Stereospecific Anionic Polymerization of α-(Hydroxymethyl)acrylate with Protective Group

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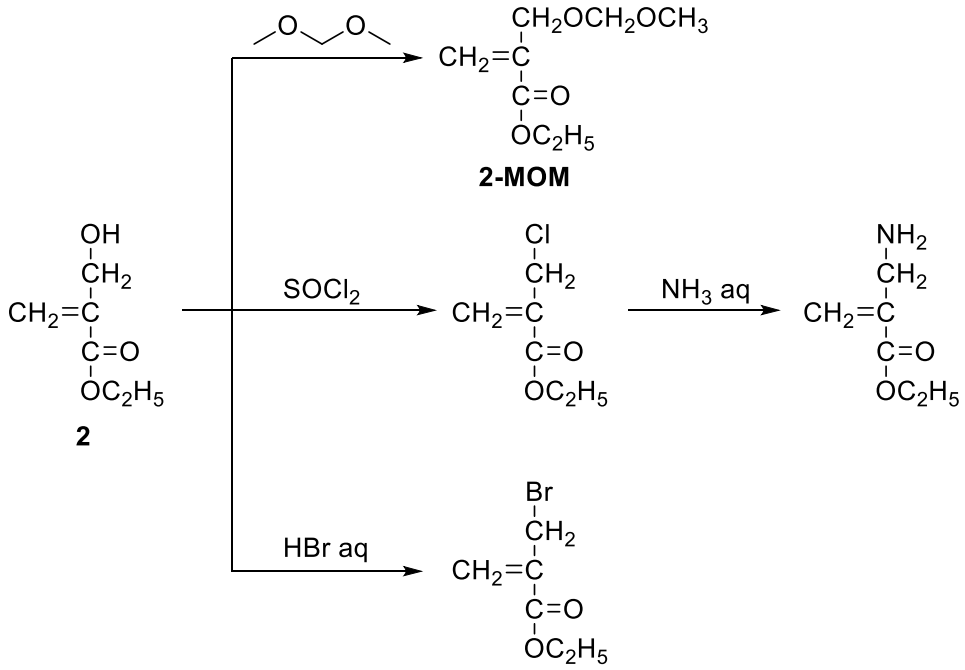
Summary: Anionic polymerizations of hydroxyl-protected α-(hydroxymethyl) acrylates were investigated. The methyl ester with methoxymethyl (**1-MOM**) and allyl (**1-allyl**) protecting groups were polymerized by isopropyl α-lithioisobutyrate (Li-*i*PrIB) in toluene at −78 °C, affording highly isotactic polymers. Similarly, the polymerization of ethyl ester (**2-MOM**) gave an isotactic polymer, while those of *t*-butyl (**3-MOM**) and isobutyl (**4-MOM**) ester did not form any polymeric products. The hydrolysis of **poly(2-MOM)** in acidic conditions resulted in the deprotection of MOM group, although the acid also catalyzed the ester exchange between the neighboring units to form lactone units, as observed by ^{1}H NMR analysis, IR spectroscopy and thermogravimetric analysis. A film of **poly(2-MOM)** exposed to HCl vapor for 2 h became insoluble in any organic solvents due to the lactonization in solid state.

Keywords: stereoregular polymer; end-functionalization; functional monomer; α-substituted acrylates, protective group

Introduction

Ethyl α-(hydroxymethyl)acrylate (**2**), an isomer of 2-hydroxyethyl methacrylate (HEMA), is a functional monomer possessing hydroxyl and ester groups [1]. The polymer [**poly(2)**] has hydrophilicity, biocompatibility, and hydroxyl functionality, so that its applications to composites with wood [2], adhesives [3], coatings [4], curing agents [5] , and photoresists [6] have been investigated. Recently, reversible addition-fragmentation chain transfer (RAFT) polymerization of **2** has been reported, which achieved the control of molecular weight with high conversion [7,8].

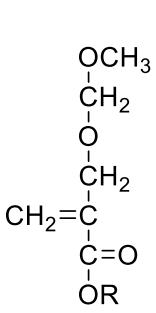
We have been utilizing α-(hydroxymethyl)acrylates as sources of a series of acrylic monomers (**Scheme 1**). Chlorination or bromination of α-(hydroxymethyl)acrylate gives α-(halomethyl)acrylate, which has been found as an efficient terminating reagent for stereospecific living polymerization of methyl methacrylate (MMA) through addition-elimination (S_N2') reaction [9]. The S_N2' reaction of α-(halomethyl)acrylate with amines, including ammonia, primary and secondary amines, gives α-(aminomethyl)acrylate, which are also interesting functional monomers.



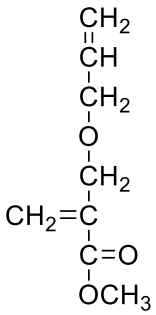
Scheme 1. Utilization of α-(hydroxymethyl)acrylates.

As well-known, the anionic polymerization of α-alkylacrylate in tetrahydrofuran (THF) affords syndiotactic-rich polymer [10]. In contrast, Okamoto *et al*. have reported remarkable stereospecificity in anionic polymerization of α-(alkoxymethyl)acrylate [11-13]; the polymerization affords highly isotactic polymers not only in non-polar solvents such as toluene but also in THF. They postulated that the counter cation is chelated at propagating chain-end by the ether oxygen of the α-alkoxy groups so as to control the stereochemistry of propagation process.

In this report, we have examined the anionic polymerization of hydroxyl-protected monomers, **1-4,** whose ether or acetal group at α-position of the propagating terminal may facilitate stereospecific propagation as in the case of the above-mentioned anionic polymerization of α-(alkoxymethyl)acrylate to form highly isotactic polymers. The subsequent deprotection reaction was also investigated to obtain **poly(1)**-**poly(4)** with high isotacticity.



1-MOM (R =Me)
2-MOM (R = Et)
3-MOM (R = *t*-Bu)
4-MOM (R = *i*-Bu)



1-allyl

Experimental

Materials α-(Hydroxymethyl)acrylates, **1** and **2**, were kind gifts from Nipppon Shokubai Co. Ltd. Toluene (Aldrich, anhydrous grade) dehydrated with red-colored adduct of butyllithium (*n*-BuLi) and 1,1-diphenylethylene, and distilled under high vacuum just before use. Ethylaluminum bis(2,6-di-*tert*-butylphenoxide) [EtAl(ODBP)$_2$] was prepared according to our previous report [14] and stored as a toluene solution under nitrogen atmosphere. MMA (Nacalai Tesque) was fractionally distilled and stored over CaH_2. All monomers were distilled over CaH_2 under reduced nitrogen pressure just before use. Me_3SiOLi (Aldrich) was dried *in vacuo* at 100 °C for several hours and used as a dry toluene solution. The received reagent contains a significant amount of toluene-insoluble material, and thus the supernatant solution was used for polymerization. Isopropyl α-lithioisobutyrate (Li-*i*PrIB) was prepared and recrystallized in toluene according to our previous report [15].

Instruments ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ (Aldrich) or DMSO-d_6 (Aldrich) on a JEOL JNM-ECS400 spectrometer or a JEOL JNM-GSX270 or a Varian Unity-Inova500. Chemical shifts in ^{1}H NMR spectra were referred to the signal of tetramethylsilane (TMS). Molecular weight and its distributions of the polymers were determined at 40 °C by size-exclusion chromatography (SEC) using a JASCO model GPC-900 chromatograph equipped with two Polymer Laboratories SEC columns [PL-gel, Mixed C (300 mm × 7.5 mm)], using THF as an eluent, and calibrated against standard PMMA samples (Shodex, MW: 1.25×10^6, 6.59×10^5, 1.95×10^5, 4.96×10^4, 2.06×10^4, 6.82×10^3, 2.00×10^3). Purity of monomers were determined from the gas chromatogram (GC) recorded on a GC-2014 (Shimadzu) equipped with a HP-5 capillary column (Hewlett-Packard). Thermogravimetry / differential thermal analysis (TG/DTA) were

performed with an EXSTAR TG/DTA6000 (SII NanoTechnology) (scan rate = 10 °C / min) under N_2 atmosphere (flow rate = 100 mL / min).

***Isobutyl α-(Hydroxymethyl)acrylate* (3)** To a solution of 1,4-diazabicyclo-[2,2,2]-trioctane (DABCO) (8.97 g, 80.0 mmol) in 1,4-dioxane (300 mL)–water (300 mL) were added 37 wt% HCHO aq (35.7 g, 0.440 mol) and isobutyl acrylate (51.3 g, 0.400 mol). The reaction mixture was stirred at 60 °C for 10 h (conversion = 86 wt%, product yield = 64 wt% by GC). The product was extracted with hexane (250 mL × 2) and the combined organic layer was concentrated. The residue oil was purified on silica gel column chromatography (eluent: hexane / EtOAc = 10 / 0, 8 / 1, and then 4 / 1) to give **3** (30.9 g) as colorless oil.

3: Yield 48.7%; purity 98.9%; ^{1}H NMR (400 MHz, 30 °C, $CDCl_3$) δ 6.27 (s, 1H, CH_2=), 5.84 (s, 1H, CH_2=), 4.34 (q, *J* = 5.5 Hz, 2H, –CH_2OH), 3.98 (d, *J* = 6.4H, 2H, C=C–CH_2OCH_2), 2.38 (br, 1H, OH), 2.05-1.95 (m, 1H, –CH<), 0.97 (d, *J* = 6.4 Hz, 3H, CH_3) ppm..

t-Butyl α-(Hydroxymethyl)acrylate (4) was prepared in a similar way to **3**.

4: Yield 31%; purity 97.3%; ^{1}H NMR (400 MHz, 30 °C, $CDCl_3$) δ 6.15 (s, 1H, CH_2=), 5.74 (s, 1H, CH_2=), 4.29 (q, *J* = 5.9 Hz, 2H, OCH_2), 4.11 (s, 2H, CH_2OH), 1.51 (s, 9H, CH_3–) ppm.

Methyl α-(Methoxymethoxymethyl)acrylate (1-MOM) To a solution of **1** (23.2 g, 0.200 mol) in dimethoxymethane (88.5 mL, 1.00 mol) were added *p*-toluenesulfonic acid (0.380 g, 0.200 mol) and a trace amount of 4,4'-methylenebis(2,6-*t*-butylphenol) as a polymerization inhibitor. The reaction mixture was refluxed for 11 h. After cooling to room temperature, the reaction mixture was neutralized with 5 wt% $NaHCO_3$ aq and extracted with Et_2O, and the organic layer was concentrated. The product was purified on silica gel column chromatography (eluent: hexane/EtOAc = 5/1, R_f = 0.34) and distillation under reduced pressure to afford **1-MOM** (19.4 g) as colorless oil.

1-MOM [16]: Yield 60.6%; Purity 100%; bp 32.5 °C/ 0.20 mmHg; *d* = 1.06 g/mL; ^{1}H NMR (400 MHz, 30 °C, $CDCl_3$): δ 6.32 (s, 1H, CH_2=), 5.89 (s, 1H, CH_2=), 4.68 (s, 2H, –OCH_2O–), 4.29 (s, 2H, C=CCH_2O–), 3.78 (s, 3H, –OCH_3), 3.39 (s, 3H, –CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 166.2, 167.0, 126.2, 96.0, 65.7, 55.3, 51.8 ppm.

Caution: 1 and the products may cause severe skin inflammation, and use leather gloves.

Ethyl α-(methoxymethoxymethyl)acrylate (**2-MOM**), isobutyl α-(methoxymethoxy-

methyl)acrylate (**3-MOM**), and *t*-butyl α-(methoxymethoxymethyl)acrylate (**4-MOM**) were synthesized in a similar way to **1-MOM**. **3-MOM** and **4-MOM** were dried *in vacuo* over molecular sieves 4A after column chromatography instead of distillation.

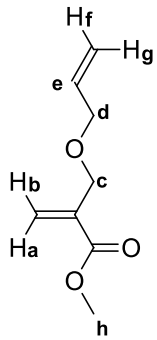
2-MOM [17]: bp 39-40 °C / 0.3 mmHg; *d* = 0.994 g/mL; ^{1}H NMR (400 MHz, 30 °C, $CDCl_3$): δ 6.31 (s, 1H, CH_2=), 5.88 (s, 1H, CH_2=), 4.69 (s, 2H, –OCH_2O–),4.29 (s, 2H, –CH_2O–), 4.24 (q, 2H, J = 7.2 Hz, –$COOCH_2$–), 3.39 (s, 3H, –OCH_3), 1.31 (t, 3H, *J* = 7.2 Hz, –CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 165.8, 13..4, 125.9, 96.0, 65.7, 60.7, 55.3, 14.1 ppm.

3-MOM: ^{1}H NMR (400 MHz, 30 °C, $CDCl_3$): δ 6.31 (s, 1H, CH_2=), 5.87 (s, 1H, CH_2=), 4.69 (s, 2H, –OCH_2O–), 4.23 (s, 2H, –C=C–CH_2O–), 3.96 (q, 2H, *J* = 3.2 Hz, –$COOCH_2$–), 3.39 (s, 3H, –OCH_3), 2.00-1.97 (m, 1H, –CH<), 0.96 (q, *J* = 3.2 Hz, –CH_3) ppm.

4-MOM: ^{1}H NMR (400 MHz, 30 °C, $CDCl_3$): δ 6.21 (d, *J* = 1.6 Hz, 1H, CH_2=), 5.80 (d, *J* = 1.6 Hz, 1H, CH_2=), 4.68 (s, 2H, –OCH_2O–), 4.24 (dd, J_1 = J_2 =1.6 Hz, 2H, –CH_2O–), 3.38 (s, 3H, –OCH_3), 1.50 (s, 9H, –CH_3) ppm.

Methyl α-(Allyloxymethyl)acrylate (1-allyl) To a three-necked flask equipped with Dean-Stark trap and nitrogen-gas inlet tube were added **1** (58.1 g, 0.500 mol), allyl alcohol (51.0 mL, 0.750 mol), DABCO (2.80 g, 25.0 mmol), acetic acid (2.86 mL, 50.0 mmol), zinc acetate dihydrate (1.10 g, 5.00 mmol), diisopropyl ether (21 mL), and catalytic amount of methylene bis(3,5-di-*t*-butyl-2-hydroxyphenyl). The reaction mixture was heated at 100 °C under nitrogen flow (*ca.* 20 mL/min). After 12 h, water (4 mL) was removed from a Dean-Stark trap, and the reaction mixture was heated for 3 h. After cooling to room temperature, the reaction mixture was washed with water (200 mL) and the organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. After distillation, the obtained **1-allyl** (39.6 g) was stored in the presence of CaH_2 and methylene bis(3,5-di-*t*-butyl-2-hydroxyphenyl) at −20 °C and distilled just before use.

1-allyl [18]: Yield 50.7%; purity 97.5%; colorless oil; bp 54.8–55.0 °C / 2.0 mmHg; *d* 0.986 g/mL: ^{1}H NMR (270 MHz, $CDCl_3$, 30 °C) δ 6.30 (d, *J* = 1.3 Hz, 1H, a), 5.98-5.85 (m, 2H, b and e), 5.30 (ddd, J_1 = 17.1 Hz, J_2 = 1.6 Hz, J_3 = 1.5 Hz, 1H, f), 5.19 (ddd, J_1 = 10.2 Hz, J_2 = 1.6 Hz, J_3 = 1.3 Hz, 1H, g), 4.20 (t, *J* = 1.5 Hz, 2H, d), 4.04 (dt, 2H, J_1 = 5.4 Hz, J_2 = 1.5 Hz, c),



3.76 (s, 3H, h) ppm; ^{13}C NMR (67.5 MHz, $CDCl_3$, 30 °C) δ 166.01, 137.0, 134.3, 125.5, 116.9, 71.6, 68.1, 51.7 pm.

Anionic polymerization A typical procedure (Table 1, Run 1): To a glass ampoule filled in dried nitrogen passed through Molecular Sieves 4A at −78 °C, toluene (5.0 mL) and Li-*i*PrIB (0.25 mmol) were added at room temperature. The reaction mixture was cooled to −78 °C, and the polymerization was started by the addition of **1-MOM** (5.0 mmol). After 48 h, polymerization was finally quenched by CH_3COOH—MeOH solution. A small amount of reaction mixture was dissolved in $CDCl_3$ to determine the conversion of monomer by ^{1}H NMR spectroscopy. The residual reaction mixture was poured into hexane (300 mL). The precipitate was collected by filtration and dried *in vacuo*.

poly(1-MOM) (Table 1, Run 1): Yield 44%; M_n = 15000; $Đ$ = 16.8; *mm* : *mr* : *rr* = 100 / 0 / 0; ^{1}H NMR (400 MHz, $CDCl_3$, 55 °C) δ/ppm 6.15 (s, 1H, ω1), 5.61 (s, 1H, ω2), 4.89 (sep, J = 6.0 Hz, 1H, α), 4.57 (s, 233H, c), 3.70 (s, 233H, b), 3.57 (s, 349.5H, e), 3.38 (s, 349.5H, d), 2.02 (br, 233 H, a).

poly(2-MOM) (Table 1, Run 4): Yield 26%; M_n = 23000; $Đ$ = 6.56; *mm* : *mr* : *rr* = 100 / 0 / 0; ^{1}H NMR (400 MHz, $CDCl_3$, 55 °C) δ/ppm 6.13 (s, 1H, ω1), 5.61 (s, 1H, ω2), 4.89 (sep, J = 6.0 Hz, 1H, α), 4.57 (s, 327H, c), 4.01 (q, J = 6.9 Hz, 327H, e), 3.74 (s, 327H, b), 3.38 (s, 490.5H, d), 2.04 and 2.03 (AB quartet, J = 14.2 Hz, 327H, a), 1.25 (t, J = 7.1 Hz, 490.5H, f); ^{13}C NMR (100 MHz, $CDCl_3$, 55 °C) δ/ppm 173.88 (C=O), 97.58 (c), 68.86 (b), 60.55 (e), 56.3 (d), 49.7 (4°-C), 43.7-43.5 (a), 14.1 (f).

Radical polymerization (Table 1, Run 7): **2-MOM** (1.75 g, 10.0 mmol) and AIBN (83.0 mg, 0.500 mmol) was dissolved in toluene (5.0 mL) and freeze-dried three times. The reaction mixture was heated at 60 °C for 15 h under nitrogen atmosphere and poured into hexane. The precipitate was collected by centrifugation and dried *in vacuo* to afford **poly(2-MOM)** (1.30 g, 74%). **2** was polymerized in a similar way.

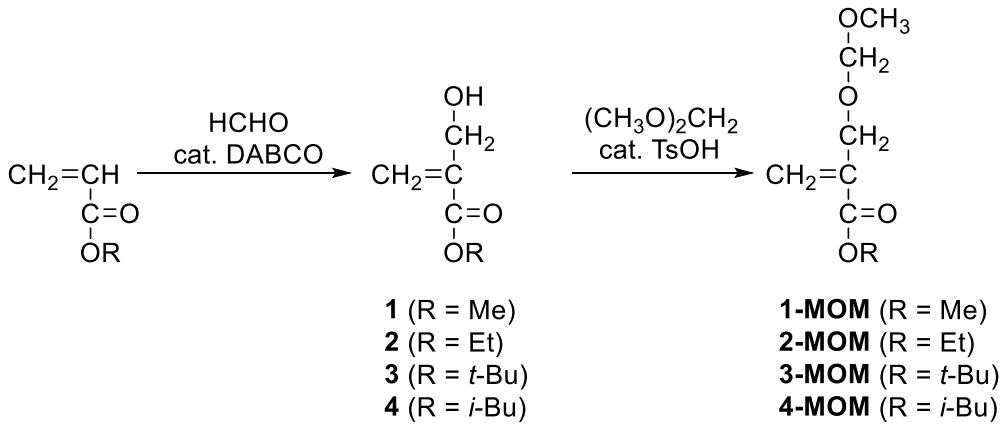
poly(2-MOM) (Table 1, Run 7): Yield 74%; M_n = 2600; $Đ$ = 2.07; *mm* : *mr* : *rr* = 14 / 50 / 36; ^{1}H NMR (400 MHz, $CDCl_3$, 55 °C) δ/ppm 4.55 (s, 2H, c), 4.00 (br, 2H, e), 3.87-3.50 (m, 7H, b), 3.38 (br, 3H, d), 2.42-1.66 (m, 2H, a), 1.27-1.24 (m, 3H, f); ^{13}C NMR (100 MHz, $CDCl_3$, 55 °C) δ/ppm 174.3-173.7 (C=O), 97.6-97.5 (c), 70.5-68.5 (b), 60.63-60.58 (e), 56.5-56.0 (d), 50.2-49.4 (4°-C), 45.0-43.5 (a), 14.1-14.0 (f).

poly(2): Yield 91%; ^{1}H NMR (400 MHz, $CDCl_3$, 55 °C) δ/ppm 4.4-2.70 (m, 5H, –OCH_2– and –CH_2OH), 2.28-1.50 (m, 2H, –CH_2–), 1.38–1.17 (μ, 3H, –CH_3).

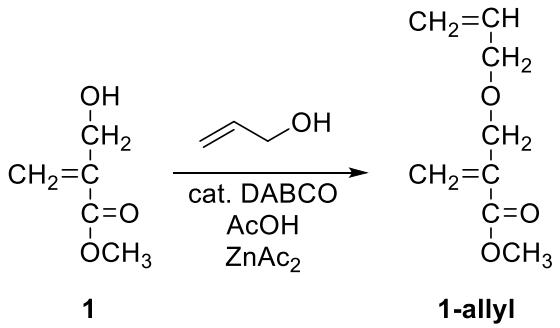
Deprotection of MOM group [19] To a solution of **poly(2-MOM)** (0.21 g) in 1,4-dioxane (6.0 mL) was added dropwise *conc.* HCl aq (2.0 mL) at 0 °C. The reaction mixture was stirred at room temperature for 12 h and poured into water. The precipitation was collected by centrifugation to afford white solids (97 mg).

Results and Discussion

Protection of Hydroxy Group Since bulky protective groups for the hydroxyl group of **1** such as tetrahydropyranyl (THP) and trityl (Tr) groups are expected to hinder the polymerization due to large steric demand [11-13], smaller protective groups, methoxymethyl (MOM) and allyloxy groups, were chosen in the present research. Protection of **1** and **2** with MOM group was achieved via standard acetal-exchange reaction (Scheme 2). Monomers with longer ester substituent, **3-4**, were synthesized by Baylis-Hillman reaction of the corresponding acrylates, and protected with MOM groups [1]. Allyl protection of **1** was achieved by condensation with allyl alcohol (Scheme 3).

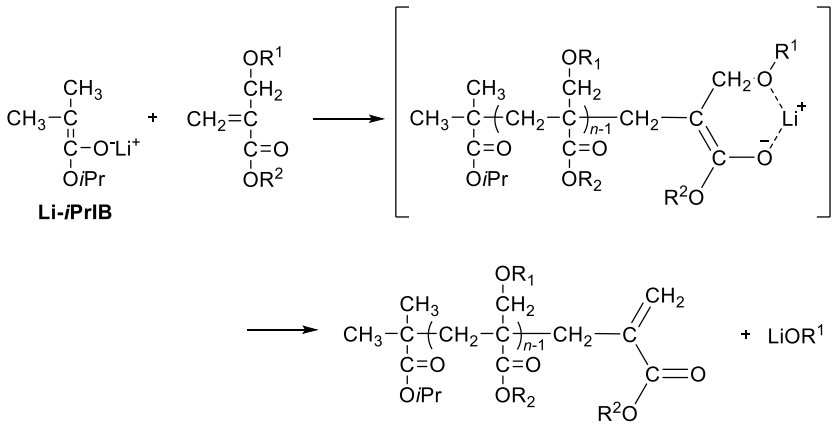


Scheme 2. MOM protection of **1-4**.



Scheme 3. Allyl protection of **1**.

Anionic Polymerization Anionic polymerization of **2-MOM** initiated with Li-*i*PrIB in toluene at −78 °C for 24 h afforded a polymeric product, which was recovered by precipitation in hexane (Scheme 4; Table 1, Run 4). ^{1}H NMR spectrum of the resulting polymer, **poly(2-MOM)**, is shown in Fig. 1-A. All signals were sharply observed. In particular, signal **a** around 2.0 ppm assignable to methylene protons of the main-chain was observed as an AB quartet, indicating highly isotactic structure. Fig. 2 shows partial ^{13}C NMR spectra of **poly(2-MOM)** synthesized by anionic (A, Run 4) and radical (B, Run 7) polymerizations. Both in carbonyl and α-CH_2 signal regions, **poly(2-MOM)** by anionic polymerization shows sharp and single peaks, whereas that by radical polymerization exhibits complicated split signals due to low stereoregularity. Thus, it is evident that the anionic polymerization of **2-MOM** proceeded in a highly isotactic-specific manner. Similarly, the anionic polymerization of **1-MOM** (Run 1) and **1-allyl** (Run 2) afforded the corresponding highly isotactic polymers. The ^{1}H NMR spectra showed clear AB-quartet pattern of the main-chain methylene protons (Fig.1B and 1C). The isotactic-specific polymerization behavior of these monomers is consistent with the reported observation for α-(alkoxymethyl)acrylates [11-13]. Okamoto *et al.* reported the spontaneous terminating reaction in anionic polymerization of α-(alkoxymethyl)acrylates; that is, the alkoxyl group at the terminal anion leaves as the alkoxide anion to generate the vinylidene group at ω-end [12].



Scheme 4. Anionic polymerization of α-(alkoxymethyl)acrylate and spontaneous terminating reaction.

In the ^{1}H NMR spectrum of **2-MOM** (Fig. 1A), weak signals **ω1** and **ω2** at 6.13 and 5.61 ppm assignable to the vinylidene protons at ω-end were observed. It should be noted that the integration of these signals completely agreed with that of the isopropyl methine

proton (signal **α**) at α-end, indicating that all the propagating anions underwent the spontaneously terminating reaction. Actually, the molar mass dispersities (*Đ*) of the resulting polymers were large, and SEC traces of **poly(2-MOM)** spread over 10^6-10^2 range. Fig. 3 shows the time-conversion plots of the anionic polymerization of **2-MOM** in toluene at −78 °C. The conversion reached 29% at 5 min, and then the polymerization rate became much slower thereafter probably due to the spontaneous terminating reaction. Polymerization of **3-MOM** (Run 5) and **4-MOM** (Run 6) did not afford any polymeric products.

Table 1. Anionic polymerization of protected α-(hydroxymethy)acrylates with Li-*i*PrIB in toluene at −78 °C.

Run	Monomer	Time /h	Conv.[b] /%	Yield /%	M_n / 10^3 (Calcd)	M_n / 10^3 (SEC)[c]	*Đ*[c]	Tacticity[d] /% *mm* / *mr* / *rr*
1	**1-MOM**	60	71	44	3.3	15	16.8	100 / 0 / 0
2	**1-allyl**	24	56	49	3.2	23	4.27	100 / 0 / 0
4	**2-MOM**	24	68	26	3.5	23	6.56	100 / 0 / 0
5	**3-MOM**	24	~0	0	-	-	-	-
6	**4-MOM**	24	~0	0	-	-	-	-
7[e]	**2-MOM**	15	-	74		2.6	2.07	14 / 50 / 36

a) Monomer 5.0 mmol, $[monomer]_0$ / $[Li\text{-}iPrIB]_0$ = 20 / 1, toluene 5.0 mL.
b) Determined by ^1H NMR spectroscopy (400 MHz, $CDCl_3$, 30 °C).
c) Determined by SEC (PMMA standards, THF, 40 °C).
d) Estimated by ^{13}C NMR spectroscopy (100 MHz, $CDCl_3$, 55 °C).
e) Radical polymerization initiated by AIBN (5 mol% of monomer) in toluene at 60 °C.

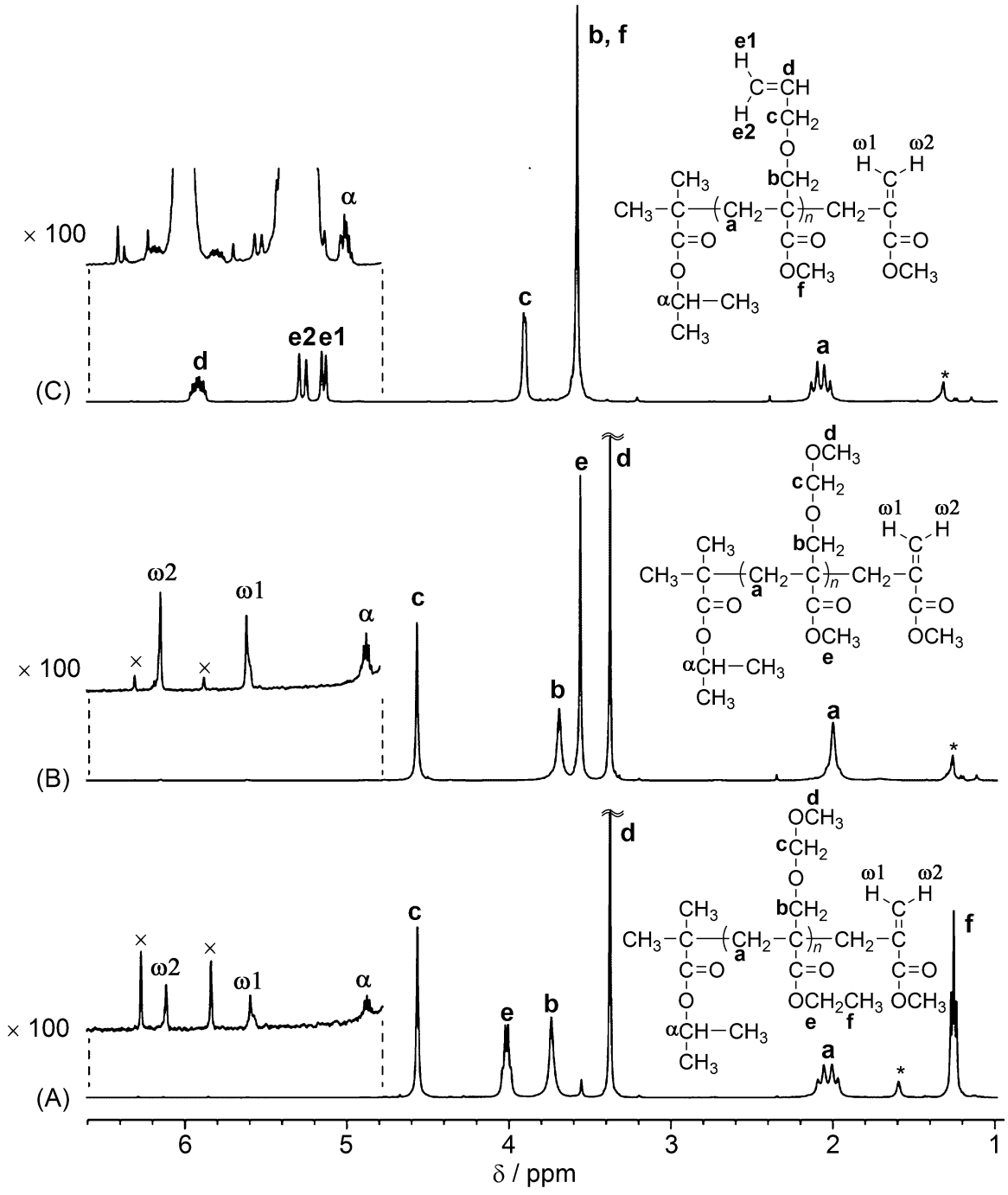


Fig. 1. ^{1}H NMR spectra of (A) **poly(2-MOM)** (Run 4), (B) **poly-(1-MOM)** (Run 1), and (C) **poly(1-allyl)** (Run 2) (400 MHz, $CDCl_3$, 55 °C).
* solvent peaks, × unreacted monomer peaks.

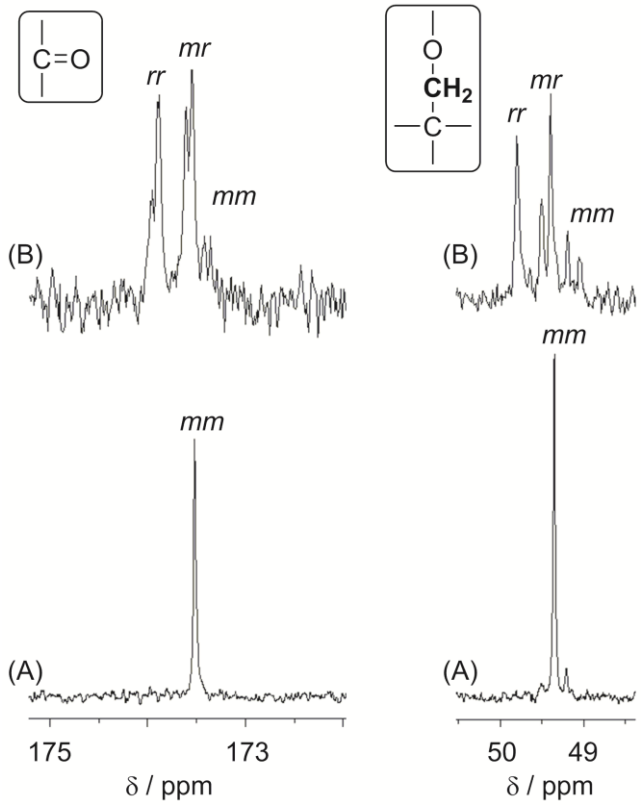


Fig 2. ^{13}C NMR spectra of **poly(2-MOM)** synthesized by (A) anionic (Run 4) and (B) radical (Run 7) polymerizations (100 MHz, $CDCl_3$, 55 °C).

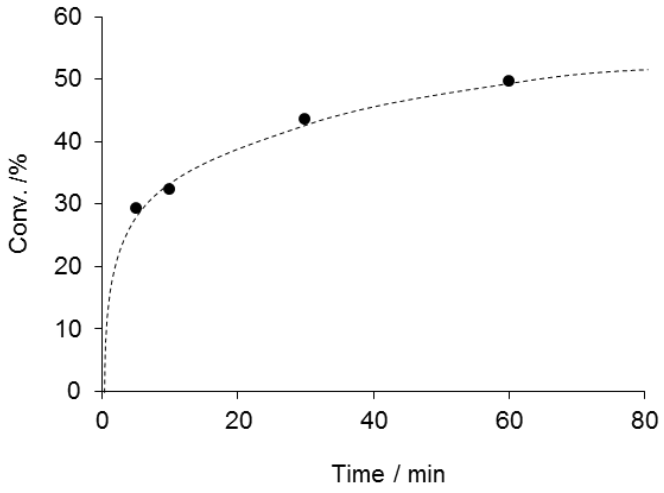


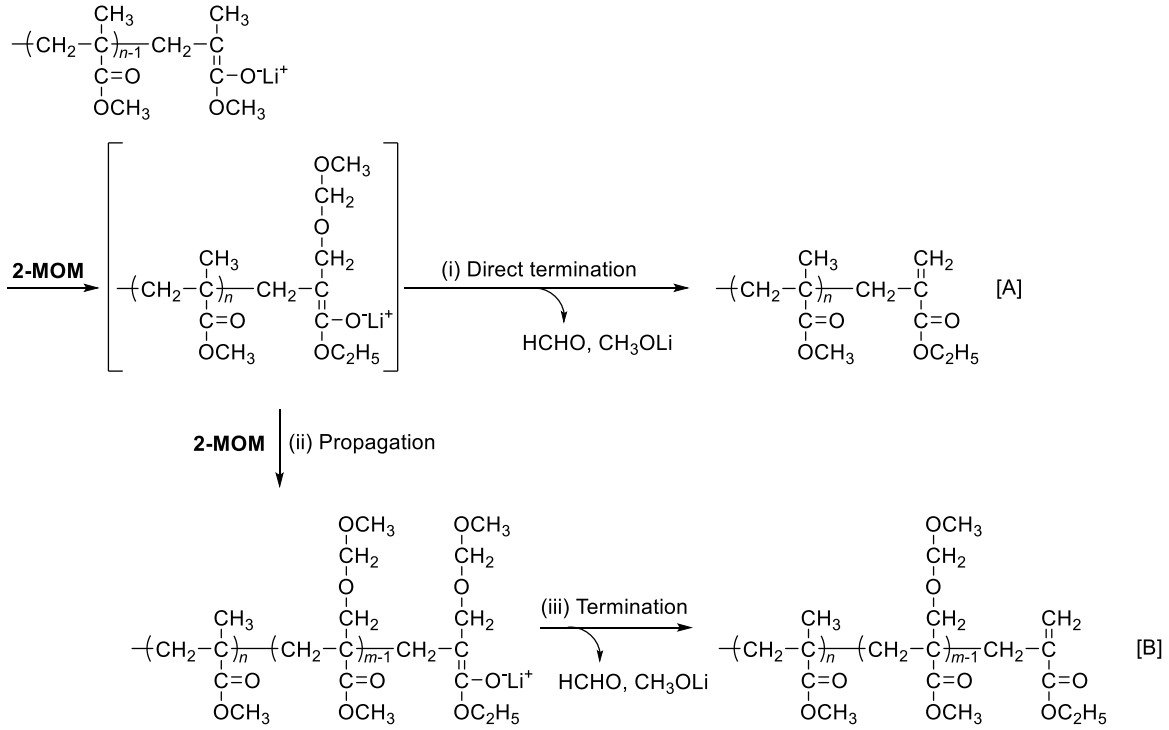
Fig. 3. Time vs. conversion plots in the polymerization of **2-MOM** with Li-*i*PrIB in toluene at −78 °C.

We have reported that organoaluminum compounds stabilize the living anion in anionic polymerization of MMA to prevent side reactions, resulting in controlled molecular weight and high syndiotacticity [14], whereas the addition of Me_3SiOLi effects isotactic-

specific living polymerization [15]. With the aim of controlling the polymerization in a similar manner, *n*-Bu_3Al, *i*-Bu_3Al, $EtAl(ODBP)_2$, and Me_3SiOLi were used as additives for the polymerization of **2-MOM** with Li-*i*PrIB. However, any polymeric products were not obtained in all the cases. In order to examine if the reaction of **2-MOM** and Li-*i*PrIB is completely prohibited or not, syndiotactic- (*st*-) poly(methyl methacrylate) (PMMA) living anion, prepared with Li-*i*PrIB in the presence of $EtAl(ODBP)_2$ in toluene at −78 °C, was reacted with **2-MOM** as a macroinitiator, and the resulting polymeric product recovered was analyzed by ^{1}H NMR spectroscopy (Fig. 4). The resulting polymer showed signal **ω3** at 4.17 ppm assignable to OCH_2 of ethyl ester in **2-MOM** unit but signals assignable to the MOM group were not observed (Fig. 4A). More interestingly, signals **ω1** (5.44 ppm) and **ω2** (6.18 ppm) assignable to vinylidene protons and signal **ω4** (2.50 ppm) assignable to allylic protons were observed. Recently, we reported that ethyl α-(chloromethyl)acrylate functions as a terminating agent against stereoregular living PMMA anions to form α,β-unsaturated structure at the ω-end quantitatively [9]. It is noteworthy that the characteristic ^{1}H NMR signals mentioned above (Fig. 4A) completely agreed with those observed for *st*-PMMA terminated with α-(chloromethyl)acrylate. Thus, it is concluded that the *st*-PMMA living anion attacks **2-MOM** to form the unsaturated ω-end unit with a release of MOM group as an alkoxide anion without any propagation reaction (Scheme 5). It might be due to the slow propagation rate in the presence of the propagating species stabilized by the aluminum compound. In fact, the relative intensity of signal **ω1** (5.44 ppm) at ω-end to signal **α** (4.95 ppm, methine proton of isopropyl group of the initiator fragment at α-end) was close to unity, indicating the quantitative termination.

In a similar way, an isotactic- (*it*-) PMMA living anion prepared in the presence of Me_3SiOLi was reacted with **2-MOM** at −78 °C. In contrast to the case of *st*-PMMA anion, the ^{1}H NMR spectrum of the resulting polymer (Fig. 4B) exhibits signals assignable to MOM group, *e.g.* acetal signal **c** at 4.04 ppm, indicating that the propagation of **2-MOM** took place. In addition, two sets of vinylidene signals, **ω1** (6.17 ppm) / **ω2** (6.17 ppm) and **ω5** (5.60 ppm) / **ω6** (6.15 ppm), were observed. The former signals **ω1**/ **ω2** agreed with those of the unsaturated ω-end of *it*-PMMA obtained by termination with α-(chloromethyl)acrylate [9]. The latter signals are close to those observed in the spectrum of poly(**2-MOM**) (cf. Fig. 1A) and assignable to the unsaturated ω-end formed after the addition of several units of **2-MOM.** The sum of intensities of the two types of vinylidene

signals was close to unity against the intensity of signal **α** representing the initiator fragment. The results indicate that the product consists of two types of polymers; (i) *it*-PMMA with one unsaturated ω-end unit formed through direct termination with **2-MOM** as in the case of *st*-PMMA, and (ii) the polymer with a few units of **2-MOM** and one unsaturated ω-end unit, which should be formed by oligomerization of **2-MOM** by the living *it*-PMMA followed by the termination reaction with a release of MOM anion. The relative intensities of signal **ω1** and signal **ω5** against signal **α** (initiator fragment) revealed that the product comprised 28% of type [A] polymer and 72% of type [B] polymer. From the relative intensity of signal **c** against signal **α**, type [B] polymer was found to contain 3.3 units of **2-MOM** per chain. Thus, it is concluded that **2-MOM** can be attacked by PMMA living anions even in the presence of additives such as $EtAl(ODBP)_2$ and Me_3SiOLi, but the propagation of **2-MOM** is hindered by the dominant spontaneous terminating reaction. It is worth noting that **2-MOM** can be an effective terminating agent against the living PMMA as far as it is stabilized by the aluminum additives.



Scheme 5. Polymerization of **2-MOM** by PMMA living anion as a macroinitiator.

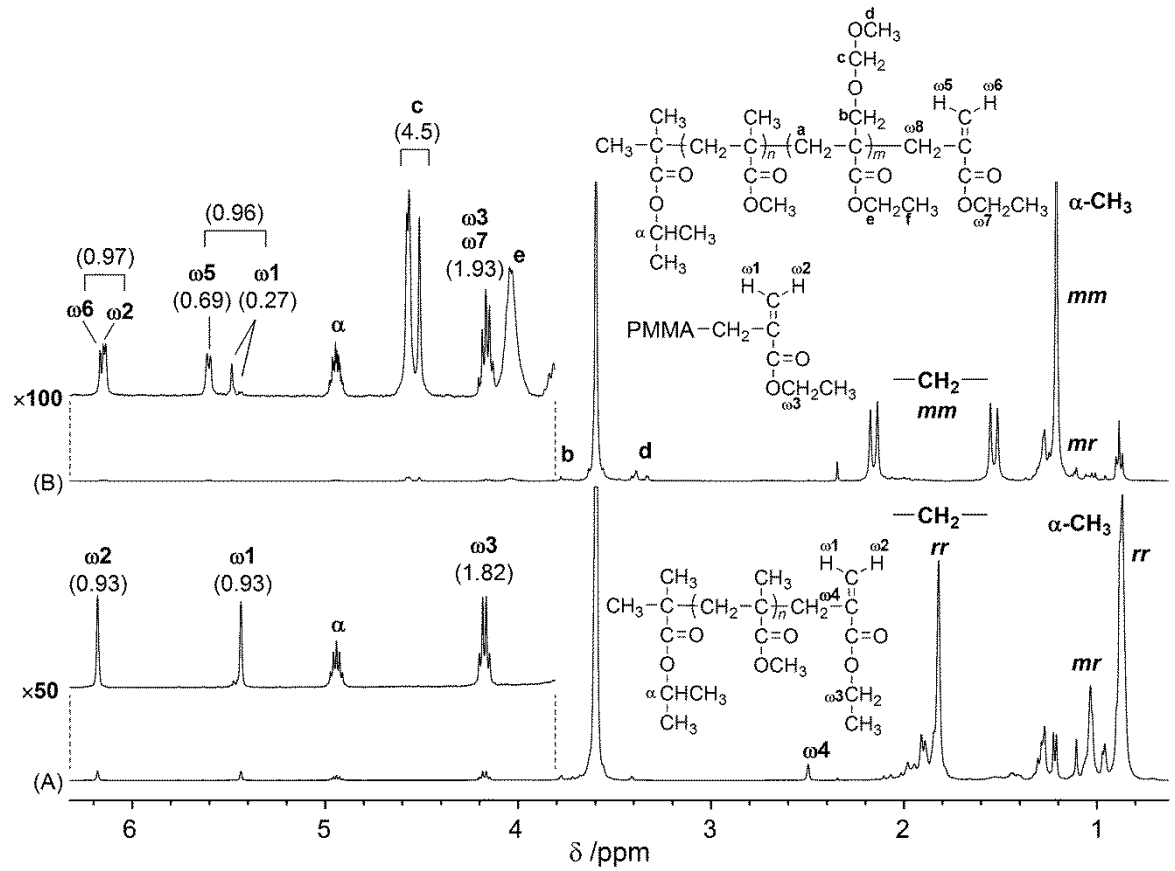


Fig. 4. ^{1}H NMR spectra of polymers prepared by the reaction of **2-MOM** with (A) *st*-PMMA and (B) *it*-PMMA living anions (400 MHz, $CDCl_3$, 55 °C). Numerals in parentheses are intensity of the respective signal(s) relative to signal **α**.

Deprotection of poly(2-MOM) Acid-catalyzed hydrolysis of MOM group for **poly(2-MOM)** was carried out according to the literature [16]. **Poly(2-MOM)** was treated with *conc.* HCl aq in 1,4-dioxane to afford a white precipitate within a few hours. The precipitate was insoluble in acetone, THF, and chloroform, which were good solvents for **poly(2-MOM)**. Fig. 5 shows the carbonyl absorption in IR spectra of **poly(2-MOM)**, the hydrolysis product, and **poly(2)** obtained directly from **2** by radical polymerization. While carbonyl absorption of **poly(2-MOM)** was observed at 1736 cm^{-1}, that of **poly(2)** shifted to lower wavenumber (1725 cm^{-1}), probably due to the hydrogen bonding with hydroxyl groups. On the other hand, the hydrolysis product showed a broad peak from 1739 cm^{-1} to 1714 cm^{-1} different from that of **poly(2),** suggesting the possibility of formation of other types of carbonyl groups. It should be noted that treatment of **poly(2)** with hydrochloric acid also caused a similar broadening of carbonyl absorption (Fig. 5D). To investigate further details, the reaction was monitored by ^{1}H NMR spectroscopy. **Poly(2-MOM)** was

dissolved in DMSO-d_6 and a catalytic amount of *conc.* HCl aq was added. Fig. 6 shows the change of ^{1}H NMR spectrum of the reaction mixture. At room temperature, no change was observed even after 12 h. Then, the mixture was heated at 80 °C for 12 h (Fig. 6B). The decrease of MOM signals was observed, while the signals assignable to EtOH (1.06 and 3.44 ppm) also evolved, indicating ester exchange reaction in the pendant groups. Under similar conditions, the lactonization between two neighboring units of **poly(2)** have been reported [7]. Thus, it was revealed that the deprotection of MOM group led to lactonization instantaneously (Scheme 6).

Ueda *et al.* have reported a similar intramolecular lactonization of **poly(2)** in the bulk when heated up to 320 °C [5]. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out on the hydrolysis product and **poly(2)** prepared directly by radical polymerization (Fig. 7). The thermal degradation of **poly(2)** occurred in two steps, where the lactonization occurred in the first step with 26% weight loss under 295 °C. On the other hand, the hydrolysis product decomposed in one step; weight loss at 295 °C was 7% and rapid degradation was observed above 320 °C. The much lower weight loss of the hydrolysis product in the first stage than that for **poly(2)** implies that most of the repeating units had already formed lactone skeletons in the hydrolysis process.

Poly(2-MOM) has good solubility in common organic solvents such as acetone, THF, and chloroform. Casting of an acetone solution onto a glass plate gave a tough self-standing film. Upon exposure to *conc.* HCl *aq* vapor for 2 h, the film became insoluble in any organic solvents (Fig. 8), since the acid-catalyzed hydrolysis and lactonization proceeded fast even in the solid state so as to drastically change its solubility. The phenomenon may be used for a new acid-resist.

Conclusion

Anionic polymerization of methyl or ethyl α-(hydroxymethyl)acrylates protected by MOM or allyl groups at −78 °C afforded highly isotactic polymers, although the inevitable spontaneous terminating reaction deteriorated the livingness of polymerization so as to prevent sufficient molar-mass control. The acid-treatment of **poly(2-MOM)** resulted in the deprotection of MOM group and following lactonization between neighboring two repeating units to afford insoluble polymers. Though the clean deprotection of **poly(2-MOM)** to obtain stereoregular **poly(2)** was so far unsuccessful, this reaction proceeded even in film state with a vapor of HCl aq, which might provide a new acid-resist. The polymerization of α-(hydroxymethyl)acrylates protected by other protective groups which

can be cleaved under milder conditions are underway.

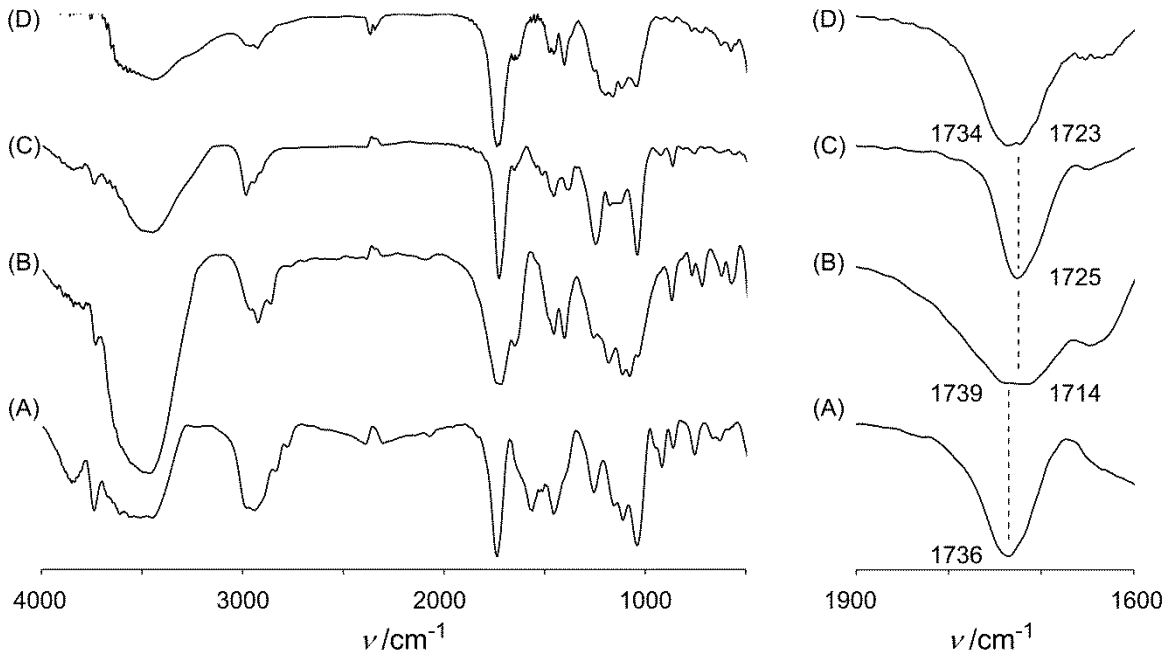
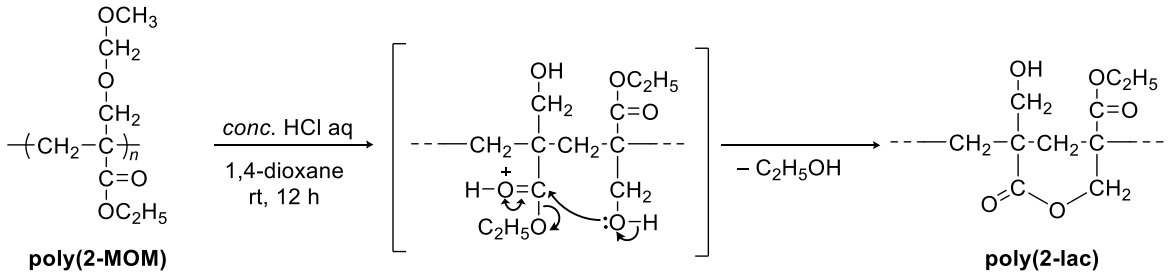


Fig. 5. IR spectra of **poly(2-MOM)** (A) before and (B) after hydrolysis, and those of **poly(2)** (C) before and (D) after hydrolysis: [Left] Full spectra and [Right] expanded around 1750 cm^{-1}.



Scheme 6. Acid hydrolysis of **poly(2-MOM)** and following lactonization.

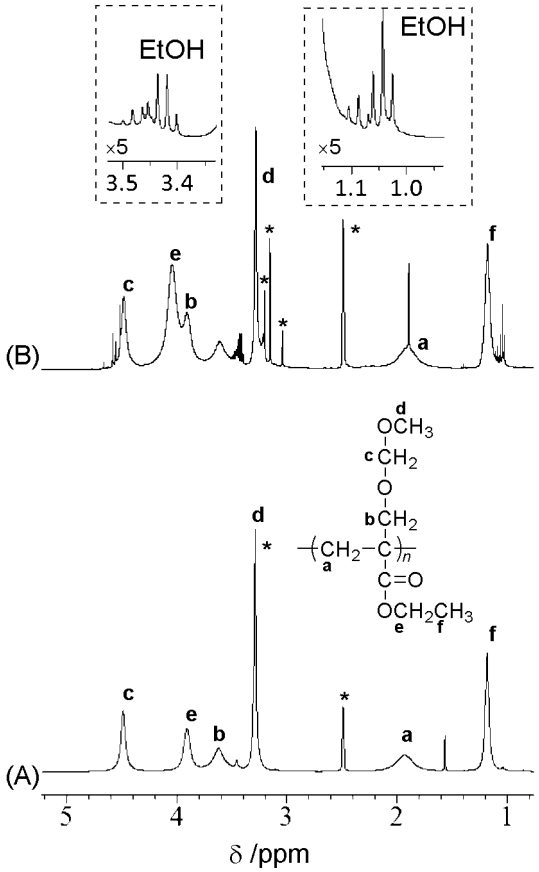


Fig. 6. ^{1}H NMR spectra of **poly(2-MOM)** (A) before hydrolysis and (B) after heating at 80 °C with a catalytic amount of *conc.* HCl aq (400 MHz, DMSO-d_6, 30 °C).

* solvent peaks.

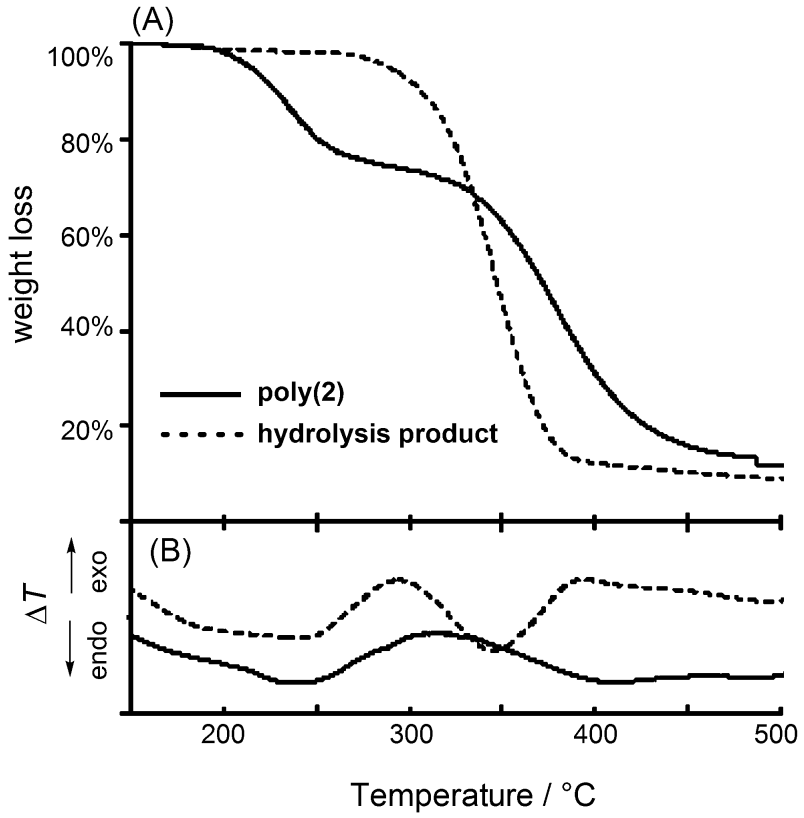


Fig. 7. (A) TGA and (B) DTA curves of **poly(2)** (solid line) and hydrolysis product of **poly(2-MOM)** (dashed line).

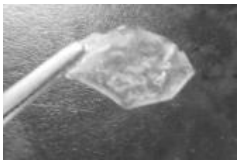


Fig. 8. A picture of after exposure of **poly(2-MOM)** film to *conc.* HCl aq vapor for 2 h.

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