Solvent Effect on the Radical Copolymerization of N-Methyl- and N,N-Dimethylacrylamides and N-Methylmethacrylamide with Methyl Methacrylate

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ABSTRACT: Solvent effect on radical copolymerizations of N-methylacrylamide (AA) and N-methylmethacrylamide (MA) with methyl methacrylate (MMA, M_2) was studied using benzene (BZ), dioxane (DO), acetonitrile (ACN), ethanol (EtOH), and N,N-dimethylformamide (DMF). Spectroscopic studies revealed that the solvents influence these amide monomers (M_1) with regards to their association by hydrogen-bonding and dipole–dipole interaction. The solvent ability which makes the self-associations of AA and MA more effective decreases in the order of BZ > DO > ACN > EtOH > DMF. The higher the solvent ability for the self-associations of the amide monomers, the larger the values of r_1. The extent of the solvent effect on both the monomers decreased with decreasing order of their self-association tendencies, *i.e.*, AA > MA. M_1 concentration around $M_1 \cdot$ radical is considered to be enhanced by its association with M_1 in the solvent with higher ability for the self-association of M_1. This enhances the propagation-rate between $M_1 \cdot$ radical and M_1 and increases apparently k_{11} as compared with k_{12}. The r_2 values did not change depending on solvents except the copolymerization in BZ. The interactions between MMA and the amide monomers are too weak to raise their local concentrations around $M_2 \cdot$ radical. BZ increases extraordinarily r_1 and decreases r_2, respectively. Copolymers precipitated during copolymerization in BZ are considered to adsorb the amide monomers, since their interactions with BZ are extremely weak. This increases the local M_1 concentration around both $M_1 \cdot$ and $M_2 \cdot$ radicals. BZ influences even the copolymerization of N,N-dimethylacrylamide which has been considered to be independent of the solvents. Dipole–dipole interaction has been ascribed to this solvent effect.

KEY WORDS   Solvent Effect / Radical Copolymerization / NMR / IR / Hydrogen-Bond / Dipole–Dipole Interaction / Derivatives of Acrylamide / N-Methylmethacrylamide /

It has been reported that solvents influence strongly the radical copolymerizations of acrylamide,[1-8] methacrylamide[9] and their N-monosubstituted derivatives,[10,11] though the copolymerization behavior of N,N-dimethylacrylamide (DMA)[12] is not affected by the solvent employed. The solvent effect on the copolymerizations has been discussed in terms of the influence of the solvent properties, *i.e.*, polarity, dielectric constant, hydrogen-bonding ability, etc., on the monomer associa-

tion,[3-6] keto-enol equilibrium,[12] and conjugation between C=C and C=O double bonds.[11] There is, however, no comprehensive understanding of its mechanism, because of the lack of adequate data which describe these aspects of monomers and solvents. On the other hand, during the study on the cyclopolymerization of *sym*-dimethacryloyldimethylhydrazine and N,N'-dimethacryloylmethyl hydrazine (DMUM), it was found that polymerization of the latter strongly depends

on the solvents employed as reaction media, while the former did not. The change with regard to molecular association through hydrogen-bonding and dipole-dipole interaction in polymerization system depending on solvents has been ascribed to the solvent effect in the polymerization of DMUM.[13] For this reason, the studies on the copolymerization of N-methylacrylamide (AA) and N-methylmethacrylamide (MA) with methyl methacrylate (MMA) were undertaken along with NMR and IR studies on the two amide monomers, using benzene (BZ), dioxane (DO), acetonitrile (ACN), ethanol (EtOH), and N,N-dimethylformamide (DMF) as solvents. AA and MA were chosen, since the fairly high solubility of these monomers in the solvents with extremely different properties mentioned above permits us to study the copolymerization in widely different conditions. Copolymerizations of N,N-dimethylacrylamide (DMA) with MMA in BZ and DMF were also carried out for comparison.

EXPERIMENTAL

Materials

Monomers were prepared by reactions between corresponding acid chlorides and amines according to the procedure reported.[14]

Commercial azobisisobutyronitrile (AIBN) was recrystallized twice from EtOH.

All common solvents were purified by usual methods. EtOH and ACN for spectroscopic measurements were used without further purification.

Polymerization

Copolymerizations were carried out at constant total monomer concentration (0.80 mol dm^{-3}) in the presence of AIBN (2.4×10^{-3} mol dm^{-3}) at 70°C. The copolymerization solutions placed in glass ampoules were subjected to several freeze-pump-thaw cycles and sealed. Polymers were isolated by pouring the polymerization mixture into a precipitant and

drying them at 80°C under reduced pressure for 48 h. The precipitants used are mixtures of diethyl ether (DE) and petroleum ether (PE). Volume ratios of DE to PE were 3 : 1 for AA and DMA systems and 1 : 1 for MA system. The polymers were reprecipitated from DMF solution into the precipitants to obtain pure polymers for the composition analysis.

Measurements

IR spectra were recorded on Hitachi 260-30 infrared spectrometer at room temperature. NMR spectra were taken on a JEOL GX-270 FT NMR spectrometer. Copolymer compositions were determined for the polymers obtained with conversion less than 10% according to Fineman–Ross method[15] by measuring the intensity of the specific absorption for the respective monomer units in the NMR spectra of copolymers: AA and MA, $\geqslant$NCH$_3$ protons; DMA, $-$N(CH$_3$)$_2$ protons; MMA, $-$OCH$_3$ protons. The mean values at least for five measurements were adopted. In cases where measurements were made in DMSO-d_6 solution, trifluoroacetic acids was added to shift the peak due to H$_2$O to a lower magnetic field.

RESULTS

Copolymerization of AA, MA, and DMA with MMA

Copolymer composition curves obtained from the copolymerization of the three amide monomers with MMA in various solvents are illustrated in Figures 1, 2, and 3. Monomer reactivity ratios calculated based on these data are summarized in Table I together with those reported. It can be seen that the tendencies of the solvent effects are common for AA and MA, though their extents are different. Effect of BZ on these copolymerizations is extraordinarily large and it influences even the copolymerization of DMA which has been considered to be almost independent of the solvents where copolymerizations are carried out.
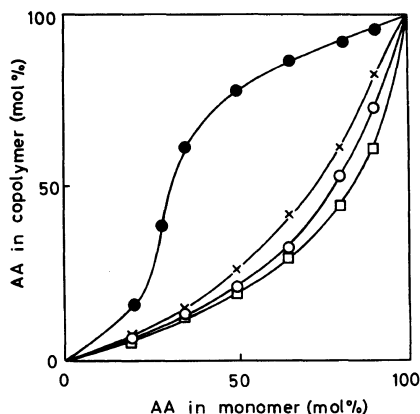
Figure 1. Copolymer composition curves of AA with MMA. (●), BZ; (○), ACN; (□), DMF; (×), mixed solvent of BZ and DMF, BZ/DMF is 3/1 in volume ratio, temp, 70°C; total monomer concn, 0.80 mol dm^{-3}; [AIBN]$_0$, 2.4×10^{-4} mol dm^{-3}.
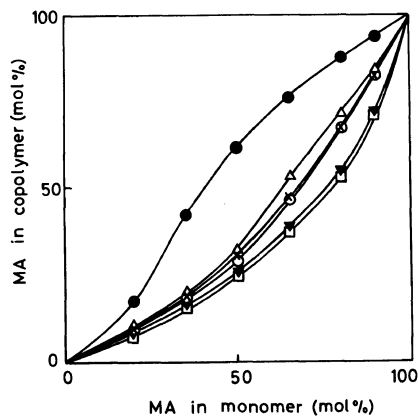

Figure 2. Copolymer composition curves of MA with MMA. (△), DO; (▼), EtOH. Other notations and conditions are the same as in Figure 1.

IR studies on monomer solvent mixture

The lowering of stretching frequencies of certain groups such as OH and NH in the IR spectra is well known to occur when they are associated with hydrogen-bonding.[17] The lower the frequency of the absorption, the stronger the interaction.[18] The absorption maxima of the NH stretching frequency of AA measured in various solvents at monomer concentrations of 0.017 and 0.84 mol dm^{-3} are summarized in Table II along with the physical
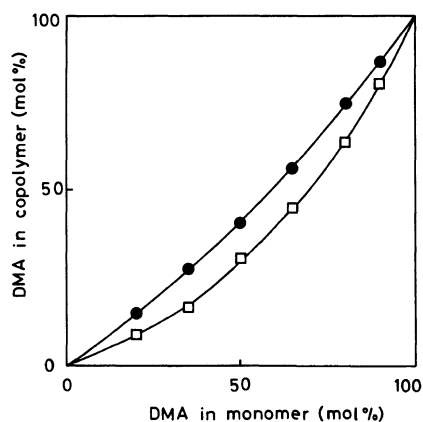

Figure 3. Copolymer composition curves of DMA with MMA. Notations and conditions are the same as in Figure 1.

Table I. Copolymerization of amide monomers (M$_1$) with MMA (M$_2$) in various solvents

M$_1$	Solvent	r_1	r_2
AA	BZ	2.43 ± 0.22	0.45 ± 0.14
	DO^a	1.03 ± 0.04	3.50 ± 0.20
	BZ/DMF^b	0.59 ± 0.28	3.55 ± 0.03
	ACN	0.32 ± 0.04	3.88 ± 0.00
	EtOH^a	0.28 ± 0.02	3.30 ± 0.10
	DMF	0.13 ± 0.03	3.59 ± 0.00
MA	BZ	1.92 ± 0.10	0.96 ± 0.04
	DO	0.81 ± 0.09	2.45 ± 0.01
	BZ/DMF^b	0.57 ± 0.07	2.49 ± 0.01
	ACN	0.56 ± 0.07	2.52 ± 0.01
	EtOH	0.24 ± 0.04	2.45 ± 0.00
	DMF	0.24 ± 0.03	2.66 ± 0.02
DMA	BZ	0.71 ± 0.01	1.39 ± 0.03
	TL^c	0.45 ± 0.08	1.80 ± 0.18
	DO^d	0.51 ± 0.08	2.04 ± 0.11
	EtOH^d	0.42 ± 0.10	2.30 ± 0.24
	DMF	0.46 ± 0.03	2.53 ± 0.00

[a] Cited from ref 10.
[b] Mixed solvent: volume ratio of BZ to DMF, 3:1.
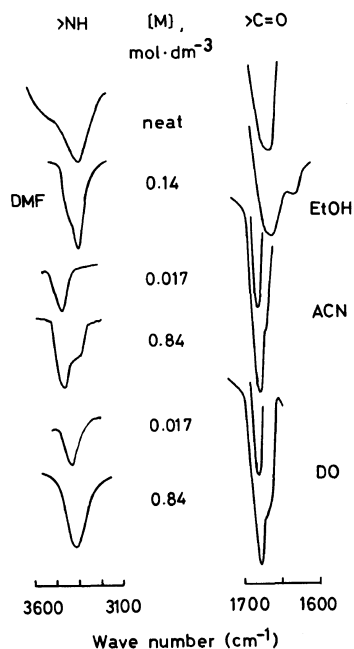[c] TL, toluene. Cited from ref 16.
[d] Cited from ref 12.

properties of the solvents. Dependence of spectral patterns of NH and C=O stretching frequencies on AA concentration in BZ are depicted in Figure 4. The NH frequency at 3445 cm^{-1} corresponds to AA in monomeric state

Table II. Stretching vibration of the NH group of AA in various solvents and their physical properties

Solvent	Wave number/cm^{-1}		μ^c	ε^d	γ^e
	$\nu_1{}^a$	$\nu_2{}^b$			
BZ	3445	3300	0	2.22	0
DO	3365	3360	0.45	2.21	9.7
ACN	3400	3398	3.37	32.5	6.3
EtOH	—	—	1.68	25.7	18.7
DMF	3305	3305	3.82	37.6	11.7
BZ/DMF^f	3330	3328	—	—	—
Neat^g	—	3300	—	—	—

^{a} [M], 0.017 mol dm^{-3}.
^{b} [M], 0.84 mol dm^{-3}.
^{c} Dipole moment.
^{d} Dielectric constant.
^{e} Hydrogen bonding parameter.[19]
^{f} Mixed solvent: volume ratio of BZ to DMF, 3:1.
^{g} Measured in neat.
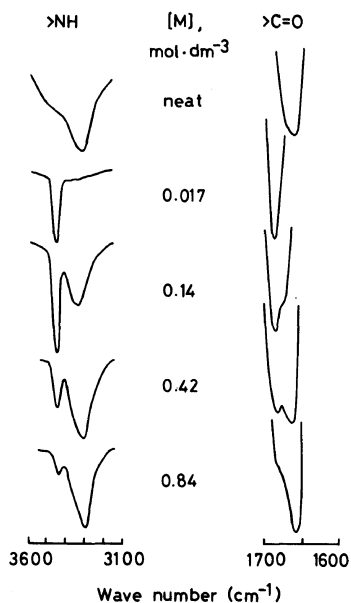
Figure 4. Concentration dependence of IR spectra of AA in BZ.

Figure 5. Concentration dependence of IR spectra of AA in various solvents.

and that at 3300 cm^{-1} to self-associated AA. The variation of carbonyl absorption indicates that the self-association of AA occurs through hydrogen-bonding between its NH and C=O groups. This assignment is supported by the fact that the NH and C=O stretching fre-

quencies of AA in neat are observed nearly at the same regions as those of AA in BZ with its higher concentration. The frequencies of the absorption maxima of NH stretching vibration in various solvents at monomer concentration of 0.017 mol dm^{-3} reflect the strength of hydrogen-bonding between NH hydrogen and solvents, since AA is dissolved in monomeric state at the concentration. The absorption maxima of NH groups varies in accordance with the hydrogen-bonding ability[19] of the solvents (Table II). Increase in the AA concentration does not bring about distinct change in absorption maxima of NH absorption except in BZ (Table II). However, the shoulder at a lower wave number and broadening to a lower wave number of the absorptions of NH and C=O groups observed in DO or ACN show that association of AA takes place through hydrogen bonding between NH and C=O groups in these solvents, too, though the extent is not so high as in BZ (Figure 5). The absorption due to carbonyl group in EtOH

Table III. Stretching vibration of the NH group of MA in various solvents

Solvent	Wave number/cm^{-1}	
	$v_1{}^a$	$v_2{}^b$
BZ	3470	3345
DO	3395	3390
ACN	3435	3430
DMF	3370	3370
Neat^c		3340

^{a} [M], 0.015 mol dm^{-3}.
^{b} [M], 0.80 mol dm^{-3}.
^{c} Measured in neat.

indicates clearly that the C=O group is involved with hydrogen-bonding. The stretching vibration of NH group of MA observed in various solvents are shown in Table III. The change of absorption maxima depending on solvent and monomer concentration has similar tendency to that of AA. The appearance of spectral pattern of NH and C=O groups also showed similar change observed in AA, though the change was less sensitive than that observed in AA. These results suggest that weaker but essentially the same association as that in AA takes place in MA.

Aspects of the NH absorptions of AA and MA measured in MMA are depicted in Figure 6. It can be said that the hydrogen-bonding ability of MMA is almost the same as that of ACN, since the absorption maxima observed at lower concentration of AA and MA exhibit almost the same values as those observed for AA and MA dissolved in monomeric state in ACN (Tables II and III).

^{1}H NMR Studies on Monomer–Solvent Mixture

Features of the molecular association in these monomer-solvent systems examined by measuring ^{1}H NMR spectra are summarized in Table IV. A down field shift is usually observed when the NH proton is placed in an environment of proton affinity.[20] The observed chemical shifts show that the proton affinities
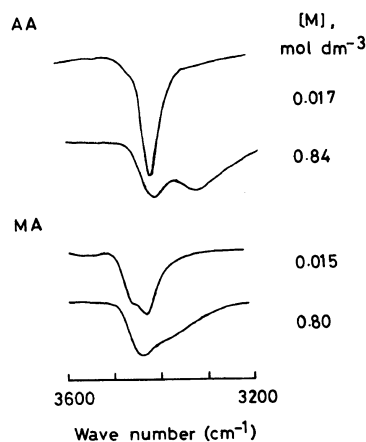
Figure 6. Concentration dependence of NH absorption in IR spectra of AA and MA in MMA.

Table IV. Chemical shifts of the NH protons of AA and MA in various solvents^a

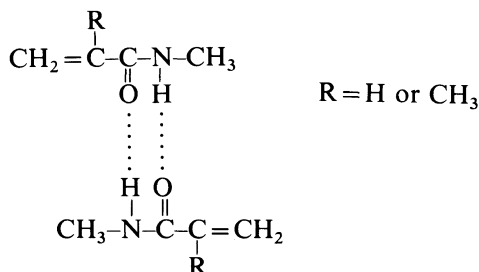| Monomer	Solvent	$\delta_1{}^b$/ppm	$\delta_2{}^c$/ppm	$\Delta\delta^d$/ppm
AA	BZ-d_6	4.18	6.58	2.40
	DO-d_8	6.38	6.82	0.44
	BZ-d_6/DMF-$d_7{}^e$	7.23	7.55	0.32
	ACN-d_6	6.37	6.52	0.15
	DMF-d_7	7.71	7.75	0.04
MA	BZ-d_6	4.70	6.10	1.40
	DO-d_8	6.46	6.72	0.26
	ACN-d_3	6.35	6.52	0.17
	DMF-d_7	7.52	7.59	0.07

^{a} Temp, 70°C.
^{b} 0.015 mol dm^{-3}.
^{c} 0.80 mol dm^{-3}.
^{d} $\delta_2 - \delta_1$.
^{e} Mixed solvent: volume ratio of BZ to DMF, 3:1.

of the solvents decrease with an order DMF-$d_7 >$ DO-$d_8 >$ ACN-$d_3 >$ BZ-d_6, which is in agreement with the order found by IR measurements. Increase in monomer concentration in BZ-d_6 shifted remarkably the chemical shift of NH proton to lower magnetic field. This is because weak affinity of BZ-d_6 toward the NH proton and dipole-dipole interaction between amide monomers favor their association. Down field shift was also observed in ACN-d_3 and DO-d_8, but the extents are small compared

with those in BZ-d_6, which indicates weaker self-association of AA and MA in these solvents than in BZ-d_6. Furthermore, the shift brought about by increasing monomer concentration in ACN-d_3 is less than that in DO-d_8, in spite of the fact that the proton affinity of ACN-d_3 is lower than that of DO-d_8. Judging from much higher polarity of ACN-d_3 than that of DO-d_8, molecular association in these solvents is considered to be governed by the relative strength of the proton affinity toward dipole–dipole interaction. The chemical shifts of the NH protons in DMF-d_7 are independent of amide monomer concentration. A monomer can interact with solvent to the same extent as with the monomer itself in this solvent. BZ is at one extreme and DMF, at another extreme in terms of proton affinity and polarity among the solvents investigated. AA and MA dissolve homogeneously in DMF, but the strong interactions between themselves make the BZ solutions of AA and MA inhomogeneous. These results together with those of IR spectroscopic studies suggest that the strength of the molecular association between amide monomers in these solvents decreases in the order of BZ > DO > ACN > DMF. Properties of EtOH given in Table II suggest that EtOH solutions of AA and MA have similar characteristic features to their DMF solution in terms of molecular association.

$$
\begin{array}{c}
R \\
| \\
CH_2 = C-C-N-CH_3 \\
\| | \\
O H \\
\vdots \vdots \\
H O \\
| \| \\
CH_3-N-C-C=CH_2 \\
| \\
R
\end{array}
\qquad R = H \text{ or } CH_3
$$

Self-association constants K for dimer (self associated monomer pair) were determined at 70°C in BZ-d_6 by the procedure reported,[21] since it was found that AA and MA have strong self-association tendencies in BZ. The K value is written as

$$
K = \frac{[C_d]}{[C_m]^2} \tag{1}
$$

where $[C_m]$ and $[C_d]$ are concentrations of free monomer and the dimer, respectively. The initial concentrations of AA and MA [M] are related to $[C_m]$ and $[C_d]$ by

$$
[M] = [C_m] + 2[C_d] \tag{2}
$$

The observed chemical shifts δ_{obs} is expressed by

$$
\delta_{obs} = \frac{(\delta_m[C_m] + 2\delta_d[C_d])}{[M]} \tag{3}
$$

where δ_m and δ_d are the chemical shifts characteristic of the free monomer and the dimer. From (1), (2), and (3) it follows that

$$
\left(\frac{\delta_{obs} - \delta_m}{[M]} \right)^{1/2} = [2(\delta_d - \delta_m)K]^{1/2}
$$
$$
- \left(\frac{2K}{\delta_d - \delta_m} \right)^{1/2} (\delta_{obs} - \delta_m) \tag{4}
$$

The product of slope and intercept obtained by plotting $\{(\delta_{obs} - \delta_m)/[M]\}^{1/2}$ vs. $(\delta_{obs} - \delta_m)$ just corresponds to $-2K$. The δ_m values were evaluated from extrapolation of δ_{obs} vs. [M] plots in Figure 7. The K values obtained from the plots in Figure 8 are $0.45\, dm^3\, mol^{-1}$ for AA and $0.22\, dm^3\, mol^{-1}$ for MA at 70°C.

The effect of the addition of MMA to solutions of AA and MA in BZ-d_6 and ACN-d_3 was examined. This is because C=O group of MMA can possibly form hydrogen-bond with NH protons of AA and MA which affects their associations in copolymerization systems. The results are summarized in Table V. Lower field shifts of NH proton was slightly observed only in the solution of MA in BZ-d_6 on addition of equimolar amount of MMA to the amide monomers, which indicates that the interactions between MMA and the amide monomers are weak even in BZ-d_6. This result is reasonable, since the IR spectroscopic studies showed that MMA has similar hydrogen bonding ability to ACN (Figure 6).
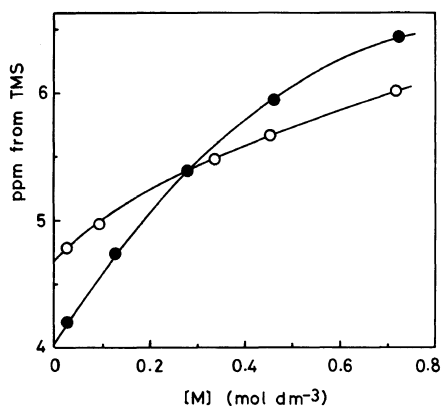
Figure 7. Concentration dependence of NH absorption in ^1H NMR spectra of AA and MA in BZ-d_6 at 70°C. (●), AA; (○), MA.
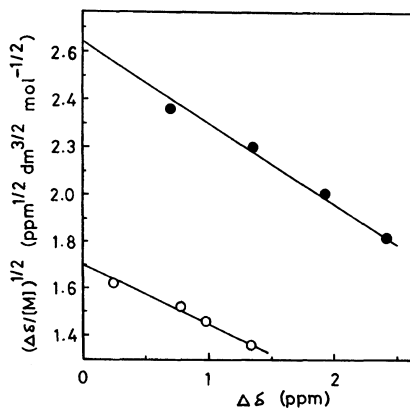

Figure 8. Plots of $(\Delta\delta/[M])^{1/2}$ vs. $\Delta\delta$ where $\Delta\delta$ is $\delta_m - \delta_{obs}$ obtained in BZ-d_6 at 70°C.

Table V. Variation of chemical shifts of the NH proton on addition of MMA (M_2) to AA and MA (M_1) solution

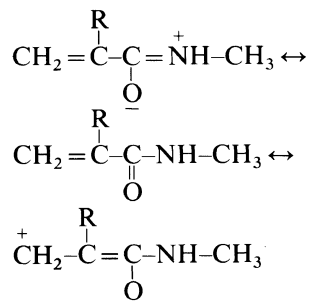| Monomer	Solvent	$\dfrac{[M_2]^a}{[M_1]}$	$\Delta\delta^b$/ppm	
			30°C	70°C
AA	BZ-d_6	1.06	−0.01	0.00
	ACN-d_3	1.05	0.01	0.00
MA	BZ-d_6	0.96	0.05	0.08
	ACN-d_3	1.05	0.01	−0.01

[a] MMA added to AA and MA solutions in a molar ratio.
[b] Difference in chemical shifts after and before the addition of MMA.

No ^1H NMR spectra obtained in these measurements show any signals which are ascribable to the enol-form of these monomers. Further, NH signals observed in these measurements were broad singlet. This result along with the observation of strong carbonyl absorption in IR spectra indicates that the amide monomers exist exclusively in keto-form in these solutions.

Conjugation between C=C and C=O Double Bonds

The change in conjugation between the C=C and C=O double bonds of AA and MA varies the stretching vibration of these bonds, since the bond order changes depending on the conjugation as can be seen from the scheme shown below. Stretching vibrations of C=C and C=O double bonds measured in various solvents are given in Table VI. It can be seen

$$CH_2 = \overset{\overset{R}{|}}{C} - \overset{}{C} = \overset{+}{N}H - CH_3 \leftrightarrow$$
$$\underset{O}{\overset{|}{}}$$

$$CH_2 = \overset{\overset{R}{|}}{C} - \overset{}{C} - NH - CH_3 \leftrightarrow$$
$$\underset{O}{\overset{\|}{}}$$

$$\overset{+}{C}H_2 - \overset{\overset{R}{|}}{C} = \overset{}{C} - NH - CH_3$$
$$\underset{O}{\overset{|}{}}$$

that solvents do not influence the stretching vibrations of C=C double bonds of AA and MA. The strong concentration dependence of the stretching vibration of C=O groups of AA and MA in BZ is due to its participation in hydrogen-bonding as already discussed and not due to the change in conjugation. This can be reasonably understood by the almost negligible change in the stretching vibration of their C=C double bonds. Increase in the amide monomer concentration in DO and ACN does not bring about distinct change in absorption maxima of their C=O groups. However, shoulders at lower wave length region of their spectra are clearly observed (Figure 5).

Table VI. Stretching vibrations of C=C and C=O double bonds of AA, MA, and DMA

Monomer	Solvent	Wave number/cm^{-1}			
		C=C$_1$[a]	C=C$_2$[b]	C=O$_1$[a]	C=O$_2$[b]
AA	BZ.	1634	1630	1685	1660
	DO	1632	1630	1683	1681
	ACN	1631	1631	1678	1678
	Neat[c]	—	1623	—	1658
MA	BZ	1627	1624	1677	1661
	DO	1627	1626	1672	1669
	ACN	1625	1625	1667	1667
	Neat[c]	—	1618	—	1655
DMA	BZ	1619	1619	1655	1653
	Neat[c]	—	1612	—	1647

[a] [M], 0.017 mol dm^{-3}.
[b] 0.84 mol dm^{-3}.
[c] Measured in neat.

Table VII. Dependence of chemical shifts of the olefin and carbonyl carbons of amide monomer concentration in BZ-d_6[a]

Monomer	[M] mol dm^{-3}	δ/ppm		
		>C=O	>C=	CH$_2$=
AA	0.022	165.15	131.38	125.40
	0.73	166.66	131.87	125.19
MA	0.015	168.25	141.20	118.10
	0.71	169.10	140.82	118.85

[a] At 30°C.

Resonance forms written above show that such conjugations change the electron densities of these carbons if they exist. Chemical shifts of olefin and carbonyl carbons in the ^{13}C NMR spectra of AA and MA measured in various solvents did not show any essential difference. This means that the conjugation between C=C and C=O double bonds in these monomers are not influenced by the environment surrounding them. Table VII shows the effect of amide monomer concentration in BZ-d_6 solution on the chemical shifts of olefin and carbonyl carbons. The values in diluted and concentrated solutions represent

those of the monomeric and self-associated amide monomers in BZ-d_6 solution, respectively. In concentrated solution, chemical shifts of the carbonyl carbons are observed at slightly lower magnetic field than in diluted solution probably due to the lower electron density induced by the hydrogen bonding of the carbonyl group. However, no fundamental difference in chemical shifts of the olefin carbons is observed between monomeric and self-associated amide monomers. This leads to the conclusion that formation of hydrogen bonds does not affect the conjugation between C=C and C=O double bonds.

Signals attributable to enol-form of AA and MA have not been detected in these ^{13}C NMR spectra.

DISCUSSION

Spectroscopic studies revealed that solvents influenced AA and MA with regard to their association conditions. They showed that conjugation between C=C and C=O double bonds of these amide monomers did not change depending on solvents. It was also found that AA and MA existed exclusively in the keto-form. Both IR and NMR studies revealed that the hydrogen-bond and dipole–dipole interactions played important roles in molecular association. Based upon these spectroscopic studies, the copolymerization behavior of AA and MA is interpreted as follows.

The results of the copolymerization in Table I show that the solvent in which monomers have stronger self-association tendency tends to increase r_1 values. This means that k_{11} increases in the solvent with monomer associated tightly as compared with k_{12}. The extent of the solvent effects on AA and MA decreases in the order of AA > MA, which is the order of decreasing self-association tendency of the monomers. Increase in the self-association of AA and MA (M$_1$) possibly leads to increase in the association between M$_1$· radical and M$_1$ monomer, since it is neither a

$C=C$ double bond nor an unpaired electron of the propagating radical but the $C=O$ and NH groups which participate mainly in the molecular association. This results in enhanced local concentration of M_1 monomer around $M_1 \cdot$ radical. As a result, it can be reasonably assumed that k_{11} increases apparently owing to the enhanced propagation rate between $M_1 \cdot$ radical and M_1 as compared with k_{12} to yield higher r_1 value.

If the molecular association between MMA and the amide monomers is strong enough to increase their local concentration around the propagating radical of MMA, k_{21} value increases apparently, which in turn decreases r_2 value. However, Table V shows that the interaction of MMA with AA and MA is weak. In fact, r_2 did not change except the copolymerization in BZ which yielded exceptionally small r_2 values. BZ seems to increase r_1 values in the copolymerization of AA and MA more than the expected. These extraordinary effects of BZ on the copolymerization might be explained as follows. Copolymers obtained in BZ are insoluble except those formed under the monomer composition containing 20 mol% of M_1 monomer. Thus, the amide monomers are considered to be adsorbed on the polymers precipitated because of weaker affinity of AA and MA to BZ. This adsorption causes the increase of local concentration of the amide monomers at the propagating chain ends. For this reason both k_{11} and k_{21} increase extensively. Some of the copolymers obtained in ACN and EtOH also precipitate during copolymerization. In these cases, however, the adsorption of the amide monomers to copolymers precipitated would not occur so much as in BZ, since the affinity of AA and MA to solvents was fairly large.

BZ influences even the copolymerization behavior of DMA which has been considered to be independent of the solvents where the copolymerizations are carried out. Dipole–dipole interaction between monomers or monomer and polymer may be responsible for this solvent effect.

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