

Radiation-Induced Solid-State Polymerization in Binary Systems. VIII. Polymerization and Foaming of Multicomponent Systems Including Acrylamide and Acrylic Acid

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

Radiation-induced polymerization and foaming of multicomponent systems including acrylamide, acrylic acid, and foaming agents were studied. Eutectic mixtures such as acrylamide-itaconic acid were polymerized in solid state and then foamed by heating at 130 ~ 200°C. The solution systems such as acrylamide-itaconic acid-water and acrylamide-maleic anhydride-urea-water were polymerized in liquid and supercooled phases at higher rates and foamed to a higher degree of expansion. Foams of poly(acrylic acid) and poly(methacrylic acid) were obtained by polymerization and heating of acrylic acid (methacrylic acid)-urea-water systems. It was deduced that the non-melting or flowing property of these acrylic polymers, especially the semithermosetting property of polyacrylamide, had an important effect on the foaming mechanism.

INTRODUCTION

The authors have studied radiation-induced polymerization of binary and multicomponent systems in solid and supercooled phases.¹⁻³ It is one of the characteristics of polymerization in multicomponents systems that all components are dispersed homogeneously and compactly in polymerized mixtures. Therefore, formation of multicellular product is expected when heating the polymerized mixture including foaming agents as a component. Foaming is one of the interesting application of radiation polymerization, because a relatively low temperature is desirable for the polymerization of such systems to avoid the uncontrolled decomposition of foaming agent due to the accumulation of polymerization heat.

In this report, γ -ray-induced polymerization and foaming of multicomponent systems including acrylamide or acrylic acid as a monomer were studied.

EXPERIMENTAL

All substances used were purified by recrystallization or distillation according to conventional methods.

All components were mixed homogeneously, if necessary by heating, then charged into glass ampoules, and irradiated with γ -rays from a 5000 Ci⁶⁰Co source.

The polymerized mixtures were separated from ampoule glass and put into the oven to be heated at the given temperature. The apparent specific weight and the degree of expansion were determined from weight and volume of the foams. The polymer yield was determined gravimetrically. Content of imide-crosslinking formation was determined by measurement of ammonia gas.

Glass transition temperatures (T_g) were estimated by differential thermal analysis (DTA).

RESULTS

Polymerization and Foaming of Polyacrylamide Obtained by Solid-State Polymerization of Eutectic Mixtures

In previous studies,¹ it was found that polymerization rates of acrylamide in radiation-induced solid-state polymerization were much accelerated in various eutectic mixtures, and it was deduced that the acceleration of the polymerization rate is due to the small grain and increased dislocations in the crystal of the eutectic composite. Polymerization and foaming of eutectic mixtures consisting of acrylamide and foaming agent were investigated.

The following substances were found to be effective for the foaming of polyacrylamide: effective (degree of expansion over 10 times): itaconic

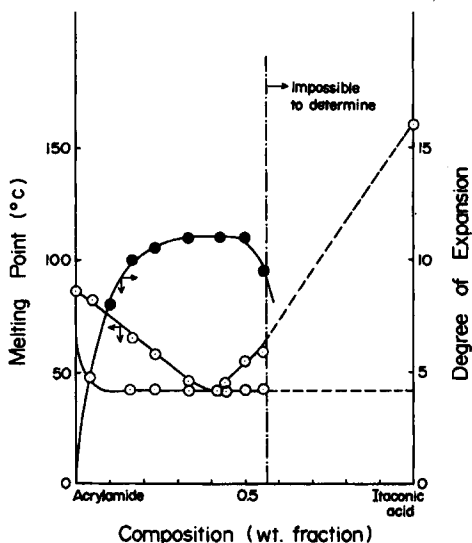


Fig. 1. Phase diagram and degree of expansion as a function of composition in acrylamide-itaconic acid system. Polymerization: dose rate 1×10^5 r/hr, dose 7×10^5 r, temperature 25°C, in air.

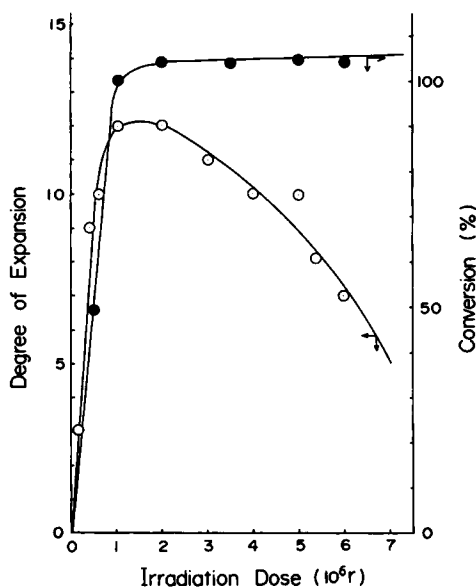


Fig. 2. Conversion and degree of expansion as a function of irradiation dose in acrylamide-itaconic acid system. Composition: acrylamide 0.67 wt fraction; polymerization: dose rate 1×10^6 r/hr, temperature 25°C , in air; foaming: temperature 210°C , time 30 min.

acid, citric acid, urea, trichloroacetic acid, chloral hydrate, phosphonitrilic chloride; somewhat effective foaming agent (degree of expansion less than 10 times): maleic anhydride, succinic acid, dicyandiamide, thiourea, oxalic acid, malonic acid, *d*-tartaric acid.

Such substances as crotonic acid, sorbic acid, terephthalic acid, and benzoic acid were not effective at all.

The acrylamide-itaconic acid system was studied in details. Phase diagrams and the degree of expansion as a function of composition are shown in Figure 1. The phase diagram in itaconic acid-rich composition was impossible to determine because of the violent thermal polymerization. From the result in Figure 1 it was found that the expansion degree had a maximum at the eutectic composition, probably due to the finely mixed structure of polymer and foaming agent in the eutectic composite.

Conversion and the degree of expansion as a function of irradiation dose are shown in Figure 2. The degree of expansion had a maximum at a certain irradiation dose, and then decreased with increase in dose. This may be the result of excess crosslinking of the polymer.

Polymerization and Foaming of Polyacrylamide Obtained in the Liquid and Supercooled Phases

Acrylamide-itaconic acid eutectic mixture could be dissolved into a homogeneous liquid phase by the addition of a small quantity of water. It was found that the polymerized mixture of acrylamide-itaconic acid-

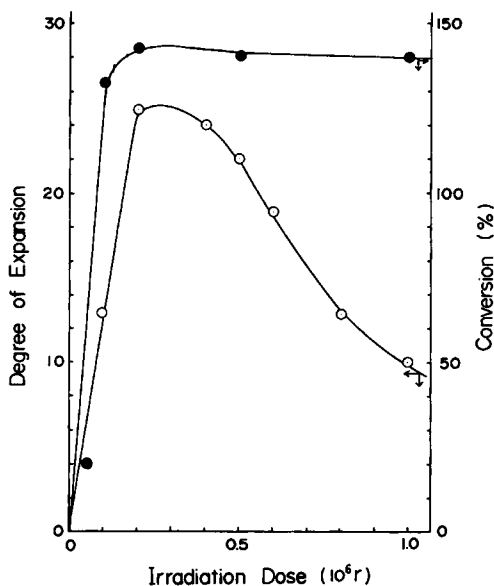


Fig. 3. Conversion and degree of expansion as a function of irradiation dose in acrylamide-itaconic acid-water system. Composition: acrylamide:itaconic acid:water = 10:5:3 wt ratio; polymerization: dose rate 5×10^4 r/hr, temperature 25°C , in air; foaming: temperature 210°C , time 30 min.

water solution gave a foam of greater degree of expansion and better quality than those obtained by solid-state polymerization without water. The conversion and the expansion degree in liquid-phase polymerization are shown in Figure 3 against irradiation dose. In the acrylamide-itaconic acid-water solution system, maximum degree of expansion occurred at an irradiation dose below 0.5 Mr, which was much smaller than the corresponding dose in the solid-state polymerization system. Moreover, the irradiation dose necessary for high foaming in the solution polymerization system was smaller than that in the solid-state polymerization system. These differences in irradiation dose dependence of foaming by the two polymerization phases perhaps can be attributed to the difference in polymerization and crosslinking rates.

Both foams obtained by solid and solution polymerization had a discontinuous cell structure, but excess increase in water content caused a gradual change in structure from discontinuous to continuous cell structure.

It was also found that the acrylamide-maleic anhydride-urea-water solution system also could be foamed to a high degree of expansion. The expansion degree as a function of irradiation dose is shown in Figure 4. According to the result of Figure 4, irradiation dose dependence of expansion degree in this system much depends on the content of urea-water. The irradiation dose necessary for high foaming and the dose at maximum expansion degree increased with increasing urea-water content. These results suggest that the rates of polymerization and crosslinking were very large in a composition of small urea-water content. The relationship be-

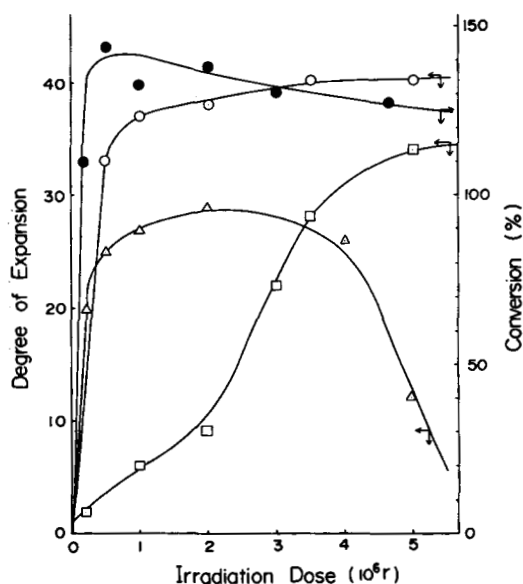


Fig. 4. Conversion and degree of expansion as a function of irradiation dose in acrylamide-maleic anhydride-urea-water system. Polymerization: dose rate 5×10^4 r/hr, temperature 25°C , in air; foaming: temperature 200°C , time 30 min; composition: acrylamide: maleic anhydride = 10:6 wt parts; (●) urea 3.0 wt parts, water 3.0 wt parts; (△) urea 0.85 wt parts, water 0.85 wt parts; (○) urea 6.0 wt parts, water 6.0 wt parts; (◻) urea 8.8 wt parts, water 8.8 wt parts.

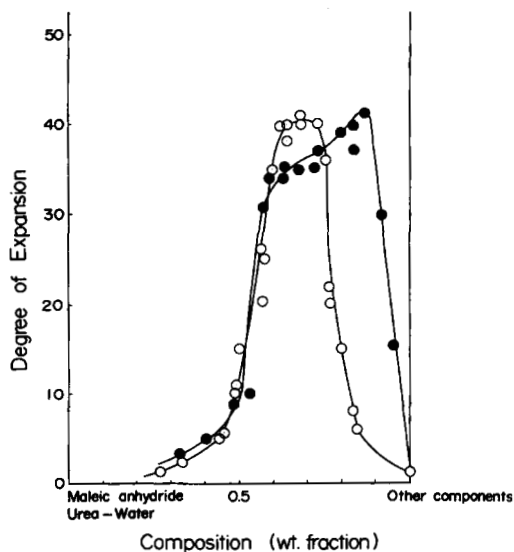


Fig. 5. Effect of the composition on the degree of expansion in acrylamide-maleic anhydride-urea-water system. Polymerization: dose rate 5×10^4 r/hr, dose 1.4×10^6 r, temperature 25°C , in air; foaming: temperature 200°C , time 30 min; composition: (○) maleic anhydride content, acrylamide:urea:water = 10:1.5:1.5 wt ratio; (●) urea-water content (equal quantity), acrylamide: maleic anhydride = 10:6 wt ratio.

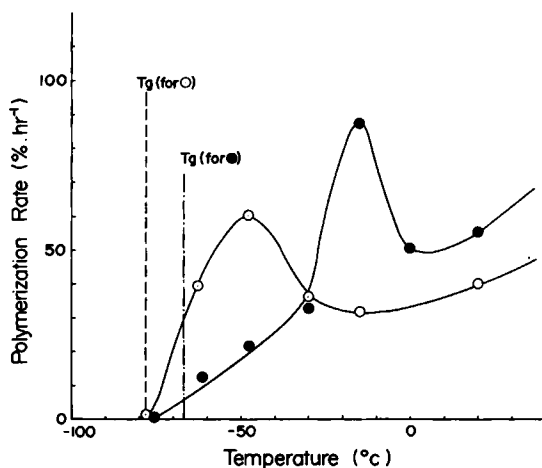


Fig. 6. Effect of temperature on polymerization rate in liquid and supercooled phase polymerization of some foaming systems. (○) Acrylamide-maleic anhydride-urea-water system, acrylamide: maleic anhydride: urea: water = 10:6:3:3 wt ratio; polymerization: dose rate 2×10^4 r/hr, in vacuum; (●) acrylamide-itaconic acid-water system, acrylamide: itaconic acid: water = 10:5:3 wt ratio; polymerization: dose rate 5×10^4 r/hr, in vacuum.

tween composition and degree of expansion in this system is shown in Figure 5.

In the previous studies,^{2,3} it was found that organic binary systems consisting of acid and amide form a glassy phase owing to large molecular interaction between the components. Binary foaming systems such as acrylamide-itaconic acid and acrylamide-malonic acid were found to be glassified at eutectic composition. However, it was found that multi-component solution systems such as acrylamide-itaconic acid-water and acrylamide-maleic anhydride-urea-water system formed a more stable glassy phase. The radiation polymerization of these solution systems in the supercooled phase was investigated. The polymer yield was plotted as a function of polymerization temperature in Figure 6. The polymerization rate had a maximum at a temperature, 30–50° higher than T_g . This result agreed with the characteristics of radical polymerization of glass-forming system in the supercooled phase.²⁻⁴

It may be an advantage of polymerization in the supercooled phase that the polymerization can be carried out at a very high rate without uncontrolled elevation of temperature or much formation of strain and shrinkage.

Foaming of Poly(acrylic Acid) and Poly(methacrylic Acid)

Acrylic acid and methacrylic acid hardly dissolved the solid foaming agent directly, but dissolved an aqueous solution of urea in any composition. It was found that the polymerized mixture of an acrylic acid- or methacrylic acid-urea-water solution system had a high foaming property. The results are shown in Figure 7.

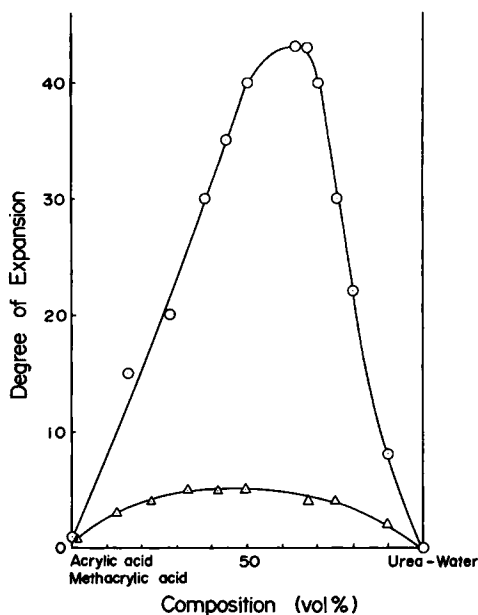


Fig. 7. Effect of the composition on the degree of expansion in acrylic acid-urea-water and methacrylic acid-urea-water systems. Polymerization: dose rate 4×10^4 r/hr, dose 7×10^4 r, temperature 25°C , in air; foaming: temperature 210°C , time 30 min; (\circ) acrylic acid-urea-water system; (Δ) methacrylic acid-urea-water system.

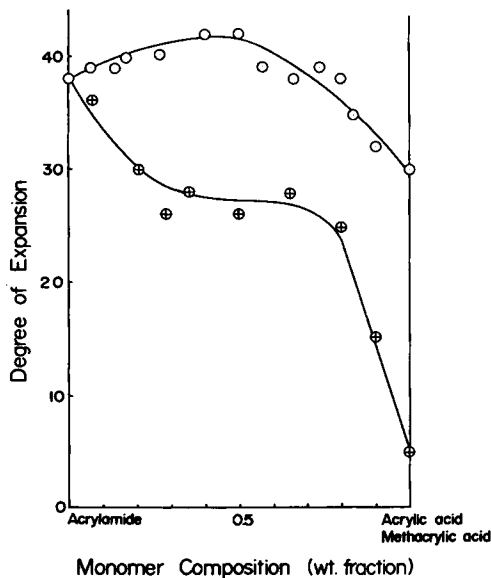


Fig. 8. Effect of monomer composition on degree of expansion in acrylamide-acrylic acid (methacrylic acid)-maleic anhydride-urea-water system. Polymerization: dose rate 4×10^4 r/hr, dose 5×10^5 r, temperature 25°C , in air; foaming: temperature 210°C , time 30 min; composition: acrylamide: maleic anhydride: urea: water = 10:6:3:3; (\circ), acrylamide-acrylic acid-maleic anhydride-urea-water system; (\oplus) acrylamide-methacrylic acid-maleic anhydride-urea-water system.

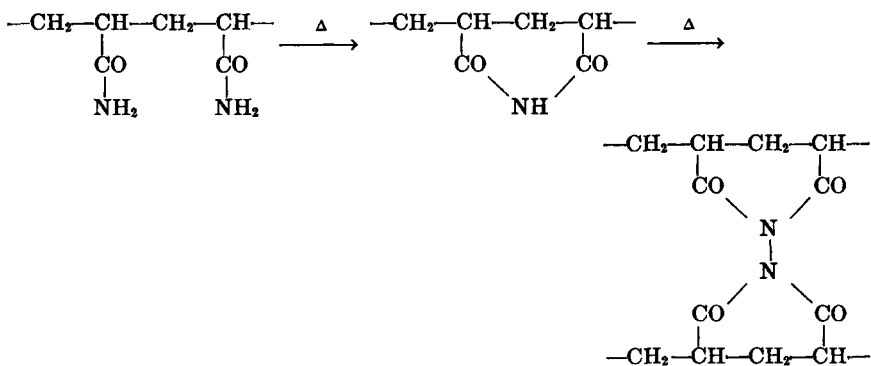
Foams of poly(acrylic acid) had continuous cell structure with rough and strong cells.

It was also found that addition of acrylic acid improved the degree of expansion and quality of polyacrylamide foam, and acrylamide-acrylic acid-maleic anhydride-urea-water system gave the highest degree of expansion and the most excellent foams. In Figure 8 relationship between composition and degree of expansion is shown.

DISCUSSION

It is known that itaconic acid decomposes giving water and citraconic anhydride at a temperature above its melting point (161°C). Citric acid decomposes to itaconic anhydride liberating water and carbon dioxide above 153°C. All effective foaming agents give gaseous products at temperatures between 130° and 200°C, which roughly agrees with the thermal softening temperature of polyacrylamide, poly(acrylic acid), and poly(methacrylic acid).

It is the characteristic of these acrylic polymers that they do not melt or flow but are only softened gradually at elevated temperatures. Moreover, heating of polyacrylamide causes an imide-type crosslinking which gives a nonsoftening three-dimensional polymer according to the following mechanism:



The content of imide crosslinking and the swelling ratio of polymer after heating were plotted as a function of heating temperature in Figure 9. The swelling ratio increased at ca. 160°C, at which polyacrylamide began to soften considerably, then it rapidly decreased at ca. 190°C to reach a constant value at 220°C. The formation of imide-crosslinking rapidly increased at 190°C in correspondence with the decrease of swelling ratio. This result was also in correspondence with the result of foaming as shown in Fig. 10, in which the active foaming began at ca. 160°C and highly expansion was completed at ca. 220°C.

From these results it can be deduced that the semithermosetting property of polyacrylamide gives a foaming capability to the foaming system. That is, a softening but nonmelting or flowing property prevents the break

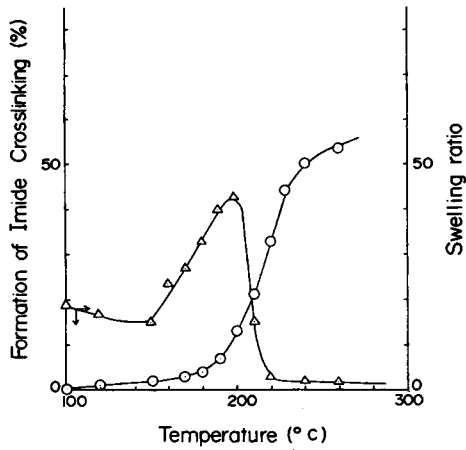


Fig. 9. Effect of heating temperature on imide crosslinking formation and swelling ratio of polyacrylamide. Polymerization of polyacrylamide: dose rate 1×10^6 r/hr, dose 5×10^6 r, temperature 25°C , in air; (○) formation of imide crosslinking; (△) swelling ratio of polymer.

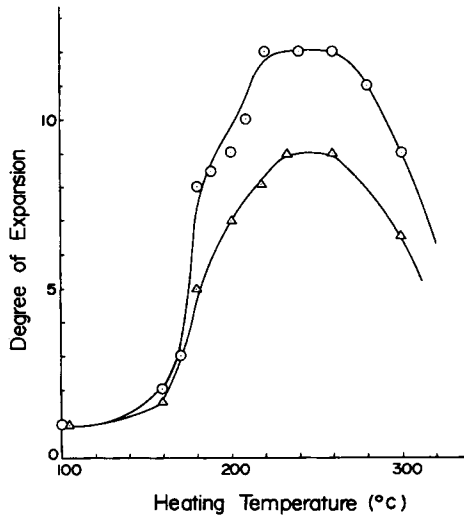


Fig. 10. Effect of heating temperature on degree of expansion. (○) Acrylamide-itaconic acid system: polymerization: dose rate 1×10^5 r/hr, dose 4×10^6 r, temperature 25°C , in air; composition: acrylamide 0.67 wt fraction. (△) Acrylamide-urea system: polymerization: dose rate 4×10^4 r/hr, dose 1×10^6 r, temperature 25°C , in air; composition: acrylamide 0.50 wt fraction.

of cell membranes and dissipation of gas to complete effective expansion, and formation of imide crosslinking improves the cell structure to prevent shrinkage of the expanded product both by cooling and excess heating. Rheological study of multicomponent foaming systems will be performed in the future to clarify the foaming mechanism.

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