Cyclopolymerization. 22. Radical Polymerization of *N*-Methyl-*N*-allyl-2-(methoxycarbonyl)allylamine: Design of Unconjugated Dienes with High Polymerizability and High Cyclization Tendency Using Functional Groups of Low Polymerizabilities

Toshiyuki Kodaira,* Tadahiro Fujisawa, Qing-Qing Liu, and Michio Urushisaki

Department of Materials Science and Engineering, Faculty of Engineering, Fukui University, Fukui 910, Japan

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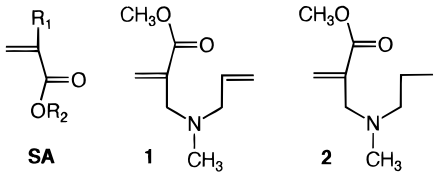
Polymerization of 1,6-dienes usually leads to soluble polymers which have cyclic structures in the main chain. The degrees of cyclization of the polymers formed depend on the monomers and the polymerization conditions. For this reason, the most important aspect of structural control in the cyclopolymerization of 1,6-dienes is how to regulate the degree of cyclization. We have already proposed the principle for monomer design for the synthesis of highly cyclized polymers.[1] It states that bifunctional monomers whose monofunctional counterparts do not polymerize will give rise to highly cyclized polymers, if they polymerize at all. The validity of the principle has been proved by investigating the cyclopolymerizability of several monomers.[2,3] However, the problem has been the lower polymerization tendencies of the unconjugated dienes synthesized under this principle. This is why we have searched for monomers with high tendencies for both intramolecular cyclization and polymerization.

α-Substituted acrylates (SA) have a wide variety of polymerization tendencies from high polymerizability to nonpolymerizability, depending on the α-substituents.[4] This variation is assumed to be due to steric factors of the substituents, since the reported spectroscopic data of SA have suggested that the conjugative nature of their C═C and C═O double bonds is not much different from that of methyl methacrylate (MMA) irrespective of the nature of the substituents.[4,5] This suggests that 1,6-dienes which have C═C double bonds of this type would have high polymerizability, even if they do not polymerize as monoene compounds. This is because steric factors fatal to intermolecular propagation leading to uncyclized pendant units are not necessarily unfavorable to intramolecular cyclization. Unconjugated dienes were sought which have higher polymerizability as well as higher tendencies toward intramolecular cyclization, using these functional groups. Cyclopolymerizations of several symmetrical and unsymmetrical unconjugated dienes having α-substituted acryloyl groups have already been reported.[5−7] However, their cyclopolymerizabilities have not been investigated in terms of the polymerizabilities of their monofunctional counterparts. Thus, *N*-methyl-*N*-allyl-2-(methoxycarbonyl)allylamine (**1**) was synthesized and its polymerization behavior studied. This compound has the added advantage that *N*-methyl-*N*-propyl-2-(methoxycarbonyl)allylamine (**2**), one of the monoene counterparts of **1**, can be synthesized easily and the other monofunctional counterpart of **1** is well known.

Monomers **1** and **2** were synthesized by the equimolar reaction between methyl α-(bromomethyl)acrylate (BMA) and *N*-methylallylamine (MA) or *N*-methylpropylamine (MP), based on the procedure reported for a similar compound.[8] Repeated distillations gave pure liquids with about 60% yields for both compounds. Their



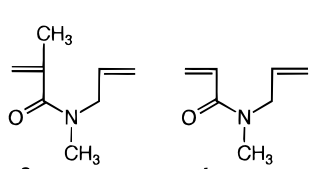
SA 1 2

boiling points (40 °C/0.2 mmHg, not corrected) were almost identical. ^{1}H NMR for **1**: δ = 6.28 (s, 1H), 5.86 (m, 1H), 5.79 (s, 1H), 5.17 (t, 2H), 3.77 (s, 3H), 3.21 (s, 2H), 3.05 (d, 2H), and 2.23 ppm (s, 3H). ^{13}C NMR for **1**: δ = 167.4, 137.8, 135.7, 126.8, 117.4, 60.7, 57.3, 51.8, and 42.1 ppm. ^{1}H NMR for **2**: δ = 6.25 (s, 1H), 5.76 (s, 1H), 3.79 (s, 3H), 3.18 (s, 2H), 2.34 (t, 2H), 2.21 (s, 3H), 1.51 (sextet, 2H), and 0.89 ppm (t, 3H). ^{13}C NMR for **2**: δ = 167.5, 138.1, 126.5, 59.8, 58.0, 51.8, 42.3, 20.5, and 11.8 ppm.

BMA,[9] MA,[10] and MP[10] were prepared by the reported procedures. Polymerizations were carried out as described previously[11] using azobis(isobutyronitrile) (AIBN) as initiator. Petroleum ether was used to precipitate polymers. Samples for NMR and viscosity measurements were precipitated from benzene solution.

^{1}H NMR and ^{13}C NMR spectra were taken on a JEOL JNM-GX-270 FT NMR spectrometer using $CDCl_3$ as a solvent and tetramethylsilane as an internal standard. Viscosities were measured in an Ubbelohde viscometer at 30 °C in *N*,*N*-dimethylformamide.

The results of the polymerizations of **1** and **2** are listed in Table 1 together with those of related compounds. The former was polymerized to high polymers, while no detectable polymer could be obtained from the latter, even after a prolonged polymerization time. This leads to the conclusion that both the monoene counterparts of **1** have essentially no polymerization tendency, because it may be reasonably assumed that the other monofunctional counterpart of **1** has an extremely low polymerizability based on ^{13}C NMR studies of the allyl group of **1** shown later. Poly(**1**)s are soluble in common solvents, which suggests formation of highly cyclized polymers. In fact, no pendant double bonds could be detected in the ^{1}H NMR spectrum of poly(**1**) (Figure 1). The fact that even the polymers obtained in bulk polymerization did not contain any pendant unsaturation shows how high the cyclization tendency of **1** is. For the present, we do not have sufficient data to determine the repeating cyclic unit, 5- and/or 6-membered rings (Chart 1), and further study is necessary. Comparison of the polymerization results of **1** with those reported for *N*-methyl-*N*-allylmethacrylamide (**3**)[2] and *N*-methyl-*N*-allylacrylamide (**4**)[11] clearly indicates the high polymerization tendency of **1**. Both of the monofunctional counterparts of **3** do not polymerize,[2] while *N*-methyl-*N*-propylacrylamide, one of the monofunctional counterparts of **4**, can be polymerized to high polymer.[11] Accordingly, **3** is polymerized to yield highly



3 4

cyclized polymers but with a lower polymerization rate, while **4** has a high polymerizability but its cyclization tendency is low. Similar polymerization tendencies of **1** and **4** are observed, irrespective of the fact that both monofunctional counterparts of **1** have extremely low polymerization tendencies. The characteristic features

* To whom correspondence should be addressed.

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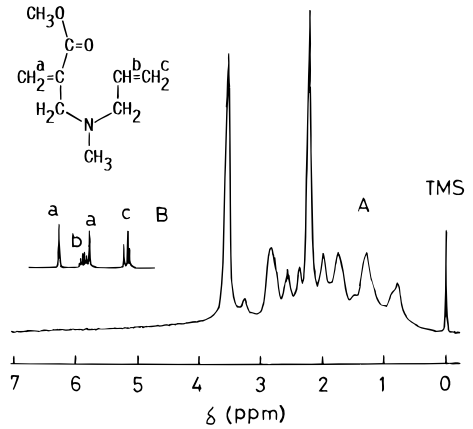


Figure 1. ^{1}H NMR spectra of poly(**1**) and **1**: (A) poly(**1**) (no. 2 in Table 1) measured at 50 °C; (B) olefin protons of **1** measured at room temperature.

Table 1. Polymerizations of 1 and Related Compounds at 60 °C

no.	monomer	$[M]_0$, M	10^{-3} $[AIBN]_0$, M	time, h	DC,[a] %	$[\eta]$, dL/g	convn, %
1	**1**	bulk	6.06	0.3	100	0.24	7
2	**1**	bulk	6.06	0.7	100	0.28	20
3	**1**	2.32	6.06	1	100		21
4	**2**	bulk	112	48			0
5[b]	**3**	bulk	143	15	93		35
6[c]	**4**	2.31	6.06	1	60		23

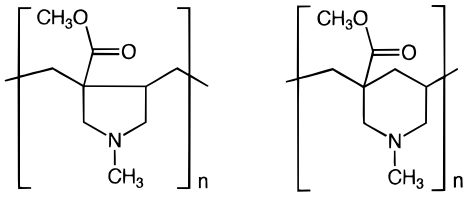
[a] Degree of cyclization. [b] Quoted from ref 2. [c] Quoted from ref 11.

Table 2. ^{13}C Chemical Shifts of $C_\beta H_2{=}C_\alpha<$ and Carbonyl Carbons of Acryloyl Groups of 1 and Related Compounds in $CDCl_3$

compd	δ_{C_β}, ppm	δ_{C_α}, ppm	$\delta_{C=O}$, ppm	$\Delta\delta$,[a] ppm
1	126.8	137.8	162.4	11.0
2	126.5	138.1	167.5	11.6
MMA	125.5	136.3	168.0	10.8
3[b]	117.3	148.8	172.9	23.5
MA	115.1[c]	141.4[c]		26.3
4[b]	127.8	127.8	166.5	0
1	117.4[d]	135.7[d]		18.3
MI			177.6[e]	

[a] $\delta_{C_\alpha} - \delta_{C_\beta}$. [b] Quoted from ref 13. [c] Chemical shifts of olefin carbons of methallyl chloride (MA). [d] Chemical shifts of allyl carbons of **1**. [e] Chemical shifts of carbonyl carbon of methyl isobutyrate (MI).

Chart 1



of **1**, high polymerization and cyclization tendencies, correspond to what was expected.

Chemical shifts of the C=C double bonds ($C_\beta H_2{=}C_\alpha$-XY) of **1** and related compounds are summarized in Table 2. It has been reported that the δ_{C_β} and δ_{C_α} values shift to lower and higher magnetic fields, respectively, with a linear relationship when the *e* values of the monomers become larger with increasing electron-attracting power of substituents.[12] This means that the values, $\Delta\delta$, obtained by subtracting δ_{C_β} from δ_{C_α} reflect the influence of substituents more effectively than their absolute values. The stronger the electron-attracting power of the substituents, the smaller the value. Comparison of the values of the compounds listed clearly shows that the conjugative nature of MMA is much higher than that of the methacryloyl group of **3**[13] and that of the α-substituted acryloyl groups of **1** and **2** is as effective as the former, because effective conjugation between C=C and C=O double bonds reduces the electron density on their C=C double bonds. This conclusion can also be drawn from the chemical shifts of the carbonyl carbons of these compounds, since effective conjugation in α,*β*-conjugated carbonyl compounds moves electrons in the olefin double bond into the carbonyl group and shifts the chemical shifts of the carbonyl carbons to higher magnetic field. 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 similarity that their monofunctional counterparts, **2** and *N*-methyl-*N*-propylmethacrylamide,[2] respectively, do not have any polymerization tendency. Thus, polymerization of **1** is considered to proceed initially from the α-substituted acryloyl group, in contrast to the polymerization of **3**, which proceeds from the side of its allyl group.[14] Further studies are in progress to confirm this. Radical polymerizabilities of allyl monomers were also correlated to their $\Delta\delta$ values to show that those with a value of more than 6 ppm for $\Delta\delta$ are reluctant to polymerize.[15] This clearly indicates that the polymerization tendency of the allylic monofunctional counterpart of **1** would be extremely low because of the large $\Delta\delta$ value (18.3) observed for the allyl group of **1**.

The unconjugated dienes which have both high polymerization and cyclization tendencies could be synthesized using functional groups with essentially no polymerization tendency such as α-substituted acryloyl and allyl groups. Judging from the fact that the conjugative natures of the acryloyl groups of **1**, **2**, and MMA are almost the same, the steric factor which inhibits the vinyl polymerization of **1** leading to pendant unsaturation does not influence the intramolecular cyclization unfavorably.

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