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### The Fundamental Basis for Cyclopolymerization. IV. Radiation Initiated Solid-State Polymerization of Certain Dimethacrylamides

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## The Fundamental Basis for Cyclopolymerization. IV. Radiation Initiated Solid-State Polymerization of Certain Dimethacrylamides\*

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### SUMMARY

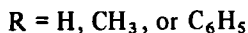
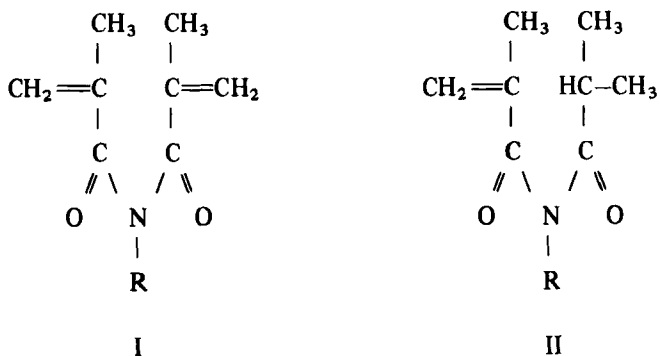
The purpose of this investigation was to study the solid-state polymerization of suitable 1,6-diene monomers, to compare the structure of the polymers with those obtained by free radical initiated solution polymerization, and to use this information in postulating the most probable conformation of the monomer in the crystal. An additional purpose was to compare the polymerization characteristics of these dienes with suitable monoolefinic counterparts. The compounds studied were dimethacrylamide, N-isobutyrylmethacrylamide, and their N-methyl and N-phenyl derivatives. Solution polymerization of all monomers and solid-state polymerization of solid monomers (N-methyl- and N-phenyl-N-isobutyrylmethacrylamide were liquids which did not polymerize) led to polymers of comparable structure in each case. Dimethacrylamide yielded a polymer consisting primarily of six-membered rings. N-Methyldimethacrylamide gave a polymer consisting predominantly of five-membered rings but up to 30% six-membered rings. N-Phenyldimethacrylamide gave a polymer containing almost exclusively five-membered rings. The formation of comparable cyclic polymers by both methods is interpreted to mean that the 1,6-diene molecules are present in the crystal in a conformation favorable for cyclopolymerization.

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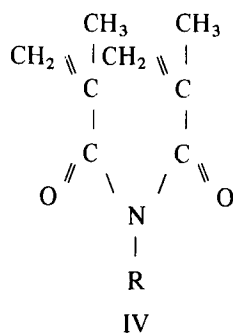
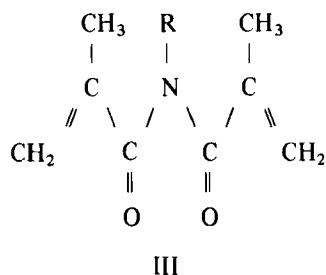
\*Presented in part at the IUPAC Symposium on Macromolecular Chemistry, Budapest, Hungary, August, 1969.

## INTRODUCTION

In the previous paper of this series [1], the synthesis, and UV and NMR spectral studies of dimethacrylamide, N-isobutyrylmethacrylamide, and their N-methyl and N-phenyl derivatives were reported. The three dimethacrylamides are solids at room temperature and represent suitable monomers for a comparative study of their free radical initiated solution polymerization and  $\gamma$ -ray initiated solid-state polymerization. The three N-isobutyrylmethacrylamides represent suitable monoolefinic monomers for comparative polymerization studies. The structures of these monomers are shown as I and II.



It was the purpose of this investigation to compare the polymerization characteristics of the 1,6-dienes with their monoolefinic counterparts, and to compare the structure of the polymers obtained by  $\gamma$ -ray initiated solid-state polymerization of the 1,6-dienes with those obtained by free radical solution polymerization. It was postulated that solid-state polymerization of these monomers could lead to cyclic polymer only if the intramolecular double bonds of the 1,6-dienes were preoriented in the crystal in a conformation favorable for cyclization. This means that a conformation represented by III could only lead to cross-linked polymer, or to a linear polymer containing one pendent double bond per monomer unit. Thus, the assumption was made that if cyclization were the predominant mode of propagation in the solid-state polymerization, the intramolecular double bonds were preoriented in the crystal either as shown in I or in IV, or some conformation approximating one or both of these. The most probable distance for a one-dimensional five-link carbon chain has been



calculated by Treloar [2] to be 4.93 Å. This would not favor cyclization since the distance is too great to permit bond formation without considerable migration of the intramolecular double bond toward the reactive center, a degree of freedom that the molecule is not generally conceded to have in the solid state. This favorable conformation for cyclization, otherwise highly improbable, could be accounted for on the basis of a homoconjugative, interspatial interaction between the double bonds [3, 4] and would lend considerable additional support to this hypothesis.

An obvious extension of this investigation would include an x-ray crystallographic study of the 1,6-dienes. Such experiments are under consideration at the present time.

For comparative purposes, free radical initiated solution polymerization of these 1,6-dienes was carried out in each case and the polymers characterized in the usual manner.

## RESULTS AND DISCUSSION

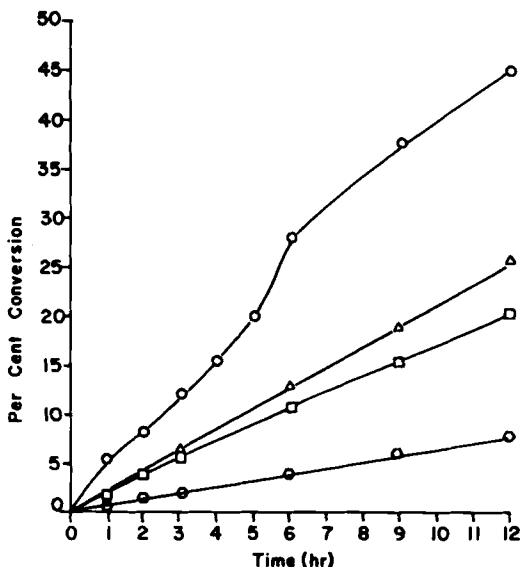
### Free Radical Polymerization

The free radical polymerization of the dimethacrylamides used in this study had been reported previously [5, 6]. In the present work polymerization of the dimethacrylamides has been compared with the polymerization of the N-isobutyrylmethacrylamides. Relative rates of polymerization of the different monomers were determined by measuring the amount of polymer produced in a given time under identical conditions.

In Fig. 1 the results of the polymerization of the monomers at 50° in dimethylformamide (DMF) are plotted. Azobisisobutyronitrile (AIBN) was used as an initiator. Surprisingly, the mixed diacylamide, N-isobutyryl-

methacrylamide, polymerizes much faster than the dimethacrylamides. From Fig. 1 the conversion plot for *N*-phenyldimethacrylamide is similar to but slightly below that of the dimethacrylamide. For *N*-methylmethacrylamide the over-all rate of polymerization is even slower.

No polymer was isolated when the *N*-phenyl and *N*-methyl derivatives of *N*-isobutyrylmethacrylamide were polymerized in DMF at 50° and attempts made to isolate the polymer by the procedure used for the corresponding dimethacrylamides. It seemed possible that the mixed diacylamides might form low molecular weight polymers that did not precipitate. For this reason, solutions of the same monomer and initiator concentration as used in Fig. 1 were prepared in NMR tubes and the ratio of the HC=O proton of DMF to the vinyl protons of the mixed diacylamide determined. After heating for 24 hr at 50°, the ratio was again determined and found to be unchanged. The *N*-methyl and *N*-phenyl derivatives of *N*-isobutyrylmethacrylamide did not polymerize free radically under these conditions. Other attempts to polymerize these mixed diacylamides, in bulk, at higher temperature and with different initiators were unsuccessful.



**Fig. 1.** Polymerization of *N*-isobutyrylmethacrylamide (○), dimethacrylamide (△), *N*-phenyldimethacrylamide (□), and *N*-methylmethacrylamide (×) in DMF. Conditions:  $[M] = 2.0$  moles/l,  $[I] = 2.0 \times 10^{-2}$  moles/l, 50°.

Of all the monomers studied, the two with hydrogen on the nitrogen polymerized the fastest; it seemed this difference must be due to the hydrogen. One possibility would be monomer-polymer association through hydrogen bonding. In a nonpolar solvent, hydrogen bonding would increase and possibly affect the rate of conversion and structure of the polymer. For this reason, plots of conversion vs time were also determined in benzene. A comparison of the polymerization of N-phenyldimethacrylamide in benzene and DMF is shown in Fig. 2. The plots are almost the same, showing no solvent effect as expected. A similar plot for N-methyldimethacrylamide is shown in Fig. 3. The lower conversions obtained in benzene could be due to increased repulsion between the carbonyl groups of the polymer and monomer. Because of their low solubility, dimethacrylamide and N-isobutyrylmethacrylamide were not polymerized in benzene at 50°. Polymerization at 50° gave soluble polymers whose intrinsic viscosities are shown in Table 1.

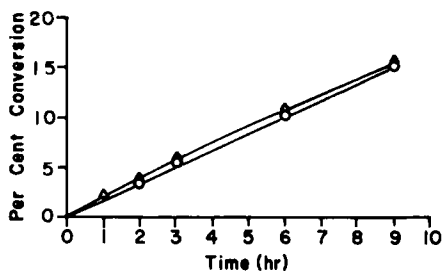


Fig. 2. Polymerization of N-phenyldimethacrylamide in benzene (○) and DMF (△). Conditions:  $[M] = 2.0$  moles/l,  $[I] = 2.0 \times 10^{-2}$  moles/l, 50°.

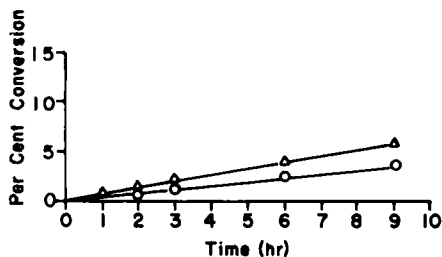


Fig. 3. Polymerization of N-methyldimethacrylamide in benzene (○) and DMF (△). Conditions:  $[M] = 2.0$  moles/l,  $[I] = 2.0 \times 10^{-2}$  moles/l, 50°.

**Table 1.** Polymerization of Monomers at 50°

Monomer <sup>a</sup>	Solvent	Conversion (%)	$[\eta]^b$
1 N-Isobutyrylmethacrylamide	DMF	44	0.46
2 Dimethacrylamide	DMF	23	0.65
3 N-Methyldimethacrylamide	DMF	8.8	0.08
4 N-Methyldimethacrylamide	C <sub>6</sub> H <sub>6</sub>	5.0	0.07
5 N-Phenyldimethacrylamide	DMF	19	0.11
6 N-Phenyldimethacrylamide	C <sub>6</sub> H <sub>6</sub>	17	0.11

<sup>a</sup>[M] = 2.0 mole/l, [I] =  $2 \times 10^{-3}$  mole/l.

<sup>b</sup> $[\eta]$  = intrinsic viscosity.

The three dimethacrylamides and N-isobutyrylmethacrylamide were polymerized as 2.5 M solution in DMF at 75°. Some properties of the polymers obtained are given in Table 2.

**Table 2.** Polymerization of Monomers in DMF at 75°

Monomer <sup>a</sup>	40 min conversion (%)	$[\eta]^b$	10 hr conversion (%)	$[\eta]^b$
1 N-Isobutyrylmethacrylamide	16	0.410	73	0.35
2 Dimethacrylamide	9.7	0.252	74 <sup>c</sup>	0.09 <sup>d</sup>
3 N-Methyldimethacrylamide	3.3	0.09	30	0.08
4 N-Phenyldimethacrylamide	8.9	0.12	55	0.10

<sup>a</sup>[M] = 2.5 mole/l, [AIBN] =  $0.85 \times 10^{-2}$  mole/l.

<sup>b</sup> $[\eta]$  = intrinsic viscosity.

<sup>c</sup>Only 10% soluble.

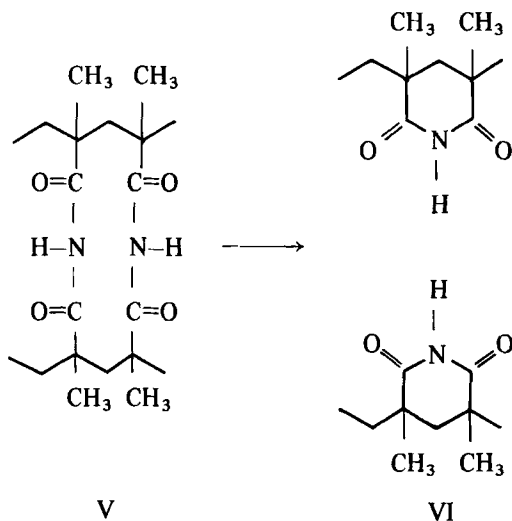
<sup>d</sup>Soluble fraction.

With the conditions used in Table 2, all of the monomers gave soluble polymers at low conversions. At high conversions only 10% of the polymer formed by dimethacrylamide was soluble in DMF. Insolubility indicates that pendent double bonds are formed and cross-link during the polymerization of

dimethacrylamide. This insoluble polymer would dissolve upon prolonged heating in DMF at 100°. Possibly an exchange reaction occurs between adjacent imide groups. This could be represented as shown by V and VI. A similar exchange reaction has been proposed to occur in poly(methacrylic anhydride) [7]. Another possibility is an exchange reaction between DMF and the imide cross-link.

In order to compare the polymerization of dimethacrylamide and N-isobutyrylmethacrylamide in benzene and DMF, it was necessary to use dilute solutions. In Fig. 4 the conversion curves for these two monomers in benzene and DMF are shown. Some properties of the polymers obtained are listed in Table 3.

Figure 1 and the data in Table 3 show that N-isobutyrylmethacrylamide polymerizes faster than dimethacrylamide in DMF. The polymers formed are soluble in DMF. When benzene is the solvent, both monomers polymerize faster and at very similar rates. For the polymerizations in benzene the polymer precipitated from solution was granular and seemed not to be swollen



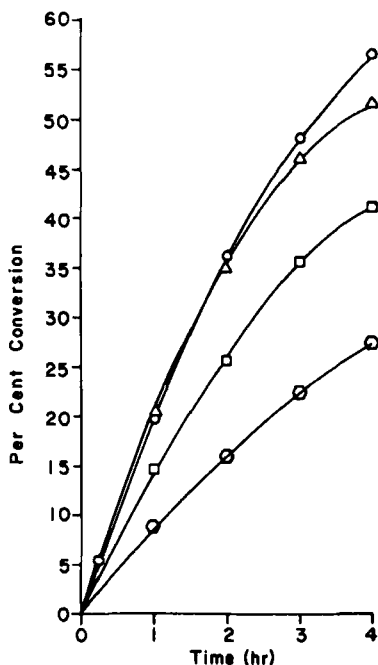
by the solvent. The increased polymerization rate in benzene with polymer separating from solution is not surprising. As the polymer separates, propagation and termination will be diffusion controlled. The monomer can reach the growing chain but, in a heterogeneous medium, bimolecular termination is inhibited by the decreased mobility of the polymer chain [8]. Hayden and Melville [9] studied the polymerization of methyl methacrylate in a heterogeneous medium. They found that both the prop-



agation and termination rate constants decreased, but the decrease was much greater for the termination step, so the over-all rate increased.

Polymerization of N-isobutyrylmethacrylamide in benzene gave a polymer that was soluble in DMF. Polymerization of dimethacrylamide in benzene gave a polymer that was only partially soluble in DMF and the solubility decreased as conversion increased (Table 3, 7-11).

It has been found that acrylic anhydride [10] and methacrylic anhydride [11] polymerize faster in cyclohexanone than in DMF. The polymers precipitate in cyclohexanone and the increased rate is due to the heterogeneous nature of the system. Gray [12] observed that for the polymerization of methacrylic anhydride the amount of cyclization in cyclohexanone is greater than in DMF. This indicates that precipitation of the growing polymer chain favors cyclization. The reason cyclization may be enhanced by precipitation is the lower the solvation of a polymer chain the tighter it will coil [13].



**Fig. 4.** Polymerization of dimethacrylamide in dimethylformamide (X) and benzene (O), N-isobutyrylmethacrylamide in dimethylformamide (□) and Benzene (△). Conditions:  $[M] = 0.85$  moles/l,  $[I] = 0.85 \times 10^{-2}$  moles/l,  $75^\circ$ .

Table 3. Polymerization of N-Isobutyrylmethacrylamide and Dimethacrylamide at 75°

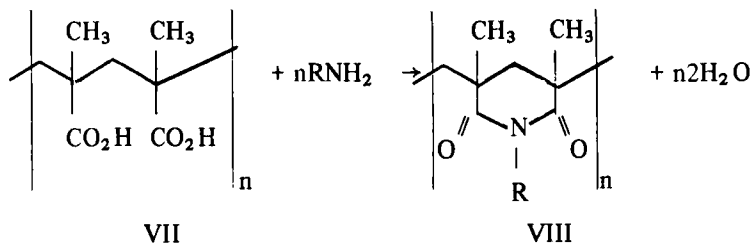
Monomer <sup>a</sup>	Solvent	Time	Conversion (%)	Soluble in DMF (%)	$[\eta]^b$ 30° DMF
1 N-Isobutyrylmethacrylamide	DMF	1 hr	15	100	0.20
2 N-Isobutyrylmethacrylamide	DMF	4 hr	41	100	0.17
3 N-Isobutyrylmethacrylamide	C <sub>6</sub> H <sub>6</sub>	1 hr	20	100	0.24
4 N-Isobutyrylmethacrylamide	C <sub>6</sub> H <sub>6</sub>	4 hr	51	100	0.24
5 Dimethacrylamide	DMF	1 hr	8.9	100	0.09
6 Dimethacrylamide	DMF	4 hr	28	100	0.09
7 Dimethacrylamide	C <sub>6</sub> H <sub>6</sub>	18 min	4.2	37	0.10
8 Dimethacrylamide	C <sub>6</sub> H <sub>6</sub>	1 hr	20	29	—
9 Dimethacrylamide	C <sub>6</sub> H <sub>6</sub>	2 hr	30	24	—
10 Dimethacrylamide	C <sub>6</sub> H <sub>6</sub>	3 hr	41	23	—
11 Dimethacrylamide	C <sub>6</sub> H <sub>6</sub>	4 hr	56	23	0.10

<sup>a</sup>[M] = 0.85 mole/l, initiator AIBN [I] = 0.85 × 10<sup>-2</sup> moles/l.<sup>b</sup>[ $\eta$ ] = intrinsic viscosity.

The N-methyl and N-phenyl derivatives of dimethacrylamide were polymerized in bulk at  $100^\circ$ , using tert-butyl hydroperoxide as an initiator. The N-methyl derivative gave a 74% yield of a soluble polymer ( $[\eta] = 0.07$ ). The N-phenyl derivative gave a 90% yield of a soluble polymer ( $[\eta] = 0.10$ ).

Götzen and Schröder [5] compared the IR spectra of the polymers of dimethacrylamide and its N-methyl derivative with the products obtained by heating poly(methacrylic acid) with ammonia and methyl amine. The reaction of the poly(methacrylic acid) with an amine would yield a six-membered ring polymer (VII and VIII).

The free radical polymerization of dimethacrylamide gave a polymer whose IR spectrum was similar to that obtained by heating poly(methacrylic acid) with ammonia. This indicates the polymer contains six-membered rings. Free radical polymerization of the N-methyl derivative gave a product

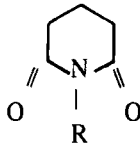
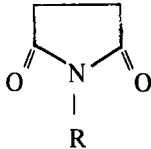
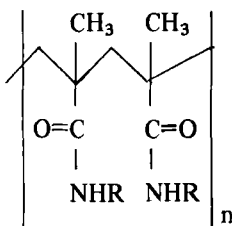
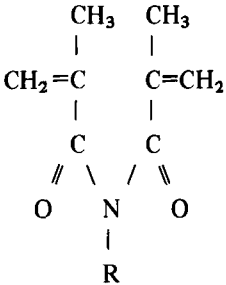


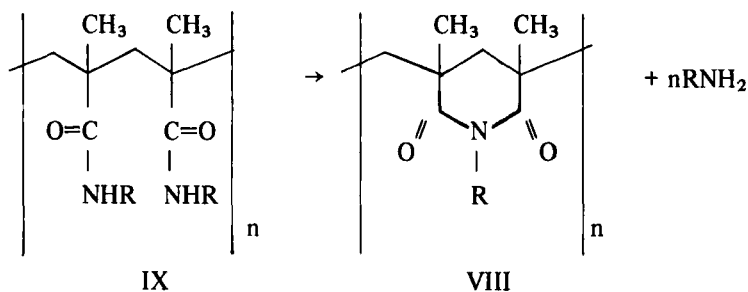
whose IR spectrum was different from the polymer obtained by heating poly(methacrylic acid) with methyl amine. Pyrolysis of the poly(N-methyl dimethacrylamide) gave ethylene and trimethylmaleimide. Thus the polymer contained primarily units of five-membered rings.

Sokolova and Rudkovskaya [6] compared the IR spectra of the carbonyl region of the polymers obtained by free radical polymerization of dimethacrylamide and its N-methyl, ethyl, propyl, and phenyl derivatives with the polymer formed by deamination of the appropriate poly(methacrylamide). The deamination of the poly(methacrylamide) (IX) would give a polymer containing six-membered rings. The IR spectra of the polymers were also compared with the appropriate N-substituted succinimides and glutarimides. These IR spectral comparisons indicate that substituted dimethacrylamides give polymers containing five-membered rings and dimethacrylamide gives a polymer containing six-membered rings. The results of this IR spectral study are summarized in Table 4.

The IR spectra of the polymers prepared in this work are in agreement with those found in the literature; also, changing temperature of polymeriza-

Table 4. Infrared Spectra of the Polymers and Cyclic Imides [6]

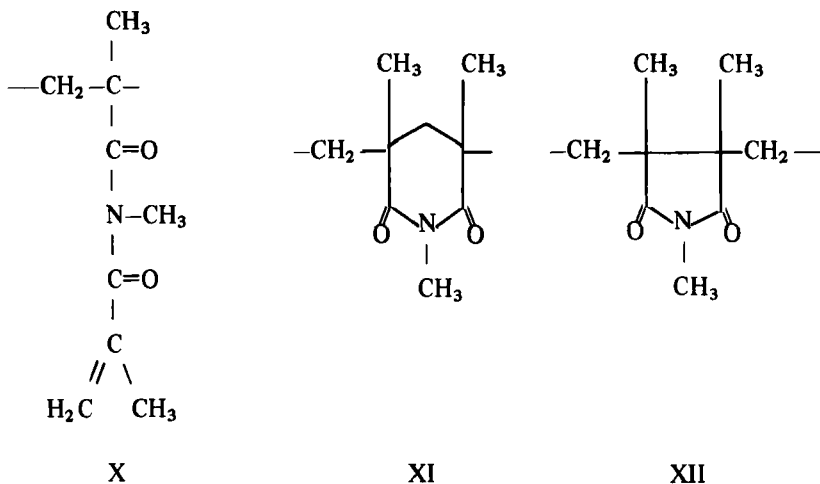
Compound type	R	C=O (cm <sup>-1</sup> )		Difference (cm <sup>-1</sup> )
		1	2	
	H	1694	1746	52
	CH <sub>3</sub>	—	—	—
	C <sub>6</sub> H <sub>5</sub>	1678	1730	52
	H	1700	1774	74
	CH <sub>3</sub>	1700	1774	70
	C <sub>6</sub> H <sub>5</sub>	1712	1780	68
Deamination of	H	1695	1755	60
	CH <sub>3</sub>	1672	1722	50
	C <sub>6</sub> H <sub>5</sub>	1680	1730	50
	H	1700	1755	55
Polymerization of	H	1700	1755	55
	CH <sub>3</sub>	1705	1778	73
	C <sub>6</sub> H <sub>5</sub>	1715	1787	72



tion, solvent, and concentration did not change the appearance of the IR spectra.

In this work the NMR spectra of the polymers were studied in the hope of learning more about the structure of the polymers. The spectra of polymer from N-methyl- and N-phenyldimethacrylamide were determined in nitrobenzene; polymers from dimethacrylamide, in deuterated dimethylsulfoxide.

For poly(N-methyldimethacrylamide) three structural units are possible; X, XI, and XII.



The NMR spectra of these units would be expected to be different. The chemical shift of the N-CH<sub>3</sub> protons would be different. Also, Structure X contains allyl and vinyl protons. In Table 5 are the chemical shifts of some model compounds.

The NMR spectrum of a sample of poly(*N*-methylmethacrylamide) is shown in Fig. 5. Proton resonances corresponding to vinyl or allyl protons were not observed, so the polymer does not contain pendent groups (X). Signals at 6.77 and 6.98  $\tau$  correspond to the  $\text{N}-\text{CH}_3$  protons of XI and XII, respectively. Both signals are shifted 0.1 ppm downfield from the  $\text{N}-\text{CH}_3$  protons of *N*-methylglutarimide and *N*-methylsuccinimide, as shown in Table 5. The IR spectral data indicate that the polymer is primarily of the five-membered rings (XII), so the upfield  $\text{N}-\text{CH}_3$  signal should be larger, as

Table 5. Proton Chemical Shifts of Some Methyl Substituted Imides

Compound	Chemical shift ( $\tau$ ) <sup>a</sup>			
	$\text{N}-\text{CH}_3$	$\text{CH}_2=$	$\text{CH}_3-\text{C}=\text{C}$	$\text{CH}_3-\text{C}-\text{CH}_3$
1 <i>N</i> -Methyl- <i>N</i> -isobutyryl-Methacrylamide	6.80	4.59	7.97	8.65
2 <i>N</i> -Methylglutarimide	6.87			
3 <i>N</i> -Methylsuccinimide	7.07			

<sup>a</sup>Measured in nitrobenzene at 145°.

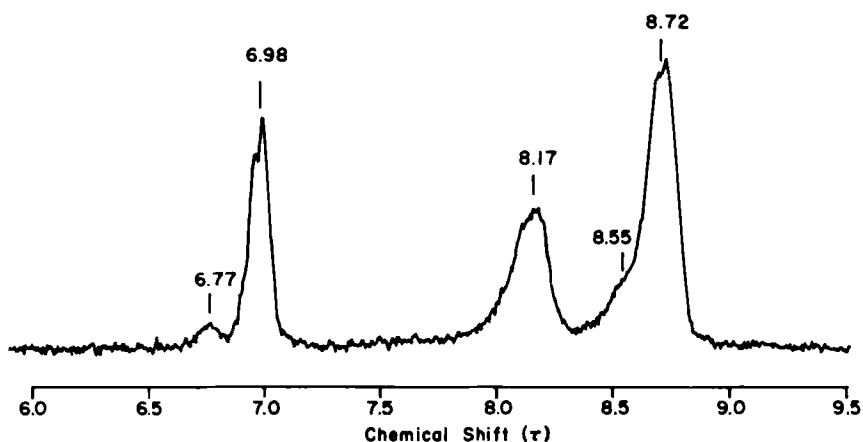


Fig. 5. NMR spectrum of poly(*N*-methylmethacrylamide) in nitrobenzene at 145°.

is observed. The proton resonances centered at 8.17 and 8.72  $\tau$  were assigned to the methylene and methyl proton, respectively, of the five-membered rings (XII).

The shoulder at 8.55  $\tau$  is assigned to the methyl protons of six-membered rings (XI). The NMR spectra of samples polymerized in benzene and DMF were identical. Estimation of the areas of the N-CH<sub>3</sub> proton resonances by planimetry indicates that the polymer contains about 10% six-membered rings and 90% five-membered rings. The percentage of six-membered rings seems to increase as the polymerization temperature is raised.

The NMR spectrum of a sample of poly(N-phenyldimethacrylamide) is shown in Fig. 6. The spectra of polymers polymerized in benzene, DMF, and at different temperatures were identical. There are no resonances corresponding to vinyl or allyl protons. The polymer contains only cyclic

units, and, judging from the sharpness of the CH<sub>3</sub>-C- signal, only five-membered rings, in agreement with IR spectral data. Poly(dimethacrylamide)

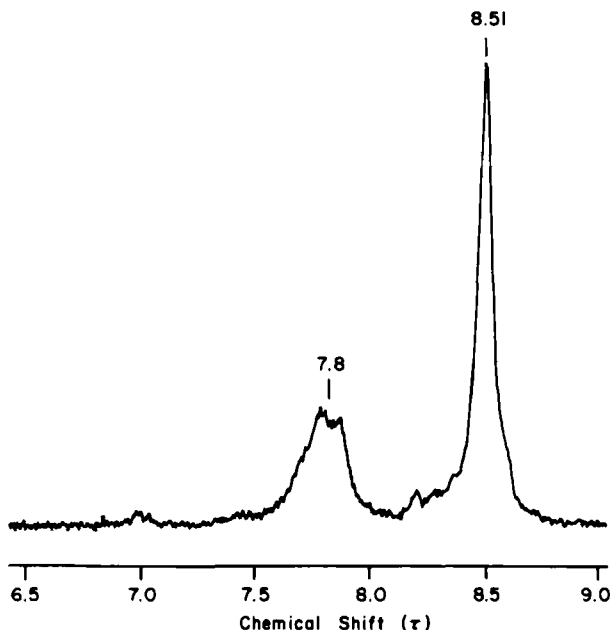


Fig. 6. NMR spectrum of poly(N-phenyldimethacrylamide) in nitrobenzene at 145°.

was not soluble in nitrobenzene, so the NMR spectra were determined in deuterated dimethylsulfoxide (DMSO). This polymer could be composed of structural units like X, XI, and XII with N-CH<sub>3</sub> replaced by N-H. It was thought that the different units could be distinguished by the N-H proton resonance, but the signal was too broad for this to be done. Some chemical shifts of related model compounds are shown in Table 6.

The NMR spectrum of a sample of poly(dimethacrylamide) is shown in Fig. 7. The IR spectrum indicates this polymer contains primarily six-membered rings, so the signal at 8.71  $\tau$  was assigned to the methyl protons of the six-membered rings, the shoulder at 8.88  $\tau$  assigned to the methyl of the five-membered rings. The signal at 8.08  $\tau$  is the allyl protons of the pendent double bond (see Table 6, 2). The broad signal at 7.3  $\tau$  is the

Table 6. Proton Chemical Shifts of Some Imides

Compound	Chemical shift ( $\tau$ ) <sup>a</sup>				
	$\begin{array}{c}   \\ \text{CH}_3-\text{C}-\text{CH}_3 \\   \end{array}$	$\begin{array}{c}   \\ \text{CH}_3-\text{C}=\end{array}$	$\begin{array}{c}   \\ \text{H}-\text{C}- \\   \end{array}$	$\begin{array}{c}   \\ \text{H}_2\text{C}=\end{array}$	
1 Diisobutyramide	8.95	—	7.05	—	
2 N-Isobutyrylmethacrylamide	8.94	8.10	6.91	4.43	4.16

<sup>a</sup>Measured in deuterated dimethylsulfoxide at 95°.

methylene protons. The multiplet at 7.48  $\tau$  is CD<sub>2</sub>HSOCD<sub>3</sub> and the signal at 7.0  $\tau$  is water. In the region 4.2-4.4  $\tau$  signals due to the vinyl protons are present. This polymer contains about 15% uncyclized units. If this spectrum is compared with that of the N-methyl derivative in Fig. 8, notice that signals which have been assigned to the five-membered and six-membered rings, 8.93  $\tau$  and 8.75  $\tau$ , respectively, in deuterated dimethylsulfoxide, are both within 0.05  $\tau$  of the same assignments for poly(dimethacrylamide). In Fig. 9 are two more spectra of samples of poly(dimethacrylamide), one prepared in DMF and the other a soluble fraction from a polymerization in benzene. They are very similar (both seem to contain the same amount of unsaturation), but it does seem that polymerization in benzene gives a polymer containing more of the five-membered rings.



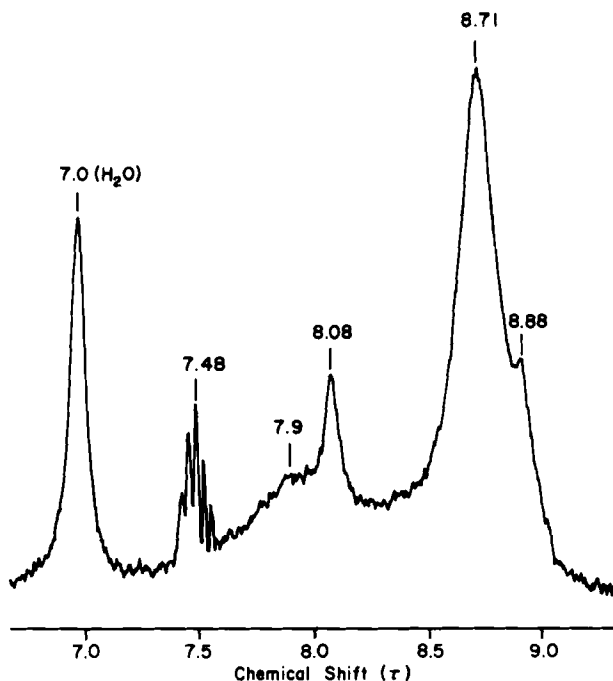
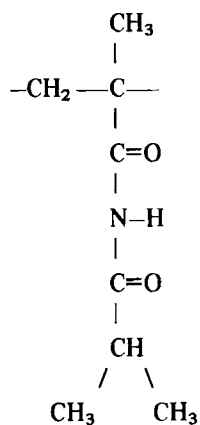


Fig. 7. NMR spectrum of poly(dimethacrylamide) in DMSO- $d_6$  at  $95^\circ$ . Polymerization conditions: 2.5 moles/l in DMF at  $75^\circ$ .

The NMR spectrum of poly(*N*-isobutyrylmethacrylamide) is shown in Fig. 10; this is consistent with the expected structure (XIII). The signal at 8.95  $\tau$  is the  $\text{CH}_3\text{-C-CH}_3$  group ( $J = 6.5$ ), and overlapping the methyl of the polymer chain at 8.0  $\tau$  is the methylene of the chain. It appears that the H-C-absorption is obscured by the water signal. The nitrogen proton is near 0.5  $\tau$ . Spectra of samples polymerized at different temperatures, concentrations, and using different solvents were identical.

The IR spectrum of the polymer had the following absorption: 3600-3300  $\text{cm}^{-1}$  (N-H stretch); 2975, 2935, and 2875  $\text{cm}^{-1}$  (C-H stretch); 1755 and 1695  $\text{cm}^{-1}$  (C=O); 1470  $\text{cm}^{-1}$  (N-H); 1375-1355  $\text{cm}^{-1}$  (C-H deformation); 1195, 1155, and 1100  $\text{cm}^{-1}$  (skeletal). It seemed possible that an exchange reaction might occur during the polymerization of *N*-isobutyrylmethacrylamide to produce the symmetrical diacylamides, but



## XIII

when the unreacted monomer was recovered from a polymerization, it was found to be unchanged.

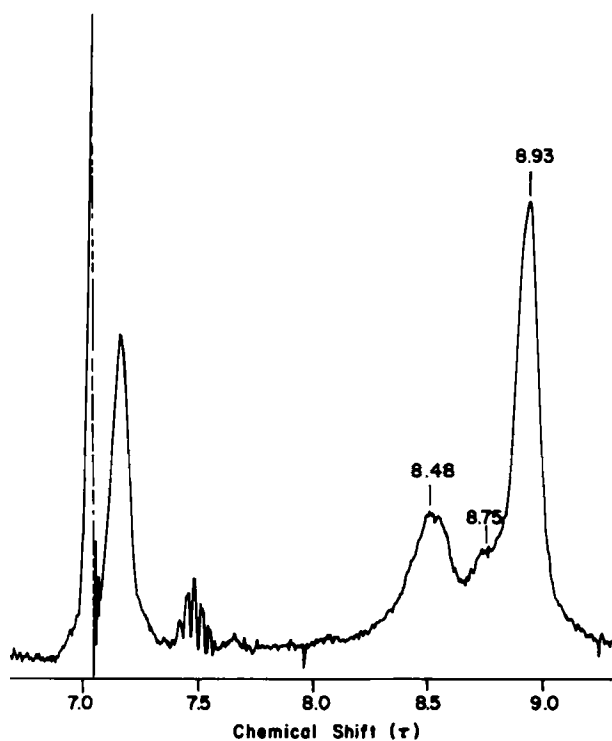
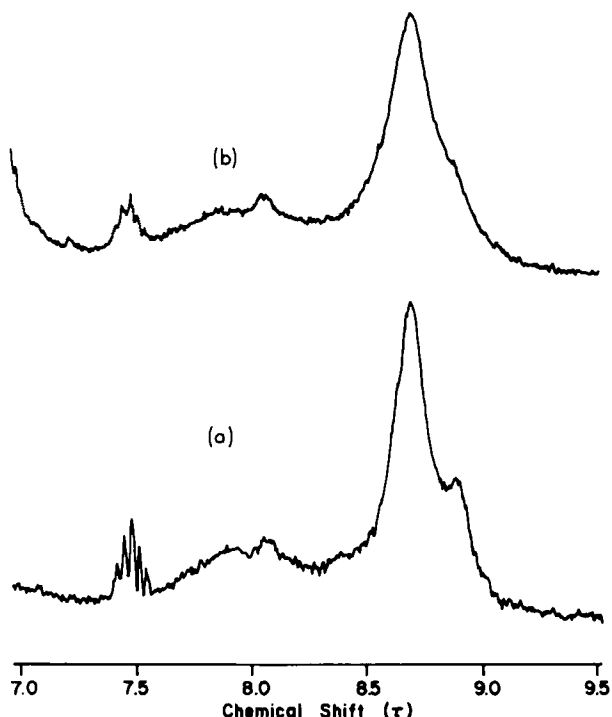


Fig. 8. NMR spectrum of poly(N-methyldimethylacrylamide) in DMSO-d<sub>6</sub> at 95°.



**Fig. 9.** NMR spectra of poly(dimethacrylamide) in DMSO- $d_6$ . Polymerization conditions: 0.85 moles/l at 75° in DMF (a), and in benzene (b).

Of the compounds studied, *N*-isobutyrylmethacrylamide polymerizes at the fastest rate. The *N*-phenyl and *N*-methyl derivatives of *N*-isobutyrylmethacrylamide do not polymerize. For the dimethacrylamides, dimethacrylamide polymerizes fastest, *N*-phenyl dimethacrylamide at a slightly lower rate, and *N*-methyl dimethacrylamide considerably slower. The polymerization rate of *N*-phenyl- and *N*-methyl dimethacrylamide is slower in benzene than in DMF. Both *N*-isobutyrylmethacrylamide and dimethacrylamide polymerize faster in benzene, probably due to the heterogeneous nature of the system. Also, dimethacrylamide will crosslink, while the *N*-phenyl and *N*-methyl derivatives will not.

The structures of the polymers produced by the dimethacrylamides are different. Polymerization of dimethacrylamide yields a polymer consisting primarily of six-membered rings. Five-membered rings and units resulting from linear propagation with the formation of pendent double bonds are also formed. Polymerization of *N*-methyl dimethacrylamide yields a polymer

consisting of about 90% five-membered rings and 10% six-membered rings. For N-phenyldimethacrylamide, the polymer seems to contain only five-membered rings.

In attempting to explain the results of the polymerization study, it must be kept in mind that a number of steps are involved in addition polymerization. The fact that one compound polymerized, while another does not, could be due to differences in propagation, termination, or chain transfer reactions. However, because of the similarity of the compounds used in this study, their polymerizations should be similar.

For the dimethacrylamides and N-isobutyrylmethacrylamides, the substituent on nitrogen controls the course of free radical polymerization. Dimethacrylamide polymerizes to give a polymer containing predominantly six-membered rings and significant amounts of five-membered rings and pendent double bonds. The N-methyl- and N-phenyldimethacrylamides polymerize to form polymers containing five-membered rings. There are only small amounts of six-membered rings and no detectable pendent

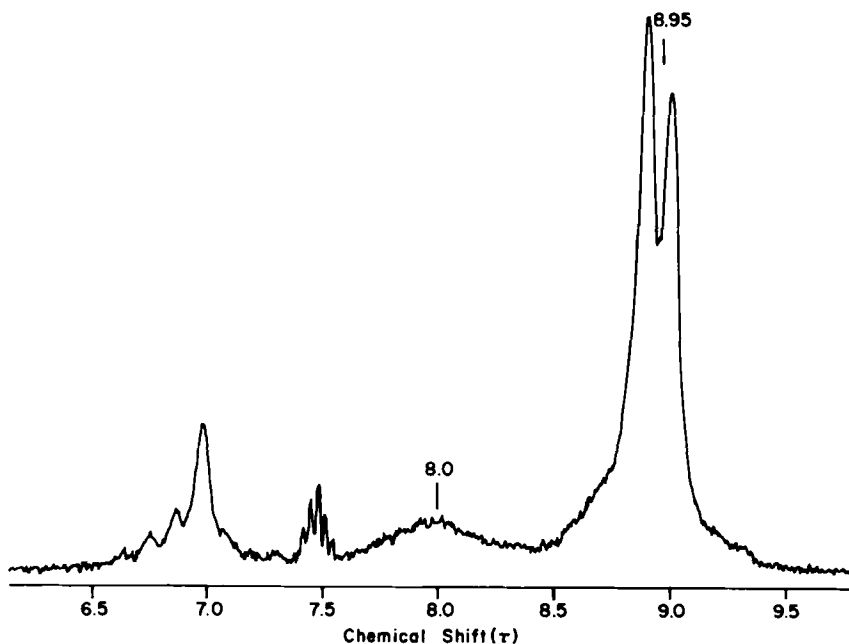
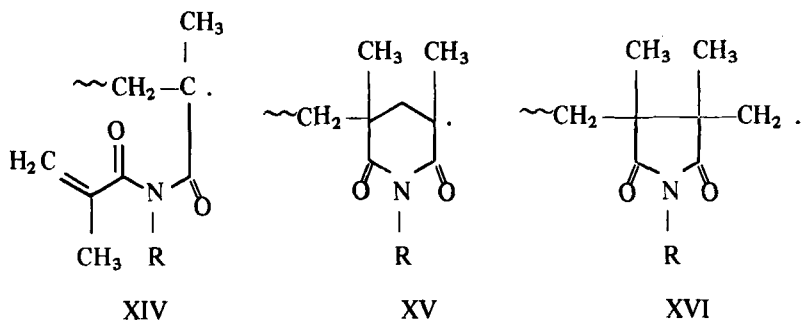


Fig. 10. NMR spectrum of poly(N-isobutyrylmethacrylamide) in DMSO- $d_6$  at 95°.

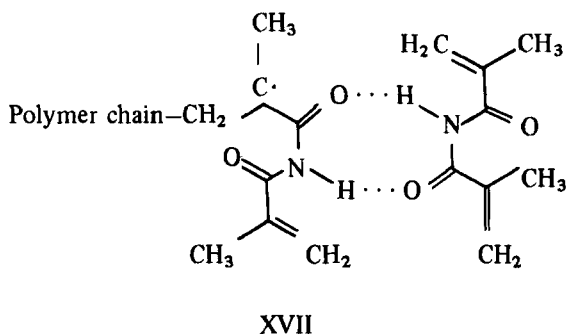
double bonds remain. The effect of hydrogen is strikingly demonstrated in that *N*-isobutyrylmethacrylamide readily polymerizes, but the *N*-methyl and *N*-phenyl derivatives do not. The effect of the nitrogen substituent is best seen by considering the possible propagating radicals, XIV, XV, and XVI.



R = H, CH<sub>3</sub>, or C<sub>6</sub>H<sub>5</sub>

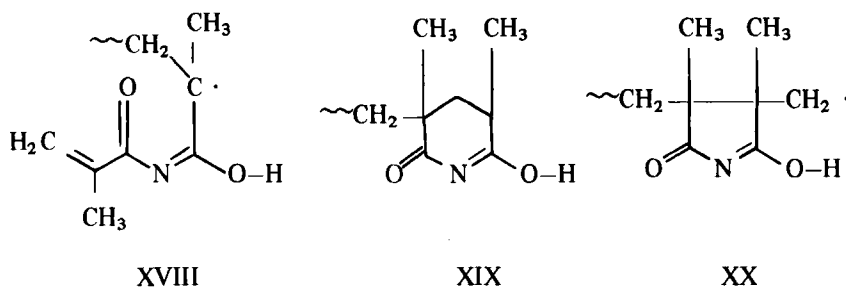
If R is methyl or phenyl, polymerization occurs predominantly through XVI. If R is hydrogen, polymerization occurs predominantly through XV but XIV and XVI are also formed.

The effect of hydrogen could be due to a number of factors. One possibility is hydrogen bonding. Lee and Kumler [14] have presented evidence that diacetamide forms a hydrogen bond dimer in solution. For the compounds in this work the monomer association or monomer-polymer association through hydrogen bonding could increase the rate of polymerization of the unsubstituted diacylamides. In a structure such as XVII monomer association with the growing polymer chain would favor propagation without cyclization.



It seems monomer-polymer association would be more effective for XIV than for XV and XVI. This could account for the high rate of polymerization of N-isobutyrylmethacrylamide and dimethacrylamide, but does not readily explain the formation of six-membered rings. That dimethacrylamide and N-isobutyrylmethacrylamide form hydrogen bonds in solution is shown by the upfield shift of the nitrogen proton as the concentration decreases. Nakayama and Smets [15] have suggested the possibility of monomer association being responsible for the differences in the polymerization of maleimide and N-butylmaleimide. If hydrogen bonding is a factor, the polymerization of dimethacrylamide in a nonpolar solvent should be faster and contain more unsaturation than polymerization in a polar solvent. When polymerized in benzene the rate of polymerization of dimethacrylamide increased and the polymer cross-linked. However, NMR spectral studies did not show any increase in unsaturation and the results could be explained by the heterogeneous nature of the polymerization.

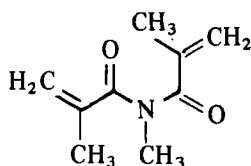
Another possibility with hydrogen is enolization of the propagating radical (XVIII-XX). The enolized radical could complex with the monomer through hydrogen bonding. Also, enolization would decrease repulsion between the carbonyl of the growing chain and the next monomer.



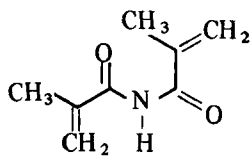
Resonance effects could also be important in the polymerization of the dimethacrylamides. Addition of the monomer to the propagating radical produces XIV, then cyclization gives either XV or XVI. Resonance stabilization of the radical by conjugation with the carbonyl would favor XV. However, if there were considerable interaction of the carbonyl groups through the nitrogen, conjugation between the carbonyl and radical in the six-membered ring (XV) would be reduced and formation of XV would be less favorable. This would mean nitrogen substituents which increase resonance stabilization of the imide group would be less likely to form six-membered rings. Resonance forms of the imide such as XIV and XVI

reduce the electron density on nitrogen. Electron donation by the methyl group would stabilize a positive charge on nitrogen and it is possible that the phenyl group would also act as an electron donor in the dimethacrylamides. This increased resonance stabilization of the imide group by methyl or phenyl substituents on nitrogen could account for the formation of five-membered rings. Another factor is that the imide group in a five-membered ring is more likely to be planar than a six-membered ring. Therefore, substituents which increase resonance stabilization of the imide group would be more likely to form the planar five-membered ring.

Götzen and Schröder [5] have attributed differences in polymerization to steric effects. Examination of molecular models predicts that the most probable conformation of N-methyldimethacrylamide is XXI; for dimethacrylamide, XXII.



XXI



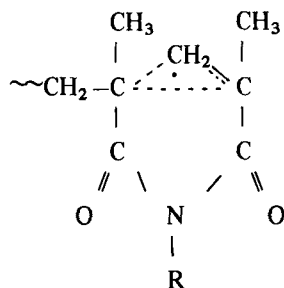
XXII

If it is assumed that one methacryl group adds to the propagating chain and the other retains its s-cis or s-trans conformation until cyclization occurs, the structure of the polymers can be explained. For XXI no matter which methacryl group the propagating radical attacks, the remaining one will be in a s-cis conformation and will most easily form a five-membered ring by rotation about an N-C bond. For XXII there are two possibilities; addition to the s-trans methacryl group gives a structure which forms a five-membered ring by cyclization. If addition occurs at the s-cis methacryl group, cyclization to a six-membered ring is favored. Cyclopolymerization of dimethacrylamide to give predominantly six-membered rings is attributed to the greater reactivity of the s-cis methacryl group. This argument based on different conformations for dimethacrylamide and N-methyldimethacrylamide explains the results. But conformation XXI for N-methyldimethacrylamide is different from the structure which was proposed [1] to explain the unusual NMR chemical shifts of the vinyl protons of N-methyldimethacrylamide. Also, the study of the solvent shifts did not indicate any significant differences in the conformations of the dimethacrylamides.

Another possibility is steric repulsions in the different size rings. The

angle between the carbonyl group in the five-membered ring is larger than in the six-membered ring. Therefore, the large methyl and phenyl substituents would favor formation of the five-membered ring.

Another possible explanation for the formation of five- as well as six-membered rings is an intermediate nonclassical radical (XXIII) [3, 16].



XXIII

Attack at the least hindered tertiary position by the electron cloud of a neighboring monomer molecule would lead to the six-membered ring. Attack at the most hindered primary carbon would lead to the five-membered ring. Neither attack, however, would be required to generate the postulated intermediate radical, the relatively stable tertiary radical in the case of six-membered ring formation, or the less stable primary radical in the case of five-membered ring formation.

Of the various factors discussed, it seems that monomer association or monomer-polymer association through hydrogen bonding would be important in the polymerization of dimethacrylamide and N-isobutyrylmethacrylamide. For the N-phenyl- and N-methyldimethacrylamides, steric and resonance effects of the nitrogen substituent can explain the results. Considering that the resonance effect of the methyl and phenyl would be expected to be different, steric effects may be more important.

### Solid State Polymerization

The first reported example of cyclopolymerization in the solid state was by Gibbs and Van Deusen [17]. They found that irradiation of N,N-diallylmelamine with  $\gamma$ -rays from a cobalt-60 source gave an acid-soluble polymer that contained negligible amounts of unsaturation as indicated by NMR and IR spectroscopy. Solubility and absence of unsaturation in the polymer were taken as evidence for formation of a cyclopolymer.



Azori et al. [18] have reported the radiation-induced polymerization of N-phenyldimethacrylamide. The polymerization was initiated by radiation from an x-ray tube at a dose rate of 0.2 Mrad/hr. The polymerization temperature was 75°, which is 5° below the melting point of the monomer. Irradiation for 100 min gave a 10% yield of a polymer with an intrinsic viscosity of 0.26. Irradiation for 300 min gave a 60% yield of a polymer with an intrinsic viscosity of 0.16. The intrinsic viscosities of the polymers obtained by irradiation of solid N-phenyldimethacrylamide are higher than values reported for solution polymerization. The IR spectra of the polymers obtained by radiation-induced polymerization and free radical initiated polymerization were identical. Absorption bands characteristic of vinyl unsaturation were absent in the IR spectrum. The presence of absorption bands at 1700-1710 and 1780  $\text{cm}^{-1}$  indicate that the cyclopolymerization occurred to give a polymer containing five-membered rings.

In this work the crystalline monomers, N-isobutyrylmethacrylamide, dimethacrylamide, N-methyldimethacrylamide, and N-phenyldimethacrylamide, were polymerized by  $\gamma$ -ray irradiation from a cobalt-60 source. The monomers, sealed in evacuated Pyrex tubes, were irradiated at two dose rates, 0.5 and 1.4 Mrad/hr. After irradiation, the samples were left standing at room temperature (25°) for 6 days. In Table 7 are listed per cent conversion and viscosities of the polymers. Polymerization at the low-dose rate gave similar conversion for all monomers except the phenyl derivative. The lower conversions observed for N-phenyldimethacrylamide could be due to differences in crystal structure or to the absorption of energy by the phenyl ring. At the higher-dose rate the conversion varied. For N-isobutyrylmethacrylamide polymerization increased, but the intrinsic viscosity of the polymer is lower. N-Methyldimethacrylamide polymerized completely, and also the viscosity is higher than that of the polymer obtained at low conversion.

For N-phenyldimethacrylamide the yield is still low, but the increase is greater than that of the other monomers. A comparison of this work with the work of Azori et al. [18], described above, shows that increasing the temperature gave a higher yield of polymer in less time and at a lower radiation dose. It is not possible to tell what the per cent conversion was for dimethacrylamide. The product was unaffected by DMF at room temperature and only partially soluble when heated at 150° for 40 hr. The IR spectrum was similar to that of the polymer obtained by free radical solution polymerization except that the bands were much broader. Dimethacrylamide has a strong absorption at 938  $\text{cm}^{-1}$  due to out-of-plane deformation of the methylene group. The irradiated product has only a weak absorption of

Table 7. Radiation Induced Polymerization of Monomers

Monomer	Dose <sup>a</sup> 13 Mrad		Dose <sup>b</sup> 91 Mrad	
	Conversion (%)	$[\eta]^c$	Conversion (%)	$[\eta]^c$
1 N-Isobutyrylmethacrylamide	4.5	0.13	34	0.09
2 Dimethacrylamide	4.0	Insoluble	Insoluble	Insoluble
3 N-Methylmethacrylamide	4.3	0.062	100	0.07
4 N-Phenyldimethacrylamide	0.6	—	22	0.06

<sup>a</sup>Irradiated for 26.5 hr at a dose rate of 0.5 Mrad/hr.

<sup>b</sup>Irradiated for 65.3 hr at a dose rate of 1.4 Mrad/hr.

<sup>c</sup>Intrinsic viscosity.

940  $\text{cm}^{-1}$  which could be unreacted monomer or pendent double bonds. Although some monomer may be left in the product, the IR spectrum indicates considerable polymerization occurred.

Information about the structure of the polymers produced by radiation-initiated polymerization was obtained by comparing their IR and NMR spectra with those of the polymers obtained by free radical polymerization. The IR and NMR spectra of poly(N-isobutyrylmethacrylamide) obtained by the two methods are identical and, as discussed previously, consistent with the expected structure.

Irradiation of dimethacrylamide gave an insoluble polymer, indicating polymerization occurs without complete cyclization and cross-linking occurs through the pendent double bond. The IR spectrum is similar to that of the polymer obtained by free radical solution polymerization, except for a broadening of the absorption bands and changes in intensity. In particular, free radical polymerization gives a polymer with a strong absorption at 1220  $\text{cm}^{-1}$  and a weak absorption at 1130  $\text{cm}^{-1}$  due to skeletal vibrations of the methyl on the six-membered ring and five-membered ring. In the polymer produced by irradiation of the solid, these bands are nearly of equal intensity, indicating an increase in the amount of the five-membered ring. It seems likely that this polymer consists of five- and six-membered rings and units resulting from linear propagation without cyclization.

The IR spectrum of the polymer obtained by irradiation of N-methylmethacrylamide is almost identical to the spectrum of the polymer obtained by free radical polymerization. The only difference is a shoulder at 1670

$\text{cm}^{-1}$  on the carbonyl band, indicative of the presence of six-membered rings. More information about the structure is obtained from the NMR spectrum shown in Fig. 11. The two absorptions at 6.77 and 6.98  $\tau$  are indicative of the presence of five- and six-membered rings in the polymer.

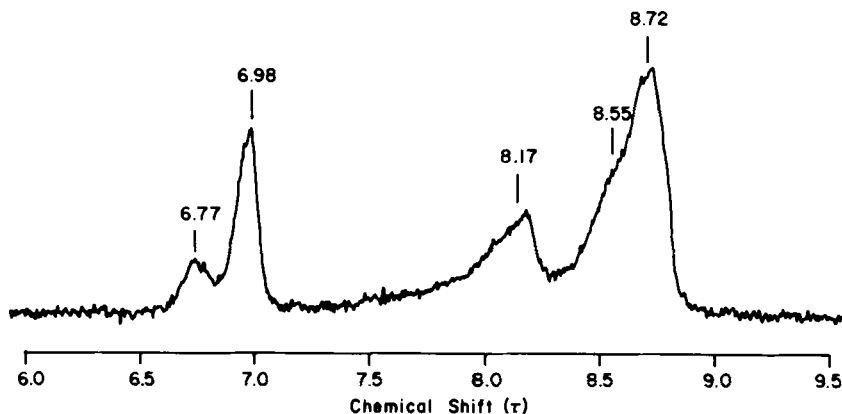
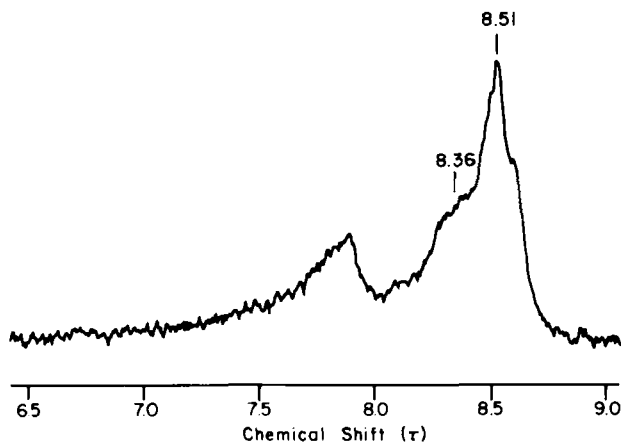


Fig. 11. NMR spectrum of poly(N-methyldimethacrylamide) in nitrobenzene at  $145^\circ$ . Polymerization induced by  $\gamma$ -ray irradiation of the monomer.

The signal at 8.72  $\tau$  and the shoulder at 8.55  $\tau$  also show the polymer is a mixture of five- and six-membered rings. The spectrum contained no absorptions due to vinyl or allyl protons. Measurement of the areas of the two absorptions at 6.77 and 6.98  $\tau$  indicates this polymer is a mixture of about 30% six-membered rings and 70% five-membered rings.

Radiation-induced polymerization of N-phenyldimethacrylamide gave a polymer with an IR spectrum similar to that of the polymer obtained by free radical polymerization. In the carbonyl region there were absorptions at 1710 and 1778  $\text{cm}^{-1}$  associated with the five-membered ring and also a shoulder at 1680  $\text{cm}^{-1}$  due to the presence of six-membered rings. The NMR spectrum of this polymer is shown in Fig. 12. If this is compared with the spectrum of polymer obtained by free radical polymerization, Fig. 6, one can see a broadening of the methylene protons near 7.8  $\tau$  and a shoulder in the methyl region near 8.4  $\tau$ . This is due to six-membered rings in the polymer structure.

Radiation-induced polymerization in the solid state has been studied extensively in the past few years. No single pattern of behavior emerges from the various monomers studied [19]. For some monomers, polymerization rate is considerably enhanced by monomer orientation in the



**Fig. 12.** NMR spectrum of poly(N-phenyldimethacrylamide) in nitrobenzene at  $145^{\circ}$ . Polymerization induced by  $\gamma$ -ray irradiation of monomer.

crystal lattice and an oriented polymer may be formed. In other monomers, crystallinity impedes the reaction which then tends to be initiated at crystalline defects to give an amorphous polymer.

In cyclic monomers such as trioxane, the crystal structure enhances polymerization [20]. For trioxane large crystals formed by sublimation polymerize faster than small crystals formed by rapid cooling. Additives such as benzene, water, and methanol greatly decrease the rate of polymerization. This could be because of a disordering effect on the crystal lattice or these additives may act as terminating agents. Another feature of the solid-state polymerization of trioxane is that rate of polymerization decreases with conversion and only a certain fraction of the initial monomer crystal can be polymerized. This could be due to a destruction of crystallinity by the growing polymer chain [18]. The polymerization of trioxane is believed to proceed by an ionic mechanism.

Acrylamide is a monomer in which the crystal structure impedes radiation-induced solid-state polymerization. Samples of acrylamide, which were melted and shock-cooled, polymerize faster than large slowly grown crystals [21]. Also the presence of 1% water greatly increases the rate of polymerization. Solid solutions of acrylamide containing 10% propionamide or 10% acetamide polymerize faster than pure acrylamide. It seems that factors that increase imperfections in the crystal lattice increase the rate of polymerization. The polymer obtained by irradiation of acrylamide is

amorphous [22]. Electron spin resonance studies [23] indicate that polymerization of acrylamide occurs by a free radical mechanism.

The radiation-induced polymerization of methacrylamide has been studied [24] and appears to be very much like the polymerization of acrylamide, except that polymerization is much slower. Electron spin resonance studies indicate polymerization is by a free radical mechanism [25].

It would seem that the radiation-induced polymerization of the dimethacrylamides used in this study probably propagates by a radical mechanism like acrylamide and methacrylamide. That the structures of the polymers are similar to structures obtained by free radical solution polymerization would be consistent with this mechanism.

Direct comparison of the rate of polymerization of methacrylamide and the dimethacrylamides is not possible because of differences in experimental conditions. Irradiation of methacrylamide at a dose rate of 0.42 Mrad/hr for a total dose of 12 Mrad gave 6.5% conversion to polymer. Comparison with the low-dose rate figures in Table 7 indicates that methacrylamide polymerizes faster. It is reported that methacrylanilide does not polymerize when the solid is irradiated in a cobalt-60 source, presumably because of intermolecular hydrogen bonding.

The reason for irradiating the dimethacrylamides used in this study was to see if cyclopolymerization would occur. It was thought that the occurrence of cyclopolymerization in the solid state would be indicative of the existence of the monomer in the crystal lattice in a conformation that favored cyclization. It would seem that if the crystal structure were a major factor in the cyclization step, then the polymer obtained would have a simple structure. Since the polymers formed contain mixtures of five- and six-membered rings, it does not seem that the crystal structure is controlling the cyclization step.

## EXPERIMENTAL

### Preparation of Model Compounds

**N-Methylsuccinimide.** With shaking and cooling, 5.0 g (0.05 moles) of succinic anhydride were dissolved in 15 ml of 30% aqueous methyl amine. The mixture was distilled and the fraction distilling between 227 and 230° collected. Two recrystallizations from isopropanol left 2.0 g of N-methylsuccinimide, mp 65.7-67.5°. Literature: [26] mp 65.5-67.5°.

**N-Methylglutarimide.** With shaking and cooling 10 g (0.088 moles) of glutaric anhydride were added to 30 ml of 30% aqueous methyl amine. The solution was distilled and the fraction distilling between 240 and 250° collected. Redistillation through a microspinning band column gave 5.0 g of N-methylglutarimide; bp 123° (14 mm);  $n_D^{25}$  1.4940. Literature: [26] bp 124° (14 mm);  $n_D^{25}$  1.4944.

**Solution Polymerizations.** The free radical polymerizations of the various monomers were carried out in sealed tubes, using benzene or DMF as a solvent. Azobisisobutyronitrile (AIBN) and tert-butyl hydroperoxide were used as initiators.

As a general procedure the polymerization tube was charged with the appropriate amount of monomer, initiator, and solvent, then flushed with nitrogen and sealed. After heating in an oil bath at a constant temperature for the appropriate length of time, the tube was opened and the contents added dropwise to a nonsolvent. The precipitated polymer was filtered off through a sintered glass crucible and dried to a constant weight in a vacuum desiccator at 50° to determine the yield. Polymers were then reprecipitated twice to provide samples for measurement of properties and spectra. Polymerizations were carried out using 0.25-0.26 g of monomer in 0.5 to 15 ml of solvent. The polymer was precipitated in 100-300 ml of nonsolvent. Many attempts were made to polymerize N-methyl and N-phenyl-N-isobutyrylmethacrylamide under the same conditions that N-methyl and N-phenyldimethacrylamide polymerized. In no case was there any evidence that polymerization had occurred.

The intrinsic viscosities of all polymers were determined in DMF at 30°. IR data were obtained on all polymers, using potassium bromide pellets. NMR data were obtained on the polymers, using a Varian A-60A Analytic NMR Spectrometer equipped with a variable temperature probe. Spectra of polymers of dimethacrylamide and N-isobutyrylmethacrylamide were determined, using deuterated dimethylsulfoxide as a solvent. The  $CD_2HSOCD_3$  multiplet, chemical shift 7.48  $\tau$  at the normal probe temperature [27], was used as a reference for measuring the position of absorptions. Spectra of polymers of N-methyldimethacrylamide and N-phenyldimethacrylamide were determined using nitrobenzene as a solvent. That component of the nitrobenzene multiplet which had a chemical shift of 2.39  $\tau$ , measured with respect to internal TMS at the normal probe temperature, was used as a reference point for measuring the positions of absorptions.

**Solid-State Polymerization.** The crystalline monomers, dimethacrylamide, N-methyldimethacrylamide, N-phenyldimethacrylamide, and N-isobutyrylmethacrylamide, were polymerized by irradiation from a  $\text{Co}^{60}$   $\gamma$ -ray source of 600 Ci. The design and construction of the irradiator have been described in the literature [28].

Weighed samples of the monomers were placed in 13 mm Pyrex tubes, evacuated to  $10^{-3}$  mm, and sealed. The samples were placed in a rack which positioned the tubes adjacent to the source in the  $\text{Co}^{60}$   $\gamma$  irradiator. Two positions at different distances from the source were used. At the closest position the dose rate was about 1.4 Mrad/hr; at the outer distance, 0.5 Mrad/hr.

The samples were irradiated at room temperature, removed from the source, and allowed to stand at room temperature. After opening, the contents were dissolved in a suitable solvent, the polymer precipitated in a nonsolvent, collected by filtration, and vacuum dried at  $50^\circ$ . Irradiated dimethacrylamide was stirred with DMF. At low conversion the monomer dissolved but the polymer was insoluble. At high conversion the product was unaffected by DMF at room temperature and dissolved only upon prolonged heating at  $100^\circ$ . Irradiated N-isobutyrylmethacrylamide was dissolved in DMF and the polymer precipitated in ether.

For N-methyldimethacrylamide and N-phenyldimethacrylamide, the irradiated product was dissolved in acetone and the polymer precipitated in hexane.

## CONCLUSIONS

The marked similarity between the polymers of dimethacrylamides obtained by free radical solution polymerization and  $\gamma$ -ray initiated solid-state polymerization indicates that the latter process also involves a free radical mechanism. Structural comparisons also indicate that the degree of cyclization of these monomers in solid-state polymerization is equal to that observed in solution polymerization. These results are interpreted to mean that the conformation of the monomers in the crystalline state is such that the intramolecular double bonds are preoriented in a manner favorable for cyclization to occur. These conclusions lend considerable additional support to the hypothesis that a homoconjugative interspatial interaction exists between the intramolecular double bonds of 1,6-dienes, thus providing a lower energy pathway from monomer to cyclic polymer.

## ACKNOWLEDGMENTS

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