

Radiation-Induced Solid-State Polymerization of Vinyl Compounds in Binary Systems

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Synopsis

The radiation-induced solid-state polymerization in the binary systems such as acrylamide-methacrylamide and acrylamide-acenaphthylene was studied. The former system forms a solid solution, and the latter one forms a eutectic mixture. In the solid solution, the polymerization proceeds homogeneously and copolymer is formed, while in the eutectic mixture, it proceeds heterogeneously, forming only homopolymer. The post-polymerization of the same binary systems was also studied. Linearity between the conversion and the logarithm of the post-polymerization time was found for the various monomer compositions at various temperatures. This relationship satisfied the kinetic equation presented by Morawetz et al. for the post-polymerization of acrylamide. The kinetics of the binary systems might be considered similarly to the single system, considering that the crystalline state of the system is changed by the monomer compositions.

A number of reports have been presented on the radiation-induced solid-state polymerization of various vinyl compounds.¹⁻⁷ In particular, it was reported by many researchers that acrylamide was polymerized by γ -irradiation in the solid state.¹⁻³ However, there are few reports describing binary systems.^{3,8} The polymerization in the binary system is studied in order to elucidate the mechanism of reaction in the solid state. It is very favorable that the crystal structures of monomer mixtures are already known and monomer mixtures remain in the solid state at room temperature.

The monomer mixtures might form either a solid solution or a eutectic mixture in the binary solid, and the composition and the structure of the polymer obtained should be different. The effect of the radiation field on the phase equilibria in solids was studied by comparing results of in-source and post-polymerization.

In this report, the relationship of the structure of the monomer mixtures, kinetic behavior, and the compositions of the polymer obtained in the binary systems with both in-source and post-polymerization are described.

One of the binary systems is a mixture of acrylamide (AA) and methacrylamide (MAA) which forms a solid solution. Another system is a mixture

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of acrylamide and acenaphthylene (ACN) which forms a eutectic mixture. The reaction is expected to proceed homogeneously in the former system, but heterogeneously in the latter one.

EXPERIMENTAL

Materials

Acrylamide (AA), methacrylamide (MAA), and acenaphthylene (ACN) were recrystallized twice from chloroform, acetone, and methanol, respectively.

Preparation of Solid Solution and Eutectic Mixture

The monomer mixtures were prepared in glass ampules by weighing various compositions, then warmed to the liquid state and cooled gradually to room temperature. The samples were sealed at a reduced pressure of 10^{-4} mm. Hg or in air.

Irradiation Procedure

In-source polymerization was performed in a ^{60}Co facility at various dose rates, the temperature being controlled to $25 \pm 0.5^\circ\text{C}$. The irradiation dose rate was determined by ferrous sulfate dosimetry.

Post-Polymerization

Samples sealed in a thin glass ampule in vacuum were irradiated by an electron beam from a Van de Graaff electron accelerator at -78°C ., then post-polymerization was carried out at various temperatures.

Isolation of Polymer

The polymers were isolated by extracting the residual monomer from the partially polymerized samples with dry methanol. The polymers were separated, washed several times with dry methanol, and dried in vacuum at room temperature.

Phase Equilibria

The measurement of melting temperature of small amounts of monomer mixtures was made with a micro melting point measurement apparatus. The samples used were prepared in the same way as the samples used for polymerization.

X-Ray Diffraction

The x-ray diffraction peaks of powdered acrylamide, methacrylamide, acenaphthylene, and their mixtures were measured by use of a Shimadzu x-ray diffractometer, type GX-II, employing $\text{CuK}\alpha$ radiation in the angular range of $10\text{--}35^\circ$.

Composition of Polymers

Determination of the composition of the polymer obtained was by high-resolution NMR spectra or elementary analysis.

RESULTS AND DISCUSSION

Structure of Monomer Mixtures

Phase equilibria of the two monomer mixtures are shown in Figures 1 and 2. The AA-MAA system forms a solid solution, and the AA-ACN system forms a eutectic mixture. This result is confirmed by x-ray diffraction patterns (Figs. 3 and 4). In the case of the AA-MAA system, the angles of the diffraction peaks change continuously with monomer composition, but in the case of the AA-ACN system, they overlap each other.

However, Figure 1 indicates the possibility, in the narrow range of 65–90 mole-% AA, of existence of a eutectic mixture of two solid solutions having different compositions.

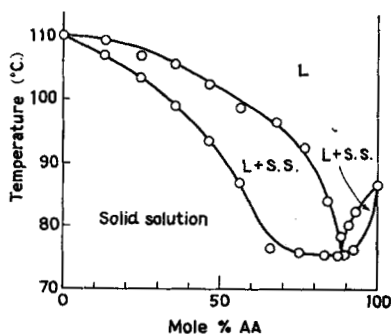


Fig. 1. Phase equilibria of acrylamide-methacrylamide system.

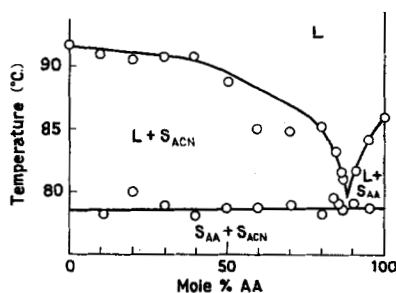


Fig. 2. Phase equilibria of acrylamide-acenaphthylene system.

In-Source Polymerization

The effects of monomer composition on the rate of polymerization in the solid state of the AA-MAA and AA-ACN systems are shown in Figures

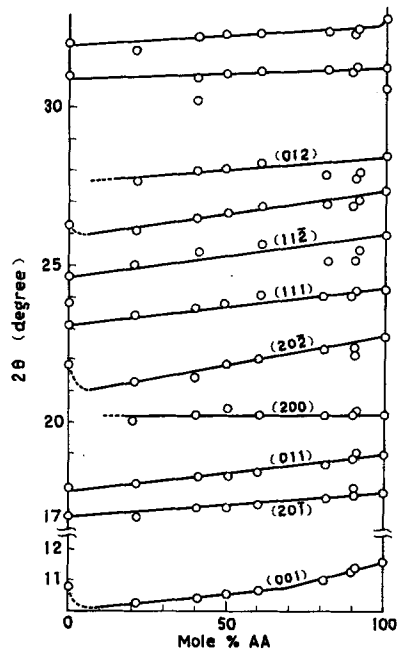


Fig. 3. X-ray diffraction diagrams of AA-MAA system.

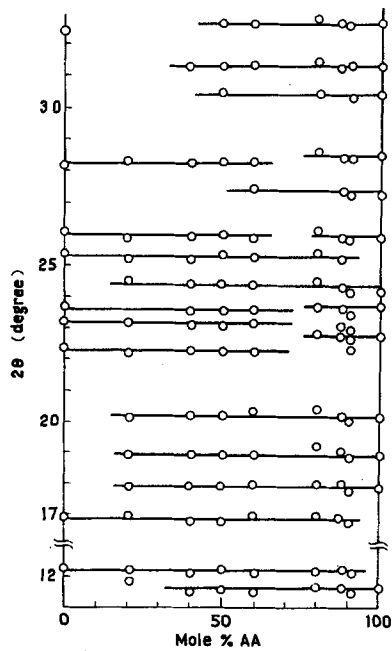


Fig. 4. X-ray diffraction diagrams of AA-ACN system.

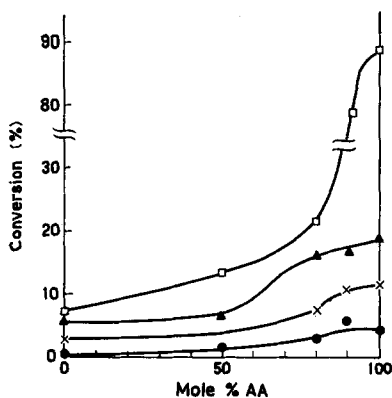


Fig. 5. Effect of monomer composition on the polymer yield in the AA-MAA system at 25°C.: (●) 1.3×10^5 rad; (×) 2.4×10^5 rad; (▲) 3.6×10^5 rad; (□) 5.1×10^5 rad.; $I = 8.0 \times 10^3$ rad/hr.

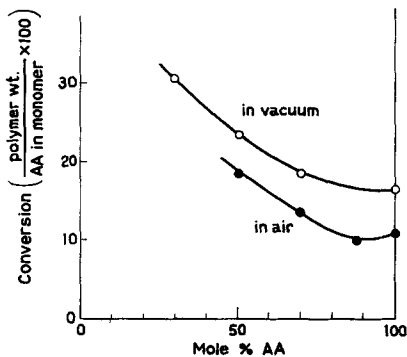


Fig. 6. Effect of monomer composition on the polymer yield in the AA-ACN system at 25°C. $D = 4.2 \times 10^5$ rad; $I = 8.0 \times 10^3$ rad/hr.

5 and 6. In the former system, the rate of polymerization appears to be accelerated by the effect of gel formation with increasing AA content. For the latter system, infrared spectra of the polymers obtained indicate that only homopolymers of AA were obtained in this case, because the rate of polymerization of ACN is lower than that of AA. Accordingly, it is obvious that the polymerization of AA is accelerated by the addition of ACN (Fig. 6). This result indicates that the polymerization of AA in the solid phase is advanced in the disordered region of the monomer crystal.

Figure 7 shows that the copolymers of 1:1 composition were obtained from the AA-MAA system, and homopolymers of AA from the AA-ACN system.

On the other hand, the results of polymerizations of both systems in acetone solution at the same temperature are shown in Figures 8 and 9. In the AA-MAA system, the effect of monomer composition on the polymer

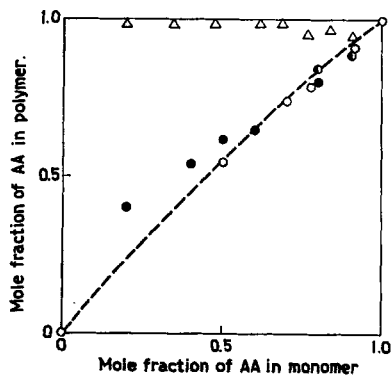


Fig. 7. Composition curves of the polymers obtained by the polymerization of AA-MAA systems: (O) AA-MAA, in-source polymerization (by elementary analysis); (◐) AA-MAA, in-source polymerization (by NMR); (●) AA-MAA, post-polymerization (by NMR); (Δ) AA-ACN, in-source polymerization (by elementary analysis); (---) calculated based on Q, e values.

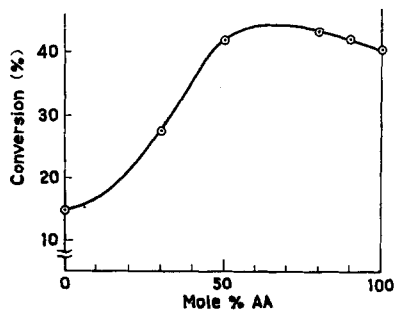


Fig. 8. Effect of monomer composition on the polymer yield in acetone solution of AA-MAA system at 25°C. Monomer concentration = 10 g./100 ml.; $D = 5.2 \times 10^4$ rad; $I = 8.0 \times 10^8$ rad/hr.

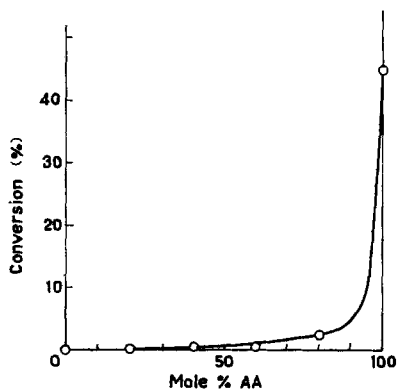


Fig. 9. Effect of monomer composition on the polymer yield in acetone solution of AA-ACN system at 25°C. Monomer concentration = 30 g./100 ml.; $D = 1.4 \times 10^4$ rad; $I = 8.0 \times 10^8$ rad/hr.

yield is similar to that of the solid state. However, in the AA-ACN system, the polymer yields decreased remarkably on addition of ACN. A similar phenomenon was found in the polymerization of this system initiated by AIBN. ACN inhibits the homopolymerization of AA in the eutectic mixture.

It was clearly shown that the reaction proceeds homogeneously, and copolymer is formed in the solid solution, while in the eutectic mixture, it proceeds heterogeneously with formation only of homopolymer.

Post-Polymerization

The time dependence of the polymerization of the AA-MAA system is shown in Figure 10. It is found that the linearity comes into existence for the various monomer compositions.

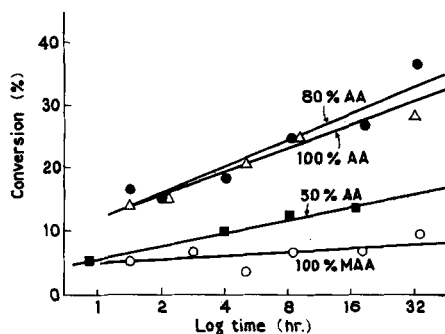


Fig. 10. Kinetics of AA-MAA system post-polymerization on various monomer compositions. Preirradiation at $-78^{\circ}\text{C}.$; $D = 5.1 \times 10^6$ rad; post-polymerization at $50^{\circ}\text{C}.$

The kinetic equation, eq. (1), presented by Morawetz et al. for the radiation-induced post-polymerization of AA³ is used for this system.

$$Y \doteq (k_p/k_t)(\ln t + \ln k_i[R_0]) \quad (1)$$

Here Y is polymer yield, k_p and k_t are the rate constants of propagation and termination, respectively, and $[R_0]$ is the initial concentration of radicals trapped in the monomer mixture.

k_p and k_t should change with the crystalline state of the system transformed by the monomer composition. Moreover, $[R_0]$ is proportional to the preirradiation dose, and the possibility of trapping the radicals is influenced by the monomer compositions.

It is shown that the time dependence of the polymerization yield is linear and eq. (1) is still useful. If the monomer concentration changes, the slope and intercept should be changed because k_p/k_t and $[R_0]$ is function of monomer composition. It is thus obvious that the kinetic behavior of the binary system is similar to the single phase of AA.

Figure 11 shows the dependence of the monomer composition on the post-polymerization of the AA-MAA system. The curve indicates no

maximum or minimum, and the same tendency as in-source polymerization in the solid state and the liquid state. The linearity of Y and $\log t$ does not change with preirradiation dosage and it moves parallel with dosage based on the equation (1) (Fig. 12).

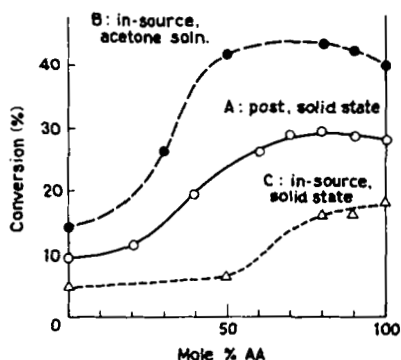


Fig. 11. Effect of monomer composition on the post-polymerization of AA-MAA system: (A) preirradiation at -78°C ., $D = 5.1 \times 10^6$ rad, post-polymerization at 50°C ., 33.2 hr.; (B) γ -irradiation at 25°C ., $D = 5.2 \times 10^4$ rad, monomer concentration = 10 g./100 ml.; (C) γ -irradiation at 25°C .; $D = 3.6 \times 10^6$ rad.

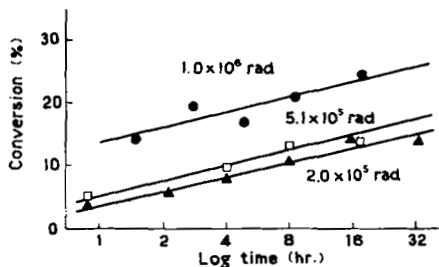


Fig. 12. Effect of preirradiation dose on the post-polymerization of AA-MAA system. Monomer composition: 50 mole-% AA, preirradiation at -78°C ., post-polymerization at 50°C .

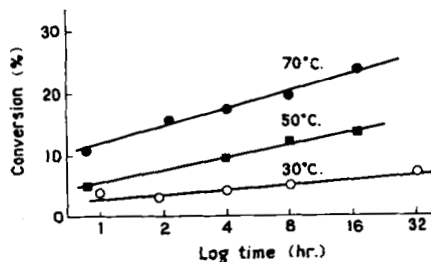


Fig. 13. Effect of post-polymerization temperature on the post-polymerization of AA-MAA system. Monomer composition: 50 mole-% AA, preirradiation at -78°C ., $D = 5.1 \times 10^6$ rad.

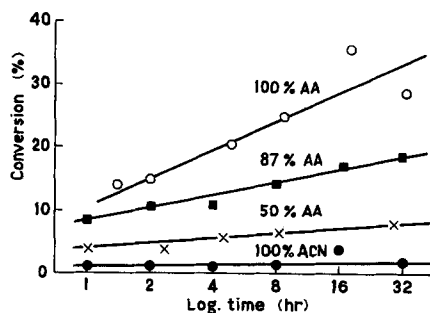


Fig. 14. Kinetics of AA-ACN system post-polymerization at various monomer compositions. Preirradiation at -78°C ., $D = 5.1 \times 10^6$ rad, post-polymerization at 50°C .

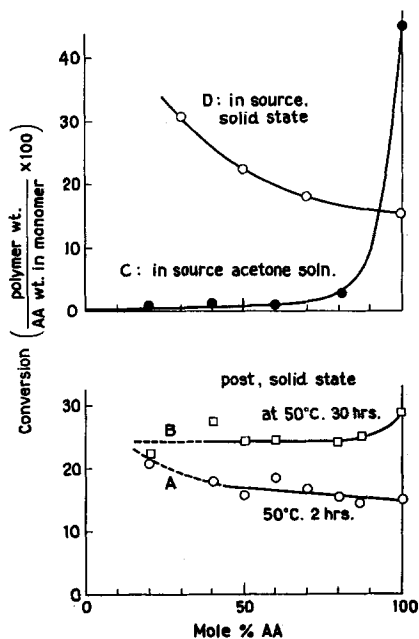


Fig. 15. Effect of monomer composition on the post-polymerization of AA-ACN system: (A,B) preirradiation at -78°C ., $D = 5.1 \times 10^6$ rad; (C) γ -irradiation at 25°C ., $D = 1.4 \times 10^6$ rad, monomer concentration = 30 g./100 ml.; (D) γ -irradiation at 25°C ., $D = 4.2 \times 10^6$ rad.

The post-polymerization proceeds at temperatures higher than room temperature. Linearity of the time dependence of the polymerization was observed at various temperatures, but the slopes changed as a function of the temperature (Fig. 13). This change of the slope is attributed to the variations of k_p , k_t , and the crystalline states of the systems.

The polymers obtained are copolymers of AA and MAA, the compositions of which are approximately the same as that of the monomer mixtures,

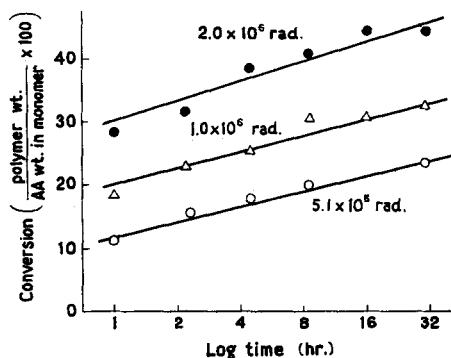


Fig. 16. Effect of preirradiation dose on the post-polymerization of AA-ACN system. Monomer composition: 50 mole-% AA, preirradiation at -78°C ., post-polymerization at 50°C .

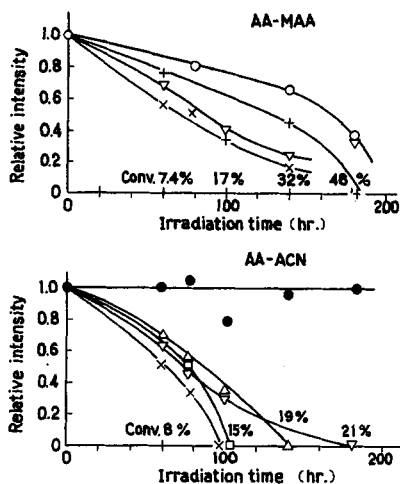


Fig. 17. Change of intensity of x-ray diffraction in the irradiated monomer mixtures: (●) diffraction from ACN crystal, irradiation at 25°C .; $I = 8.0 \times 10^3$ rad/hr., monomer composition of both systems: 50 mole-% AA.

as reported for the solid solution of oxetanes,⁹ while this value is similar to that calculated based on Q , e values ($Q = 1.18$, $e = 1.30$ for AA, $Q = 1.46$, $e = 1.24$ for MAA).¹⁰ (Fig. 7).

ACN produces hardly any polymer in the solid or liquid phase, and the eutectic mixture of AA and ACN does not produce AA homopolymer because of inhibition by ACN. In the solid phase of the AA-ACN system, AA homopolymer is produced.

The linearity of the time dependence of the polymerization is similar to that for the AA-MAA system at various monomer compositions, and the slopes change with the monomer composition (Fig. 14).

Figure 15 shows the monomer composition dependence of the polymerization. The polymerization is inhibited by ACN in the liquid state; in the solid state, however, many imperfections in the crystal of AA are produced by the addition of ACN, so the homopolymerization of AA is accelerated as a result of disordering of monomer crystal.

However, in the case of post-polymerization, the trapping of radicals in the solid state is prevented by the imperfections. So the polymer yield decreases slightly in the latter stages of polymerization. The effect of preirradiation dosage on the polymer yield in AA-ACN system is linear as in the AA-MAA system, and it changes parallel with the variations of dosage. The slope changes with the temperature of polymerization, but it decreases at temperatures higher than 50°C. This result should be explained by the difficulty of trapping radicals at temperatures near the eutectic point (78°C.).

The kinetics of the binary systems might be considered similarly to single system, considering that the crystalline state of the system is changed by the monomer composition.

X-Ray Diffraction Analysis of the Monomer Mixtures

Changes in intensity of x-ray diffraction were observed for the polymerization of monomer mixtures. In the AA-MAA system, the intensities of all diffraction peaks decreased continuously as polymerization proceeded; that is, the reaction takes place homogeneously in the solid solution. On the other hand, in the AA-ACN system, the intensities of diffraction peaks of AA decreased, but that of ACN did not change. Therefore, the polymerization should proceed only in the crystals of AA. The same result was observed in the case of the post-polymerization of these systems.

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Résumé

La polymérisation à l'état solide, induite par radiation, d'un système binaire tel qu'acrylamide-méthacrylamide et acrylamide-acénaphthylène a été étudiée. Le premier système forme une solution solide, tandis que le second forme un mélange eutectique. On a montré que à l'état solide la polymérisation progresse de façon homogène et un copolymère est formé, tandis que dans le mélange eutectique, elle avance de façon hétérogène en formant uniquement un homopolymère. La post-polymérisation de ces systèmes binaires a également été étudiée. La linéarité entre le degré de conversion et le logarithme de la durée de post-polymérisation a été vérifiée pour diverses compositions en monomères à des températures variables. Cette relation satisfait l'équation cinétique présentée par Morawetz et collaborateurs sur la post-polymérisation de l'acrylamide. La cinétique du système binaire peut être considérée de façon similaire à un système simple en considérant que l'état cristallin du système est modifié suivant les compositions en monomères.

Zusammenfassung

Die strahlungsinduzierte Polymerisation in festem Zustand wurde in binären Systemen, wie Acrylamid-Methacrylamid und Acrylamid-Acenaphthylen untersucht. Ersteres System bildet eine feste Lösung und letzteres eine eutektische Mischung. Es wurde klar gestellt, dass in der festen Lösung die Polymerisation homogen verläuft und ein Copolymeres liefert, während sie in der eutektischen Mischung heterogen ist und nur zu Homopolymerem führt. Die Nachpolymerisation in den gleichen binären Systemen wurde ebenfalls untersucht. Bei verschiedener Monomierzusammensetzung und verschiedenen Temperaturen wurde eine lineare Abhängigkeit des Umsatzes von der Nachpolymerisationsdauer gefunden. Diese Beziehung entsprach der von H. Morawetz et al. für die Nachpolymerisation von Acrylamid angegebenen kinetischen Gleichung. Die Kinetik der binären Systeme könnte unter Berücksichtigung der Änderung des kristallinen Zustands des Systems durch die Monomierzusammensetzung in ähnlicher Weise wie diejenige des einfachen Systems behandelt werden.

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