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Polymer 44 (2003) 4157–4164
polymer
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Anionic polymerization of 2-haloethyl methacrylates

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Received 2 December 2002; received in revised form 17 April 2003; accepted 24 April 2003

Abstract

The anionic polymerizations of 2-chloroethyl methacrylate (**1**), 2-bromoethyl methacrylate (**2**), and 2-iodoethyl methacrylate (**3**) were carried out in THF at −78 °C with 1,1-diphenyl-3-methylpentyllithium in the presence of LiCl. The polymerizations proceeded in a controlled manner to quantitatively afford polymers with predictable molecular weights and narrow molecular weight distributions. Under similar conditions, the anionic block copolymerizations by the sequential addition of methyl methacrylate (MMA) followed by **1**, **2**, and **3** generated the corresponding diblock copolymers with well-defined structures. On the other hand, in the block copolymerization by the reverse addition of monomer, a well-defined diblock copolymer, poly(**1**)-*block*-PMMA, could be synthesized only by the sequential addition of **1** followed by MMA, whereas the block copolymerizations using **2** and **3** were not successful because of instabilities of the propagating chain-end anions derived from **2** and **3**. The side reactions which occurred during the polymerization were discussed.

Keywords: 2-Haloethyl methacrylate; Anionic polymerization; Block copolymer

1. Introduction

It is known that the anionic polymerizations of methyl methacrylate (MMA) and its derivatives usually suffered from inherent undesired reactions of ester carbonyl groups with anionic initiators and/or growing chain-end anions. Considerable efforts have been expended in suppressing such reactions to achieve living anionic polymerization of methacrylate monomers. There have been so far reported several effective systems of the living anionic polymerization by carefully setting reaction conditions and designing appropriate initiators and additives, which can allow the precise synthesis of controlled homopolymers in chain length and well-defined block copolymers [1–18]. In practice, molecular weights can be controlled across a wide range of 10^2–10^5 simply by the stoichiometry of the polymerization. Molecular weight distribution can be narrowed, the M_w/M_n values usually being less than 1.2 and often reaching to 1.05.

Methacrylate monomers are also polymerized in a controlled fashion by the polymerizations using aluminum–porphyrin [19,20] and rare-earth metal complexes [21] as initiators as well as group transfer polymerization [22,23], whose mechanisms are similar to anionic systems. Furthermore, several living radical polymerizations of methacrylate monomers have successfully been achieved in recent years [24–27]. Among these controlled polymerization systems, the anionic polymerization has an advantage especially for the synthesis of well-defined block copolymers because a variety of vinyl and cyclic monomers are usable and therefore block copolymers with various structures can be synthesized in this system.

The propagating chain-end anions of living poly(alkyl methacrylate)s are enolate-type anions much lower in reactivity than the chain-end carbanions of living anionic polymers of styrene and 1,3-diene monomers. Accordingly, there must be present certain functional groups that react with the carbanions but are compatible with the enolate-type anions. Provided functional groups are appropriately chosen, the living anionic polymerization of alkyl methacrylates substituted with such functional groups can be achieved. Indeed, it has been reported that several alkyl methacrylates substituted with functional groups such as allyl [28], 2,4-hexadienyl [29], alkynyl [30], perfluoroalkyl [31], 2-(trimethylsilyloxy)ethyl [32], 2-(*tert*-butyldimethylsilyloxy)ethyl [33], glycidyl [34], 3-(trialkoxysilyl)propyl [35], cyanobiphenyl groups [36], and even a hindered

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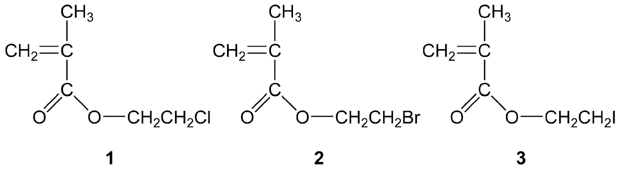
doi:10.1016/S0032-3861(03)00350-1

phenolic function [37] undergo living anionic polymerization.

It is known that enolate anions readily react with alkyl halides in a S_N2 fashion under normal conditions. However, we have recently found that the alkyl chlorides and bromides are sufficiently stable towards the living polymer anion of *tert*-butyl methacrylate initiated with 1,1-diphenylhexyllithium in the presence of LiCl in THF at −78 °C even for a longer reaction time of 24 h [38]. We therefore anticipated that methacrylate monomers substituted with chloroalkyl or bromoalkyl moieties could undergo living anionic polymerization. In this contribution, we report on the anionic polymerization of three 2-haloethyl methacrylates, 2-chloroethyl methacrylate (**1**), 2-bromoethyl methacrylate (**2**), and 2-iodoethyl methacrylate (**3**), shown below.



Monomers

The objective of this study is to extend the possibility of living anionic polymerization of functionalized methacrylate monomers and to understand the limitation of compatibility of enolate-type anion towards functional group.

2. Experimental

2.1. Materials

Reagents (reagent grade) are purchased from Aldrich, Japan, unless otherwise stated. THF was refluxed over sodium wire, distilled over $LiAlH_4$ under a nitrogen atmosphere, and then distilled from its sodium naphthalene solution on the vacuum line. *sec*-Butyllithium (*sec*-BuLi) was used as received. Diphenylmethylpotassium (Ph_2CHK) was prepared by the reaction of a 1.1-fold excess of diphenylmethane with potassium naphthalene in THF at 25 °C for 24 h by modifying the method previously reported [39]. Diethylzinc (Et_2Zn) (Tosoh Akuzo, 99.9%) was used as received. 1,1-Diphenyl-3-methylpentyllithium (DPMPLi) was prepared by the reaction of 1,1-diphenylethylene (DPE) with *sec*-BuLi at −78 °C for 5 min just before the polymerization. DPE was distilled over CaH_2 under a reduced pressure and finally distilled from its *sec*-BuLi solution on the vacuum line (10^{-6} Torr). 1,1-Bis(4-trimethylsilylphenyl)ethylene was synthesized by the method previously reported [40] and purified by the same procedures used in the case of DPE mentioned above. MMA was twice distilled over CaH_2 and finally purified by distillation from its 3 mol% trioctylaluminum solution on the vacuum line. Lithium chloride (LiCl) was dried at 110 °C under the high vacuum condition (10^{-6} Torr) for a few days and dissolved in THF (1 g/100 ml). Haloalkyl alcohols were distilled over CaH_2 under an atmosphere of nitrogen. 2-Iodoethanol was synthesized from the reaction of 2-chloroethanol with a 10-fold excess of sodium iodide in acetone at 60 °C for 24 h under an atmosphere of nitrogen.

2.2. Measurements

Both ^1H and ^{13}C NMR spectra were measured on a BRUCKER DPX300 in $CDCl_3$. Chemical shifts were recorded in ppm downfield relative to $(CH_3)_4Si$ (δ 0) for ^1H NMR and relative to $CDCl_3$ (δ 77.1) for ^{13}C NMR as standards. Size exclusion chromatography (SEC) was measured by Tosoh HLC-8020 at 40 °C with refractive index detection using THF as a carrier solvent at a flow rate of 1.0 ml/min. Infrared spectra were recorded on a JEOL JIR-AQS20M FT-IR spectrometer. Vapor pressure osmometry (VPO) measurement for absolute M_n determination was made with Corona 117 in benzene at 40 °C. The M_n values up to 10^5 were measured within ±5%.

2.2.1. Synthesis of 2-chloroethyl methacrylate (1)

The title methacrylate, **1**, was synthesized by the reaction of methacryloyl chloride with 2-chloroethanol. Under an atmosphere of nitrogen, in a 200 ml two-necked round-bottomed flask equipped with a mechanical stirrer and a dropping funnel were placed 6.35 g (78.9 mmol) of 2-chloroethanol, 12 ml of pyridine, and 30 ml of dry ether. The solution was cooled down in an ice bath and then 8.71 g (83.3 mmol) of methacryloyl chloride dissolved in 10 ml dry ether was slowly added over a period of 30 min under stirring. Then, the reaction mixture was stirred at room temperature overnight. After the precipitated pyridine hydrochloride salt was removed by filtration, the organic layer was washed with 2N hydrochloric acid, water, saturated $NaHCO_3$ solution, and dried over anhydrous $MgSO_4$. After filtration, the organic layer was concentrated under a reduced pressure. The residual oil was distilled under a reduced pressure (bp: 51.5–52.0 °C/4 Torr) to yield 9.83 g (66.2 mmol, 84%) of **1** as a colorless liquid: $C_6H_9O_2Cl$: calcd C 48.50, H 6.11; Found C 48.28, H 6.20. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.97 (s, 3H, CH_3), 3.73 (t, 2H, CH_2Cl, $J = 5.7$ Hz), 4.41 (t, 2H, OCH_2, $J = 5.8$ Hz), 5.62 and 6.18 (m, 2H, CH_2=); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.3 (CH_3), 41.7 (CH_2Cl), 64.3 (OCH_2), 126.4 (CH_2=), 135.9 (=CCH_3), 167.1 (C=O); IR (neat): 813 (C=C), 1159 (C–O), 1641 (C=C), 1721 cm^{-1} (C=O).

2.2.2. Synthesis of 2-bromoethyl methacrylate (2) and 2-iodoethyl methacrylate (3)

For the synthesis of **2** and **3**, the similar procedures described above were followed using the corresponding alcohols in place of 2-chloroethanol. Yields and characterizations of **2** and **3** are summarized below. They were purified by column chromatography (hexane/ethyl acetate = 10/1) and distilled over CaH_2 twice or more

Table 1
Anionic polymerizations of **1**, **2**, and **3** in THF at − 78 °C for 1 h

Run	Monomer (mmol)	Initiator (mmol)	LiCl (mmol)	$M_n/10^3$			M_w/M_n[a]
				Calcd	SEC[a]	Obsd[b]	
1[c]	**1**, 4.51	DPMPLi[d], 0.0994	0.316	7.0	6.4	7.1	1.06
2	**1**, 6.30	DPMPLi, 0.0950	0.443	10	9.5	10	1.04
3	**1**, 5.60	DPMPLi, 0.0410	0.313	21	21	23	1.11
4	**1**, 7.40	DPMPLi, 0.0391	0.234	28	29	32	1.04
5	**2**, 1.83	TMSMPLi[e], 0.0712	0.297	5.3	4.3	5.8	1.02
6[c]	**2**, 2.99	TMSMPLi, 0.0811	0.392	7.4	5.8	8.3	1.04
7	**2**, 4.86	TMSMPLi, 0.0663	0.429	14	14	18	1.12
8	**3**, 3.23	DPMPLi, 0.111	0.368	7.2	3.7	6.7	1.06
9[c]	**3**, 4.47	TMSMPLi, 0.0895	0.526	12	6.9	11	1.05
10	**3**, 4.39	DPMPLi, 0.0522	0.667	20	11	18	1.12

Yields of polymers were quantitative in all cases.

[a] Estimated by SEC using standard PMMA calibration curve.

[b] Determined by ^{1}H NMR and VPO, respectively.

[c] For 10 min.

[d] 1,1-Diphenyl-3-methylpentyllithium.

[e] 1,1-Bis(4-trimethylsilylphenyl)-3-methylpentyllithium.

under reduced pressures. Finally, they were distilled over CaH_2 on the high vacuum line.

2-Bromoethyl methacrylate (**2**). Yield: 94% (bp: 57.5–58.0 °C/5 Torr): $C_6H_9O_2Br$: calcd C 37.34, H 4.70; Found C 37.81, H 4.79. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.96 (s, 3H, CH_3), 3.56 (t, 2H, CH_2Br, $J = 6.1$ Hz), 4.46 (t, 2H, OCH_2), 5.62 and 6.17 (m, 2H, CH_2=); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.3 (CH_3), 28.8 (CH_2Br), 64.0 (OCH_2), 126.4 (CH_2=), 135.8 (=CCH_3), 166.9 (C=O); IR (neat): 813 (C=C), 1157 (C–O), 1637 (C=C), 1721 cm^{-1} (C=O).

2-Iodoethyl methacrylate (**3**). Yield: 84% (bp: 53.5–54.0 °C/2 mm Hg): $C_6H_9O_2I$: calcd C 30.03, H 3.78; Found C 29.95, H 3.63. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.97 (s, 3H, CH_3), 3.35 (t, 2H, CH_2I, $J = 6.7$ Hz), 4.40 (t, 2H, OCH_2), 5.62 and 6.18 (m, 2H, CH_2=); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 0.60 (CH_2I), 18.3 (CH_3), 64.7 (OCH_2), 126.4 (CH_2=), 135.9 (=CCH_3), 166.7 (C=O); IR (neat): 813 (C=C), 1155 (C–O), 1637 (C=C), 1721 cm^{-1} (C=O).

2.3. Anionic polymerization

All operations were carried out under the high vacuum condition (10^{-6} Torr) in the all glass apparatus equipped with break-seals. The polymerization was usually carried out in THF at − 78 °C with vigorous shaking. The polymerization reaction was terminated by the addition of a small amount of degassed methan{ol. The polymer was precipitated by pouring the polymerization mixture into a large amount of methanol. The precipitated polymer was collected by filtration, purified by reprecipitation from THF solution to methanol two times, and freeze-dried from its benzene solution. The initiators used were 1,1-diphenyl-3-methylpentyllithium and diphenylmethylpotassium. In some cases, 1,1-bis(4-trimethylsilylphenyl)-3-methylpentyllithium prepared from 1,1-bis(4-trimethylsilylphenyl)-ethylene and *sec*-BuLi was used as an initiator. This initiator is suitable to accurately determine the molecular weight of the polymer by end-group analysis, since it possesses eighteen silyl methyl protons (1.96 ppm).

The block copolymerizations of MMA with 2-haloalkyl methacrylates were performed as follows. After the polymerization of each of 2-haloalkyl methacrylates in THF at − 78 °C for 10 min, a small amount of the polymer was taken to determine the molecular weight and molecular weight distribution. Then, MMA was added to the mixture to polymerize at − 78 °C for 1 h. The polymerization was quenched with a small amount of degassed methanol. The polymers were precipitated by pouring the reaction mixture into a large amount of methanol. The collected polymers were purified by reprecipitation two times from THF solution to methanol and finally freeze-dried from their benzene solutions.

The block copolymerizations by the reverse addition of two monomers, namely, 2-haloethyl methacrylates followed by MMA, were similarly carried out.

3. Results and discussion

Previously, two research groups reported the anionic polymerization of **1** and **2** with *n*-BuLi, PhMgBr, and $LiAlH_4$ [41,42]. In these literatures, however, molecular weights and molecular weight distributions of the resulting polymers were not characterized. Therefore, reliable information was not available on the behaviors and influences of their haloethyl functions of **1** and **2** on the anionic polymerization.

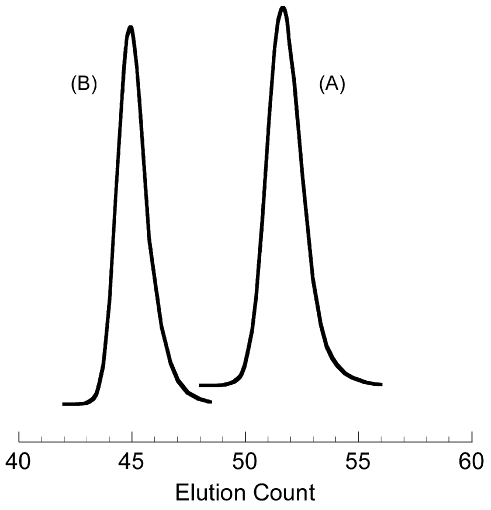


Fig. 1. SEC profiles of poly(1): (A) Run 1 and (B) Run 4 in Table 1.

3.1. Anionic polymerizations of **1**, **2**, and **3**

Alkyl methacrylate monomers were generally purified by distillation over CaH_2 and further purified by distillation after addition of trialkylaluminum to completely remove impurities such as unreacted alcohols [43]. However, this purification method could not be applied to 2-haloethyl methacrylate monomers, **1**, **2**, and **3**, since undesirable polymerization presumably via radical-induced mechanism always occurred significantly on mixing each of **1**–**3** with trioctylaluminum. Therefore, they were carefully purified up to the purities of more than 99.9% by column chromatography several times, followed by fractional distillation over CaH_2 twice under reduced pressures. Finally, they were again distilled over CaH_2 using the system of high vacuum line and used in the polymerization.

With use of the monomer, **1**, thus purified, the anionic polymerization was first carried out in THF at −78 °C with the initiator system including 1,1-diphenyl-3-methylpentyllithium (DPMPLi) prepared from *sec*-BuLi and DPE in the presence of ca. a 5-fold excess of LiCl as an additive. This is a well-established system very effective for the living anionic polymerization of methyl and other alkyl methacrylates. Upon addition of **1** to DPMPLi solution, an intense red color characteristic of DPMPLi immediately disappeared. The anionic polymerization was usually completed within 10 min, but continued for an additional 1 h at −78 °C by way of precaution. The polymerization was then quenched with degassed methanol. A yield of polymer was quantitative in every case. The results are summarized in Table 1.

The relative signal intensity of the methylene protons of main chain with the chloromethylene protons of side chain in ^{1}H NMR spectrum of the resulting polymer proved that the vinyl polymerization proceeded exclusively and the chloroethyl moiety remained intact. All polymers showed sharp monomodal SEC distributions without any shoulders and tailings, the M_w/M_n values being in the range of 1.04–1.11. Fig. 1 shows representative SEC profiles.

The observed M_n values by SEC relative to poly(methyl methacrylate) (PMMA) were in good agreement with those calculated on the basis of the polymerization stoichiometry. The absolute molecular weights were also determined by ^{1}H NMR (end-group analysis) and VPO measurements. Agreement between M_n values observed and calculated is quite satisfactory. Thus, the molecular weight could be precisely controlled in the range of 7.1–32 kg/mol with narrow molecular weight distribution maintained.

Similarly, the anionic polymerizations of **2** and **3** were carried out in THF at −78 °C. It was observed that both **2** and **3** were quantitatively polymerized within 10 min to afford near-monodisperse polymers with M_w/M_n values of 1.02–1.12 (Table 1). Since the estimated M_n values by SEC relative to PMMA were somewhat smaller than those calculated, their M_n values were determined by ^{1}H NMR and VPO measurements, respectively. To accurately determine the molecular weight of the resulting polymer by end-group analysis with ^{1}H NMR, 1,1-diphenylalkyllithium having eighteen silylmethyl protons prepared from 1,1-bis(4-trimethylsilylphenyl)ethylene [40] and *sec*-BuLi, TMSMPLi, was used instead of DPMPLi in some cases. The M_n values thus determined were in good agreement with those calculated for both poly(**2**) and poly(**3**) samples. Accordingly, the anionic polymerizations

Table 2
Anionic polymerizations of **1**, **2**, and **3** with diphenylmethylpotassium in THF at −78 °C for 1 h

Run	Monomer (mmol)	Ph_2CHK (mmol)	Et_2Zn (mmol)	Yield (%)	$M_n/10^3$			M_w/M_n [a]
					Calcd	SEC [a]	Obsd [b]	
11	**1**, 5.90	0.108	–	46	3.9	5.8	6.4	1.92
12	**1**, 4.21	0.0655	0.878	94	9.8	9.1	10	1.12
13	**1**, 8.34	0.0679	1.09	98	18	20	22	1.35
14	**2**, 5.09	0.0811	–	0	–	–	–	–
15	**2**, 5.69	0.0812	0.768	63	8.7	6.2	8.7	1.57
16	**3**, 4.17	0.0723	–	0	–	–	–	–
17	**3**, 3.42	0.0655	1.20	41	5.3	3.6	5.8	1.45

[a] Estimated by SEC using standard PMMA calibration curve.
[b] Determined by VPO and ^{1}H NMR, respectively.

Table 3
Block copolymerizations of **1**, **2**, and **3** with MMA in THF at −78 °C with DPMPLi in the presence of LiCl

Run	DPMPLi (mmol)	1^{st} Stage		2^{nd} Stage		$M_n/10^3$		M_w/M_n[a]
		Time (min)	Monomer (mmol)	Time (min)	Monomer (mmol)	Calcd	Obsd[b]	
18	0.0973	60	MMA, 9.32	10	**1**, 2.09	13	13	1.04
19	0.124	60	MMA, 8.40	10	**2**, 5.14	15	15	1.04
20	0.111	60	MMA, 8.45	10	**3**, 3.63	15	15	1.02
21	0.0596	10	**1**, 3.97	60	MMA, 10.1	27	29	1.04
22	0.107	10	**2**, 4.86	60	MMA, 8.63	17	20, 7.1	[c]
23	0.106	120	**2**, 3.28	60	MMA, 9.92	16	18, 6.2	[c]
24	0.106	10	**3**, 3.54	60	MMA, 9.60	17	68, 31, 6.8	[d]

Yields of polymers were quantitative in all cases.

[a] Estimated by SEC using standard PMMA calibration curve.

[b] Determined by both VPO and ^{1}H NMR, respectively.

[c] Bimodal distribution.

[d] Trimodal distribution.

of **2** and **3** also proceeded in a controlled manner under the conditions employed here.

On the other hand, the anionic polymerizations of **1**, **2**, and **3** in THF at −78 °C with diphenylmethylpotassium (Ph_2CHK) as an initiator were problematic. The results are summarized in Table 2.

In the anionic polymerization of **1**, a polymer with a broad molecular weight distribution ($M_w/M_n = 1.92$) was obtained only in 46% yield. An improvement has been made by the addition of diethylzinc (Et_2Zn) to the polymerization system. The polymerization with $Ph_2CHK-Et_2Zn$ proceeded efficiently to quantitatively afford polymers possessing M_n values close to the predicted ones and relatively narrow molecular weight distributions ($M_w/M_n = 1.12-1.35$). This result is consistent with our recent results that demonstrate the effectiveness of Et_2Zn in controlling the anionic polymerizations of *tert*-butyl acrylate [44], alkyl methacrylates [45], and *N*,*N*-dialkyl acrylamides [46,47]. In these cases, a possible side reaction of carbonyl attack by chain-end anion may be suppressed by stabilizing the growing chain-end anions by coordination of Et_2Zn having a weak Lewis acidic character.

Difficulties also arose in the anionic polymerizations of **2** and **3** with use of either Ph_2CHK or $PhCH_2K-Et_2Zn$ system. No polymerizations of both monomers occurred at all with Ph_2CHK alone in THF at −78 °C for 1 h. To elucidate the reaction mechanism, the oligomerization of **3** was carried out in THF at −78 °C for 1 h with low monomer to initiator ratio ($[M]/[I] = 5$) and the product was characterized by NMR, SEC, and gas chromatography. The SEC curve of the product showed mutimodal peaks in the range from monomer to 20mer. From the number average molecular weight of the product, the initiation efficiency can be estimated ca. 50%, suggesting that the initiator is deactivated. Tentatively, halogen attacks by the initiator or propagating chain-end may occur during the initiation and propagation steps. Unfortunately, the evidence of a cyclization of chain-end has not been clearly observed by NMR study, although the content of the iodoethyl moiety is relatively lower than that calculated. By adding Et_2Zn to the systems, the polymers of **2** and **3** with broad molecular weight distributions could be obtained in 63 and 41% yields, respectively. Yields did not increase even for a longer reaction time of 24 h. Thus, the polymerizations of **2** and **3** were improved to some extents by the addition of Et_2Zn, but not far from quantitative and control manners.

In our previous paper [38], we observed that living poly(*tert*-butyl methacrylate)s bearing K^+ as a countercation readily and quantitatively reacted with alkyl bromides and iodides in THF at −78 °C, while these halides remained intact toward the corresponding living polymers bearing Li^+ as a countercation under the identical conditions. It is therefore highly probable that, in the polymerizations of 2-haloethyl methacrylates with Ph_2CHK, the reaction of their 2-haloethyl moieties with Ph_2CHK and/or the growing chain-end anions if produced will terminate the polymerizations. The higher reactivity of the enolate anion bearing K^+ over that bearing Li^+ may possibly be explained by higher degree of dissociation of the ion-pair, since the radius of K^+ is bigger than that of Li^+, thereby promoting the dissociation of ion-pair.

3.2. Block copolymerizations of 1, 2, and 3 with MMA

One of the main advantages of living polymerization is capable of synthesizing block copolymers with well-defined structures. The synthesis of novel block copolymers containing polymer segments of **1**, **2**, and **3** is especially of interest, since these polymer segments have alkyl halide moieties in each monomer unit that can undergo a wide variety of reactions and quaternarization with amines or phosphines. Furthermore, it is possible to estimate stabilities and reactivities of the living chain-end anions from the results of block copolymerization.

At first, the block copolymerization was carried out with DPMPLi in the presence of LiCl in THF at −78 °C by the sequential addition of MMA followed by **1**. The first and

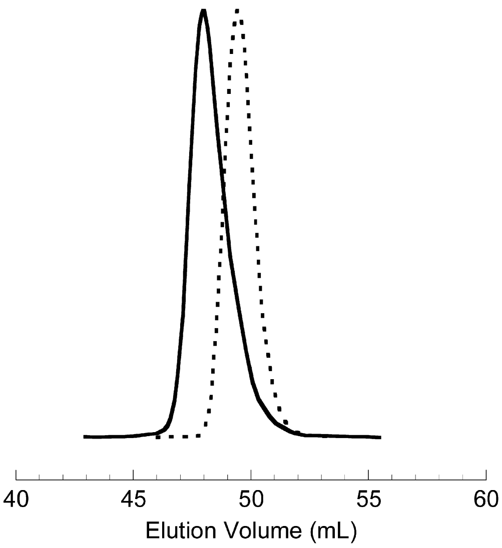


Fig. 2. SEC profiles of PMMA-*block*-poly(**1**) (solid line) and PMMA obtained at the 1st stage of polymerization (dashed line).

second stages of polymerization were carried out for 1 h and 10 min, respectively. Yields of polymers were quantitative in both cases. The results are summarized in Table 3.

Fig. 2 shows SEC profiles of the polymers obtained by the first and second stages of the polymerization.

PMMA with a narrow molecular weight distribution was obtained at the first stage. On addition of **1** at the second stage, the SEC peak completely moved toward the higher molecular weight side, while the molecular weight distribution remained narrow. The SEC peak corresponding to the PMMA produced at the first stage was not observed in this chromatogram. The molecular weight could be controlled at each stage as desired (Table 3). The composition determined by ^{1}H NMR was in good agreement with that designed. A well-defined diblock copolymer, PMMA-*block*-poly(**1**), could thus be successfully synthesized.

The block copolymerization of MMA with either **2** or **3** in this addition order was conducted under the identical conditions. Polymers were quantitatively obtained in both cases. The resulting two block copolymers, PMMA-*block*-poly(**2**) and PMMA-*block*-poly(**3**), showed sharp monomodal SEC distributions and possessed the M_n values and compositions very close to the predicted values determined by SEC and ^{1}H NMR analyses. Thus, novel well-defined diblock copolymers consisting of polymer segments having reactive haloalkyl functions could be synthesized by means of anionic polymerization.

Next, the block copolymerization was carried out under the similar conditions by the reverse addition of two monomers, namely, **1** followed by MMA. The polymerization times for **1** and MMA were 10 min and 1 h, respectively. Yields of polymers were quantitative under the conditions. The SEC profile of the resulting polymer showed a sharp monomodal distribution very similar to Fig. 2 and no peak corresponding to the poly(**1**) obtained at the first stage was observed. The M_n value and composition determined by VPO and ^{1}H NMR agreed quite well with those calculated. A well-defined diblock copolymer, poly(**1**)-*block*-PMMA was thus successfully synthesized. The success of this block copolymerization also confirms the living character of the anionic polymerization of **1** under the conditions employed.

In contrast, the block copolymerizations by the addition of **2** and **3** followed by MMA were problematic. Fig. 3 shows the SEC profile of the polymerization mixture obtained by the block copolymerization of **2** and MMA.

There were two distinct sharp SEC peaks presumably for the block copolymer, poly(**2**)-*block*-PMMA, and the homopolymer of **2**, indicating that the propagating chain-end anion derived from **2** was partly deactivated prior to the addition of MMA. Estimating from the peak area and the M_n values of both polymers, ca. 9% of the original chain-end anion was deactivated after 10 min. We also observed by the post-polymerization of **2** that ca. 10% of the chain-end anion was deactivated after 10 min under the conditions similar to that of the block copolymerization. The deactivation of the growing chain-end anion derived from **3** was more serious as evidenced from the result of the block copolymerization of **3** and MMA. In this case, ca. 45% of the growing chain-end anion was already deactivated even after 10 min. The influence of both 2-bromoethyl and 2-iodoethyl functions on stability of growing chain-end anion is thus crucial.

Since the growing chain-end anion of poly(**1**) is stable under the same conditions, the deactivation observed in the polymerizations of **2** and **3** is undoubtedly attributed to the 2-bromoethyl and 2-iodoethyl moieties. Furthermore, the growing chain-end anion of PMMA is also stable under the same conditions, indicating that the deactivation is not due to the intramolecular carbonyl attack by growing chain-anion well-known in the polymerization of MMA.

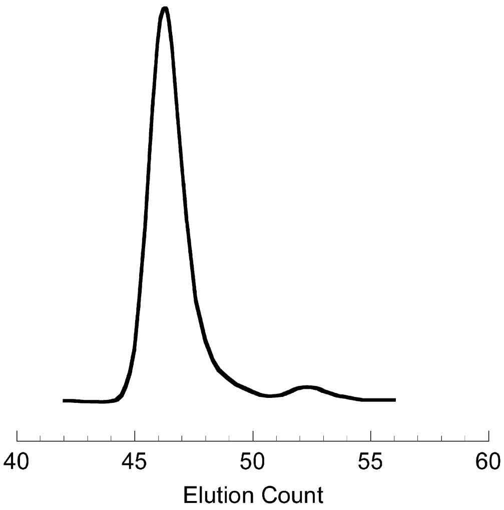
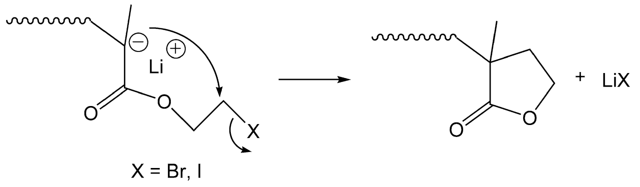


Fig. 3. SEC profile of the resulting polymer obtained by the block copolymerization of **2** with MMA.



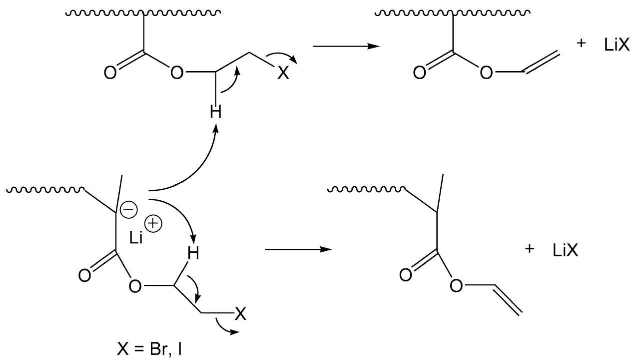
Scheme 1.

Sharp monomodal SEC distributions were realized by the polymerizations of **2** and **3** within 10 min and remained unchanged even after allowing the reaction mixtures for 1 h. It is therefore considered that the polymerizations of **2** and **3** proceed in a living manner during the polymerizations and the deactivation of growing chain-end anions starts after depletion of monomers. Any intermolecular coupling reactions may be ruled out from the fact that the SEC peak shapes remain unchanged after 1 h. Accordingly, a most likely side reaction responsible for the deactivation is an intramolecular nucleophilic substitution reaction between the growing chain-end anion and 2-bromoethyl or 2-iodoethyl moieties via five-membered ring formation at the chain-end as illustrated in Scheme 1.

A β-elimination reaction of the hydrogen adjacent to ester moieties is also considered as a possible side reaction candidate to deactivate the chain-end anion [48] (Scheme 2). These reactions may occur both intra- and intermolecularly.

Similar side reactions may take place in the block copolymerizations. However, three SEC peaks eluted at M_n values corresponding to 68, 31, and 6.8 kg/mol were observed in the block copolymer synthesized by the sequential monomer addition, **3** followed by MMA, as shown in Fig. 4.

The two peaks (M_n's = 31 and 6.8 kg/mol) are readily estimated to the block copolymer of poly(**3**)-*block*-PMMA and poly(**3**) at the first stage of the polymerization, respectively, based on their molecular weight values. Obviously, the poly(**3**) was partly deactivated prior to the addition of MMA as mentioned above. Since the peak showing M_n of 68×10^3 was almost doubly increased for the block copolymer ($M_n = 31 \times 10^3$), it might be the coupling product. In this case, the growing chain-end anion derived from MMA is likely to attack the 2-iodoethyl moieties of another polymer chain, resulting in the formation of the product coupled between two polymer chains as shown in Scheme 3. However, the peak eluted at higher molecular weight than 68×10^3 was not present, indicating that a few part of the propagating chain-end anion derived from MMA might participate in the reaction shown in Scheme 3. The occurring of the reaction was indeed supported by the fact that the coupling product ($M_n = 15 \times 10^3$) was produced in ca. 10% yield by the reaction of poly(**3**) ($M_n = 5 \times 10^3$) with living polymer of MMA ($M_n = 10 \times 10^3$) in THF at −78 °C for 1 h. In this case, no formation of the coupling products with higher molecular weight than 15×10^3 was also observed.



Scheme 2.

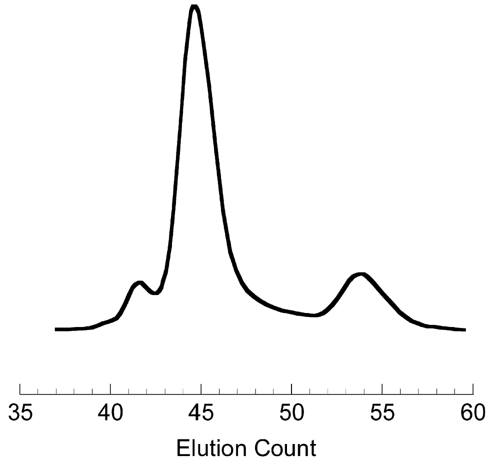
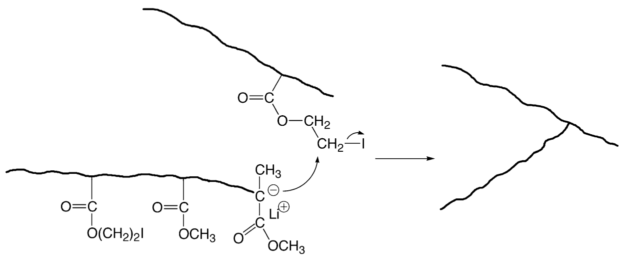


Fig. 4. SEC profile of the resulting polymer obtained by the block copolymerization of **3** with MMA.

In conclusion, **1**, **2**, and **3** undergo living anionic polymerization with DPMPLi in THF at −78 °C. It has been found that the growing chain-end anion derived from **1** is stable, while those derived from both **2** and **3** may become unstable to deactivate after depletion of monomers as shown in Scheme 1. For this reason, the addition order is very important to synthesize well-defined block copolymers. In practice, well-defined block copolymers can be synthesized without problem by the sequence of monomer addition, MMA followed by **1**, **2**, or **3**. Whereas it is feasible to synthesize only a well-defined block copolymer of poly(**1**)-*block*-PMMA by reversing the sequence of monomer addition



Scheme 3.

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