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Head-to-Head Vinyl Polymers

9. Preparation and Characterization of Head-to-Head Cyclopolymer Through Radical Head-to-Head Cyclopolymerization of N,N'-Dimethyl-N,N'-Dimethacrylurea

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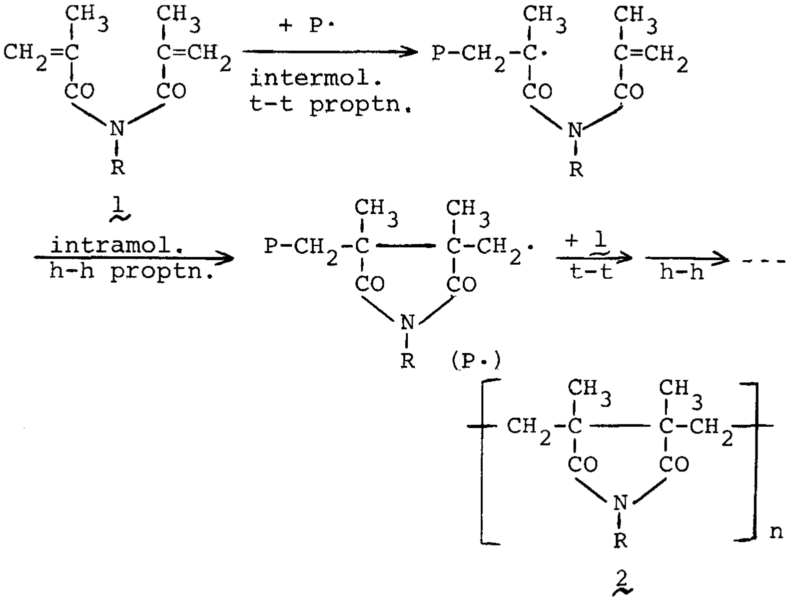
Summary

The radical cyclopolymerization of N,N'-dimethyl-N,N'-dimethacrylurea(DMDMU) was investigated. The resulting polymer was completely soluble in benzene, and was found to compose of a seven-membered cyclized unit by means of IR and NMR spectra. This observation indicated that this cyclopolymerization was performed with alternating inter- and intra-molecular head-to-head(h-h) propagations, i.e. h-h cyclopolymerization mechanism to give a h-h cyclopolymer. When the cyclopolymer was heated, it was found to convert to a h-h cyclopolymer of N-methyl-N,N-dimethacrylamide(MDMA). The hydrolysis of the cyclopolymers of DMDMU and MDMA to h-h polymethacrylic derivatives was not succeeded.

Introduction

In previous papers[OTSU 1977; OTSU et al. 1970, 1979, 1981a, 1981b; QUACH et al. 1981a, 1981b, 1982c, 1982d], a number of h-h polymers and copolymers of acrylic acid and its esters were prepared through alternating copolymerization of ethylene with maleic and citraconic anhydrides, followed by chemical reactions, and characterized. However, the above route is not effective for preparing the pure h-h polymers of methacrylic acid and its esters, because alternating copolymerization of ethylene with 2,3-dimethylmaleic anhydride is not induced[TANAKA et al. 1974].

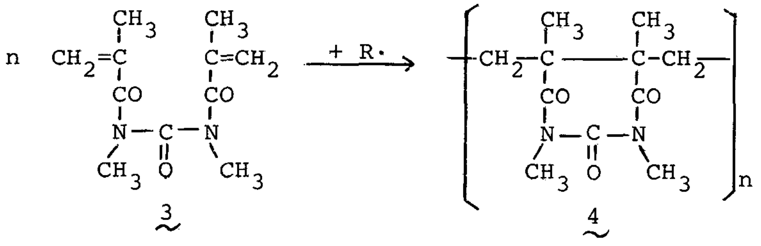
To synthesize pure h-h poly(methacrylic esters), it seems to be better to use a route of h-h cyclopolymerization of dimethacrylamide derivatives, followed by chemical reactions. Since N,N-disubstituted methacrylamides have been known to be not homopolymerized [OTSU et al. 1975], i.e. no head-to-tail(h-t) propagation occurs, N-substituted-N,N-dimethacrylamides(1), one of N,N-disubstituted methacrylamides, seem to be homopolymerized via only h-h(plus t-t) propagation. The most reasonable way for this is a h-h(i.e. plus t-t) cyclopolymerization leading to h-h cyclopolymer(2) as follows[eq.(1)]:

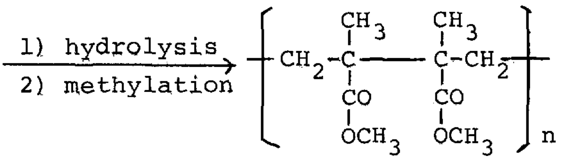


(1)

Such h-h cyclopolymerization was first pointed out by Kodaira et al. for N-n-propyl-N,N-dimethacrylamide (PDMA) and the other N-alkyl derivatives[KODAIRA et al. 1973, 1974a, 1974b], and then they extended this idea to N,N'-dimethyl-N,N'-dimethacrylhydrazine(DMDMH)[KODAIRA et al. 1975, 1979]. In previous papers, we analyzed kinetically the h-h cyclopolymerization of PDMA[YAMADA et al. 1982a] and also found that N-methyl-N-methacrylcrotonamide underwent h-h cyclopolymerization[YAMADA et al. 1982b].

To extend this concept to other methacrylamide derivatives, and to synthesize new h-h vinyl polymer from the h-h cyclopolymer obtained, we prepared DMDMU (3) which then polymerized in the presence of radical initiator. Moreover, the resulting h-h cyclopolymer (4) was attempted to convert new h-h polymer of methyl methacrylate(MMA)(5)[eq.(2)]. The results obtained are described in this paper.





(2)

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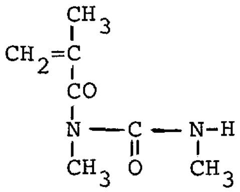
Experimental

Monomer 3 was prepared by the reaction of N,N'-dimethylurea with methacryl chloride in the presence of triethylamine in chloroform at temperatures below 0°C: yield 31.2%, mp 37.5-38.5°C. N,N'-dimethyl-N-methacrylurea(6), a N,N-disubstituted methacrylamide was synthesized according to the reported method[MERGER et al. 1968]: yield 51.5%, mp 44-45°C.



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The polymerizations were carried out in a sealed glass tube in the presence of 1,1'-azobisisobutyronitrile(AIBN). After polymerization for a given time, the content of the tube was poured into a large amount of methanol to isolate the polymer. The polymer was then filtered and dried undder a reduced pressure.

The intrinsic viscosity$[\eta]$ of the polymer was determined in chloroform at 30°C. The structure of the polymer was checked by IR and ^{1}H-NMR spectra. The softening and thermal degradation temperatures were determined by micromelting point apparatus and thermogravimetric analysis(TGA), respectively.

Results and Discussion

The results of radical polymerizations of DMDMU and DMMU initiated by AIBN are shown in Table 1, in which those of PDMA and DMDMH and also indicated as comparison.

From this table, DMMU does not polymerized because it consists of a N,N-disubstituted methacrylamide structure, but DMDMU easily undergoes homopolymerization, as same as PDMA and DMDMH. The resulting polymer is completely soluble in benzene, indicating that no h-t ordinary vinyl polymerization leading to cross-linked polymer formation occurs.

The IR spectrum of the polymer showed no absorption due to methacryl double bond which appeared in the DMDMU monomer. Similar result was also observed in ^{1}H-NMR spectrum which is shown in Fig. 1.

TABLE 1

Radical Polymerizations of DMDMU, DMMU, and Other Dimethacrylamides

Monomer (g)	AIBN (mg)	Benzene (ml)	Temp. (°C)	Time (hr)	Yield (%)	[η] (dl/g)
DMDMU(1)	30	2	60	48	7.4	-
DMDMU(1)	30	1	70	24	18.4	-
DMDMU(1)	30	1	20-30	100*	5.9	-
DMDMU(5)	60	0	70	13	51.9	0.10
DMMU (1)	30	1	70	15	0	-
DMMU (1)	30	0	70	15	0	-
PDMA (1)	4	0	60	10	20.3	0.16
DMDMH(5)	60	0	70	27	29.0	-

* Polymerized under irradiation of UV light(Toshiba SHL-100W) from a distance of 10 cm.

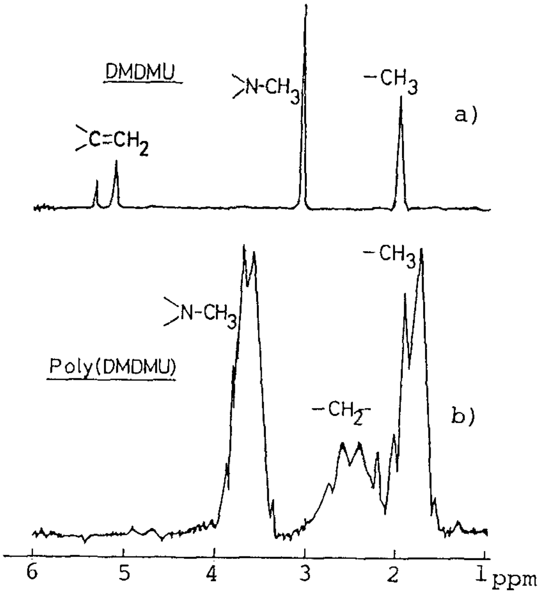

Fig. 1 ^{1}H-NMR spectra: a) DMDMU in CCl_4 at room temperature; b) poly(DMDMU) in $CDCl_3$ at 50°C

The fact that DMMU(6) did not give any polymer would mean that no h-t propagation proceeds in DMDMU polymerization. Therefore, this polymerization is performed via an alternating t-t intermolecular propagation and intramolecular h-h cyclization mechanisms [eq.(1)], similarly to the cyclopolymerization of dimethacrylamide derivatives stated above. Thus, we may call these cyclopolymerizations a h-h cyclopolymerization in distinction from ordinary h-t cyclopolymerization which proceeds via h-t propagation.

Since the main chain of the cyclopolymers obtained from h-h cyclopolymerization consists of a h-h structure, we may also propose to call these cyclopolymers a h-h cyclopolymer in distinction from a h-t cyclopolymer. The h-h cyclopolymer of DMDMU is a white powder with intrinsic viscosity of ca. 0.1 dl/g and melted at 227 -228°C. The TGA thermogram of the h-h cyclopolymer from DMDMU is shown in Fig. 2, in which that from MDMA is also indicated.

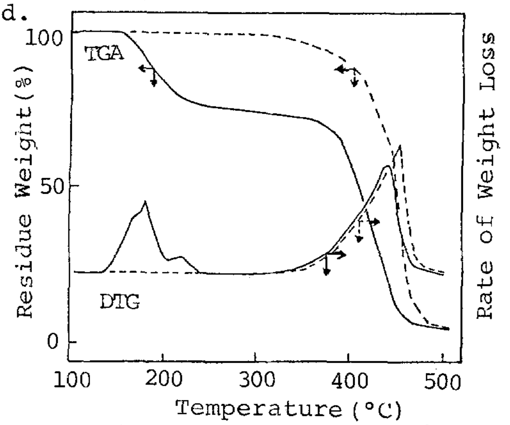

Fig. 2 TGA and DTG thermogramas of poly(DMDMU) (——) and poly(MDMA) (---). Heating rate: 10 °C/min, nitrogen atmosphere

The poly(DMDMU) decomposes with two steps contrary to 2; the first decomposition occurs from 130 to 220°C and the weitht loss is about 25%, which corresponds to the amount of the elimination of methyl isocyanate from the cyclic urea unit(4) giving the h-h cyclopolymer, 7 (R=CH_3 of 2). The formation of methyl isocyanate was also proved by pyrolysis gas chromatography at 235°C.

The second decomposition occurs at temperatures above 350°C and it corresponds to the decomposition of 7. The thermal properties of the h-h cyclopolymers, 4, and 7 are summarized in Table 2.

It is noted that the h-h cyclopolymers with imide ring are thermally stable. Moreover, to prepare h-h poly(MMA) (5), the hydrolyses of 4 and 7 were attempted

TABLE 2

Thermal Properties of Cyclized Polymers

Polymer	Soft. temp. (°C)	Degrad. temp. (°C)		Residue at 500°C(%)
		Initial	Maximum	
Poly(MDMA)	180-187	305	450	5.22
Poly(DMDMU)	227-228	130	178, 434	4.58

under various acidic and alkaline conditions. However both polymers did not hydrolyze even with heating up to 120°C in concentrated sulfuric acid or in 60% potassium hydroxide aqueous solution. This result also suggests that the h-h cyclopolymers with imide ring had strong resistance for acid or alkaline.

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