

Radiation-Induced Solid-State Polymerization in Binary Systems. IX. Polymerization and Foaming of Multicomponent Systems Including Inorganic Acid and Acrylic Monomers

ISAO KAETSU and AKIHIKO ITO, *Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Takasaki, Japan*, and NORIO SAGANE, *Research Laboratory, Sekisui Chemical Company, Osaka, Japan*

Synopsis

It was found that binary systems consisting of inorganic acid and organic amide or nitrile form a stable glassy phase owing to the large molecular interaction between the components. The change in T_g values with change in composition of these binary systems was studied. Gamma ray-induced polymerization of inorganic acid and acrylamide or acrylonitrile systems was carried out in a supercooled phase. The polymerization rates in acrylamide-inorganic acid systems had a maximum at a temperature T_p (30°–50°C higher than the glass transition temperature), but in acrylonitrile-inorganic acids systems there was no maximum rate at any temperature. Foaming occurred during irradiation in the polymerization of acrylamide-urea-sulfuric acid system. The in-source foaming was attributed to the promoting effect of sulfuric acid for the decomposition of urea and the heat accumulation by the acceleration of the polymerization.

INTRODUCTION

In the previous studies,¹⁻⁵ glassification and polymerization of glass-forming monomeric systems have been investigated. It was found that binary systems consisting of organic acid and amide formed a stable glassy phase owing to large molecular interaction between the components and that they were polymerized at a very high rate in the supercooled phase.¹⁻³ It was also expected that some combinations of organic amide and inorganic acid also have large molecular interaction between the components. In the present study, glassification and polymerization of binary systems consisting of inorganic acid-organic amide or organic nitrile systems were investigated.

EXPERIMENTAL

All components were purified according to the conventional method. Polymerization, foaming, and T_g estimation were carried out in the same way as described in the previous report.⁶

RESULTS AND DISCUSSION

Glass Formation of Binary Systems Consisting of Inorganic Acid and Organic Amide or Nitrile

In the previous study,^{1,2} it was found that binary systems consisting of organic acid and amide have an evident glass-forming tendency owing to large molecular interaction between acid and amide.

The authors have also found that binary systems consisting of inorganic acid and organic amide or nitrile have large molecular interaction and could be easily glassified. The change in T_g (glass transition temperature) as a function of composition in those binary systems is shown in Figures 1 and 2.

It was found in a previous study⁵ that in binary systems with large molecular interaction between the components, T_g 's of binary systems were higher than those of the pure components and the molecular complex of the two components often formed. According to the result of Figures 1 and 2, the T_g 's of inorganic acid-organic amide or nitrile systems greatly increased in comparison with the original value of single component. Moreover, the formation of a molecular complex was observed in some systems such as acrylamide-sulfuric acid. A large amount of mixing heat was observed by mixing inorganic acid and organic amide or nitrile. These results support the assumption of large molecular interaction between the two components of these systems.

Phosphoric acid by itself had the glass forming property, but sulfuric acid and nitric acid could not be glassified by themselves. The stability

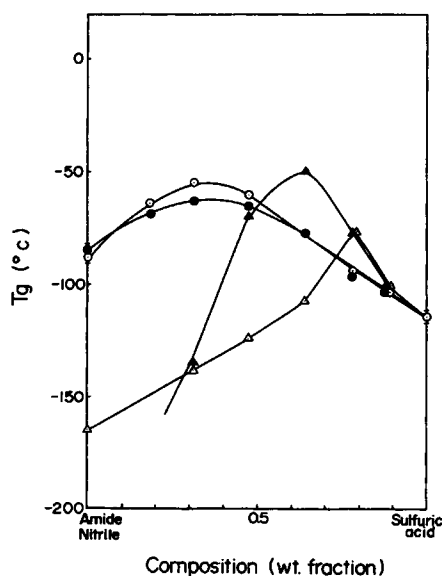


Fig. 1. Change of T_g as function of composition in sulfuric acid-organic amide or nitrile systems. Amide or nitrile: (O) acrylamide; (●) propionamide; (Δ) acrylonitrile; (▲) acetonitrile.

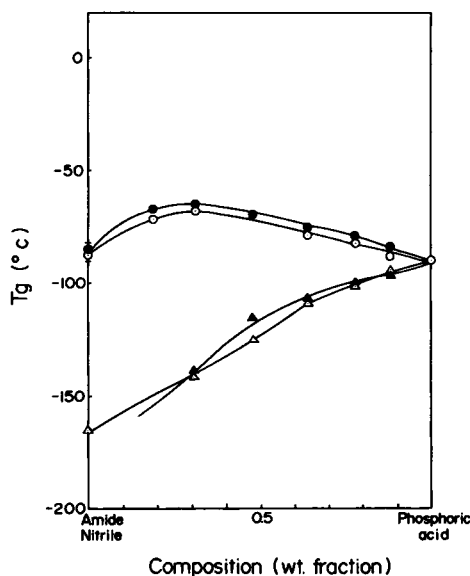


Fig. 2. Change of T_g as function of composition in phosphoric acid-organic amide or nitrile systems. Amide or nitrile: (O) acrylamide; (●) acetoamide; (Δ) acrylonitrile; (▲) propionitrile.

of the glassy phase increased in the order of binary systems including nitric acid, sulfuric acid, and phosphoric acid.

Radiation-Induced Polymerization of Binary Systems Consisting of Inorganic Acid and Acrylamide or Acrylonitrile System

Polymerization of glass-forming systems consisting of inorganic acid and acrylamide or acrylonitrile by γ -irradiation was studied. The polymer yield as a function of polymerization temperature is shown in Figures 3 and 4.

It was clarified in previous studies⁴ that polymerization rate had a maximum at a temperature T_p (30° – 50°C higher than T_g) in the polymerization of glass-forming systems by radical mechanism. The temperature dependence of the polymerization rate in acrylamide-inorganic acid systems shown in Figure 3 agreed with the characteristics of typical radical polymerization of glass-forming system in the supercooled phase. However, the result of the polymerization of the acrylonitrile-inorganic acid system showed no maximum polymerization rate at T_p , as shown in Figure 4. This result may be attributed to the fact that the polymerization of acrylonitrile proceeds in the heterogeneous phase owing to the precipitation of polymer.

It was surprising that the polymerization rate was extremely large in acrylamide-inorganic acid systems, and postpolymerization occurred also very rapidly after their irradiation. In nitric acid-acrylamide or acrylo-

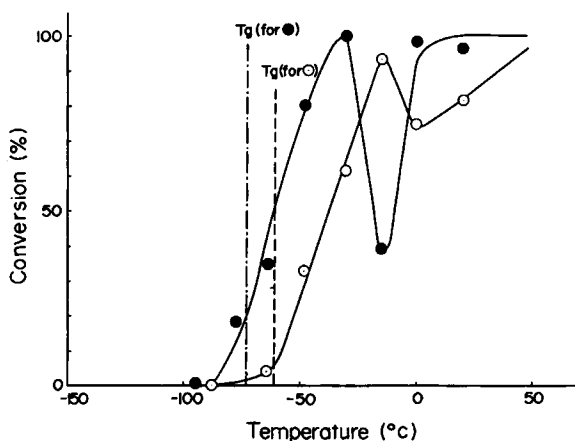


Fig. 3. Relationship between conversion and temperature in acrylamide-inorganic acid systems: (O) acrylamide-sulfuric acid (1:0.95 wt fraction), dose rate 2×10^4 r/hr, dose 3.3×10^3 r, in vacuum; (●) acrylamide-phosphoric acid (1:0.95 wt fraction), dose rate 3×10^3 r/hr, dose 5.0×10^3 r, in vacuum.

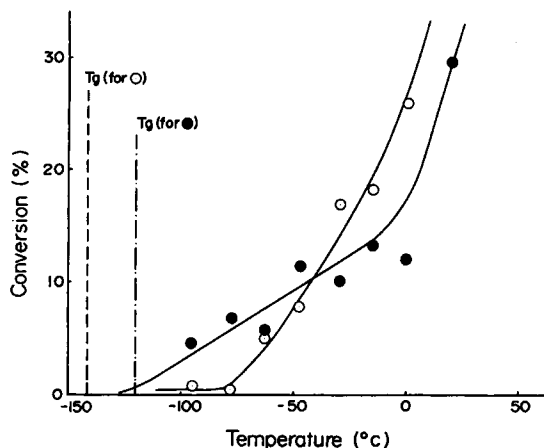


Fig. 4. Relationship between conversion and temperature in acrylonitrile-inorganic acid systems: (O) acrylonitrile-sulfuric acid (1:0.46 wt fraction), dose rate 5×10^4 r/hr, dose 5×10^4 r, in vacuum; (●) acrylonitrile-phosphoric acid (1:0.95 wt fraction), dose rate 5×10^4 r/hr, dose 5×10^4 r, in vacuum.

nitrile systems, the polymerization rate was much retarded owing to inhibitory effect of nitrogen compound.

Foaming of Sulfuric Acid-Acrylamide-Urea System by Irradiation

It was found that sulfuric acid-acrylamide-urea systems could be foamed during irradiation. Acrylamide and urea easily dissolved in sulfuric acid to form a homogeneous viscous solution. This solution suddenly began to expand at a certain irradiation dose, when it was polymerized by

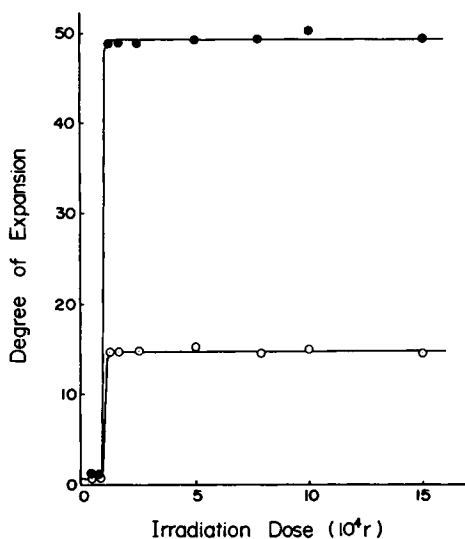


Fig. 5. Effect of irradiation dose on foaming of acrylamide-urea-sulfuric acid system: (O) expansion degree in foaming during irradiation; (●) final expansion degree after irradiation and postheating. Composition: acrylamide-urea-sulfuric acid = 1:1:0.95 wt fraction; irradiation dose rate 5×10^4 r/hr, in air; heating 160°C , 30 min.

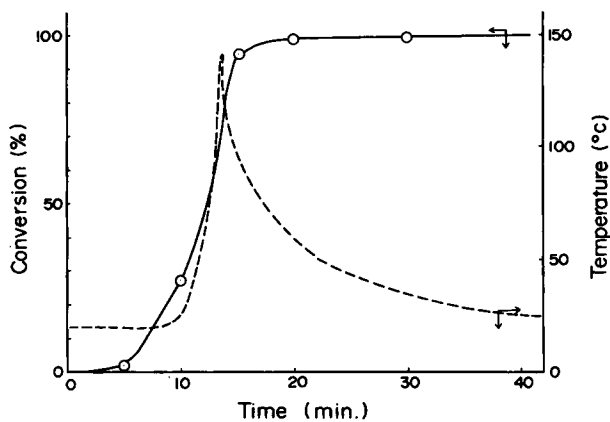


Fig. 6. Change of conversion and inner temperature as function of irradiation time in in-source foaming of acrylamide-urea-sulfuric acid system. Composition: acrylamide-urea-sulfuric acid = 1:1:0.95 wt fraction; irradiation dose rate 5×10^4 r/hr, in air.

irradiation. The foaming did not complete during irradiation and the in-source foaming polymer could be further expanded by heating after irradiation to reach an expansion of 60–80 times. The results are shown in Figure 5.

In-source foaming can be attributed to the promoting effect of sulfuric acid for the decomposition of urea and heat accumulation of the system by

the acceleration of the polymerization rate. In Figure 6, conversion and temperature change inside the polymerization system measured by a thermocouple were plotted against irradiation dose. From the result of Figure 6 it was clear that the temperature rapidly increased with acceleration of polymerization and reached a maximum above 130°C , which was enough to soften the polymer and decompose the urea.

The effect of sulfuric acid content on the degree of expansion is shown in Figure 7. The foam had a rough continuous cell structure and soft flexible property as if made of paper owing to very thin cell membranes. Further

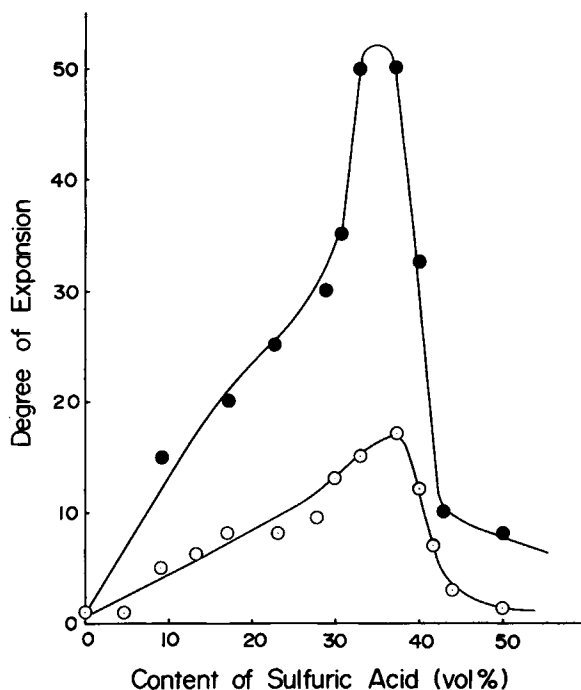


Fig. 7. Relationship between degree of expansion and content of sulfuric acid in foaming of acrylamide-urea-sulfuric acid system; (O) expansion degree in foaming during irradiation; (●) final expansion degree after irradiation and postheating. Composition: acrylamide-urea = 1:1 volume fraction; irradiation dose rate 5×10^4 r/hr, dose 1×10^6 r, in air; heating 160°C , 30 min.

addition of acrylic acid to acrylamide-urea-sulfuric acid systems increased greatly the degree of expansion.

The promoting effect of various acids on the foaming during irradiation was also tested. Such organic acid as tartaric acid, malonic acid, oxalic acid, and succinic acid increased the expansion of acrylamide-urea-water systems, but none of them caused in-source foaming. Only iodic anhydride showed a promoting effect of in-source foaming, but the degree of expansion was not so high as in sulfuric acid.

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