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Cyclopolymerization. 20. Anionic Cyclopolymerization of *N-tert*-Butyl-*N*-allylacrylamide: Five-Membered Ring Formation through Head-to-Head and Tail-to-Tail Additions

Toshiyuki Kodaira,* Michio Urushisaki, Mitsuhiro Usugaya, Kenji Ohora, and Miyuki Okumura

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

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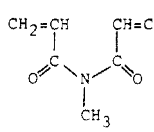
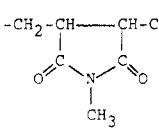
ABSTRACT: The possibility for five-membered ring formation, i.e., head-to-head and tail-to-tail additions, in anionic cyclopolymerization of 1,6-dienes was investigated using *N-tert*-butyl-*N*-allylacrylamide (BAA), *N*-2,6-xylyl-*N*-allylacrylamide (XAA), *N,N*-diallylacrylamide (DAA), and *N*-methyl-*N*-allylacrylamide (MAA) as monomers and *tert*-butylmagnesium chloride as an initiator. It was found that BAA forms polymers, with five-membered rings as a repeating cyclic unit and, in addition, the degree of cyclization of poly(BAA) obtained was about 81%, in spite of the fact that the anionic polymerization tendency of an allyl group is extremely low. XAA, DAA, and MAA yielded polymers without any cyclized units leaving the allyl group as pendant unsaturation. Conformational analysis of these monomers suggested that only BAA has favorable conformation for five-membered ring formation. ^{13}C NMR spectroscopic studies revealed that conjugations between C=C and C=O double bonds of BAA and XAA are less effective than those of DAA and MAA probably due to steric hindrance. This indicates that the propagating anions derived from acryloyl groups of the former are more active than those of the latter. Based on these results it has been concluded that conformational advantage of BAA and higher reactivity of propagating anion derived from its acryloyl group make possible this unusual addition reaction to form five-membered ring.

Introduction

During the studies on cyclopolymerization of a series of 1,6-dienes, it has been found that *N*-methyldiacrylamide (MDA) forms almost completely cyclized polymers with a five-membered ring as a repeating cyclic unit not only in its radical polymerization[1,2] but also in its anionic polymerization.[3] This observation is extremely curious, since a five-membered ring and its anion (**I**) are considered to be more unstable than a six-membered ring and its anion (**II**), respectively. In addition, five-membered ring formation means occurrence of head-to-head and tail-to-tail additions, which have never been observed in the anionic polymerization of vinyl monomers.


MDA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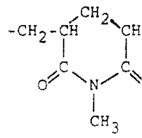
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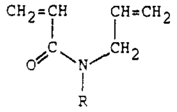
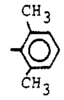
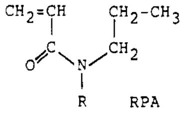
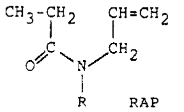
In the present paper, anionic polymerization of *N-tert*-butyl-*N*-allylacrylamide (BAA) was undertaken in order to see whether the unusual addition reactions, i.e., five-membered ring formation, can generally occur or not in anionic polymerization of 1,6-dienes. BAA was chosen since this monomer has been reported to yield almost completely cyclized polymers with a five-membered ring as a repeating cyclic unit in its radical polymerization.[4] BAA has an advantage for the clarification of the mechanism of the five-membered ring formation in the case where it occurs, since its anionic cyclopolymerizability can be compared with that of various N-substituted *N*-allylacrylamides (RAA), such as *N*-methyl-*N*-allylacrylamide (MAA), *N,N*-diallylacrylamide (DAA), and *N*-2,6-xylyl-*N*-allylacrylamide (XAA). All these RAA compounds are known to yield polymers with considerably different degrees of cyclization in their radical cyclopolymerizations, though polymers with five-membered rings as repeating cyclic unit are formed.[5-7] Further advantage of this polymerization system is that the monofunctional counterparts of RAA (RPA and RAP) can be obtained easily and their polymerization tendencies can be compared with those of RAA.



RAA	-R
BAA	$-C(CH_3)_3$
MAA	$-CH_3$
DAA	$-CH_2-CH=CH_2$
XAA	



RPA	-R
MPA	$-CH_3$
BPA	$-C(CH_3)_3$



RAP	-R
MAP	$-CH_3$
BAP	$-C(CH_3)_3$

Experimental Sections

Materials. All the amide monomers employed in this study were synthesized by interfacial condensation reaction between corresponding amines and acid chlorides based on the procedure for the preparation of *sym*-dimethyldimethacryloylhydrazine.[8] The supposed structure was confirmed by NMR and infrared spectra and results of elementary analyses. *N-tert*-Butyl- and *N*-2,6-xylylallylamines were synthesized according to the procedure reported for the synthesis of *N*-ethylallylamine.[9] *N*-Methylallylamine was synthesized according to Morrison.[10]

Tetrahydrofuran (THF) was purified in the usual way. Commercial *tert*-butylmagnesium chloride (*t*-BuMgCl) solution in THF (Tokyo Kasei) was used as received. Commercial azobis-

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* To whom all correspondence should be addressed.

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Table 1. Anionic Polymerization of RAA[a]

no.	RAA	$[M]_0$, mol/dm^3	time, min	convn, %	IP,[b] %	M_n[c]	M_w[d]/M_n	DC,[e] %	A,[f] %
1	BAA	0.46	10	4	0	3600	1.8	81	9
2	BAA	0.46	30	4	0	3200	1.8	81	9
3	XAA	0.46	30	2	79	1700	1.3	0	100
4	XAA	0.46	60	3	58	2200	1.4	0	100
5	MAA	0.23	5	100					
6	MAA	0.23	10	100	68	5200	1.2	0	100
7	DAA	0.23	0.5	74	63	5200	1.7	0	100
8	DAA	0.23	1	95	63	5000	1.9	0	100

[a] $[t\text{-BuMgCl}]_0$, 2.5×10^{-2} mol/dm^3. Temperature, −78 °C. [b] Insoluble part. [c] Number average molecular weight. [d] Weight average molecular weight. [e] Degree of cyclization. [f] Content of pendant allyl group.

Table 2. Radical Polymerization of RAA

no.	RAA	$[M]_0$, mol/dm^3	$[AIBN]_0$, mol/dm^3 × 10^3	time, min	convn, %	IP,[a] %	M_n[b]	M_w[c]/M_n	DC,[d] %	A,[e] %
1	BAA	2.00	2.5	20	7	0	43 000	2.5	100	0
2	XAA	0.30[f]	2.5						46	54
3	MAA	0.46[g]	6.1	30	8	0			60	40
4	DAA	1.00	2.5	7	2	90	2800	3.1	96	4

[a] Insoluble part. [b] Number average molecular weight. [c] Weight average molecular weight. [d] Degree of cyclization. [e] Content of allyl group. [f] Quoted from ref 7. [g] Quoted from ref 6.

(isobutyronitrile) (AIBN) was recrystallized from ethyl alcohol. All common solvents were purified by usual methods.

Polymerization. Anionic polymerizations were carried out according to the procedure reported.[3] The precipitant used was petroleum ether. In the case of BAA, XAA, and *N-tert*-butyl-*N*-propylacrylamide (BPA), solvent of the polymerization systems was evaporated under vacuum at temperatures lower than 20 °C to get concentrated solution which was poured into petroleum ether. The precipitate obtained was filtered on a sintered glass crucible. The precipitates were extracted with chloroform and reprecipitated in petroleum ether. The insoluble fraction in chloroform obtained from the polymerization systems of BAA and BPA was assigned to magnesium chloride by comparing its IR spectrum with that of an authentic sample. In the case of DAA and MAA, the insoluble fraction in chloroform consists of a three-dimensional network of polymers derived from these monomers. The insoluble fraction obtained from the polymerization of XAA is considered to contain magnesium chloride and three-dimensional network polymer in almost the same amount. However, the quantitative analysis of their contents was not attempted.

Radical polymerization was carried out according to the procedure reported.[5] Polymer was isolated by pouring the polymerization mixture into petroleum ether.

All the polymers were dried under reduced pressure at 80 °C for 48 h. The polymer yield was determined gravimetrically.

Measurements. ^{1}H NMR and ^{13}C NMR spectra were taken on a JEOL JNM-GX-270 FT NMR spectrometer using tetramethylsilane as an internal standard. IR spectra were recorded on Hitachi 260-30 IR spectrometer. Gel-permeation chromatography was performed on a JASCO TRI ROTAR-II using THF as eluent. The column set consisted of Shodex KF-802.5, A-800P, and A-80M. A molecular weight calibration curve was obtained by using standard polystyrene. Viscosity was measured using a Ubbelohde viscometer at 30 °C in *N,N*-dimethylformamide.

Results

Anionic Polymerization of RAA. Table 1 summarizes the results of the anionic polymerization of RAA. Polymerization tendencies of BAA and XAA are significantly low as compared to those of DAA and MAA. The poly(BAA) obtained is soluble in various common solvents, which suggests formation of polymers with a higher degree of cyclization. In fact the degree of cyclization (DC) of poly(BAA) was 81%. The other *N*-allylacrylamide derivatives studied yielded polymers containing insoluble parts. The soluble parts of these polymers was found not to contain any cyclized units. Typical radical polymerization behavior of RAA is shown in Table 2 for comparison. The values of DC and structure of pendant unsaturations given in Tables 1 and 2 were determined based on the structural studies of poly(RAA) which are described below.

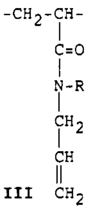
Table 3. Anionic Polymerization of Monofunctional Counterparts of BAA and MAA[a]

monomer	$[M]_0$, mol/dm^3	convn, %	M_n[b]	M_w[c]/M_n
BPA	0.46	6	6400	1.3
MPA	0.31	75	0.26[d]	
BAP	0.46	0		
MAP	0.46	0		

[a] $[t\text{-BuMgCl}]_0$, 2.5×10^{-2} mol/dm^3; temp, −78 °C; time, 30 min. [b] Number average molecular weight. [c] Weight average molecular weight. [d] $[\eta]$, dL/g in DMF at 30 °C.

Anionic Polymerization of the Monofunctional Counterparts of BAA and MAA. Anionic polymerization behavior of the corresponding monofunctional counterparts of BAA and MAA was investigated in order to judge the polymerizabilities of the four double bonds of these two dienes. The results are listed in Table 3. It can be noticed that polymerizability of BPA is extremely low as compared to that of *N*-methyl-*N*-propylmethacrylamide (MPA). This polymerization behavior is in accordance with that of BAA and MAA. *N-tert*-Butyl-*N*-allylpropanamide (BAP) and *N*-methyl-*N*-allylpropanamide (MAP) do not yield any detectable polymer as has been expected from the reactivity of the allyl group.

Structure of Poly(RAA). The repeating units which are expected in the polymers prepared from RAA have the structures **III–VI**. To get information on the structure of poly(BAA), spectroscopic studies were undertaken. ^{1}H NMR spectrum of poly(BAA) obtained is shown in Figure 1 together with the spectra of poly(BAA) obtained by using a radical initiator and olefin protons of BAA. The comparison of these spectra clearly indicates that poly(BAA) formed through an anionic mechanism has a rather similar structure to that of the polymer derived from radical mechanism. The fundamental difference is that the former contains an allyl group as a pendant unsat-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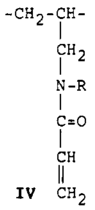
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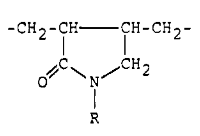
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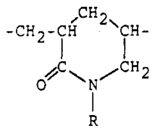

VI

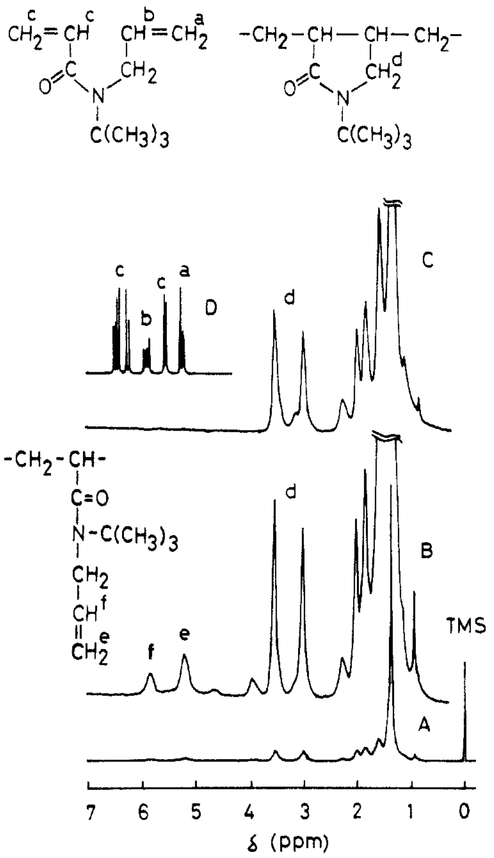


Figure 1. ^{1}H NMR spectra of poly(BAA) and BAA: A, poly(BAA) (no. 1 in Table 1); B, measured in increased gain for the spectrum A; C, poly(BAA) (no. 1 in Table 2); D, BAA. Measured in $CDCl_3$.

Table 4. ^{13}C Chemical Shifts of >C=O Carbons and Stretching Vibration of >C=O Double Bonds

compound	δ^a, ppm	WN,^{b} cm^{-1}
poly(BAA)^c	179.2^d	1674^e
poly(BAA)^f	179.2^d	1674^e
poly(BAMA)^g	179.2^d	1674^e
telo(BAMA)^h	177.6, 177.2	1678^i
methyl-Pyr^j	175.0	1669^i
methyl-Pip^k	170.0	1628^i
poly(MAA)^l	174.5	1638^e

[a] Measured in $CDCl_3$. [b] Wavenumber. [c] Obtained by anionic polymerization (no. 1 in Table 1). [d] Broad singlet. [e] Measured in KBr pellet. [f] Obtained by radical polymerization (no. 1 in Table 2). [g] Poly(*N*-*tert*-butyl-*N*-allylmethacrylamide) obtained by radical polymerization, which has a five-membered ring as a repeating cyclic unit.[11] [h] A five-membered cyclic compound obtained by telomerization of *N*-*tert*-butyl-*N*-allylmethacrylamide.[11] [i] Measured neat. [j] *N*-Methylpyrrolidone. [k] *N*-Methylpiperidone. [l] Obtained by anionic polymerization (no. 6 in Table 1).

uration while the latter does not. Observation of >N–CH_2– protons of a five-membered ring (signal d) indicates that head-to-head and tail-to-tail additions also occur in the anionic polymerization of BAA. The assignment of the >N–CH_2– protons was established in the previous paper.[11]

The stretching vibrations of >C=O double bonds and chemical shifts of the carbonyl carbons of poly(BAA) and related compounds are summarized in Table 4. Comparison of these data indicates that cyclic repeating units of poly(BAA) consist almost exclusively of a five-membered ring in accordance with the observation of >N–CH_2– protons of a five-membered ring in the ^{1}H NMR spectrum mentioned above.

The degree of cyclization given in Table 1 was determined based on the peak intensities of pendant unsaturation and those of >N–CH_2– protons of a five-membered repeating cyclic unit, since it appeared that poly(BAA) does not contain any six-membered ring as a repeating cyclic unit. Judging from the fact that allyl groups have essentially no anionic polymerization tendency (see Table 3), it can be said that the value of DC, 81%, is exceptionally high.

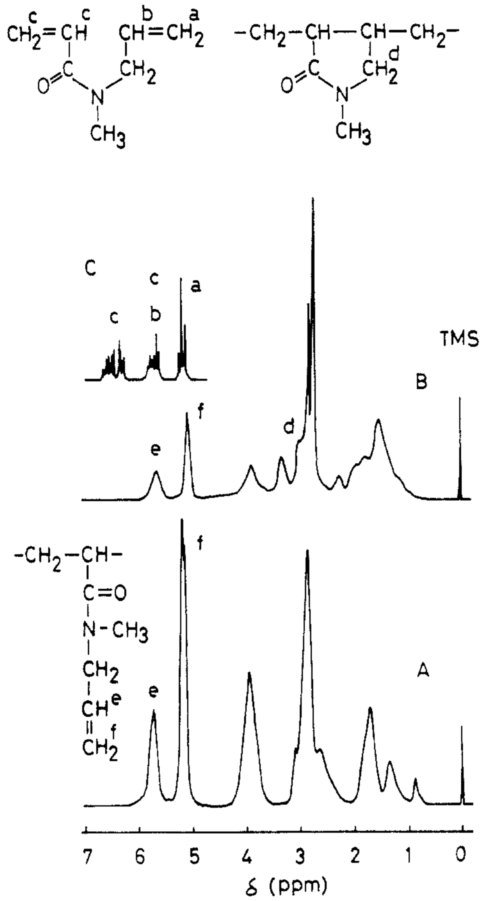


Figure 2. ^{1}H NMR spectra of poly(MAA) and MAA: A, poly(MAA) (no. 6 in Table 1); B, poly(MAA) (no. 3 in Table 2); C, MAA. Measured in $CDCl_3$.

^{1}H NMR spectra of poly(MAA) and olefin protons of MAA are illustrated in Figure 2. Absence of a five-membered repeating cyclic unit in the poly(MAA) obtained by an anionic mechanism can be recognized, since the signal due to >N–CH_2– protons of the five-membered ring is not detected in the spectrum. The chemical shift of carbonyl carbon and stretching vibration of the >C=O double bond of poly(MAA) listed in Table 4 indicate that poly(MAA) contains neither a five- nor six-membered ring. The pendant unsaturation is ascribed to an allyl group based on the comparison with spectra of monomeric olefin protons and poly(MAA). The same polymerization behavior, i.e., formation of uncyclized polymers with allyl groups as pendant unsaturation, was also confirmed in the anionic polymerization of DAA and XAA based on a similar structural investigation. Detection of the allyl group as pendant unsaturations in these polymers formed with the anionic initiator is understood considering the reactivities of the acryloyl group and allyl group involved. The typical results of the radical polymerizations shown for comparison in Table 2 indicate that the polymerization mechanism significantly affects the polymerization tendencies and structure of the polymers formed.

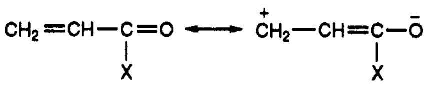
NMR Spectroscopic Studies on BAA and Related Compounds. Chemical shifts of C=C double bonds ($C_\beta H_2$=$C_\alpha H$—X) of RAA and related compounds obtained by measuring ^{13}C NMR spectra are summarized in Table

Table 5. ^{13}C Chemical Shifts of $C_\beta H_2{=}C_\alpha H{-}CO{-}$ Carbons of Acryloyl Groups of MDA and Related Compounds

monomer	δ_{C_β}, ppm	δ_{C_α}, ppm	$\Delta\delta^a$, ppm
MAA	127.8	127.8	0.0
DAA	128.0	128.0	0.0
BAA	126.5	131.6	5.1
XAA	127.7	132.9	5.2
BPA	126.1	131.4	5.3
BAP	115.5^b	136.3^b	20.8

^{a} $\delta_{C_\alpha} - \delta_{C_\beta}$. ^{b} Chemical shifts of $C_\beta H_2{=}C_\alpha H{-}$ carbons of allyl group.

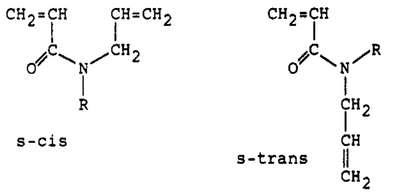
Scheme 1



$$CH_2{=}CH{-}\underset{\underset{\displaystyle X}{|}}{C}{=}O \longleftrightarrow \overset{+}{C}H_2{-}CH{=}\underset{\underset{\displaystyle X}{|}}{C}{-}\overset{-}{O}$$

5. It has been reported that the δ_{C_α} and δ_{C_β} values shift to a higher and lower magnetic field, respectively, with a linear relationship when the *e* values of the monomers become larger with increasing electron-attracting power of substituents.[12] This means that the values, $\Delta\delta$, obtained by subtracting δ_{C_α} from δ_{C_β} reflect the influence of substituents more effectively than their respective value. The stronger the electron-donating power of substituents, the larger the value. Comparison of the $\Delta\delta$ values of BAA and XAA with those of MAA and DAA indicates that the conjugations between olefin and carbonyl double bonds (Scheme 1) in the former are less effective than those in the latter. This is because the effective conjugation in α,β-unsaturated carbonyl compounds moves the electron in the olefin double bond into the carbonyl group and decrease the $\Delta\delta$ values.

Conformational Analyses of RAA. It is well-known that rotational rates around the amide C–N bond of many compounds with amide group are in the range which can be measured by means of NMR spectroscopic analyses and s-trans and s-cis isomers can be recognized.[13] In order to see the effect of conformation on the five-membered ring formation in the anionic polymerization of BAA, conformations of RAA were compared based on the ^{13}C NMR spectroscopic studies of carbon attached to nitrogen. ^{13}C NMR studies on the conformational isomerism of BAA and MAA have already been reported.[11] They revealed that rotation around the amide C–N bond of BAA is restricted even at a temperature as high as 120 °C and that of MAA is considerably free as can be seen from the fact that the temperature where the peaks due to >N–CH$_2$– carbons of the allyl group of the s-cis and s-trans isomers coalesce is at around 80 °C.[11] Temperature dependence of spectral patterns of *N*-methylene carbons of DAA illustrated in Figure 3 shows that the rotational behavior of the amide C–N bond of DAA is similar to that of MAA. In the case of XAA, the signal derived from carbons attached to the nitrogen remained as a sharp singlet over the temperature range from −80 °C to 120 °C. This means that the amide C–N bond of XAA is restricted even at temperatures as high as 120 °C as in the case of BAA.



N-Methyl protons of MAA were observed as a doublet with intensity ratio of 0.56:0.44 at temperatures lower than the coalescence temperature. In the dilution of a 50 wt % solution of MAA in CDCl$_3$ with benzene to 10 wt % solution, both *N*-methyl resonance peaks in the NMR spectra of MAA are shifted upfield (Figure 4). The lower-field peak with lower intensity is shifted by $\Delta\delta$ = 0.60 ppm, while the higher-field peak with higher intensity of the doublet is shifted by only $\Delta\delta$ = 0.20 ppm. The lower-field and higher-field peaks are attributed to the s-trans and s-cis forms, respectively, by analogy with the results reported for *N,N*-dimethylacetamide and similar compounds on the basis of dilution studies using aromatic solvents.[14]

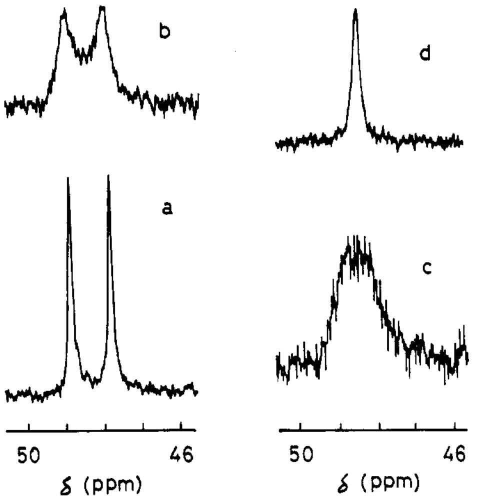


Figure 3. Temperature dependence of ^{13}C NMR spectra of >N–CH$_2$– carbons of DAA measured in (CD$_3$)$_2$SO: a, 40 °C; b, 60 °C; c, 70 °C; d, 100 °C.

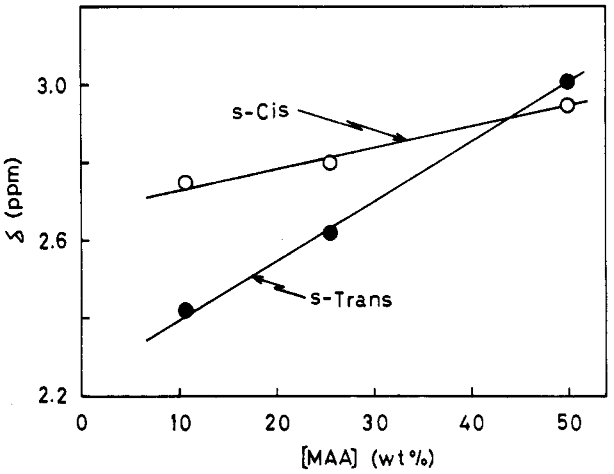


Figure 4. Upfield shift of the *N*-methyl proton resonance of MAA in CDCl$_3$ (50 wt % solution) on dilution with C$_6$D$_6$ at 25 °C.

Discussion

The allyl group of BAA is considered to have an extremely lower anionic polymerization tendency as can be judged from the polymerizability of BAP (Table 3). Nevertheless, BAA yields polymers with degree of cyclization higher than 80%, which indicates participation of the allyl group of BAA in the anionic polymerization. One reason for its peculiar reaction behavior might be attributed to a higher reactivity of the propagating anion derived from the acryloyl group of BAA. This can be reasonably expected from the fact that conjugation between its C=C and C=O double bonds is less effective than the acryloyl group of acrylamide derivatives such as MAA and DAA. However, the results shown in Table 1 indicate that the cyclopolymerizability of XAA is extremely low, though the reactivity of the propagating anion of its acryloyl group would be comparable to that of BAA, judging from the ^{13}C NMR data given in Table 5. This difference might be interpreted by taking into consideration the structural difference of the conformational isomers of BAA and XAA.

It has been concluded that BAA has just a favorable conformation for five-membered ring formation, since it forms completely cyclized polymers with a five-membered ring as a repeating cyclic unit irrespective of the fact that the rotation around its amide C–N bond is restricted.[11] The following consideration reasonably leads to the conclusion that this conformation plays an important role in five-membered ring formation in the anionic polymerization of BAA. Conformational analysis of XAA revealed that the rotation around its amide C–N bond is restricted even at temperatures as high as 120 °C. Accordingly, XAA is considered to assume fundamentally s-cis structure, because it can form a five-membered ring as a cyclic repeating unit in the radical polymerization, though the cyclization tendency is low (Table 2). This result suggests that the structure of s-cis conformer of XAA is considerably different from that of BAA; i.e., the two double bonds in XAA are thought to be fairly far from each other. In the case of radical polymerization, the uncyclized propagating radicals of XAA are considered to approach the double bonds of its own by oscillation, since the polymerizations are carried out at higher temperature where molecular motion is more active. The rotation around the amide C–N bonds of DAA and MAA is possible at the temperature range where radical polymerizations were undertaken. However, the fact that anionic polymerization was carried out at −78 °C suggests that it is practically restricted in the polymerization systems. In the case of DAA, its s-cis and s-trans forms have essentially the same structure, which means that one of its allyl groups is inevitably in s-cis arrangement with respect to its acryloyl group. Nevertheless, it does not yield any cyclized repeating units. In the case of MAA, the ratio of s-cis to s-trans isomer is 0.56:0.44. If the s-cis conformer has just favorable conformation for five-membered ring formation, it should yield polymers with a five-membered ring as the main repeating unit. In this case too, the polymers obtained do not contain any cyclized unit in their repeating units. These results together with the lower cyclopolymerization tendencies of these monomers than those of BAA in radical polymerization suggest that the s-cis conformers of DAA and MAA are considerably different from the structure of s-cis conformer of BAA as in the case of XAA. One reason for extremely lower cyclization tendencies of these two monomers would be attributable to their less favorable conformation and the other to lower reactivity of their propagating anions derived from the acryloyl groups. In the case of radical polymerization, the oscillation or rotation around the amide C–N bond is considered to allow encounter of the propagating radical with the double bond of their own. These results indicate that just favorable conformation of BAA for five-membered ring formation is one of the most important factors for these head-to-head and tail-to-tail additions, and in addition, higher reactivity of the propagating anion derived from the acryloyl group of BAA is considered to assist its attack to allyl group with lower reactivity.

Another characteristic feature of the polymerization behavior of BAA is its extremely lower anionic polymerizability. One reason for this might be ascribed to the lower rate of initiation reaction due to steric hindrance between the *N-tert*-butyl group and *tert*-butyl anion. The fact that BPA has also lower polymerization tendency supports this conclusion. The other might be attributed to the occurrence of side reaction owing to higher reactivity of the five-membered cyclized anion.

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References and Notes

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