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RADIATION-INDUCED SOLID-STATE POLYMERIZATION OF ALLYLTHIOUREA AND CRYSTAL STRUCTURE EFFECTS

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ABSTRACT

Allylthiourea crystals grown from water and from ethanol have been found to belong to the space group $P2_{1/c}$ and $P2_{1/m}$ or related, respectively. The corresponding unit cell parameters are a = 13.45 Å, b = 17.33 Å, c = 14.38 Å, β = 96.6°, and d = 1.18 g/cm^3 for water-grown crystals, and a = 14.65 Å, b = 17.18 Å, c = 13.15 Å, β = 95.5°, and 1.17 g/cm^3 for ethanol-grown crystals.

Solid-state in-source polymerization of allylthiourea crystallized from water and ethanol both follows an S-shaped curve with limiting conversion of 88% (at 18 and 0°C in vacuum and 18°C at atmospheric pressure) and 92% (at 18°C) and 98% (at 33 and 45°C), respectively. It was shown by optical microscope that the polymerization does not proceed at the monomer-polymer interphase when the irradiation is stopped. The mechanism of polymerization was studied by ESR as well as by IR and UV spectroscopy, and structure effects by x-ray diffraction. The activation energy was calculated to be 54.1 kJ/mol for in-source polymerization. Postpolymerization and polymerization under UV-radiation gave less than 3% conversion.

INTRODUCTION

It has been reported [1] that crystallization of allylthiourea from water gives a monoclinic crystal with a melting point of 78°C and that rapid cooling from organic solvents or from melts gives another crystal form with a melting point of 71°C, i.e., allylthiourea is a compound that shows polymorphism. Dragonette and Karle [2] reported the crystal structure of allylthiourea as monoclinic with space group $P2_{1/c}$ and cell parameters of $a = 8.39$ Å, $b = 8.58$ Å, $c = 9.77$ Å, and $\beta = 119°45'$. However, they gave no information about the conditions of single crystal growth.

Polymerization of allylthiourea was first observed in 1844 [1]. It was observed to form a dark, viscous polymer with the evolution of great amounts of heat when reacted with an excess of lead oxide or lead hydroxide. The copolymerization with SO_2 under ^{60}Co gamma irradiation at -40°C in ethanol was reported in a patent [3]. Due to chain transfer to monomer in the polymerization of allyl compounds, the molecular weight is expected to be low.

The effect of monomer crystal structure upon the course of polymerization is the most important feature of solid-state polymerization [4, 5].

In this work the radiation-induced polymerization of allylthiourea is investigated, and the monomer crystalline structure effect upon solid-state polymerization is examined.

EXPERIMENTAL

Single crystals of allylthiourea were grown from water (ATU-1) and from ethanol (ATU-2) solutions by slow evaporation of the solvent at room temperature and atmospheric pressure. The melting point of ATU-1 was 72°C and of ATU-2 70°C. The structures of these crystals were studied by using Weissenberg single crystals and Guinier powder cameras.

The densities of the crystals were measured by flotation using isobutanol and carbon tetrachloride as the solution mixture. Densities were 1.18 g/cm^3 for ATU-1 and 1.17 g/cm^3 for ATU-2.

About 1-3 g samples of monomer were placed in Pyrex tubes and connected to the vacuum line. They were evacuated for 6-7 h at a reduced pressure of 10^{-4}-10^{-5} torr. After evacuation, the tubes were sealed off and irradiated in a Gamma Cell 220, manufactured by Atomic Energy of Canada Ltd., that has a dose rate of 0.110 Mrd/h for the desired periods. Irradiation in air was done with samples that were not evacuated. Irradiation at 0°C was done in an ice-water bath, and a thermostated system was used for other temperatures. The tubes were opened by breaking after irradiation times, and samples were first dissolved in a small amount of water and then precipitated in ethanol. The percent conversion values were found gravimetrically.

The allylthiourea crystallized from water (ATU-1) was powdered and irradiated at -196°C in the presence of oxygen for a period long enough to give 5 Mrd gamma ray total dose. The ESR spectra of each sample were taken immediately after it was taken out of the γ-ray source and warmed to room temperature. The sample was kept at room temperature and ESR spectra was taken from time to time.

The allylthiourea crystallized from ethanol (ATU-2) was powdered and irradiated under vacuum at -196°C with up to 3.0 Mrd irradiation. The ESR spectrum was taken at the end of the irradiation period. Then the behavior of the free radicals was followed for 2 weeks while the sample was kept at 50°C during the intervals.

The IR spectra of the monomer and the polymer were taken in the form of KBr pellets. The UV spectra of ATU-1 and the compound remaining unpolymerized at the end of the polymerization were taken from their water solutions.

Intrinsic viscosities of the polymer samples in *N,N*,-dimethylformamide solution at 25°C were determined in an Ubbelohde-type glass viscometer.

Single crystals of ATU were irradiated by x-rays, and the polymerization was followed by taking periodic photographs magnified 200 times under a polarizing microscope for 15 months time interval.

The powdered samples of ATU-2 were irradiated under vacuum at -196°C by γ-rays for 5 and 19.5 h. Postpolymerization of these samples was carried out at 63°C constant temperature. The powdered samples of ATU-2 were irradiated by UV light under vacuum at room temperature. The UV lamp used was of 55 mV/cm^2 power and of 365 nm maximum wavelength.

RESULTS AND DISCUSSION

X-Ray Diffraction

Reflections obtained from the indexing of Weissenberg photographs of ATU-1 showed that the space group was $P2_{1/c}$ and the cell parameters were a = 13.45 Å, b = 17.33 Å, c = 14.38 Å, and β = 96.6°.

Weissenberg photographs of ATU-2 revealed the space groups $P2_{1/m}$ or $P2_1$ and the cell parameters a = 13.65 Å, b = 17.18 Å, c = 13.15 Å, and β = 95.5°.

Although Dragonette and Karle [2] gave no information about the conditions of crystallization of allylthiourea in their article, it can still be concluded that allylthiourea crystallizes in a monoclinic crystal structure with different unit cell parameters and space groups, depending on the conditions of crystallization.

In-Source Polymerization

Solid-state in-source polymerization of ATU-1 was followed at 0 and at 18°C under vacuum, and at 18°C in the presence of atmospheric oxygen. Plots of conversion against time of irradiation are given in Figs. 1 and 2.

For both types of crystals, polymerization at all temperatures follow S-shaped kinetic curves, and the polymerization rate increases with increasing temperature. A limiting conversion of 88% was obtained for the in-source polymerization of ATU-1 at the polymerization temperatures studied and for polymerization in air. The limiting conversion for ATU-2 samples increased to 92% at 18°C and to 98% at 33 and 45°C. The difference in the limiting conversion can be attributed to the difference in crystal structure of the mono-

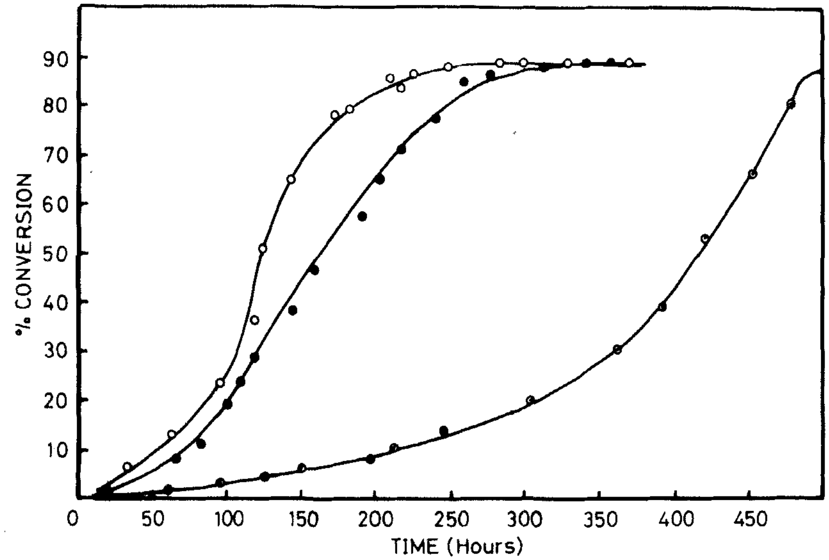

FIG. 1. Polymerization of allylthiourea crystallized from water by gamma radiation (⊛, 0°C; ●, 18°C in vacuum; ○, 18°C open to air).

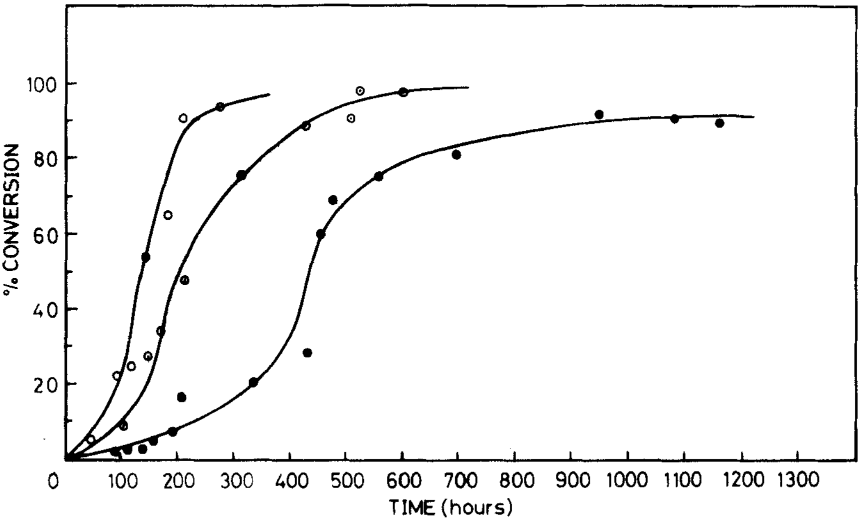

FIG. 2. Polymerization of allylthiourea crystallized from ethanol by gamma radiation in vacuum (●, 18°C; ◉, 33°C; ○, 45°C).

mer. Since the mechanism of polymerization is greatly influenced by the monomer crystal geometry in the solid state, the change in crystal structure most probably orients the molecules in a more favorable arrangement for polymerization, leading to a higher maximum conversion in ATU-2 samples. In 33 and 45°C polymerization of ATU-2, the mobility of molecules increases and distortion of the crystals places the —C═C— double bonds at more favorable distances for addition to growing chains.

Figure 1 shows that the rate of polymerization is higher in the presence of oxygen. The accelerating effect of oxygen is clearer at conversions above about 40%. This suggests that the crystal structure becomes distorted with the formation of polymer to allow easier diffusion of oxygen.

ESR Spectroscopy

The ESR spectrum of ATU-1 that had been irradiated with 5 Mrd total dose at liquid nitrogen temperature is given in Fig. 3. The spectrum was taken after the completion of the irradiation period and after various times at room temperature and open to the atmosphere. The first spectrum was also taken at room temperature. The peak intensities increase first, then start to decrease.

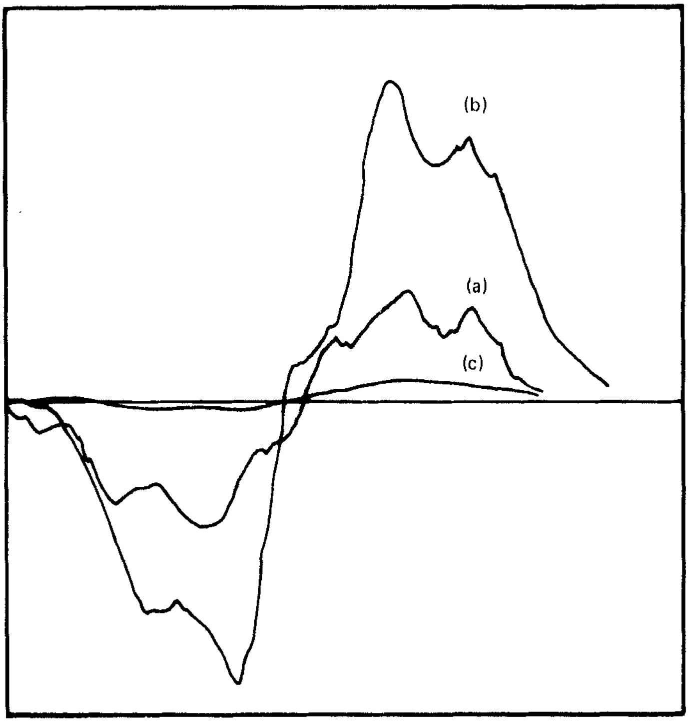

FIG. 3. ESR spectrum of allylthiourea crystallized from water. Spectrum taken (a) immediately at −196°C and at room temperature; (b) at room temperature and 2 weeks after irradiation; and (c) at room temperature and 2 months after irradiation.

This may be due to the easy diffusion of oxygen in the crystal matrix when the crystal was warmed to room temperature and the crystal structure distortion by radiation. After the concentration of radicals reaches a maximum, radical termination becomes more effective and, therefore, peak intensity decreases.

The ESR spectrum of powdered ATU-2 irradiated under various conditions shows similarity to the spectrum of ATU-1 (Fig. 4). The radicals are quite stable, even at 50°C, for a reasonable long period. However, in this case no initial increase of peak intensities was observed. This also suggests that the peak intensity increase in the spectrum of ATU-1 is due to the presence of

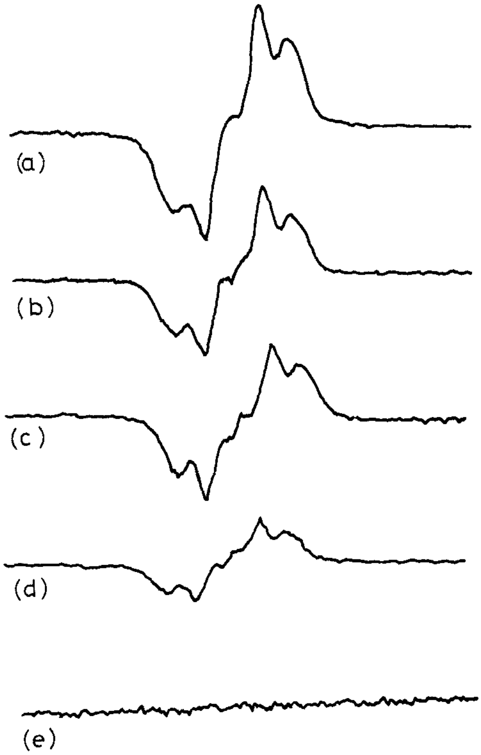

FIG. 4. ESR spectrum of allylthiourea crystallized from ethanol taken at room temperature: (a) after irradiation; (b) after being kept at 50°C for 1 d; (c) at 50°C for 5 d; (d) at 50°C for 15 d; and (e) after 245 h of irradiation at room temperature with UV light.

oxygen. The ESR spectrum of ATU-2 irradiated by UV showed no peaks and, therefore, no radical formation.

The appearance of the ESR spectrum and the decrease in the intensity of the peaks with time suggests the probability of a free-radical mechanism. This is also supported by the high activation energy, found to be 54.1 kJ/mol.

IR Spectroscopy

The IR spectrum of allylthiourea monomer (the same for both ATU-1 and ATU-2) and the polymer are shown in Fig. 5.

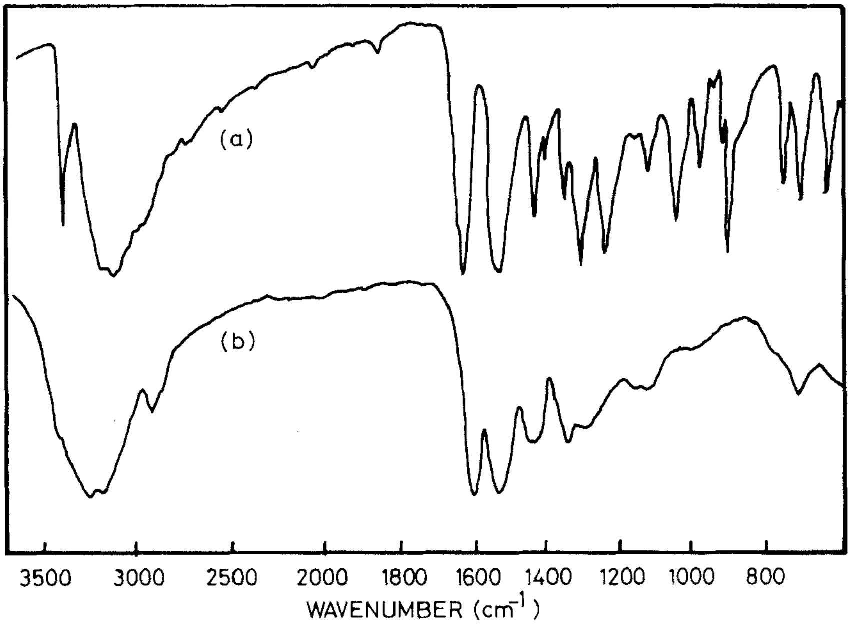

FIG. 5. IR spectrum of allylthiourea: (a) monomer; (b) polymer.

The $-C{=}S$ bond present in the monomer molecule does not give a peak but causes $-NH$ and $-NH_2$ groups to show peaks at 1 665-1 540 cm^{-1}. The two peaks due to primary and secondary amines remain unchanged in the spectrum of polymer. Peaks due to the $-C{=}CH_2$ (1 000-700 cm^{-1}) group that are present in the spectrum of the monomer cannot be observed in that of the polymer.

There is no evidence in the IR spectra of the monomer and the polymer to show the formation of S–H or C–S bonds during polymerization. This shows that the $-C{=}S$ bond stays unchanged during polymerization, excluding a cyclization reaction by opening of the $-C{=}S$ bond. The vinyl groups $-C{=}CH_2$ seen at 1 000-700 cm^{-1} in the monomer spectrum do not appear in the spectrum of the polymer. The intensity of the $-CH_2-$ group at 732 cm^{-1} is greater after polymerization.

When the polymer is heated, it softens between 160-190°C. Around 190°C it turns yellow with NH_3 gas evolution and resolidifies. The IR spectrum of this newly formed solid is the same as that of the polymer, except that it contains an additional peak at 2 050 cm^{-1}. It is concluded that this new peak shows the presence of $-C(NH_2)-S-S-C(NH_2)-$ groups formed by inter- and intramolecular reaction. This is also supported by quantitative analysis of NH_3 gas that formed during the phase transition.

UV Spectroscopy

The UV spectra of allylthiourea monomer has two peaks, at 200 and 237 nm. The UV spectrum of the unpolymerized, 12% sample is identical with that of the monomer. This suggests that the unpolymerized part is most probably unchanged monomer. This was also indicated by the IR spectrum and the melting point.

Changes in Crystal Structure upon Polymerization

Indexing of diffraction peaks in the x-ray powder-diffraction patterns, shown in Fig. 6, were done by using cell parameters obtained from single-crystal data. When Figs. 6(a) and 6(b) are compared, it is seen that, although the monomer peaks are partially covered by the broad amorphous polymer peak, the monomer molecules still retain their crystalline structure at 46% conversion. The changes in relative intensities of monomer peaks during polymerization are most probably due to distortion of the crystal morphology [5]. The fact that all diffraction peaks are effected similarly shows that there is no selective propagation of polymer chain in a certain crystallographic direction.

The x-ray pattern of the polymer and completely polymerized (88%) monomer are exactly the same (Fig. 6c). The single broad x-ray diffraction peak suggests that the polymer is amorphous and has limited structural regularity.

Similar results were also observed from single-crystal diffraction photographs of monomer and partially polymerized monomers. However, in order to understand it better, more work will have to be done with single crystals of monomer using a single-crystal diffractometer instead of the photographic method. This will provide quantitative data about the intensity changes [5].

Molecular Weight Determination

An interesting feature of the plots in Fig. 7 is that the intrinsic viscosity shows a sharp decrease between 20 and 30% conversion, at the beginning of autocatalysis, the minimum being reached at about 30%. This suggests

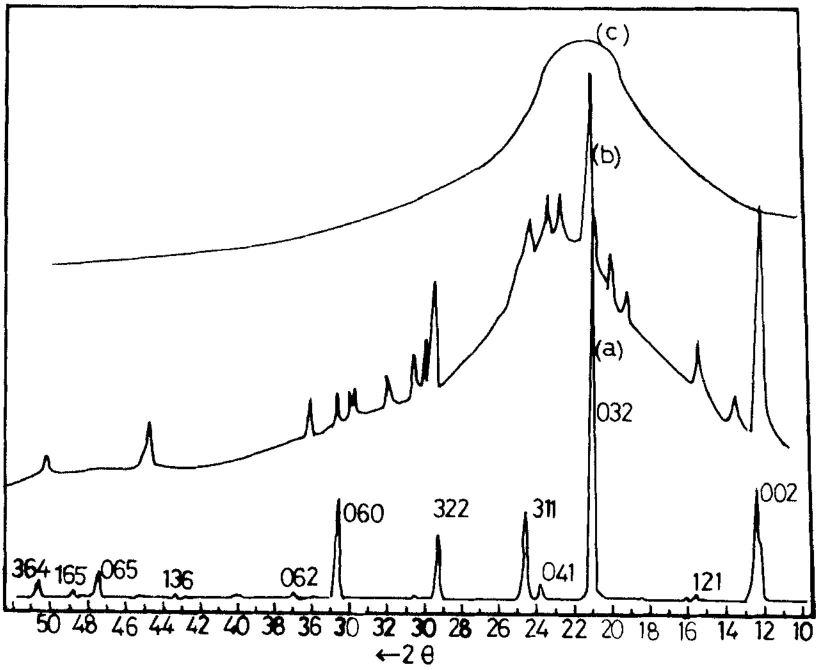

FIG. 6. X-ray powder diffraction of allylthiourea crystallized from water (CuK$_\alpha$, 15 mA, 35 kV): (a) monomer; (b) partially polymerized monomer (46%); (c) completely polymerized (88%).

the probability that, at the beginning of autocatalysis, the number of newly initiated small polymer chains increases so much that it causes a sharp decrease in the average molecular weight. On formation of long polymer chains during autocatalysis, the average molecular weight increases again and reaches a second maximum at the end of autocatalysis. On further irradiation, degradation or branching again decreases the intrinsic viscosity.

The intrinsic viscosities of polymers obtained at 18°C are much larger than those of the polymers obtained at 33 and 45°C. This might be related to the high polymerization rate at higher temperatures giving shorter molecules. Also, chain termination and branching is more probable at higher temperatures due to the higher mobility of the active centers.

It was attempted to determine the molecular weight of the polymer samples by cryscopic and osmometric methods. The cryscopic method was too insensi-

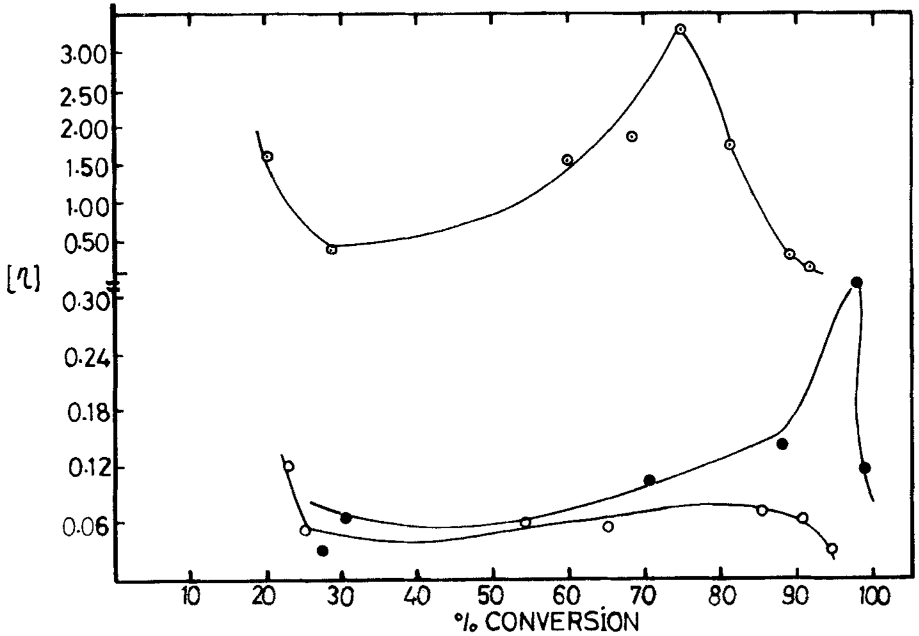

FIG. 7. Intrinsic viscosity change with conversion for polyallylthiourea (ATU-2) (⊙, 18°C; ●, 33°C; ○, 45°C).

tive for our samples. Osmometric measurements, by comparison with standard samples, indicated that the molecular weights of our polymer samples were around one million. The results were not very reproducible because of instrument difficulties. In contrast to the generally reported low molecular weights of allyl-type polymers, the molecular weight of polyallylthiourea obtained in the solid state seems to be very high.

Polarizing Microscope

Comparison of photographs of x-ray-irradiated allylthiourea crystals taken at a 15-month interval showed that polymerization occurred only in those parts on the crystal that had been under direct irradiation. The polymer is amorphous and isotropic; it always looks dark between crossed polarizers, where the monomer is anisotropic and looks bright except at the extinction positions. The results proved that polymerization does not proceed by a two-phase mechanism like the monomer-polymer interphase polymerization observed, for instance, in the radiation-induced polymerization of acrylamide crystals [5]. Polymerization does not proceed in the unirradiated part of the single crystal, as is observed for other monomers such as *N*,-vinylcarbazole [6].

The fact that polymerization does not proceed with time in the monomer single crystal can be attributed to the low mobility and the relatively high resonance or transfer reactions of the active species, most probably free radicals produced under irradiation. This can also explain the low conversions obtained for the postpolymerization (see below).

Postpolymerization of Allylthiourea

It has been shown that postpolymerization of allylthiourea is possible but gives only very low conversion (less than 3%) due to the low mobility of radicals and the stability of the active species produced by irradiation. The polymer obtained was found to be amorphous by x-ray diffraction.

Polymerization under UV Light

A 2.7% conversion to polymer was obtained for about 860 h of irradiation under UV light. It can be concluded that UV light is not energetic enough to activate great numbers of allylthiourea molecules.

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