Solid-State Polymerization of Acrylamide and Methacrylamide by Chlorine under Ultraviolet Irradiation

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SUMMARY

Crystalline monomers of acrylamide (AAm) and methacrylamide (MAAm) could be polymerized in the presence of chlorine gas under ultraviolet (uv) irradiation, the shape of the solid crystals remaining unchanged during the polymerization. The yield of polymer increased with increasing amounts of chlorine. It was deduced that chlorine atoms formed by the decomposition of chlorine molecules on the monomer crystals with uv irradiation initiate the polymerization, which proceeds from the surface to the inner part of the crystals. One apparent characteristic of the catalytic solid-state polymerization is that the molecular weight of the polymer increases as polymerization temperature is raised.

After the unreacted AAm was sublimated from a partially polymerized crystal, the polymer obtained was found by polarized microscopic investigation to be well oriented and to show sharp Debye-Scherrer rings in X-ray diagram due to crystalline polymer. Polymethacrylamide obtained in the solid-state polymerization by the Cl_2-uv system was also crystalline in the untreated state. On the basis of these results, the mechanism of the catalytic solid-state polymerization is discussed.

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INTRODUCTION

The catalytic solid-state polymerization of cyclic compounds such as trioxane has been extensively studied [1], but that of vinyl compound, with the exception of N-vinylcarbazole [2-7] and acenaphthylene [8], has not been investigated.

In the case of radiation-induced solid-state polymerization, the polymerization is initiated homogeneously at all parts of the monomer crystal, whereas it takes place only on the surface of monomer crystal in the case of catalytic solid-state polymerization. Indeed, the crystallinity and the molecular weight distribution of the polymers obtained were found to be different [6, 7] in radiation- and catalyst-induced solid-state polymerizations of N-vinylcarbazole.

In the present work, the solid-state polymerizations of acrylamide (AAm) and methacrylamide (MAAm) by radical catalyst were studied; the radiation-induced solid-state polymerizations of these compounds have already been extensively investigated. Moreover, the different orientation and crystallinity behavior of the polymers of AAm and MAAm as opposed to those of N-vinylcarbazole or acenaphthylene should be expected because of the existence of hydrogen bonding in AAm and MAAm monomer crystals.

It was found that crystalline AAm or MAAm can be polymerized by chlorine under ultraviolet (uv) irradiation, starting from the crystal surface and propagating into the inside part of the crystal without destroying the crystal shape. The polymerization behavior and the structure of the polymer formed were studied, and the mechanism of the catalytic solid-state polymerizations of AAm and MAAm systems is discussed.

EXPERIMENTAL

Materials

AAm was recrystallized twice from solution in a mixed solvent of benzene and chloroform (5:1) (mp, 84°C; lit., 84°C [9]). MAAm was recrystallized twice from solution in a mixed solvent of benzene and ethanol (4:1) (mp, 109°C; lit., 110°C [9]). Chlorine (commercial product) was used without further purification.

Procedures

Polymerization. The solid-state polymerization of AAm by chlorine and uv irradiation was carried out as follows: A small amount of liquid chlorine was added at -50 ~ -60°C to the crystalline AAm in a glass ampoule (1 cm in diam.) under nitrogen gas, and then the temperature of the reaction vessel was gradually raised under uv irradiation to room temperature over a 1-hr period. A high-pressure mercury lamp (100 W) was used without filtration for uv irradiation. The distance between the center of the glass ampoule and the mercury lamp was 5 cm. During this procedure, the initiation of polymerization took place and the surface of the monomer crystal was covered with a thin film of polymer (conversion about 2%). This process is called "prepolymerization" in this paper. The prepolymerization favors the suppression of any side reaction between chlorine and AAm taking place at high temperature. Following this procedure, the reaction vessel was maintained at a given temperature under uv irradiation. The polymerization was stopped by adding the excess of methanol-containing hydroquinone at a fixed time.

MAAm was polymerized in a similar manner except that the period of prepolymerization was longer than in the case of AAm because of the lower degree of polymerizability of MAAm.

The polymer formed was usually washed several times with methanol and dried under reduced pressure at room temperature.

Viscosity Measurement. The η_{sp}/c value of the polymer produced was measured in water at 30°C. As the viscosity of the aqueous solution of polyacrylamide (PAAm) changes with time [10], it was measured 24 hr after the preparation of polymer solution.

Orientation and Crystallinity of the Polymer. A thin, plate-like crystal was used for observation by a polarized microscope. The microscopic measurement took place under constant low temperature (20°C) and low moisture (40%) because of the hygroscopic character of the polymer. For the measurement of the crystallinity of the polymer by X-ray diffraction, the partially polymerized crystal was used without further purification.

Table 1. Solid-State Polymerization of AAm by
Cl$_2$ under uv-irradiation in N$_2$ atmosphere[a]

[Cl$_2$], mmole/liter	Polymerization time, hr	Conversion, %
0	20	Trace
14[b]	20	0
14	4	7.1
14	10	7.8
14	16	7.0
14	20	7.3
14[c]	20	7.1

[a]weight of monomer, 1 g/33-ml vessel; poly-
merization temperature, 32.4°C.
[b]No uv irradiation.
[c]In air.

RESULTS

Solid-State Polymerization of AAm by Chlorine under uv Irradiation

The results of the solid-state polymerization of AAm by chlorine under
uv irradiation are summarized in Table 1. The solid-state polymerization
of AAm under uv irradiation hardly occurred without chlorine, and AAm
did not produce polymer in the presence of chlorine without uv irradiation.
These facts show that both chlorine and uv irradiation are necessary to
initiate the solid-state polymerization of AAm.

Figure 1 shows the time-conversion curves in the solid-state polymeriza-
tion of AAm by chlorine under uv irradiation. AAm was polymerized
rapidly even at 32.4°C. The shape of monomer crystal remained unchanged
during polymerization, and the transparent monomer crystal became opaque
as the polymerization proceeded. Although the initial rate of polymeriza-
tion was high, it decreased markedly with increasing conversion. The
polymerization rate was enhanced by chlorine added during the polymeri-
zation, as shown in Fig. 2. The saturation of the time-conversion curve
might therefore be due to the consumption of chlorine.

Figure 3 shows the relationships between the concentration of chlorine,
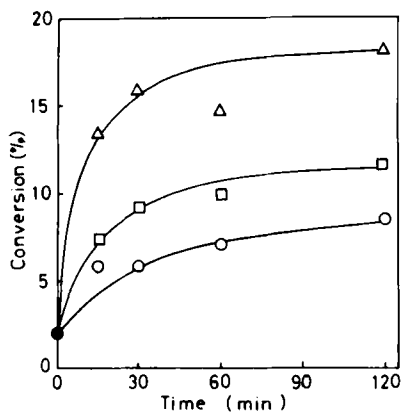the initial rate of polymerization, and the saturated yield of polymer in

Fig. 1. Effect of temperature on the rate of solid-state polymerization of AAm in Cl_2-uv system. ●: Conversion in prepolymerization. $[M]_0$: 1 g/33-ml vessel, $[Cl_2]$: 21 mmoles/liter. ○: 32.4°C, □: 40°C, △: 45°C.
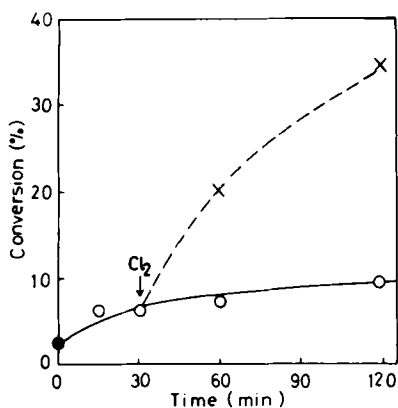

Fig. 2. Effect of chlorine addition during polymerization on the rate of solid-state polymerization of AAm. ●: Conversion in prepolymerization. $[M]_0$: 1 g/33-ml vessel, 32.4°C. Initial concentration of Cl_2: 21 mmoles/ liter. —○—: No addition of Cl_2, - - X - -: addition of 21 mmoles of Cl_2/ liter at 30 min.
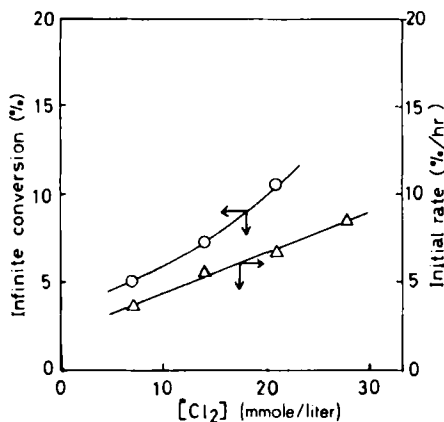
Fig. 3. Effect of chlorine concentration on the infinite conversion and the initial rate of solid-state polymerization of AAm at 32.4°C. (Polymerization conditions as in Fig. 1.)
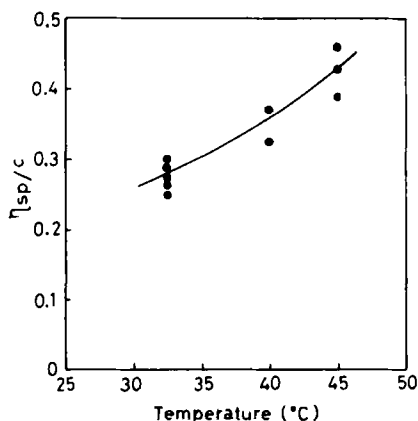
Fig. 4. Relationship between temperature and η_{sp}/c of the polymer obtained in solid-state polymerization of AAm. (Polymerization conditions as in Fig. 1).

the solid-state polymerization. Both the initial rates and the saturated yields increased with increasing amounts of added chlorine.

Figure 4 shows the effect of polymerization temperature on η_{sp}/c of the polymer obtained. The η_{sp}/c of the polymer was almost independent of
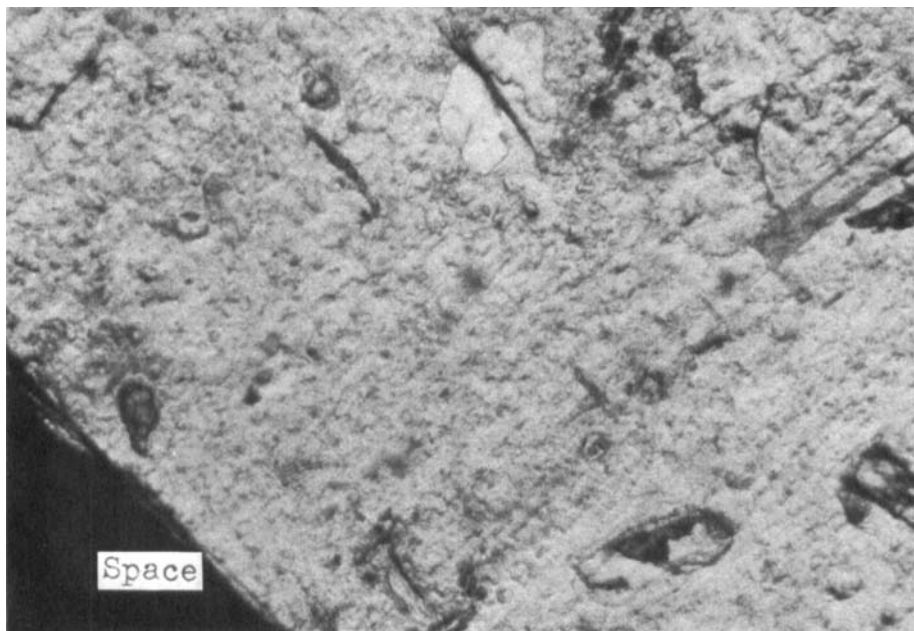
Fig. 5. Photomicrograph of the surface of partially polymerized AAm crystal at 11.6% conversion. (Temperature: 40°C, other polymerization conditions as in Fig. 1.)

the polymer yield. The molecular weight of the polymer formed increased with increasing polymerization temperature, as in the case of radiation-induced solid-state polymerization [11].

The reaction product in the present method was confirmed to be PAAm by infrared spectroscopy in which the infrared spectrum of the polymer was exactly the same as that of the PAAm obtained in the solution polymerization by radical catalysts. No evidence for the occurrence of the hydride transfer polymerization of AAm was found in the solid-state polymerization by chlorine and uv irradiation. Also, side reactions such as the displacement reaction between chlorine and hydrogen in an amide of monomer molecules or the addition reaction of chlorine to carbon-carbon double bond of AAm were not predominant, because the content of chlorine in the polymer obtained was less than 3 ~ 5 wt%.
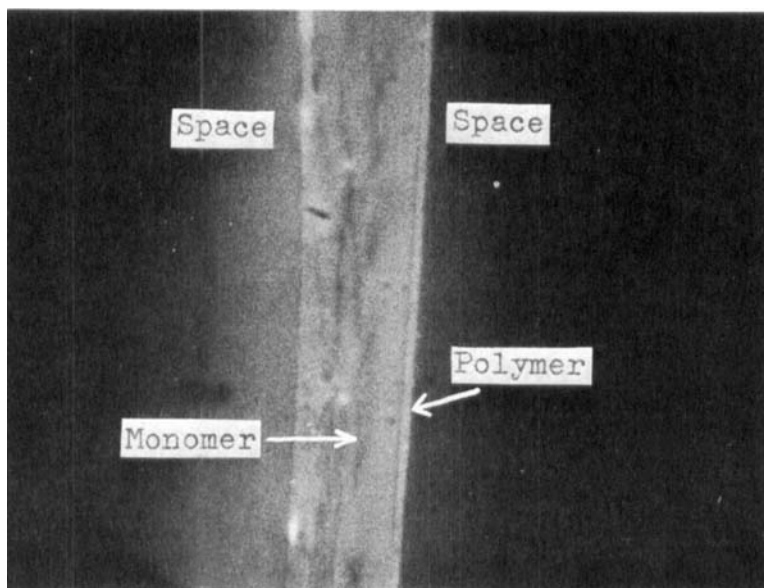
Fig. 6. Photomicrograph of the cross section of partially polymerized AAm crystal. (Polymerization conditions as in Fig. 5.)

Orientation and Crystallinity of PAAm

Polarized photomicrographs of the surface and a cross section of a partially polymerized monomer crystal are shown in Figs. 5 and 6, respectively. As shown in Fig. 6, the polymer can be distinguished from the unreacted monomer; the polymer layer which covered the unreacted monomer in Fig. 6 was about 1/100 mm thick.

When the unreacted monomer was excluded from the partially polymerized crystal of AAm by sublimation, a tube-like polymer was obtained. As shown in Fig. 7, birefringence was observed by polymerized microscope. This fact shows that PAAm obtained in the solid-state polymerization of AAm by chlorine under uv irradiation is well oriented. However, the tube-like polymer obtained by extracting the unreacted monomer with acetone from the partially polymerized crystal of AAm did not show the birefringence.

The results in Figs. 6 and 7 make it possible to draw the conclusion that the solid-state polymerization of AAm by chlorine under uv irradiation
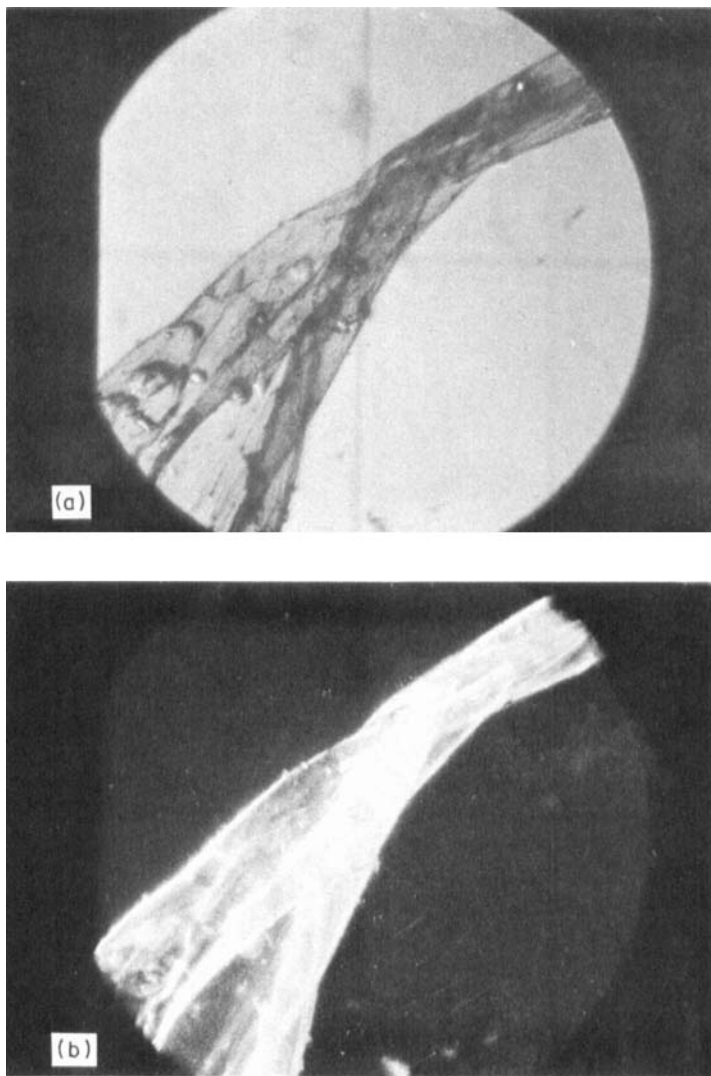
Fig. 7. Photomicrographs of PAAm film obtained by sublimation of residual monomer at 7.4% conversion. (Temperature: 32.4°C, other polymerization conditions as in Fig. 1.) (a) Bright field, (b) Polarized light.
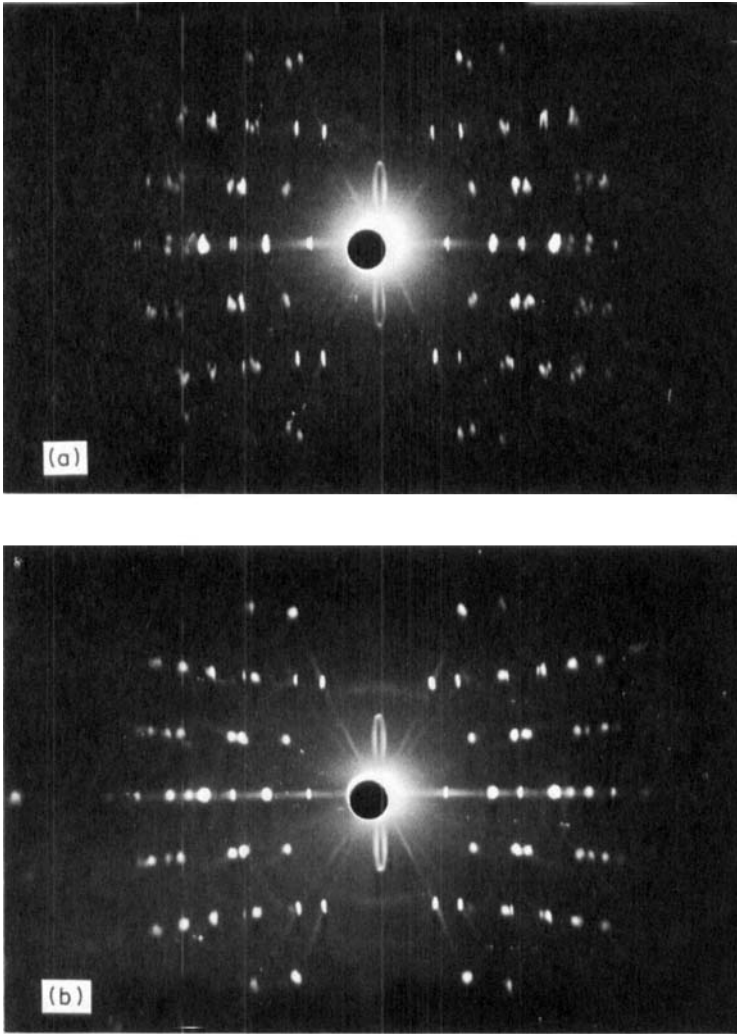
Fig. 8. X-ray diffraction patterns of AAm and PAAm. (a) AAm. (b) Par-
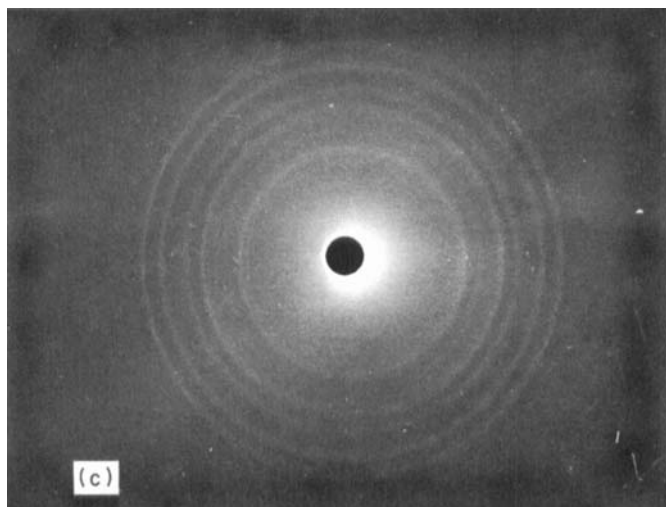tially polymerized AAm crystal. Conversion: 7.4%.

Fig. 8. (Continued) (c) Conversion: ca. 100%. (Polymerization conditions in (a) and (b) as in Fig. 7.)

proceeds from the crystalline surface to the inside of the crystal. In order to confirm this conclusion, PAAm obtained in the solid-state polymerization by chlorine and uv irradiation was investigated by X-ray analysis. Figure 8 shows the X-ray diffraction patterns of AAm crystal and PAAm obtained at various conversions in the solid-state polymerization. As can be seen in Fig. 8(b), Debye-Scherrer rings due to the crystalline polymer were observed with the partially polymerized crystal of AAm, in addition to the spots due to the unreacted monomer at low (about 7%) conversion. In these rings, the arc, which was weak, was observed in equatorial and meridional direction. As the polymerization proceeded further, the spots due to the monomer disappeared and Debye-Scherrer rings due only to the polymer were observed (Fig. 8(c)). The interface distance of the rings due to the crystalline polymer did not correlate with that of spots due to the unreacted monomer that is shown in Fig. 8.

On the other hand, the polymer obtained by extracting the unreacted monomer with acetone from the partially polymerized crystal of AAm was also confirmed by X-ray analysis to be amorphous.
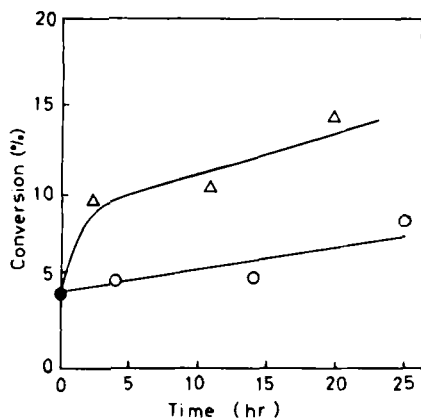
Fig. 9. Effect of temperature on the rate of solid-state polymerization of MAAm in Cl_2-uv system. ●: Conversion in prepolymerization. ○: 35°C, △: 50°C. (Polymerization conditions as in Fig. 1.)
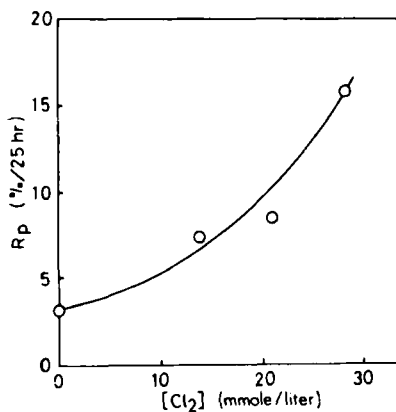

Fig. 10. Effect of chlorine concentration on the initial rate of solid-state polymerization of MAAm at 35°C. (Polymerization conditions as in Fig. 1.)

The Solid-State Polymerization of MAAm by Chlorine under uv Irradiation and the Structure of the Polymer

It was found that the solid-state polymerization of MAAm by chlorine could also take place under uv irradiation as in the case of AAm.

Figure 9 shows the dependence of the polymerization rate on the polymerization temperature in the solid-state polymerization of MAAm. The long prepolymerization was required because MAAm has a lower reactivity than AAm. About 4% of the monomer was converted to polymer during the prepolymerization. The polymerization rate of MAAm was much smaller than that of AAm. In the polymerization of MAAm at 50°C, a large amount of polymer was obtained within 2 hr, but the polymerization rate decreased markedly after 2 hr.

Figure 10 shows the effect of concentration of chlorine on conversion. Chlorine accelerated the polymerization of MAAm as well as AAm.

The relationship between the polymerization temperature and η_{sp}/c of the polymer obtained is shown in Fig. 11. The molecular weight of the polymer increased with increasing polymerization temperature.

The structure of the product was confirmed by infrared spectroscopy to be the same as that of polymethacrylamide (PMAAm) obtained by an ordinary radical catalyst in solution.

The thin polymer film was also obtained by extracting with methanol the unreacted monomer from the partially polymerized crystal of MAAm. The polymer film thus obtained showed a weak birefringence, while the film of PAAm similarly obtained showed no birefringence. Therefore, it might be deduced that PMAAm molecules are better oriented than PAAm during the polymerization.

Figure 12 shows the X-ray diffraction pattern of the partially polymerized crystal of MAAm. Debye-Scherrer rings ascribed to the formation of the crystalline polymer were observed in addition to many spots due to the unreacted monomer.

DISCUSSION

Since Mesrobian et al [11] obtained PAAm by high-energy radiation from crystalline AAm in 1954, the radiation-induced solid-state polymerization of AAm has been investigated extensively [9, 12-18]. No papers, however, have been published on the catalytic solid-state polymerization of AAm. On the other hand, a few papers (e.g., [9, 19]) on the
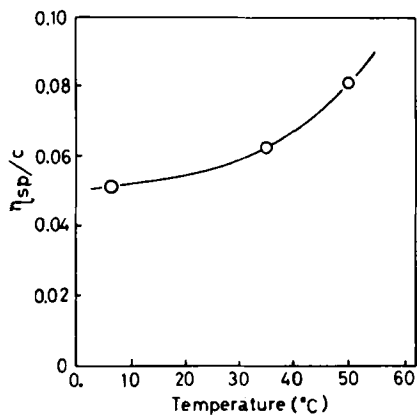
Fig. 11. Relationship between temperature and η_{sp}/c of the polymer obtained in solid-state polymerization of MAAm. (Polymerization conditions as in Fig. 1.)
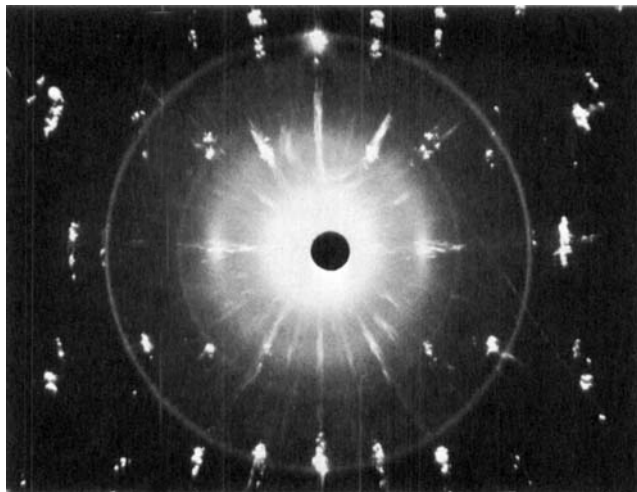

Fig. 12. X-ray diffraction pattern of partially polymerized MAAm crystal at 50°C. Conversion: 14.2%. (Polymerization conditions as in Fig. 1.)

radiation-induced solid-state polymerization of MAAm have appeared. The reactivity of MAAm was found to be smaller than that of AAm.

In the present work, it was observed that crystalline AAm or MAAm could be polymerized in the presence of gaseous chlorine under uv irradiation, the shape of monomer crystals remaining unchanged during the polymerization. It was also found that the chemical structure of PAAm or PMAAm thus obtained was the same as that of PAAm or PMAAm obtained by an ordinary radical catalyst.

The solid-state polymerization of AAm could not be initiated by uv irradiation without the addition of chlorine. The addition of chlorine caused the polymerization of AAm under uv irradiation and the yield of polymer was changed by changing the amount of chlorine added.

On the other hand, it is well known that chlorine molecules decompose easily to atoms under uv irradiation. Therefore, the solid-state polymerization of AAm (or MAAm) by chlorine under uv irradiation seems to be initiated by chlorine atom produced on the surface of the monomer crystal. The content of chlorine included in the polymer was less than 3-5%. This small value suggests that the main reaction is the polymerization.

The molecular weight of polymer increased with increasing polymerization temperature, as shown in Figs. 4 and 11. This might be explained in terms of the enhanced movement of monomer molecules in the crystal at high temperature. The molecular weight of PAAm obtained in the solid-state polymerization was smaller than that of the polymer obtained by the radiation-induced solid-state reaction, as in the case of N-vinylcarbazole. The difficulty in producing the high-molecular-weight polymer in the catalytic solid-state polymerization might be due to the limited mobility of monomer molecules in the solid, since the catalytic solid-state polymerization proceeds from the surface into the inner part of the crystal.

PAAm obtained in the radiation-induced solid-state polymerization was amorphous, and no report has been published so far on the formation of crystalline polymer of AAm or MAAm. Nevertheless, PAAm and PMAAm obtained in the solid-state polymerization by chlorine under uv irradiation were well oriented and showed crystalline Debye-Scherrer rings in X-ray diagrams during polymerization.

Nitta et al. [20] discussed the mechanism of the radiation-induced solid-state polymerization on the basis of the analysis of the crystal structures of AAm or MAAm. As the molecules of AAm and MAAm are well oriented in crystal by hydrogen-bonding between

$$\diagdown \atop \diagup NH$$

and

$$O=C \Big\langle$$

groups, they concluded that the polymerization propagates in specified layers in monomer crystals. A similar mechanism may be applied to the system mentioned here. The monomers in the first layer on the surface will be polymerized into a well-oriented polymer layer by hydrogen-bonding, with the second layer of monomers acting as a bed surface. Then the second layer of monomers will be polymerized, their form protected by the hydrogen-bonding both with the first layer of the polymer formed and with the third layer of monomers. Thus, the polymerization proceeds into the inside of the crystal, by producing the well-oriented, crystalline polymer layers. Therefore, the hydrogen-bonding plays an important role in maintaining the regularity of the polymer formed. The mechanism mentioned above might be supported by the fact that no birefringence was observed in the polymer after swelling by solvents such as methanol or acetone. It is not clear, however, whether the well-oriented PAAm and PMAAm obtained in the present systems have stereoregularities or not. This will be the subject of a future study.

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