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Electron Spin-Resonance Studies of Irradiated N-(p-Bromophenyl)dimethacrylamide and Solid-State Polymerization of sym-Dimethacryloyldimethylhydrazine

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ABSTRACT

An electron spin resonance study of the intermediate radicals formed in the cyclopolymerization of certain nitrogen-containing monomers has been carried out. An initiation radical, both in N-(p-bromophenyl)dimethacrylamide (BrPhDMA) and sym-dimethacryloyldimethylhydrazine (DMMH), could be observed. The crystalline structure of DMMH is not known at present, but the comparison of the crystalline structure of BrPhDMA with that of N-methyldimethacrylamide suggests that the crystalline structure in these cyclization reactions is very important. In the glassy state of BrPhDMA, an anion radical of the methacryl group was detected as was the case in the glassy state of propyl- and benzyldimethacrylamides. It is significant that only the 5-membered cyclic radical was detected in the glassy state of BrPhDMA, because only the noncyclic initiation radical was observed in irradiated crystalline

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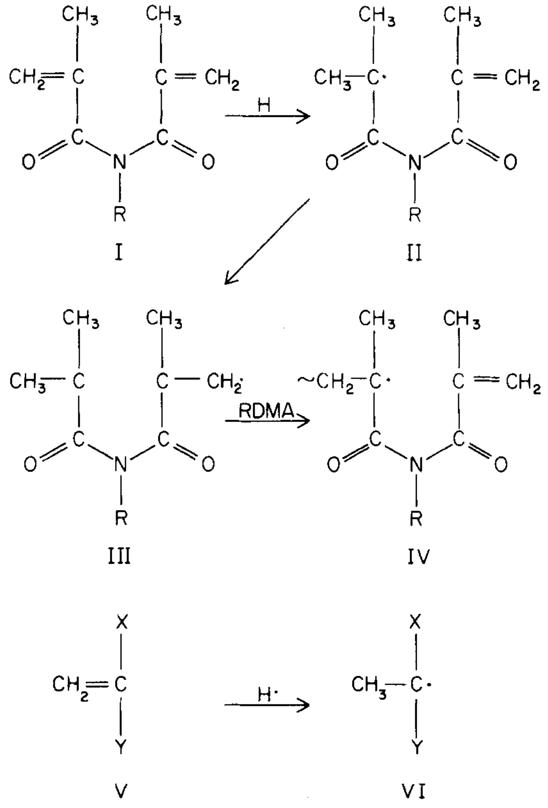
BrPhDMA at -196°C, and only the 5-membered cyclic radical was detected in propyl- and benzyldimethacrylamide in both the crystalline and glassy states.

INTRODUCTION

Cyclopolymerization of N-substituted dimethacrylamides (RDMA) has been carried out by several researchers [1-4]. Structural investigation has shown that their main repeating unit is a 5-membered ring. They contain small amounts of 6-membered ring but do not contain any detectable pendant double bond. Detailed investigation on the cyclopolymerization of RDMA has led to the conclusion that the high tendency of RDMA to cyclization is due to the nonpolymerizability of their monofunctional counterparts [4]. The hypothesis that the lower the polymerizability of the monofunctional counterpart, the higher the cyclopolymerizability of the bifunctional monomer has been deduced, and this hypothesis has been verified in several monomers [5-7].

During these studies it was found that the rate-determining step of the cyclopolymerization in the solid and supercooled liquid states is the intramolecular cyclization reaction [4, 8, 9]. This conclusion has been deduced because only a noncyclic propagating radical (IV in Scheme 1) was observed on measurements of ESR spectra of irradiated RDMA at polymerization temperature. Radiation polymerization of unsaturated monomers in the solid state proceeds through the initiation radical (VI in Scheme 1) which is formed by the addition of hydrogen atom to the double bond. Based upon these facts, the formation of the initiation radical in RDMA (II Scheme 1) is reasonably assumed. This initiation radical cyclizes to give 5-membered cyclic radical which reacts with other monomer to yield an uncyclized propagating radical. At higher temperature where polymerization proceeds, only the noncyclic propagating radical was detected as mentioned previously. A decrease in temperature reduces the molecular motion, and the polymerization does not proceed. These considerations suggest that it might be possible to observe the initiation radical (II in Scheme 1) and 5-membered cyclic radical (III in Scheme 1) at lower temperature, and then the noncyclic radical (IV) with a gradual increase in temperature. These reactions should be strongly influenced by the phases where the reactions are carried out. The effect of phases on these reactions can be studied by using RDMA because the propyl and benzyl derivatives can form glassy, supercooled liquids and crystalline states [8].

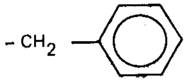
As summarized in Table 1, the initiation radical at -196°C could not be observed. This radical had already cyclized to form a 5-membered cyclic radical. The crystalline structure of the methyl derivative [12] shows that the formation of the 5-membered ring is the most favorable reaction in this monomer. The distance between the two carbon atoms that react to form the 5-membered ring is 2.9 Å in crystalline N-methyldimethacrylamide. It can be assumed that the crystalline



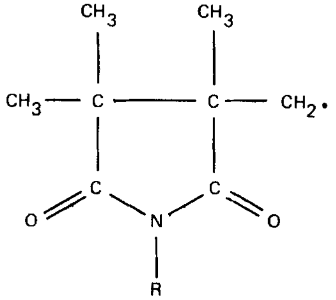
SCHEME 1.

structures of the propyl and benzyl derivatives are also favorable for the cyclization reaction. These results show that to observe the initiation radical, the experimental temperature must be reduced to below -196°C, or some other system must be chosen. It would be interesting to know what the distance between two intramolecular double bonds should be to permit detection of the initiation radical. For this purpose, N-(p-bromophenyl)dimethacrylamide (BrPhDMA) and sym-dimethacryloyldimethylhydrazine (DMMH) were chosen (Scheme 2). The crystalline structure of BrPhDMA has already been determined [13]. As opposed to the methyl derivative, the distances between the possible reaction sites are rather long (~4 Å), and in addition the planes containing the two methacryl double bonds are perpendicular to each other. Solution and solid-state polymerization of this monomer has also been carried out, and the results show that it gives polymer with no detectable pendant double bonds [13]. The content of 5-

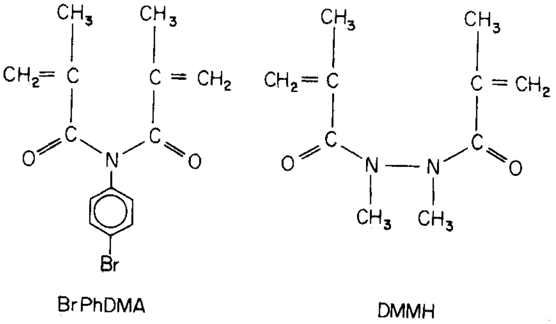
TABLE 1. Radicals Observed in RDMA Irradiated at -196°C [10, 11]

	Radicals	
Substituents	Crystalline state	Glassy state
CH_3	A	-
$-C_3H_7$	A	A, B
	A	A, B

A.



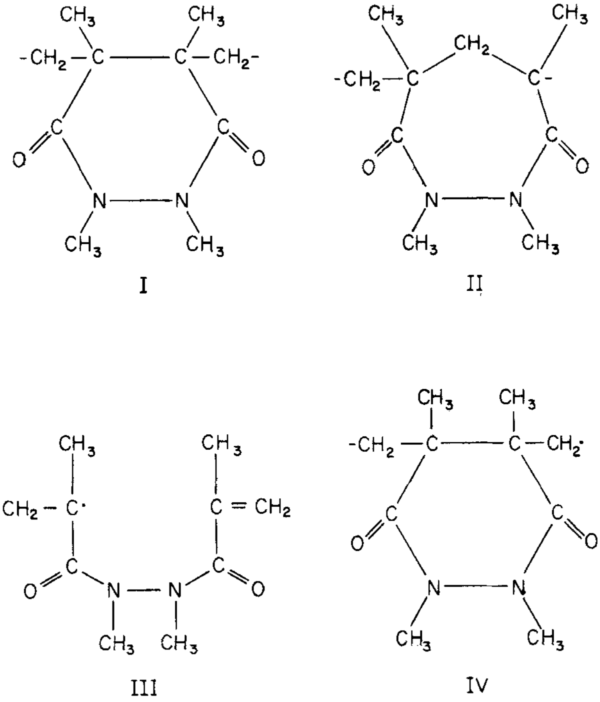
B. Anion radical of methacryl group.



SCHEME 2.

membered ring in the polymer obtained in solution and solid states are 80 and 60%, respectively. This monomer has the same polymerization behavior as other RDMA, but its crystalline structure is different from that of the methyl derivatives. This monomer was chosen for this reason.

At present the crystalline structure of DMMH is not known, but it can be assumed that the distance between two intramolecular double bonds is rather long as compared with the methyl derivative because DMMH is a 1,7-diene. A 1,7-diene is an unfavorable monomer for cyclopolymerization, but DMMH gives highly cyclized polymer in solution polymerization due to the nonpolymerizability of its monofunctional counterpart. DMMH is considered to possess an unfavorable conformation for cyclization as compared with N-methyldimethacrylamide, and the initiation radical may be observed, but it would yield polymer with a rather higher degree of cyclization. This monomer is considered to be suitable for showing how the crystalline structure influences the initial stage and how polymerization proceeds independently from the crystalline structure. That the crystalline structure of the methyl substituent does not influence the polymer has al-



SCHEME 3.

ready been shown. DMMH could be another example. The cyclic units which are expected from this monomer are 6- and 7-membered rings. Judging from the stability of the cyclic structure, the 6-membered ring is the more favorable one. The possible propagating radicals are the 6-membered cyclic radical (IV in Scheme 3) and the noncyclic propagating radical (III in Scheme 3). These two radicals can easily be distinguished from each other. As a result, some additional information about the mechanism of cyclopolymerization should be obtained.

EXPERIMENTAL

Syntheses of Monomers

BrPhDMA and DMMH were synthesized according to the procedures previously described [5, 13].

Polymerization

The crystalline monomer was placed in a 20-mm Pyrex tube, evacuated to 10^{-5} mmHg, sealed, and irradiated at ambient temperature. After irradiation for the desired time, the crystals were poured into chloroform, and then the mixture was poured into diethyl ether to precipitate the polymer. The polymer yield was determined gravimetrically.

ESR measurements were made using a Varian E-3 EPR spectrometer after evacuation of the sample to 10^{-5} mmHg.

X-ray Powder Diffractometer using copper as a target.

NMR spectra were taken on a JEOL FX-100 spectrometer.

Thermal analyses were carried out on a Perkin-Elmer Differential Scanning Calorimeter DSC-1B.

RESULTS AND DISCUSSION

ESR Studies of Irradiated Polycrystalline BrPhDMA

ESR spectra of polycrystalline BrPhDMA irradiated at -196°C are shown in Fig. 1. With increasing temperature the intensity of the signal decreases slightly but is almost constant up to 0°C. Above 0°C the intensity of the spectrum decreases and the spectral pattern changes to a 12-line spectrum. The 7-line spectrum (a or b in Fig. 1) can be ascribed to the initiation radical (II in Scheme 1) and the 12-line spectrum (d in Fig. 1) to the noncyclic propagating radical (IV in Scheme 1). These results show that only an initiation radical is formed in irradiated BrPhDMA at -196°C which is stable up to 0°C. When the irradi-

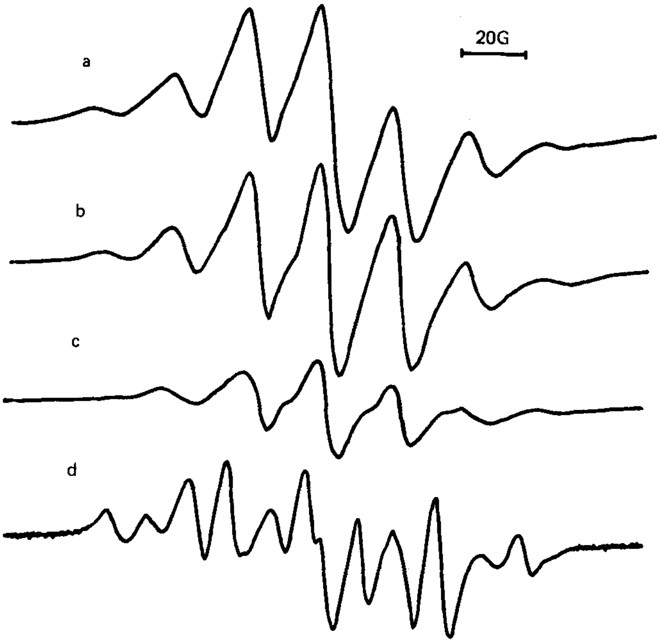


FIG. 1. ESR spectra of polycrystalline BrPhDMA irradiated at -196°C for 8 h (dose rate: 0.95 Mrd/h): a, measured at -196°C after irradiation; b, recorded at -155°C after warming to 0°C for 15 min. Spectra c and d were measured at 20 and 50°C, respectively, after heat treatment at the temperature of measurement for 5 min. Sensitivity ratio of spectrum d is 3.2 times as large as the others.

ated sample was allowed to stand at 0°C for a longer period, the spectral pattern changed gradually to the 12-line spectrum (Fig. 2). The intramolecular and intermolecular reactions (Scheme 4) occur at ~0°C. This is a very different result from that observed in other RDMA, and shows how the crystalline structure is important in this cyclization reaction in the monomeric unit.

ESR Studies of Irradiated Glassy BrPhDMA

During the ESR studies of irradiated polycrystalline BrPhDMA, it was found that BrPhDMA forms the glassy and supercooled liquid state when it is quenched rapidly to liquid nitrogen temperature from above its melting point. T_g was found to be -18°C by measuring the DSC. Its thermogram is shown in Fig. 3. Propyl- and benzyl-substituted RDMA cyclized to give a 5-membered ring in both crystalline and glassy states

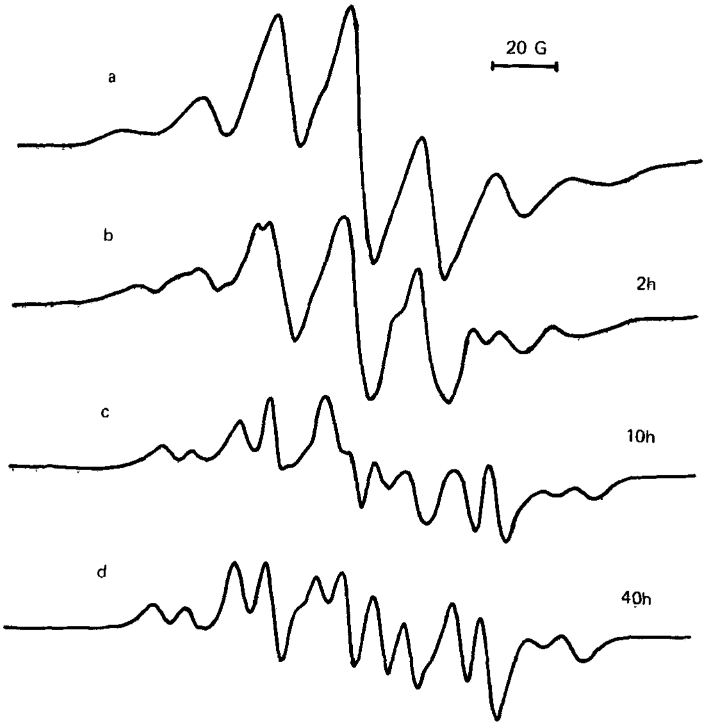
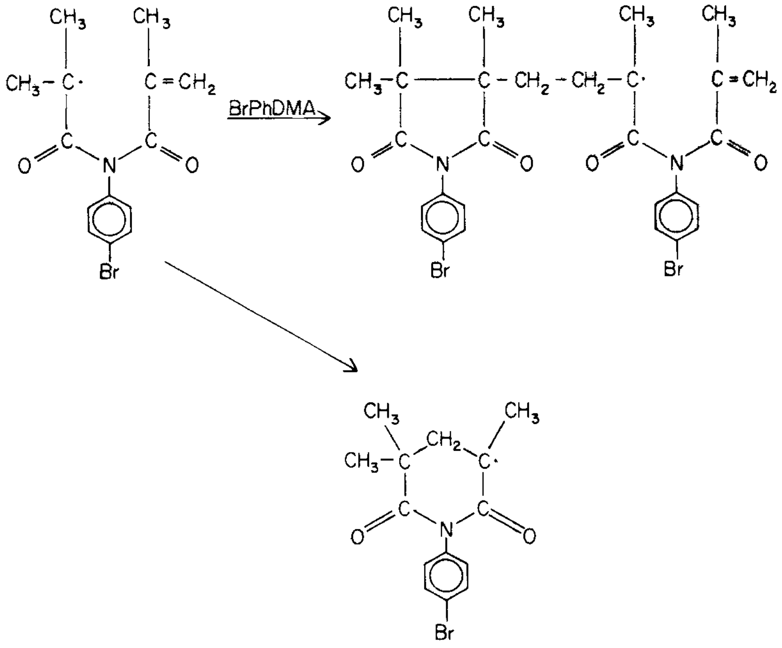


FIG. 2. ESR spectra of polycrystalline BrPhDMA irradiated at -196°C for 8 h (dose rate: 0.95 Mrd/h): a, measured at -196°C after irradiation, Spectra b, c, and d were recorded at -196°C after warming to 0°C for the period described on the right side of the spectra.

at -196°C. In the case of BrPhDMA, it was found that it does not cyclize in its crystalline state over the temperature range from -196° to ~0°C. Thus, it is interesting to know how BrPhDMA in the glassy state responds to γ-ray irradiation at -196°C.

ESR spectra of glassy BrPhDMA irradiated at -196°C are shown in Fig. 4. The triplet with a separation of 10 gauss (a in Fig. 4) can be attributed to the anion radical of the methacryl group. This triplet was observed in glassy propyl and benzyl derivatives and was identified as the anion radical based upon the ESR spectra of the deuterated propyl derivative [11]. With increasing temperature the triplet due to the anion radical gradually disappears, and a triplet with a separation of 20 gauss that is not clear at -196°C can be observed (b in Fig. 4). When the temperature is increased further, the central part sharpens strongly, leaving the side band almost unaltered (c in Fig. 4). If the temperature is lowered at this stage, the spectral pattern changes



SCHEME 4.

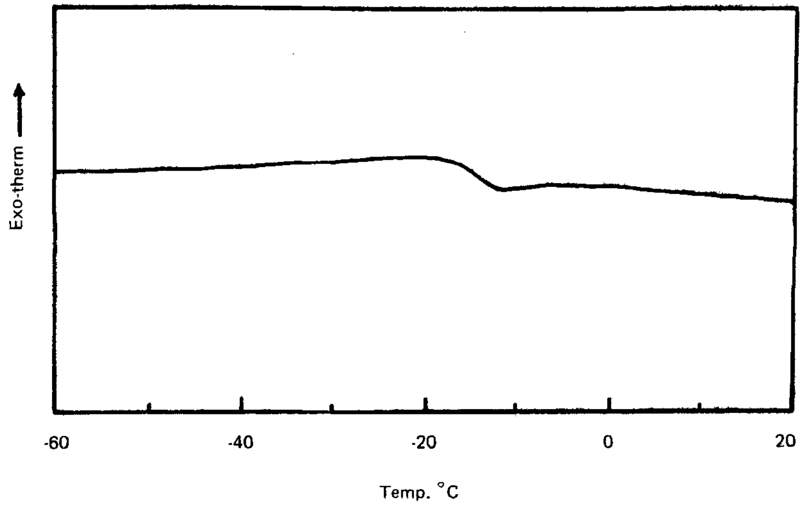


FIG. 3. DSC heating curve of glassy BrPhDMA, measured after a rapid quenching to -196°C from above its melting point. Heating rate = 10°C/min.

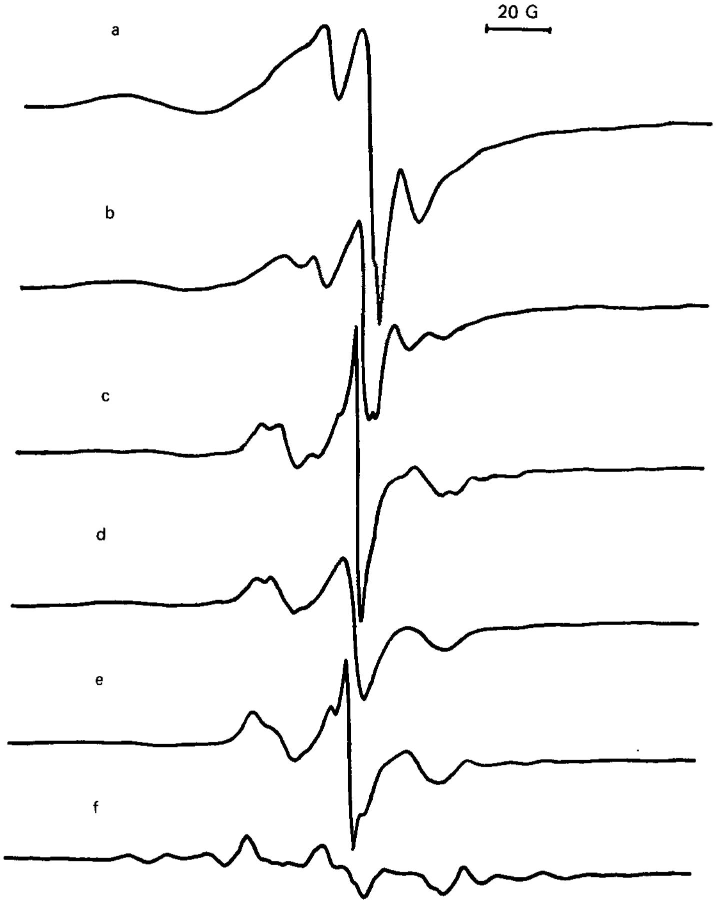


FIG. 4. ESR spectra of glassy BrPhDMA irradiated at -196°C for 2 h with a dose rate of 0.95 Mrd/h. Recorded at -196°C, a; -120°C, b; -100°C, c; -196°C, d; -60°C, e; and -20°C, f. Spectra other than a and d were measured after heating to the respective temperature for 5 min. Spectrum d was recorded after the measurement of spectrum c. Sensitivity ratio of a:d:the others = 1:2:4.

to that shown in d in Fig. 4. This is not the original pattern observed at -196°C immediately after irradiation, because some of the active species have disappeared. When the temperature was increased and decreased repeatedly, the spectral change between b and c could be reproduced precisely. This is what had been observed in the other RDMA. Therefore, this triplet can be attributed to the 5-membered cyclic radical, and the temperature dependence of the spectral pattern is ascribed to free rotation about the C–C bond of C–$CH_2\cdot$ groups at higher temperature and its restricted rotation at lower temperature. On further increase in temperature, this triplet disappeared and changed partly to a 12-line spectrum at the temperature near T_g (f in Fig. 4). The molecular structure in the glassy state is not known; if it is assumed that the molecules trapped in the glassy state take a conformation similar to that in the crystalline state, the result suggests that the molecule in the glassy state is rather more mobile than in the crystalline state.

Polymerization of DMMH in the Solid State

The time-conversion curve obtained in the solid-state polymerization of DMMH at ambient temperature is shown in Fig. 5. It is a typical sigmoid curve. The polymers formed at longer polymerization

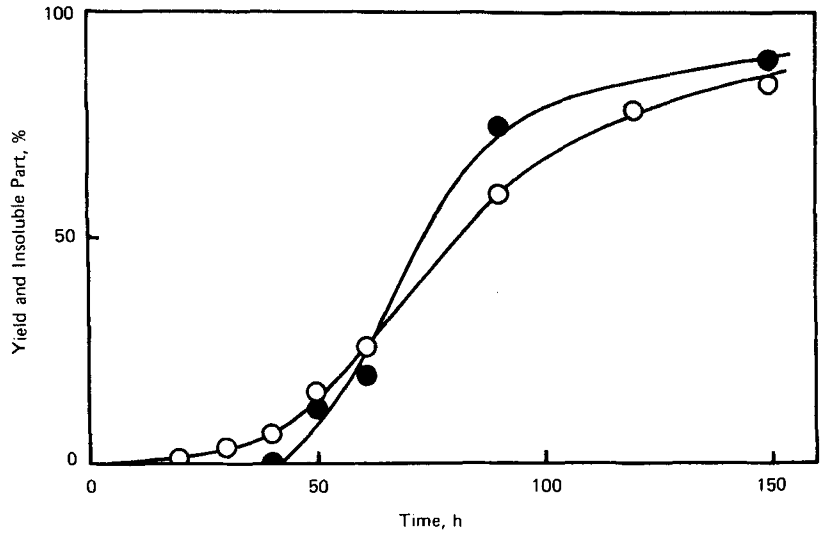


FIG. 5. Irradiation polymerization of DMMH at ambient temperature. Dose rate: 0.95 Mrd/h. (○) Polymer yield, (●) insoluble part in polymer obtained.

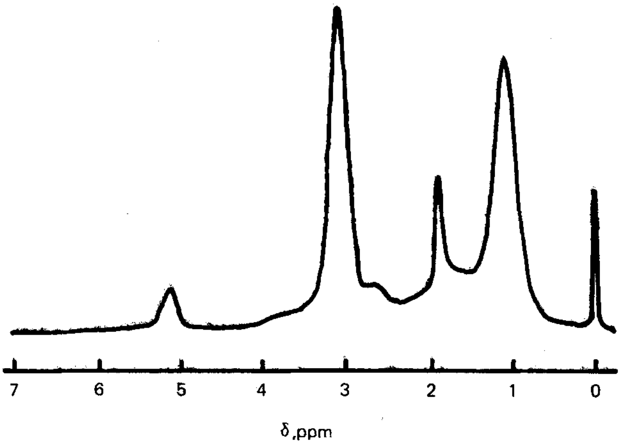


FIG. 6. ^{1}H-NMR spectrum of poly-DMMH obtained after 40 h irradiation with a dose rate of 0.95 Mrd/h at ambient temperature. Spectrum was recorded at 100°C in $CDCl_3$ using tetramethylsilane as an internal standard.

time than 40 h contain an insoluble part. Fractions of the insoluble part are also shown in Fig. 5. A ^{1}H-NMR spectrum of the polymer obtained at the initial stage of polymerization (polymerization time 40 h) is shown in Fig. 6. The degree of cyclization determined based upon absorption due to the methylene proton of the pendant methacryl group and other protons is 75%. It is less than 91%, which is the value obtained in solution polymerization ([M] = 1 g/2 mL) at 45°C [7]. Considering the differences in conditions, this value is believed to be reasonable. Some of the x-ray diffraction diagrams obtained from unirradiated and irradiated DMMH are shown in Fig. 7. They show that the characteristic peaks of the monomer disappear rapidly as the irradiation dose increases. Decreases of peak heights of irradiated samples at $2\theta = 11.3$ and 15.5°, as compared with that of unirradiated DMMH, were plotted against polymerization time (Fig. 8). This figure shows how the amorphous phase increases with polymerization time. When the increase in polymer yield is compared with the decrease in crystallinity, it is clear that the crystalline structure is destroyed much faster than the increase in polymer yield. These results suggest that the crystalline structure does not play an important role in the solid-state polymerization of DMMH.

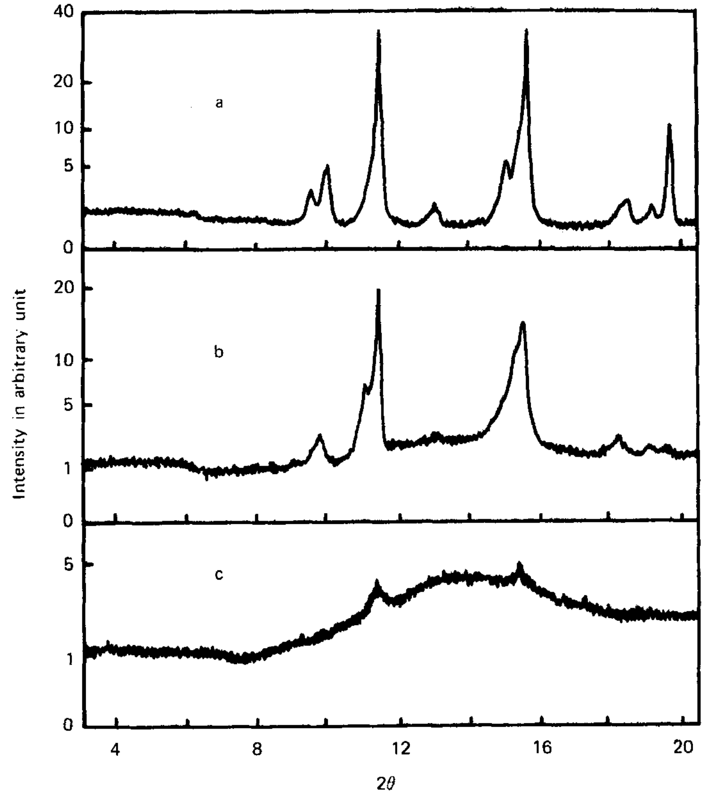


FIG. 7. X-ray diffraction diagrams observed during the course of the solid-state polymerization of DMMH: a, DMMH unirradiated; b, 31.0% polymer content; c, 77.8% polymer content. Polymer contents were determined gravimetrically after the x-ray diffraction measurements. Irradiated at ambient temperature with a dose rate of 0.95 Mrd/h.

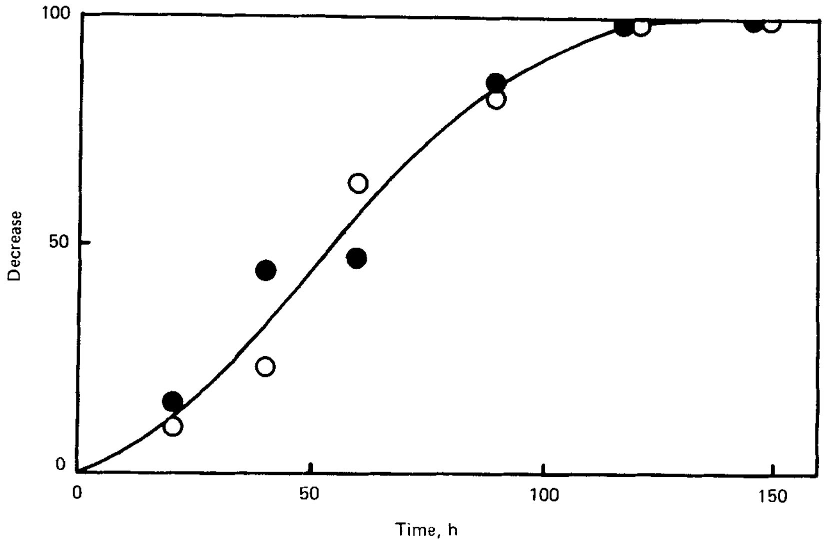


FIG. 8. Decrease of peak height in the x-ray diagrams of irradiated DMMH at $2\theta = 11.3°$ (●) and $2\theta = 15.5°$ (○).

$$\text{Decrease} = \frac{(\text{peak height of DMMH} - \text{peak height of irradiated DMMH}) \times 100}{\text{peak height of DMMH}}$$

ESR Studies of Polycrystalline DMMH

ESR spectra of polycrystalline DMMH irradiated at -196°C are shown in Fig. 9. At liquid nitrogen temperature the sample contains some unknown species. On increasing the temperature this unknown species disappears, and at -100°C a 7-line spectrum (b in Fig. 9) was observed. This 7-line spectrum can be ascribed to the initiation radical. By comparing these spectra it can reasonably be assumed that the 7-line spectrum is present at -196°C. This means that the initiation radical has been formed at -196°C. On further increase in temperature the 7-line spectrum decreases in intensity and changes to a broad 5-line spectrum (c in Fig. 9). Only a small difference between spectra b and c in Fig. 9 can be seen, but if the sensitivity of the instrument is increased, it is clear that the 7-line spectrum has already disappeared and changed to the 5-line spectrum. The pattern in c (Fig. 9) corresponds to the spectrum derived from a propagating radical of methyl methacrylate [14]. Thus, this radical can be attributed to the noncyclic propagating radical (III in Scheme 3). The 7-line spectrum could still be observed after the heat treatment at 0°C for 180 h, but could not be detected after the heat treatment at room

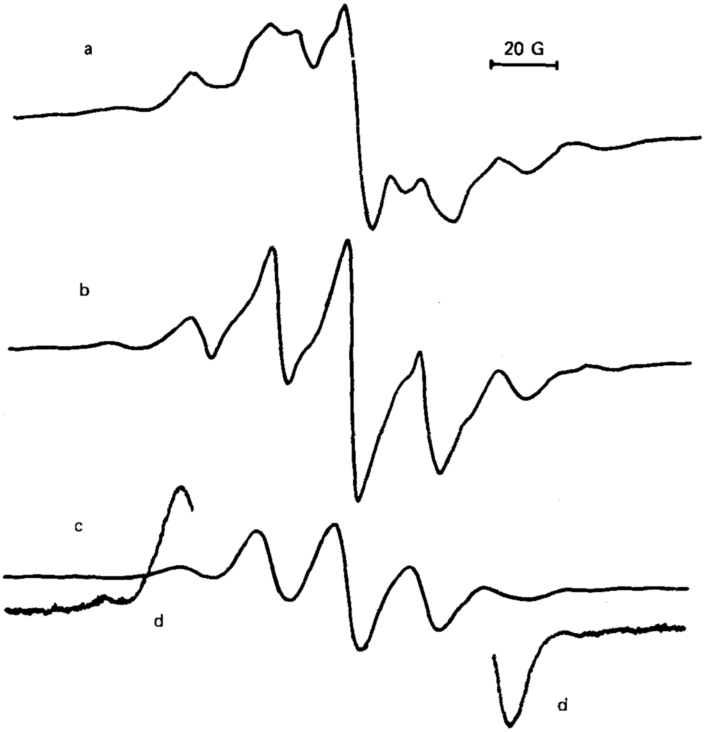
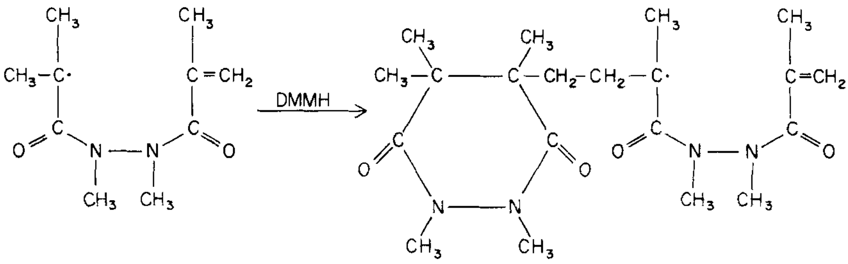


FIG. 9. ESR spectra of polycrystalline DMMH irradiated at -196°C to 3.8 Mrd. Recorded at -196°C, a; -100°C, b; and ambient temperature, c, d. Spectrum b was measured after heat treatment at -100°C for 20 min. Spectra c and d were recorded after standing for 100 h at ambient temperature. Sensitivity ratio of a:b:c:d = 1:1.3:1.3:9.



SCHEME 5.

temperature. These results show that the intramolecular cyclization and intermolecular propagation (Scheme 5) begin to occur over the temperature range from 0°C to room temperature.

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