Cyclopolymerization. 25. Five-Membered Ring Formation through Head-to-Head and Tail-to-Tail Additions in Radical and Anionic Polymerizations of α-(Allyloxymethyl)acrylates

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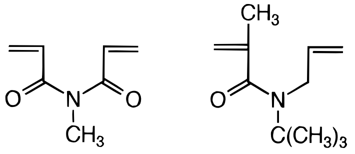
ABSTRACT: Radical and anionic polymerizations of methyl and *tert*-butyl α-(allyloxymethyl)acrylates (AMA and ABA, respectively) were undertaken to see whether five-membered ring formation through head-to-head and tail-to-tail additions can occur irrespective of the polymerization mechanism. Both the monomers yielded highly cyclized polymers with a five-membered ring as a repeating cyclic unit in their radical polymerizations. Lithium compounds such as *n*-butyl- and *tert*-butyllithiums yielded highly isotactic uncyclized poly(AMA)s, while *tert*-butylmagnesium chloride afforded polymers with a considerably higher degree of cyclization (70%), the repeating cyclic units of which consist of a five-membered ring. Poly(ABA)s obtained through an anionic mechanism were found to have a five-membered ring as a repeating cyclic unit and degrees of cyclization higher than 80% irrespective of the initiator used. The structure of the anionically obtained cyclopolymers was fundamentally the same as those formed through a radical mechanism. These results along with those obtained from methyl and *tert*-butyl α-(propoxymethyl)acrylates, one of the monofunctional counterparts of AMA and ABA, respectively, led to the conclusion that anionic cyclopolymerizations proceed in the case where interaction of a countercation with the propagating chain end and the monomer is weak.

Introduction

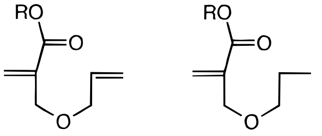
1,6-Dienes such as *N*-methyldiacrylamide (MDA) (Chart 1) and *N*-*tert*-butyl-*N*-allylacrylamide (BAA) form selectively a five-membered ring as a repeating cyclic unit in their anionic polymerizations[1,2] as well as in their radical counterparts,[3,4] though they have two possible cyclic repeating structures, i.e., five- and six-membered rings. These polymers were essentially free from pendant unsaturations except for poly(BAA) obtained through an anionic mechanism, which contained pendant allyl groups less than 20% in its repeating units.[2] Such a high tendency toward five-membered ring formation in their anionic polymerizations is extremely curious, because it means occurrence of head-to-head and tail-to-tail additions, which have never been observed in the anionic polymerization of vinyl monomers. In connection with these results, the radical polymerizations of ethyl α-(allyloxymethyl)acrylate (AEA) (Chart 2)[5] caught our attention, since it yields completely cyclized polymers with a five-membered ring as a repeating cyclic unit. Investigations on the anionic cyclopolymerizability of α-(allyloxymethyl)acrylates (ARA) are expected to afford information on whether the unusual addition reactions, i.e., five-membered ring formation, can generally occur or not in the anionic polymerizations of 1,6-dienes which form selectively a five-membered ring in their radical polymerizations. Methyl and *tert*-butyl α-(allyloxymethyl)acrylates (AMA and ABA, respectively) were chosen as monomers, and the effect of ester substituents on their cyclopolymerizabilities was also investigated.

Chart 1



MDA BAA

Chart 2



ARA PRA

ARA	R	PRA
AMA	CH_3	PMA
ABA	$C(CH_3)_3$	PBA
AEA	CH_2CH_3	—

Another interesting point of the anionic polymerization of ARA to be noted is as follows. α-(Alkoxymethyl)acrylates yield polymers with highly isotactic stereoregularity when they are polymerized with anionic initiators such as lithium reagents.[6] The strong intra- and intermolecular coordination powers of the polar groups of a growing polymer chain end and α-(alkoxymethyl)acrylate monomer to the countercation (Li^+) have been attributed to the main factor controlling the stereochemistry of the polymerization. Since such a coordination is considered to influence strongly the structure of poly(ARA), a detailed investigation on the

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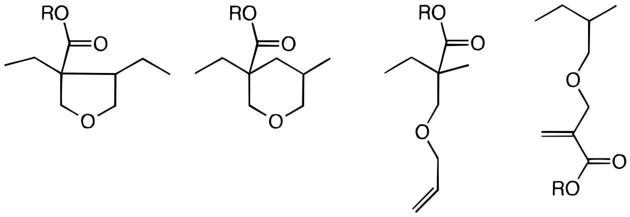
Table 1. Radical Polymerization of ARA

no.	ARA	$[M]_0$, mol/dm^3	$[AIBN]_0$, mol/dm^3 × 10^2	temp, °C	time, h	convn, %	M_n[a]	M_w[b]/M_n	DC,[c] %	*A*,[d] %
1	AMA	6.4	6.1	50	0.17	16	47 000	2.6	86	14
2	AMA	1.0	0.1	70	12	80	19 000	2.1	96	4
3	AMA	1.0	0.1	70	24	100	19 000	2.6	98	2
4	ABA	5.04	6.1	50	0.33	19	35 500	2.3	90	10
5	ABA	5.04	6.1	50	1	42	64 500	2.6	91	9
6	ABA	1.0	0.1	70	12	71	32 900	2.3	100	0

[a] Number-average molecular weight. [b] Weight-average molecular weight. [c] Degree of cyclization. [d] Content of pendant allyl group.

anionic polymerization of these monomers would provide valuable information on the correlation between polymerization conditions and polymer structure. Polymerization behavior of α-(propoxymethyl)acrylates (PRA), one of the monofunctional counterparts of ARA, was also investigated to gain a deep insight into the aspect of the intermolecular coordination at the growing polymer chain end.

Chart 3. Possible Structures of Poly(ARA)



1 **2** **3** **4**

Experimental Section

Materials. ARA and PRA were synthesized by the reactions between methyl and *tert*-butyl α-(bromomethyl)acrylates and the corresponding alcohol according to the procedure reported for the synthesis of AEA.[5] Repeated distillations gave pure liquids with about 70% yields for all of them. The boiling points of methyl and *tert*-butyl esters were observed at around 48 °C/3 mmHg and 54 °C/0.4 mmHg (not corrected), respectively. Chemical shifts of the characteristic absorption peaks of ^{1}H and ^{13}C NMR spectra of ARA and PRA are as follows. For AMA, ^{1}H NMR: δ = 3.76 (s, 3H), 4.04 (d, 2H), 4.20 (s, 2H), 5.17–5.33 (2H, doublet of doublet), 5.90 (s, 1H), 5.91 (m, 1H), 6.30 (s, 1H), ^{13}C NMR: δ = 51.8 (CH_3O-), 68.2 (allyl $-CH_2O-$), 71.7 (acryl $-CH_2O-$), 117.1 (allyl $CH_2=$), 126.8 (acryl $CH_2=$), 134.5 (allyl $-CH<$), 137.2 (acryl $>C<$), 166.3 ($>C=O$). For ABA, ^{1}H NMR: δ = 1.50 (s, 9H), 4.05 (d, 2H), 4.16 (s, 2H), 5.18–5.33 (2H, doublet of doublet), 5.81 (s, 1H), 5.92 (m, 1H), 6.21 (s, 1H), ^{13}C NMR: δ = 28.1 (*tert*-butyl CH_3-), 68.4 (allyl $-CH_2O-$), 71.7 (acryl $-CH_2O-$), 80.9 (*tert*-butyl $>C<$), 117.0 (allyl $CH_2=$), 124.5 (acryl $CH_2=$), 134.6 (allyl $-CH<$), 138.4 (acryl $>C<$), 165.2 ($>C=O$). For PMA, ^{1}H NMR: δ = 0.94 (t, 3H), 1.63 (sextet, 2H), 3.45 (t, 2H), 3.77 (s, 3H), 4.18 (s, 2H), 5.88 (s, 1H), 6.29 (s, 1H), ^{13}C NMR: δ = 10.4, (propyl CH_3-), 22.7 (propyl $-CH_2-$), 51.5 (CH_3O-), 68.6 (propyl $-CH_2O-$), 72.4 (acryl $-CH_2O-$), 125.2 (acryl $CH_2=$), 137.3 (acryl $>C<$), 166.2 ($>C=O$). For PBA, ^{1}H NMR: δ = 0.94 (t, 3H), 1.50 (s, 9H), 1.62 (sextet, 2H), 3.44 (t, 2H), 4.14 (s, 2H), 5.78 (s, 1H), 6.19 (s, 1H), ^{13}C NMR: δ = 10.6 (propyl CH_3-), 23.0 (propyl $-CH_2-$), 28.1 (*tert*-butyl CH_3-), 69.0 (propyl $-CH_2O-$), 72.6, (acryl $-CH_2O-$), 80.7 (*tert*-butyl $>C<$), 124.2 (acryl $CH_2=$), 139.1 (acryl $>C<$), 165.3 ($>C=O$). Methyl and *tert*-butyl α-(bromomethyl)acrylates were prepared based on the reported procedures.[7]

Toluene was washed successively with concentrated sulfuric acid, water, 5% aqueous sodium hydroxide, and finally water and subsequently refluxed over sodium metal and distilled. Just before use, it was redistilled from calcium hydride. Commercial *tert*-butylmagnesium chloride (*t*-BuMgCl) in tetrahydrofuran, *tert*-butyllithium (*t*-BuLi) in pentane, and *n*-butyllithium (*n*-BuLi) in hexane (Kanto Chemicals, respectively) were used as received. Commercial azobis(isobutyronitrile) (AIBN) was recrystallized from ethyl alcohol. All common solvents were purified by usual methods.

Polymerization. Anionic polymerizations were carried out in toluene according to the procedure reported.[2] The precipitant used was hexane except for poly(PBA). In the polymerization systems of ABA and PMA initiated with *n*-BuLi and *t*-BuMgCl, respectively, where the conversion is low, solvent was evaporated under vacuum at temperatures lower than 20 °C to obtain a concentrated solution which was poured into hexane. The precipitates obtained were filtered on a sintered glass crucible. The precipitates were extracted with chloroform and reprecipitated in hexane. The insoluble fractions in chloroform were assigned to lithium chloride and magnesium chloride, respectively, by comparing their IR spectra with those of authentic samples. Methanol was employed as a precipitant for poly(PBA).

Radical polymerizations were performed in sealed tubes. A given amount of monomer and initiator (and toluene when polymerized in solution) was placed in glass ampules, which were then subjected to several freeze–pump–thaw cycles and sealed. After polymerization in a constant-temperature bath, polymers were isolated by pouring the polymerization mixture into precipitant. Polymerizations at −78 °C were carried out under the irradiation of a 100 W high-pressure mercury lamp (Toshiba Electric Works, model SHL-100UV-2) using AIBN as photosensitizer. The precipitants used for poly(PMA) and poly(PBA) were hexane and methanol, respectively.

Measurements. ^{1}H and ^{13}C NMR spectra were obtained at room temperature in $CDCl_3$ with tetramethylsilane as an internal standard using JEOL GX-270 (270 MHz for ^{1}H and 68 MHz for ^{13}C) and LA-500 (500 MHz for ^{1}H and 125 MHz for ^{13}C) FT NMR spectrometers. Size exclusion chromatography (SEC) was performed on Shimazu LC-10AD liquid chromatograph equipped with three polystyrene gel columns (Shodex K-804L) and ultraviolet/refractive index dual detectors using chloroform as eluent. A molecular weight calibration curve was obtained by using standard polystyrene. Samples for NMR measurements were collected by preparatory SEC using Jasco Megapack 201 as a column in the case where conversions are low, since polymer separation from monomer was difficult.

Results

Radical Polymerizations of AMA and ABA. The results of the radical polymerizations of AMA and ABA are summarized in Table 1. Both the monomers yielded soluble polymers even in bulk polymerizations, which suggests formation of highly cyclized polymers. The repeating units which are expected to appear in poly(AMA) and poly(ABA) are **1**–**4** (Chart 3). Their ^{1}H NMR spectra are illustrated in Figure 1 along with absorption due to olefin protons of both the monomers. Formation of polymers with allyl groups as a pendant unsaturation (**3**) can be recognized by the absorption at around 5.3 and 5.8 ppm. This is the characteristic that differentiates these two monomers from AEA, since even poly(AEA) obtained by bulk polymerization does not contain essentially any uncyclized units.[5] The degrees of cyclization of poly(AMA) and poly(ABA) given in Table 1

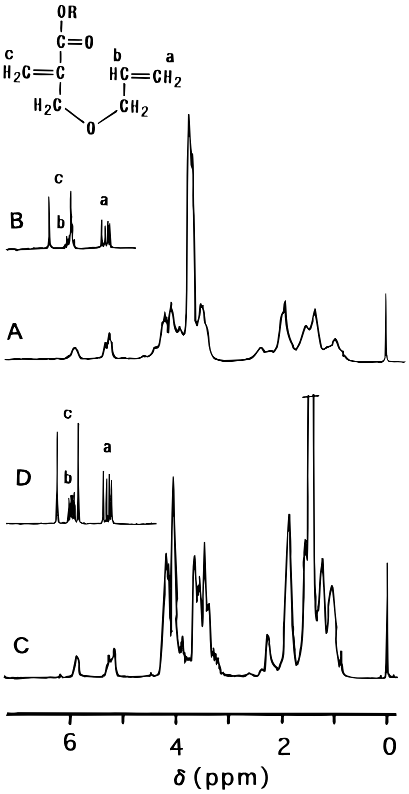


Figure 1. ^{1}H NMR spectra of poly(ARA) and ARA: (A) poly(AMA) (no. 1 in Table 1); (B) AMA; (C) poly(ABA) (no. 4 in Table 1); (D) ABA. Measured in 270 MHz for (A) and (B) and in 500 MHz for (C) and (D).

were determined based on the signal intensities of the methine proton of the allyl group at 5.8 ppm and the protons on the carbons adjacent to oxygen observed at around 3.9 ppm. ABA yields polymers with slightly higher degrees of cyclization than AMA. This is in accordance with the reported results that bulky substituents enhance the cyclopolymerizability of 1,6-dienes.[4,8,9]

To obtain information on repeating cyclic units of poly(AMA) and poly(ABA), their ^{13}C NMR spectra were compared with that of poly(AEA) in Figure 2. This is because the repeating cyclic structure of poly(AEA) has been identified unambiguously as a five-membered ring (**1**) by using the INADEQUATE NMR method (incredible natural abundance double quantum transfer experiment).[5] The spectral patterns of both the polymers are identical with that of poly(AEA) to every detail except for the difference due to the absorption of their ester alkyl carbons. This means that poly(AMA) and poly(ABA) have substantially the same structure as that of poly(AEA) and accordingly that repeating cyclic units of the former two polymers consist exclusively of a five-membered ring (**1**). The fact that every carbon other than ester alkyl carbons and methylene carbons adjacent to the ether oxygen is detected as two absorption peaks as in the case of poly(AEA)[5] suggests that those with stronger intensity and the other with weaker intensity are due to trans and cis forms (see Figure 2), respectively, based on the assignment reported for poly(AEA).

Anionic Polymerization of AMA and ABA. Anionic polymerizations of AMA and ABA were undertaken to see whether polymers with a five-membered ring as a repeating unit are formed or not, since both the monomers yielded highly cyclized polymers with a five-membered ring as a repeating cyclic unit in their radical polymerizations. The results of the polymerizations summarized in Table 2 indicate strong influence of initiators on the anionic polymerization of AMA. The polymerizations initiated with *n*-BuLi proceeded to much higher conversion than those initiated with *t*-BuMgCl and *t*-BuLi. Further, the NMR studies on poly(AMA) revealed that the structures of the anionically obtained poly(AMA) are significantly dependent on the initiators used.

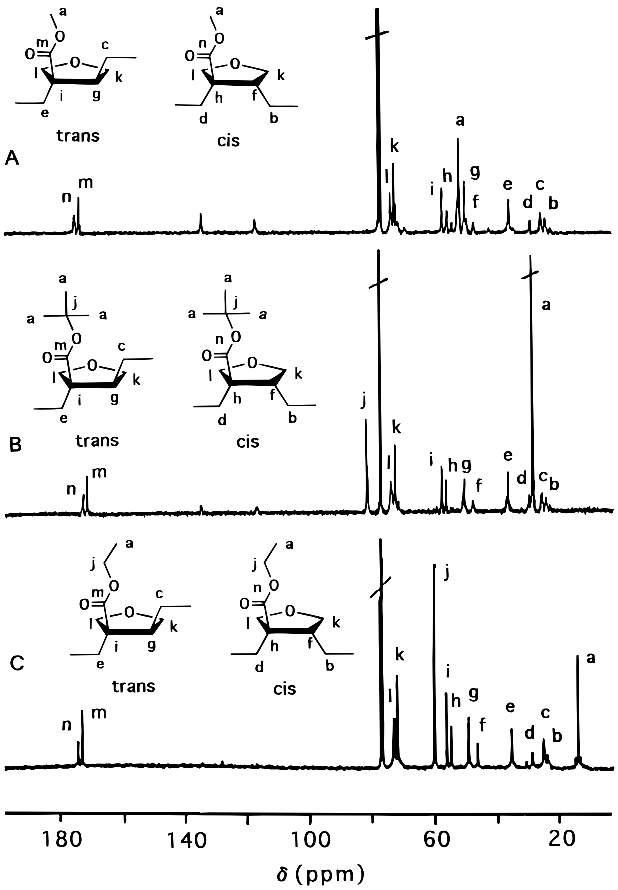


Figure 2. ^{13}C NMR spectra of poly(ARA): (A) poly(AMA) measured in 68 MHz; (B) poly(ABA) measured in 125 MHz; (C) poly(AEA) measured in 100 MHz, which was reprinted in part with permission from ref 5.

Table 2. Anionic Polymerization of ARA[a]

no.	ARA	initiator	convn, %	M_n[b]	M_w[c]/M_n	DC,[d]%	A,[e]%
1[f]	AMA	*n*-BuLi	72	20100	3.5	0	100
2[f]	AMA	*n*-BuLi	83	23600	3.6	0	100
3[f]	AMA	*t*-BuLi	22	9600	2.0	0	100
4	AMA	*t*-BuMgCl	17	9900	4.5	70	30
5	ABA	*n*-BuLi	2			80	20
6	ABA	*n*-BuLi	1	4000	1.4	80	20
7	ABA	*t*-BuLi	8	15800	2.0	91	9
8	ABA	*t*-BuMgCl	8	4700	3.0	87	13

[a] [Monomer]/[initiator] = 10. $[M]_0$, 1.0 mol/dm^3. Temperature, −78 °C. Time, 96 h. [b] Number-average molecular weight. [c] Weight-average molecular weight. [d] Degree of cyclization. [e] Content of pendant allyl group. [f] Highly isotactic.

^{1}H NMR spectra of poly(AMA) derived from the anionic polymerizations are depicted in Figure 3 along with the absorption due to olefin protons of AMA. Polymers obtained using *t*-BuMgCl (Figure 3C) and AIBN (Figure 1A) have essentially the same spectral pattern, which indicates that *t*-BuMgCl yielded consid-

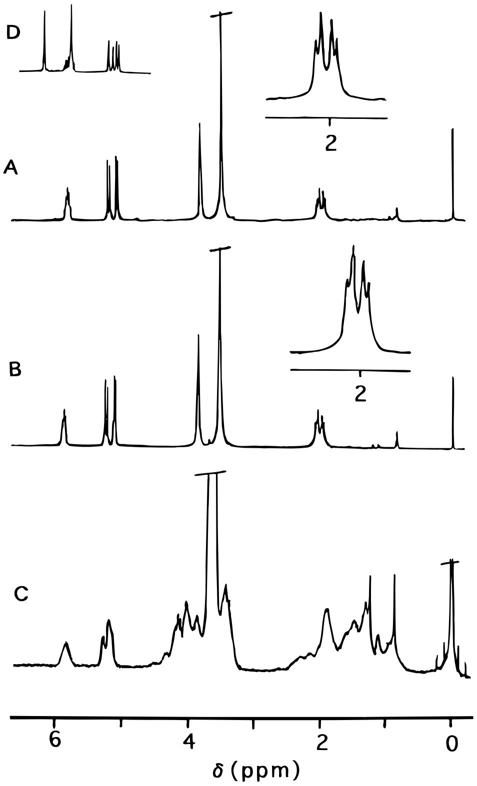


Figure 3. The 500 MHz ^{1}H NMR spectra of poly(AMA) obtained with *n*-BuLi (A) (no. 2 in Table 2), *t*-BuLi (B) (no. 3 in Table 2), and *t*-BuMgCl (C) (no. 4 in Table 2) and AMA (D). Spectrum C was measured in 270 MHz.

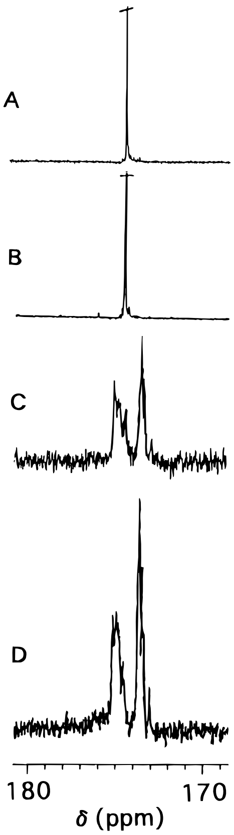


Figure 4. The 125 MHz ^{13}C NMR spectra of the carbonyl carbon in poly(AMA) obtained with *n*-BuLi (A) (no. 2 in Table 2), *t*-BuLi (B) (no. 3 in Table 2), *t*-BuMgCl (C) (no. 4 in Table 2), and AIBN (D) (no. 1 in Table 1). Spectra C and D were measured in 68 MHz.

erably highly cyclized polymers with a five-membered ring as a main repeating unit. On the contrary, their spectral patterns are completely different from those derived using lithium compounds (Figure 3A,B). It was found that *t*-BuMgCl yielded polymers with a degree of cyclization as high as 70%, while polymers derived using *t*-BuLi and *n*-BuLi as initiators do not contain any cyclic units as a repeating unit. The main chain methylene protons of poly(AMA)s obtained with lithium reagents were observed as a clean AB quartet pattern as shown in enlarged scale in Figure 3A,B. This result led us to the conclusion that AMA initiated with lithium reagents formed highly isotactic uncyclized polymers, since this characteristic of ^{1}H NMR spectra was essentially the same as that observed for highly isotactic poly(α-(alkoxymethyl)acrylates).[6] The high isotacticity of poly(AMA)s obtained with lithium compounds was also confirmed by the absorption due to a carbonyl carbon in ^{13}C NMR spectra (Figure 4). Its sharp singlet was considered to be an evidence for the high isotacticity of poly(α-(alkoxymethyl)acrylates).[6] The carbonyl carbons of poly(AMA)s prepared with lithium compounds are detected as a sharp singlet, while those formed with *t*-BuMgCl and AIBN have broader absorption with complex spectral patterns. The strong intra- and intermolecular coordination powers of the polar groups of a growing polymer chain end and α-(alkoxymethyl)acrylate monomer to the countercation (Li$^+$) have been attributed to the main factor controlling the stereochemistry of the polymerizaton.[6]

Results of the polymerizations of ABA indicate that ester substituents also influence strongly the polymerization procedures of these monomers. Bulky ester *tert*-butyl group retards considerably its polymerization. Further, the effect of the initiators on its polymerizations is somewhat different from that observed in the polymerizations of AMA. *n*-BuLi is the least effective initiator for ABA while it was the most effective one for AMA. The polymerization tendency of AMA and ABA initiated with lithium reagents is considered to be determined by how steric factor influences the initiation, propagation, and side reactions during their polymerizations.

^{1}H NMR spectra of poly(ABA) obtained with *t*-BuMgCl and lithium compounds were found to be substantially the same as those of poly(ABA) obtained through a radical mechanism (Figure 1C), which indicates formation of polymers with a high degree of cyclization with a five-membered ring as a repeating cyclic unit irrespective of the initiators employed. This is the most characteristic feature of the anionic polymerization behavior of ABA which differs from that of AMA.

Radical and Anionic Polymerization of PRA. Since polymerization behavior of AMA and ABA changes significantly depending on polymerization conditions, polymerizations of α-(propoxymethyl)acrylates (PRA), one of the monofunctional counterparts of ARA, were undertaken to get information on the aspect of the intermolecular coordination at the growing polymer chain end. The results obtained are given in Table 3. The polymerizations of PMA initiated with *n*-BuLi proceeded to considerably higher conversion, while only a small amount of poly(PMA) was obtained in the polymerization initiated with *t*-BuMgCl. This is in accordance with the reported results that benzyl α-(methoxymethyl)acrylate initiated with ethylmagnesium

Table 3. Radical and Anionic Polymerization of PRA

no.	PRA	initiator	temp, °C	time, h	convn, %	M_n[a]	M_w[b]/M_n
1[c,e]	PMA	*n*-BuLi	−78	48	67	49 500	2.6
2[c,e]	PMA	*n*-BuLi	−78	96	66	83 500	1.9
3[c,f]	PMA	*t*-BuMgCl	−78	96	1	4 600	7.7
4[d]	PMA	AIBN	50	6	56	267 000	1.4
5[d]	PMA	AIBN	−78	19	3	25 000	3.7
6[c]	PBA	*n*-BuLi	−78	96	*g*		
7[c]	PBA	*t*-BuMgCl	−78	96	*g*		
8[d]	PBA	AIBN	50	39	29	8 480	1.4

[a] Number-average molecular weight. [b] Weight-average molecular weight. [c] $[M]_0$, 1.0 mol/dm^3. $[I]_0$, 0.1 mol/dm^3. [d] Bulk polymerization. $[I]_0$, 6.0×10^{-2} mol/dm^3. [e] Highly isotactic. [f] Atactic. [g] Trace.

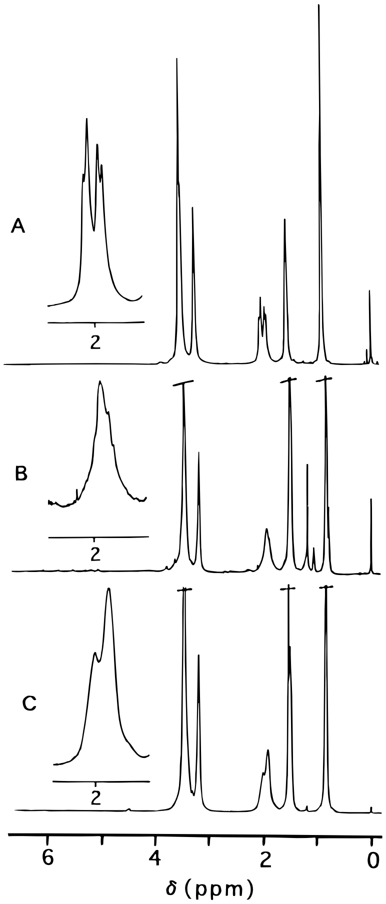


Figure 5. The 500 MHz ^{1}H NMR spectra of poly(PMA) obtained with *n*-BuLi (A) (no. 2 in Table 3), *t*-BuMgCl (B) (no. 3 in Table 3), and AIBN (C) (no. 4 in Table 3).

bromide yields substantially no polymer.[6] Low polymerizability of PBA as compared with that of ABA can be recognized from the results listed in Table 3.

^{1}H NMR spectra of poly(PMA) are illustrated in Figure 5. Poly(PMA) obtained using *n*-BuLi has a spectral pattern characteristic of poly(α-(alkoxymethyl)acrylate) with high isotacticity,[6] i.e., AB quartet of the main chain methylene protons. Its high isotacticity can also be recognized by the sharp absorption of carbonyl carbon as compared with that of radically obtained poly(PMA) (Figure 6). On the contrary, the ^{1}H NMR spectra of main chain methylene protons of poly(PMA)s obtained with *t*-BuMgCl and AIBN have essentially the same spectral pattern, which means that *t*-BuMgCl forms poly(PMA) with atactic structure. Poly(PMA) obtained through radical mechanism at −78 °C (no. 5 in Table 3) also afforded an ^{1}H NMR spectrum which is not a different pattern from that shown in Figure 6C.

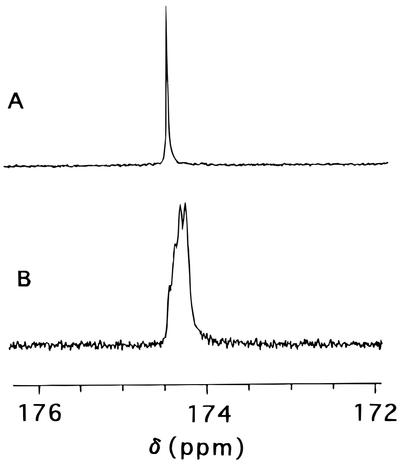


Figure 6. The 125 MHz ^{13}C NMR spectra of poly(PMA) obtained with *n*-BuLi (A) (no. 2 in Table 3) and AIBN (B) (no. 4 in Table 3).

Table 4. ^{13}C Chemical Shifts of $C_\beta H_2{=}C_\alpha <$ Carbons of Acryloyl Groups of ARA, PRA, and Related Compounds in $CDCl_3$

compd	δ_{C_β}, ppm	δ_{C_α}, ppm	$\Delta\delta$,[a] ppm
AMA	126.8	137.2	11.5
ABA	124.5	138.4	13.9
PMA	125.2	137.3	12.1
PBA	124.2	139.1	14.9
MMA	125.5	136.3	10.8
MA	115.1[b]	141.4[b]	26.3

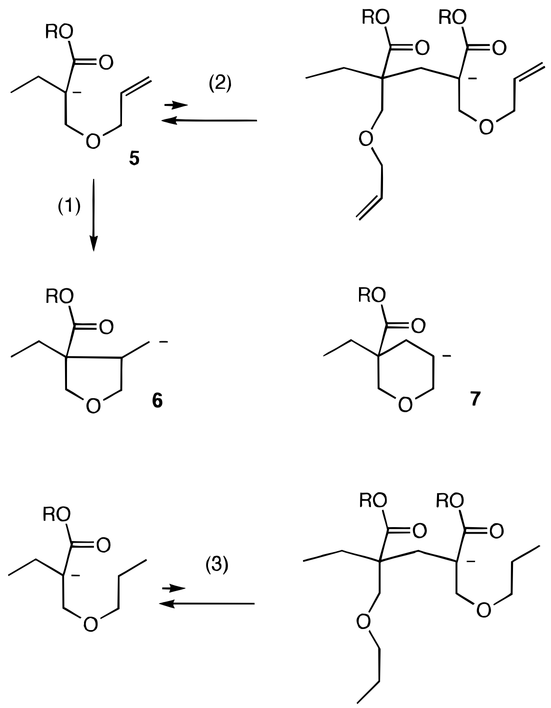
[a] $\delta_{C_\alpha} - \delta_{C_\beta}$. [b] Chemical shifts of olefin carbons of methallyl chloride (MA).

Conjugative Nature of α-Substituted Acryloyl Groups of ARA and PRA. ^{13}C chemical shifts of olefin carbons of the α-substituted acryloyl groups ($C_\beta H_2{=}C_\alpha <$) of ARA and PRA are summarized in Table 4. It has been reported that the δ_{C_α} and δ_{C_β} values shift to a higher and lower magnetic field, respectively, with a linear relationship when the *e* values of the monomers become larger with increasing electron-attracting power of substituents.[10] This means that the values, $\Delta\delta$, obtained by subtracting δ_{C_β} from δ_{C_α} reflect the influence of substituents more effectively than their respective value. The more effective the conjugation between their C═C and C═O double bonds, the smaller the value. The comparison of the values of the compounds listed in Table 4 clearly shows that the conjugative nature of the α-substituted acryloyl groups of methyl esters is as effective as that of methyl methacrylate (MMA), while that of *tert*-butyl esters is less effective. The bulky *tert*-butyl group is considered to distort the coplanarity of the C═C and C═O double bonds. A similar dependence of $\Delta\delta$ on substituents was also observed in a series of ether dimers of α-(hydroxymethyl)acrylic acid esters.[9,11] However, the conjugation of the acryloyl groups of ABA and PBA is considerably effective, judging from the $\Delta\delta$ values of these compounds and methallyl chloride (MC), the one of typical unconjugative monomers.

Discussion

The results obtained by the anionic polymerizations of AMA and ABA suggest that cyclopolymerizations proceed in the case where the countercation does not have strong interaction with the growing polymeric

Scheme 1



chain end and/or the monomer. The polymerization systems of AMA initiated with *t*-BuMgCl which yield cyclized polymers are considered not to have any such strong specific interaction in their propagating chain ends different from the polymerizations with lithium reagents. This is because poly(PMA) obtained using *t*-BuMgCl was confirmed to have an atactic structure, while PMA initiated with *n*-BuLi afforded highly isotactic polymers. The importance of strong coordination power of lithium cation for the formation of highly isotactic poly(PMA) can also be recognized by the fact that PMA polymerized with AIBN at −78 °C yielded an atactic polymer. The bulky *tert*-butyl group in ABA is supposed to interfere with the strong interaction at the growing chain end. This might be the reason cyclized polymers are formed from ABA even in the polymerization initiated with lithium compounds which yielded highly isotactic uncyclized polymers from AMA. The strong interaction of the countercation with the growing polymeric chain end and/or monomer is considered to prevent the intramolecular cyclization in the polymerizations of AMA initiated with lithium compounds.

^{13}C NMR studies on olefin carbons of the acryloyl groups of ARA and PRA revealed that the conjugations between their C═C and C═O double bonds are considerably high, especially in the case of AMA. This result leaves a question why the rather stable uncyclized propagating anion **5** (Scheme 1) derived from the α-substituted acryloyl group can attack the allyl group to form the unstable five-membered ring anion **6**. This is because the first step in the polymerization of ARA is considered to involve predominantly the α-substituted acryloyl group, judging from the reactivity of the two C═C double bonds of ARA and the detection of only allyl groups as pendant unsaturations. The fact that PRA showed extremely low polymerizability under the conditions where anionic cyclopolymerizations of ARA proceeded suggests that the mechanism for cyclization might be interpreted based on the consideration developed for the radical polymerization of unconjugated dienes, the monofunctional counterparts of which do not homopolymerize.[12]

It can be understood that intermolecular propagation (2) (Scheme 1) is difficult under the conditions where anionic polymerization of PRA does not proceed (3). The disappearance of one π-bond and the formation of one σ-bond during the intramolecular cyclization (1) can compensate for the loss of entropy in a cyclization, even if the enthalpy change derived from the transformation of one π-bond to one σ-bond cannot in intermolecular propagation reaction (2), because the entropy decrease in the former is small compared with that in the latter. The favorable enthalpy change due to the formation of a stable σ-bond is considered to compensate also for the unfavorable enthalpy change caused by the transformation from **5** to **6**. There still remains a question why the ring formed is not a six-membered anion **7** but **5**, because the former is considered to be more stable than the latter. This might be explained again in a manner similar to the mechanism for the five-membered ring formation in radical cyclopolymerizations.[8] The uncyclized propagating anions are assumed to have a favorable conformation for five-membered ring formation when the anions approach the double bonds of their own by oscillation or rotation. These considerations can also be supported by the fact that anionic cyclopolymerizations proceeded in the case where interaction at growing polymeric chain end is weak.

Specific intramolecular interaction between the propagating anion and its pendant double bond through countercation might exist in ARA, which is not in PRA because of the lack of one of two C═C double bonds in the latter. Such interaction could be the reason for the occurrence of the intramolecular cyclization reaction. However, this possibility would be small, because the cyclopolymers obtained anionically from AMA and ABA have substantially the same structure as those obtained through radical mechanism. If such intramolecular interaction exists, formation of cyclopolymers with stereospecificity would be highly expected.

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