Cyclopolymerization XXVIII. Radical Polymerizations of *N*-Substituted *N*-Methallyl-2-(methoxycarbonyl)allyl amines : Polymerizability of Unconjugated Dienes with Functional Groups with Low Homopolymerization Tendency

Toshiyuki KODAIRA[†], Michio URUSHISAKI, and Norio KASAJIMA

Department of Materials Science and Engineering, Faculty of Engineering, Fukui University,
3-9-1 Bunkyo, Fukui 910-8507, Japan

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ABSTRACT: Radical cyclopolymerizations of *N*-substituted-*N*-methallyl-2-(methoxycarbonyl)allyl amines (**1**) were studied to compare their cyclopolymerizabilities with those of *N*-substituted-*N*-allyl-2-(methoxycarbonyl)allyl amines (**2**). Monomers **1** with a phenyl(**1a**) and a *t*-butyl(**1b**) group as an *N*-substituent were employed. The phenyl group was chosen, since **2** with an *N*-phenyl group(**2a**) was reported to have exceptionally low polymerization tendency among **2**. Monomer **1b** was polymerized to see whether the bulky *N*-*t*-butyl group enhances the cyclization tendency of **1** or not, since **1** with an *N*-methyl group(**1c**) was reported to yield polymers with pendant unsaturations, though their content is low. It was found that polymerizations of **1a** proceed very slowly like **2a**, but the reason for their slow polymerizations was left unsolved. Polymers with high degree of cyclization, 96% for poly(**1a**) and 100% for poly(**1b**), were obtained even in their bulk polymerizations. This could be an additional support for the proposal made previously. It states that unconjugated dienes, for which monofunctional counterparts do not have homopolymerization tendency yield highly cyclized polymers. This is because both the monofunctional counterparts of **1** are considered to have essentially no homopolymerization tendency. The bulky *t*-butyl group was found to be effective to enhance cyclization tendency also in **1**. Structural studies showed that poly(**1a**) and poly(**1b**) contain both six- and five-membered rings as repeat cyclic units. Mechanism for intramolecular cyclization was discussed.

KEY WORDS Radical Cyclopolymerization / 1,6-Diene / α -Substituted Acryloyl Group / Methallyl Group / Repeat Cyclic Unit / Degree of Cyclization /

Cyclopolymerizations of *N*-phenyl- and *N*-*t*-butyl-*N*-methallyl-2-(methoxycarbonyl)allyl amines (**1a** and **1b**, respectively)(see Scheme 1) were undertaken to see the effect of the *N*-substituents on their cyclopolymerization behavior. The reasons why these groups were chosen as *N*-substituents are as follow. 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.¹ *N*-Substituted-*N*-allyl-2-(methoxycarbonyl)allyl amines (**2**)^{1,2} and *N*-methyl-*N*-methallyl-2-(methoxycarbonyl) allylamine (**1c**)³ are the monomers that were synthesized and polymerized to establish the validity of the proposal. Their α -substituted acryloyl groups were found to have a high conjugative nature, though they do not show homopolymerization tendency when they exist as monoene compounds.^{1,2} However, polymerization behavior of **2** changed considerably depending on their *N*-substituents. For examples, **2a** polymerized exceptionally slowly despite the fact that its α -substituted acryloyl group has a high conjugative nature. Polymerizations of **1a** were undertaken to see how is the effect of *N*-phenyl group on the polymerizations of **1**, because **1c** polymerized rapidly in accordance with the proposal.³ Bulky substituents have been known to enhance the cyclization tendency of unconjugated dienes.^{4–6} This led us to the studies of cyclopolymerizations of **1b** to see whether the bulky *N*-*t*-butyl group enhances the cyclization tendency of **1** or not, since **1c** yielded polymers with a small amount of pendant methallyl groups.

Scheme 1.

Another interesting point of this study is structural investigations on repeat cyclic units of poly(**1**). The structures of the polymers derived from various diallyl compounds were compared in the previous paper.⁷ 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. Monomers **1** which have a structure with an additional methyl group on the allyl group of **2** are supposed to yield polymers with a considerable amount of a six-membered ring as a repeat cyclic unit, different from poly(**2**) which consist exclusively of a five-membered ring.^{1,2} In fact, **1c** yielded polymers which consist almost exclusively of a six-membered ring as a repeat cyclic unit.³ Present investigation may provide us valuable information on how

[†]To whom correspondence should be addressed.

the influence of the *N*-substituents on the structures of the repeat cyclic units of poly(**1**) is.

EXPERIMENTAL

Materials

Monomers **1** were synthesized by the equimolar reaction between methyl α -(bromomethyl)acrylate (BMA) and corresponding amines based on the procedure for the preparation of **2**.^{1,2} Crude products obtained were subjected to repeated distillations to give pure liquids. Yields of the final stage of the synthesis of these monomers were from 40 to 60% after distillations two times. The supposed structures were confirmed by NMR. The boiling points and chemical shifts of the characteristic absorption peaks of ¹H and ¹³C NMR spectra of **1** are as follow. Boiling point of **1a**: 124°C/0.4 mmHg. ¹H NMR for **1a**: δ = 7.17 (m, *m*-C₆H₅), 6.67 (t, *p*-C₆H₅), 6.60 (d, *o*-C₆H₅), 6.26 (s, CH₂=, acryloyl), 5.55 (s, CH₂=, acryloyl), 4.86 (s, CH₂=, methallyl), 4.80 (s, CH₂=, methallyl), 4.19 (s, >N-CH₂-), 3.80 (s, >N-CH₂-), 3.79 (s, -O-CH₃), and 1.73 (s, CH₂=C (CH₃)-) ppm. ¹³C NMR for **1a**: δ = 166.9 (>C=O), 148.2 (>N-C=), 140.2 (CH₂=C (CH₃)-), 135.3 (CH₂=C<, acryloyl), 129.0 (*m*-C₆H₅), 124.9 (CH₂=C<, acryloyl), 116.5 (*p*-C₆H₅), 111.9 (*o*-C₆H₅), 110.6 (CH₂=C (CH₃)-), 56.2 (>N-CH₂-), 51.8 (-O-CH₃), 51.3 (>N-CH₂-), and 20.0 (CH₂=C (CH₃)-) ppm. Boiling point of **1b**: 82°C/0.1 mmHg. ¹H NMR for **1b**: δ = 6.16 (s, CH₂=, acryloyl), 5.94 (s, CH₂=, acryloyl), 4.84 (s, CH₂=, methallyl), 4.69 (s, CH₂=, methallyl), 3.73 (s, -O-CH₃), 3.32 (s, >N-CH₂-), 3.00 (s, >N-CH₂-), 1.68 (s, CH₂=C (CH₃)-), and 1.08 (s, (CH₃)₃C-) ppm. ¹³C NMR for **1b**: δ = 167.7 (>C=O), 145.7 (CH₂=C (CH₃)-), 141.3 (CH₂=C<, acryloyl), 125.5 (CH₂=C<, acryloyl), 111.7 (CH₂=C (CH₃)-), 57.3 (>N-CH₂-), 55.2 ((CH₃)₃C-), 51.5 (-O-CH₃), 50.8 (>N-CH₂-), 27.0 ((CH₃)₃C-), and 20.7 (CH₂=C (CH₃)-) ppm.

Bis(2-methoxycarbonylallyl)aniline (**10**) was prepared by the reaction of BMA with aniline based on the procedure reported for a similar compound.⁸ White crystal with mp 67–68°C was obtained in 80% yield by recrystallization from methanol. ¹H NMR for **10**: δ = 7.18 (t, *m*-C₆H₅), 6.71 (t, *p*-C₆H₅), 6.59 (d, *o*-C₆H₅), 6.28 (s, CH₂=, acryloyl), 5.59 (s, CH₂=, acryloyl), 4.19 (s, >N-CH₂-), and 3.80 (s, -O-CH₃) ppm. ¹³C NMR for **10**: δ = 166.8 (>C=O), 147.6 (>N-C=), 134.9 (CH₂=C<), 129.2 (*m*-C₆H₅), 125.1 (CH₂=C<), 116.9 (*p*-C₆H₅), 111.8 (*o*-C₆H₅), 51.9 (>N-CH₂-), and 51.2 (-O-CH₃) ppm.

BMA was prepared by the reported procedure.⁹ *N*-*t*-Butyl-, and *N*-phenylallyl amines were synthesized according to the procedure reported for the synthesis of *N*, *N*-diethylallylamine.¹⁰

Commercial 2,2'-azobisisobutyronitrile (AIBN) was recrystallized from ethyl alcohol. 1-Methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (MTMP, Tokyo Kasei) was used as received. Tetrabutylammonium bibenzoate (TBABB) was synthesized based on the reported procedures.¹¹ All common solvents were purified by the usual methods.

Polymerization

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, 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 their polymers was found to be soluble in petroleum ether. The polymers were reprecipitated from benzene solution into petroleum ether to obtain pure polymers for measurements.

Group-transfer polymerizations were carried out according to the procedure reported,^{8,11} using MTMP and TBABB as initiator and catalyst, respectively.

Measurements

¹H NMR and ¹³C NMR spectra were taken on a JEOL JNM-GX-270 (270 MHz for ¹H and 68 MHz for ¹³C) or a JEOL LA-500 (500 MHz for ¹H and 125 MHz for ¹³C) FT NMR spectrometer using CDCl₃ and tetramethylsilane as a solvent and an internal standard, respectively. 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 chloroform 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). Viscosity was measured using a Ubbelohde viscometer at 30°C in *N*, *N*-dimethylformamide.

RESULTS

Polymerizations of **1a** and **1b**

The results of the polymerization of **1a** and **1b** are summarized in Table I along with the reported results of **1c** and **2**.^{1,2} that are given for comparison. The degrees of cyclization determined based on ¹H NMR spectra were found to be 96% for poly(**1a**) and 100% for poly(**1b**) (see next section). In accordance with these structural characteristics, both poly(**1a**) and poly(**1b**) samples are soluble in common solvents. It can be reasonably assumed that both the monoene counterparts of **1**, *N*-substituted *N*-isobutyl-2-(methoxycarbonyl)allyl amines (**3**) (see Scheme 2) and *N*-substituted *N*-methallyl-2-(methoxycarbonyl)propyl amines (**4**), have extremely low homopolymerizability. This is because *N*-substituted *N*-propyl-2-(methoxycarbonyl)allyl amines (**5**) which have almost the same structure as **3**, have been reported to have essentially no homopolymerization tendency^{1,2} and extremely low homopolymerizabilities of methallyl compounds is well-known. For this reason, high cyclization tendency of these monomers could be an additional support for the principle for the monomer design for the synthesis of highly cyclized polymers. It states 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.^{12,13} However, the results of the polymerizations of **1** show that the cyclization tendency of **1** is slightly lower than that of **2**. This is because **1c** investigated previously yielded poly-

Scheme 2.

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

No.	Monomer	[AIBN] ₀ (M × 10 ³)	Time h	<i>M_n</i>	<i>M_w/M_n</i>	[η] dL g ⁻¹	DC ^a %	Conversion / % Pre ^b GC ^c
1	1a	112	24	5100	2.3		96	11 23
2	1b	112	12				100	32 49
3	1b	28	4				100	5
4	1b	28	12			0.08	100	16
5 ^d	1c	112	1.2	6400	2.5	0.22	97	74
6 ^d	1c	28	4	9300	2.3	0.24		78
7 ^e	2a	28	2	20000	2.0		100	5
7 ^e	2a	28	10				100	36
8 ^e	2b	28	4			0.16	100	73
9 ^d	2c	112	0.3				100	80
10 ^f	2c	6	0.7			0.28	100	22
11 ^g	10	—	5	5900	1.5		97	84

^aDegree of cyclization. ^bDetermined by weight. ^cDetermined by GC. ^dQuoted from ref 3. ^eQuoted from ref 2. ^fQuoted from ref 1. ^gGroup transfer polymerization of bis(2-methoxycarbonylallyl) aniline (**10**) at ambient temperature: monomer, 6.7 mmol; MTMP, 0.50 mmol; TBABB, 5×10^{-3} mmol; THF, 6.5 ml. *M_n* calculated, 3300. Degree of cyclization was determined based on signal due to phenyl protons and weak absorptions observed at 5.28 and 6.15 ppm in a ¹H NMR spectrum, assuming that the latter two absorptions are derived from pendant unsaturations, though olefin protons of **10** resonate at 5.59 and 6.28 ppm.

mers with degree of cyclization of 97%,³ while all **2** investigated afforded completely cyclized polymers irrespective of the *N*-substituents.^{1,2}

The results summarized in Table I show that polymerization tendency of **1** decreases with a following order, **1c** > **1b** > **1a**. It is clear that *N*-substituents influence in a similar manner for both **1** and **2**. This is because **2c** polymerizes most rapidly and **2a** most slowly among **2**. When polymerizabilities of **1** are compared with those of **2** with a same *N*-substituent, the former are always lower than the latter.

Pendant Unsaturations of Poly(**1a**) and Poly(**1b**)

A methallyl group (**6**) and a 2-(methoxycarbonyl)allyl amino group (**7**) are the pendant unsaturations which are expected to appear in poly(**1**) (see Scheme 3). ¹H NMR spectra of poly(**1**) are illustrated in Figure 1 along with absorptions due to olefin protons of **1**. Comparison of these spectra clearly indicates that poly(**1a**) contains small amount of pendant methallyl groups, while the spectrum of poly(**1b**) shows formation of completely cyclized polymers. Degrees of cyclization of poly(**1a**) listed in Table I were determined based on the signal intensities of methallyl protons detected at around 4.7 ppm and the absorptions due to phenyl protons detected over the region from 6.3 to 7.5 ppm.

Repeat Cyclic Units of Poly(**1a**)

Extremely lower contents of pendant unsaturations indicate that repeat cyclic units of poly(**1**) are **8** and/or **9**

Figure 1. 270 MHz ¹H NMR spectra of poly(**1**) and **1**. (A) Poly(**1a**) (No. 1 in Table I); (B) olefin protons of **1a**; (C) poly(**1b**) (No. 2 in Table I); (D) olefin protons of **1b**.

illustrated in Scheme 3. Proton noise decoupled ¹³C NMR spectra of poly(**1a**) for higher and lower magnetic field regions are depicted in Figures 2A and 3A, respectively. The spectra shown in Figures 2B and 3B were obtained by DEPT (Distortion Enhancement by Polarization Transfer) measurements of poly(**1a**) under the conditions where methyl and methine carbons appear upwards and methylene carbons downwards. Comparison of these spectra allows the assignment of the absorption signals of ¹³C spectrum of poly(**1a**) shown in Figure 2A. However, the complicated spectral pattern does not allow detailed assignment of the each peak. Further, the appearance of the absorptions due to phenyl carbons is also complicated, as can be seen from the observation of

Figure 2. 125 MHz ^{13}C NMR spectra. (A) Poly(**1a**) (No. 1 in Table I); (B) DEPT spectrum of poly(**1a**) measured under the conditions where CH_3 and CH carbons are detected upwards and CH_2 carbons downwards; (C) poly(**10**) (No. 11 in Table I); (D) poly(**1c**) (No. 5 in Table I).

two peaks for a quaternary carbon adjacent to nitrogen (peaks 1 and 1' in Figure 3A). For this reason, the spectra of polymers derived from compounds with similar structures to **1a** were compared with those of Figures 2A and 3A. ^{13}C NMR spectra for higher and lower magnetic field regions of a polymer obtained by a group transfer polymerization (GTP) of bis(2-methoxycarbonylallyl) aniline(**10**) are shown in Figures 2C and 3C, respectively. Its repeat cyclic unit is supposed to be a six-membered ring, judging from the mechanism of GTP.^{8,11} Figure 2D is the spectrum of a higher magnetic field region observed for poly(**1c**) which consists almost exclusively of six-membered rings.³ Figure 3D shows the stick spectrum of phenyl carbons of a polymer derived from *N*-phenyldiallylamine(**11**). It was depicted based on the spectrum of poly(**11**) and its peak analysis reported by Johns *et al.*¹⁴ The polymer was obtained by a radical polymerization and its repeat cyclic unit has been identified to a five-membered ring.¹³ Chemical shifts reported for model compounds with piperidine and pyrrolidine ring structures (Scheme 4) are listed in Table II,^{7,15} which were used to assign the spectrum of Figure

Figure 3. 125 MHz ^{13}C NMR spectra. (A) Poly(**1a**) (No. 1 in Table I); (B) DEPT spectrum of poly(**1a**) measured under the conditions where CH_3 and CH carbons are detected upwards and CH_2 carbons downwards; (C) poly(**10**) (No. 11 in Table I); (D) stick spectrum of poly(**11**) depicted based on the spectrum reported for the polymer.

2A.

Considerable differences can be seen between the spectral patterns of the phenyl carbons of poly(**10**) and poly(**11**) which are illustrated in Figures 3C and 3D, respectively. Substituent effect on ^{13}C chemical shifts of monosubstituted benzenes was studied extensively.¹⁶ It revealed that they are influenced strongly by electron withdrawing or electron donating power of the substituents. The assignment for the phenyl carbons shown in Figure 3C was made based on these reported results. Appearances of the absorption signals of poly(**10**) and poly(**11**) indicate that conjugation between the lone pair electrons on nitrogen and the benzene ring is more efficient in the latter than in the former.¹⁶ This suggests that a bulkier six-membered ring than a five-membered ring interferes with the coplanar conformation between piperidine and benzene rings. Comparison of the spectra of Figures 3 indicates that poly(**1a**) contains both five- and six-membered rings as repeat cyclic units and the former is the main component. This structural characteristic can also be recognized from the spectral analysis at higher magnetic field. Methylene carbons detected at the region from 26 to 37 ppm in Figure 2A are attributable to those of main chain attached to five-membered rings (C6 and C7 carbons of **9**), because main chain

Table II. ^{13}C NMR chemical shifts of **12**,^a **13**,^a and poly(**2c**)^b in ppm

Model compounds	C2	C3	C4	C5	C6	N-CH ₃
12	69.1	31.5	50.4	31.5	69.1	47.1
13	69.8	44.1	44.1	69.8		42.6
poly(2c)	61.6–64.3	54.6, 56.8	46.7, 50.6	61.6–64.3		42.4

^aQuoted from ref 15. ^bQuoted from ref 7.

methylene carbons (C4 and C7) of poly (**1c**) (Figure 2D) that consists of six-membered rings were detected at definitely different chemical shifts. A quaternary carbon detected at 59 ppm in Figure 2A can be attributed to C3 carbon of **9** of poly(**1a**). This is because C3 carbon of poly (**2c**) (Scheme 4) was detected at around 55 ppm (Table II). No quaternary carbon was observed in this region for the spectrum of poly(**1c**) (Figure 2D). The peaks due to quaternary carbons can also be seen at around 36 and 46 ppm in Figure 2A. The former can be attributable to a C5 carbon of **8**, since C3 and C5 carbons of **12** are observed at 31.5 ppm, while C3 and C4 carbons of **13** are detected at 44.1 ppm. The peaks at around 46 ppm are assigned to a C3 carbon of **8** according to the spectral analysis of poly(**1c**) (Figure 2D) and poly(**10**) (Figure 2C). However, the peak detected at around 36 ppm is significantly weak as compared with that observed at around 46 ppm. The ratio, 3 to 5, was obtained for the former to the latter, based on the peak intensities determined by the measurements under suppressed NOE as described below. Furthermore, the signal at 36 ppm is overlapped with that of methylene carbons as can be seen from the comparison with DEPT spectrum (Figure 2B). The peaks observed at around 46 ppm are considered to be contaminated with signals due to the C4 carbon of **9**. The chemical shifts of C3 and C4 carbons of **13** given in Table III rationalize this consideration. The methylene carbons adjacent to nitrogen of poly(**1a**) were detected at considerably higher magnetic field than those of poly(**1c**). One reason for this might be ascribed to the effect of benzene ring through diamagnetic anisotropy and the other to γ -gauche effect. Two ortho carbons could be gauche to these methylene carbons. In the polymers derived from *N*-substituted diallyl amines, it was reported that $>\text{N}$ -methylene carbons of poly(**11**) were shifted to higher magnetic field by about 9 ppm as compared with those of *N*-methyl derivative.¹⁴

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).¹⁷ The longest T_1 value determined using a progressive saturation method was 2.8 s for the carbonyl carbon of poly(**1a**). ^{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 five-membered ring content was determined to be 72% based on the peak intensities of the phenyl carbons adjacent to nitrogen (peaks 1 and 1' in Figure 3A).

Repeat Cyclic Units of Poly(**1b**)

A ^{13}C NMR spectrum of poly(**1b**) is illustrated in Figure 4. The assignment given in the figure was made by comparing its spectral pattern with that of poly(**1a**) and poly(**1c**). A spectrum obtained by DEPT measurements also supported the assignment. Characteristic peaks which have been attributed to C3 and C5 quaternary

Scheme 4.

carbons of **8** in poly(**1a**) and poly(**1c**) are detected at around 46 and 36 ppm, respectively, almost the same chemical shifts as those of these two polymers. This suggests that poly(**1b**) also contains a six-membered ring as a repeat cyclic unit. However, the peak intensity at around 36 ppm is considerably weak as compared with that at around 46 ppm, which indicates the presence of a considerable amount of a five-membered ring as a repeat cyclic unit as in the case of poly(**1a**). Peak analysis at the region from 52 to 54 ppm also supports this consideration. This is because two peaks due to quaternary carbons, one at 52 and the other at 54 ppm, are detected. The one should be attributed to the C3 carbon of **9** and the other to $>\text{N}-\text{C}(\text{CH}_3)_3$. The absence of the characteristic peaks attributable to the two repeat cyclic units does not allow to estimate accurately the contents of these two rings. The observations of $>\text{N}-\text{CH}_2-$ carbons of poly(**1b**) at considerably high magnetic field as compared with those of poly(**1c**) can be interpreted by taking the γ -gauche effect into considerations. These *N*-methylene carbons have possibility to be gauche to the three methyl carbons in the *t*-butyl group of poly(**1b**). No such carbon exists for *N*-methylene carbons of poly(**1c**). It has been reported that signals due to *N*-methylene carbons of poly(**2b**) are observed at higher magnetic field than those of poly(**2c**) by about 10 ppm.⁷ This result also rationalizes the rather large difference between the chemical shifts of the *N*-methylene carbons of poly(**1b**) and poly(**1c**).

^{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 III. 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.¹⁸ This means that the stronger the electron-attracting power of the substituents, the smaller the $\Delta\delta$ values, which was obtained by subtracting δ_{C_β} from δ_{C_α} values. Comparison of the $\Delta\delta$ of **1** indicates that conjugation between the olefin and carbonyl double bonds in these compounds changes depending on the substituents on nitrogen according to the same trend as in the case of **2**. The extent of conjugation between $\text{C}=\text{C}$ and $\text{C}=\text{O}$

Figure 4. 68MHz ^{13}C NMR spectrum of poly(**1b**) (No. 4 in Table I).

double bonds decreases, as the bulkiness of *N*-substituent on nitrogen increases. However, the conjugation of the acryloyl groups of **1** is considerably effective even in **1b**, judging from $\Delta\delta$ of these compounds and methallyl groups, the one of typical unconjugative groups.

DISCUSSION

The results obtained indicate that *N*-substituents influence polymerizabilities of **1** in a similar manner to those of **2**. Steric hindrance of the bulky *t*-butyl group of **1b** distorts the coplanarity between the $\text{C}=\text{C}$ and $\text{C}=\text{O}$ double bonds of its α -substituted acryloyl group. This would be the reason for a lower conjugative nature of its α -substituted acryloyl group. Monomers **1** are considered to be incorporated into the polymeric chain at first through their acryloyl groups, since their conjugative nature is higher than that of methallyl groups even in **1b**. The fact that only methallyl group was detected as pendant unsaturations in poly(**1a**) and poly(**1c**) supports this consideration. For this reason, the polymerization rate would decrease, as the conjugative nature of the acryloyl groups decreases. Bulky substituents that decrease the extent of conjugation might also be unfavorable sterically for the addition of the attacking radical to the α -substituted acryloyl group.

Bulky substituents have been known to enhance the cyclization tendencies of unconjugated dienes.⁴⁻⁶ This can also be seen in the polymerization of **1**. Completely cyclized polymers were obtained from **1b**, while **1a** and **1c** yielded polymers with a small amount of pendant unsaturations. It can be understood that bulky substituents can generally be utilized to enhance the cyclization tendency of 1,6-dienes.

The reason for the lowest polymerization tendency of **1a** among **1** is not clear at present, since its acryloyl group

Table III. ^{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
1a	126.2	138.2	12.0
1b	125.5	141.3	15.8
1c ^b	124.9	135.3	10.4
MMA ^c	125.5	136.3	10.8
2a ^d	126.8	137.8	11.0
2b ^d	125.7	141.1	15.4
2c ^e	125.0	135.6	10.6
1a	112.7 ^f	143.6 ^f	30.9

^a $\delta_{\text{C}_\alpha} - \delta_{\text{C}_\beta}$. ^b Quoted from ref 3. ^c Methyl methacrylate. ^d Quoted from ref 2. ^e Quoted from ref 1. ^f Chemical shifts of methallyl carbons.

has high conjugative nature. In the case of **2**, the lowest polymerizability was also observed for **2a**, though the conjugative nature of its α -substituted acryloyl group was found to be as effective as that of **2c** which has the highest polymerization tendency.² One possible reason for their slow polymerizations might be ascribed to lower conjugation between an unpaired electron and a $\text{C}=\text{O}$ double bond in a propagating radicals, which is brought about by conformational change during addition reactions of the monomers to polymeric chain ends.¹⁹ Another is side reactions which are common to both **1a** and **2a**. They might be playing important roles to suppress the overall polymerization rate in these two monomers, though they are unknown at present. Anyhow further study is necessary to elucidate the cause for the slow polymerization of **1a** and **2a**.

High cyclization tendency of **1a** and **1b** can be explained by a similar manner to that of **1c**.³ The intramolecular cyclization reactions of **14** (eq 1 and eq 1') proceed preferentially over the intermolecular propagation reaction (eq 2) to form cyclized radicals **15** and **15'** because extremely low homopolymerization tendency of **3** can be reasonably assumed. The methyl group on the methallyl group seems to interfere slightly with the cyclization reactions in these monomers, which results in lowering the reactivity of the uncyclized radical (**14**) to the intramolecular cyclization reactions (eq 1 and eq 1'). This could be the reason why slower polymerizations proceed in **1** than **2**, when their polymerizabilities were compared among those with a same *N*-substituent. Only the uncyclized propagating radical related to the α -substituted acryloyl group was considered in the reaction scheme illustrated in Scheme 5, since the first attack of a propagating radical to **1** is considered to be made on the acryloyl group as mentioned above.

One of the characteristics that differentiate the polymerizations of **1** from those of **2** exists in their repeat cyclic structures. Detailed examination on the influence of substituents of diallyl compounds on the repeat cyclic units of polymers derived therefrom revealed that these 1,6-dienes tend to form a six-membered ring, as substituents are introduced on olefinic double bonds.⁷ Based on the investigation, **1** have been expected to yield polymers with a considerable amount of a six-membered ring as a repeat cyclic unit different from **2** that formed selectively polymers with five-membered rings for their repeat cyclic units. This is what has really been observed. It can be understood that the 2-methyl group of the

Scheme 5.

methallyl double bond works in favor of six-membered ring formation due to steric and radical stabilizing effects. However, the contents of six-membered rings of poly(**1**) were found to change significantly depending on *N*-substituents. Poly(**1a**) and poly(**1b**) contain considerable amounts of five-membered rings, while **1c** yielded polymers which consist almost exclusively of a six-membered ring. This indicates that *N*-substituents change the conformations of **14** that are responsible for the reaction paths for the intramolecular cyclizations. One of the interesting aspects of these results is that the bulky *N*-*t*-butyl group enhances the cyclization ten-

dency, though the conformations of uncyclized radicals leading to five- and six-membered rings are considerably different.

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19. This was added based on the suggestion by a referee.