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Polymer 44 (2003) 7113–7120

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Cyclopolymerization. Part XXXI. An attempt to control the reaction courses of the polymerizations of *N*-methyl-*N*-allyl-2-(ethoxycarbonyl)allylamine by using anionic and radical initiators

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Received 18 April 2003; received in revised form 7 August 2003; accepted 22 August 2003

Abstract

Anionic and radical polymerizations of *N*-methyl-*N*-allyl-2-(ethoxycarbonyl)allylamine (**1**) were undertaken to search the possibility for controlling the structure of the polymers therefrom. Completely cyclized polymers with a five-membered ring as a repeat cyclic unit were obtained by radical polymerizations. Anionic polymerizations by lithium compounds such as *tert*-butyl lithium and lithium 4-benzylpiperidide yielded highly isotactic uncyclized poly(**1**)s, while *tert*-butylmagnesium chloride afforded polymers with higher degree of cyclization (97%), the repeat cyclic units of which consist of a five-membered ring. The anionically obtained cyclopolymers were found to have fundamentally the same structure as those formed through a radical mechanism. These results along with those obtained from *N*-methyl-*N*-propyl-2-(ethoxycarbonyl)allylamine, one of the monofunctional counterparts of **1**, led to the conclusion that anionic cyclopolymerizations proceed in the case where interaction of a counter cation with the propagating chain end and/or the monomer is weak and the mechanism of the five-membered ring formation is essentially the same as that in the radical polymerization. On the contrary, the strong intra- and intermolecular coordination power of the amino nitrogen of a growing polymer chain end and/or the monomer to the counter cation (Li^+) have been attributed to the main factor controlling the stereochemistry leading to the highly isotactic uncyclized polymers. Polymers with six-membered rings as repeat units could not be obtained under the conditions employed. It is needed to seek an initiator that has specific interaction at a propagating chain end for the formation of six-membered rings.

Keywords: 1,6-Diene; Cyclopolymerization; Stereospecific polymerization

1. Introduction

Polymerizations of 1,6-dienes usually yield polymers with complicated structure as can be seen from their elemental reactions illustrated schematically for their radical polymerization in (1)–(5) in Scheme 1. However, if one can control these reaction courses, polymers with various structures can be obtained from one monomer. Among them, those with only a single repeat structural unit are three; one consists of a five-membered ring, another a six-membered ring, and the other an uncyclized unit. The purpose of the present investigation is to obtain the polymers with these structural characteristics by anionic and radical polymerizations of *N*-methyl-*N*-allyl-2-(ethoxycarbonyl)allylamine (**1**) (see Scheme 2). Monomer **1** has possibility to form four repeat structural units as shown in Scheme 3, since it is an unsymmetrical unconjugated diene. Radical polymerizations of **1** are expected to provide completely cyclized polymers with only five-membered rings as their repeat units. This is because repeat units of the polymers derived from radical polymerizations of *N*-methyl-*N*-allyl-2-(methoxycarbonyl)allylamine (**2**) consist of only a five-membered ring [1]. Monomer **1** was chosen instead of **2**, since it appeared that methyl (2-hydroxymethyl)acrylate, a precursor to **2**, is much more hazardous to skin than the ethyl ester, a precursor to **1**. The structure of the polymers derived from anionic polymerizations changes extensively depending on the aspect of the intermolecular coordination at a growing polymer chain end [2]. Accordingly, polymers with uncyclized units or with six-membered rings as their repeat units might be formed from **1** in its anionic polymerizations. In fact, we have already reported that methyl-2-(allyloxymethyl)acrylate (**3**) yields highly

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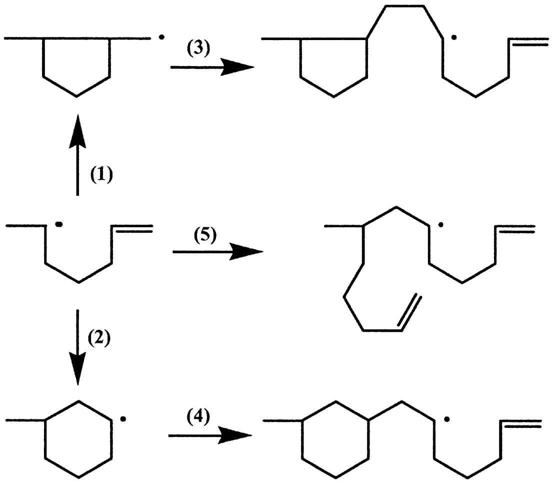
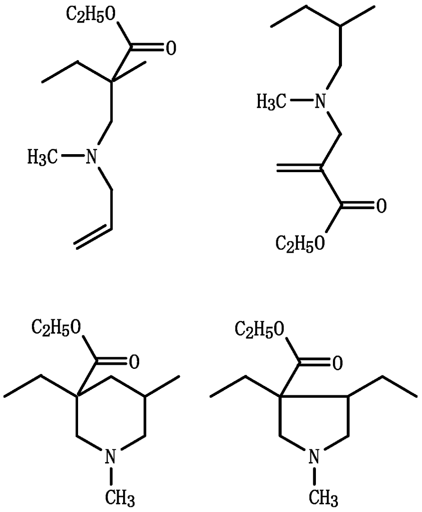
doi:10.1016/j.polymer.2003.08.034

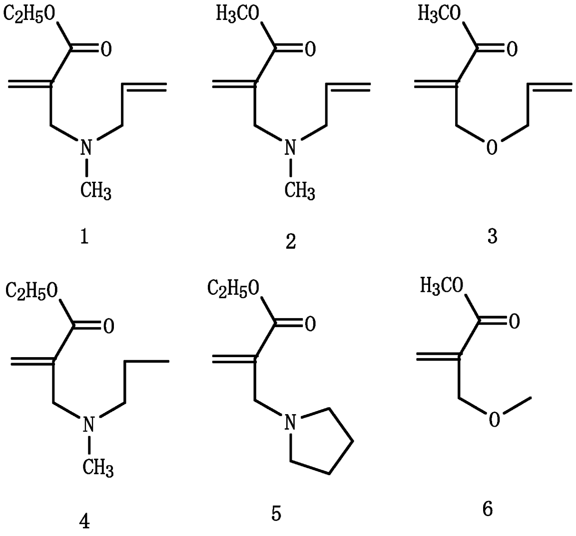


Scheme 1. Possible reaction courses for radical polymerization of 1,6-dienes.



Scheme 3. Possible repeat units of poly(**1**).

isotactic uncyclized polymers with allyloxy groups as pendant unsaturations, when it is polymerized with lithium compounds, though polymers with five-membered rings as their repeat cyclic units are formed through a radical mechanism [3]. The strong intra- and intermolecular coordination power of the ether oxygen in the allyloxy group of a growing polymer chain end to the counter cation (Li^+) have been attributed to the main factor controlling the stereochemistry of the polymerization. Polymerizations leading to the polymers with six-membered rings did not proceed in the case of **3**, though *tert*-butylmagnesium chloride (*t*-BuMgCl) afforded poly(**3**) with a high degree of cyclization [3]. Even in an anionic polymerization, polymers with only a five-membered ring were formed from **3**. Such a high tendency towards five-membered ring formation in its anionic polymerization 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. Accordingly, whether five-membered ring formation can occur or not in the anionic polymerizations of **1** is also an interesting problem, because the formation of polymers with only a five-membered ring as repeat cyclic units is expected with extremely high possibility in the radical polymerizations of **1** as mentioned above. It should be a key problem for the present investigation how the coordination power of amino nitrogen of **1** to the counter cation influences its polymerization courses. Possibility for the formation of the uncyclized polymer with α-substituted acryl groups as pendant unsaturations from **1** would be small, since allyl groups have an extremely low anionic polymerization tendency. Polymerization behavior of *N*-methyl-*N*-propyl-2-(ethoxycarbonyl)allylamine (**4**), one of the monofunctional counterparts of **1**, was also investigated to gain a deep insight into the aspect of the intermolecular coordination at the growing polymer chain end.



Scheme 2. Structural formulae of **1–6**.

2. Experimental part

2.1. Materials

Monomers **1** and **4** were synthesized by the equimolar reaction between ethyl 2-bromomethylacrylate (BMA) and *N*-methylallylamine (MA) or *N*-methylpropylamine (MP), based on the procedure reported for the synthesis of **2** [4]. Repeated distillations gave pure liquids with about 60% yields for all of them. The boiling points of **1** and **4** were observed at around 40 °C/0.15 mm Hg and 47 °C/0.4 mm Hg (not corrected), respectively. The supposed structures were confirmed by measuring NMR spectra and results of elementary analyses.

Anal. calcd for $C_{10}H_{17}NO_2$ (**1**): C, 65.63%; H, 9.28%; N, 7.64%. Found: C, 65.73%; H, 9.53%; N, 7.51%. Calcd for $C_{10}H_{19}NO_2$ (**4**): C, 64.83%: H, 10.34%; N, 7.56%. Found: C, 64.94%; H, 10.41%; N, 7.35%.

Chemical shifts of the characteristic absorption peaks of ^{1}H and ^{13}C NMR spectra of **1** and **4** are as follow. For **1**, ^{1}H NMR: $\delta = 1.31$ (t, 3H), 2.22 (s, 3H), 3.04 (s, 2H), 3.20 (s, 3H), 4.22 (q, 2H), 5.16 (m, 2H), 5.76 (s, 1H), 5.86 (m, 1H), 6.27 (s, 1H), ^{13}C NMR: $\delta = 14.2$ ($O{-}CH_2{-}\mathit{C}H_3$), 42.1 ($>\mathit{N}{-}CH_3$), 57.2 ($-O{-}CH_2{-}$), 60.7 ($>\mathit{N}{-}CH_2{-}$), 117.5 (allyl $CH_2{=}$), 126.5 (acryl $CH_2{=}$), 135.6 (allyl $-CH<$), 138.0 (acryl $-\overset{|}{\underset{|}{C}}-$), 166.9 ($>C{=}O$). For **4**, ^{1}H NMR: $\delta = 0.68$ (t, 3H), 1.08 (t, 3H), 1.29 (sext, 2H), 1.99 (s, 3H), 2.13 (t, 2H), 2.98 (s, 2H), 4.01 (q, 2H), 5.69 (s, 1H), 6.18 (s, 1H), ^{13}C NMR: $\delta = 11.3$ (propyl $CH_3{-}$), 13.7 ($\mathit{C}H_3{-}CH_2{-}O{-}$), 41.7 ($>\mathit{N}{-}CH_3$), 57.6 ($-CH_2{-}O{-}$), 59.3 ($>\mathit{N}{-}\mathit{C}H_2{-}CH_2{-}$), 60.0 ($>\mathit{N}{-}CH_2{-}C{=}$), 125.3 (acryl $CH_2{=}$), 138.1 (acryl $-\overset{|}{\underset{|}{C}}-$), 166.4 ($>C{=}O$).

BMA [5], MA [6], and MP [6] were prepared by the procedures reported.

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 *t*-BuMgCl in tetrahydrofuran, *tert*-butyl lithium (*t*-BuLi) in pentane, and *n*-butyl lithium (*n*-BuLi) in hexane (Kanto Chemicals, respectively) were used as received. Lithium 4-benzylpiperidide (BPNLi) was prepared according to the procedure reported [7]. Commercial azobis(isobutyronitrile) (AIBN) was recrystallized from ethyl alcohol. All common solvents were purified by usual methods.

2.2. Polymerization

Anionic polymerizations were carried out in toluene according to the reported procedure [3]. The precipitant used was petroleum ether, the polymerization systems of **1** and **4** 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 get concentrated solution which was poured into petroleum ether. The precipitates obtained were filtered on a sintered glass crucible. The precipitates were extracted with chloroform and reprecipitated in petroleum ether. The insoluble fractions in chloroform were assigned to lithium chloride and magnesium chloride, respectively, by comparing their IR spectra with those of authentic samples.

Radical polymerizations were performed in sealed tubes. A given amount of monomer and initiator were placed in glass ampoules, 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.

2.3. Measurements

^{1}H and ^{13}C NMR spectra were obtained at room temperature in $CDCl_3$ with tetramethylsilane as an internal standard using JEOL LA-500 (500 MHz for ^{1}H and 125 MHz for ^{13}C) FT NMR spectrometer. IR spectra were recorded on a Hitachi 260-30 IR spectrometer. Viscosities were measured in Ubbelohde viscometer at 30 °C in *N*,*N*-dimethylformamide (DMF) or in chloroform.

3. Results

3.1. Anionic and radical polymerizations of **1**

The results of the anionic and radical polymerizations of **1** are summarized in Table 1 along with those reported for **3**. They indicate strong influence of initiators on the anionic polymerization of **1**. It can be seen that *t*-BuMgCl, *t*-BuLi, and BPNLi are effective for the polymerization of **1** as in the case of **3**. However, *n*-BuLi has yielded essentially no polymer from **1**, though it is the most effective initiator for the polymerization of **3** [3]. No polymer has been obtained in the anionic polymerization of ethyl-α-(1-pyrrolidinylmethyl)acrylate (**5**) initiated with *n*-BuLi [7]. A preferential 1,2-attack (carbonyl attack) has been attributed to the most plausible side reaction that prevents the polymerization of **5**. This type of side reactions is considered to occur also in **1**. The degrees of cyclization listed in Table 1 were obtained based on ^{1}H NMR spectra shown later. They show that lithium compounds afford polymers with essentially no cyclized unit, while *t*-BuMgCl forms highly cyclized polymers. As expected from the polymerization behavior of **2**, the radical polymerizations of **1** proceeded smoothly to yield completely cyclized polymers even in a bulk polymerization that is unfavorable conditions for intramolecular cyclization. Molecular weights and their distribution of poly(**1**) obtained could not be determined by SEC as in the case of poly(**2**). For this reason, viscosities were measured to obtain information on molecular size.

3.2. ^{1}H NMR spectra of poly(**1**)

^{1}H NMR spectra of poly(**1**) obtained using various initiators are shown in Fig. 1 along with the absorption due to olefin protons of **1**. Spectra with rather complicated patterns were obtained for the polymers derived using AIBN (Fig. 1(A)) and *t*-BuMgCl (Fig. 1(B)). Their patterns are somewhat different from each other, but common characteristics can be recognized. On the contrary, these two spectral patterns are completely different from those of the polymers derived using lithium compounds (Fig. 1(C)). Comparison of the spectrum B and that of the olefin protons of **1** indicates that *t*-BuMgCl yielded highly cyclized polymers with a small amount of allyl groups as pendant

Table 1
Anionic and radical polymerizations of **1** and **3**

No.	Monomer	Initiator	Time (h)	DC[a] (%)	[η] (dl/g)	M_n[b]	M_w/M_n	Conversion (%)	Reference
1	**1**	*n*-BuLi	96	0	–	–	–	~1	This work
2	**1**	*t*-BuLi	96	0	0.19[c]	–	–	41	This work
3	**1**	BPNLi	24	0	0.31[c]	–	–	47	This work
4	**1**	*t*-BuMgCl	96	97	0.14[d]	–	–	22	This work
5	**1**	AIBN	0.8	100	0.19[d]	–	–	16	This work
6	**3**	*n*-BuLi	96	0	–	23,600	3.6	83	[3]
7	**3**	*t*-BuLi	96	0	0.13[c]	9600	2.0	22	[3]
8	**3**	*t*-BuMgCl	96	70	–	9900	4.5	17	[3]

Conditions of anionic polymerization: $[M]_0 = 1.0$ mol/l; $[I]_0 = 0.1$ mol/l; temperature, -78 °C; solvent, Toluene. Conditions of radical polymerization: $[M]_0 =$ bulk; $[I]_0 = 6.06 \times 10^{-3}$mol/l; temperature, 60 °C.

[a] Degree of cyclization.

[b] Determined by SEC (polystyrene standard, eluent: chloroform).

[c] Measured in chloroform.

[d] Measured in DMF.

unsaturations. It was found that *t*-BuMgCl formed polymers with a degree of cyclization as high as 97%, while polymers derived using *t*-BuLi and BPNLi as initiators did not contain any cyclic units as a repeat unit. These were determined based on the signal intensities of allyl methylene protons and $-OCH_2-$ protons detected at 5.1 and 4.1 ppm, respectively. The signals due to main chain methylene protons of poly(**1**)s obtained with lithium reagents are considered to be an AB quartet pattern judging from resonance peaks depicted in enlarged scale in Fig. 1(D), though the half part of its pattern is overlapped with a peak derived from $>N$-methyl protons. This result led us to the conclusion that **1** 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 polymers derived from **5** [7] and α-(alkoxymethyl)acrylates (**6**) [8].

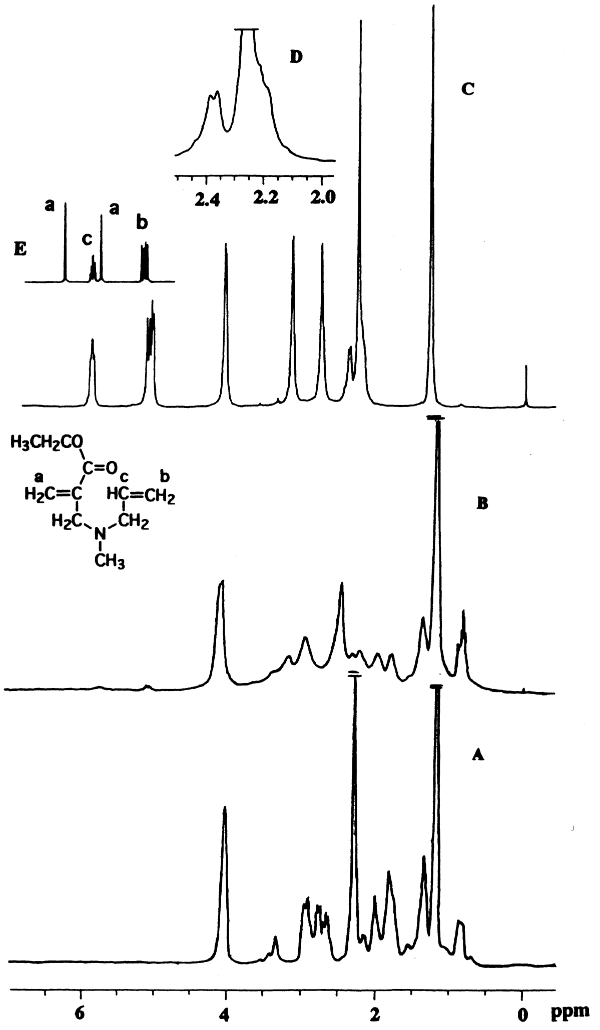


Fig. 1. ^{1}H NMR spectra of poly(**1**)s and **1**: (A) poly(**1**) (No. 5 in Table 1); (B) poly(**1**) (No. 4 in Table 1); (C) poly(**1**) (No. 3 in Table 1); (D) expanded pattern for spectrum C; (E) olefin protons of **1**.

3.3. ^{13}C NMR spectra of poly(*1*)

^{13}C NMR spectra of poly(**1**) and poly(**2**) obtained using AIBN are shown in Fig. 2. The repeat cyclic structure of poly(**2**) obtained using AIBN has been identified unambiguously as a five-membered ring by using INADEQUATE (Incredible Natural Abundance Double Quantum Transfer Experiment) NMR method [1]. These studies along with the comparison of the spectra of poly(**2**) with those of related compounds revealed that the poly(**2**) consists of two sets of five-membered rings. The main chain methylene carbons attached to the ring have a *trans* configuration for one of them and a *cis* arrangement for the other as shown in Fig. 2(A). The spectral pattern of poly(**1**) obtained with AIBN is identical with that of poly(**2**) to every detail except for the difference due to the absorption of their ester alkyl carbons. This means that poly(**1**) has substantially the same structure as that of poly(**2**) and accordingly that repeat cyclic units of the former consist exclusively of a five-membered ring. The

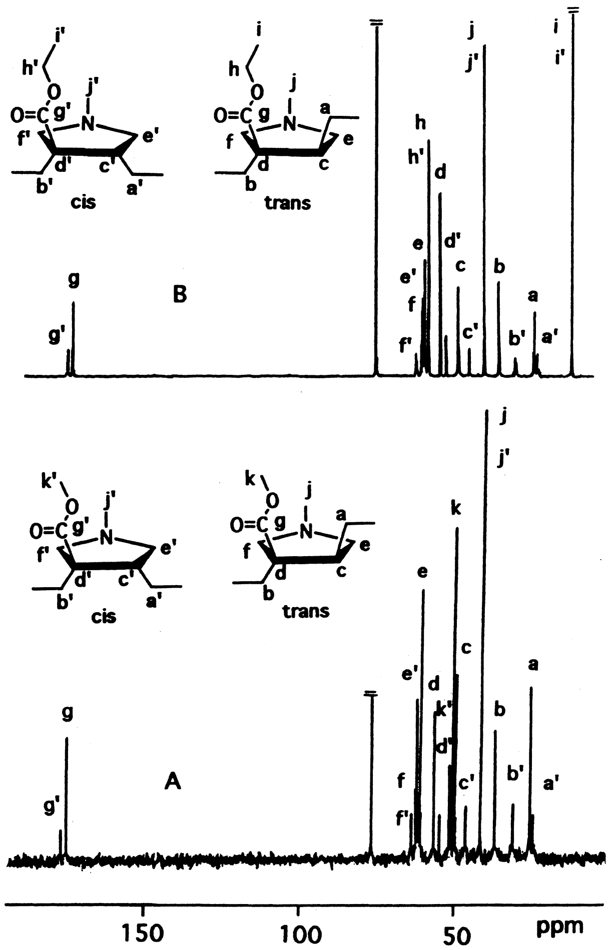


Fig. 2. ^{13}C NMR spectra of poly(**1**) (B, No. 5 in Table 1) and poly(**2**) (A, No. 6 in Table 2).

fact that every carbon other than ester alkyl carbons and >*N*-methyl carbon is detected as two absorption peaks as in the case of poly(**2**) suggests that those with stronger intensity and the other with weaker intensity are due to *trans* and *cis* forms (see Fig. 2(B)), respectively, based on the assignment reported for poly(**2**) [1].

^{13}C NMR spectra of poly(**1**) obtained using various initiators are shown in Fig. 3 together with the absorption due to olefin carbons of **1**. Comparison of the two spectral patterns of Fig. 3(A) and (B) clearly shows that peaks observed for poly(**1**) derived using *t*-BuMgCl completely coincide with those assigned to a *trans* form of poly(**1**) formed through a radical mechanism. This led us to the investigation on temperature effect on the polymerization initiated with *t*-BuMgCl, because it has been reported that *trans* contents in poly(**2**) increase with decreasing polymerization temperature in the radical polymerizations of **2**, and poly(**2**) formed at −78 °C consists almost exclusively of a *trans* form [1]. The results obtained are compared in Table 2 with those reported for the radical polymerizations of **2**. They indicate that *trans* contents in poly(**1**) increase with decreasing temperature as in the case of the radical polymerization of **2**.

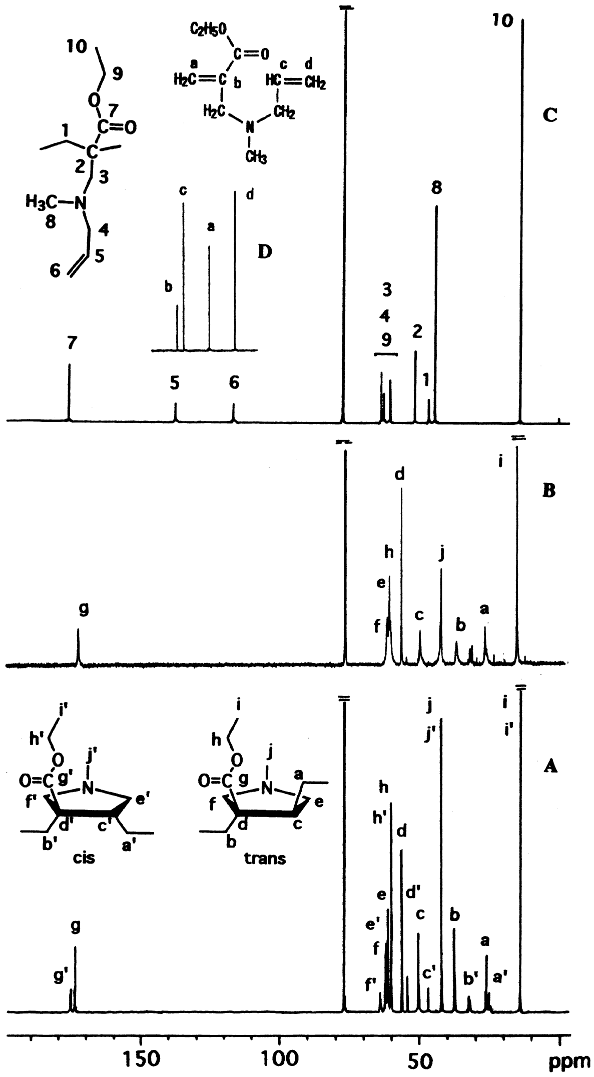


Fig. 3. ^{13}C NMR spectra of poly(**1**)s obtained with AIBN (A, No. 5 in Table 1), *t*-BuMgCl (B, No. 4 in Table 1), BPNLi (C, No. 3 in Table 1), and olefin protons of **1** (D).

On the contrary, the spectral patterns of poly(**1**) obtained with lithium compounds are completely different from those derived using AIBN and *t*-BuMgCl. A typical example is shown in Fig. 3(C). The presence of pendant allyl groups can be confirmed by the comparison of the spectrum with that of olefin carbons of **1** (Fig. 3(D)). The other signals can be assigned as indicated in Fig. 3(C) and accordingly, the conclusion can be drawn that polymers with no cyclic repeat units are formed through the anionic polymerization initiated with lithium compounds. A characteristic feature of the spectrum is that all the absorption peaks are observed as sharp singlet. Appearance of carbonyl carbons in ^{13}C NMR spectrum of poly(**5**) and poly(**6**) as sharp singlet was regarded as an evidence for their high isotacticity [7,8]. The carbonyl carbons of poly(**1**) prepared with lithium compounds are detected as sharp singlet, while those formed with *t*-BuMgCl have broader absorption (Fig. 4). This must be an additional evidence that supports the high isotacticity

Table 2
Anionic polymerizations of **1** and radical polymerizations of **2** at various temperatures

No.	Monomer	Temperature (°C)	$[M]_0$ (mol/l)	Time (h)	DC[a] (%)	*trans/cis*[b]	$[\eta]$[c] (dl/g)	Conversion (%)	Reference
1	**1**	−78	1.0	96	97	100/0	0.14	22	This work
2	**1**	−30	1.0	24	~100	87/13	0.23	54	This work
3	**1**	0	1.0	24	99	79/21	0.17	57	This work
4[d]	**2**	−78	2.32	6	100	90/10	–	2	[1]
5	**2**	0	Bulk	5	100	83/17	–	20	[1]
6	**2**	60	Bulk	0.7	100	72/28	0.28	21	[1]
7	**2**	120	Bulk	0.7	100	67/33	–	9	[1]
8	**2**	180	Bulk	0.07	100	66/34	–	15	[1]

$[t-\text{BuMgCl}]_0 = 0.1$ mol/l; solvent, toluene. $[\text{AIBN}]_0 = 6.06 \times 10^{-3}$ mol/l.

[a] Degree of cyclization.

[b] Ratio of peak area of the *trans* isomer to that of the cis isomer.

[c] Measured in DMF.

[d] $[\text{AIBN}]_0 = 0.112$ mol/l; Solvent, DMF.

of poly(**1**) obtained with lithium compounds. The strong intra- and intermolecular coordination power of the amino nitrogen and ether oxygen of a growing polymer chain end and/or a monomer to the counter cation (Li^+) have been attributed to the main factor controlling the stereochemistry of the polymerizations of **5** and **6**, respectively [7,8]. The results of the anionic polymerizations of **1** indicate that the nitrogen atom of the amino methyl group has also strong coordination power to the Li^+ counter cation.

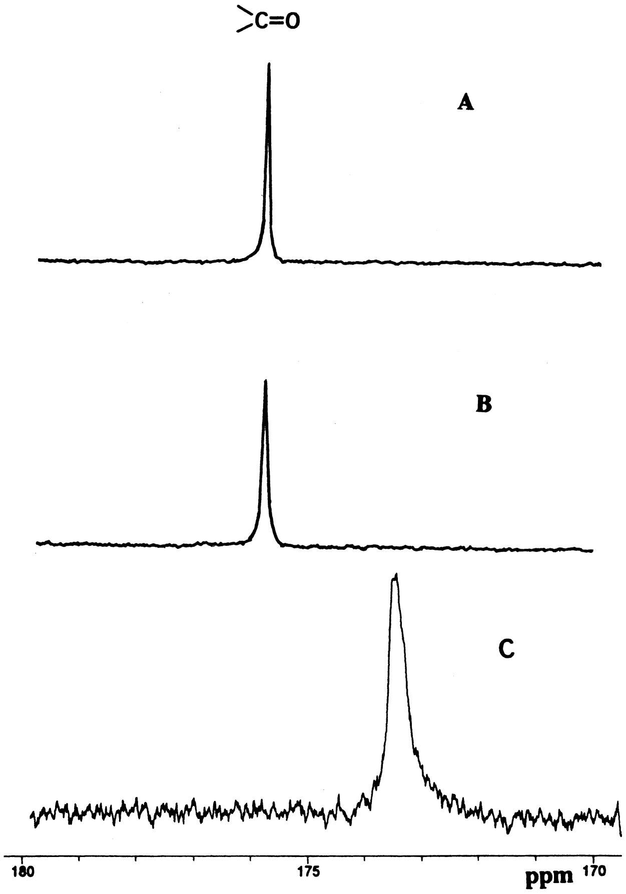


Fig. 4. ^{13}C NMR spectra of the carbonyl carbon in poly(**1**) obtained with *t*-BuLi (A, No. 2 in Table 1), BPNLi (B, No. 3 in Table 1), and *t*-BuMgCl (C, No. 4 in Table 1).

3.4. Anionic polymerization of 4

Since anionic polymerization behavior of **1** changes significantly depending on polymerization conditions, polymerizations of **4** 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. Among the lithium compounds employed, *n*-BuLi was found to be ineffective for the polymerizations of **4** as in the case of **1**. The viscosity value of the product obtained with *t*-BuMgCl suggests that it is a considerably low molecular weight compound.

^{1}H NMR spectrum of poly(**4**) obtained using *t*-BuLi is shown in Fig. 5(A). A clear AB quartet pattern of the main chain methylene protons, which is a characteristic of poly(**5**) and poly(**6**) with high isotacticity [7,8], is not observed in this spectrum (Fig. 5(B)). However, the sharp absorption of carbonyl carbon of poly(**4**) (Fig. 6(B)) suggests that it has considerably high isotacticity. BPNLi has also yielded poly(**4**) with similar spectral characteristics, though its spectra are not shown. ^{1}H NMR spectrum of the lower molecular weight product derived from **4** using *t*-BuMgCl is substantially different from that of poly(**4**) obtained with

Table 3
Anionic polymerizations of **4**

No.	Initiator	Time (h)	Conversion (%)	$[\eta]$[a] (dl/g)
1	*n*-BuLi	96	~1	–
2	*t*-BuLi	96	20	0.12
3	BPNLi	48	60	0.19
4	*t*-BuMgCl	96	19	0.04

$[M]_0 = 1.0$ mol/l; $[I]_0 = 0.1$ mol/l; temperature, −78 °C; solvent, toluene.

[a] Measured in chloroform.

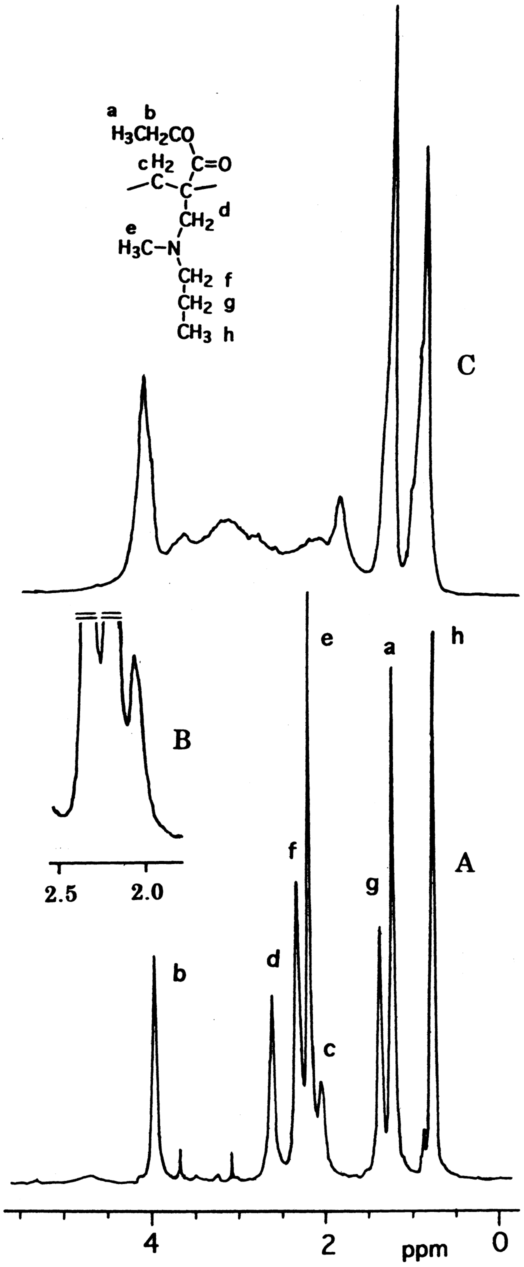


Fig. 5. ^{1}H NMR spectra: (A) poly(**4**) obtained with *t*-BuLi (No. 2 in Table 3); (B) expanded pattern for spectrum A; (C) a reaction product from **4** initiated with *t*-BuMgCl (No. 4 in Table 3).

lithium compounds (see Fig. 5(C)). In addition, broad and complicated absorption pattern was observed for carbonyl carbon as shown in Fig. 6(B). These results suggest that attempted polymerizations of **4** by *t*-BuMgCl proceed with various side reactions to yield low molecular weight compounds with complicated structures.

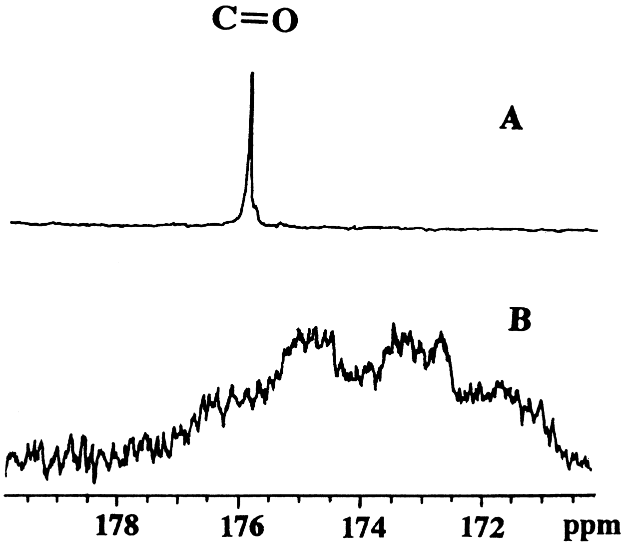


Fig. 6. ^{13}C NMR spectra of the carbonyl carbon in poly(**4**)s obtained with *t*-BuLi (A, No. 2 in Table 3) and *t*-BuMgCl (B, No. 4 in Table 3).

3.5. Conjugative nature of α-substituted acryloyl groups of *1* and *4*

^{13}C chemical shifts of olefin carbons of the α-substituted acryloyl groups ($C_\beta H_2{=}C_\alpha <$) of **1** and **4** 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 [9]. This means that the more effective the conjugation between their C=C and C=O double bonds, the smaller the value, $\Delta\delta$, obtained by subtracting δ_{C_β} from δ_{C_α}. 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 **1** and **4** is as effective as that of methyl methacrylate (MMA).

4. Discussion

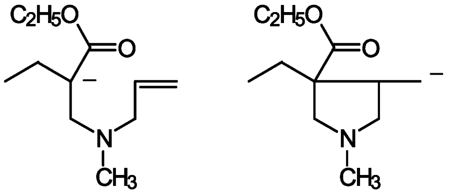
The results obtained by the anionic polymerizations of **1** suggest that cyclopolymerizations proceed under the conditions, where the counter cation does not have strong interaction with the growing polymeric chain end and/or the monomer. The polymerizations initiated with *t*-BuMgCl are the case. This is because the structural characteristics of poly(**1**) obtained by the system and those of poly(**1**) formed through a radical mechanism are essentially the same. For example, almost completely cyclized polymers with a

Table 4
^{13}C chemical shifts of $C_\beta \mathbf{H}_2{=}C_\alpha <$ carbons of acryloyl groups of **1**, **4**, and related compounds in $CDCl_3$

Compounds	δ_{C_β} (ppm)	δ_{C_α} (ppm)	$\Delta\delta^a$ (ppm)
1	126.5	138.0	11.5
4	125.3	138.1	12.8
3	126.8	137.3	11.5
MMA^b	125.5	136.3	10.8
MA	115.1^c	141.4^c	26.3

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

five-membered ring as a repeat cyclic unit are obtained for both the systems. Furthermore, the proportion of *trans* to *cis* contents in poly(**1**) formed with *t*-BuMgCl increases with decreasing polymerization temperature in a similar manner to poly(**2**) obtained with AIBN. Formation of highly cyclized polymers from **1** initiated with *t*-BuMgCl can be understood under the light of the principle developed for the monomer design for the synthesis of highly cyclized polymers. It states that bifunctional monomers, the monofunctional counterparts of which do not polymerize are likely to give rise to highly cyclized polymers, if they can be polymerized at all [10]. The validity of the principle has been established by the polymerizations of various bifunctional compounds [11]. Monomer **4**, one of the monofunctional counterparts of **1**, yielded only a low molecular weight compound with an unknown structure, when it was initiated with *t*-BuMgCl. *N*-Methyl-*N*-allyl-2-(ethoxycarbonyl)propylamine, the other monofunctional counterparts of **1**, would have essentially no polymerization tendency, since extremely low anionic polymerizability of allyl compounds are well-known. This means that both the monofunctional counterparts of **1** have a lower homopolymerization tendency, which satisfies the conditions for the formation of highly cyclized polymers. However, one may doubt why the rather stable uncyclized propagating anion **7** (Scheme 4) derived from the α-substituted acryloyl group can attack the allyl group to form the unstable five-membered ring anion **8**. This is because ^{13}C NMR studies on the olefin carbons of the acryloyl groups of **1** and **4** revealed that the conjugations between their C=C and C=O double bonds are considerably effective. The first step in the polymerization of **1** is considered to involve predominantly the α-substituted acryloyl group, judging from its conjugative nature. In fact, only allyl groups were detected as a pendant unsaturation. We do not have a clear answer to the question, but conformational effect is considered to play the most important role in the cyclization reaction as in the case of radical cyclopolymerizations. A series of studies has been undertaken on the anionic polymerizations of unconjugated dienes that form highly cyclized polymers with five-membered rings as their repeat cyclic units in their radical polymerizations. The monomers investigated are *N*-methyldimethacrylamide [12,13], *N*-tert-butyl-*N*-allylacrylamide [14], and **3** [3]. Interestingly, polymers with five-membered rings are formed from all these monomers even in their anionic polymerizations in the case where cyclopolymerization proceeds. These results suggest that the uncyclized propagating anions are assumed to have favorable conformation for five-membered ring formation when the anions approach the double bonds of their own by oscillation or rotation. To obtain polymers with six-membered rings as repeat units, it is suggested that one must seek an initiator that has specific interaction at the propagating chain end for the formation of six-membered rings.



7 **8**

Scheme 4. Propagating anions of **1**.

In the case of polymerizations of **1** initiated with lithium compounds, the strong interaction of the counter cation with the growing polymeric chain end and/or the monomer is considered to prevent the intramolecular cyclization reaction to form uncyclized polymers. Monomer **1** that has an $>N$-methyl group instead of ether oxygen of **3** exhibited almost the same anionic polymerization behavior except for the activity of *n*-BuLi. This indicates that the nitrogen atom of the amino methyl group of **1** has similar coordination power to ether oxygen of **3** and **6** toward lithium cation.

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