A New Type of Solid-State Crystalline Photopolymerization

ZHANG XIAOLIN and MAO YOUAN, *Department of Material and Applied Chemistry, Changsha Institute of Technology, Changsha, Hunan, China*

Synopsis

A new type of solid-state crystalline photopolymerization is researched in which, different from the topochemical polymerization, vinyl monomers are filmed under the induction of other macromolecular compound, crystallized, and polymerized after photoirradiation. Therefore, it may be also known as induction-filming polymerization. The crystalline polyacrylamide film with large spherulite structures was obtained from the crystalline acrylamide by this means. Microscopy, differential scanning colorimetry, and infrared measurements were carried out. Mechanism is proposed for the induction-filming polymerization involved.

INTRODUCTION

Some organic monomers in the crystalline state can be polymerized into crystalline polymers under the irradiation of ultraviolet light.[1-3] This method of polymerization is regarded as the solid-state crystalline photopolymerization. The monomers usually used are diacetylenes and dienes with aromatic rings or heterocyclic rings.[4] Two triple bonds, or double bonds in the adjacent monomer molecules react with each other, and the crystalline polymers are formed in which crystal structure is nearly in agreement with that of the monomer. The center of gravity of the monomer molecules becomes that of the units in macromolecules. This method is, therefore, also referred to as topochemical polymerization.

In this paper, a new type of solid-state crystalline photopolymerization is researched in which, different from the topochemical polymerization, vinyl monomers are filmed under the induction of other macromolecular compound, crystallized, and polymerized after irradiation. Thus it may be also known as the induction-filming polymerization.

So far, there is no report on the preparation of crystalline polyacrylamide through solid-state crystalline photopolymerization.[5] It is here reported that polyacrylamide film made of spherulites with diameters several centimeters has been prepared from crystalline acrylamide by the new type of solid-state crystalline photopolymerization, i.e., the induction-filming polymerization. With the help of microscopy, IR spectra, and thermal analysis, the possible mechanism of the induction-filming polymerization is discussed.

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Acrylamide is one of vinyl monomers. Because of the extensive applicability of acrylamide monomer, the utilization and exploitation of the products of solid-state crystalline photopolymerization is full of promise.

EXPERIMENTAL

Materials

Commercial acrylamide, gelatin, and photosensitizer all were used in chemical grade reagents. Acrylamide is a white crystal with the melting point of 83–84°C.

Procedure

The mixed aqueous solution of acrylamide, gelatin, and photosensitizer is coated on a glass surface, and then crystallized at room temperature. The monomer spherulites, the diameters of which are up to several centimeters, are obtained. The transparent coating changes into turbid one with growth of the monomer spherulites. Under a high-volt mercury-arc lamp irradiating, monomer spherulites are converted into polymer spherulites, and the coating film is still turbid.

Measurements

IR spectra of acrylamide monomer spherulites and polyacrylamide spherulites obtained by the induction-filming polymerization have been measured using the infrared spectrophotometer of Shimadzu IR-500. DSC curves have been measured using Thermoflex, Rigaku. The microstructure of acrylamide monomer spherulite and polyacrylamide spherulite has been observed using a general optical microscope, across-polarizing microscope and Hitachi H-800 electron microscope.

RESULTS AND DISCUSSION

The Induction-Filming Polymerization

The polyacrylamide spherulite obtained by the induction-filming polymerization is shown in Figure 1. The spherulite of acrylamide monomer obtained by induction filming is similar to that in Figure 1.

The IR spectra of acrylamide and polyacrylamide obtained by the induction-filming polymerization are shown in Figure 2. After irradiating, peaks at 3100, 3040, and 990 cm^{-1}, which are characteristics of $CH_2{=}CH{-}$ have disappeared, and peaks at 2930, 2850, and 1455 cm^{-1}, which are characteristics of methylene have appeared. It is indicated, therefore, that acrylamide monomers have been polymerized into polyacrylamide.

DSC curves of acrylamide monomer and its spherulite obtained by the induction filming are shown in Figure 3. DSC curve of the induction-filming polymerization product is shown in Figure 4. According to Figures 3 and 4, the melting point of acrylamide monomer is 83°, acrylamide monomer spherulite is 65°C, and the product is 258°C, which is much higher than 160°C which is the glass-transition temperature of amorphous polyacrylamide. It is indicated

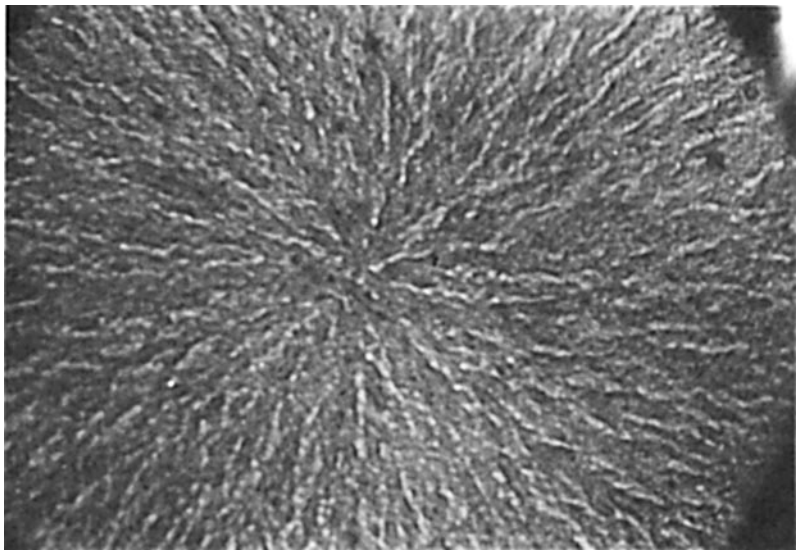


Fig. 1. A photograph of PAM spherulite.

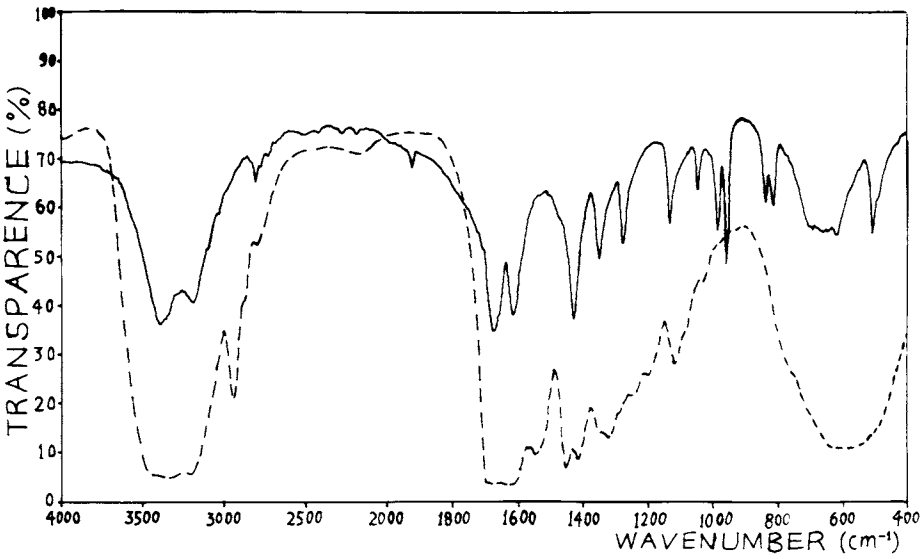


Fig. 2. IR spectra of AM (—) and of PAM (---).

that the crystal acrylamide has been changed into crystalline polyacrylamide through the induction-filming polymerization. In Figure 4, the glass-transition temperature cannot be identified, and this means that the crystallinity of the polyacrylamide obtained by this means is very high, which is in agreement with the general solid-state crystalline photopolymerization. In addition, the DSC curve of gelatin, from which it is shown that gelatin is an amorphous substance, has been also measured.

The microstructure of acrylamide monomer spherulite is shown in Figure 5. The radiative band of the monomer spherulite consists of many small pieces of

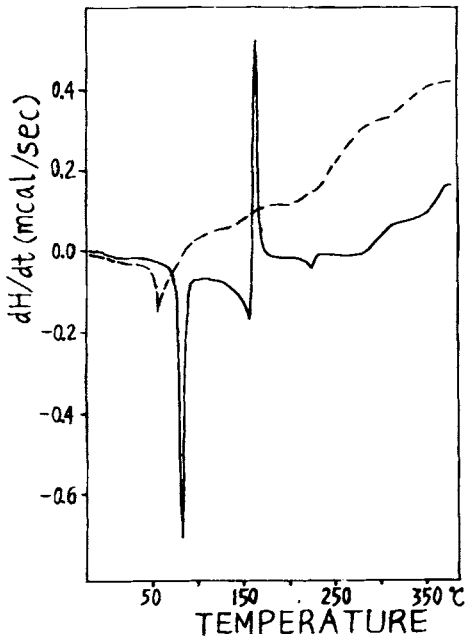


Fig. 3. DSC curves of AM monomer and of film-forming AM spherulite.

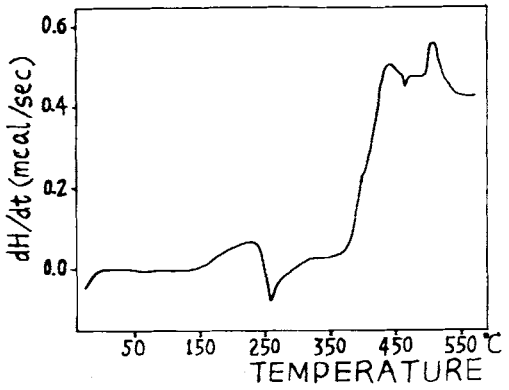


Fig. 4. DSC curve for film-forming PAM spherulite.

Fig. 5. A microphotograph for a part of film forming AM spherulite (100×).

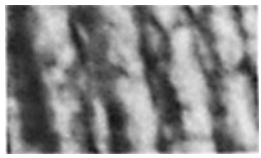


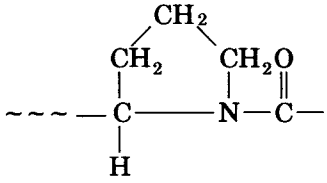
Fig. 6. A cross-polarizing microscope photograph for a part of film-forming PAM spherulite (100×).

regular brick-shaped crystal. These small crystalline pieces lose their sharp edges and corners in the photopolymerization procedure, and the radiative band of polyacrylamide spherulite appears as the chain form (see Fig. 1). A part of polyacrylamide spherulite observed by the cross-polarizing microscope is shown in Figure 6. These results show the crystalline polyacrylamide has been obtained by the induction-filming polymerization.

The Mechanism of the Induction-Filming Polymerization

Acrylamide is a polar molecule and can be dissolved in water to increase the surface tension of water. The drop of its concentrated solution does not wet on the glass surface and, thus, cannot form a liquid film.

The gelatin in which intramolecular and intermolecular hydrogen bondings can form is a natural polar macromolecular compound. The intramolecular hydrogen bondings make the macromolecule in the helical conformation. However, there are many planar rings of proamino acids (I) in gelatin molecule, and in these rings, there are no longer the hydrogen atoms connecting with nitrogen atoms; thus, the hydrogen bonding of N—HO(N) cannot form, and the peptide chain in which there is a ring of proamino acid is more easily mobile:



(I)

As a result, the wettability and filmability of aqueous gelatin solution are good at glass surface, and the gelatin molecules possess the stronger interaction with the polar glass surface. In addition, the gelatin molecule would also form the hydrogen bonding with acrylamide or water molecule. Gelatin can be used, therefore, as the induction-filming agent of an aqueous acrylamide solution. It is possible that the aquoacrylamide molecules separate out from the liquid film when a mixed transparent aqueous solution of acrylamide, gelatin, and photosensitizer is coated on glass surface (see Figs. 7–9), and the acrylamide aquocrystal will form on the gelatin lamella with the evaporation of the extra water molecules (see Fig. 4).

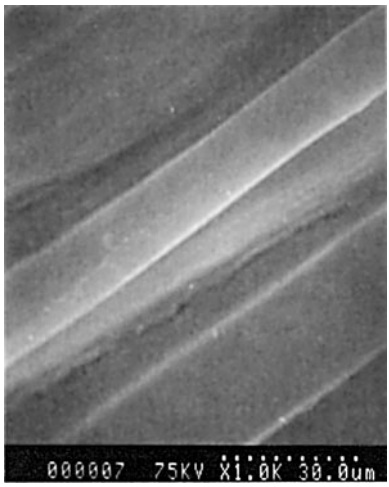


Fig. 7. A SEM graph of the free surface of the film-forming PAM spherulite.

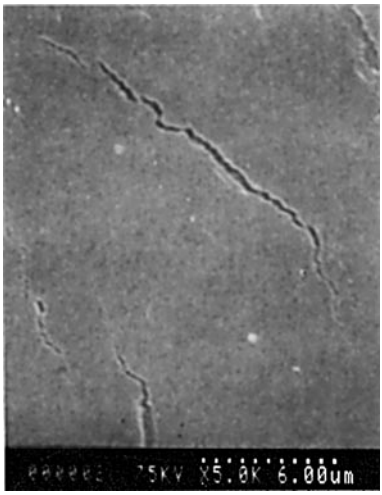


Fig. 8. A SEM graph of the surface contacted with glass plate for the film-forming PAM spherulite.

According to the principle of mechanics, the probability of a crystal growing for all directions in space is the same for a uniform system, and the growth of spheric crystal, therefore, is easier. In fact, the discoid crystal will form when the coating film is very thin.

The light energy makes the water molecules associated with acrylamide disassociated and evaporate when aquoacrylamide spherulite is irradiated by the ultraviolet light. At the same time, acrylamide molecules can obtain more mobility and can arrange themselves in some orientation, which leads to the form of crystalline structure of polyacrylamide when light energy makes acrylamide monomers polymerize. In appearance, this structure is in agreement with the spherulitic structure of acrylamide monomers (see Fig. 1). In fact, some water molecules have been lost after photopolymerization. Under a

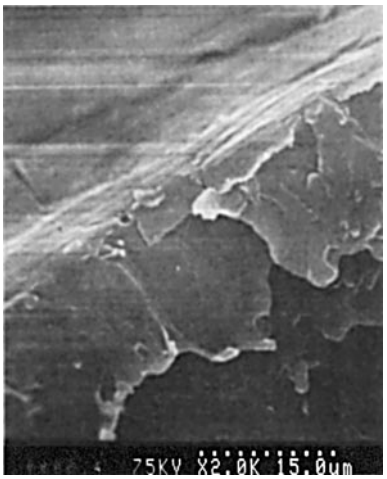


Fig. 9. A SEM graph of the cross section of the film-forming PAM spherulite.

microscope, it was observed that the small crystal pieces of the monomer spherulite have attenuated and its sharp edges corners have become smooth. The whole radiative band of the polyacrylamide spherulite appears as the chain form (see Figs. 5 and 6).

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