of nitrogen with magnetic stirring. The anionic polymerization of GMA was performed in THF, at −45 °C, in the presence of LiCl ($[\text{LiCl}]/[\text{DPHL}]_0 = 3$). After THF, DPE, and a THF solution of LiCl were added with dry syringes, the flask was cooled to −45 °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 the prechilled GMA to the above system, and the reaction was allowed to last 1.0 h. Without termination and polymer separation, this THF solution was directly used in the next coupling reaction step with the living poly(St) or/and living poly(Is).

The preparation of the THF solution of the living block copolymer of MMA and GMA was carried out in a manner similar to that for living poly(GMA). However, as soon as the reaction of DPE and *n*-BuLi was completed, the solution was cooled to −70 °C and prechilled MMA added. After the polymerization lasted 40 min, the temperature was raised to −50 °C, and then prechilled GMA was added and the block copolymerization was allowed to last 1.0 h. This THF solution of the living poly(MMA-*b*-GMA) was used in the preparation of DAB_x graft and DaB_x star-shaped copolymers.

Preparation of the Benzene Solution of Living Poly(St) (or Poly(Is)) by the Anionic Polymerization of St (or Is). The anionic polymerization of St or Is was carried out using *n*-BuLi as initiator, in benzene, in the presence of a small amount of THF ($[\text{THF}] = [n\text{-BuLi}]_0$). After benzene, THF and the hexane solution of *n*-BuLi were introduced into a flask placed in a 10 °C water bath, the polymerization was started by adding St (or Is) to the above system. After 10 min, the temperature was raised to 25 °C and the polymerization reaction was allowed to last 1.0 h. The benzene solution thus obtained was directly employed in the next coupling reaction step.

Syntheses of AB_x and AB_xC_y Graft, DAB_x Block–Graft, and DaB_x Star-Shaped Copolymers by the Coupling Reaction between the Epoxy Groups of Living Poly(GMA) or Poly(MMA-*b*-GMA) with the Living Sites of Poly(St) or/and Poly(Is). The coupling reaction was carried out with vigorous magnetic stirring, at −30 °C, for 30 min. For the preparation of AB_x graft copolymer, the benzene solution of living poly(St) was transferred to the THF solution of living poly(GMA). In the case of AB_xC_y graft copolymer, the benzene solutions of both living poly(St) and poly(Is) were sequentially transferred. The DAB_x block–graft copolymer or DaB_x star-shaped copolymer was prepared in the same way as the AB_x graft copolymer, except that the THF solution of living poly(GMA) was replaced by that of living poly(MMA-*b*-GMA). Although the coupling reaction occurred rapidly, it was still allowed to last 30 min to ensure a complete conversion. Then, the reaction was quenched, by adding a small amount of methanol, and the reaction mixture was poured into the methanol to precipitate the polymer. The polymer was reprecipitated by pouring again its THF solution into methanol and finally vacuum-dried overnight.

Measurements. ^{1}H NMR spectra were recorded in $CDCl_3$ on a VXR-400 spectrometer. M_n and M_w/M_n of the polymer were determined by gel permeation chromatography (GPC) on the basis of a polystyrene calibration curve. 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

Synthesis of AB_x (or AC_y) Graft Copolymer. The THF solution of living poly(GMA) was prepared by the living anionic polymerization according to a reported method.[10−13] The initiator DPHL was first prepared by reacting *n*-BuLi with DPE ($[DPE]/[n\text{-BuLi}]_0 = 1.2$) at −45 °C for 15 min. The anionic polymerization of GMA was carried out in THF, at −45 °C, in the presence of LiCl[16] ($[LiCl]/[n\text{-BuLi}]_0 = 3$). The initial monomer concentration was fixed at $[GMA]_0 = 0.47$ M in all cases. The polymerization degree ($m = [GMA]_0/[DPHL]_0$) and the theoretical average number molecular weight ($M_n = mM_{GMA} + M_I$, where M_{GMA} and M_I are the molecular weights of GMA and the initiator moiety 1,1-diphenylhexyl, respectively) were controlled by changing the initial concentration of DPHL. For instance, for $[DPHL]_0 = 14.0$ mM, the determined M_n of the obtained poly(GMA) was 4940, which is close to the calculated value ($M_k = 5000$). In addition, the molecular weight distribution of the polymer was very narrow ($M_w/M_n = 1.06$) and the GPC chromatogram exhibited a single sharp peak (peak **b** in Figure 2). In the other cases, the determined molecular weights are also in good agreement with those calculated and the molecular weight distributions are narrow ($M_w/M_n = 1.06-1.15$, see Tables 1 and 3). These results indicate that the anionic polymerization of GMA proceeded in a living manner. After the polymerization lasted 1.0 h, a small amount of solution (about 0.1 mL) was taken out with a dry syringe for the GPC measurement, and the remaining solution was directly used in the next coupling reaction step.

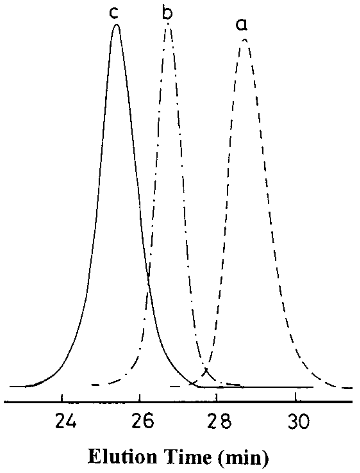


Figure 2. GPC traces of the AB_x graft copolymer and its precursors: (a) living poly(St) ($M_n = 1180$; $M_w/M_n = 1.13$); (b) living poly(GMA) ($M_n = 4940$; $M_w/M_n = 1.06$); (c) graft copolymer prepared by the coupling reaction of **a** and **b** (AB_x-2 in Tables 1 and 2; $M_n = 1.21 \times 10^4$; $M_w/M_n = 1.19$).

The benzene solution of living poly(St) or poly(Is) was prepared by a traditional method.[17] The anionic polymerization was carried out in benzene, using *n*-BuLi as initiator, at 25 °C. To promote the dissociation of *n*-BuLi and accelerate the polymerization, a small amount of a polar solvent, THF, was added ($[THF] = [n\text{-BuLi}]_0$). Because of the THF, the living poly(St) solution acquired a deep red color and this allowed us to observe via the color change the end of the next coupling reaction step. The living polymer possesses controlled molecular weight and narrow molecular weight distribution ($M_w/M_n = 1.08-1.14$; see Tables 1, 3 and 5). After a small amount of sample (about 0.1 mL) was taken out from the system for the GPC measurement, the remaining solution was immediately used in the next coupling reaction step.

The coupling reaction between the epoxy groups of living poly(GMA) and the living sites of poly(St) or poly(Is) was carried out with vigorous magnetic stirring, at −30 °C, for 30 min. As soon as the benzene solution of the living poly(St) was introduced into the THF solution of the living poly(GMA), the deep red color of the living poly(St) disappeared, which implies that the coupling reaction takes place instantaneously. As shown in Figure 2, the GPC peaks corresponding to living poly(St) (peak **a**; $M_n = 1180$; $M_w/M_n = 1.13$) and the living poly(GMA) (peak **b**; $M_n = 4940$; $M_w/M_n = 1.06$) disappeared completely and a new single peak due to the formation of the graft copolymer emerged (peak **c**; $M_n = 1.21 \times 10^4$; $M_w/M_n = 1.19$; see AB_x-2 in Tables 1 and 2). As depicted in the ^{1}H NMR spectrum (I in Figure 3), besides the peaks (**a**, **b**, **c**, **d**, and **e**) belonging to the backbone polymer, poly(GMA), the peaks (**f**, **g**, and **i**) of the poly(St) side chains are also present. The combination of GPC and ^{1}H NMR measurements indicates that a pure graft copolymer, free of precursor polymers and consisting of a poly(GMA) backbone and poly(St) side chains, was obtained.

As shown in Tables 1 and 2, the grafting efficiency (f) can be controlled through the molar ratio of the living poly(St) and epoxy groups, $f = \mathrm{mol}_{PSt}/\mathrm{mol}_{epoxy}$. The graft number in each poly(GMA) backbone is given by $N = fm$, where m is the polymerization degree of GMA. Furthermore, the calculated molecular weight (M_k) of the graft copolymer is given by the expression $M_k = M_{n(poly(GMA))} + NM_{n(PSt)}$. Because of the living polymerization, the real molecular weight is expected to be near

Table 1. Preparation Conditions of AB_x (or AC_y) Graft Copolymer[a]

	living poly(GMA)				living poly(St) or poly(Is)			
no.	M_n[b]	M_w/M_n[b]	m[c]	$mmol_{epoxy}$[d]		M_n[b]	M_w/M_n[b]	mmol[e]
AB_x-1	4050	1.07	26.8	14.1	PSt	1330	1.10	2.22
AB_x-2	4940	1.06	33.1	14.1	PSt	1180	1.13	3.04
AC_y-1	3900	1.09	25.8	14.1	PIs	1430	1.14	2.06

[a] The coupling reaction was carried out by introducing the benzene solution of living poly(St) or poly(Is) into the THF solution of living poly(GMA) with vigorous magnetic stirring. The reaction was allowed to last 30 min at −30 °C. [b] Determined by GPC. [c] Polymerization degree (m) of poly(GMA). [d] Molar amount of epoxy groups (equal to the amount of GMA). [e] Molar amount of living poly(St) or poly(Is) (equal to the amount of n-BuLi used for the preparation of the corresponding living polymer).

Table 2. Characterization of AB_x (or AC_y) Graft Copolymer

			$10^{-3}M_n$		
no.	f,[a] %	N[b]	calcd[c]	obsd[d]	M_w/M_n[d]
AB_x-1	15.7	4.2	9.64	9.32	1.18
AB_x-2	21.6	7.1	13.3	12.1	1.19
AC_y-1	14.6	3.8	9.33	8.2	1.18

[a] Grafting efficiency, $f = mol_{(PSt\ or\ PIs)}/mol_{epoxy}$ (see Table 1). [b] Graft number in each poly(GMA) chain, $N = fm$. [c] Calculated with the expression $M_k = M_{n(poly(GMA))} + NM_{n(PSt\ or\ PIs)}$. [d] Determined by GPC.

the calculated one. As shown in Table 2, the calculated M_k is close, but somewhat larger than that determined by GPC. It should be emphasized that a polystyrene calibration curve was employed for the determination of the molecular weight by GPC and that polystyrene is a linear molecule. The molecular weights determined by GPC for the branched molecules are, therefore, expected to be smaller than the true ones, because their hydrodynamic volumes are smaller than those of the corresponding linear molecules.

Synthesis of AB_xC_y Graft Copolymer. The “grafting from” method cannot be applied to the synthesis of the graft copolymer possessing two or more different side chains (AB_xC_y graft copolymer). However, the “grafting onto” technique (coupling method) is suitable for the preparation of this kind of copolymer. For the graft copolymer AB_xC_y-1 (Table 3), three kinds of living polymers were prepared at the same time. As shown in Table 3 and Figure 4, the M_n of living poly(St) (peak **a** in Figure 4; $M_n = 1420$; $M_w/M_n = 1.12$) is almost equal to that of living poly(Is) (peak **b** in Figure 4; $M_n = 1490$; $M_w/M_n = 1.10$) and their molar amounts are almost the same. The coupling reaction was carried out by sequentially transferring the benzene solutions of the above two living polymers to the THF solution of living poly(GMA) (peak **c** in Figure 4; $M_n = 5960$; $M_w/M_n = 1.10$). As shown in Figure 4, after the coupling reaction, a new single peak corresponding to the graft copolymer appears in the higher molecular weight range (peak **d** in Figure 4; $M_n = 1.71 \times 10^4$; $M_w/M_n = 1.21$), and no peak due to the precursor polymers remains. The ^{1}H NMR spectrum of this graft copolymer is presented in part II of Figure 3 and, compared to part I, contains the additional absorptions **j**, **k**, **l**, **r**, **s**, **t**, and **v** due to the poly(Is) side chains. Therefore, this graft copolymer consists of a poly(GMA) backbone and both poly(St) and poly(Is) side chains.

The calculated grafting efficiencies and graft numbers of both poly(St) and poly(Is) are listed in Table 4. For AB_xC_y-1, the grafting efficiency is $f = f_{PSt} + f_{PIs} = 28.6\%$ and the graft number in each poly(GMA) backbone $N = N_{PSt} + N_{PIs} = 11.5$. The calculated molecular weight ($M_k = 2.27 \times 10^4$) is larger than the value ($M_n = 1.71 \times 10^4$) determined by GPC.

Synthesis of DAB_x Block−Graft Copolymer. It has been reported that the carbonyl groups of poly(MMA) can react with the living poly(St) to generate a graft copolymer,[6] although the coupling reaction did not proceed quantitatively and a part of the living poly(St) remained unreacted. However, in the presence of poly(GMA), we have shown that the living poly(St) reacts with the epoxy groups of poly(GMA) and that the poly(MMA) remains unreacted.[18] In other words, the reactivity of epoxy is much higher than that of carbonyl. Therefore, when the living poly(St) is mixed with the block copolymer of MMA and GMA, the former will selectively react with the epoxy groups of the poly(GMA) segment. In this manner, a block−graft copolymer consisting of a poly(MMA-*b*-GMA) block backbone and poly(St) side chains attached to the poly(GMA) segment can be generated.

The block copolymer of MMA and GMA was prepared under conditions similar to those used for the homopolymerization of GMA. However, MMA was first polymerized at −70 °C, and GMA was sequentially added at −50 °C. One example is given in Figure 5. The living poly(MMA) (peak **b**; $M_n = 1780$; $M_w/M_n = 1.09$) was prepared in THF, at a ratio $[MMA]_0/[DPHL]_0 = 0.67/0.04$, in the presence of LiCl ($[LiCl]/[DPHL]_0 = 3$). After GMA was introduced into the above system, the GPC peak shifted to a higher molecular weight position (peak **c**), and no poly(MMA) precursor remained. This indicates that all the living sites of poly(MMA) were consumed to initiate the polymerization of GMA and the block copolymer thus obtained had a controlled molecular weight and a narrow molecular weight distribution ($M_n = 3400$; $M_w/M_n = 1.07$). For other block copolymers of MMA and GMA (Table 5), similar results were obtained. As shown by ^{1}H NMR spectrum in part I of Figure 6, besides the peaks **a**, **b**, **c**, **d**, and **e** due to the poly(GMA) segment, the absorptions **a**, **b**, and **f** due to the poly(MMA) segment are also present. Without termination and polymer separation, the THF solution of the block copolymer was immediately used in the coupling reaction.

The coupling reaction was carried out in a way similar to that used in the preparation of AB_x graft copolymer (Table 5). As shown in Figure 5, the benzene solution of the living poly(St) (peak **a**; $M_n = 1260$; $M_w/M_n = 1.09$) was introduced into the THF solution of poly(MMA-*b*-GMA) (peak **c**; $M_n = 3400$; $M_w/M_n = 1.07$), and the block−graft copolymer thus produced had a high molecular weight and narrow molecular weight distribution (peak **d**; $M_n = 7410$; $M_w/M_n = 1.12$; DAB_x-2 of Table 6). The ^{1}H NMR spectrum (part II of Figure 6) confirms the presence of poly(MMA-*b*-GMA) backbone, and of poly(St) side chains (peaks **g**, **i**, and **j**). The above results indicate that a pure block−graft copolymer consisting of a poly(MMA-*b*-GMA) backbone and poly(St) side chains was obtained.

Table 3. Synthetic Conditions of AB$_x$C$_y$ Graft Copolymer[a]

	living poly(GMA)				lving poly(St)			living poly(Is)		
no.	M_n[b]	M_w/M_n[b]	m[c]	mmol$_{epoxy}$[d]	M_n[b]	M_w/M_n[b]	mmol[e]	M_n[b]	M_w/M_n[b]	mmol[f]
AB$_x$C$_y$-1	5960	1.10	40.3	14.1	1420	1.12	2.06	1490	1.10	1.97
AB$_x$C$_y$-2	8360	1.15	57.2	14.1	1090	1.14	3.29	1070	1.13	3.35

[a] The coupling reaction was carried out by introducing the benzene solutions of living poly(St) and poly(Is) into the THF solution of living poly(GMA) sequentially, with vigorous magnetic stirring. The reaction was allowed to last 40 min at −30 °C. [b–d] See Table 1. [e] Molar amounts of living poly(St). [f] Molar amounts of living poly(Is).

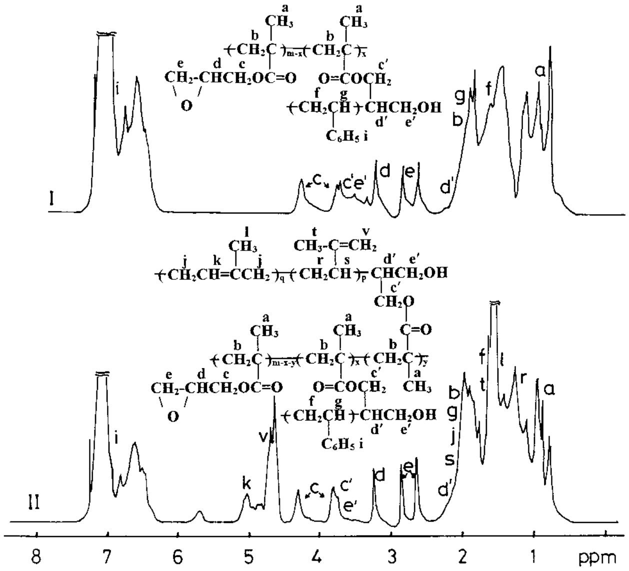


Figure 3. ^{1}H NMR spectra of AB$_x$ (I; AB$_x$-2 in Tables 1 and 2) and AB$_x$C$_y$ (II; AB$_x$C$_y$-1 in Tables 3 and 4) graft copolymers.

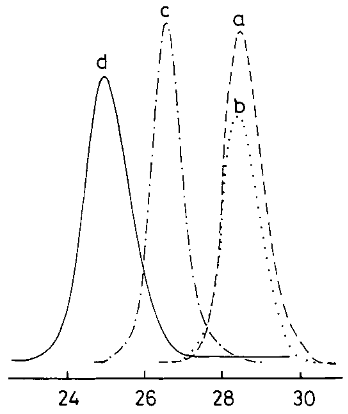


Figure 4. GPC traces of the AB$_x$C$_y$ graft copolymer and its precursors: (a) living poly(St) (M_n = 1420; M_w/M_n = 1.12); (b) living poly(Is) (M_n = 1490; M_w/M_n = 1.10); (c) living poly(GMA) (M_n = 5960; M_w/M_n = 1.10); (d) graft copolymer obtained after the coupling reaction of **a**, **b**, and **c** (AB$_x$C$_y$-1 in Tables 3 and 4; M_n = 1.71 × 10^4; M_w/M_n = 1.21).

Table 4. Characterization of AB$_x$C$_y$ Graft Copolymer

					10^{-3} M_n		
no.	f_{PSt},[a] %	N_{PSt}[b]	f_{PIs},[c] %	N_{PIs}[d]	calcd[c]	obsd[f]	M_w/M_n[f]
AB$_x$C$_y$-1	14.5	5.9	14.0	5.6	22.7	17.1	1.21
AB$_x$C$_y$-2	23.3	13.3	23.8	13.6	37.4	27.5	1.23

[a] Grafting efficiency of poly(St), f_{PSt} = mol$_{PSt}$/mol$_{epoxy}$. [b] Graft number of poly(St) in each poly(GMA) chain, $N_{PSt} = mf_{PSt}$. [c] Grafting efficiency of poly(Is), f_{PIs} = mol$_{PIs}$/mol$_{epoxy}$. [d] Graft number of poly(Is) in each poly(GMA) chain, $N_{PIs} = mf_{PIs}$. [e] Calculated with the expression: $M_k = M_{n(poly(GMA))} + N_{PSt}M_{n(PSt)} + N_{PIs}M_{n(PIs)}$. [f] Determined by GPC.

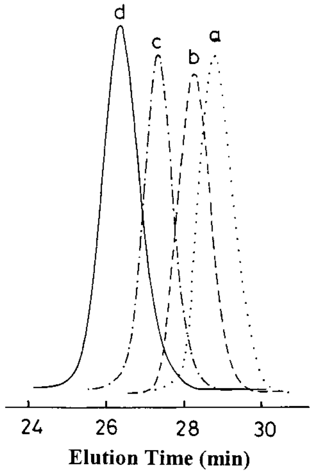


Figure 5. GPC traces of the DAB$_x$ block–graft copolymer and its precursors: (a) living poly(St) (M_n = 1260; M_w/M_n = 1.09); (b) living poly(MMA) (M_n = 1780; M_w/M_n = 1.09); (c) living poly(MMA-*b*-GMA) (M_n = 3400; M_w/M_n = 1.07) prepared by the anionic block copolymerization of GMA from **b**; (d) block–graft copolymer obtained by the coupling reaction of **a** and **c** (DAB$_x$-2 in Tables 5 and 6; M_n = 7410; M_w/M_n = 1.12).

As shown in Table 6, when the graft number and the molecular weight are smaller (DAB$_x$-1 and DAB$_x$-2), the determined M_n of the block–graft copolymer is close to the calculated value. In this case, the molecular architecture is close to a linear one, and the GPC determination is expected to provide a value near the real one. However, as the graft number and the molecular weight increase (DAB$_x$-3), Table 6 shows that the determined value is smaller than the calculated value.

Synthesis of DaB$_x$ Star-Shaped Copolymer. As described above, a well-defined block copolymer of MMA and GMA can be prepared by the sequential anionic polymerization method. For the above synthesis of DAB$_x$ block–graft copolymer, the block copolymer with a weight ratio W_{MMA}/W_{GMA} = 50/50 was employed. Because the polymerization proceeds in a living manner, the polymerization degree of GMA in the block copolymer can be restricted to a small value by reducing the amount of GMA. As listed in Tables 5 and 7, the block copolymers in DaB$_x$-1, DaB$_x$-2, and DaB$_x$-3 have a very short poly(GMA) segment with average polymerization degrees of GMA of 3.0, 3.0, and 6.4, respectively. These block copolymers were employed for the synthesis of the star-shaped copolymers that contain a poly(MMA) arm and several poly(St) arms (DaB$_x$ star-shaped copolymer, **4** in Figure 1).

In the coupling reaction, the molar amount of living poly(St) employed was selected to be equal to that of epoxy groups (Table 5). As illustrated in Figure 7, when the benzene solution of living poly(St) (peak **a**; M_n = 1020; M_w/M_n = 1.10; 6.50 mmol) was added to the THF solution of the living poly(MMA-*b*-GMA) (peak **b**; M_n = 3150; M_w/M_n = 1.08; amount of epoxy, 6.34 mmol), the coupling reaction took place and a star-shaped copolymer with a high molecular weight and narrow molecular

Table 5. Preparation Conditions of DAB$_x$ Block–Graft and DaB$_x$ Star-Shaped Copolymers[a]

	living poly(MMA-*b*-GMA)				living poly(St)		
no.	M_n[b]	M_w/M_n[b]	W_{MMA}/W_{GMA}[c]	mmol$_{epoxy}$[d]	M_n[b]	M_w/M_n[b]	mmol[e]
DAB$_x$-1	3670	1.08	50/50	14.1	1750	1.08	3.13
DAB$_x$-2	3400	1.07	50/50	14.1	1260	1.09	3.75
DAB$_x$-3	5830	1.07	50/50	14.1	930	1.13	5.63
DaB$_x$-1	2340	1.09	80/20	3.52	1010	1.10	3.60
DaB$_x$-2	2350	1.10	80/20	3.52	1740	1.09	3.60
DaB$_x$-3	3150	1.08	69/31	6.34	1020	1.10	6.50

[a] The coupling reaction was carried out by introducing the benzene solution of living poly(St) into the THF solution of the living block copolymer of MMA and GMA with vigorous magnetic stirring. The reaction was allowed to last 30 min at −30 °C. [b] Determined by GPC. [c] Weight percent of poly(MMA) and poly(GMA) segments, respectively. [d] Molar amounts of epoxy groups. [e] Molar amounts of living poly(St).

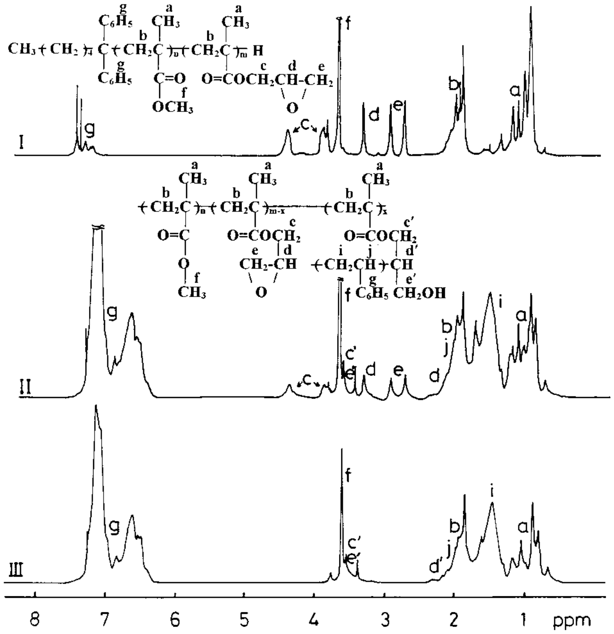


Figure 6. ^{1}H NMR spectra of poly(MMA-*b*-GMA) (I; M_n = 5830; M_w/M_n = 1.07; the weight ratio of two components, W_{MMA}/W_{GMA} = 50/50), DAB$_x$ block–graft copolymer (II; DAB$_x$-1 in Tables 5 and 6), and DaB$_x$ star-shaped copolymer (III; DaB$_x$-2 in Tables 5 and 7; its structure is similar to that of DAB$_x$-1 in part II).

Table 6. Characterization of DAB$_x$ Block–Graft Copolymer

				10^{-3} M_n		
no.	*f*,[a] %	*m*,[b] %	N[c]	calcd[d]	obsd[e]	M_w/M_n[e]
DAB$_x$-1	22.2	12.1	2.7	8.40	9.42	1.18
DAB$_x$-2	26.6	11.4	3.0	7.18	7.41	1.12
DAB$_x$-3	40.0	19.7	7.9	13.2	10.8	1.15

[a] Grafting efficiency, f = mol$_{PSt}$/mol$_{epoxy}$. [b] Polymerization degree (m) of poly(GMA) segment. [c] Graft number in each backbone, $N = fm$. [d] Calculated with the expression $M_k = M_{n\,(block)} + NM_{n(PSt)}$. [e] Determined by GPC.

Table 7. Characterization of DaB$_x$ Star-shaped Copolymer

				10^{-3} M_n		
no.	m[a]	N[b]	$M_{n(PMMA)}/M_{n(PSt)}$[c]	calcd[d]	obsd[e]	M_w/M_n[e]
DaB$_x$-1	3.0	4.0	1680/1010	5.37	4.40	1.12
DaB$_x$-2	3.0	4.0	1690/1740	7.57	6.80	1.14
DaB$_x$-3	6.4	7.4	2010/1020	9.68	7.83	1.10

[a] Polymerization degree (m) of poly(GMA) segment. [b] Arm number of the star-shaped copolymer, $N = m + 1$. [c] The molecular weights of poly(MMA) arm and each poly(St) arm, respectively. [d] Calculated with the expression $M_k = M_{n(block)} + mM_{n(PSt)}$. [e] Determined by GPC.

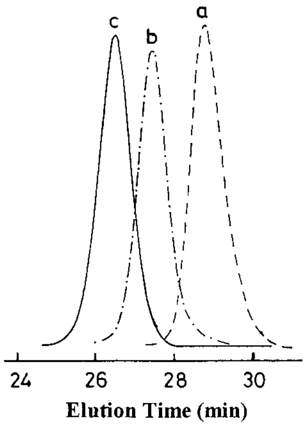


Figure 7. GPC traces of the DaB$_x$ star-shaped copolymer and its precursors: (a) living poly(St) (M_n = 1020; M_w/M_n = 1.10); (b) living poly(MMA-*b*-GMA) (M_n = 3150; M_w/M_n = 1.08); (c) star-shaped copolymer obtained by the coupling reaction of **a** and **b** (DaB$_x$-3 in Tables 5 and 7; M_n = 7830; M_w/M_n = 1.10).

weight distribution was generated (peak **c**; M_n = 7830; M_w/M_n = 1.10; DaB$_x$-3 in Table 7). As for the above graft and block–graft copolymers, the single, very sharp GPC peak implies that this star-shaped copolymer is not mixed with its precursor polymers.

Part III of Figure 6 presents the ^{1}H NMR spectrum of a star-shaped copolymer (DaB$_x$-2 in Tables 5 and 7). The absorptions due to poly(MMA) component (**a**, **b**, and **f**) and poly(St) component (**g**, **i**, and **j**) can be easily detected. However, the absorptions corresponding to the poly(GMA) segment can hardly be detected, because the weight ratio of the three components in this copolymer is W_{MMA}:W_{GMA}:W_{St} = 4:1:14. This copolymer can be considered a star-shaped copolymer that consists of just two components, poly(MMA) and poly(St).

As shown in Tables 5 and 7, in the preparation of DaB$_x$-1 and DaB$_x$-2, the block copolymers of MMA and GMA employed have almost the same molecular weight, molecular weight distribution, and composition. Therefore, the star-shaped copolymers based on them possess the same arm number, namely a poly(MMA) arm and three poly(St) arms, and the molecular weights of the poly(MMA) arms are almost equal (Table 7). However, the poly(St) arms in DaB$_x$-2 have a larger molecular weight ($M_{n(PSt)}$ = 1740) than those in DaB$_x$-1 ($M_{n(PSt)}$ = 1010). This causes a difference in the total molecular weights of the final star-shaped copolymers. Comparing DaB$_x$-1 with DaB$_x$-3, the lengths of poly(St) arms are almost the same. However, their poly(St) arm numbers are different (m = 3 and 6.4, respectively). As shown in Table 7, the final molecular weight of DaB$_x$-3 (M_n = 7830) is much larger than that of DaB$_x$-1 (M_n = 4400). The molecular weights of the star-shaped copolymers determined by GPC on the basis of a polystyrene calibration curve are smaller than the calculated values. They have smaller hydrodynamic volumes than the corresponding linear polymers, and for this reason the determined values should be smaller than the real ones.

Conclusion

The coupling reaction between the epoxy groups of living poly(glycidyl methacrylate) (poly(GMA)) and the propagating sites of living polystyrene (poly(St)) or polyisoprene (poly(Is)) can generate a graft copolymer with a polar backbone and nonpolar side chains. When both the living poly(St) and poly(Is) were reacted with the epoxy groups of living poly(GMA), a graft copolymer possessing two kinds of nonpolar side chains attached to a poly(GMA) backbone was obtained. If the backbone polymer is a block copolymer of MMA and GMA, the coupling reaction with living poly(St) can produce a block−graft copolymer, which contains a poly(MMA-*b*-GMA) block backbone and poly(St) side chains attached to the poly(GMA) segment. In addition, when the poly(GMA) segment is short, a star-shaped copolymer possessing one poly(MMA) arm and several poly(St) arms are obtained.

Because both the backbone and side chain polymers are prepared in situ prior to the coupling reaction and the living polymer solutions were directly employed, no impurity was introduced into the system. Both the backbone and side chain polymers prepared separately have controlled molecular weights and narrow molecular weight distributions. On the basis of these well-defined living precursor polymers, model copolymers with designed molecular architectures, controlled molecular weights, and narrow molecular weight distributions can be synthesized.

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