

PHOTOPOL YMERIZA TION OF MALEIMIDE ANDITS N-SUBSTITUTED DERIVATIVES

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PHOTOPOLYMERIZATION OF MALEIMIDE AND ITS N-SUBSTITUTED DERIVATIVES

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1. Introduction

To the best knowledge of the present authors, the photopolymerization of maleimide and its N-substituted derivatives has not so far been reported.

We found that the photopolymerization of these monomers proceeds without the sensitizer under various conditions. This communication is concerned with the results of polymerization in both the solid state and the solution. It is emphasized that some kinds of the polymers obtained have crystalline structures.

2. Experimental

Procedure.- A typical solid state polymerization procedure is described below.

A fine crystalline monomer (1.000g) was placed in a glass ampule which was then outgassed under vacuum, purged, and sealed under pure nitrogen. With stirring at 40°C, the ampule was exposed to a 100 W high pressure mercury lamp (Toshiba SHL 100UV-2) which was placed at the distance of 17.5 cm. After the polymerization, the reaction mixtures were kept overnight in about 100 ml of acetone, methanol, or ethylacetate in order to remove residual monomers. The polymers were separated from the mixtures by filtration and dried in vacuo.

The solution polymerization was carried out in methanol at 40°C. The precipitated polymer on the wall of the ampule was dissolved in cyclohexanone, and the solution was poured into a large amount of ether or isopropanol. The reduced viscosities of the polymers were measured in N,N-dimethylformamide(DMF) solution(0.5g polymer in 100 ml DMF) at 30°C with an Ostwald viscometer. X-ray diffractions were obtained with a powder camera in a Shimadzu x-ray diffraction apparatus(Model GX-1). The infrared spectra were determined with a Hitachi infrared spectrometer(Model EPI-2) in KBr pellets.

3. Results and Discussion

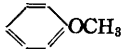
Table 1 shows that all of the monomers were photopolymerized in both the solid state and the solution.

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Table 1
Experimental Results of Photo-Polymerization of Maleimide and Its N-substituted Derivatives^a

No.	R in $\begin{array}{c} \text{CHCO} \\ \parallel \\ \text{CHCO} \end{array} \text{N-R}$	Irradiation temperature, °C.	Irradiation time, hr.	Polymer yield, wt.-%	Reduced viscosity	Softening point, °C.	Polymerization phase	Polymer structure ^b
1	H (1)	40	20	0.34	—	—	Solid state	Crystalline
2	CH ₂ OH (2)	40	20	20.0	0.08	338-350	Solid state	Amorphous
3	CH ₂ CH ₂ OH (3)	40	16	5.5	0.10	258-264	Solid state	Crystalline
4	CH ₂ CH ₂ OH (3)	40	11	25.0	0.21	284-304	Solution	Amorphous
5	CH ₂ CH ₂ OCOCH ₃ (3)	40	20	26.7	0.04	220-224	Solid state	Crystalline
6	CH ₂ CH ₂ OCOCH ₃ (3)	40	2	72.0	0.11	143-162	Solution	Amorphous
7	CH ₂ CH ₂ OCOCH ₂ CH ₃ (4)	30	20	26.9	0.22	175-198	Solid state	Crystalline
8	CH ₂ CH ₂ OCOCH ₂ CH ₃ (4)	40	20	70.8	Insoluble	320-350 with decomposition	Solid state	Amorphous
9	CH ₂ CH ₂ OCOCH ₂ CH ₃ (4)	40	6	40.5	0.11	132-151	Solution	Amorphous
10	 (5)	40	16	1.0	—	310-330	Solid state	Amorphous

a Condition : Solution polymerization was carried out in the concentration of 1.000g. monomer in 6 ml. methanol.

b From the x-ray diffraction diagram and the infrared absorption spectrum.

From this table it can be seen that, in general, the solution polymerization gave higher yields of polymers. In the solid state polymerization at 40°C, N-2-propionyloxyethyl maleimide polymerized much more rapidly than the other monomers and the polymer obtained was found to be insoluble in DMF or other solvents, unlike the polymer prepared at 30°C. It is supposed that, in this case, a part of the monomer (mp 50°C) melted with accumulation of the heat of polymerization, therefore a partial liquid state polymerization occurred and some crosslinked polymers were formed.

All of the polymers obtained from the solution polymerization were soluble in DMF and cyclohexanone. On the other hand, the polymers obtained from the solid state polymerization were soluble only in DMF.

In further experiments, some post effects on polymer yield in the solid state polymerization were observed.

Figure 1 shows the x-ray diffraction photographs of the monomers and of the polymers obtained from the solid state polymerization. The diagrams of some of the polymers display clear crystalline peaks in contrast to those of the polymers obtained from the solution polymerization as shown in Figure 2.

The infrared absorption spectra of the polymers obtained by solution polymerization and by radical initiator (*a,a'*-azobisisobutyronitrile) were very similar to each other, as shown in Figure 3. On the other hand, in the chart of the polymer obtained from the solid state polymerization, a few new absorption bands were observed as shown in Figure 4. These bands will be assigned to the characteristic absorption corresponding

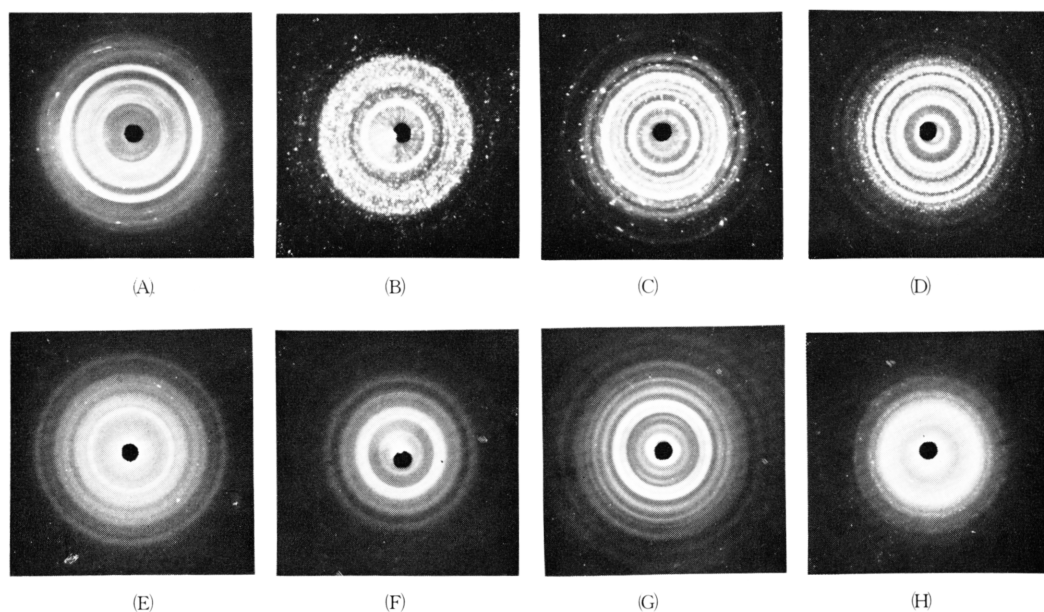


Figure. 1. X-ray diffraction diagrams of the monomers and of the polymers obtained from the solid state polymerization; (A) maleimide; (B) N-2-hydroxyethyl maleimide; (C) N-2-acetoxyethyl maleimide; (D) N-2-propionyloxyethyl maleimide; (E) poly-maleimide; (F) poly-N-2-hydroxyethyl maleimide; (G) poly-N-2-acetoxyethyl maleimide; (H) poly-N-2-propionyloxyethyl maleimide (30°C)

to the crystalline structure of the polymer.

Further detailed studies on the mechanism of this polymerization and on other N-substituted derivatives will be reported in subsequent papers.

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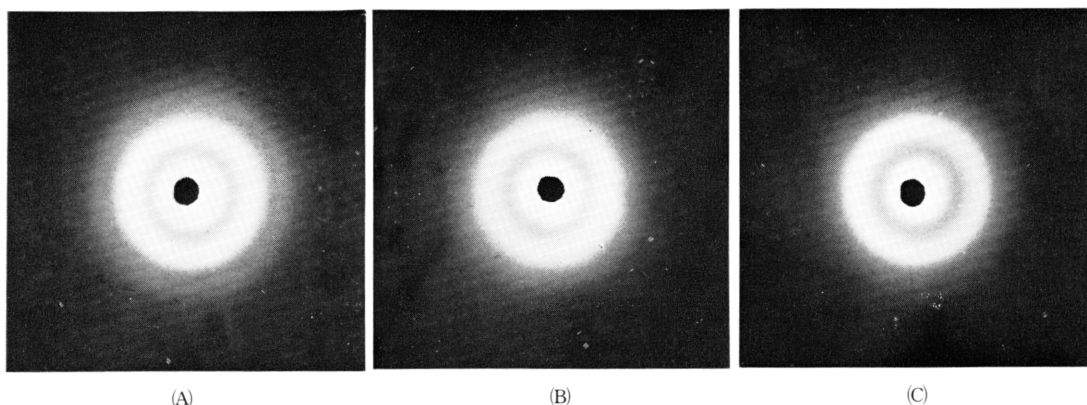


Figure. 2. X-ray diffraction diagrams of the polymers from the solution polymerization at 40°C.; (A) poly-N-2-hydroxyethyl maleimide; (B) poly-N-2-acetoxyethyl maleimide; (C) poly-N-2-propionyloxyethyl maleimide.

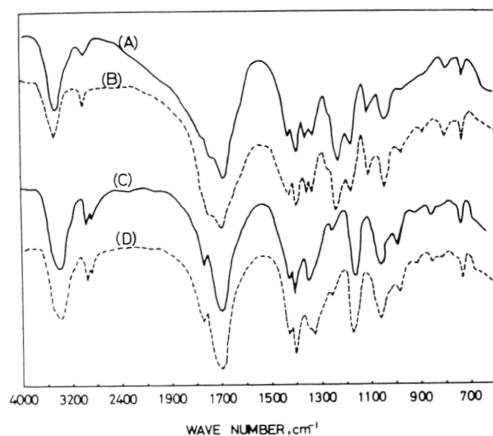


Figure. 3. Infrared spectra of the polymers from the solution polymerization and of the radical-initiated polymers; (A) radical-initiated poly-N-2-acetoxyethyl maleimide; (B) poly-N-2-acetoxyethyl maleimide from the solution polymerization; (C) radical-initiated poly-N-2-hydroxyethyl maleimide; (D) poly-N-2-hydroxyethyl maleimide from the solution polymerization.

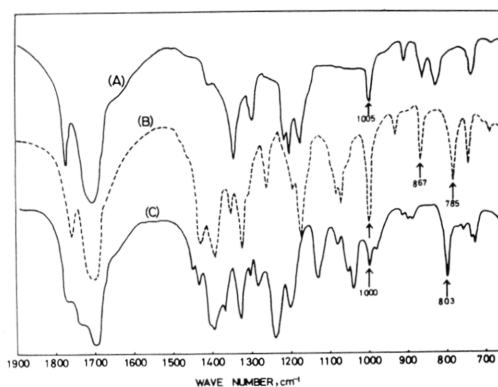


Figure. 4. Infrared spectra of the polymers obtained from the solid state polymerization; (A) poly-maleimide; (B) poly-N-2-hydroxyethyl maleimide; (C) poly-N-2-acetoxyethyl maleimide; ↑ shows new characteristic absorption bands.

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