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Cyclopolymerization. VIII. Polymerization of *sym*-Dimethacryloyldimethylhydrazine and Related Compounds

Toshiyuki KODAIRA, Kazuyuki YAMAZAKI, and Tadahiro KITOH

Department of Industrial Chemistry, Faculty of Engineering, Fukui University, Fukui 910, Japan.

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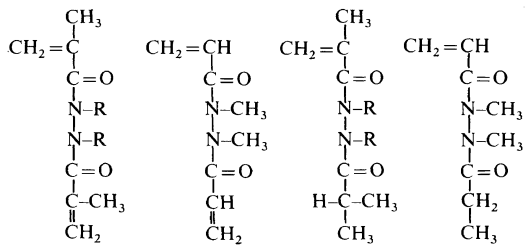
ABSTRACT: Polymerization behaviors of several 1,7-dienes were investigated in order to see the correlation between their cyclopolymerizability and the polymerizability of their monofunctional counterparts. In connection with this problem, studies on the effect of the intermolecular hydrogen bonds between monomers or between a monomer and a solvent on the cyclopolymerizability of these dienes have also been undertaken. *sym*-Dimethacryloyldimethylhydrazine, whose monofunctional counterpart does not polymerize, showed high cyclopolymerizability irrespective of the solvents used. *sym*-Dimethacryloylhydrazine and *sym*-diacryloyldimethylhydrazine, whose monofunctional counterparts polymerize, showed low cyclopolymerizability, though their ability to form hydrogen bonds is extremely different. The results thus obtained support the idea that the high and low cyclopolymerizabilities of these monomers are mainly associated with the low and high polymerizabilities of their monofunctional counterparts, respectively, but not with the ability to form hydrogen bonds, in agreement with the theory proposed previously.

KEY WORDS Cyclopolymerization / Highly Cyclized Polymer / 1,7-Diene / Hydrogen Bond / Solvent Effect /

During the study of the cyclopolymerization of unconjugated dienes, it was found that the unconjugated dienes whose monofunctional counterparts do not polymerize are likely to give rise to highly cyclized polymers, if the unconjugated dienes polymerize.[1,2] Preliminary results[3] were reported on the polymerization of *sym*-dimethacryloyldimethylhydrazine (DMMH) and *sym*-dimethacryloylhydrazine (DMH), which was carried out in an attempt to test the validity of the above hypothesis. The monofunctional counterpart of the former (*N*-isobutyryl-*N'*-methacryloyl-*sym*-dimethylhydrazine, IMMH) can be polymerized only with difficulty, while that of the latter (*N*-isobutyryl-*N'*-methacryloylhydrazine, IMH) can be easily polymerized. In accordance with the above-mentioned hypothesis, DMMH and DMH exhibited high and low cyclopolymerizability, respectively. However, the lower cyclopolymerizability of DMH might be due to the interruption of cyclization by the intermolecular association through hydrogen bonds between some DMH molecules and other DMH or solvent molecules. In order to clarify the contribution from such associations, the cyclopolymerizability of *sym*-diacryloyldimethylhydrazine (DAMH) has been investigated. DAMH has no hydrogen atom attached to nitrogen capable of forming hydrogen bonds, but it is predicted that it would give a polymer with a lower degree of cyclization and that its monofunctional counterpart (*N*-acryloyl-*N'*-propionyl-*sym*-dimethylhydrazine, APMH) would polymerize easily.



R=CH_3, DMMH DAMH R=CH_3, IMMH APMH
H, DMH H, IMH

The mechanism of the cyclopolymerization of DMMH will be discussed here, based upon the results on the polymerization of the above-mentioned dienes and their monofunctional counterparts.

EXPERIMENTAL

Materials

Syntheses of Unconjugated Dienes. DMMH and DMH were synthesized as reported previously.[3] DAMH was prepared according to essentially the same method of synthesis as that of DMMH, by the reaction between *sym*-dimethylhydrazine dihydrochloride and acryloyl chloride. The oily residue obtained after the evaporation of the reaction medium was purified by repeated distillation.

Syntheses of Monofunctional Counterparts. IMH was obtained by the reaction of isobutyryl chloride and monomethacryloylhydrazine, based upon the procedure used for the syntheses of the aforementioned dienes. Monomethacryloylhydrazine was synthesized according to Kolb and Honig.[4] IMMH and APMH were prepared through a similar synthetic route to that of IMH, *i.e.*, the reaction of isobutyryl chloride or acryloyl chloride with monomethacryloyl- or monopropionyl-*sym*-dimethylhydrazine. The preparation of the latter two hydrazides was due to that of monomethacryloylhydrazine. IMH was recrystallized three times from benzene solution. IMMH and APMH were distilled twice to yield pure compounds.

The supposed structures of the compounds obtained were confirmed by NMR and IR spectra and by the results of elementary analyses. The yields, physical constants, and the results of elementary analyses for the new monomers are shown in Table I.

Commercial azobisisobutyronitrile (AIBN) was recrystallized twice from ethyl alcohol.

All common solvents were purified by the usual techniques.

Polymerization

Polymerizations were carried out as described previously.[1] Diethyl ether was used to precipitate polymers, except for IMMH, which was poured into petroleum ether. In a previous work,[3] acetonitrile was adopted as a precipitating agent for poly-DMH, but it appeared that diethyl ether is better for poly-DMH containing non-cross-linked fractions. Polymers for NMR and viscosity measurements were reprecipitated from chloroform solution, with the exception of poly-DMH and poly-IMH, which were dissolved in *N,N*-dimethylformamide (DMF).

Measurements

NMR and IR spectra were taken as reported.[1] The viscosity was measured in DMF at 30°C using an Ubbelohde viscometer. The degree of cyclization was calculated based upon the absorption related to pendant double bonds and the absorption specific to the respective polymers in NMR spectra. The mean values of at least five measurements were adopted.

RESULTS

Polymerization of DMMH and Related Compounds

The results of the polymerization of DMMH and related compounds are summarized in Table II. The solvents do not affect at all the cyclopolymerizability of DMMH. When DAMH was polymerized under comparable polymerization conditions with those of DMMH, it afforded polymers insoluble in all solvents examined. But in a highly diluted solution polymerization, a soluble polymer was obtained from DAMH. IMH and APMH polymerized easily, but the polymerizability of IMMH is quite low. Only faint turbidity was observed when the polymerization system of IMMH was poured into petroleum ether after the polymerization for a longer period using a higher dosage of the initiator as compared with the polymerization of IMH or APMH. The

Table I. Yields, physical constants, and elementary analyses

Monomer	Yield,[a] %	bp,[b] °C/mmHg	mp,[b] °C	C, %		H, %		N, %	
				Calcd	Found	Calcd	Found	Calcd	Found
DAMH	28.3	~ 80/0.1	—	57.13	56.85	7.19	7.46	16.66	16.81
APMH	50.1	~ 80/0.1	—	56.45	56.73	8.29	8.51	16.46	16.25
IMMH	62.5	~110/1.0	~32	60.58	60.33	9.15	8.90	14.13	13.87
IMH	38.7	—	142–143	56.45	56.65	8.29	8.18	16.46	16.45

[a] Values obtained for the last steps of the syntheses after purification.
[b] Not corrected.

Table II. Polymerization of DMMH, DMH, DAMH, and their monofunctional counterparts

No.	Monomer, mmol	Temp, °C	Time	[AIBN], mmol	Solvent, ml	Yield, %	DC,[a] %	$\eta_{sp/C}$, dl/g
1	DMMH, 5.10	60	24 hr	0.12	Benzene, 2	17.4	93.5	0.09
2	DMMH, 5.10	60	24 hr	0.12	DMF, 2	19.0	92.9	0.08
3	IMMH, 5.05	70	24 hr	0.12	Benzene, 2	trace	—	
4	DMH,[b] 5.95	60	80 min	0.03	DMF, 14	11.9	18.9[c]	—
5	IMH, 5.88	70	50 min	0.03	DMF, 10	27.4	—	0.17
6	IMH, 5.88	70	30 min	0.03	DMF, 10	16.1	—	—
7	DAMH,[d] 5.95	60	50 min	0.03	DMF, 4	11.7	—	—
8	DAMH, 5.95	60	140 min	0.03	DMF, 12	11.3	58.7	0.07
9	APMH, 5.88	70	10 min	0.03	Benzene, 2	52.2	—	1.75

[a] Degree of cyclization. [b] Partly insoluble. [c] Values obtained from the soluble part. [d] Insoluble.

polymerization of DMH in a highly diluted solution proceeded apparently in a homogeneous state, but it was found that poly-DMH contains an insoluble fraction when it was subjected to a reprecipitation procedure to purify the polymer.

Structure of Polymer

The NMR spectrum of poly-DMMH formed in DMF, illustrated in Figure 1, is essentially the same as that obtained in benzene.[3] The solvents used do not influence the degree of cyclization or the polymerizability of DMMH, as is seen in Table II, though the properties of both the solvents are extremely different. Measurements of NMR spectra of poly-DMH and poly-DAMH revealed that both the polymers contain considerable amounts of pendant double bonds (Figure 1), in spite of the fact that they were formed in the highly diluted solution, where an intramolecular cyclization reaction is favored over an intermolecular propagation reaction. The degree of cyclization calculated based upon the NMR spectra is given in Table II.

There are two possible cyclic structural units in the polymers from 1,7-dienes, *viz.*, six- and seven-membered rings. The available data at present do not allow us to distinguish the two cyclic structures in the polymers formed from DMMH, DMH, and DAMH. Therefore, the six-membered ring is tentatively adopted as the repeating cyclic structure in the scheme which appears later.

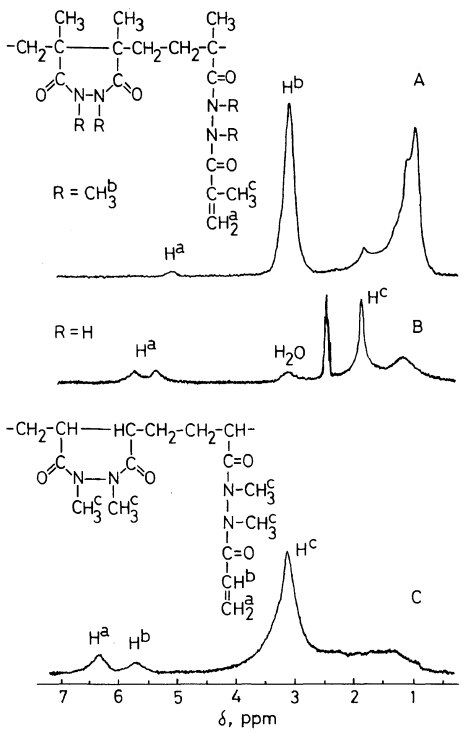


Figure 1. NMR spectra of polymers: A, Poly-DMMH (2 in Table II); B, Poly-DMH (4 in Table II); C, Poly-DAMH (8 in Table II). A and C were recorded at 80°C in deuterochloroform, and B in hexadeuterodimethylsulfoxide at the same temperature.

Effect of Temperature on the Structure of Poly-DMMH

The structure of poly-DMMH is determined by the value of the ratio of the rate of the intramolecular cyclization reaction (R_c) to that of intermolecular propagation (R_p). Smets, *et al.*,[5] deduced eq 1, which

$$\frac{R_c}{R_p} = \frac{k_c}{2k_p[M]} = \left(\frac{DC}{1-DC}\right) \quad (1)$$

permits a graphical evaluation of the difference $E_c - E_p$ from a plot of the logarithmic values of R_c/R_p *vs.* the reciprocal of absolute temperature: here k_p is the rate constant for R_p, k_c is that for R_c, DC is the degree of cyclization, E_c and E_p are the activation energies of the intramolecular cyclization reaction and of the intermolecular propagation reaction, respectively, and [M] is the monomer concentration. The polymerization of DMMH was carried out in the range from 45 to 85°C; the results are shown in Table III. The values were plotted according to eq 1 in Figure 2. From the slope, $E_c - E_p$ was determined to be 14.2 kJ/mol.

Table III. Dependence of DC[a] on temperature in the polymerization of DMMH in benzene[b]

Temp, °C	Time, h	Yield, %	DC	R_c/R_p
45	90	11.7	0.909	9.87
55	24	9.5	0.912	10.4
70	6	9.8	0.936	14.6
85	3	12.6	0.947	17.5

[a] Degree of cyclization in mole fraction.
[b] [M], 5.10 mmol; benzene, 2 ml; [AIBN], 0.12 mmol.

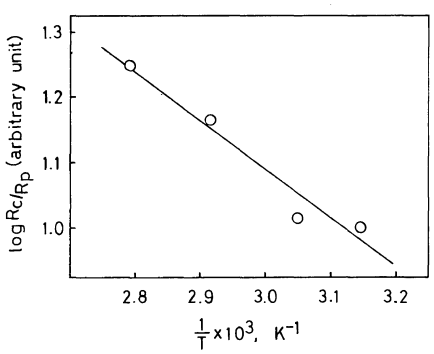
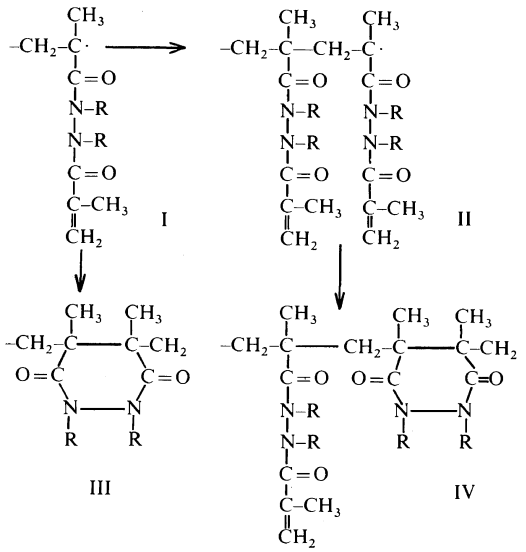


Figure 2. Difference between the activation energies of intramolecular cyclization and intermolecular propagation in the cyclopolymerization of DMMH. Conditions are the same as described in Table III.

DISCUSSION

The polymerization behaviors of DMMH, DMH, DAMH, and their monofunctional counterparts are consistent with, and correspond to, what had been expected from the beginning. It should be noted that DMMH and DAMH are similar in their inability to form hydrogen bonds. But their cyclopolymerizability is extremely different and is in accordance with what has been anticipated from the polymerizability of their monofunctional counterparts. A study of the solvent effect on the polymerization of DMH could not be undertaken because of its poor solubility to hydrophobic solvents, but the polymerization of DMMH was not affected at all by the solvents used. These results led to the conclusion that the polymerization of DMMH proceeds by the mechanism proposed for the cyclopolymerization of *N*-substituted dimethacrylamide (RDMA).[1] The definitely lower polymerizability of IMMH indicates that the probability of the formation of sequence II during the polymerization of DMMH is quite low and a chain end I would react with the double bond of its own to yield the cyclized unit III, which results in the formation of a highly cyclized polymer. The reason why the polymerizability of IMMH is so low in comparison with IMH and APMH is not known, but perhaps it is attributable to the steric hindrance originating from



the α-methyl and *N*-methyl groups introduced.

One must, however, bear in mind that poly-DMMH contains pendant double bonds, unlike poly-RDMA which does not have any detectable trace of a pendant double bond. The faint turbidity observed when the polymerization system of IMMH was poured into the precipitating agent suggests that the

formation of long chain segments for this monomer is quite improbable, but short chain segments are probably formed. This means that a propagating chain end II possibly appears during the polymerization of DMMH and it cyclizes to form sequence IV, though only to a small extent, leaving pendant double bonds.

The lower cyclopolymerizability of DMH is easily understood by considering the high polymerizability of its monofunctional counterpart and the energetically less favored repeating cyclic structures of poly(1,7-diene)s as compared with those of 1,6-dienes. The latter factor could be an additional cause which assists the formation of sequence II during the polymerization of DMMH mentioned above. It is well known that a seven-membered ring has considerable ring strain. The six-membered repeating unit which appears in cyclized poly(1,7-diene)s has fundamentally no strain inside itself, but the mutual repulsion between the bulky rings spread laterally along a backbone chain is considered to decrease the stability of cyclized poly(1,7-diene)s. This view is supported by the non-polymerizability of pyridazinone derivatives[6] and the high polymerizability of maleimide derivatives.[7] Thus, in the DMH polymerization, the propagating chain end I adds to a monomer to yield the sequence II in preference to the cyclization reaction which forms the cyclized unit III. This explanation is completely applicable to the polymerization procedure of DAMH. Therefore, the main reason for the lower cyclopolymerizability of DMH is the high polymerizability of its monofunctional counterpart and not its ability to form hydrogen bonds.

The results of the dependence of polymerization behavior on temperature agreed with its effect observed in the cyclopolymerization of other unconjugated dienes.[8] Namely, the activation energy for the intramolecular cyclization is larger than that of intermolecular propagation. This fact is interesting when one notices that the intermolecular addition of DMMH to the propagating chain end I rarely occurs; it suggests that an entropy factor is important in the competition between the intramolecular cyclization of chain end I and its intermolecular propagation to yield sequence II.

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