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Head-to-Head Polymers. XII.* Preparation, Thermal Properties, and Reaction of Head-to-Head Cyclopolymers by Head-to-Head Cyclopolymerization of N-Substituted Dimethacrylamide Derivatives

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ABSTRACT

N-Methyl- and N-n-propyl-N,N-dimethacrylamides (MDMA and PDMA), N,N'-dimethyl-N,N'-dimethacrylhydrazine (DMDMH), N,N'-dimethyl-N,N'dimethacrylethylenediamine (DMDME), and N,N'-di-methyl-N,N'-dimethacrylurea (DMDMU) were synthesized and polymerized with a radical initiator. All of these monomers were homopolymerized to give soluble head-to-head (h-h) cyclopolymers which were obtained through a h-h cyclopolymerization, i.e., a repeated cycle of intermolecular tail-to-tail (t-t) propagation and intramolecular h-h cyclization. The thermal properties of these h-h cyclopolymers were determined. In order to obtain h-h poly(methacrylic esters), the hydrolysis of these polymers was attempted under various acidic and alkaline conditions. It was confirmed by IR spectra that h-h poly(methacrylic

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*For Part XI of this series, see T. Ohya and T. Otsu, J. Polym. Sci., Polym. Chem. Ed., 21(12) (1983).

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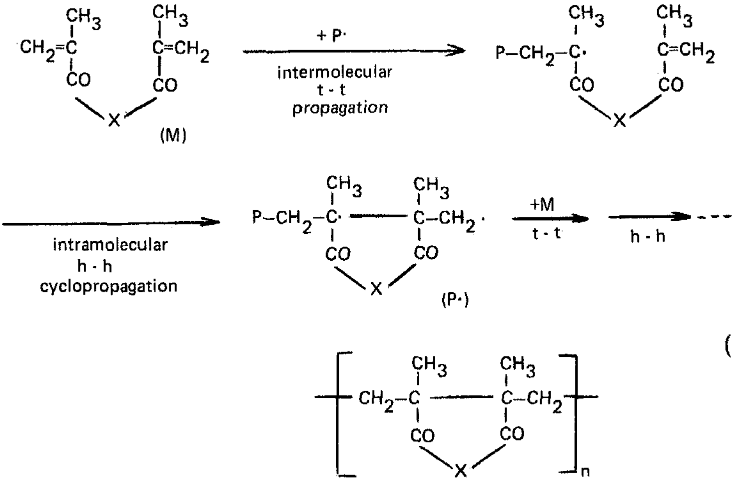
acid) and h-h poly(ethyl methacrylate) were obtained by hydrolysis of poly(PDMA) with concentrated KOH aqueous solution and by alcoholysis of poly(DMDMH) with KOH-ethanol solution, respectively. However, the isolation of these h-h polymers was not successful.

INTRODUCTION

In a previous paper [1] it was reported that N,N'-dimethyl-N,N'-dimethacrylurea (DMDMU) underwent head-to-head (h-h) cyclopolymerization to give a seven-membered h-h cyclopolymer. These h-h cyclopolymerizations were originally found by Kodaira et al. [2-6] for radical polymerizations of N-methyl-N,N-dimethacrylamide (MDMA), N-n-propyl-N,N-dimethacrylamide (PDMA), N,N'-dimethyl-N,N'-dimethacrylhydrazine (DMDMH), and N,N'-dimethyl-N,N'-dimethacrylethylenediamine (DMDME).

Such h-h cyclopolymerizations proceed via a repeating tail-to-tail (t-t) propagation and h-h cyclization:



(1)

where X is $\overset{|}{\mathrm{N}}(\mathrm{CH_3})\mathrm{CO}\overset{|}{\mathrm{N}}(\mathrm{CH_3})$ (DMDMU), $-\overset{|}{\mathrm{N}}\mathrm{CH_3}$ (MDMA), $-\overset{|}{\mathrm{N}}\mathrm{C_3H_7}$ (PDMA), $\overset{|}{\mathrm{N}}(\mathrm{CH_3})\overset{|}{\mathrm{N}}(\mathrm{CH_3})$ (DMDMH), and $\overset{|}{\mathrm{N}}(\mathrm{CH_3})\mathrm{CH_2CH_2}\overset{|}{\mathrm{N}}(\mathrm{CH_3})$ (DMDME).

Because the main chain of the cyclopolymers thus obtained consists of h-h (plus t-t) structures which were proposed by us [1] and called h-h cyclopolymers, it may be interesting to evaluate their physical, chemical, thermal, and mechanical properties. Moreover, if these polymers are hydrolyzed and then methylated, various new h-h polymers of methacrylic derivatives are prepared. In a previous paper [1] we attempted to hydrolyze the h-h cyclopolymer of DMDMU under various acidic and alkaline conditions, but proof of hydrolysis was not obtained. Therefore, this h-h cyclopolymer was considered to have strong resistance to acids and alkalines.

To further clarify these problems, cyclopolymerizations of MDMA, PDMA, DMDMH, DMDME, and DMDMU were undertaken, and the thermal properties and hydrolyses of the resulting h-h cyclopolymers were investigated. The results obtained are described in this paper.

EXPERIMENTAL

Preparation of Dimethacrylamide Derivatives

MDMA, PDMA, DMDMH, and DMDME were prepared and purified by the methods of Kodaira et al. [2-6], and confirmed to be pure by their ^{1}H-NMR spectra.

DMDMU was synthesized by reaction of N,N'-dimethylurea with methacryloyl chloride. In a four-necked flask cooled in a Dry Ice-methanol bath, 33.4 g (0.38 mol) of N,N'-dimethylurea, 76.8 g (0.76 mol) of triethylamine, and 300 mL of chloroform were placed. With vigorous stirring, 118.6 g (1.14 mol) of methacryloyl chloride in 100 mL of chloroform was added dropwise for 3 h while keeping the temperature below 0°C. After the mixture was gradually heated to 65-75°C, the triethylammonium chloride that precipitated was removed by filtration and the chloroform was then evaporated under reduced pressure. The resulting residual liquid was passed through an activated alumina column, and the effluent was distilled under reduced pressure. The boiling fraction of 92-93°C/2 mmHg was collected and recrystallized from methyl ethyl ketone-n-hexane mixed solvent: mp 37.5-38.5°C, yield 31.2%.

Analysis Calculated for $C_{11}H_{16}N_2O_3$: C, 58.91; H, 7.19; N, 12.49%; Found: C, 58.78; H, 7.19; N, 12.39%.

The ^{1}H-NMR spectra of DMDMU thus obtained showed absorption peaks at 5.37, 5.12 ($CH_2=$), 3.02 ($-N-CH_3$), and 1.88 ppm ($CH_3-C=$) in tetrachloromethane. These are peak areas of 2:3:3, in agreement with the structure of DMDMU.

Other Reagents

Commercial α,α'-azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol. Solvents and precipitants were used after purification by ordinary methods.

Polymerization

Polymerizations were carried out in sealed glass tubes in bulk or in benzene in the presence of AIBN as an initiator. Photopolymerization was also conducted in benzene at 0°C or at room temperature under irradiation of a Toshiba SHL-100 high pressure mercury lamp. After polymerization for a given time, the content of the tubes was poured into a large amount of diethyl ether to precipitate the polymer, which was then dried in vacuo. The yield of polymers was determined gravimetrically.

Hydrolysis and Alcoholysis

An attempt was made to hydrolyze the polymers obtained from various dimethacrylamide derivatives under various acidic and alkaline conditions (see Table 3) or to alcoholyze them with potassium hydroxide or cupric chloride in alcohols (See Table 4). After a given reaction time, the polymers were recovered and checked for the change in absorption of the imide group by their IR spectra.

Measurements

^{1}H-NMR measurements were made by means of a JEOL JNM PS-100 (100 MHz) spectrometer with deuterochloroform or tetrachloromethane as the solvent and tetramethylsilane as the internal standard. The IR spectra of the polymers were recorded on a JASCO IR-G spectrometer as they KBr pellets or as films on an NaCl plate.

The melting points of the monomers and the softening temperatures of the polymers were measured by a micromelting point apparatus. Thermal degradation studies were carried out in a nitrogen atmosphere using about 1.5 mg of the polymer by means of Shimadzu TGC-20 thermobalance with a heating rate of 10°C/min. The initial and maximum degradation temperatures of the polymers were analyzed from thermogravimetric analysis (TGA) and differential thermogravimetry (DTG), respectively.

The pyrolysis of the polymers was performed at 235 and 300°C by using a Curie point pyrolyzer, and the pyrolysis products were analyzed by gas chromatography (column: PEG-6000 at 60°C).

The intrinsic viscosities of the polymers were measured in benzene or in chloroform at 30°C by using an Ubbelohde viscometer.

RESULTS AND DISCUSSION

h-h Cyclopolymerization

The results of the radical polymerization of these monomers with the AIBN initiator are summarized in Table 1. The polymers obtained are white powder and their intrinsic viscosities are less than 0.09-0.16 dL/g.

As reported by Kodaira et al. [2-6] (except for DMDMU [1]), these substituted dimethacrylamides were found to homopolymerize to give cyclopolymers soluble in most organic solvents. It is noted, however, that in the radical polymerization of these divinyl monomers, completely soluble polymers are obtained even in bulk system.

Since the methacryl double bonds in these monomers are not known to undergo no h-t propagation, they must be polymerized by a repeated t-t propagation and h-h cyclopropagation mechanism to give h-h cyclopolymers (Eq. 1). This conclusion was also obtained through the IR and ^{1}H-NMR spectra of these polymers which were identical to those reported previously [1-6]. Figures 1 and 2 show, for example, the IR and ^{1}H-NMR spectra of the poly(DMDMH) obtained here.

The strong absorptions due to the vinyl protons appeared in the DMDMH monomer almost disappear in its polymer, and a strong peak by methylene protons appears (Fig. 2). A similar conclusion was reached from the IR spectrum (Fig. 1). Recently the polymers of DMDMU obtained under various conditions were found by ^{1}H-NMR spectra to consist of more than 96.2 to 98.3% h-h cyclized units [7]. Therefore, these polymers were concluded to be the h-h cyclopolymer.

Thermal Properties of h-h Cyclopolymers

TGA curve of the h-h cyclopolymers of MDMD and DMDMU, for example, are shown in Fig. 3, and some thermal properties of these h-h cyclopolymers are summarized in Table 2.

The h-h cyclopolymers obtained from MDMA, PDMA, and DMDMH are found to be thermally stable, probably because of existence of cyclic imide bonds in the main polymer chain. However, thermal degradation of the h-h cyclopolymer of DMDMU starts as low as 130°C and proceeds via two steps. The weight loss in the first degradation step is about 25%, which agrees with that calculated by assuming that methyl isocyanate has been eliminated. Therefore, it is thought the methyl isocyanate is eliminated quantitatively from h-h cyclopoly(DMDMU) to convert to h-h cyclopoly(MDMA):

TABLE 1. Radical Polymerizations of Substituted Dimethacrylamides

Monomer	[AIBN] × 10^2	Benzene (mL)	Temperature (°C)	Time (h)	Yield (%)
MDMA (1.50 mol/L)	2.01 mol/L	2	60	4.5	11.1
MDMA (1.50 mol/L)	2.01 mol/L	2	60	12	18.5
PDMA (4.99 mol/L)	2.26 mol/L	0	60	10	20.3 (0.155)[a]
PDMA (4.99 mol/L)	4.63 mol/L	0	60	9	17.1
PDMA (4.99 mol/L)	4.70 mol/L	0	60	28	62.3
PDMA (4.99 mol/L)	5.00 mol/L	0	60	36	69.3
PDMA (4.99 mol/L)	4.78 mol/L	0	60	18	46.8
PDMA (4.00 mol/L)	2.01 mol/L	2	60	20	30.1
PDMA (3.00 mol/L)	2.00 mol/L	2	60	27	17.7

PDMA (2.01 mol/L)	2.00 mol/L	2	60	27	11.1
DMDMU (1 g)	20 mg	2	70	34	5.7
DMDMU (1 g)	30 mg	2	60	48	7.4
DMDMU (1 g)	30 mg	1	70	24	18.4
DMDMU (1 g)	30 mg	2	0	43 (hν)	0
DMDMU (1 g)	30 mg	1	RT	100 (hν)	5.9
DMDMU (5 g)	60 mg	0	70	13	51.9 (0.10)[a]
DMDMH (1 g)	30 mg	0	70	10	36.4
DMDMH (5 g)	60 mg	0	70	27	29.0
DMDMH (10 g)	100 mg	0	70	12	30.0 (0.09)[a]
DMDME (5 g)	100 mg	0	70	30	9.8

[a] Values in parentheses indicate intrinsic viscosities determined in benzene or chloroform at 30°C.

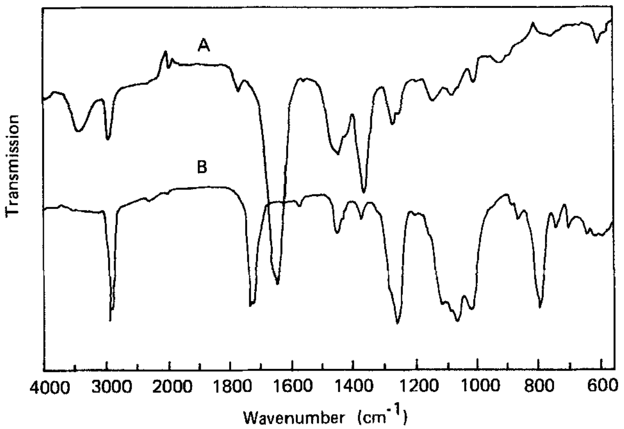


FIG. 1. IR spectra of the polymers. A: h-h cyclopoly(DMDMH). B: Polymer obtained from alcoholysis of h-h cyclopoly(DMDMH).

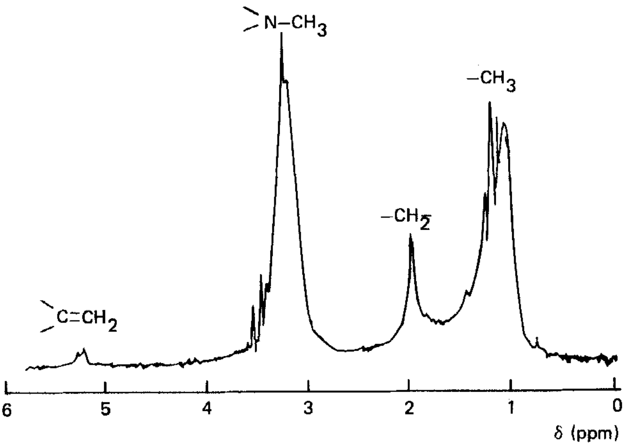


FIG. 2. ^{1}H-NMR spectrum of h-h cyclopoly(DMDMH) in deuterochloroform.

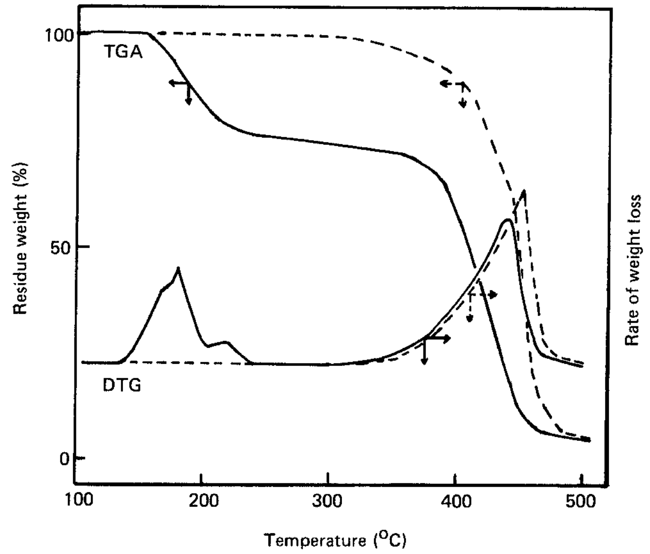
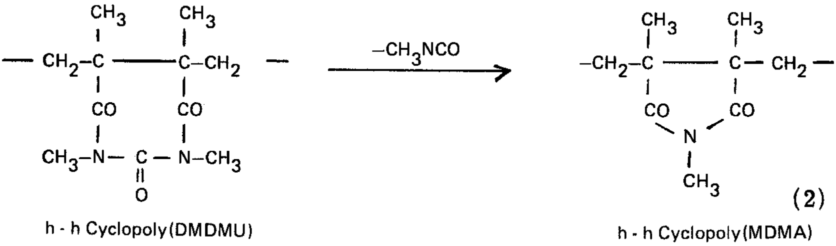


FIG. 3. TGA and DTG curves of h-h cyclopoly(DMDMU) (—), and h-h cyclopoly(MDMA) (- -).



(2)

The formation of methyl isocyanate was also confirmed by pyrolytic gas chromatography.

Hydrolysis of h-h Cyclopolymers

Since the polymers obtained here consist of the h-h structure as stated above, it is expected their hydrolysis and methylation would give h-h poly(methyl methacrylate). Therefore, the h-h cyclopolymers shown in Table 1 were hydrolyzed under various conditions and, after

TABLE 2. Thermal Properties of h-h Cyclopolymers

Polymer	Softening temperature (°C)	Degradation temperature (°C)[a]		Residue at 500°C (%)[a]
		Initial	Maximum	
Poly(MDMA)	180-187	305	450	5.22
Poly(PDMA)	140-145	300	442	3.64
Poly(DMDMU)	227-228	130	178, 434	4.58
Poly(DMDMH)	266-270	288	415	8.26
Poly(DMDME)	168-172	208	428	15.22

[a] Determined by TGA (10°C/min, N_2).

having reacted for an appropriate time, the change in IR absorption due to the imide group of the polymers recovered was checked. The results obtained are shown in Table 3.

As shown in Table 3, these polymers are not hydrolyzed under acidic and alkaline conditions. These results suggest that these cyclic imide polymers are very stable against acids and alkalies. When poly(PDMA) was heated at 100°C in a strong alkali for about 2 weeks, no absorption of the imide group in the neutralized polymer was observed, probably indicating the formation of h-h poly(methacrylic acid). However, we were not successful in isolating the pure acid polymer.

Alcoholysis of the h-h Cyclopolymers

Nishizaki et al. [8] reported that the phthalimide polymer, which is known as a heat-resistant polymer, was hydrolyzed with potassium hydroxide in alcohols. Therefore, this technique was adopted for the hydrolysis of these polymers. The results are shown in Table 4.

Although only h-h cyclopoly(PDMA) and h-h cyclopoly(DMDMH) were used, the polymers recovered after reactions carried out in the presence of potassium hydroxide in ethanol at temperatures above 60°C for long reaction times did not show the IR absorption of the imide group, and a new band due to the ester carbonyl group appeared, as shown in Fig. 1. This result indicates that h-h poly(ethyl methacrylate) was produced. Because the yield of this polymer was very small, the pure product could not be isolated.

TABLE 3. Hydrolysis of h-h Cyclopolymers

Polymer	Reaction reagents	Temperature (°C)	Time (h)	Imide IR band[a]
Poly(MDMA)	10 N NaOH aq soln	100	48	+
Poly(MDMA)	conc H_2SO_4	120	48	+
Poly(PDMA)	conc HCl:H_2O:acetic acid = 1:1:1 (mL)	140	26	+
Poly(PDMA)	conc HCl:H_2O:dioxane = 2:2:8 (vol)	140	26	+
Poly(PDMA)	50-60% KOH aq soln	100	14 d	-
Poly(PDMA)	conc HCl	130	163	+
Poly(PDMA)	48% aw HBr:acetic acid = 1:1 (vol)	120	79	+
Poly(PDMA)	48% HBr	Reflux	72	+
Poly(PDMA)	2 N HCl:glacial acetic acid = 1:4 (vol)	105	19 d	+
Poly(PDMA)	conc H_2SO_4	RT	120	+
Poly(PDMA)	conc H_2SO_4	85-130	95	+
Poly(PDMA)	18-crown-6, 40% KOH aq soln, benzene	60	141	+
Poly(PDMA)	18-crown-6, KOH pellet, benzene	60	27 d	+

(continued)

TABLE 3 (continued)

Polymer	Reaction reagents	Temperature (°C)	Time (h)	Imide IR band[a]
Poly(PDMA)	$[CH_3(CH_2)_{15}N(CH_3)_3]Br$, 40% KOH aw soln, benzene	60	185	+
Poly(DMDMU)	conc HCl	130	42	+
Poly(DMDMU)	conc H_2SO_4	95-97	50	+
Poly(DMDMU)	60% KOH aq soln	160	143	+
Poly(DMDMH)	conc H_2SO_4	RT	13 d	+
Poly(DMDMH)	conc H_2SO_4	100	132	+
Poly(DMDMH)	60% KOH aq soln	160	102	+
Poly(DMDME)	conc H_2SO_4	RT	32 d	+
Poly(DMDME)	60% KOH aq soln	120	24 d	+

[a] Imide groups in the polymers recovered after reactions were checked by their IR spectra: + presence, - absence.

TABLE 4. Alcoholysis of h-h Cyclopolymers

Polymer	Reagents	Temperature (°C)	Time	Imide IR band[a]
Poly(PDMA)	$CuCl_2$–CH_3OH	Reflux	200 h	+
Poly(DMDMH)	$CuCl_2$–CH_3OH	Reflux	107 h	+
Poly(DMDMH)	KOH–CH_3OH	Reflux	14 d	+
Poly(DMDMH)	KOH–C_2H_5OH[b]	60	26 d	-
Poly(DMDMH)	KOH–CH_3OH	Reflux	16 d	+
Poly(DMDMH)	KOH–CH_3OH–dioxane[b]	80-85	14 d	+
Poly(DMDMH)	KOH–C_2H_5OH–dioxane[b]	80-85	155 h	-
Poly(DMDMH)	KOH–C_2H_5OH[b]	120	110 h	-

[a] Imide groups in the polymers recovered after reactions were checked by their IR spectra; + presence, - absence.

[b] Reacted in a sealed tube.

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