Cyclopolymerization XI. Cyclopolymerizability of *N,N'*-Dimethacryloylmethylhydrazine and Solvent Effect on Its Polymerization

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(Received May 8, 1984)

ABSTRACT: The polymerization behavior of *N,N'*-dimethacryloylmethylhydrazine (DMUM) was investigated. The two methacryloyl groups in DMUM have essentially different reactivities; one, attached to the nitrogen with a methyl group, definitely has a lower polymerizability than the other. Cyclopolymerizability of DMUM is explained by taking into account the difference in the reactivities of the two methacryloyl groups. Solvent effects on the cyclopolymerizations of DMUM and *sym*-dimethacryloyldimethylhydrazine (DMMH) have also been studied in connection with the hydrogen-bonding ability of DMUM. Solvents influenced not only the polymerization rate of DMUM but also the structure of the resulting poly-DMUM to a small extent. However, the polymerization of DMMH is not affected by solvents. These results and spectroscopic studies on the molecular interaction in solution have led to the conclusion that molecular association through hydrogen-bonding is responsible for the solvent effects observed.

KEY WORDS Cyclopolymerization / Solvent Effect / Hydrogen-Bond / NMR / IR / 1,7-Diene /

The present work is a study of the cyclopolymerizability of *N,N'*-dimethacryloylmethylhydrazine (DMUM) on the basis of the hypothesis that the lower the polymerizability of the monofunctional counterparts of bifunctional monomers, the higher their cyclopolymerizability, if they polymerize at all.^{1,2} The validity of this hypothesis is supported by the cyclopolymerization of several monomers.²⁻⁵ Two methacryloyl groups of DMUM should have essentially different reactivities, *viz.*, the polymerization tendency of the double bond attached to the nitrogen having a methyl group (A) is definitely low compared to that of the other (B). This assumption is based on the polymerizability of a *N,N*-disubstituted methacrylamide and *N*-monosubstituted methacrylamide. The former does not polymerize to yield a high

polymer but the latter does.⁶ The cyclopolymerization behavior of DMUM was compared with that of *sym*-dimethacryloyldimethyl-

hydrazine (DMMH) and *sym*-dimethacryloylhydrazine (DMH).^{4,5} DMUM possesses a hydrogen atom with hydrogen-bonding ability. For this reason, the influence of molecular association on cyclopolymerizability has been investigated. DMUM is helpful for this purpose since its polymerization proceeds homogeneously in various solvents such as

benzene, acetonitrile (ACN), dioxane (DO), *N,N*-dimethylformamide (DMF), and ethanol (EtOH).

EXPERIMENTAL

Materials

DMUM was prepared by a reaction between monomethylhydrazine and methacryloyl chloride using a procedure similar to that for DMMH.⁵ The solid residue obtained after evaporation of the reaction medium was purified by repeated recrystallization from benzene. The mp was 88–89°C and the crude yield, almost quantitative. The structure was confirmed by NMR, IR, and elementary analysis. *Anal.* Calcd for $C_9H_{14}N_2O_2$: C, 59.32%; H, 7.74%; N, 15.37%. Found: C, 59.43%; H, 7.74%; N, 15.37%.

DMMH was prepared as reported previously.⁵

Commercial azobisisobutyronitrile (AIBN) was recrystallized twice from EtOH.

All common solvents were purified by usual methods.

Polymerization

Polymerizations were carried out in sealed glass tubes under vacuum ($<10^{-4}$ mmHg). The polymers were isolated by pouring the polymerization mixtures into ethyl ether and drying them under reduced pressure at 80°C for 48 h. The polymer yield was determined gravimetrically. The polymers were reprecipitated from DMF solutions into ethyl ether to obtain samples for property and spectra measurements.

Measurements

IR spectra were recorded on a Hitachi 260-30 infrared spectrophotometer. NMR spectra were taken as reported previously.¹ Hexamethyldisiloxane was used as the internal standard for NMR measurements at 150°C. The chemical shifts of the NH proton of DMUM in various solvents were determined

with a JEOL GX-270 FT NMR spectrometer. The degree of cyclization was calculated on the basis of the peak areas of pendant double bond protons and those of $>N-CH_3$ protons at 3.07 ppm in the NMR spectra of the polymers. The mean values of at least five measurements were adopted. Viscosities were measured in DMF at 30°C using an Ubbelohde viscometer.

RESULTS AND DISCUSSION

Polymerization of DMUM

Polymerizations of DMUM were carried out in various solvents. The time-conversion curves thus obtained are illustrated in Figure 1. The polymerization rates change significantly, depending on the solvents. The important role of the NH proton of DMUM is evident because polymerization of DMMH proceeds in a similar manner in both benzene and DMF solutions (Figure 2). In Figure 3, the polymerization rates of DMUM in benzene and DMF are plotted against monomer concentration. The addition of a small amount of DMF to DMUM caused a striking decrease in the polymerization rate. The viscosities of the polymers obtained with nearly the same conversions are shown in Figure 4 as a function of monomer concentration. These results are consistent with the polymerization rates.

Structure of Poly-DMUM

Repeating units expected in poly-DMUM have the structures I, II, and III (Figure 5). The NMR spectrum of poly-DMUM is shown in Figure 5 along with the resonance signals of $CH_2=C<$ protons of DMUM and related monomers. The doublet (H_b) centered at $\delta = 5.46$ ppm of DMUM has the same area as that of the singlet (H_a) at $\delta = 5.06$ ppm. The methylene protons of methacryloyl groups of DMH (H_b) and DMMH (H_a) give doublets centered at $\delta = 5.48$ and 5.11 ppm, respectively. The peaks (H_b) at 5.34 and 5.58 ppm in the spectrum of DMUM are thus attributable to the methylene protons of the double bond B

Figure 1. Polymerization of DMUM in various solvents at 60°C. $\diamond$, benzene; $\blacklozenge$, DO; $\circ$, EtOH; $\bullet$, ACN; $\triangle$, DMF; [DMUM], 1.10 mol dm^{-3} ; [AIBN], $5.9 \times 10^{-3} \text{ mol dm}^{-3}$.

Figure 2. Polymerization of DMMH at 60°C. $\bullet$, DMF; $\circ$, benzene; [DMMH], 1.70 mol dm^{-3} ; [AIBN], $4.0 \times 10^{-2} \text{ mol dm}^{-3}$.

Figure 3. Dependence of the polymerization rate of DMUM on monomer concn at 60°C. $\circ$, benzene; $\bullet$, DMF; [AIBN], $5.9 \times 10^{-3} \text{ mol dm}^{-3}$.

Figure 4. Dependence of the intrinsic viscosity (in DMF at 30°C) of poly-DMUM on monomer concn at 60°C. $\circ$, benzene; $\bullet$, DMF; [DMUM], 1.10 mol dm^{-3} ; [AIBN], $5.9 \times 10^{-3} \text{ mol dm}^{-3}$.

* Conversion, %.

Figure 5. NMR spectra of poly-DMUM, DMUM, and related monomers measured at 150°C in $(\text{CD}_3)_2\text{SO}$. Polymerization conditions of DMUM: [DMUM], 1.83 mol dm^{-3} ; [AIBN], $5.9 \times 10^{-3} \text{ mol dm}^{-3}$; solvent, benzene; time, 1 h.

and signal (H_a) at 5.06 ppm to those of the double bond A. The broad singlet (H_a) at 5.11 ppm of poly-DMUM can be assigned to the methylene protons of the double bond A and the weak doublet (H_b) centered at $\delta = 5.58 \text{ ppm}$ to those of the double bond B. The

Table I. Structure of poly-DMUM and related polymers formed at 60°C

Monomer	Solvent	Time	Conv.	Concn	[AIBN] × 10 ³	II ^a	III ^a	DC ^b
		h	%	mol dm ⁻³	mol dm ⁻³	%	%	%
DMUM	DMF	12	11.6	1.10	5.9	72	6	22
DMUM	ACN	8	12.1	1.10	5.9	74	11	15
DMUM	EtOH	8	12.7	1.10	5.9	72	11	17
DMUM	DO	3	12.4	1.10	5.9	70	17	13
DMUM	Benzene	1	9.1	1.10	5.9	71	16	13
DMMH	DMF	12	10.4	1.70	40.0	—	—	92
DMMH	Benzene	12	8.1	1.70	40.0	—	—	92
DMH ^c	DMF	1.3	11.9	0.40	2.0	—	—	19

^a See Figure 5. ^b Degree of cyclization. ^c Cited from ref 4.

Table II. Structural change in poly-DMUM formed in benzene and DMF solutions, according to monomer concentration^a

Concn	Time	Solvent	Conv.	II ^b	III ^b	DC ^c
mol dm ⁻³	h		%	%	%	%
1.83	1	Benzene	11.4	71	17	12
1.10	1	Benzene	9.1	71	16	13
0.68	1	Benzene	11.1	70	17	13
1.83	6	DMF	11.2	72	8	20
1.10	12	DMF	11.6	72	6	22
0.68	24	DMF	13.3	75	1	24

^a AIBN, 5.9×10^{-3} mol dm⁻³; temp, 60°C. ^b See Figure 5. ^c Degree of cyclization.

degree of cyclization and proportion of the two pendant double bonds of poly-DMUM obtained under various experimental conditions are listed in Tables I and II. These results show the structure of the polymers to change depending on the solvent, though this change is not very large. The data available at present does not permit a distinction between the two cyclic structures in poly-DMUM, *viz.*, 6- and 7-membered rings. Thus, the 6-membered ring was tentatively adopted as the repeating cyclic structure in the Scheme depicted in this article.

The structure of poly-DMMH was not affected by the solvents used, as shown in Table I in accordance with the polymerization behavior in these solvents. This reconfirms the results obtained under other experimental conditions.⁴

The cyclopolymerizability of DMUM in DMF (Table II) was compared with that of DMH (Table I) to eliminate the influence of solvents. These data show that the cyclopolymerizabilities of the two monomers are almost the same. Further, it can be seen that the extent of cyclization of poly-DMMH is much higher than that of poly-DMUH. The reactivity differences in methacryloyl groups of DMUM suggest that DMUM is attacked by radicals primarily through the double bond B. The propagating radical IV formed should add the double bond B of another DMUM to yield sequence V. The cyclization reaction of IV seldom occurs, judging from the low cyclopolymerizability of DMH (Table I). There are a few monomers which do not homopolymerize but copolymerize. The formation of sequence VI is thus probable, though the

possibility for this is very low. The extremely low homopolymerizability of the double bond A may not permit formation of sequence VII, thus leading to the reappearance of propagating radical IV. This is the reason why the extent of the cyclization of poly-DMUM is almost the same as that of DMH and its cyclization tendency is considerably low compared to that of poly-DMMH. This also explains the fact that the pendant double bond consists almost exclusively of structure II.

Molecular Association in Solution

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.⁷ The lower the frequency of the absorption, the stronger is the interaction.⁸ Consequently, the NH vibrational bands of DMUM in various solvents were measured and the results are listed in Table III along with the physical constants of the solvents. The spectral change in NH and C=O stretching vibrations at various mixture ratios of DMUM–benzene is given in Figure 6. These spectra indicate that the spectrum in dilute solution corresponds to DMUM in a monomeric state and that at a higher concentration, to DMUM self-associated through NH and C=O groups. Accordingly, the strength of the proton affinity of these solvents can be judged by NH frequencies in the dilute solutions listed in Table III. It is clear that benzene has the weakest affinity toward the NH proton of DMUM and DMF, the strongest among the solvents investigated.

The resonance frequencies and spectral patterns of C=O groups of DMMH did not change when IR spectra were measured in benzene at different DMMH concentrations (0.016–0.16 mol dm⁻³). The interaction between DMMH monomers may be weak and DMMH may dissolve homogeneously in benzene to a greater extent than DMUM. The

Table III. Stretching vibration of NH groups in the IR spectra of DMUM in various solvents and their physical properties

Concn mol dm ⁻³	Wave number/cm ⁻¹					
	KBr	Benzene	ACN	DO	DMF	EtOH
0.016	—	3390	3336	3298	3246	—
0.16	3265 ^c	3292	3335	3296	3252	—
μ^a	—	0	3.37	0.45	3.82	1.68
ϵ^b	—	2.28	32.5	2.21	37.6	25.7

^a Dipole moment. ^b Dielectric constant. ^c Measured in KBr pellets.

Figure 6. IR spectra of DMUM. Conc: a, 0.016 mol dm⁻³; b, 0.05 mol dm⁻³; c, 0.11 mol dm⁻³; d, 0.16 mol dm⁻³; a, b, c, and d were measured in benzene; e, KBr pellet; f, EtOH solution; [DMUM], 0.16 mol dm⁻³.

poor solubility of poly-DMH and DMH preclude studies on its polymerization and aspect of its association with DMH itself and/or a solvent molecule in these solvents.

The molecular association of a DMUM solution was investigated in greater detail by measuring the NMR spectra, since the concentration dependence of the IR spectra could not be observed in ACN, DO, and DMF solutions. The signal due to the NH proton is dependent on the solvent. A downfield shift is usually observed when the NH proton is placed in an environment of proton affinity,⁹ as evident from Table IV. The resonance peak of the NH proton in a dilute solution shifts to the lower magnetic field, depending on solvent, in the order of benzene, ACN, DO, and DMF. In a concentrated solution, a large

Table IV. Chemical shifts of the NH proton of DMUM in various solvents

Concn mol dm ⁻³	Temp ^a °C	δ /ppm			
		Benzene	ACN	DO	DMF
0.016	22	7.16	8.81	9.04	10.50
1.10	22	10.06	9.15	9.54	10.49
0.016	60	7.00	8.62	8.82	10.24
1.10	60	9.53	8.91	9.25	10.22

^a Not corrected.

downfield shift of the NH proton occurs in benzene, owing to a strong interaction between DMUM monomers because of the weak affinity of benzene toward the NH proton. In ACN and DO as well, resonance frequencies decrease as the monomer concentration increases, though not as much as when benzene is the solvent. On contrast, the NMR in DMF shows the affinity of the NH proton of DMUM toward DMUM itself to be almost the same as that toward DMF.

Benzene is at one extreme and DMF, at the other extreme in terms of proton affinity and polarity among the solvents investigated. The interaction between DMUM monomers is so strong in benzene that they associated with each other even in solutions much more dilute than those for the polymerization. The interaction between DMUM and DMF is as possible as that between DMUM molecules, meaning that the association between DMUM monomers in DMF increases with increasing DMUM concentration. Accordingly, the structure of poly-DMUM obtained in benzene is independent of monomer concentration, while that of poly-DMUM formed in DMF changes depending on concentration and tends to approach that of poly-DMUM in benzene, with increasing monomer concentration (Table II). Behavior in DO and ACN solutions is rather complicated. The interaction between DMUM molecules in DO is stronger than that in ACN even though ACN has weaker proton affinity than DO. Thus, molecular association

Table V. Correlation of polymerization rates with the viscosity of polymerization systems^a

Solvent	η	$R_p \times 10^5$
	cP	mol dm ⁻³ s ⁻¹
DMF	0.861	0.45
Benzene	0.812	2.95

^a Temp, 60°C; [DMUM], 1.10 mol dm⁻³; [AIBN], 5.9×10^{-3} mol dm⁻³.

in these solvents may be governed by the relative strength of the proton affinity toward a dipole-dipole interaction. The proton attracting power of EtOH is comparable to that of DMF.¹⁰ Its physical constants are listed in Table III. The interaction between the OH proton and C=O of DMUM affects the molecular association in EtOH as evident from the spectrum in Figure 6f. The behavior of DMUM in EtOH is thus influenced by all these factors. The data in Table I indicate the structural change dependent on the solvent to be correlated to the solution properties. But such a change is very small. This shows that the influence of the reactivity of the two methacryloyl groups of DMUM on the structure of poly-DMUM is too strong to be affected by molecular association through NH and C=O groups. The data at present do not permit an adequate understanding of the self-association of DMUM and how it is correlated to the structure of poly-DMUM. However, the structural change suggests that it suppresses the cyclization reaction.

Striking variation in polymerization rates was observed to depend on the solvent. The stronger the self-association of DMUM, the higher tends to be the rate of polymerization. Intermolecular hydrogen-bonding between NH and C=O of DMUM may affect the reactivity of DMUM and/or its propagating

radical¹¹ so that the polymerization rate increases. However, the data from the polymerization in EtOH exclude this possibility in that the rate of polymerization is low in EtOH even though the C=O groups of DMUM are associated with the OH protons of EtOH (Figure 6). Since the benzene solution has a lower viscosity than that of DMF (Table V), the possibility that the termination reaction is controlled by the propagating radical diffusion rate in benzene is also ruled out.¹² The most plausible explanation for this solvent effect is that linear plurimolecular aggregates of DMUM, which promote polymerization, exist in benzene. Such plurimolecular aggregates of monomers have been proposed for the polymerization of acrylic acid.¹³ As the interaction between DMUM and solvent proceeds, the plurimolecular aggregates decompose, causing a decrease in the polymerization rate.

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