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Living Anionic Polymerization of 1-(Alkoxy)ethyl Methacrylates and the Preparation of Well-Defined Poly(methacrylic acid)

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ABSTRACT: Three novel methacrylate monomers, 1-(ethoxy)ethyl methacrylate (EEMA), 1-(butoxy)-ethyl methacrylate (BEMA), and 1-(*tert*-butoxy)ethyl methacrylate (tBEMA), were prepared through the addition reaction of methacrylic acid (MAA) and ethyl, butyl, or *tert*-butyl vinyl ether, respectively. These monomers have been subjected to anionic polymerization in tetrahydrofuran (THF), using (1,1-diphenyl)-hexyllithium (DPHL) as initiator. In contrast to the common alkyl methacrylates, their anionic polymerizations were very sensitive to temperature and to the amount of LiCl added. A $[\mathrm{LiCl}]/[\mathrm{DPHL}]_0$ molar ratio of unity was most beneficial, but a high excess of LiCl had a negative effect. Suitable polymerization temperatures were found to be in the range −60 to −20 °C, with an optimum at about −40 °C, but even at +20 °C tBEMA could be polymerized quantitatively to a poly(tBEMA) with a relatively narrow molecular weight distribution ($M_w/M_n = 1.18$). However, the very low temperature of −80 °C, which is optimum for the common alkyl methacrylates, was not suitable for the new monomers. For $[\mathrm{LiCl}]/[\mathrm{DPHL}]_0 \approx 1$ and a temperature in the range −60 to −20 °C, the anionic polymerizations of EEMA, BEMA, and tBEMA could proceed in a living manner and generate polymers with controlled molecular weights and narrow molecular weight distributions ($M_w/M_n = 1.06-1.09$). Poly(EEMA), poly(BEMA), or poly(tBEMA) could be easily hydrolyzed, to generate well-defined poly(MAA).

Introduction

The living anionic polymerization is a most suitable method to synthesize well-defined polymers, since it allows the precise control of the molecular architecture and of the molecular weight.[1] However, the functional monomers containing an active proton and/or an electrophilic functional group, such as the aldehide group, cannot be subjected to anionic polymerization, because they cannot coexist with an anionic initiator. To overcome this difficulty, the following three-step method was developed:[2] (i) the active proton or the functional group was masked using an appropriate group; (ii) the anionic polymerization was carried out; (iii) the protecting group was eliminated. This procedure broadened the capabilities of the anionic polymerization, because it allowed one to synthesize well-defined functional polymers with controlled molecular weights, narrow molecular weight distributions, special properties, and useful performances.

Methacrylic acid (MAA) cannot undergo anionic polymerization, because of the presence of the active proton which deactivates instantaneously the carbanion of the initiator. To prepare well-defined poly(MAA), particularly its block copolymers with other hydrophobic polymers, the following anionically synthetic method was usually employed.[3] First, the anionic polymerization of *tert*-butyl methacrylate or its copolymerization with other monomers was carried out in tetrahydrofuran (THF) at −78 °C. This was followed by the elimination of the *tert*-butyl side chains of the obtained polymers. The latter step was usually accomplished by hydrolysis using either aqueous hydrochloric acid in 1,4-dioxane at 85 °C for about 5 h or *p*-toluenesulfonic acid in wet toluene at 80 °C for 4 h.

In the present paper, we report a more suitable protecting method for the anionic synthesis of a well-defined poly(MAA). This method has the following advantages: (1) The monomers can be easily prepared under temperate conditions. (2) The anionic polymerization of the monomer can proceed at higher temperatures. (3) The elimination of the protecting group is

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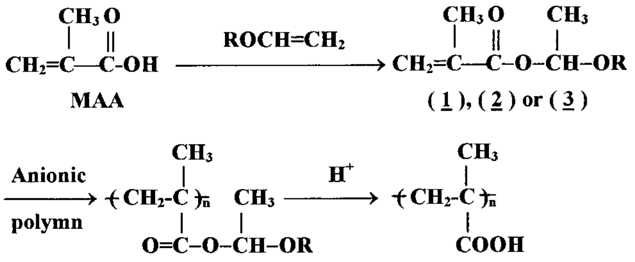
Scheme 1



(**1**) R = ethyl; 1-(ethoxy)ethyl methacrylate (EEMA)

(**2**) R = butyl; 1-(butoxy)ethyl methacrylate (BEMA)

(**3**) R = *tert*-butyl; 1-(tert-butoxy)ethyl methacrylate (tBEMA)

much easier than in the previous method.

Three novel monomers, 1-(ethoxy)ethyl methacrylate (EEMA), 1-(butoxy)ethyl methacrylate (BEMA), and 1-(*tert*-butoxy)ethyl methacrylate (tBEMA), were prepared through the addition reaction of MAA and the corresponding alkyl vinyl ether, namely, ethyl, butyl, or *tert*-butyl vinyl ether, respectively (Scheme 1). The anionic polymerization of these monomers under appropriate conditions generated polymers with controlled molecular weights and narrow molecular weight distributions. The protecting groups, 1-(ethoxy)ethyl, 1-(butoxy)ethyl, and 1-(*tert*-butoxy)ethyl, could be easily eliminated under mild acidic conditions to obtain a well-defined poly(MAA).

EEMA and BEMA possess protecting groups of different molecular weights. On the other hand, the protecting groups in BEMA and tBEMA have the same molecular weight, but the ester group of tBEMA is bulkier than that of BEMA. One can thus investigate the effect of the protecting group on the anionic polymerizations of the new monomers. To determine the optimum polymerization conditions, the effects of polymerization temperature, additives, and initiator concentration were investigated. The prepared polymers were characterized by GPC, ^{1}H NMR, and FT-IR. In addition, the differences between the polymerizabilities of these novel protected monomers and the common alkyl methacrylates are discussed.

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-diphenylhexyl)lithium (DPHL) just before use. Hexane was first dried and distilled over CaH_2 and then distilled from a solution of *n*-BuLi. 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.[4] *n*-BuLi (Aldrich, 1.6 M solution in hexane) was diluted with purified hexane.

Preparation and Purification of 1-(Ethoxy)ethyl Methacrylate (EEMA), 1-(Butoxy)ethyl Methacrylate (BEMA), and 1-(*tert*-Butoxy)ethyl Methacrylate (tBEMA). As shown in Scheme 1 and Table 1, EEMA, BEMA, and tBEMA were prepared through the reaction of methacrylic acid (MAA) and the corresponding alkyl vinyl ether, namely, ethyl, butyl, and *tert*-butyl vinyl ether, respectively. To avoid the polymerization of the monomer during this reaction, the reaction was carried out in the presence of a trace amount of the inhibitor 4-*tert*-butylcatechol, under the protection of nitrogen, with magnetic stirring. First, the inhibitor was added to the flask which contained the alkyl vinyl ether. Then, the temperature was raised to a value indicated in Table 1 and MAA was dropwise added. After the reaction was allowed to last a selected time, the crude product was distilled under reduced pressure. Prior to polymerization, it was further purified by distillation twice over CaH_2 under reduced pressure. The monomer thus obtained was identified by FT-IR and ^{1}H NMR spectroscopy. ^{1}H NMR ($CDCl_3$). EEMA: δ 6.15 and 5.58 (s, 2H, $\mathrm{CH_2}{=}$), 5.95 (m, 1H, $\mathrm{OC}H(\mathrm{CH_3})\mathrm{O}$), 3.70 and 3.55 (m, 2H, $\mathrm{C}H_2\mathrm{CH_3}$), 1.92 (s, 3H, α-$CH_3$), 1.41 (d, 3H, $\mathrm{OCH(C}H_3\mathrm{)O}$), 1.20 (t, 3H, $\mathrm{CH_2C}H_3$). BEMA: δ 6.15 and 5.58 (s, 2H, $\mathrm{CH_2}{=}$), 5.95 (m, 1H, $\mathrm{OC}H(\mathrm{CH_3})\mathrm{O}$), 3.65 and 3.45 (m, 2H, $\mathrm{C}H_2\mathrm{CH_2CH_2CH_3}$), 1.93 (s, 3H, α-$CH_3$), 1.55 (m, 2H, $\mathrm{CH_2C}H_2\mathrm{CH_2CH_3}$), 1.41 (d, 3H, $\mathrm{OCH(C}H_3\mathrm{)O}$), 1.33 (m, 2H, $\mathrm{CH_2CH_2C}H_2\mathrm{CH_3}$), 0.90 (t, 3H, $\mathrm{CH_2CH_2CH_2C}H_3$). tBEMA: δ 6.18 (m, 1H, $\mathrm{OC}H(\mathrm{CH_3})\mathrm{O}$), 6.10 and 5.52 (s, 2H, $\mathrm{CH_2}{=}$), 1.90 (s, 3H, α-CH_3), 1.39 (d, 3H, $\mathrm{OCH(C}H_3\mathrm{)O}$), 1.20 (s, 9H, $\mathrm{C(C}H_3)_3$).

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 or absence of LiCl. After THF, DPE, and a THF solution of LiCl were added with dry syringes, the flask was cooled to a selected temperature 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 EEMA, BEMA, or tBEMA to the above system. After a certain time, the system was quenched by adding a small amount of methanol, evaporated to dryness, and then vacuum-dried overnight to obtain the polymer.

Elimination of the Protecting Groups. The protecting groups, 1-(ethoxy)ethyl, 1-(butoxy)ethyl, and 1-(*tert*-butoxy)ethyl, were eliminated by hydrolysis in a mild acidic environment. For instance, 2.9 g of vacuum-dried poly(tBEMA) was redissolved in 30 mL of THF, to which 3.0 mL of aqueous HCl solution (5.0 M) was added with magnetic stirring at room temperature. After 2 min, this mixture, which was transparent, was poured into water to precipitate the polymer. The polymer thus obtained was washed with water and vacuum-dried at 40 °C for more than 24 h.

Measurements. ^{1}H NMR spectra were recorded in $CDCl_3$ or CD_3OD on a VXR-400 spectrometer. The M_n and M_w/M_n values 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 mm × 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. After polymerization, a trace of THF solution (ca. 0.1 mL) was taken out, diluted with THF, and injected immediately. The FT-IR spectra were recorded on a Perkin-Elmer 1760-X spectrometer.

Results and Discussion

Anionic Polymerization of EEMA. DPHL, a bulky initiator with a low nucleophilicity, was employed. It was prepared in situ before the monomer addition, via the reaction of *n*-BuLi with DPE ($[\mathrm{DPE}]/[n\text{-BuLi}]_0 = 1.2$), at the selected polymerization temperature, for about 15 min. The anionic polymerization was carried out in THF, in the presence or absence of LiCl. It was found that the polymerization temperature and the amount of added LiCl affected greatly the anionic polymerization of EEMA. LiCl has been reported to have remarkably positive effects on the living character of the anionic polymerization of either the common[4] or the functional[5] methacrylates. Keeping the polymerization temperature at −60 °C, the effect of the amount of added LiCl was first investigated (PEEMA-1 to PEEMA-4 in Table 2). Although EEMA can undergo

Table 1. Preparation of 1-(Ethoxy)ethyl, 1-(Butoxy)ethyl, and 1-(*tert*-Butoxy)ethyl Methacrylates[a]

		Alkyl vinyl ether						
monomer	moles of MAA	alkyl	moles of	temp (°C)	time (h)	yield[b] (%)	bp (°C/Torr)	d
EEMA	0.60	ethyl	1.00	reflux	8	92	60/16	0.95
BEMA	0.32	butyl	0.38	75	6	96	36/1	0.91
tBEMA	0.30	*t*-butyl	0.35	80	6	94	34/2	0.90

[a] The reaction was carried out in the presence of a small amount of 4-*tert*-butylcatechol, in an atmosphere of nitrogen, with magnetic stirring. [b] Calculated based on the amount of MAA employed.

Table 2. Anionic Polymerization of EEMA[a]

						10^{-3} M_n		
no.	[n-BuLi]$_0$ (mM)	[LiCl]/[n-BuLi]$_0$	temp (°C)	time (min)	conv %	calcd	obsd[b]	M_w/M_n[b]
PEEMA-1	16.2	0	−60	45	100	7.26	7.10	1.42
PEEMA-2	16.2	1	−60	45	100	7.26	6.98	1.09
PEEMA-3	16.2	2	−60	45	88	6.42	10.6	1.20
PEEMA-4	15.0	3	−60	60	95	7.44	8.99	1.15
PEEMA-5	16.2	1	−80	55	85	6.21	5.54	1.16
PEEMA-6	16.2	1	−40	45	100	7.26	6.90	1.06
PEEMA-7	16.2	1	−20	35	100	7.26	7.04	1.09
PEEMA-8	16.2	1	0	30	93	6.77	6.43	1.14
PEEMA-9	16.2	1	0	60	94	6.84	5.55	1.15
PEEMA-10	16.2	2	0	60	84	6.14	5.55	1.15
PEEMA-11	16.2	1	20	60	56	4.17	3.45	1.29
PEEMA-12	16.2	2	20	60	49	3.68	3.34	1.21
PEEMA-13	15.0	3	−40	45	65	5.17	5.06	1.18
PEEMA-14	5.5	1	−40	75	100	20.9	20.5	1.11
PEEMA-15	6.7	1	−50	60	100	17.2	18.6	1.12

[a] The initiator DPHL was first prepared by the reaction of n-BuLi with DPE ([DPE]/[n-BuLi]$_0$ = 1.2), at the corresponding polymerization temperature, for 15 min. The initial concentration of the monomer was fixed at [EEMA]$_0$ = 0.720 M. [b] Determined by GPC.

anionic polymerization in the absence of LiCl, the poly(EEMA) obtained has a broad molecular weight distribution (PEEMA-1, M_n = 7100, M_w/M_n = 1.42). For [LiCl]/[n-BuLi]$_0$ = 1, a poly(EEMA) with a controlled molecular weight and a narrow molecular weight distribution is obtained (PEEMA-2 in Table 2, M_n = 6980, M_w/M_n = 1.09). However, a too large amount of added LiCl caused a negative effect. Indeed, for PEEMA-3 ([LiCl]/[n-BuLi]$_0$ = 2) and PEEMA-4 ([LiCl]/[n-BuLi]$_0$ = 3), the monomer conversion does not reach 100%, the molecular weights are out of control, and the molecular weight distributions are broad. Therefore, the molar ratio [LiCl]/[n-BuLi]$_0$ ≈ 1 is most suitable for the anionic polymerization of EEMA.

To determine the suitable polymerization temperature range for EEMA, the [LiCl]/[n-BuLi]$_0$ molar ratio was fixed at 1 and the anionic polymerization was carried out at different temperatures. As shown in Table 2 for PEEMA-2 and for PEEMA-5 to PEEMA-12, the anionic polymerization of EEMA does not proceed smoothly at either a too high (>0 °C) or a too low temperature (−80 °C). When the temperature is kept at 0 °C, the polymer yield is 93% after 30 min (PEEMA-8), and the increase of the polymerization time from 30 to 60 min does not increase the polymer yield (94%, PEEMA-9). At the same temperature, the increase in the amount of LiCl ([LiCl]/[n-BuLi]$_0$ = 2, PEEMA-10) results in a decline of the monomer conversion (84%). For the temperature 20 °C (PEEMA-11 and -12), the monomer conversion is just about 50% and the molecular weight distribution is broad (M_w/M_n = 1.29 and 1.21). These results indicate that, at a higher temperature (>0 °C), the propagating site is not stable and cannot be maintained until the completion of the polymerization. When the temperature was lowered in the range −20 to −60 °C (PEEMA-2, -6, and -7), the determined M_n values were not too different from those calculated, and narrow molecular weight distributions were achieved (M_w/M_n = 1.06−1.09). The polymerization carried out at −40 °C (PEEMA-6) appears to provide the best results. As shown in Figure 1A, the GPC chromatogram of the obtained polymer exhibits a single and symmetrical peak, which can be compared with that of the polystyrene standard (Figure 1D). Therefore, the optimum polymerization temperature for EEMA is about −40 °C.

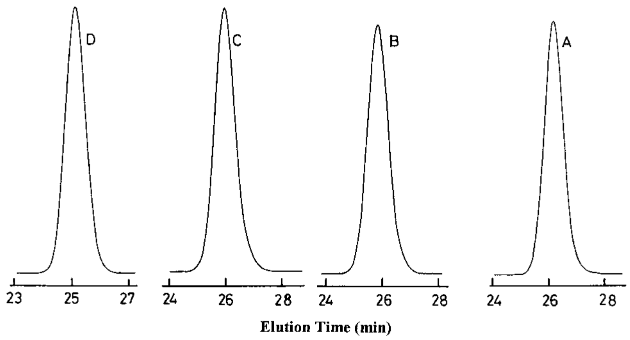


Figure 1. GPC traces of poly(EEMA) (A; PEEMA-6 in Table 2, M_n = 6900, M_w/M_n = 1.06), poly(BEMA) (B; PBEMA-5 in Table 3, M_n = 7980, M_w/M_n = 1.07), poly(tBEMA) (C; PtBEMA-8 in Table 4, M_n = 7440, M_w/M_n = 1.09), and polystyrene standard (D; from Pressure Chemical, Lot No. 41220; M_n = 17 500, M_w/M_n less than 1.06).

When the temperature was kept at −40 °C, the effects of the amount of LiCl and the initial concentration of n-BuLi on the anionic polymerization of EEMA were again investigated. For [LiCl]/[n-BuLi]$_0$ = 3 (PEEMA-13), the monomer conversion was still low (65%) and the molecular weight distribution of the obtained polymer (M_w/M_n = 1.18) was not as narrow as that obtained for [LiCl]/[n-BuLi]$_0$ = 1 (PEEMA-6). This means that [LiCl]/[n-BuLi]$_0$ ≈ 1 is a most suitable ratio even at the optimum temperature. As shown in Table 2 (PEEMA-14 and -15), when [LiCl]/[n-BuLi]$_0$ = 1 and the temperature is kept in a suitable range, a completely controllable anionic polymerization can be achieved even for a

Table 3. Anionic Polymerization of BEMA[a]

no.	$[n\text{-BuLi}]_0$ (mM)	$[\text{LiCl}]/[n\text{-BuLi}]_0$	temp (°C)	time (min)	conv %	$10^{-3}M_n$ calcd	$10^{-3}M_n$ obsd[b]	M_w/M_n[b]
PBEMA-1	20.0	3	−60	45	56	3.26	4.77	1.09
PBEMA-2	13.3	3	−60	60	63	5.35	8.48	1.12
PBEMA-3	13.6	1	−80	60	96	7.86	8.03	1.14
PBEMA-4	13.6	1	−60	60	100	8.17	8.10	1.10
PBEMA-5	13.6	1	−40	60	100	8.17	7.98	1.07
PBEMA-6	13.6	1	−20	60	100	8.17	7.70	1.07
PBEMA-7	13.6	1	0	60	94	7.70	7.10	1.12
PBEMA-8	13.6	1	20	60	86	7.06	5.14	1.19
PBEMA-9	5.3	1	−30	80	98	20.2	19.8	1.09

[a,b] As in Table 2 except $[\text{BEMA}]_0 = 0.580$ M.

Table 4. Anionic Polymerization of tBEMA [a]

no.	$[n\text{-BuLi}]_0$ (mM)	$[\text{LiCl}]/[n\text{-BuLi}]_0$	temp (°C)	time (min)	conv %	$10^{-3}M_n$ calcd	$10^{-3}M_n$ obsd[b]	M_w/M_n[b]
PtBEMA-1	21.3	0	−60	40	100	5.30	5.38	1.58
PtBEMA-2	21.3	3	−60	40	51	2.82	4.71	1.15
PtBEMA-3	14.1	3	−60	40	41	3.38	2.60	1.20
PtBEMA-4	14.1	3	−60	40	38	3.15	1.99	1.13
PtBEMA-5	6.7	3	−60	120	50	8.29	19.1	1.12
PtBEMA-6	14.8	1	−80	60	85	6.44	5.85	1.21
PtBEMA-7	14.8	1	−60	60	100	7.53	7.23	1.10
PtBEMA-8	14.8	1	−40	60	100	7.53	7.44	1.09
PtBEMA-9	14.8	1	−20	60	100	7.53	7.00	1.09
PtBEMA-10	14.8	1	0	60	100	7.53	6.81	1.11
PtBEMA-11	14.8	1	20	60	100	7.53	6.80	1.18
PtBEMA-12	5.6	1	−20	75	100	19.5	18.6	1.09

[a,b] As in Table 2 except $[\text{tBEMA}]_0 = 0.580$ M.

low initial concentration of initiator ($[n\text{-BuLi}]_0 = 5.5$ and 6.7 mM) and poly(EEMA)s with high molecular weights, and narrow molecular weight distributions can be obtained.

Anionic Polymerization of BEMA and tBEMA. The anionic polymerization of BEMA is summarized in Table 3. As for EEMA, the anionic polymerization is not well controlled for the high ratio $[\text{LiCl}]/[n\text{-BuLi}]_0 = 3$ at −60 °C (PBEMA-1 and -2). The monomer conversion hardly reaches 100%, and the determined M_n is not close to that calculated. For $[\text{LiCl}]/[n\text{-BuLi}]_0 = 1$ and for a polymerization temperature in the range −60 to −20 °C (PBEMA-4 to -6), the monomer is quantitatively polymerized and the molecular weight distribution of the obtained polymer is almost as narrow as that of poly(EEMA) ($M_w/M_n = 1.07-1.10$, Table 3 and Figure 1B). Even at a low initial concentration of initiator ($[n\text{-BuLi}]_0 = 5.3$ mM, PBEMA-9 in Table 3), a poly(BEMA) with a high molecular weight and a narrow molecular weight distribution (M_n = 19 800, $M_w/M_n = 1.09$) is obtained.

The anionic polymerization of tBEMA in the absence of LiCl generates a polymer with a broad molecular weight distribution ($M_w/M_n = 1.58$, PtBEMA-1 in Table 4). For the high molar ratio $[\text{LiCl}]/[n\text{-BuLi}]_0 = 3$, the polymerization cannot be controlled either (PtBEMA-2 to -5). The temperature range from −60 to −20 °C is also suitable for this monomer. As shown in Table 4 (PtBEMA-7 to -9) and Figure 1C, satisfactory polymerization results are obtained for $[\text{LiCl}]/[n\text{-BuLi}]_0 = 1$. The polymer yield is quantitative, the molecular weight is under control, and the molecular weight distribution is narrow ($M_w/M_n = 1.09-1.10$). At high temperatures (0 and 20 °C), the polymerization results for this monomer are different from those of EEMA and BEMA; the monomer conversion reaches 100%, and the polymers have relatively narrow molecular weight distributions ($M_w/M_n = 1.11$ and 1.18, PtBEMA-10 and -11). These results could be relevant from a practical point of view.

Comparison of the Polymerization Results. The anionic polymerization of (1-alkoxy)ethyl methacrylate is surprisingly different from those of the common alkyl methacrylates. (1) The latter can undergo anionic polymerization only at very low temperatures (−78 °C or lower), and the lower the temperature, the better the polymerization results.[3−5] In contrast, the suitable temperature for 1-(alkoxy)ethyl methacrylate is in the range −40 to −20 °C, and even at +20 °C, poly(tBEMA) with a controlled molecular weight and a narrow molecular weight distribution ($M_w/M_n = 1.18$) is obtained. (2) For both the common alkyl methacrylates and the novel monomers prepared in the present paper, the addition of LiCl is effective in controlling the molecular weight and the molecular weight distribution. However, the latter monomers are much more sensitive to the amount of added LiCl than the former. As noted above, the best results are obtained for a $[\text{LiCl}]/[n\text{-BuLi}]_0$ molar ratio of about unity; the further increase of the molar ratio makes the anionic polymerization uncontrollable. In contrast, the common alkyl methacrylates,[4] including some functional methacrylates,[5] can undergo living anionic polymerization smoothly even for a $[\text{LiCl}]/[\text{n-BuLi}]_0$ ratio of 5.

The anionic polymerizations of the common alkyl methacrylates are very fast and, for this reason, difficult to control. A low temperature and/or a large amount of LiCl make the polymerization proceed at an appropriate lower rate. EEMA, BEMA, and tBEMA can be considered as products in which the ethyl of ethyl methacrylate is substituted by the ethoxy, butoxy, or *tert*-butoxy group, respectively. The introduction of these strong electron-donor groups greatly reduces the reactivity of the methacrylate and thus reduces the polymerization rate compared to that of ethyl meth-

Table 5. Two Monomer Addition Experiments[a]

				first addition			second addition		
no.	$[n\text{-BuLi}]_0$ (mM)	$[M]_0$ (M)	temp (°C)	$10^{-3}M_k$[b]	$10^{-3}M_n$[c]	M_w/M_n[c]	$10^{-3}M_k$[b]	$10^{-3}M_n$[c]	M_w/M_n[c]
PEEMA-16	17.7	0.42 + 0.42	−60	3.99	4.00	1.10	7.75	7.69	1.10
PEEMA-17	18.5	0.42 + 0.42	−40	3.83	3.50	1.09	7.42	7.12	1.11
PBEMA-10	13.3	0.36 + 0.36	−30	5.27	5.13	1.06	10.3	9.70	1.13
PtBEMA-13	33.3	0.48 + 0.48	−60	2.92	2.91	1.17	5.60	5.61	1.09
PtBEMA-14	20.0	0.34 + 0.34	−30	3.16	3.08	1.15	6.56	6.41	1.12

[a] The initiator DPHL was first prepared by the reaction of *n*-BuLi with DPE ($[\text{DPE}]/[n\text{-BuLi}]_0 = 1.2$), at the corresponding polymerization temperature, for 15 min. The polymerization was carried out in THF, for $[\text{LiCl}]/[n\text{-BuLi}]_0 = 1$. The polymerization time was 45 min for every time monomer addition. The monomer conversion was 100% for every case. [b] Calculated average number molecular weight. [c] Determined by GPC.

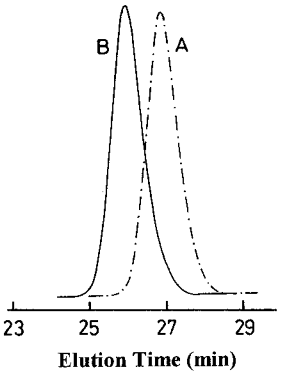


Figure 2. GPC traces of poly(EEMA)s obtained in the two monomer addition experiments (PEEMA-16 in Table 5): (A) first time monomer addition, $M_n = 4000$, $M_w/M_n = 1.10$; (B) second time monomer addition, $M_n = 7690$, $M_w/M_n = 1.10$.

acrylate. Therefore, the addition of a too large amount of LiCl and the use of a very low temperature may hinder the anionic polymerization to proceed at a suitable rate.

For the common methacrylates, the bulkier the ester group, the better the polymerization results; indeed, comparing the anionic polymerizations of methyl methacrylate, butyl methacrylate, and *tert*-butyl methacrylate, the last one provides the best molecular control and the narrowest molecular weight distribution under the same conditions.[3,6] Similarly, tBEMA possessing the bulkiest ester group undergoes anionic polymerization at high temperatures (0 and 20 °C) more smoothly than EEMA and BEMA. This likely occurs because the bulky *tert*-butyl is effective in stabilizing the propagating site for both the common alkyl methacrylates and the new monomers.

Two Monomer Addition Experiments. To verify the living characteristics of the anionic polymerization of EEMA, BEMA, and tBEMA, two successive monomer addition experiments were carried out for a $[\text{LiCl}]/[n\text{-BuLi}]_0$ ratio of unity. As summarized in Table 5, after the second monomer addition, the molecular weight of the polymer increases, remaining close to the calculated value, and the molecular weight distribution remains narrow. An example is presented in Figure 2 (PEEMA-16 in Table 5). In the first stage, poly(EEMA) with a narrow molecular weight distribution ($M_n = 4000$, $M_w/M_n = 1.10$) is obtained. After the same amount of EEMA is added to the system, the GPC peak shifts toward the higher molecular weight ($M_n = 7690$, $M_w/M_n = 1.10$), the molecular weight distribution does not change, and no precursor polymer is present. The above results clearly indicate that the anionic polymerization of 1-(alkoxy)ethyl methacrylate proceeds in a living manner.

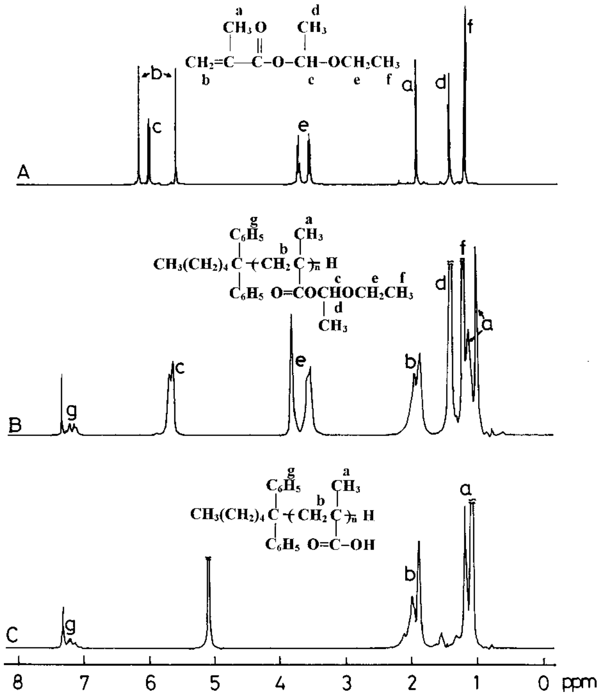


Figure 3. ^{1}H NMR spectra of EEMA (A; in $CDCl_3$), poly(EEMA) (B; in $CDCl_3$; PEEMA-7 in Table 2), and poly(MAA) (C; in CD_3OD) obtained by hydrolysis of PEEMA-7.

Elimination of the Protecting Groups. The 1-(alkoxy)ethyl groups of the three polymers were eliminated through mild hydrolysis reactions. As soon as a small amount of HCl aqueous solution was added to the THF solution of each polymer, the reaction became complete almost instantaneously to form a transparent solution. The polymer was precipitated by pouring this solution in water. The polymer obtained after hydrolysis had a quite different solubility than its precursor polymer. All poly(EEMA), poly(BEMA), and poly(tBEMA) possess excellent solubility. They are soluble in benzene, chloroform, *N*,*N*-dimethylformamide, 1,4-dioxane, THF, acetone, methanol, and ethanol but insoluble in hexane, water, and an aqueous solution of NaOH (5.0 M). In contrast, the polymer obtained after hydrolysis is soluble in methanol, ethanol, and an aqueous solution of NaOH (5.0 M) but insoluble in the other solvents mentioned above.

In the FT-IR spectrum of tBEMA, no broad absorption corresponding to the carboxyl group (2500−3800 cm^{-1}) could be detected. This means that the carboxyl group of MAA was completely masked by 1-(*tert*-butoxy)ethyl. However, after the hydrolysis of its polymer, the carboxyl groups were released.

Figure 3 depicts the ^{1}H NMR spectra of EEMA (A), poly(EEMA) (B), and its hydrolyzed product (C). After polymerization, peaks **a** and **b**, corresponding to the α-methyl and $H_2C=$ of the monomer, shifted to 1.0−1.3 and 1.8−2.2 ppm, respectively (see A and B). Furthermore, after the hydrolysis of poly(EEMA), peaks **c**−**f**, due to the protecting group 1-(ethoxy)ethyl, disappearedcompletely (C). The ^{1}H NMR (Figure 3C) and FT-IR spectra are consistent with the molecular structure of pure poly(MAA). The hydrolyzed polymers obtained from poly(EEMA), poly(BEMA), and poly(tBEMA) provided the same results. Therefore, the protecting groups 1-(ethoxy)ethyl, 1-(butoxy)ethyl, and 1-(*tert*-butoxy)ethyl are sufficiently stable in a basic environment to allow the corresponding monomers to proceed smoothly with anionic polymerization. In contrast, they are unstable even in a mild acidic environment, and this allows their easy elimination from the corresponding polymers.

References and Notes

(1) (a) Szwarc, M. *Adv. Polym. Sci.* **1983**, *49*, 1. (b) Van Beylen, M.; Bywater, S.; Smets, G.; Szwarc, M.; Worsfold, D. J. *Adv. Polym. Sci.* **1988**, *86*, 87. (c) Rempp, P.; Franta, E.; Herz, J. E. *Adv. Polym. Sci.* **1988,** *86*, 145. (d) Norton, M. *Anionic polymerization: Principles and Practice*; Academic Press: New York, 1983. (e) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization*; Marcel Dekker: New York, 1996.

(2) (a) Nakahama, S.; Hirao, A. *Prog. Polym. Sci.* **1990**, *15*, 299. (b) Hirao, A.; Ishino, Y.; Nakahama, S. *Macromolecules* **1988**, *21*, 261. (c) Mori, H.; Hirao, A.; Nakahama, S. *Macromolecules* **1994**, *27*, 35. (d) Ishizone, T.; Kurosawa, H.; Hirao, A.; Nakahama, S. *Macromol. Chem. Phys.* **1994**, *195*, 3173. (e) Kase, T.; Imahori, M.; Kazama, T.; Isono, Y.; Fujimoto, T. *Macromolecules* **1991**, *24*, 1714. (f) Ruckenstein, E.; Zhang, H. M. *J. Polym. Sci., Polym. Chem.* Ed. **1998**, *36*, 1865.

(3) (a) Ramireddy, C.; Tuzar, Z.; Prochazka, K.; Webber, S. E.; Munk, P. *Macromolecules* **1992**, *25*, 2541. (b) Desjardins, A.; Vandeven, T. G. M.; Eisenberg, A. *Macromolecules* **1992**, *25*, 2412. (c) Zhang, H. M.; Ishikawa, H.; Ohata, M.; Kazama, T.; Isono, Y.; Fujimoto, T. *Polymer* **1992**, *33*, 828. (d) Selb, J.; Gollot, Y. Y. In *Development in Block Copolymers*; Goodman, I., Ed.; Elsevier Publishers: London, 1988; Vol. 2. (e) Long, T. E.; Allen, R. D.; McGrath, J. E. In *ACS Symposium Series 364*; Benham, J. L., Kinstle, J. F., Eds.; American Chemical Society: Washington, DC, 1988; Chapter 19. (f) Rannard, S. P.; Billingham, N. C.; Armes, S. P.; Mykytiuk, J. *Eur. Polym. J.* **1993**, *29*, 407. (g) Pitsikalis, M.; Woodward, J.; Mays, J. W.; Hadjichristidis, N. *Macromolecules* **1997**, *30*, 5384.

(4) (a) Varshney, S. K.; Hautekeer, J. P.; Fayt, R.; Jerome, R.; Teyssie, Ph. *Macromolecules* **1990**, *23*, 2618. (b) Fayt, R.; Forte, R.; Jacobs, C.; Jerome, R.; Ouhadi, T.; Teyssie, Ph.; Varshney, S. K. *Macromolecules* **1987**, *20*, 1442. (c) Kunkel, D.; Muller, A. H. E.; Janata, M.; Lochman, L. *Makromol. Chem., Macromol. Symp.* **1992**, *60*, 315.

(5) (a) Mori, H.; Wakisawa, O.; Hirao, A.; Nakahama, S. *Macromol. Chem. Phys.* **1994**, *195*, 3213. (b) Zhang, H. M.; Ruckenstein, E. *J. Polym. Sci., Polym. Chem. Ed.* **1997**, *35*, 2901. (c) Zhang, H. M.; Ruckenstein, E. *Macromolecules* **1998**, *31*, 746. (d) Ruckenstein, E.; Zhang, H. M. *Macromolecules* **1998**, *31*, 2977. (e) Hild, G.; Lamps, J. P.; Rempp, P. *Polymer* **1993**, *34*, 2875. (f) Hild, G.; Lamps, J. P. *Polymer* **1995**, *36*, 4841.

(6) Hatada, K.; Kitayama, T.; Ute, K. *Prog. Polym. Sci.* **1988**, *10*, 189.

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