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Solid-State Polymerization in Binary Component Systems at Low Temperature

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Summary

Radiation-induced polymerization in binary component systems of acrylonitrile-methacrylonitrile and acrylonitrile-vinyl acetate was studied at -196°C . A mixture of two-component homopolymers was obtained from the acrylonitrile-methacrylonitrile system, which forms a eutectic mixture. When the mixture of acrylonitrile with vinyl acetate is cooled quickly from room temperature, a glassy state can be obtained. It was found that the copolymerization is possible in the glassy state at -196°C , and the monomer reactivity ratios were determined as $r_1 = 6.0$ and $r_2 = 0.2$ ($M_1 =$ acrylonitrile), which coincides with the reported values on the radical copolymerization at room temperature.

INTRODUCTION

It is well known that some monomers can be polymerized by initiating with ionizing radiation in the solid state at low temperatures (1-5). It seems that studies on solid-state polymerization in binary component systems are important to make clear the reaction mechanism from the point of the crystalline state of monomers, and to know the relationship between the polymerizability and the structure of monomers.

Several reports about the polymerization of ring monomers in binary component systems have been already published, but few data are available on the solid-state polymerization of the mixture

of vinyl monomers at low temperatures. Miura et al. (6) investigated in detail the polymerization of mixtures of some oxetane derivatives and showed that copolymerization is possible in the solid solution, but that in eutectic mixtures the blends of two-component homopolymers are obtained. In the former case, the monomer reactivity ratios (r_1 and r_2) are equal to unity, which means that the composition of copolymer obtained is the same as the composition of the monomer mixture. Analogous results were reported by Hayashi et al. (7). It was shown by Hardy et al. (8) that in the vinyl pyrrolidone-vinyl caproractum system, which makes a eutectic mixture, copolymerization is possible and that the composition of copolymer obtained is the same as the composition at the eutectic point.

In this paper, study of the polymerization of two binary systems, acrylonitrile-methacrylonitrile and acrylonitrile-vinyl acetate, is reported.

EXPERIMENTAL

Acrylonitrile and methacrylonitrile used were washed successively by aqueous potassium hydroxide solution, aqueous sulfuric acid solution and water, dried over CaH_2 , and distilled prior to use. Vinyl acetate was dried over CaH_2 and distilled before use. A glass ampoule containing the monomer mixture was set to a vacuum system, degassed repeatedly by the freeze-thaw technique and then sealed off under vacuum. The ampoule was cooled quickly in a liquid-nitrogen bath and irradiated with γ rays from a 1000-C Co-60 source. After irradiation the ampoule was opened, warmed as rapidly as possible to prevent the posteffects, and the content was poured into methanol. The precipitated polymer was filtered, washed with methanol, dried in vacuo, and weighed.

X-ray diffraction measurements were carried out at low temperatures, employing a sample cell with a beryllium window for which the temperature can be regulated by a cryostat (Rigaku Denki Co. Ltd.).

RESULTS

Acrylonitrile-Methacrylonitrile

In Fig. 1 the irradiation time-polymer yield curves at various monomer ratios are shown. In all cases of pure acrylonitrile, meth-

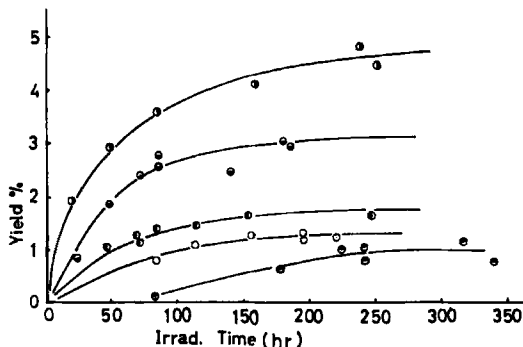


FIG. 1. Relation between yield of crude polymer and irradiation time at various concentrations of acrylonitrile in the acrylonitrile-methacrylonitrile mixture. Polymerization conditions: temperature, -196°C ; dose rate, 5×10^4 rad/hr; concentration of acrylonitrile, \bullet 100, \ominus 95, \circ 56, \circ 26, \bullet 0 mole%.

acrylonitrile, and the mixtures, the yields tend to saturate at high irradiation doses, and the limiting value decreases with increasing methacrylonitrile concentration.

The polymer yields in the initial stage of the polymerization before saturation were plotted against the composition of the monomer mixture in Fig. 2. The polymerization rate increases with increasing acrylonitrile concentration below about 90 mole% of acrylonitrile in the monomer mixture. The sharp decrease of the yield was observed at 90 to 95 mole% of acrylonitrile, where the reproducibility of the data was poor.

In Fig. 3 are shown the infrared spectra of the crude polymer and the extract and the residue obtained by acetone extraction of the crude polymer. The spectrum of the crude polymer is the super-

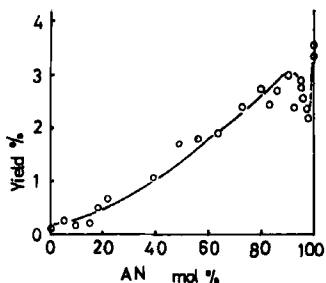


FIG. 2. Relation between polymer yield and concentration of acrylonitrile in the acrylonitrile-methacrylonitrile mixture. Polymerization conditions: temperature, -196°C ; dose rate, 5×10^4 rad/hr; irradiation time, \circ 85 hr.

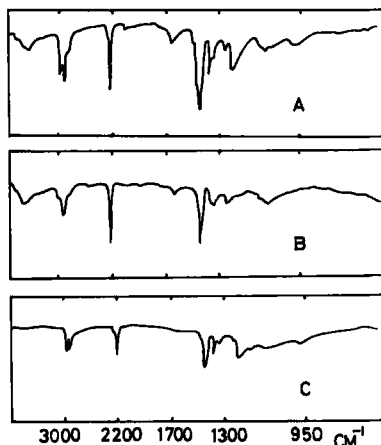


FIG. 3. Infrared spectra of polymers. A, the crude polymer; B, the insoluble part in acetone; C, the soluble part in acetone.

imposition of those of polyacrylonitrile and polymethacrylonitrile, and the spectra of the extract and the residue are in complete agreement with those of polymethacrylonitrile and polyacrylonitrile, respectively. Thus it may be concluded that the crude polymer obtained is the mixture of each homopolymer.

Acrylonitrile-Vinyl Acetate

In Fig. 4 the yield of the crude polymer is shown as the function of the irradiation time. As in the case of the acrylonitrile-methacrylonitrile system, the saturation of the yield was observed in this system.

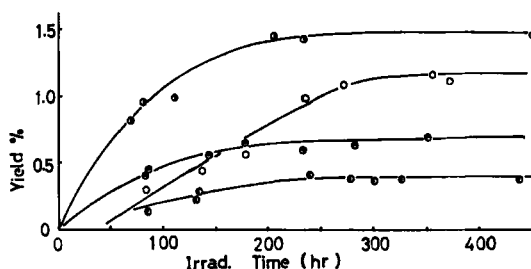


FIG. 4. Relation between copolymer yield and irradiation time at various concentrations of acrylonitrile in the acrylonitrile-vinyl acetate mixture. Polymerization conditions: temperature, -196°C ; dose rate, 5×10^4 rad/hr; concentration of acrylonitrile, \bullet 95, \bullet 79, \circ 68, \bullet 48.

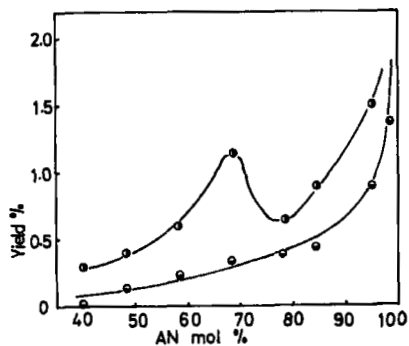


FIG. 5. Relation between copolymer yield and concentration of acrylonitrile in the acrylonitrile-vinyl acetate system. Polymerization conditions: temperature, -196°C ; dose rate, 5×10^4 rad/hr; irradiation time, \circ 85, \bullet 300 hr.

The yields in an initial stage of polymerization before saturation and in a later stage after saturation were plotted against the composition of acrylonitrile in the mixture, as shown in Fig. 5. The initial yield decreases with increasing concentration of vinyl acetate

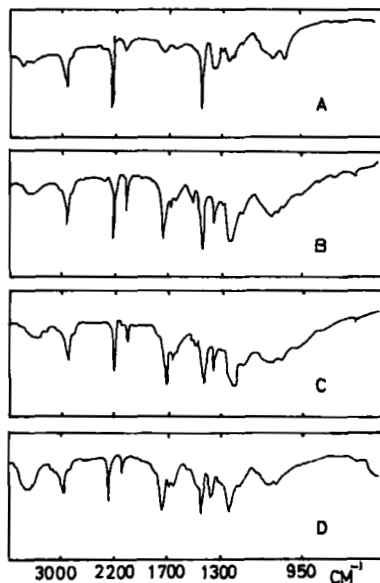


FIG. 6. Infrared spectra of acrylonitrile-vinyl acetate copolymers. The crude polymers obtained at following concentrations of acrylonitrile: A, 79; B, 68; C, 49 mole%; D, the residual part after benzene extraction.

in the monomer mixture, whereas the saturated yield shows the complicated features.

In Fig. 6 the infrared spectra of the polymers obtained are given. These spectra are different from those of two homopolymers and the spectrum changes continuously depending on the monomer composition. The homopolymer of vinyl acetate was not extracted by solvent extraction, as shown in Fig. 6. It may be concluded that the copolymer was obtained in this system.

The copolymer composition determined from elementary analysis is indicated in Fig. 7, from which the monomer reactivity ratios are estimated as $r_1 = 6.0$ and $r_2 = 0.2$ ($M_1 =$ acrylonitrile). These values are in fairly good agreement with the ones reported for radical copolymerization at 30°C (9).

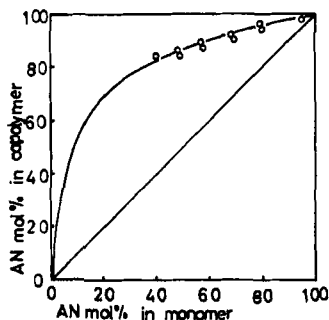


FIG. 7. Composition curve in copolymerization of the acrylonitrile-vinyl acetate system. The theoretical curve is drawn according to r_1 (AN) = 6.0, r_2 (VAC) = 0.2.

In Fig. 8 are shown the viscosities of the copolymers obtained at various monomer concentrations. The molecular weight of the copolymer decreases with decreasing concentration of acrylonitrile.

State of Monomer Aggregation

As shown in Fig. 9, the phase diagram of the acrylonitrile-methacrylonitrile system, which was obtained from thermal and X-ray analysis at low temperatures, is of a eutectic type, having a eutectic point at about 95 mole% of acrylonitrile. This means that when the monomer mixture is cooled from room temperature and solidified, each of the component monomers forms an isolated crystalline phase.

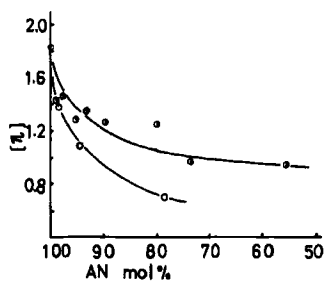


FIG. 8. Intrinsic viscosities of polyacrylonitrile and copolymer obtained at various concentrations of acrylonitrile. Polymerization conditions: dose rate, 5×10^4 rad/hr; irradiation time, 85 hr; temperature, -196°C ; ● acrylonitrile-methacrylonitrile system, ○ acrylonitrile-vinyl acetate system. Viscosities are measured in dimethylformamide at 25°C .

The X-ray diffraction curves for the acrylonitrile-vinyl acetate mixtures of 17 and 88 mole% acrylonitrile are shown in Figs. 10 and 11, respectively. In Fig. 10 the lower curve is for the sample cooled quickly, and the upper for the sample which was kept at -100°C for about 1 hr and then cooled slowly. In Fig. 11 curve C shows the "halo" of the liquid sample, B is for the sample cooled quickly, and A for the sample cooled slowly. It is evident from the figures that when the monomer mixture is cooled quickly from room temperature, a glassy state is obtained over a wide range of monomer composition except the high concentration of acrylonitrile, and that when the mixture is cooled slowly or the glassy state solidified is warmed to about -100°C , the crystallization occurs immediately. Even at the high concentration of acrylonitrile, for instance, 90 mole% of acrylonitrile, only a few very weak diffraction peaks appeared, with the weak halo due to the amorphous phase. This indi-

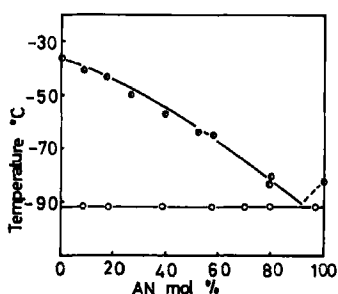


FIG. 9. Phase diagram of acrylonitrile-methacrylonitrile.

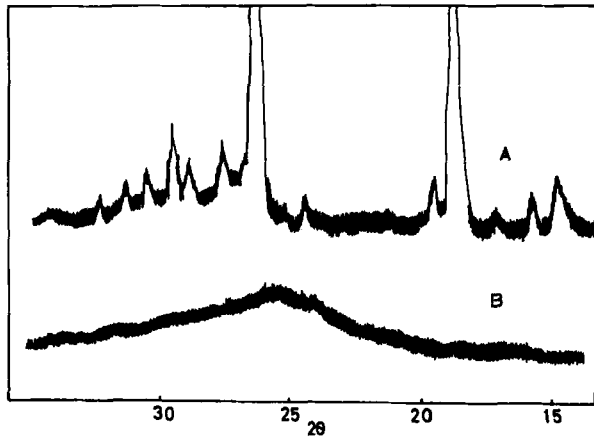


FIG. 10. X-ray diffraction curves of a acrylonitrile-vinyl acetate mixture at low temperatures. Acrylonitrile: 88 mole%. A, monomers cooled from 20 to -140°C slowly; B, monomers cooled from 20 to -160°C quickly.

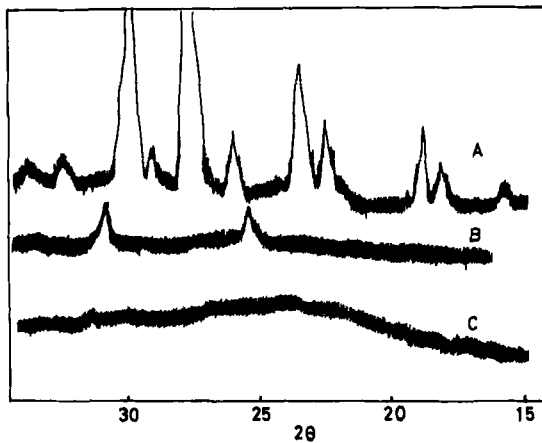


FIG. 11. X-ray diffraction curves of a acrylonitrile-vinyl acetate mixture at low temperatures. Acrylonitrile: 88 mole%. A, monomers obtained from B by warming up to -105°C ; B, monomers cooled from 20 to -160°C quickly; C, liquid state at 25°C .

cates that the monomer mixture in the solid state is far from the perfect crystalline state and extensively disordered.

DISCUSSION

From the acrylonitrile-methacrylonitrile system, which forms a eutectic mixture, a blend of two component homopolymers was obtained. This result coincides with the experimental results of Miura et al. on the polymerization of cyclic monomers. In a eutectic mixture the component monomers are isolated and form two different crystalline phases. When the solidified mixture is exposed to radiation, the polymerization seems to proceed independently in the two crystalline states. It is interesting to note that the polymerization rate decreases abnormally at a eutectic point of about 95 mole% acrylonitrile. At the eutectic point the microcrystals of the two monomers precipitate simultaneously when the mixture is cooled, whereas elsewhere one of the component monomers crystallizes along the phase separation curve in the phase diagram. The crystalline state is profoundly affected by the cooling procedure. In this system the polymerization yield tends to approach a limiting value in all monomer compositions, as was observed in the cases of pure acrylonitrile and methacrylonitrile. The limiting yields in the solid-state polymerization of pure acrylonitrile and methacrylonitrile are about 5 and 1%, respectively, at -196°C independent of dose rate. Using these values and assuming that polymerization occurs independently in the two crystalline phases, the limiting yields are calculated as 2.8 and 1.9% at the acrylonitrile concentrations of 50 and 25 mole%, respectively. The values obtained experimentally, however, are a little smaller than the calculated values. It may be partially due to the retardation of polymerization of the two monomers by the formation of eutectic mixture.

In the acrylonitrile-vinyl acetate system a glassy state is obtained over a wide range of the monomer composition. Though a transparent glass is not obtained above 70 mole% acrylonitrile, it is confirmed that the state of the monomer mixture is highly disordered at these compositions by X-ray diffraction measurements. It is interesting that the copolymerization by a radical mechanism is possible in the glass matrix at such low temperature. On the other hand, it was shown recently by Bodard and Marx (10) that acrylo-

nitrile is polymerized with γ rays by an anionic mechanism in 2-methyltetrahydrofuran glass at -196°C . The difference in the polymerization mechanism of acrylonitrile between the experiment and our copolymerization study may be due to the difference of the matrices forming glass between them, although such an effect of the matrix on the polymerization mechanism has not yet been shown. In this glass mixture system, the saturation in the polymerization yield is also observed. The total irradiation dose up to saturation is much higher in this system than in the acrylonitrile-methacrylonitrile system.

The limiting yield decreases sharply in a concentration range of 70 to 85 mole% acrylonitrile, while the initial yield increases monotonously with increasing acrylonitrile concentration. These phenomena suggest that the monomer glass in such concentrations is changeable in the course of polymerization.

It was reported by Bodard (11) that the saturation of yield is not observed in the polymerization of acrylonitrile in 2-methyltetrahydrofuran glass. However, we consider that the saturation of yield is not eliminated, but delayed, in the glass matrices. Therefore, the decrease of limiting yield mentioned above may be due to the partial crystallization in the monomer mixture during polymerization, by which the copolymerization is retarded.

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Zusammenfassung

Die strahlungsinduzierte Polymerisation in den Zweikomponentensystemen Acrylnitril-Methacrylnitril und Acrylnitril-Vinylazetat wurde bei -196°C untersucht. Im Acrylnitril-Methacrylnitril System wurde eine Mischung der zwei Komponenten der Homopolymeren erhalten da ein Eutektikum gebildet wird. Wenn das Gemisch aus Acrylnitril und Vinylazetat rasch auf Zimmertemperatur abgekühlt wird, kann eine glasige Form erhalten werden. Es wurde gefunden, dass eine Copolymerisation im Glaszustand bei -196°C möglich ist. Hierbei wurden die Monomerenreaktivitäten zu $r_1 = 6.0$ und $r_2 = 0.2$ ($M_1 = \text{Acrylnitril}$) bestimmt. Diese Werte stimmen mit den für Radikalpolymerisation bei Zimmertemperatur erhaltenen überein.

Résumé

On a étudié la polymérisation, induite par radiation, dans un système binaire d'acrylonitrile-méthacrylonitrile et acrylonitrile-acétate de vinyle à -196°C . Du système acrylonitrile-méthacrylonitrile on a obtenu un mélange d'homopolymères à deux composants, formant un mélange eutectique. Quand le mélange d'acrylonitrile avec l'acétate de vinyle est rapidement refroidi à température ordinaire, on peut obtenir un état vitreux. On a trouvé que la copolymérisation à l'état vitreux est possible à -196°C , et on a déterminé les rapports de réactivité comme $r_1 = 6.0$ et $r_2 = 0.2$ ($M_1 = \text{acrylonitrile}$), qui coïncide avec les valeurs rapportées sur la copolymérisation radicalaire à température ordinaire.