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Cyclopolymerization XVII. Anionic Cyclopolymerization Tendency of *N*-Methyldiacrylamide and *N*-Substituted Dimethacrylamides

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ABSTRACT: Anionic cyclopolymerizabilities of *N*-methyldiacrylamide (MDA), *N*-propyldimethacrylamide (PDMA), and *N*-methyldimethacrylamide (MDMA) were studied. MDA initiated by *tert*-butylmagnesium chloride at −78°C yields polymers which consists almost exclusively of 5-membered ring as repeating unit, even though the nature of solvents employed are varied widely. This indicates that MDA has strong tendency toward head-to-head and tail-to-tail additions even in anionic polymerization. NMR spectroscopic studies showed that conjugation between C=C and C=O double bonds of MDA is as effective as that of acrylic esters. Favorable conformation of MDA for the 5-membered ring formation and higher electron density of propagating anion (–CH_2–$\overline{C}$H–CO–) in spite of the fact that its acryloyl groups have conjugative nature are regarded as possible reasons for the unusual addition behavior. Attempted anionic polymerizations of PDMA and MDMA were unsuccessful. NMR spectroscopic studies revealed that conjugation between olefin and C=O double bonds in these monomers is ineffective owing to the twisted conformation between the two double bonds. This unconjugative nature of the methacryloyl groups of PDMA and MDMA is considered to be responsible for their lower polymerizability in the anionic polymerization.

KEY WORDS Anionic Cyclopolymerization / 5-Membered Ring / Head-to-Head Addition / Tail-to-Tail Addition / ^{1}H NMR / ^{13}C NMR / *N*-Methyldiacrylamide / Dimethacrylamide Derivatives / Acrylamide Derivatives / Methacrylamide Derivatives /

N-Methyldiacrylamide (MDA) and *N*-methyldimethacrylamide (MDMA) have possibility to form three structural units during polymerization as shown in Scheme 1. However, MDA yields polymers with 5-membered ring as a main repeating unit and pendant unsaturation as a minor repeating component by anionic polymerization in tetrahydrofuran (THF),[1] while MDMA affords polymers which consist almost exclusively of 6-membered ring under similar experimental conditions.[2] The 5-membered ring formation is unusual because it means that head-to-head and tail-to-tail additions proceed in anionic polymerization where such addition modes have never been observed. Radical cyclopolymerizations of *N*-substituted diacrylamides (RDA)[3−6] and dimethacrylamides (RDMA)[2,7−14] yield polymers with 5-membered ring as a main repeating unit without leaving detectable pendant double bonds. Despite the structural similarity of the polymers formed by radical cyclopolymerizations of these monomers, the reactivities of their double bonds are substantially different, *i.e.*, the monofunctional counterparts of RDA

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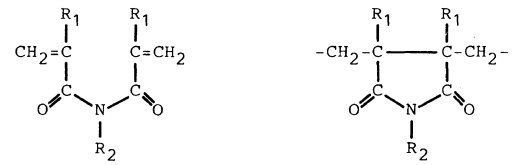
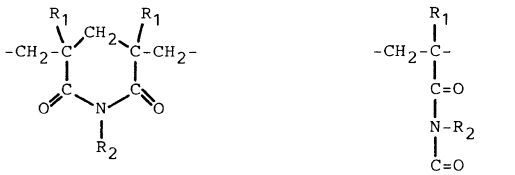




	R_1	R_2
MDA	H	CH_3
MDMA	CH_3	CH_3
PDMA	CH_3	$(CH_2)_2$-CH_3

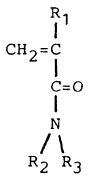
Scheme 1.

which correspond to *N,N*-disubstituted acrylamides (DSA) have high polymerization tendency,[15-17] while those of RDMA, *N,N*-disubstituted methacrylamides (DSMA), can not be polymerized to high polymers.[9,10,18] Thus, fundamental aspects for the formation of highly cyclized polymer in radical polymerization are considered to be different for RDMA[10] and RDA.[6] The effect of the difference in the reactivities of the double bonds involved in these monomers on their anionic cyclopolymerization tendencies is also the problem of interest, especially in connection with the difference observed in the repeating cyclic structures of poly(MDA)[1] and poly(MDMA).[2] However, only preliminary results are available for the anionic polymerization of MDA[1] and MDMA.[2] For this reason, anionic polymerizations of MDA, MDMA, and *N*-propyldimethacrylamide (PDMA) were undertaken together with NMR spectroscopic studies on these monomers and related compounds in order to clarify the correlation between the characteristic nature of their double bonds and their polymerizabilities. In addition to MDMA, PDMA was chosen because it can be handled easily at various experimental conditions owing to its lower melting point.[19]

EXPERIMENTAL

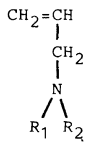
Materials

MDA,[4] PDMA,[19] MDMA,[19] and dimethacrylamide (DMA)[19] were prepared according to the reported procedure. MDA and PDMA used for polymerization were dried over molecular sieve, and distilled before use under dry nitrogen. Solvents were purified in the usual way. Commercial *tert*-butylmagnesium chloride (*t*-BuMgCl) and *n*-butyllithium (*n*-BuLi) available as solutions in THF and hexane, respectively (Tokyo Kasei), were used as initiators. Other acrylamide and methacrylamide derivatives and allylamine derivatives were synthesized by interfacial condensation reaction between corresponding amines and acid chlorides based on the procedure for the preparation of *sym*-dimethyldimethacryloylhydrazine.[20] They are *N*-methyl-*N*-propylacrylamide (MPA), *N*-methyl-*N*-allylacrylamide (MAA), *N,N*-dimethylacrylamide (DMAA), *N*-propylacrylamide (PA), *N*-methylacrylamide (MA), *N*-allylacrylamide (AA), *N*-methyl-*N*-propylmethacrylamide (MPMA), *N*-methyl-*N*-allylmethacrylamide (MAMA), *N,N*-dimethylmethacrylamide (DMMA), *N*-methylmethacrylamide (MeMA), *N*-propylmethacrylamide (PMA), *N*-allylmethacrylamide (AMA), *N*-allylpropanamide (APA), *N*-allylisobutanamide (ABA), and *N*-methyl-*N*-allylisobutanamide (MABA). Structural charactristics of these compounds are given in Schemes 1, 2, and 3. Cyclic model compounds, *N*-methylsuccinimide (MSI) and *N*-methylglutarimide (MGI), were prepared according to the procedure reported.[9] Methyl acrylate (MAC), ethyl acrylate (EAC), and methyl methacrylate (MMA) purchased from Wako pure chemical industry were subjected to NMR measurements without further purification. Poly(*N*-methylglutarimide), model polymer



	R_1	R_2	R_3
DMA	CH_3	H	$CO-C(CH_3)=CH_2$
MPA	H	CH_3	$(CH_2)_2-CH_3$
MAA	H	CH_3	$CH_2-CH=CH_2$
DMAA	H	CH_3	CH_3
PA	H	H	$(CH_2)_2-CH_3$
MA	H	H	CH_3
AA	H	H	$CH_2-CH=CH_2$
MPMA	CH_3	CH_3	$(CH_2)_2-CH_3$
MAMA	CH_3	CH_3	$CH_2-CH=CH_2$
DMMA	CH_3	CH_3	CH_3
MeMA	CH_3	H	CH_3
PMA	CH_3	H	$(CH_2)_2-CH_3$
AMA	CH_3	H	$CH_2-CH=CH_2$

Scheme 2.



	R_1	R_2
APA	H	$CO-CH_2-CH_3$
ABA	H	$CO-CH(CH_3)_2$
MABA	CH_3	$CO-CH(CH_3)_2$

Scheme 3.

which has 6-membered ring as repeating cyclic unit, was obtained based on the procedure reported.[2]

Polymerization

Polymerizations were carried out according to the procedure reported.[1] Precipitant used for polymerization mixture of PDMA was methanol. In the case of MDMA, solvents were evaporated under reduced pressure after polymerization under given conditions. Solid residue obtained was subjected to sublimation at 60°C/0.5 mmHg and finally at 90°C/0.5 mmHg to remove monomer. This process was adopted, since reproducible results on polymer yield have not been obtained in radical polymerization by precipitation method.[11]

Equimolar Reaction between PDMA and t-BuMgCl

Reaction procedures are essentially the same as those of polymerization. A solution of 1 ml (5.1×10^{-3} mol) of PDMA in 15 ml of THF was mixed with a solution of 0.53 g (5.1×10^{-3} mol) of *t*-BuMgCl in 5 ml of THF at −78°C. The reaction mixture was kept for 2 h at the temperature, to which methanol added with enough concentrated aqueous hydrochloric acid solution to neutralize anionic active species was introduced. After drying over sodium sulfate, the solvents were evaporated under reduced pressure to leave oily residue which was subjected to NMR analysis.

Measurements

^1H NMR and ^{13}C NMR spectra were taken on a JEOL JNM-GX-270 FT NMR spectrommeter using dimethyl sulfoxide-d_6 (DMSO-d_6), $CDCl_3$, and C_6D_6 as solvent and tetramethylsilane as an internal standard. Trifluoroacetic acid was added to shift signal due to water on ^1H NMR measurements in DMSO-d_6. Spectra of low molecular weight compounds were recorded at 80°C to remove the influence of restricted rotation around amide C–N bonds on their patterns. Spectral simulation on ^1H NMR spectra of vinyl protons was carried out using LAOCOON III. IR spectra were recorded on Hitachi 260-30 IR spectrometer. Viscosities were measured in Ubbelohde viscometer at 30°C in *N*,*N*-dimethylformamide (DMF).

RESULTS

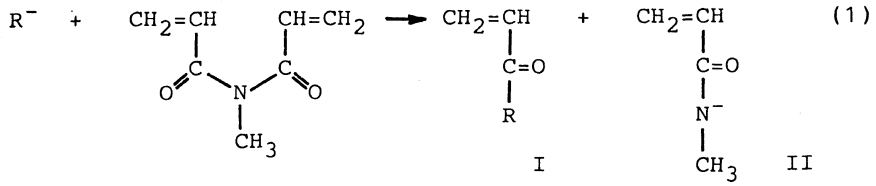
Polymerization of MDA

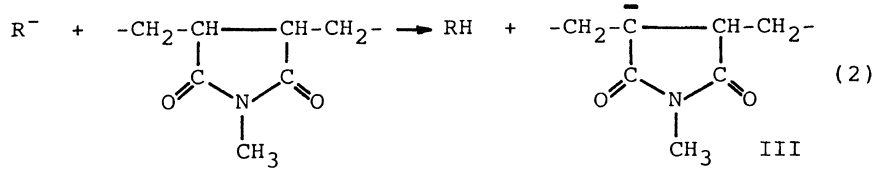
The results of the anionic polymerizations of MDA are summarized in Table I along with the reported data obtained in THF. Polymerization proceeds very rapidly after addition of initiator but it stops almost immediately. These characteristic features are common for all the polymerization systems irrespective of the solvents used, though the lower the polarity of the solvent, the higher the polymerization rate. Possible side reactions in these polymerization systems are illustrated in Scheme 4

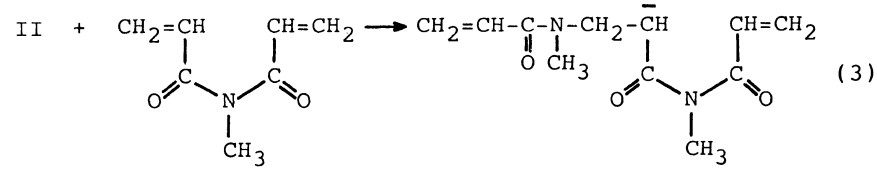
Table I. Anionic polymerization of MDA at −78°C[a]

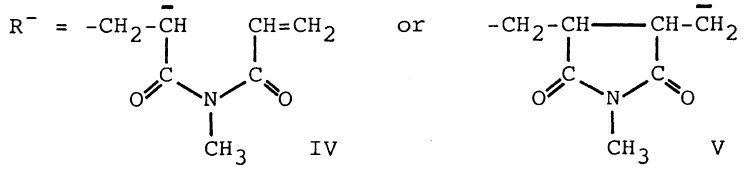
No.	Solvent	Time	Conv	$[\eta]$	DC[b]	5[c]	Ref
		min	%	$dl\,g^{-1}$	%	6	
1	Toluene[d]	0.5	26.8	0.12	—	1	This work
2		5	50.9	0.16	—	1	This work
3		30	61.2	0.14	~97	1	This work
4		60	59.0	—	~96	1	This work
6	THF	0.5	6.0	0.08	—	1	1
7		5	13.1	0.09	—	1	1
8		30	14.4	0.09	~96	1	1
9	DMF[e]	0.5	3.9	—	—	1	This work
10		5	8.6	0.08	—	1	This work
11		30	7.4	—	~100	1	This work

[a] $[M]_0 = 0.29\,mol/dm^3$, $[t\text{-BuMgCl}]_0 = 2.5 \times 10^{-2}\,mol\,dm^{-3}$.
[b] Degree of cyclization.
[c] Ratio of 5-membered ring to 6-membered ring.
[d] Contaminated with THF by 2.3 vol%.
[e] Mixed solvent with a ratio of DMF : THF = 6 : 1 in volume.









Scheme 4.

based on those which are characteristic to monomers with polar group.[21,22] These side reactions would be caused by propagating anions (IV, V) of MDA, especially by the active 5-membered cyclized anion (V), but not by sterically unfavorable *t*-butyl anion derived from initiator. Vinyl ketones (I) formed are more reactive than vinyl groups of MDA and accordingly they are consumed more rapidly than MDA.[23] Basicity of the propagating anion from vinyl ketones ($-CH_2-\overline{C}H-CO-R$) is too weak to attack MDA and polymerization stops.[23] These side reactions are considered to proceed more rapidly in polar solvent than in nonpolar solvent, because higher conversion was obtained in the polymerization in the latter than in the former. *N*-Methylacrylamide anion (II) might attack MDA to initiate polymerization (3), though the presence of these end-group vinyl protons were not detected in the ^{1}H NMR spectra of poly(MDA). Proton transfer from methine carbon to 5-membered cyclized anion yields carbanion (III) which might attack MDA to initiate its polymerization and to form branched structure. This possible structural deviation from polymer derived from radical polymerization might be responsible for the solubility behavior of poly(MDA) described below. All the polymers obtained under the conditions given in Table I are soluble in DMF and DMSO. However, they contain insoluble fraction to chloroform in which poly(MDA) obtained by radical polymerization is soluble.[6]

Structure of Poly(MDA)

^{1}H NMR spectrum of poly(MDA) obtained in DMF (Figure 1) is almost the same as that of the polymer obtained in THF, main repeating unit of which has already been identified to 5-membered ring.[1] In fact, the 5-membered ring structure of poly(MDA) obtained in DMF was confirmed by the comparison of its IR and ^{13}C NMR spectra with those of poly(MDA) obtained by radical polymerization and cyclic model compounds, *i.e.*, MGI and MSI as already reported.[1] The

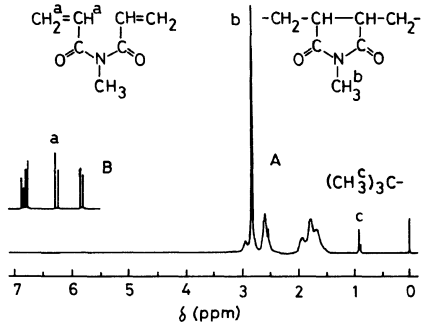


Figure 1. ^{1}H NMR spectra of poly(MDA) and MDA measured at 100°C. A, Poly(MDA) (No. 11 in Table I) in DMSO-d_6; B, $CH_2=CH-$ protons of MDA in DMSO-d_6.

characteristic features of these spectra of poly-MDA formed in DMF just correspond to what have been observed in poly(MDA) obtained in THF.[1] Only a difference found in these spectra is that signals due to pendant unsaturation is negligibly small in the ^{1}H NMR spectrum of poly(MDA) formed in DMF, while the polymers obtained in THF contains clearly detectable amount of pendant groups. Poly(MDA) formed in toluene affords essentially the same ^{1}H and ^{13}C NMR and IR spectra as those of polymers obtained in THF, though they are not shown. Very weak signals due to pendant olefin were also detected in the ^{1}H NMR spectra. The degrees of cyclization of some of these polymers were determined by comparing the signal intensity of pendant unsaturations with that of methylene protons observed at around 1.8 ppm and are also given in Table I. Repeating cyclic unit consists exclusively of 5-membered ring, since signal due to carbonyl carbon of 6-membered ring is not detected in ^{13}C NMR spectra. These results indicate that solvent effect on the structure of poly(MDA) is substantially small. Therefore, it can be concluded that MDA has extremely high tendency to 5-membered ring formation even in anionic polymerization. This is a quite anomalous observation, since head-to-head and tail-to-tail additions have never been observed in anionic polymerizations except for

the preliminary report on MDA.[1]

Attempted Polymerization of PDMA and MDMA

Polymerizations of PDMA were undertaken in THF and toluene under the same experimental conditions as those of MDA to give no polymer. *n*-BuLi was also found to be ineffective as an initiator. Almost pure PDMA was recovered quantitatively on equimolar reaction between *t*-BuMgCl and PDMA in THF at −78°C.

The result of attempted polymerization of MDMA is given in Table II. The solid residue obtained after removing monomer by sublimation was extracted with chloroform. Unextracted portion is almost soluble in DMSO (slight turbidity was observed) and has considerably higher solubility in water. It is a mixture of unknown substances and poly(MeMA) which was identified by comparing its ^{1}H NMR spectrum with that of authentic poly(MeMA). MeMA is formed by side reaction (1) but its main origin is considered to be product derived from hydrolysis of MDMA under the influence of hydrochloric acid added to terminate polymerization. MeMA is considered to be polymerized during heat-treatment to remove monomer. Portion extracted by chloroform is also a mixture of several compounds. Trace of MeMA was also confirmed as a component in the extract. It is not clear whether it contains either of 5-membered ring or 6-membered ring poly(MDMA) or both of them, because contamination with unknown substances makes difficult the comparison of ^{1}H NMR spectrum of the extract with that of poly(MDMA) obtained by radical polymerization[11] or that of poly(*N*-methylglutarimide). However, the amount of extracted portion indicates that the content of these polymers should be negligible, even if they exist.

Table II. Attempted anionic polymerization of MDMA initiated by *t*-BuMgCl in toluene at −78°C[a]

Time	Monomer[b]	Solid[c]	$CHCl_3$[d]	$MgCl_2$[e]
h	mg	mg	mg	mg
2	400	75	11	31

[a] $[M]_0 = 0.17\ mol/dm^{-3}$; $[t\text{-BuMgCl}]_0 = 2.4 \times 10^{-2}$ mol/dm.$^{-3}$
[b] Amount of monomer used.
[c] Solid residue after removing monomer by sublimation.
[d] Amount of portion extracted from the solid by $CHCl_3$.
[e] Amount of $MgCl_2$ calculated by assuming Mg is left in the solid as $MgCl_2$.

NMR Spectroscopic Studies on MDA and Related Compounds

Chemical shifts of C=C double bonds ($C_\beta H_2 = C_\alpha H\text{–}X$) of MDA and related compounds obtained by measuring ^{13}C NMR spectra are summarized in Table III. It has been reported that the δ_{C_β} and δ_{C_α} values shift to a lower and higher magnetic field, respectively, with linear relationship when the

Table III. ^{13}C Chemical shifts of $C_\beta H_2 = C_\alpha H\text{–}CO\text{–}$ carbons of acryloyl groups of MDA and related compounds

Monomer	δ_{C_β}	δ_{C_α}	$\delta_{C=O}$	$\Delta\delta$[a]
	ppm	ppm	ppm	ppm
MDA	130.0	130.5	168.9	0.5
MPA	127.4	128.0	166.4	0.6
MAA	127.8	127.8	166.5	0.0
DMAA	126.8	128.3	166.8	1.5
PA	125.7	131.7	166.0	6.0
MA	125.3	131.5	166.8	6.2
AA	126.4	130.9	165.8	4.5
MAC	130.7	128.3	166.7	−2.4
EAC	130.4	128.7	166.3	−1.7
ABA	116.0[b]	134.6[b]	177.1[c]	18.6
MABA	116.6[b]	133.3[b]	177.1[c]	15.7
MVE	84.1[d]	153.2[d]	—	69.1

[a] $\delta_{C_\alpha} - \delta_{C_\beta}$.
[b] Chemical shifts of $C_\beta H_2 = C_\alpha H\text{–}$ carbons of allyl group.
[c] Chemical shift of carbonyl carbon of isobutanamide group.
[d] Chemical shifts of $C_\beta H_2 = C_\alpha H\text{–}$ carbons of MVE.[25]

e values of the monomers become larger with increasing electron-attracting power of substituents.[24] This means that the values, $\Delta\delta$, obtained by subtracting δ_{C_β} from δ_{C_α} reflects the influence of substituents more effectively than their respective value. The stronger the electron-donating power of substituents, the larger the value. This can be seen from the values observed for the C=C double bonds of methyl vinyl ether (MVE), allyl groups, and acrylic esters. Comparison of the $\Delta\delta$ values of DSA including MDA with those of acrylic esters indicates that the conjugations between olefin and carbonyl double bonds (Scheme 5)

Scheme 5.

in the latter are slightly more effective than those in the former. The $\Delta\delta$ values of DSA and *N*-monosubstituted acrylamides (MSA) in turn suggests that conjugation of α,β-unsaturated groups is more effective in DSA than in MSA. Effective conjugation in α,β-unsaturated carbonyl compounds moves electron in olefin double bond into carbonyl group. Accordingly, the carbonyl carbons of these compounds should appear at higher magnetic field than those of unconjugated carbonyl group such as ABA and MABA in ^{13}C NMR spectra.[26] Comparison of the chemical shifts of carbonyl carbons shown in Table III affords supporting evidence for the aforementioned conclusion that conjugations between C=C and C=O double bonds in MDA and DSA are as effective as those of acrylic esters.

The results of ^1H NMR studies on MDA and related compounds are summarized in

Table IV. Chemical shifts and coupling constants of various acryloyl protons[a]

Compound	Solvent[b]	δ/ppm			Coupling const/cps			$\delta H_C^1-\delta H_B^1$	$\delta H_C^3-\delta H_B^3$
		H^1	H^2	H^3	J_{12}	J_{13}	J_{23}		
MDA	C	6.37	6.72	5.76	16.7	1.8	10.3	0.12	0.50
	B	6.25	6.42	5.26	16.8	1.9	10.3		
MPA	C	6.25	6.55	5.60	16.7	2.1	10.6	−0.13	0.25
	B	6.38	6.32	5.35	16.9	2.2	11.0		
MAA	C	6.26	6.52	5.62	16.9	2.0	10.6	−0.11	0.22
	B	6.36	6.29	5.36	16.9	2.4	10.4		
DMAA	C	6.25	6.56	5.61	16.9	2.1	10.6	−0.09	0.27
	B	6.32	6.29	5.34	16.9	2.4	10.5		
PA	C	6.20	6.15	5.56	17.3	1.7	10.6	−0.08	0.25
	B	6.28	6.13	5.31	17.1	2.0	10.2		
MA	C	6.20	6.17	5.56	17.2	1.2	10.5	−0.02	0.30
	B	6.22	6.01	5.26	17.1	1.8	10.4		
AA	C	6.22	6.17	5.59	17.0	1.4	10.2	−0.04	0.29
	B	6.26	6.10	5.30	17.1	1.9	10.6		
MAC	C	6.38	6.13	5.79	17.4	1.4	10.5	−0.14	0.44
	B	6.24	5.96	5.35	17.5	1.4	10.4		
EAC	C	6.36	6.10	5.76	17.3	1.7	10.4	−0.10	0.42
	B	6.26	5.99	5.35	17.3	1.7	10.5		
AA[c]	C	5.20	5.86	5.13	17.1	1.2	10.3	—	—
MAA[c]	C	5.18	5.80	5.20	17.0	1.1	10.1	—	—

[a] $H^1(H^3)C=C(X)H^2$

[b] C, $CDCl_3$; B, C_6D_6.

[c] Data of allyl protons.

Table IV. The chemical shifts and coupling constants are determined by computer simulation for three spin system of $CH_2=CH-$. Those obtained in $CDCl_3$ afford added evidence for the conclusion drawn above, *i.e.*, the extent of conjugation of acryloyl groups of these compounds decreases with an order of acrylic esters, DSA, and MSA. This is because chemical shifts of β-methylene protons of acrylic esters are detected at the lowest magnetic fields, while those of MSA at the highest. Solvent shifts induced by C_6D_6, which have been reported to be larger for protons *trans* than *cis* to carbonyl,[27] support the assignment of these protons along with the coupling constants shown also in Table IV.

α-Protons of DSA including MDA are observed at lower magnetic field than *cis* protons to substituents, in contrast to the results of acrylic esters and MSA. These characteristic features of proton resonance are also observed in unconjugated olefin double bonds such as allyl groups (Table IV). However, the correlation between the nature of olefin double bonds and the chemical shifts of their α-protons has not been established.[28] Diamagnetic shileding effect of carbonyl group influences the chemical shifts of α-protons of α,β-conjugated carbonyl compounds together with the electron density at α-proton.[29] For this reason detailed discussion will not be given based on these results.

NMR Studies on PDMA and Related Compounds

^1H NMR spectra of DSMA were compared with those of *N*-monosubstituted methacrylamides (MSMA) which can be polymerized (Table V). The most outstanding feature of ^1H NMR spectra of the former as compared with the latter, is the high chemical shift of CH_2 protons of their methacryloyl groups. Considering the fact that olefin protons of unconjugated monomers such as isopropenyl chloride (5.08 ppm in CCl_4)[30] and 2,5-dimethyl-1,5-hexadiene (4.74 ppm in $CDCl_3$)[31]

Table V. Chemical shifts of methylene protons of methacryloyl groups[a] of PDMA and related compounds

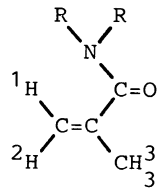
Compound	Geometry	δ_C[b]	δ_B[c]	$\delta_C-\delta_B$
		ppm	ppm	ppm
PDMA	*trans*	5.32	4.87	0.45
	cis	5.14	4.78	0.36
MDMA	*trans*	5.32	4.79	0.53
	cis	5.14	4.77	0.37
MPMA	*trans*	5.13	4.91	0.22
	cis	4.99	4.85	0.14
MAMA	*trans*	5.14	4.89	0.25
	cis	5.03	4.89	0.14
DMMA	*trans*	5.19	4.93	0.26
	cis	5.03	4.83	0.20
PMA	*trans*	5.30	5.08	0.22
	cis	5.67	5.70	−0.03
AMA	*trans*	5.37	4.96	0.41
	cis	5.75	5.45	0.30
MMA	*trans*	5.56	5.19	0.37
	cis	6.11	6.08	0.03

[a] $^{trans}H\diagdown C=C\diagup CH_3$; $^{cis}H\diagup\quad\diagdown C=O$

[b] Measured in $CDCl_3$.

[c] Measured in C_6D_6.

resonance at higher magnetic field than those of typical conjugated monomers such as MMA (Table V), this might be due to the shielding effect caused by local dimagnetic current which is effective in DSMA because of the less effective resonance between C=C and C=O double bonds.[32] The fact that *N*-methacryloylaziridine, among DSMA only monomer which can be polymerized, have rather similar chemical shifts to the corresponding shifts of methacrylic esters[33] also supports this conclusion. Another interesting feature of the ^1H NMR spectra of DSMA measured in $CDCl_3$ is that absorption due to the CH_2 proton *trans* to carbonyl appears at lower magnetic field than the *cis* proton. This is an unsual observation, since it has been reported that for many α,β-unsaturated carbonyl compounds vinyl protons *cis* to the carbonyl are deshielded to a greater extent than the *trans* protons[34] as can be seen from the data for MSMA and MMA



Scheme 6.

which are shown also in Table V. Broader peaks were assigned to protons *trans* to carbonyl, since for many α,β-unsaturated carbonyls, the long-range coupling constant $J_{2,3}$ is larger than $J_{1,3}$ (Scheme 6).[30,34] It has been reported that solvent shifts of the proton resonance produced by benzene are greater for the proton *trans* to the carbonyl.[27] The solvent shifts given in Table V are in accordance with the assignment based on the coupling constants. A large diamagnetic anisotropy of carbonyl group reasonably explains that olefin proton *cis* to the carbonyl group resonances at lower magnetic field than *trans* proton, if the C=C and C=O double bonds of α,β-unsaturated carbonyl compounds take the coplanar conformation which attains effective conjugation between the two double bonds.[32] The twisted conformation between the C=C and C=O double bonds changes the relative position of olefinic protons to carbonyl group. This brings the olefinic proton *cis* to carbonyl to the site shielded by carbonyl group less effectively while circumstance of the proton *trans* to carbonyl does not change so much. This twisted conformer reduces the conjugation between the C=C and C=O double bonds in agreement with conclusion drawn above.

^{13}C NMR spectra afforded additional evidence for the reduced conjugation between C=C and C=O double bonds in methacryloyl groups of DSMA (Table VI). This is because the values, Δδ, are larger for DSMA than for MSMA. The result of MMA, the C=C and C=O double bonds of which are in effective conjugation, also supports these considerations. In addition, the chemical shifts of the carbonyl carbons of DSMA tend to be closer to those of unconjugated carbonyl carbons

Table VI. ^{13}C Chemical shifts of $C_\beta H_2=C_\alpha<$ and carbonyl carbons of methacryloyl groups of PDMA and related compounds

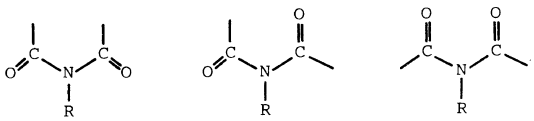
Compound	δ_{C_β}	δ_{C_α}	$\delta_{C=O}$	$\Delta\delta$[a]
	ppm	ppm	ppm	ppm
PDMA	119.6	145.0	175.0	25.4
MDMA	119.7	144.0	175.1	24.7
MPMA	114.8	141.3	172.6	26.5
MAMA	117.3	140.8	172.9	23.5
DMMA	115.4	140.8	172.5	25.4
DMA	121.9	140.2	167.3	18.3
PMA	119.0	140.4	168.6	21.4
AMA	119.5	140.0	168.4	20.5
MABA	—	—	177.1[b]	—
ABA	—	—	177.1[b]	—
MMA	125.5	136.3	168.0	10.8

[a] $\delta_{C_\alpha}-\delta_{C_\beta}$.
[b] Chemical shift of carbonyl carbon of isobutanamide group.

such as those of MABA and ABA, which shows that the conjugations in these methacryloyl groups are less effective than those in MSMA. The reduced conjugation between C=C and C=O double bonds is considered to be caused by the twisted conformation between the two double bonds. Supporting evidence for this conclusion is available from crystallographic studies of MDMA which revealed that the torsional angle between planes of C=O and C=C double bonds of its methacryloyl groups is 51.6°.[35] Some of the charactristic features of ^{1}H and ^{13}C NMR spectra mentioned above were also observed in isopropenyl *tert*-butyl ketone which could not be polymerized by radical initiator.[26] Twisted conformation between C=C and C=O double bonds has been ascribed to the reduced conjugation in its double bond.

DISCUSSION

^{1}H and ^{13}C NMR spectroscopic studies show characteristic property of α,β-conjugated double bonds in MDA is similar to those of acrylic



cis–cis *cis–trans* *trans–trans*

Scheme 7.

esters. This means that the head-to-head and tail-to-tail additions in the anionic polymerization of MDA cannot be explained by the nature of its double bonds. The reported results show that MDA has twisted *cis–cis* conformation[6] (typical three conformations of *N*-substituted imide group are illustrated in Scheme 7), which implies that its two acryloyl groups might be considerably far from each other. However, it has been also suggested that the methine carbons of the acryloyl groups are considered to have high probability to encounter when both the double bonds come closer by the oscillation around imide C–N–C bonds.[6] DMAA has been reported to have reactivity of typical conjugated monomers such as MAC toward various propagating radicals in agreement with its α,β-conjugated double bond structure, while propagating radical of DMAA was found to be much more reactive than common conjugated polymer radicals such as polystyrene or poly(MAC) radical.[15] The unexpected high reactivity of the propagating radical of DMAA was considered to be due to the less effective conjugation between unpaired electron and carbonyl group which leads to a higher electron density of the unpaired electron of the propagating radical,[15] in contrast to the effective conjugation between C=C and C=O double bonds in this monomer. These considerations suggest that the electron density of propagating anion ($-CH_2-\overline{C}H-CO-N\langle$) of acryloyl groups of DSA might be also high and, accordingly, the reactivity of the propagating anion (tail anion, IV in Scheme 4) of MDA is high enough to make possible the tail-to-tail addition to form 5-membered ring with carbanion of higher basicity (V in Scheme 4). The favorable conformation for the tail-to-tail addition is considered to assist the 5-membered ring formation.

Radical polymerization of PDMA initiated by ionizing radiation at $-78°C$ yields completely cyclized polymer with 5-membered ring as a main repeating unit and 6-membered ring as a minor repeating component.[12] However, it appeared that it can not be polymerized by *t*-BuMgCl and *n*-BuLi. Further, it was found that even the equimolar reaction between PDMA and *t*-BuMgCl does not proceed. MDMA was also found to be non-polymerizable by *t*-BuMgCl in toluene at $-78°C$. ^1H and ^{13}C NMR studies showed that *N,N*-disubstituted methacrylamide group has unconjugative nature in contrast to their appearance owing to the twisted conformation between carbonyl group and olefin double bond. This would be the reason for the low reactivity of *N,N*-disubstituted methacrylamide group toward carbanion. However, it has been reported that polymerization of MDMA by phenyl magnesium bromide in THF and toluene yields poly(MDMA) at $-78°C$ with 6-membered repeating unit.[2] The reason why MDMA shows different polymerization behavior under these experimental conditions should be the matter to be clarified in future.

IR spectra of compounds being capable of forming hydrogen bond are influenced strongly by experimental conditions, while NMR data are not.[36] It has been reported that UV spectra of these compounds are rather complicated and assignment of the observed transition was not possible.[37] For these reasons, NMR spectroscopic studies have been adopted for the investigation on conjugation between C=C and C=O double bonds.

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