

Cyclopolymerization. Part XXVII. Cyclopolymerizability of an unconjugated diene with functional groups with no homopolymerization tendency: radical polymerization of *N*-methyl-*N*-methallyl-2-(methoxycarbonyl)allylamine and structure of the polymers derived therefrom

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Abstract

Radical cyclopolymerizations of *N*-methyl-*N*-methallyl-2-(methoxycarbonyl)allylamine (**1**) were studied to see the validity of the proposal made previously. It states that the use of functional groups with a higher conjugative nature together with no homopolymerization tendency is essential for the design of 1,6-dienes with not only a high cyclization tendency but also high polymerizability. Monomer **1** was designed, since non-homopolymerizability of both the monofunctional counterparts of **1** could be assumed reasonably based on the reported polymerization behavior of compounds with similar structures. The α -substituted acryloyl group of **1** was found to have high conjugative nature and polymerizations of **1** proceeded rapidly to yield polymers with degree of cyclization of 97% even in its bulk polymerizations. The results thus obtained were fundamentally in accordance with what had been expected from the proposal. Structural studies showed that poly(**1**) consists almost exclusively of six-membered rings as repeat cyclic units. Mechanism for intramolecular cyclization during the cyclopolymerization of **1** was discussed based on the structural characteristics of poly(**1**) along with those reported for the polymers obtained from diallyl monomers. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Radical cyclopolymerization; 1,6-Diene; α -Substituted acryloyl group

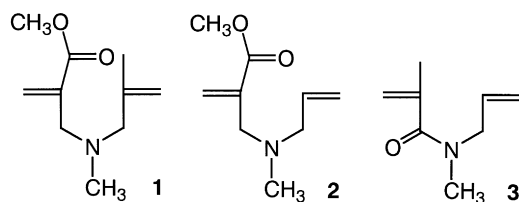
1. Introduction

It has been proposed that the bifunctional monomers, for which monofunctional counterparts do not polymerize are likely to give rise to highly cyclized polymers, if they polymerize at all [1]. The control of the degree of cyclization is the most fundamental problem with respect to the structural control in cyclopolymerization. For this reason, a series of studies on cyclopolymerizations of various 1,6-dienes have been carried out to establish the validity of the proposal for the synthesis of polymers with a high degree of cyclization [2]. However, the problem was lower polymerizability of the dienes designed under the principle. Therefore, the nature of various functional groups with low homopolymerizabilities was examined in detail and it has been proposed that the use of functional groups with a higher conjugative nature together with no homopolymerization tendency is

essential for the design of 1,6-dienes with not only a high cyclization tendency but also high polymerizability [3,4]. The purpose of this investigation is to see the validity of the proposal by comparing cyclopolymerizability of *N*-methyl-*N*-methallyl-2-(methoxycarbonyl)allylamine (**1**) (see Fig. 1) with that reported for *N*-methyl *N*-allyl-2-(methoxycarbonyl)allylamine (**2**) [3,4] and *N*-methyl *N*-allyl-methacrylamide (**3**) [5]. This is because **2** and **3** are the monomers that were synthesized and polymerized to prove the latter and former proposals, respectively. The monofunctional counterparts of **2** and **3** have extremely low homopolymerization tendencies and these two dienes yield highly cyclized polymers on polymerizations. However, the former has high polymerizability, while the latter has low. This was considered to be the consequence of the high conjugative nature of the α -substituted acryloyl group of **2** and low conjugative nature of the methacryloyl group of **3**.

Another interesting point of this study is structural investigations on repeat cyclic units of poly(**1**). The structures of

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Fig. 1. Structural formula of **1**, **2** and **3**.

the polymers derived from various diallyl compounds were compared in the previous paper [6]. It showed that the substituents on their olefinic double bonds tend to favor the formation of a six-membered ring probably due to the steric and radical stabilizing effect. Monomer **1** that has a structure with an additional methyl group on the allyl group of **2** is supposed to yield polymers with a considerable amount of a six-membered ring as a repeat cyclic unit different from poly(**2**) that consist exclusively of a five-membered ring [6], judging from the consideration made in the previous paper.

2. Experimental

2.1. Materials

Monomer **1** was synthesized by the equimolar reaction between methyl α -(bromomethyl)acrylate (BMA) and *N*-methylmethallylamine (MA) based on the procedure for the preparation of **2** [3]. Crude product obtained was subjected to repeated distillations to give pure liquid. Yield of the final stage of the synthesis of **1** was about 60% after distillations two times. The supposed structure was confirmed by NMR. The boiling point and chemical shifts of the characteristic absorption peaks of ^1H and ^{13}C NMR spectra of **1** measured in CDCl_3 are as follows. Boiling point of **1**: $40^\circ\text{C}/0.3\text{ mmHg}$. ^1H NMR for **1**: $\delta = 6.24$ (s, $\text{CH}_2=$, acryloyl), 5.80 (s, $\text{CH}_2=$, acryloyl), 4.88 (s, $\text{CH}_2=$,

methallyl), 4.84 (s, $\text{CH}_2=$, methallyl), 3.75 (s, $-\text{O}-\text{CH}_3$), 3.14 (s, $>\text{N}-\text{CH}_2-$), 2.90 (s, $>\text{N}-\text{CH}_2-$), 2.16 (s, $>\text{N}-\text{CH}_3$), and 1.74 (s, $\text{CH}_2=\text{C}(\text{CH}_3)-$) ppm. ^{13}C NMR for **1**: $\delta = 167.5$ ($>\text{C}=\text{O}$), 143.6 ($\text{CH}_2=\text{C}(\text{CH}_3)-$), 138.2 ($\text{CH}_2=\text{C} <$, acryloyl), 126.2 ($\text{CH}_2=\text{C} <$, acryloyl), 112.7 ($\text{CH}_2=\text{C}(\text{CH}_3)-$), 64.8 ($>\text{N}-\text{CH}_2-$), 57.5 ($>\text{N}-\text{CH}_2-$), 51.7 ($-\text{O}-\text{CH}_3$), 42.3 ($>\text{N}-\text{CH}_3$), and 20.6 ($\text{CH}_2=\text{C}(\text{CH}_3)-$) ppm.

MA was synthesized by the reaction between 3-chloro-2-methyl-1-propene and fourfold of *N*-methylamine in molar ratio in a mixture of solvents with tetrahydrofuran, *N,N*-dimethylformamide, and water under the presence of potassium carbonate, based on the reaction procedure reported for a similar compound [7]. After heating the reaction mixture at 55°C for 24 h, the fraction boiling at the range from 60 to 85°C was collected, which was acidified by adding concentrated hydrochloric acid to yield two separated layers. The lower layer was concentrated to a smaller volume by distilling off the fraction boiling at lower temperature than 63°C and made alkaline with 50% aqueous sodium hydroxide solution. Upper layer separated was dried over potassium hydroxide and fraction boiling at 85°C was collected. The yield was 46%. The chemical shifts of the characteristic absorption peaks of ^1H NMR spectrum of MA recorded in CDCl_3 solutions are as follows. ^1H NMR for MA: $\delta = 4.88$ (s, $\text{CH}_2=$), 4.84 (s, $\text{CH}_2=$), 3.13 (s, $>\text{N}-\text{CH}_2-$), 2.43 (s, $>\text{N}-\text{CH}_3$), 1.74 (s, $\text{CH}_2=\text{C}(\text{CH}_3)-$), and 1.57 (s, $>\text{NH}$) ppm. BMA was prepared by the reported procedure [8].

Commercial 2,2'-azobisisobutyronitrile (AIBN) was recrystallized from ethyl alcohol. 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 were placed in glass ampoules, which were then subjected to several

Table 1
Polymerizations of **1** and related compounds in bulk at 60°C

No.	Monomer	[AIBN] $_0$ ($\times 10^3\text{M}$)	Time (h)	M_n	M_w/M_n	[η] (dl/g)	DC ^a (%)	Conversion (%)	
								Pre ^b	GC ^c
1	1	112	0.3				97	22	
2	1	112	1.2	6400	2.5	0.22	97	74	
3	1	28	1					16	24
4	1	28	2					37	43
5	1	28	4	9300	2.3	0.24		71	78
6 ^d	2	112	0.3				100	80	
7 ^d	2	6	0.7			0.28	100	22	
8 ^e	3	143	15				93	35	

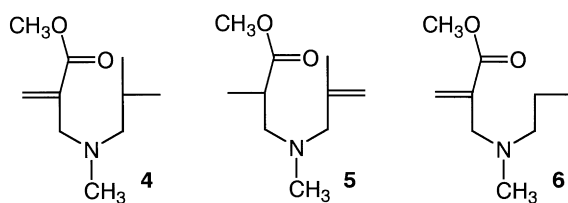
^a Degree of cyclization.

^b Determined by weight.

^c Determined by GC.

^d Quoted from Ref. [3].

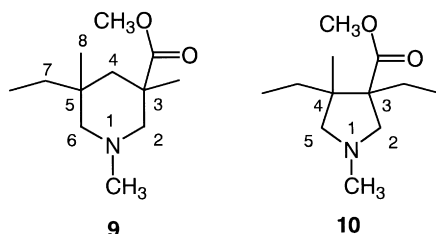
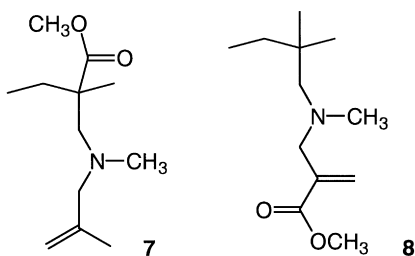
^e Quoted from Ref. [5].

Fig. 2. Structural formula of **4**, **5** and **6**.

freeze–pump–thaw cycles and sealed. After polymerization in a constant-temperature bath, the polymerization mixtures were poured into excess petroleum ether. Conversion of the monomer was calculated from the weight of the polymer along with the residual monomer concentration measured by gas chromatography (GC) with tetralin as the internal standard, since some portion of the polymers was found to be soluble in petroleum ether. The polymers were reprecipitated from benzene solution into petroleum ether and precipitates obtained were freeze-dried from benzene solution to obtain pure polymers for measurements.

2.3. Measurements

^1H NMR and ^{13}C NMR spectra were taken on a JEOL JNM-GX-270 (270 MHz for ^1H and 68 MHz for ^{13}C) or a JEOL LA-500 (500 MHz for ^1H and 125 MHz for ^{13}C) FT NMR spectrometer using tetramethylsilane as an internal standard. Size exclusion chromatography (SEC) was performed on a Shimadzu LC-10AD liquid chromatograph equipped with three polystyrene gel columns (Shodex K-804L) and ultraviolet/refractive index dual-detectors using tetrahydrofuran as eluent. A molecular weight calibration curve was obtained by using standard polystyrene. GC was carried out on a Shimadzu GC-8A gas chromatograph equipped with a silica gel column (Shimadzu DC-11).

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

Viscosity was measured using a Ubbelohde viscometer at 30°C in *N,N*-dimethylformamide.

3. Results

3.1. Polymerizations of **1**

The results of the polymerizations of **1** are summarized in Table 1. Reported results of **2** [3] and **3** [5] are also given in Table 1 for comparison. It can be reasonably assumed that both the monoene counterparts of **1**, *N*-methyl *N*-isobutyl-2-(methoxycarbonyl)allylamine (**4**) (see Fig. 2) and *N*-methyl *N*-methylallyl-2-(methoxycarbonyl)propylamine (**5**), have extremely low homopolymerizability. This is because *N*-methyl *N*-propyl-2-(methoxycarbonyl)allylamine (**6**) which have almost the same structure as **4**, have been reported to have essentially no homopolymerization tendency [3] and extremely low homopolymerizabilities of methallyl compounds is well known. Polymerizations of **1** proceeded rapidly despite these characteristics of its C=C double bonds. In addition, the poly(**1**) samples are soluble in common solvents, which suggests the formation of highly cyclized polymers. In fact, the degrees of cyclization determined based on ^1H NMR spectra were found to have the value 97% (see Section 4). That the polymerizations were carried out in bulk is an indication of how high the cyclization tendency of **1** is. These results could be an additional support for the principle for the monomer design for the synthesis of highly cyclized polymers mentioned above. However, the cyclization tendency of **1** is slightly lower than that of **2**. This is because **2** yielded completely cyclized polymers. The results summarized in Table 1 show that slower polymerizations proceed in **1** than in **2**. However, **1** polymerizes much more rapidly than **3**.

Poly(**1**) could be eluted on SEC measurements, while poly(**2**) could not be detected by either an ultraviolet or a refractive index detector [3,4]. This suggests that the adsorption behavior of these polymers is influenced strongly by a subtle structural change and information on molecular weights of the polymers of this type determined by SEC are not reliable. For this reason, viscosities were also measured for poly(**1**). Their values listed in Table 1 suggest that poly(**1**) have molecular weights comparable to those of poly(**2**).

3.2. Pendant unsaturations of poly(**1**)

The pendant unsaturations which are expected to appear in poly(**1**) are **7** and **8** shown in Fig. 3. ^1H NMR spectrum of poly(**1**) is illustrated in Fig. 4 along with absorptions due to olefin protons of **1**. Comparison of these spectra clearly indicates that poly(**1**) contains a small amount of pendant methallyl groups. Degrees of cyclization of poly(**1**) listed in Table 1 were determined based on the signal intensities of methallyl protons detected at around 4.86 ppm and the absorptions detected over the region from 4 to 0.5 ppm.

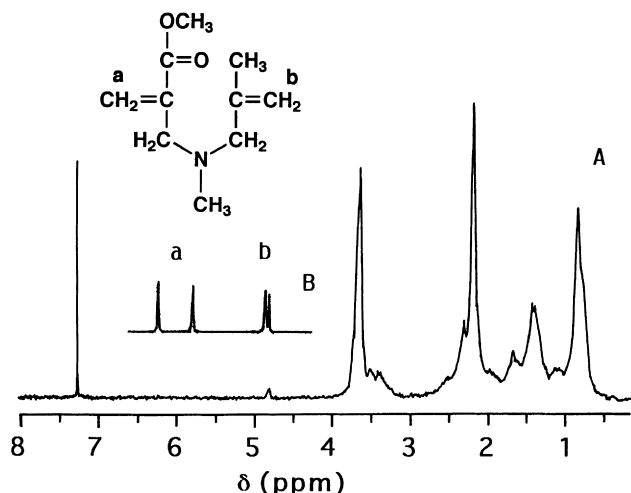


Fig. 4. 270 MHz ^1H NMR spectra of poly(**1**) and **1** measured in CDCl_3 : (A) poly(**1**) (no. 1 in Table 1); (B) **1**.

3.3. Repeat cyclic units of poly(**1**)

Extremely lower content of pendant unsaturations in poly(**1**) means that repeat units of poly(**1**) consist of structures **9** and/or **10** (see Fig. 3). A proton noise decoupled ^{13}C NMR spectrum of poly(**1**) is illustrated in Fig. 5A. DEPT

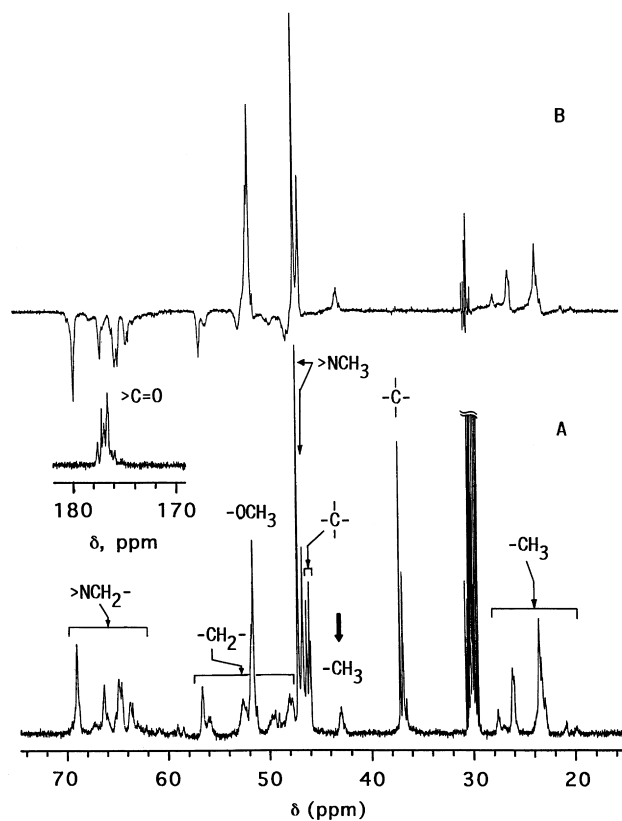


Fig. 5. 125 MHz ^{13}C NMR spectra of poly(**1**) (no. 1 in Table 1) measured in acetone- d_6 : (A) proton noise decoupled spectrum; (B) DEPT spectrum measured under the conditions where CH_3 and CH carbons are detected upwards and CH_2 carbons downwards.

Table 2

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

Carbon	Assignment ^a	δ^b (ppm)	Peak intensity ^c
– CCH_3 –	(C8)	20.0–27.5 (19.5–26.9)	0.99
> C <	(C5)	36.9 (35.9)	1.00
> C <	(C3)	46.0 (45.2)	
> NCH_3		46.6, 47.1 (46.3, 46.7)	3.00 ^d
– CH_2 –	(C4, C7)	48.0 (48.0)	
– OCH_3		51.5 (51.3)	
– CH_2 –	(C4, C7)	52.6 (51.4)	1.53 ^e
– CH_2 –	(C4, C7)	56.6 (55.7)	0.48
> NCH_2 –	(C2, C6)	63.6–68.9 (62.2–68.0)	2.02 ^f
> C=O		177.0 (176.6)	1.05

^a See **9** in Fig. 3 for the carbon number.

^b Measured in acetone- d_6 . The values in parentheses were obtained in CDCl_3 .

^c Determined as relative value to the intensity of the quaternary carbon at 36.9 ppm, assuming it as 1.00. Spectrum was measured in acetone- d_6 .

^d Total intensity of a quaternary carbon at 46.0, >*N*-methyl carbon, and a methylene carbon at 48.0 ppm.

^e Total intensity of methoxy and methylene carbons at 51.5 and 52.6 ppm.

^f Total intensity of *N*-methylene carbons.

(distortion enhancement by polarization transfer) measurements of poly(**1**) under the conditions where methyl and methine carbons appear upwards and methylene carbons downwards afforded the spectrum shown in Fig. 5B. This allows the assignment of the respective absorption signal of ^{13}C spectrum of poly(**1**) shown in Fig. 5A. The spectra measured in acetone- d_6 are well resolved as compared with those in CDCl_3 . For this reason, the former was illustrated in Fig. 5. However, the chemical shifts obtained in CDCl_3 were used for the structural analysis, since the reported spectra of model compounds that are shown in

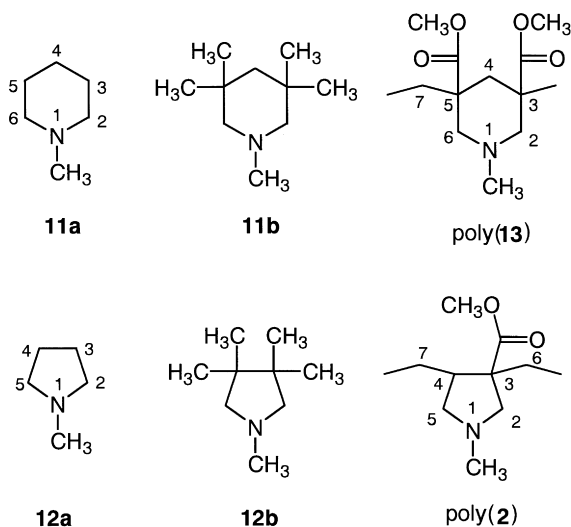


Fig. 6. Structural formula of cyclic model compounds and polymers related to poly(**1**).

Table 3
 ^{13}C NMR chemical shifts of **11**^a and poly(**13**)^b in ppm measured in CDCl_3

Compounds	C2	C3	C4	C5	C6	C7	> N-CH ₃
11a	56.7	26.2	24.3	26.2	56.7		46.9
11b	69.1	31.5	50.4	31.5	69.1		47.1
Poly(13)	59–61	~ 45	~ 45	~ 45	59–61	~ 45	~ 46

^a Quoted from Ref. [9].

^b Quoted from Ref. [7].

later section were recorded in CDCl_3 solutions. Both the chemical shifts of each carbon of poly(**1**) obtained in the two solutions were summarized in Table 2. It can be seen that there exists no significant difference between the chemical shifts obtained in the two solutions. The peaks due to the primary carbon observed at 46.3 and 46.7 ppm can be assigned to an *N*-methyl carbon and an absorption due to a methyl carbon detected at 51.3 ppm to a methoxy carbon, based on the reported results for carbons with similar structures. Thus, absorptions due to a methyl carbon observed from 19.5 to 26.9 ppm are attributable to the one on the methallyl group.

^{13}C chemical shifts reported for various compounds with *N*-methylpiperidine and pyrrolidine ring structures (see Fig. 6) are listed in Tables 3 and 4, respectively [6,7,9]. The absorptions due to *N*-methyl carbons of piperidine and pyrrolidine rings appear at considerably different chemical shifts. The former are detected at around 46.7 ppm, while the latter at around 42.4 ppm for the compounds listed in Tables 3 and 4. It is clear that these values do not depend on whether the *N*-methyl carbons are attached to low molecular weight ring structures or to repeat cyclic units of polymers, but on the size of the rings that they are linked to. These results suggest that repeat cyclic units of poly(**1**) consist almost exclusively of a six-membered ring. This is because the values 46.3 and 46.7 ppm for *N*-methyl carbon of poly(**1**) are in good agreement with the chemical shifts of *N*-methyl carbons of **11** and a polymer derived from bis(α -methoxycarbonylallyl)methylamine (**13**).

The quaternary carbon of poly(**1**) detected at around 45.2 ppm is attributable to C3 carbon of **9**, since C3 and C5 carbons of poly(**13**) are detected at around 45 ppm, while C3 carbon of poly(**2**) is observed at 54.6 and 56.8 ppm. Furthermore, the comparison of the chemical shift of the other quaternary carbon of poly(**1**) (35.9 ppm) with those of C3 and C5 of **11b** (31.5 ppm) and C3 and C4

of **12b** (44.1 ppm) suggests that the former can be attributable to the C5 carbon of **9** but not to the C4 carbon of **10**. The peak indicated by a thick arrow in Fig. 5A might be ascribed to *N*-methyl carbon of a five-membered ring, since DEPT measurements identified it as a methyl carbon and it was detected at around 42.5 ppm in CDCl_3 solution. However, its weak intensity does not allow unambiguous assignment.

Two factors influence seriously on the peak intensities of ^{13}C NMR spectra. One is the nuclear Overhauser effect and the other is the spin–lattice relaxation time (T_1) [10]. The longest T_1 value determined using a progressive saturation method was 3.2 s for the C3 carbon of **9** detected at 45.2 ppm. ^{13}C NMR spectrum of poly(**1**) 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 C5 carbon of **9** is listed in Table 2 along with the chemical shifts of each peak. It shows that the absorptions observed from 62 to 68 ppm is due to two methylene carbons, and the peaks observed at around 48.0, 51.3, 51.4 and 55.7 ppm are derived from the other two methylene carbons. The former two methylene carbons can be ascribed to those adjacent to nitrogen and the latter to C4 and C7 carbons in **9**. This is because *N*-methylene carbons are detected at lower magnetic field than methylene carbons that are sandwiched between two saturated carbons. In fact, C2 and C6 carbons of **11** and poly(**13**) are observed at lower magnetic field than their C4 carbons. The C4 and C7 carbons of poly(**1**) have definitely different ^{13}C chemical shifts from C6 and C7 carbons of poly(**2**) which have a five-membered ring as a repeat unit. The former were detected over the region from 48 to 56 ppm, while the latter from 25 to 38 ppm. This is an additional evidence for the conclusion that a six-membered ring is the repeat unit structure of poly(**1**). Observation of C4 carbons of **11b** and poly(**13**) at 50.4 and 45 ppm,

Table 4
 ^{13}C NMR chemical shifts of **12**^a and poly(**2**)^b in ppm measured in CDCl_3

Compound	C2	C3	C4	C5	C6, C7	> N-CH ₃
12a	56.3	24.2	24.2	56.3		42.1
12b	69.8	44.1	44.1	69.8		42.6
poly(2)	61.6–64.3	54.6, 56.8	46.7, 50.6	61.6–64.3	25.3–37.7	42.4

^a Quoted from Ref. [9].

^b Quoted from Ref. [6].

Table 5

^{13}C chemical shifts of $\text{C}_\beta\text{H}_2=\text{C}_\alpha <$ carbons of acryloyl groups of **1** and related compounds in CDCl_3

Compound	δ_{C_β} (ppm)	δ_{C_α} (ppm)	$\Delta\delta^a$ (ppm)
1	126.2	138.2	12.0
MMA ^b	125.5	136.3	10.8
2 ^c	126.8	137.8	11.0
3 ^d	117.3	140.8	23.5
1	112.7 ^e	143.6 ^e	30.9

^a $\delta_{\text{C}_\alpha} - \delta_{\text{C}_\beta}$.

^b Methyl methacrylate.

^c Quoted from Ref. [3].

^d Quoted from Ref. [6].

^e Chemical shifts of methallyl carbons.

respectively, and C7 carbon of the latter at 45 ppm also supports the assignment of the repeat cyclic unit of poly(**1**) to a six-membered ring, because these values are rather close to the ^{13}C chemical shifts of C4 and C7 carbons of poly(**1**). The reasons for the observation of *N*-methylene and main chain methylene carbons of poly(**1**) as multiplet are considered to be due to the unsymmetrical structure of the repeat unit. The content of a five-membered ring would be about 10%, if the assignment of the absorption observed at around 42.5 ppm to an *N*-methyl carbon of a five-membered ring is correct.

3.4. ^{13}C NMR studies of **1** and related compounds

^{13}C chemical shifts of $\text{C}=\text{C}$ double bonds ($\text{C}_\beta\text{H}_2=\text{C}_\alpha <$) of the acryloyl groups of **1** and related compounds are summarized in Table 5. δ_{C_α} and δ_{C_β} values shift to a higher and lower magnetic field, respectively, with a linear relationship when *e* values of the monomers become larger with increasing electron-attracting power of substituents [11]. This is because effective conjugation between $\text{C}=\text{C}$ and $\text{C}=\text{O}$ double bonds reduces the electron density on $\text{C}=\text{C}$ double bonds. This means that the stronger the

electron-attracting power of the substituents, the smaller the $\Delta\delta$ values, which were obtained by subtracting δ_{C_β} from δ_{C_α} values. The comparison of the values of the compounds listed clearly shows that the conjugative nature of the α -substituted acryloyl group of **1** is as high as that of MMA. Effective conjugation seems to be a common characteristic for α -substituted acryloyl groups of this type, since **2** has almost the same $\Delta\delta$ value as that of **1**. On the contrary, the chemical shifts of the methacryloyl carbons of **3** indicate that the conjugative nature of its methacryloyl group is considerably low. This result indicates the essential difference between the fundamental properties of the α -substituted acryloyl group of **1** and the methacryloyl group of **3**, despite the apparent structural similarity.

4. Discussion

High cyclization tendencies of **1** can be explained by a similar manner to the unconjugated dienes with functional groups with low homopolymerizability [1,2], as shown in Fig. 7. Since the definitely lower polymerizability of **4** has been reasonably assumed, the intramolecular cyclization of **14** (Reaction (1)) proceeds preferentially over the intermolecular propagation reaction (Reaction (2)) to form a cyclized radical **15**. The methyl group on the methallyl group seems to interfere slightly with the cyclization reaction in **1**, since **2** yielded completely cyclized polymers. Monomer **1** is considered to be incorporated into the polymeric chain at first through its acryloyl group, because its conjugative nature is higher than that of the methallyl group. For this reason, only the uncyclized propagating radical related to the α -substituted acryloyl group was considered in the reaction scheme illustrated in Fig. 7. The fact that only methallyl group was detected as pendant unsaturations in poly(**1**) supports this consideration.

The polymerization results obtained support the concept proposed in the previous papers that the use of functional groups with higher conjugative nature, along with extremely low homopolymerizability is essential for the synthesis of monomers with not only a high cyclization tendency but also high polymerizability [3,4]. This is because **1** polymerizes much more rapidly than **3** to yield highly cyclized polymers. The monomer **1** polymerizes slowly as compared with **2**. This is considered to be due to its low reactivity to the cyclization reaction (Reaction (1)). Occurrence of the intermolecular reaction leading to the sequence **16** would inevitably decrease the polymerization rate.

One of the characteristics that differentiate the polymerizations of **1** from those of **2** exists in the repeat cyclic structures of poly(**1**). Monomer **2** forms selectively polymers with five-membered rings for its repeat cyclic units [6], while **1** yields polymers that contain six-membered rings. Six-membered rings and their radicals formed during the cyclopolymerization of 1,6-dienes could be more stable than five-membered rings and their radicals, respectively.

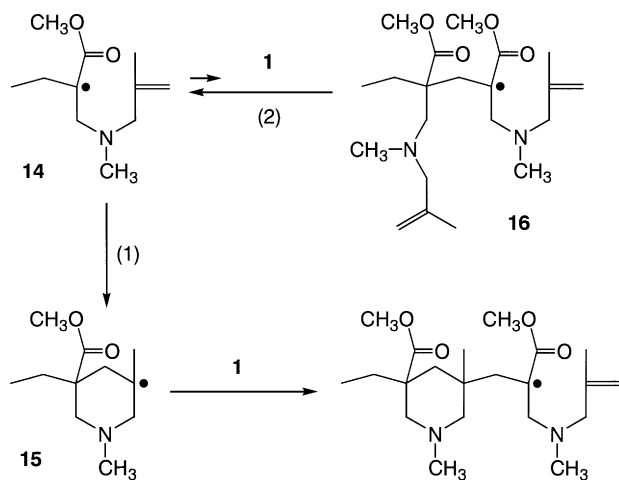


Fig. 7. Possible mechanism for the formation of poly(**1**) with high degree of cyclization.

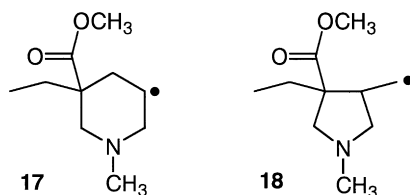


Fig. 8. Structural formula of possible cyclized radicals of poly(**2**).

However, five-membered rings are found quite often as repeat units in the polymers derived from 1,6-dienes. Therefore, there has been a discussion why a less stable five-membered ring is formed [2,12,13]. We have examined the influence of substituents of diallyl compounds on the repeat cyclic units of polymers derived therefrom [6]. It appeared that these 1,6-dienes tend to form six-membered rings as repeat cyclic units, as substituents are introduced on olefinic double bonds. This tendency was interpreted by taking the steric factor and stabilization of radicals into consideration as in the case of radical cyclization reactions of low molecular weight compounds [14]. Based on the investigation, it has been expected that **1** yields polymers with a considerable amount of a six-membered ring as the repeat cyclic unit. This is what has really been observed. The steric effect of the 2-methyl group of the methallyl double bond tends to interfere with the intramolecular cyclization leading to the five-membered ring formation and works in favor of six-membered ring formation. It is clear that the six-membered ring radical derived from **1** (**15**) is more stabilized than the one derived from **2** (**17**) (see Fig. 8).

This stabilization effect could also promote the six-membered ring formation during the polymerizations of **1**. In the case of **2**, the sterically favored reaction course realized by the absence of 2-methyl group on its allyl group allows kinetically controlled intramolecular cyclization reaction to form the less stabilized five-membered cyclized radical (**18**).

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