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Cyclopolymerization
XXVI. Repeating unit structure of cyclopolymers derived from *N*-substituted-*N*-allyl-2-(methoxycarbonyl)allylamines and mechanism of intramolecular cyclization

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Abstract

NMR studies on completely cyclized polymers derived from *N*-substituted-*N*-allyl-2-(methoxycarbonyl)allylamines (**1**) were undertaken to determine the repeat cyclic unit. NMR techniques employed are two-dimensional INADEQUATE (Incredible Natural Abundance DoublE QUAntum Transfer Experiment), DEPT (Distortion Enhancement by Polarization Transfer) measurements, and those under suppressed nuclear Overhauser effect. These studies along with the comparison of the spectra of poly(**1**) with those of related compounds revealed that the poly(**1**) consists of two sets of five-membered rings. The main chain methylene carbons attached to the ring has a *trans* configuration for one of them and a *cis* arrangement for the other. The former was found to be a main component. The value 4.5 kJ/mol as the difference of the activation energy for the formation of the respective configuration, $E_{cis} - E_{trans}$, was obtained by the investigation of temperature effect. Comparison of these results with those reported so far for polymers with similar structures led to the conclusion that five-membered ring formation could be interpreted by a kinetic mechanism as in the radical cyclization reactions in low molecular weight compounds. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Radical cyclopolymerization; Repeat cyclic unit; Intramolecular cyclization

1. Introduction

Polymers derived from radical cyclopolymerizations of 1,6-dienes have two possible repeating cyclic structures, five- and six-membered rings. A six-membered ring and its radical formed during the propagation could be more stable than a five-membered ring and its radical, respectively. However, a five-membered ring is found quite often as a repeating unit in the polymers derived from 1,6-dienes [1]. Therefore, there has been a discussion why a less stable five-membered ring is formed, but no conclusive mechanism has been found to elucidate the structural characteristics [1,2]. This indicates that much more knowledge is needed on the correlation between monomer and polymer structures to get comprehensive understanding on the mechanism of the intramolecular cyclization. These considerations led us to the structural investigations on polymers derived from *N*-substituted-*N*-allyl-2-(methoxycarbonyl)-allylamines (**1**) (see Fig. 1).

They are unique compounds, as they polymerize very rapidly despite the fact that both the monofunctional counterparts are considered to have extremely low homopolymerizability [3,4]. In fact, no homopolymerization tendency of *N*-substituted-*N*-propyl-2-(methoxycarbonyl)allylamines was confirmed and extremely low homopolymerizability of allyl compounds, which correspond to the other monofunctional counterparts of **1** is well known. Further, they yield completely cyclized polymers even in a bulk polymerization which is unfavorable conditions for intramolecular cyclization. The mechanism of the unique polymerization of **1** has already been discussed in detail in the previous papers [3,4]. However, the determination of their repeating cyclic units have remained unsolved. The recent development on the synthetic route to α-substituted acrylates [5] opened the ways to the cyclopolymerizations of a variety of 1,6-dienes with 2-substituted allyl groups, and fortunately, the repeat structural units of the polymers obtained therefrom have been determined [2,6]. This suggests that the comparison

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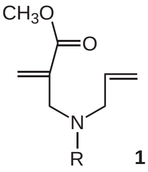


1	R
1a	CH_3
1b	$CH_2CH_2CH_3$
1c	$C(CH_3)_3$

Fig. 1. Structural formula of **1**.

of the structure of poly(**1**) and those derived from 1,6-dienes with 2-substituted allyl groups might provide us with valuable information on the mechanism for their intramolecular cyclizations.

2. Experimental

2.1. Materials

Monomers **1** were synthesized by the equimolar reaction between methyl α-(bromomethyl)acrylate (BMA) and corresponding amines [3,4]. Methyl α-[(allyloxy)methyl]-acrylate (**4a**) was synthesized by the reactions between BMA and allyl alcohol according to the procedure reported for the synthesis of ethyl α-[(allyloxy)methyl]acrylate (**4b**) [2].

BMA was prepared by the reported procedure [5].

Commercial 2,2′-azobisisobutyronitrile (AIBN) was recrystallized from ethyl alcohol. Cumene hydroperoxide (CHPO) was used as received. All common solvents were purified by the usual methods.

2.2. Polymerization

Polymerizations were performed in sealed tubes. A given amount of monomer and initiator (and *N*,*N*-dimethylformamide or toluene when polymerized in solution) 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. Polymerizations at 60°C and above 100°C were initiated with AIBN and CHPO, respectively. Polymerizations at 0°C and −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(**1**) and poly(**4a**) were petroleum ether and hexane, respectively. Poly(**1**) were reprecipitated from benzene solution into petroleum ether and finally freeze-dried from benzene solution. Poly(**4a**) was reprecipitated from chloroform solution into hexane to obtain pure polymers.

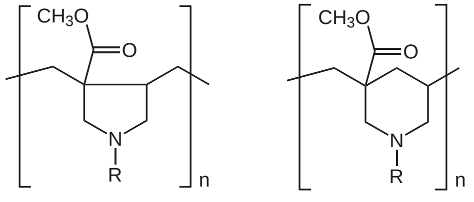
2.3. Measurements

^{1}H (500 MHz) nuclear magnetic resonance (NMR) and ^{13}C (125 MHz) NMR spectra were taken on a JEOL JNM-LA-500 FT NMR spectrometers using $CDCl_3$ and tetramethylsilane as solvent and internal standard, respectively. The two-dimensional (2D) INADEQUATE (Incredible Natural Abundance DoublE QUAntum Transfer Experiment) measurements were performed using the JEOL PFG-INADEQUATE pulse program on a JNM-α-500 FT NMR. spectrometer equipped with a NALORAC {X}-H probe and a pulse field gradient apparatus without spinning a sample. The pulse sequence [PD–90°–τ–180°–τ–90°–Δ–135°–acquire–SL1,SL2] was used. Experimental parameters were as follows: the 90° pulse width was 10.00 μs, the echo delay τ was 7.14 ms (corresponding to a ^{13}C– ^{13}C coupling of 35 Hz), the incremental delay Δ was 62.5 μs, the acquisition time was 256 ms, the purge pulses SL1 and SL2 were 1 and 0.5 ms, respectively. Gradient pulse with half sine wave of 1 ms width was applied. Intensities of field gradients, G1 and G2, were 12 and 24 G/cm, respectively. The number of increments in the F1 domain was 128, and the number of scans per FID was 3548. WAUGH decoupling was used during data acquisition in the F2 domain. The pulse delay time PD was 1.092 s. The sweep width in the F2

Table 1
Polymerizations of **1** and **4a**[a] at 60°C

No.	Monomer	$[M]_0$ (M)	$[AIBN]_0$ (M × 10^3)	Time (h)	DC[b] (%)	$[\eta]$[c] (dL/g)	Conversion (%)
1[d]	**1a**	Bulk	6.06	0.7	100	0.28	20
2[e]	**1b**	Bulk	28.0	0.5	100	0.14	15
3[e]	**1c**	Bulk	28.0	4	100	0.16	78
4[f]	**4a**	1.0	1.0	24	98		100

[a] Methyl α-[(allyloxy)methyl]acrylate.
[b] Degree of cyclization.
[c] Measured in *N*,*N*-dimethylformamide at 30°C.
[d] Quoted from Ref. [3].
[e] Quoted from Ref. [4].
[f] Polymerized in toluene solution at 70°C. Quoted from Ref. [10].



R = CH_3, $CH_2CH_2CH_3$, $C(CH_3)_3$

Fig. 2. Possible repeating cyclic units of poly(**1**).

domain was 64 ppm, which encompassed the spectral region of interest.

3. Results

3.1. ^{13}C NMR studies on poly(**1a**)

Poly(**1**) obtained under the conditions given in Table 1 were employed for this NMR study. Formation of completely cyclized polymers from **1** was concluded in the previous papers, [3,4] as any absorption due to pendant unsaturations could not be detected in the ^{1}H NMR spectra of poly(**1**). This indicates that the possible main chain structure of poly(**1**) is either of a five- or six-membered ring or the mixture of them (Fig. 2).

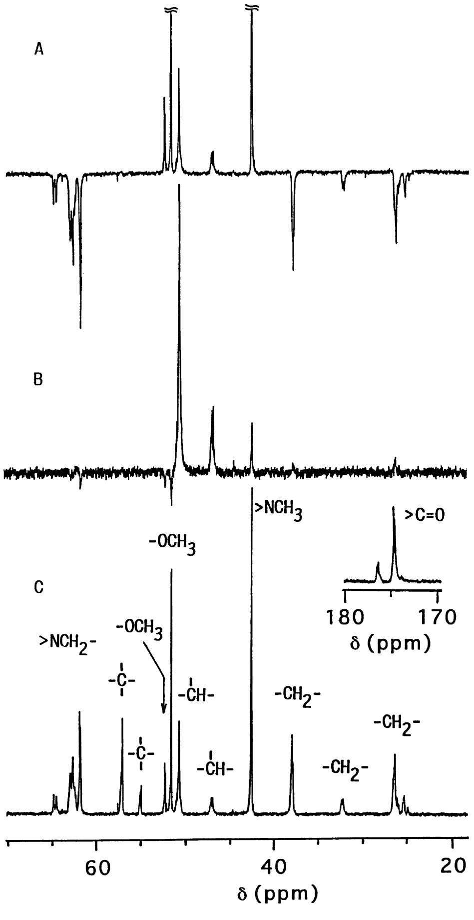


Fig. 3. ^{13}C NMR spectra of poly(**1a**) (No. 1 in Table 1). (A) DEPT spectrum measured under the conditions where CH_3 and CH carbons are detected upwards and CH_2 carbons downwards, (B) DEPT spectrum measured under the conditions where only CH carbons are detected, (C) proton noise decoupled spectrum.

DEPT (Distortion Enhancement by Polarization Transfer) measurements of poly(**1a**) under the conditions where methyl and methine carbons appear upwards and methylene carbons downwards afforded the spectrum shown in Fig. 3(A). The spectrum illustrated in Fig. 3(B) was obtained under the conditions where only methine carbons can be detected. Complete disappearance of the methyl and methylene carbons could not be attained as can be seen from the spectrum of Fig. 3(B), but comparison of these spectra allows the assignment of the respective absorption signal of poly(**1a**) as noted in Fig. 3(C). The primary carbon observed at 42.4 ppm can be assigned to a *N*-methyl carbon and absorption due to methyl carbons detected at 51.1 and 51.4 ppm to a methoxy carbon, based on the reported results for carbons with similar structures. All the quaternary, tertiary, and secondary carbons consist of two peaks, one with strong intensity and the other with weak intensity, as in the signals due to the methoxy carbon. Peaks assigned to *N*-methylene carbons are considered to consist of two strong signals overlapped with two weak signals. The chemical shifts of the two sets of the absorption are summarized in Table 2.

Two factors influence seriously on the peak intensities of ^{13}C NMR spectra. One is nuclear Overhauser effect and the other is spin–lattice relaxation time (T_1) [7]. The longest T_1 value determined using inversion recovery method [7] was 1.8 s for carbonyl and main chain quaternary carbons. ^{13}C NMR spectrum of poly(**1a**) was measured under the suppressed Overhauser effect adopting 24 s for pulse delay time which is long enough for the spins to recover. The peak intensity relative to that of the *N*-methyl carbon is given in Table 2. The ratio of the peak area with stronger intensity to that with weaker intensity is around 2.7 for all the pairs of the absorption which consist of two peaks. In addition, the peak intensity of *N*-methylene carbons is just as twice as that of the *N*-methyl carbon. This suggests that two sets of repeating ring structures exist in poly(**1a**). However, one-dimensional ^{13}C NMR does not allow further elucidation of repeating structure of poly(**1a**).

3.2. INADEQUATE studies on poly(**1a**)

The two-dimensional (2D) INADEQUATE was applied to poly(**1a**) in order to determine the ring structure. It provides the decisive structure elucidation of organic compounds in solution, as detection of double quantum coherence involving adjacent ^{13}C nuclei allows the unequivocal determination of all C,C connectivities. However, its sensitivity is the problem to be overcome. Fig. 4 shows the 2D-INADEQUATE spectrum of poly(**1a**) obtained. Each pair of connected ^{13}C nuclei forms an AX or AB spin

Table 2
^{13}C NMR chemical shifts of poly(**1a**) and peak intensities determined by the measurements under suppressed nuclear Overhauser effect

Carbon	δ (ppm)			Strong peak/Weak peak[a]
	Strong peak		Weak peak	
$-CH_2-$	26.3		25.4	73/31
$-CH_2-$	37.8		32.0	72/29
$> NCH_3$		42.4[b]		100
$> CH-$	50.6		46.7	72/28
$-OCH_3$	51.4		52.1	76/29
$> C <$	56.8		54.6	75/24
$> NCH_2-$		61.6–64.3[c]		197[d]
$> C{=}O$	174.8		176.7	84/27

[a] Ratio of peak area with strong intensity to that with weak intensity. Peak intensity was determined as relative value to that of *N*-methyl carbon, assuming the latter as 100.

[b] Observed as a singlet.

[c] *N*-methylene carbons were detected at around these values.

[d] Total intensity of *N*-methylene carbons.

system, which is found in the same frequency axis *F*1. The centers of the absorption of the pairs should fall on a diagonal line (dotted line in Fig. 4). If there exists a carbon connected to more than one carbon, the signals attributable to the carbons connected are observed at the same chemical shift in *F*2 axis, but at another double quantum frequency in *F*1 axis. This means that the carbon skeleton of the molecule under the investigation can be determined by a crisscross progression through the 2D spectrum [8].

The analysis of the 2D INADEQUATE plot illustrated in Fig. 4 clearly indicates that the set of peaks with stronger intensity were detected and they are identified unambiguously as a five-membered ring skeletal carbons. This indicates that repeating cyclic units consist mainly of a five-membered ring. The assignment for the peaks with stronger intensities in Fig. 3(C) is in good agreement with that determined by the 2D INADEQUATE measurement.

3.3. Assignment of the set of weaker peaks

The ^{13}C chemical shifts of poly(**1a**) (Fig. 3(C) and Table 2) were compared with those reported for derivatives of pyrrolidine and piperidine, five- and six-membered ring low-molecular weight model compounds, **2** and **3**, respectively (Fig. 5), [9] which are listed in Table 3. Observation of the *N*-methyl carbon of poly(**1a**) as a singlet suggests that the set of the carbons with weaker intensity is also attributable to a five-membered ring, because *N*-methyl carbons of

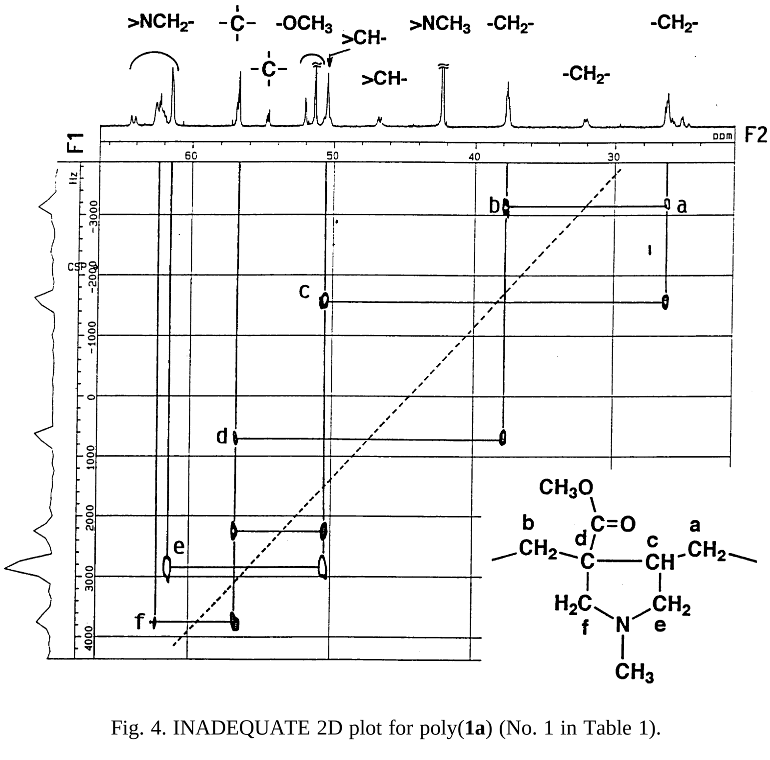


Fig. 4. INADEQUATE 2D plot for poly(**1a**) (No. 1 in Table 1).

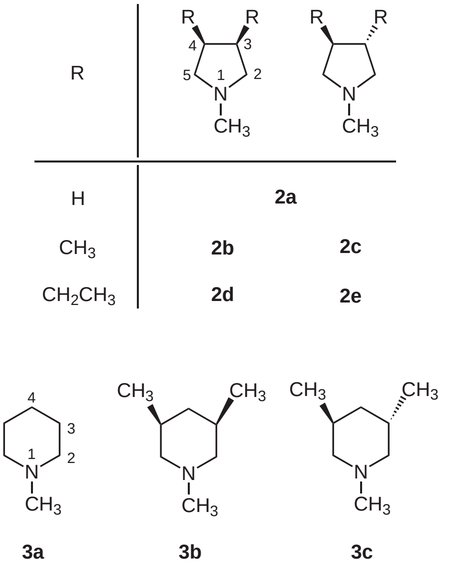


Fig. 5. Structural formula of cyclic model compounds.

2 and **3** are detected at considerably different chemical shifts. The mean values for the former and the latter listed in Table 3 are 42.6 and 46.8 ppm, respectively. The value 42.6 ppm for **2** is in good agreement with the chemical shift of *N*-methyl carbon of poly(**1a**), 42.4 ppm. The two sets of structures with a five-membered ring as a repeating unit could be attributed to configurational isomers with main chain methylene carbons attached to the five-membered ring with *trans* and *cis* arrangements as illustrated in Fig. 6(A). The one with stronger intensity in ^{13}C NMR spectrum is assigned to the *trans* isomer and the other with weaker intensity to the *cis* isomer based on the following considerations. The methylene carbons in the ethyl groups of **2e** and *C*-CH_3 carbons of **2c** are detected at lower magnetic field than those of **2d** and **2b**, respectively, while there exists essentially no change in the chemical shift of *C*-CH_3 carbons of **3b** and **3c** (Table 3). This suggests that the main chain methylene carbons with stronger intensity observed at lower magnetic field than those with weaker intensity (Table 2) can be attributable to the *trans* isomer. Tertiary carbons of **2c** and **2e** (C3 and C4 of *trans* isomers) appear at lower magnetic field than those of **2b** and **2d** (*cis* isomers), respectively. This can be additional support for the assignment, as tertiary carbons in poly(**1a**) with stronger intensity are observed at lower magnetic field than those with weaker intensity (Table 2). In the case of **3**, tertiary carbons (C3 and C5) of **3b** (*cis* isomer) are detected at lower magnetic field than those of **3c** (*trans* isomer). Further, a ^{13}C NMR study of a polymer derived from methyl α-[(allyloxy)-methyl]acrylate (**4a**), which has a structure of **1a** substituted its nitrogen by oxygen (Fig. 6(B)), also supports the conclusion. The peak assignment in Fig. 6(B) was made according to that of poly(ethyl α-[(allyloxy)methyl]acrylate) (poly(**4b**)) [10], which was established by 2D-INADEQUATE technique [2]. The fundamental concordance can be recognized between the two spectral patterns of Fig. 6. There exists a significant difference between the chemical shifts of methylene carbons (**b** and **b**$'$) connected to quaternary carbons in the two isomers of poly(**1a**), while only a small difference between those of methylene carbons (**a** and **a**$'$) connected to tertiary carbons. The former is 5.8 ppm and the latter is 0.9 ppm. This can be rationalized by considering γ-*gauche* effect as in the case of poly(**4b**). Carbon **b**$'$ is shielded more effectively than **b**, as the former is *gauche* to carbon **a**$'$, while carbons **a** and **a**$'$ are always shielded, as they are *gauche* to an ester group and carbon **b**$'$, respectively. The methylene carbons of 3,4-diethyl groups of **2d** appear at higher magnetic field than that of **2e** by 5.9 ppm. This can reasonably explain the difference of chemical shifts, 5.8 ppm, between the carbon **b** and **b**$'$ of poly(**1a**). The further fine splitting of some of the ^{13}C absorption peaks is considered to be due to difference in sequence such as *cis–cis*, *cis–trans*, and *trans–trans* as in the case of polymers derived from *N*-substituted *N*,*N*-diallylammonium salts (**6a**, see Table 6) [11].

Table 3
^{13}C chemical shifts of **2** and **3**[a]

2, **3**	C3,C4	C3,C5	*N*-CH_3	*C*-CH_3	Ethyl group	
					–CH_2–	CH_3
2a	24.2		42.1			
2b	35.3		42.6	14.4		
2c	41.7		42.6	18.8		
2d	42.9		42.9		22.4	13.1
2e	47.0		42.7		28.3	12.8
3a		26.2	46.9			
3b		31.3	46.4	19.6		
3c		27.5	47.0	19.3		

[a] Quoted from Ref. [9].

3.4. Influence of polymerization temperature on the structure of poly(1a)

If the assignment made on the ^{13}C NMR spectrum of poly(**1a**) is correct, the proportion of these two isomers is considered to change depending on polymerization temperature. This is because either of the two isomers should be more stable or one of the reaction procedures leading to these isomers is considered to be favored. Polymerizations of **1a** were carried out by changing the temperature from −78 to 180°C. Ratios of *trans* to *cis* content in the polymers formed at various temperatures are summarized in Table 4. Arrhenius plots of the ratios gave the straight line, from which the difference of the activation energies for the formation of *cis* and *trans* isomers, $E_{cis} - E_{trans}$, was obtained as 4.5 kJ/mol. The ratios of stronger peak intensities to weaker ones were always the same for all the pairs of the peaks within experimental error, when their values were compared in the polymers obtained at the same polymerization temperature. These results also support the conclusion drawn earlier that the set of peaks with stronger intensity is

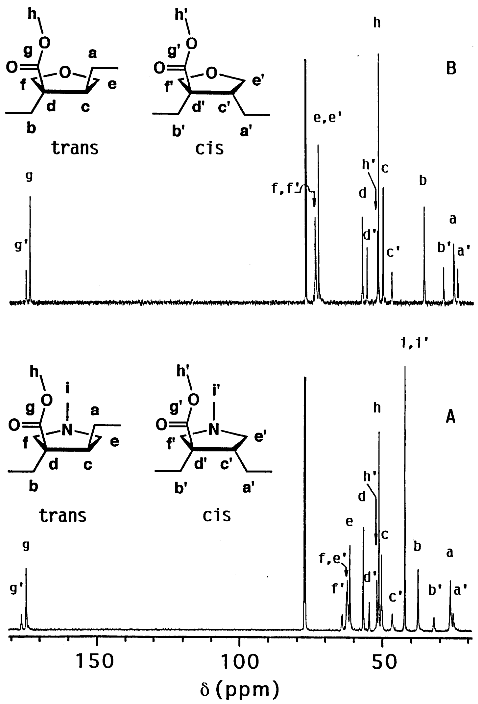


Fig. 6. Proton noise decoupled ^{13}C NMR spectra. (A) Poly(**1a**) (No. 1 in Table 1), (B) poly(**4a**) (No. 4 in Table 1).

one structural unit and that with weaker one is the other structural unit.

3.5. Structure of poly(1b) and poly(1c)

^{13}C NMR spectra of poly(**1b**) and poly(**1c**) were illustrated in Fig. 7. Their signals were assigned by comparing their spectral patterns with those of poly(**1a**). DEPT measurements also supported these assignments. Quaternary, tertiary, and main chain methylene carbons of these polymers are detected at almost the same chemical shifts as those of poly(**1a**), irrespective of the fact that bulkiness of *N*-substituents changes considerably. The peak indicated by a thick arrow in Fig. 7(C) is unknown at present, as DEPT measurements identified it as a methyl carbon. It might be attributable to methyl carbons of *tert*-butyl groups attached to some minor structural units. It can be seen that absorption due to ring methylene carbons shift to higher magnetic field as the substituents increase their bulkiness. This can be interpreted by taking the *γ-gauche* effect into considerations. These ring methylene carbons are possibly to be *gauche* to the one methylene carbon in the propyl group in poly(**1b**), while they have possibility to be *gauche* to the three methyl carbons in the *tert*-butyl group in poly(**1c**). No such carbon exists for *N*-methylene carbons of poly(**1a**). Polymers derived from **6a** have been known to yield a five-membered ring as a repeating unit. *N*-Methylene carbons of these polymers which are observed as a broad singlet shift from 62.7 to 51.8 ppm, when the *N*-substituent changes from methyl to *tert*-butyl group [11]. This result also rationalizes the rather large difference between the chemical shifts of the *N*-methylene carbons of poly(**1a**) and poly(**1c**), about 63 and 53 ppm, respectively.

4. Discussion

Much work has been reported on the radical cyclization reaction of 1-hexene derivatives which proceeds through abstraction of a hydrogen or halide atom followed by subsequent attack to a terminal double bond. A five-membered ring was found to be a main reaction product in many cases, though formation of six- and five-membered rings are possible [12]. Therefore, there has been a discussion why a more unstable five-membered ring is formed through less stable primary radicals. It is usually assumed that these reactions leading to five-membered rings are controlled by a kinetic mechanism [13,14]. However, the proportion of the five- and six-membered rings formed by these intramolecular cyclizations changes extensively depending on the substituents, especially those on olefinic double bond [12,15]. Some of the examples are shown in Table 5. Introduction of substituents on olefinic double bonds tends to favor the formation of a six-membered ring. This tendency was interpreted by taking the steric factor and stabilization of radicals into consideration [13].

The kind of atoms which constitute rings and substituents is considered to influence the ring sizes formed during cyclopolymerization. Therefore, the cyclopolymerizabilities of diallyl compounds to which **1** belong are compared in Table 6. It indicates that these 1,6-dienes tend to form a six-membered ring as a repeating cyclic unit, as substituents are introduced on olefinic double bonds. The cyclization reactions at propagating polymeric chain ends do not follow exactly the same tendency of cyclization reactions of low-molecular weight compounds. For example, the monomers **1**, **4a** and **4b** [3,10] form selectively five-membered rings during their polymerizations, though the structures of their propagating chain ends are similar to the radicals **5c**, **5e**, and **5f** in Table 5 which yield six-membered rings with considerable proportion. However, the increasing tendency for six-membered ring formation with introduction of substituents on olefinic double bonds of diallyl compounds is what has been observed in the cyclization reactions of low molecular weight compounds as mentioned before. The reason why some discrepancy exists between cyclization behavior during cyclopolymerizations and that of low molecular weight compounds is not clear at present. However, one reason might be ascribable to steric effect of a bulky polymeric chain as a substituent on the intramolecular cyclization reaction during the cyclopolymerization. Even in dimeric uncyclized radicals derived from 1,6-dienes, a substituent corresponding to R_2 or R_3 of **5** is considerably large as compared with that of **5**, which suggests the effect of remote units including penultimate, pen-penultimate, and so on on the formation of cyclic units during cyclopolymerizations. This

Table 4
Polymerizations of **1a** at various temperatures

No.	Temperature (C)	$[M]_0$ (M)	$[I]_0$ ($M \times 10^3$)	Time (h)	DC[a] (%)	Conversion (%)	*trans*/*cis*[b]
1[c]	−78	2.32	112	6	100	2	90/10
2	0	Bulk	6.06	5	100	20	83/17
3	60	Bulk	6.06	0.7	100	21	72/28
4	120	Bulk	6.06	0.7	100	9	67/33
5	180	Bulk	6.06	0.07	100	15	66/34

[a] Degree of cyclization.

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

[c] Polymerized in *N*,*N*-dimethylformamide.

steric effect might influence favorably for the five-membered ring formation. In fact, chain length dependency of reaction courses has been reported in the radical cyclopolymerization of diallyl phthalate, [19] where the ratios of the rate constants of the intramolecular cyclization to those for the intermolecular propagation of the uncyclized radical changed. These considerations suggest that intramolecular cyclizations during the cyclopolymerizations of these derivatives of diallyl compounds proceed fundamentally through the similar mechanism to the cyclization reactions of low molecular weight compounds. Thus the formation of the five-membered ring could be explained by taking a kinetic factor into considerations and six-membered ring formation by steric and stabilization factors as in the case of cyclizations in low molecular weight compounds.

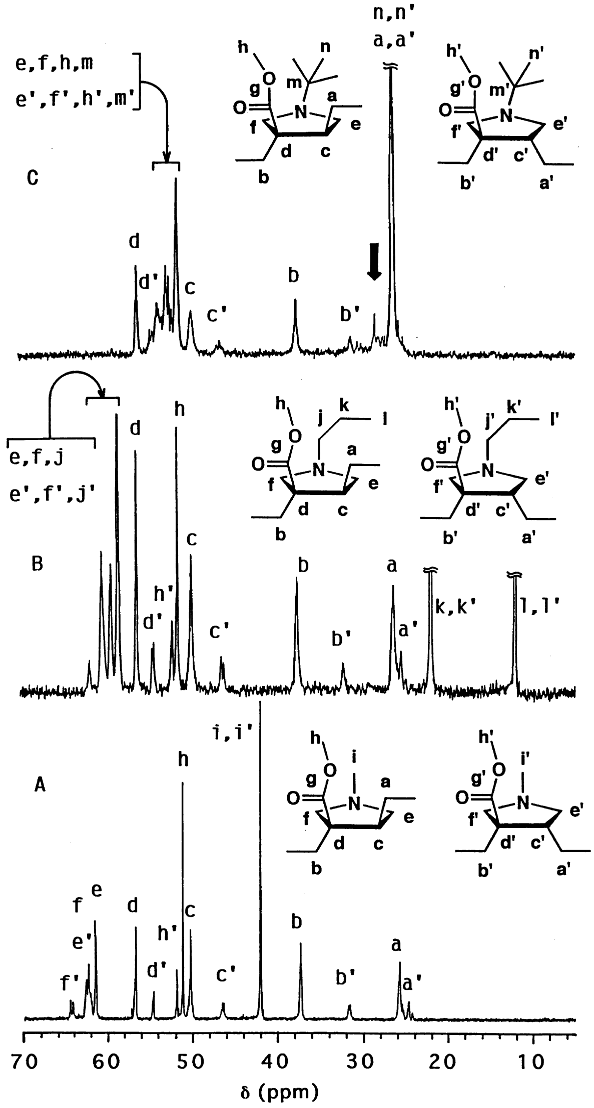
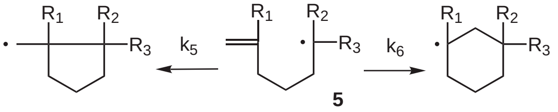


Fig. 7. Proton noise decoupled ^{13}C NMR spectra of poly(**1**). (A) poly(**1a**), (B) poly(**1b**), (C) poly(**1c**). See Table 1 for polymerization conditions.

Poly(**1**) rich with a *trans* isomer were formed and its proportion increased with the decrease of polymerization temperature. This indicates that the *trans* isomer is more stable or the reaction procedure leading to it is more favored. It has been reported that **6a** yields polymers rich with a *cis* isomer [11]. *Trans* forms are considered to be more stable in both poly(**1**) and poly(**6a**), as two polymeric chains are situated far away from each other. The presence of a carbomethoxy group in poly(**1**) is supposed to make their *trans* configurations less stable than that of poly(**6a**) because of the steric repulsion between the carbomethoxy group and a polymeric chain with *cis* arrangement to the group. On the contrary, poly(**1**) have higher content of the

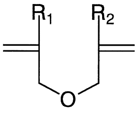
Table 5
Effect of substituents on cyclization reaction of **5**



5	R_1	R_2	R_3	k_6/k_5[a]	Reference
5a	H	H	H	<0.01	[15]
5b	H	CH_3	H	<0.03	[15]
5c	H	CH3	CH_3	0.36 ± 0.03	[15]
5d	CH_3	CH_3	CH_3	1.28 ± 0.08	[15]
5e	H	$COOC_2H_5$	H	0.79	[12]
5f	H	$COOC_2H_5$	$COOC_2H_5$	0.43	[12]
5g	H	CN	$COOC_2H_5$	1.83	[12]

[a] Ratio of the rate constant for six-membered ring and five-membered ring formation.

Table 6
Repeating cyclic units of polymers derived from various diallyl compounds



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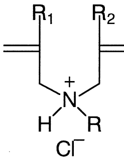

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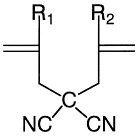

7

4, **6**, **7**	R_1	R_2	Repeating cyclic unit	Reference
4a,4b	H	COOR	5	[2], [10]
4c	COOR	COOR	6	[6]
6a[a]	H	H	5	[11]
6b[b]	CH_3	CH_3	5 and 6	[16]
7a	H	H	5	[17]
7b	COOR	COOR	6	[18]

[a] R = CH_3, $C(CH_3)_3$, C_6H_5.
[b] R = CH_3.

trans isomer and poly(**6a**) consist mainly of the *cis* isomer. A possible reason why such a difference was caused might be attributable to the fact that polymerizations of **6a** were carried out in their ammonium salts, while **1** were polymerized without neutralizing their amine groups by an acid. The ionic structure at the propagating chain end and/or at remote units in a polymeric electrolyte might influence the reaction paths or the stability of the polymeric chains. Polymerizations of **1** in their ammonium salts would be an interesting subject which should be studied in the future. Anyhow, the reported results of related compounds indicate that these reaction paths are influenced significantly by subtle changes of monomer structures. For example, poly(**7b**) consists mainly of a *cis* isomer, while poly(**4c**) contains a considerable amount of a *trans* isomer, though a six-membered ring is the repeat cyclic unit in these polymers. In addition, the difference of activation energy $E_{trans} - E_{cis}$ was estimated to be 30.1 kJ/mol for the methyl ester of **7b**, while $E_{cis} - E_{trans}$ was 2.1 kJ/mol for the *tert*-butyl ester of **4c**. In the case of **1a**, 4.5 kJ/mol is the value obtained for $E_{cis} - E_{trans}$. Limitations of available data do not allow clear explanation on what is implicated by these results.

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