A Novel Breakable Cross-Linker and pH-Responsive Star-Shaped and Gel Polymers

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ABSTRACT: A bifunctional methacrylate monomer, namely, ethylene glycol di(1-methacryloyloxy)ethyl ether (**1**), was prepared through the addition reaction between ethylene glycol divinyl ether and methacrylic acid. **1** was used as a cross-linker in the preparation of a star-shaped poly(methyl methacrylate) [poly(MMA)], a branched soluble poly(MMA), and a polymer gel. The addition of **1** to an anionically prepared living poly(MMA) solution generated a star-shaped polymer with a central poly(**1**) gel core and several poly(MMA) arms. On the other hand, when MMA and **1** were simultaneously added to a tetrahydrofuran (THF) solution of an anionic initiator, a branched soluble poly(MMA) or a polymer gel was obtained, depending on the amount of **1**. The cross-linking points in the above polymers could be easily broken by hydrolysis under acidic conditions, leading to linear polymers. In contrast to the common polymer gels, the present polymer gel could be broken to soluble polymers in an acidic medium. However, it was just swollen in a basic or a neutral medium. The hydrolyzed product from the star-shaped polymer was a block copolymer consisting of poly(MMA) and poly(methacrylic acid) segments, and those hydrolyzed from the branched polymers and polymer gels were random copolymers of MMA and methacrylic acid. All the hydrolyzed polymers possessed quite different solubilities than those of their precursors.

Introduction

Divinyl cross-linking reagents (cross-linkers) have been often employed for the preparation of star-shaped (co)polymers. A linear living polymer was first prepared using a living polymerization technique, and this was subsequently followed by the reaction of its living end with a small amount of divinyl compound. For instance, the addition of divinylbenzene (DVB) to an anionic living polystyrene [poly(St)] solution led to the formation of a star-shaped poly(St) with a central poly(DVB) gel core.[1] This method was also extended to cationic,[2] group transfer,[3] and metathesis[4] polymerizations, in which divinyl ethers, divinyl esters, and norbornadiene dimers were used as cross-linkers, respectively. This synthetic technique could be easily carried out by just adding a bifunctional monomer to a completed living polymerization system. However, the arm number of the resulting (co)polymer could be hardly controlled.

In the present paper, we synthesize a novel cross-linker, ethylene glycol di(1-methacryloyloxy)ethyl ether (**1**), whose bonds indicated by arrows in Figure 1 can be broken in acidic media. This novel cross-linker was employed in the preparation of a star-shaped poly(methyl methacrylate) [poly(MMA)], a branched soluble poly(MMA), and a polymer gel. The star-shaped poly(MMA) was prepared using a traditional method:[1−4] the living poly(MMA) was allowed to react with a small amount of **1** to form a living block copolymer, which had a short segment of **1** attached to the end of the polymer chain; the subsequent intermolecular reactions of the pendant vinyl groups of **1** with the living ends of the polymer chains resulted in a star-shaped polymer with a central poly(**1**) core. On the other hand, the simultaneous introduction of **1** and MMA into a THF solution of an anionic initiator resulted in the formation of a branched soluble poly(MMA) or a polymer gel, depending on the amount of **1** added, because the intermolecular cross-linking can occur as the polymerization proceeds. In contrast to the star-shaped polymers and polymer gels based on the conventional cross-linkers, such as ethylene glycol dimethacrylate, those prepared using **1** could be easily broken by hydrolysis under mild acidic conditions, generating linear polymers. Compared to most polymer gels, the present gels exhibited different responses in the acid and basic media. In contrast to their swelling in a basic or neutral medium, completely clear solutions of linear polymers could be obtained when an acidic medium was employed. This may be useful for controlled drug release and is relevant to the environment protection.

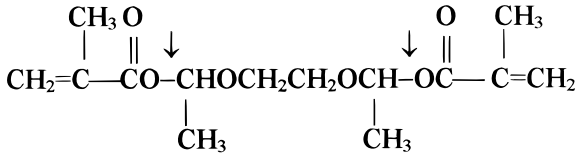

Figure 1. Molecular structure of ethylene glycol di(1-methacryloyloxy)ethyl ether (**1**). The linkages indicated with arrows can be easily broken under acidic conditions.

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 with $MgSO_4$, and distilled over CaH_2. 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 a 10% aqueous sodium hydroxide solution and then with water, dried overnight with $MgSO_4$, and distilled twice over CaH_2 prior to polymerization. 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. *n*-BuLi (Aldrich, 1.6 M solution in hexane) was diluted with purified hexane.

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Table 1. Preparation of Star-Shaped Poly(MMA) (SSP)[a]

		star[b]		hydrolyzed product[c]		
no.	$[1]_0/[DPHL]_0$	M_n[d]	M_w/M_n[d]	M_n(calcd)	M_n(obsd)[d]	M_w/M_n[d]
SSP-1	3	8 420	1.42	4760	4840	1.12
SSP-2	5	10 200	1.72	5100	5460	1.12
SSP-3	8	15 300	2.24	5620	6500	1.15

[a] The initiator, DPHL, was prepared via the reaction of *n*-BuLi with DPE ($[DPE]/[n\text{-BuLi}]_0 = 1.2$), in THF, at −40 °C, in the presence of LiCl ($[LiCl]/[n\text{-BuLi}]_0 = 1.2$), for 15 min. The anionic polymerization of MMA was performed by adding prechilled MMA ($[MMA]_0 = 0.667$ M) to the above initiator solution ($[DPHL]_0 = 16.7$ mM), and the reaction was allowed to last 50 min at −78 °C. Then, the system was warmed to −50 °C, and a toluene solution of **1** was added. This cross-linking reaction was allowed to last an additional 3 h. [b] Before reprecipitation. [c] The hydrolysis was carried out after the reprecipitation. [d] Determined by GPC.

Synthesis of Ethylene Glycol Di(1-methacryloyloxy)-ethyl Ether (1). 1 was prepared through the addition reaction between ethylene glycol divinyl ether (EGDE; Aldrich, 97%) and methacrylic acid (MAA; Aldrich, 99.8%) in the presence of a trace amount of the inhibitor 4-*tert*-butylcatechol, under the protection of nitrogen, with magnetic stirring. In a 250 mL round-bottom flask equipped with a condenser and a magnetic stirrer, 25.0 g (0.21 mol) of EGDE and a small amount of 4-*tert*-butylcatechol were introduced. After 4-*tert*-butylcatechol has dissolved and the temperature was raised to 70 °C, MAA (36.5 g, 0.42 mol) was dropwise added with a syringe in about 20 min. The reaction was allowed to last an additional 6.0 h, and the crude product was distilled under high vacuum. The monomer was dissolved in purified toluene (30% v/v), and this solution was purified with CaH_2 and filtered through a tube filter with reduced ends in a completely sealed apparatus. This purification process was repeated prior to polymerization, and the toluene solution was directly used. The high purity of **1** was confirmed by ^{1}H NMR ($CDCl_3$): δ 1.42 (d, 6H, OCH(CH_3)O), 1.95 (s, 6H, α-CH_3), 3.60−3.83 (m, 4H, OCH_2CH_2O), 5.59 and 6.15 (2s, 4H, CH_2=), 6.00 (m, 2H, OC*H*(CH_3)O).

Polymerization. The anionic polymerization was carried out in THF, in a round-bottom glass flask, under an overpressure of argon, with magnetic stirring, at a selected temperature, in the presence of LiCl.[5] 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. For the preparation of star-shaped polymer, prechilled MMA was first added, and the polymerization was allowed to last 50 min at −78 °C. Then, the system was warmed to −50 °C, and a toluene solution of **1** was added. After the cross-linking reaction lasted 3 h, the system was quenched with a small amount of methanol, and the polymer was precipitated by pouring the polymerization solution into hexane. Then, the polymer was reprecipitated in ethanol from a benzene solution and vacuum-dried overnight.

In the cases of branched poly(MMA) and polymer gels, a prechilled mixture of MMA and a toluene solution of **1** was added to the initiator solution, and the reaction was allowed to last 2 h at −50 °C. The branched poly(MMA) was purified in a way similar to that used for the star-shaped polymer. To purify the polymer gel, hexane containing a small amount of methanol was added, and after 3 h, it was dried under reduced pressure at 50 °C for 24 h.

Hydrolysis of the Star-Shaped Polymer, the Branched Polymer, and the Polymer Gel. The hydrolysis of star-shaped or branched poly(MMA) was carried out in acetone, in the presence of a small amount of an aqueous solution of HCl, at room temperature, with magnetic stirring. For instance, 1.2 g of vacuum-dried star-shaped poly(MMA) (SSP-3 in Table 1) was redissolved in 30 mL of acetone, to which 1.0 mL of HCl aqueous solution (6.0 M) was added. After 20 min, this mixture was poured into hexane to precipitate the polymer. The polymer thus obtained was washed with hexane and vacuum-dried at 40 °C for 24 h.

Table 2. Preparation of the Branched Soluble Poly(MMA) (BP) and Polymer Gel (PG)[a]

				before hydrolysis		after hydrolysis	
no.	$[DPHL]_0$ mM	$[1]_0$ mM	stirring	M_n[b]	M_w/M_n[b]	M_n[b]	M_w/M_n[b]
BP-1	14.7	29.4	OK	14 100	1.69	9 440	1.40
BP-2	14.7	58.8	OK	33 000	2.43	9 790	1.46
BP-3	7.4	29.4	OK	49 100	3.10	15 100	1.57
PG-1	7.4	58.8	NO	gel		12 900	1.63
PG-2	5.0	58.8	NO	gel		15 900	1.74

[a] The initiator, DPHL, was prepared via the reaction of *n*-BuLi with DPE ($[DPE]/[n\text{-BuLi}]_0 = 1.2$), in THF, at −40 °C, in the presence of LiCl ($[LiCl]/[n\text{-BuLi}]_0 = 1.2$), for 15 min. The polymerization was induced by adding a prechilled mixture of MMA ($[MMA]_0 = 0.588$ M) and a toluene solution of **1** to the above initiator system, and the reaction was allowed to last 2 h at −50 °C. [b] Determined by GPC.

Table 3. Response of the Poly(MMA) Gel[a]

no.	solvent	catalyst/M	time	response
1	acetone	NaOH/0.42	24 h	swelling
2	acetone	H_2O/0.95	24 h	swelling
3	THF	AA[b]/0.26	36 h	peptization
4	acetone	AA[b]/0.26	24 h	peptization
5	THF	HCl/0.015	20 min	clear solution
6	acetone	HCl/0.015	15 min	clear solution
7	acetone	HCl/0.05	10 min	clear solution
8	THF	HCl/0.2	10 min	clear solution
9	acetone	HCl/0.2	5 min	clear solution

[a] The reaction was carried out at 20 °C with magnetic stirring (solvent, 30 mL; polymer gel, 1.0 g). [b] Acetic acid.

The hydrolysis of the polymer gel was performed either in THF or in acetone, using either acetic acid or an aqueous solution of HCl. For comparison, the reaction was also carried out under basic conditions in the presence of sodium hydroxide. In 30 mL of solvent, 1.0 g of polymer gel and a certain amount of acid were added. The corresponding time to form a completely transparent solution was recorded (Table 3). The hydrolyzed polymer was purified as described above.

Measurements. ^{1}H NMR spectra were recorded in $CDCl_3$ or CD_3OD on an INOVA-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. The FT-IR spectra were recorded on a Perkin-Elmer 1760-X spectrometer using KBr tablets.

Results and Discussion

Preparation of Star-Shaped Poly(MMA). The preparation of star-shaped poly(MMA) was carried out in a two-step process,[1−4] namely, the living anionic polymerization of MMA and the reaction of the resulting living polymer with **1**. In the first step, the initiator DPHL was prepared in situ before the monomer addition, via the reaction of *n*-BuLi with DPE ($[DPE]/[n\text{-BuLi}]_0 = 1.2$), in THF, at −40 °C, in the presence of LiCl ($[LiCl]/[n\text{-BuLi}]_0 = 1.2$), [5] for about 15 min. The anionic polymerization was induced by adding prechilled MMA ($[MMA]_0 = 0.667$ M) to the above initiator solution ($[DPHL]_0 = 16.7$ mM), and the reaction was allowed to last 50 min at −78 °C. The molecular weight (M_n) of the obtained poly(MMA) was in good agreement with

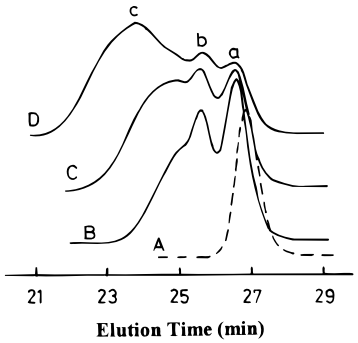

Figure 2. GPC traces of star-shaped polymers and their precursor: (A) living linear poly(MMA) ($M_n = 4140$, $M_w/M_n = 1.06$); (B, C, and D) star-shaped poly(MMA)s (Table 1; B, SSP-1; C, SSP-2; D, SSP-3) prepared by adding **1** to the above living poly(MMA) solution, for $[1]_0/[DPHL]_0$ ratios of 3, 5, and 8, respectively.

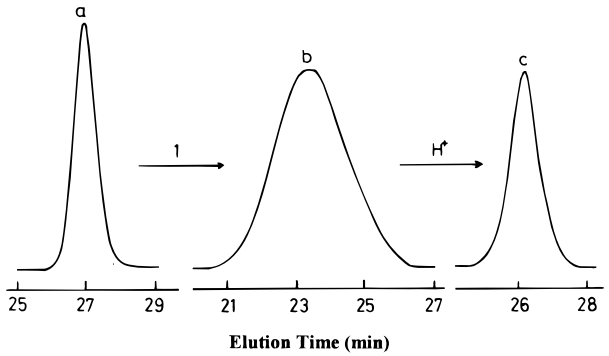

Figure 3. GPC traces of reprecipitated star-shaped poly(MMA) from SSP-3 (peak b, $M_n = 34\,000$, $M_w/M_n = 1.55$), its living poly(MMA) precursor (peak a, $M_n = 4180$, $M_w/M_n = 1.05$), and its hydrolyzed polymer (peak c, $M_n = 6500$, $M_w/M_n = 1.15$).

the designed value ($M_k = 4230$), and the molecular weight distribution (MWD) was very narrow ($M_w/M_n \leq 1.06$; see Figures 2A and 3A).

In the second step, the living poly(MMA) was allowed to react with **1** for $[1]_0/[DPHL]_0$ ratios[6] of 3, 5, or 8. The cross-linking reaction was allowed to last 3 h at −50 °C. The reaction proceeded quantitatively and produced a completely soluble product. As shown in Figure 2, the resulting polymers possess broad MWDs, and the star-shaped polymers (peak c) are accompanied by low molecular weight polymers (peaks a and b). Peak a corresponds to a higher molecular weight ($M_n \approx 5600$) than that of its living poly(MMA) precursor ($M_n = 4140$), and this can be attributed to a block copolymer of MMA and **1**. The M_n corresponding to peak b is about 14 000, and this fraction is most likely a star-shaped polymer with a low arm number (about 3). The presence of peaks a and b indicates that the cross-linking reaction was incomplete. As the amount of **1** increased, the a and b fractions decreased, being incorporated into the star-shaped polymer with high molecular weight.

It has been reported that the molecular structure of the cross-linker greatly affects the yield of the star-shaped polymer. For instance, when the cationically prepared living polymer of isobutyl vinyl ether (IBVE) was reacted with bisphenol A derived divinyl ether, a star-shaped poly(IBVE) was obtained with high selectivity.[2a] However, when this cross-linker with rigid aromatic units was replaced with a flexible divinyl ether, such as di(ethylene glycol) divinyl ether, the resulting star-shaped polymer was accompanied by low molecular weight polymers. Similarly, the cross-linker **1** also possesses a flexible spacer. After the cross-linking proceeds to a certain extent, the flexibility of the cross-linker makes its pendant double bond less exposed and hence less accessible for further reactions with the incoming living chains. The increase of the amount of **1** will generate a larger core, thus providing a larger number of accessible vinyl groups. For this reason, the fraction of star-shaped polymer will increase (Figure 2D).

Because of the presence of the low molecular weight fractions (peaks a and b), the average molecular weight of the resulting polymer was low. For instance, the M_n of SSP-3 in Table 1 is 15 300, and according to this value, the calculated arm number of the star-shaped polymer is small (3.6). However, this is not the real value, because the star-shaped polymer is not pure. To obtain a pure star-shaped polymer, reprecipitation was carried out to remove the low molecular weight fractions. For instance, 2.0 g of SSP-3 (Table 1) was redissolved in 60 mL of benzene, and this solution was poured into 400 mL of ethanol. As shown in Figure 3b, the reprecipitated polymer exhibits a single GPC peak. According to the molecular weight of the reprecipitated SSP-3 ($M_n = 34\,000$), the calculated arm number of the star-shaped polymer is about 8, which is much higher than that before reprecipitation.

Preparation of the Branched Soluble Poly(MMA) and Polymer Gel. Great attention was accorded to polymer gels, because of their applications in various fields, such as medicine, nutritive and petrochemical industries, agriculture, biotechnology, etc.[7] The synthesis of pH-sensitive polymer gels and their applications in drug delivery have been widely investigated.[8] Because of the presence of ionizable groups in this kind of polymer gels, swelling or deswelling can occur along with pH changes. However, the pH change does not affect or change their chemical composition and molecular structure. In contrast to those polymer gels, a different polymer gel was prepared using the cross-linker **1**, because this insoluble gel can be changed to soluble linear polymers by changing the pH.

In contrast to the preparation of the star-shaped poly(MMA), MMA and a toluene solution of **1** were introduced into a THF solution of the initiator (DPHL) at the same time. The reaction was allowed to last 2 h at −50 °C. Because both MMA and the cross-linker **1** participate simultaneously in the polymerization, a polymer gel could be obtained through the intermolecular cross-linking reaction.

For a fixed initial concentration of MMA ($[MMA]_0 = 0.588$ M), the characteristics of a polymer gel depend on the concentrations of both the initiator and the cross-linker **1**. Low $[DPHL]_0$ and high $[\mathbf{1}]_0$ are beneficial for the cross-linking reaction. As shown in Table 2, when $[DPHL]_0 = 14.7$ mM and $[\mathbf{1}]_0 = 29.4$ mM (BP-1), cross-linking occurred to some extent, but the polymer remained soluble. Even when the concentration of **1** was doubled to increase the number of cross-linking points (BP-2), or the concentration of DPHL was reduced to half to increase the molecular weight (BP-3), the polymers still remained soluble, and the magnetic stirring was still possible despite a very high viscosity. The resulting polymers (BP-2 and -3) have higher molecular weights and broader MWDs than BP-1 (Table 2). Consequently, when the concentration of the cross-linker **1** was sufficiently low and/or the initiator con-

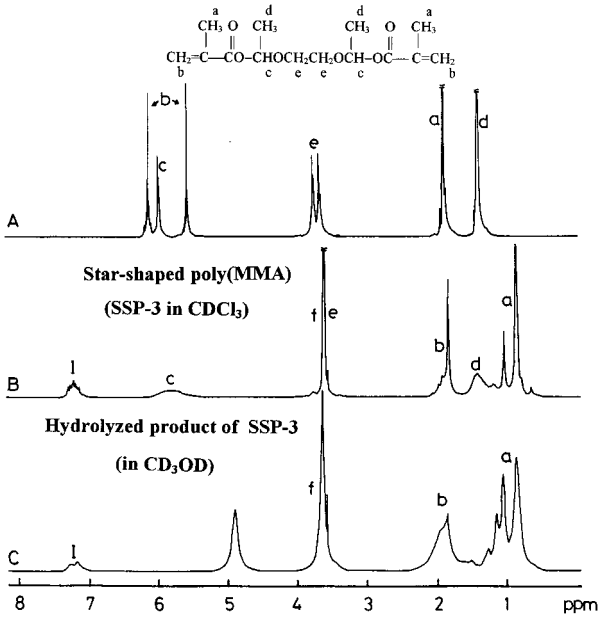

Figure 4. ^{1}H NMR spectra of **1** (A; in $CDCl_3$), star-shaped poly(MMA) (B; SSP-3 in $CDCl_3$; see Table 1 and Figure 3b) and its hydrolyzed polymer (C; in CD_3OD, see Table 1 and Figure 3c). Absorptions due to poly(MMA) segment: peak a, α-CH_3; peak b, −CH_2− in the main chain; peak f, −OCH_3 in the side chain. I: C_6H_5 of the initiator (DPHL).

centration was sufficiently high, the resulting products were soluble branched polymers, probably accompanied by some looped and cyclic polymer chains. For this reason, the MWDs were broad. However, when $[\mathbf{1}]_0$ was taken twice as large and $[DPHL]_0$ was simultaneously reduced to half that for BP-1, the magnetic stirring became impossible only after a few minutes upon the addition of MMA and **1**, and a polymer gel was generated (PG-1 in Table 2). The further reduction of $[DPHL]_0$ (PG-2 in Table 2) or the homopolymerization of **1** ($[DPHL]_0 = 7.4$ mM, $[\mathbf{1}]_0 = 0.400$ M) generated polymer gels easily.

Hydrolysis of Star-Shaped Polymers, Branched Polymers, and Polymer Gels. The hydrolysis of the star-shaped or branched polymer was carried out in acetone, at room temperature, in the presence of a small amount of hydrochloric acid (see Experimental Section). Figure 3b presents the GPC chromatogram of a reprecipitated star-shaped poly(MMA) (peak b), which has, obviously, a larger molecular weight and a broader MWD ($M_n = 34\,000$, $M_w/M_n = 1.55$) than its living linear poly(MMA) precursor (peak a, $M_n = 4180$, $M_w/M_n = 1.05$). The hydrolysis of this star-shaped polymer resulted in the formation of a polymer with a lower molecular weight and a narrower MWD (peak c, $M_n = 6500$, $M_w/M_n = 1.15$). This hydrolyzed product is most likely a block copolymer consisting of poly(MMA) and poly(methacrylic acid) [poly(MAA)] segments as described below, and for this reason, its molecular weight is larger than that of the linear poly(MMA) precursor (peak a).

To identify the cleavage point, the hydrolyzed product was characterized by ^{1}H NMR and FT-IR. Figure 4 depicts the ^{1}H NMR spectra of the star-shaped polymer (B) and its hydrolyzed product (C). For comparison, the ^{1}H NMR spectrum of **1** is also included in Figure 4A. Comparing parts A and B, one can observe that the peaks a and b, corresponding to the α-methyl and H_2C= of **1**, shifted to 0.8−1.1 and 1.8−2.1 ppm after cross-

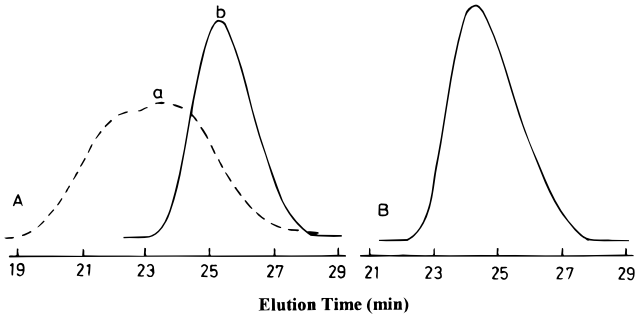

Figure 5. GPC traces of the hydrolyzed polymers from the branched soluble poly(MMA) (A) and polymer gel (B). A-a: BP-2 in Table 2, $M_n = 33\,000$, $M_w/M_n = 2.43$. A-b: Hydrolyzed polymer from A-a, $M_n = 9790$, $M_w/M_n = 1.46$. B: Hydrolyzed polymer ($M_n = 12\,900$, $M_w/M_n = 1.63$) from polymer gel, PG-1 (Table 2).

linking and overlapped with the absorptions of the α-CH_3 (B−a) and −CH_2− (B−b) belonging to poly(MMA). On the other hand, the peaks c, d, and e of the side chain of **1** did not change and could be detected in the spectrum of the star-shaped polymer (B). However, these absorptions disappeared completely in the spectrum of the hydrolyzed product (C), indicating that the ester groups of the cross-linker **1** were eliminated to yield the poly(MAA) segment. This result was also confirmed by FT-IR; the hydrolyzed polymer exhibits a broad absorption (2500−3800 cm^{-1}) corresponding to the carboxyl group of poly(MAA) segment. On the other hand, the absorption due to the ester group (−OCH_3) of poly(MMA) segment is still present quantitatively in the ^{1}H NMR spectrum of the hydrolyzed polymer (peak f in Figure 4C). The above results indicate that the hydrolysis reaction fractured selectively the cross-linking points to generate linear block copolymers of MMA and MAA.

Similarly, the hydrolysis of the branched soluble polymer can also generate a linear polymer via the same mechanism. As shown in Figure 5A, the hydrolyzed polymer possesses a lower molecular weight and a narrower MWD (peak A-b, $M_n = 9790$, $M_w/M_n = 1.46$) than its precursor polymer (peak A-a, BP-2 in Table 2, $M_n = 33\,000$, $M_w/M_n = 2.43$). Its FT-IR spectrum also confirmed the presence of the carboxyl groups of poly(MAA) units (2500−3800 cm^{-1}). However, the hydrolyzed product is a random copolymer of MMA and MAA, because MMA and the cross-linker **1** participated in the polymerization simultaneously.

The hydrolysis of the polymer gel is more interesting, because this is a process that changes the insoluble polymer to a soluble linear one. As shown in Table 3, the response of the polymer gel depends mainly on the acidity of the medium and to some extent on the solvent employed. In a basic (no. 1, NaOH) or a neutral (no. 2, H_2O) environment, the polymer gel is swollen, but the cross-linking points are not destroyed. When a weak acid, acetic acid, was used (nos. 3 and 4), the polymer gel transformed after a long time (24−36 h) into small particles which dispersed in the medium. However, in the presence of a trace amount of hydrochloric acid (nos. 5 and 6, [HCl] = 0.015 M), a transparent solution was obtained in less than 20 min, and this time became shorter with increasing acid concentration (nos. 7−9). When [HCl] = 0.2 M, a completely transparent polymer solution could be obtained in 5 min (no. 9). One can also note from Table 3 that the change occurred easier in acetone than in THF, because the former is a

Table 4. Solubility before and after Hydrolysis[a]

	CH_3OH	acetone	THF	dioxane	DMF	$CHCl_3$	benzene
SSP-1	I	S	S	S	S	S	S
h-SSP-1	D	S	S	D	S	S	I
SSP-2	I	S	S	S	S	S	S
h-SSP-2	S	S	S	D	S	C	I
SSP-3	I	S	S	D	S	S	D
h-SSP-3	S	S	D	D	S	C	I
BP-1	I	S	S	D	S	S	S
h-BP-1	W	S	S	S	S	S	C
BP-2	I	S	D	D	D	S	D
h-BP-2	W	S	S	D	S	C	I
BP-3	I	S	S	D	S	S	D
h-BP-3	W	S	S	D	S	D	C
GP-1	I	I	I	I	I	I	I
h-GP-1	W	S	S	D	S	W	I
GP-2	I	I	I	I	I	I	I
h-GP-2	W	S	S	D	S	W	I

[a] The experiment was carried out at room temperature. The amounts of polymer (or polymer gel) and solvent were 0.03 g and 1.0 mL, respectively. S = soluble; D = dissolved slowly; W = wetting; C = cloudy; I = insoluble; h- = hydrolyzed product from the corresponding polymer or polymer gel.

better solvent for both poly(MMA) and poly(MAA) segments. As for the branched soluble poly(MMA), the hydrolyzed product of the poly(MMA) gel is also a linear random copolymer of MMA and MAA. Its GPC chromatogram exhibits a single peak (Figure 5B), and the presence of carboxyl groups in the MAA units was confirmed by FT-IR (2500−3800 cm^{-1}). In addition, the polymer gel prepared via the homopolymerization of **1** could also be hydrolyzed to a linear polymer [poly(MAA)] in methanol in the presence of HCl ([HCl] = 0.2 M) in 20 min.

The hydrolyzed products of star-shaped polymers, branched polymers, and polymer gels possess quite different solubilities compared to those of their precursors (Table 4). The hydrolyzed star-shaped polymers (h-SSP-1, h-SSP-2, and h-SSP-3) are soluble in methanol, but insoluble in benzene, due to the presence of the hydrophilic poly(MAA) block. On the other hand, the polymer gel is insoluble in all solvents before hydrolysis. However, its hydrolyzed product is soluble in acetone, THF, 1,4-dioxane, and *N*,*N*-dimethylformamide (DMF), but insoluble in benzene, and only wetted by methanol due to the presence of the random MAA units.

References and Notes

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(6) The cross-linker **1** added to the living poly(MMA) solution reacts with the living end (P*) of poly(MMA). Because one initiator (DPHL) generates one living poly(MMA) chain in the first step, the living anionic polymerization of MMA, $[1]_0/[P^*]_0$ is equal to $[1]_0/[DPHL]_0$.

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