Pressure-Volume Behavior and Radiation-Induced Polymerization of Acrylic Acid-Formamide Binary System at High Pressure

Tsuneo Sasuga[a]; Masaaki Takehisa[a]

[a] Takasaki Radiation Chemistry Research, Establishment Japan Atomic Energy Research Institute Takasaki, Gunma, Japan

PLEASE SCROLL DOWN FOR ARTICLE

Pressure-Volume Behavior and Radiation-Induced Polymerization of Acrylic Acid-Formamide Binary System at High Pressure

TSUNEO SASUGA and MASAAKI TAKEHISA

Takasaki Radiation Chemistry Research Establishment
Japan Atomic Energy Research Institute
Takasaki, Gunma 370-12, Japan

ABSTRACT

Pressure-volume (P-V) measurements and radiation-induced polymerization of the acrylic acid (AA)-formamide (FA) binary system were carried out at 5 to 60°C and 1 to 8000 kg/cm^2. The mixture containing 25 vol % of FA attained the glassy state at about 5000 kg/cm^2 at 20°C. The rate of polymerization at 20°C increased with increasing pressure up to 3800 kg/cm^2 and then decreased abruptly at 4000 kg/cm^2. Overall activation volume changed with pressure and abrupt change in activation volume was not observed. The polymerization proceeded in the glassy state, and the rate increased with increasing pressure. When the polymerization temperature was varied at 3000 kg/cm^2, the rate was maximum at somewhat above the glass transition temperature. These results indicate that pressure-induced short-range order of the monomer molecules does not occur in the system having weak intermolecular interaction, and glassy states produced by compression and lowering temperature differ in the physical state.

815

INTRODUCTION

Radiation-induced polymerization of N-vinyl caprolactam, vinyl acetate, and acrylic acid anhydride in the supercooled state has been reported [1-3]. Chapiro et al. and Kaetsu et al. have studied radiation-induced polymerization of glass-forming monomer systems such as the acid-amide binary system and hydroxyethyl methacrylate, and others [4-6]. These results show that the rate of polymerization is maximum at somewhat above the glass transition temperature. This has been explained on the basis of balance of retardation of termination and propagation rates at low temperature.

We have proposed that methacrylate monomers align in short range at high pressure judging from the polymerization behavior at high pressure and pressure-volume relations of as-polymerized polymer-monomer coexistence system [7-9]. Fairly strong intermolecular interaction would be required for pressure-induced short-range alignment. To verify this assumption, we studied the radiation-induced polymerization of the acrylic acid-formamide binary system at high pressure, in which intermolecular interaction is weakened by solvation. Further, we report the polymerization behavior in the glassy state produced by compression of this binary system.

EXPERIMENTAL

Extra pure grade acrylic acid (AA) was used after passage through a column containing activated aluminum oxide (activated grade I, Pharmaceutical GmbH) in order to remove a polymerization inhibitor. Reagent grade formamide (FA) was used as received.

Pressure-volume (P-V) measurements and polymerization were performed by using a glass dilatometer described in the previous paper [7]. The AA-FA mixture introduced into the dilatometer was degassed by a freeze-thaw method several times ($\sim 10^{-3}$ Torr). After degassing, mercury was introduced under vacuum. The volume change was detected from the change in height of the mercury level in the capillary of the dilatometer. The mercury level was detected electrically as described previously [7]. Pressure was applied hydrostatically by using a high-pressure apparatus reported previously [10].

Polymerization was initiated by Co-60 γ-ray irradiation after polymerization conditions were established. The dose rate was 7×10^3 rad/hr (Fricke dosimeter) in the high pressure vessel. Time-conversion curves were obtained from dilatometric reading during polymerization and final conversion by gravimetric method.

RESULTS AND DISCUSSION

P-V Relation

Figure 1 shows the P-V isotherms of AA and a mixture containing 25 vol % FA (63.65 mole % of AA) at 20°C. The specific volume for AA decreases abruptly at 800 kg/cm^2 during increasing pressure and increases abruptly at 600 kg/cm^2 during decreasing pressure. The compressibility above 1300 kg/cm^2 is of the order of 10^{-6} (kg/cm^2)$^{-1}$. Therefore, AA crystallizes at about 700 kg/cm^2.

The P-V isotherms of AA-FA mixture having various FA contents were measured, and a typical one is shown in Fig. 1. The shape of the P-V isotherm of the AA-FA mixture differs greatly from that of AA. Formamide crystallizes at about 2000 kg/cm^2 at 20°C [11], but the specific volume of the AA-FA mixture containing 25 vol % FA decreases smoothly up to 5500 kg/cm^2 and then decreases abruptly
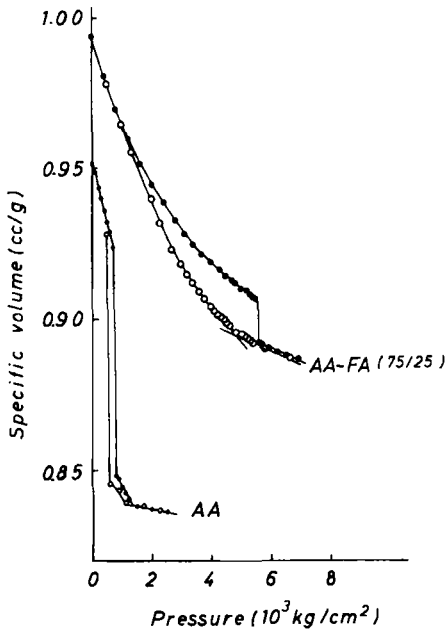
FIG. 1. P-V relations of acrylic acid and acrylic acid-formamide 75/25 vol % binary system: (●) during pressurization and (○) during depression at 20°C.

at 5600 kg/cm^2. The compressibility above 5600 kg/cm^2 is of the order of 10^{-6} (kg/cm^2)$^{-1}$. During decreasing pressure from higher pressure than 5600 kg/cm^2, an abrupt change in specific volume about 5500 kg/cm^2 is not observed, and a change in slope of P-V curve is observed at 4900 kg/cm^2. An abrupt decrease in specific volume at 5500 kg/cm^2 during increasing pressure suggests the occurrence of a first-order transition such as crystallization. This abrupt volume change, however, cannot be attributed to crystalliza-tion, for the following two reasons. Firstly, crystallization pressures of AA and FA are completely different from this pressure range. Secondly, no abrupt volume increase is observed during depression from a higher pressure than 5600 kg/cm^2. At least, however, the AA-FA mixture is solidified above 5600 kg/cm^2, since the compres-sibility above 5600 kg/cm^2 is of the order of 10^{-6} (kg/cm^2)$^{-1}$.

We have observed a similar phenomenon in the P-V study on synthetic rubbers and concluded that the abrupt volume change in Fig. 1 is attributable to the glass transition [12]. Since the glassy state and the glass transition are thermodynamically nonequilibrium in nature, the change in specific volume with temperature and pressure depends on experimental conditions, especially time scale. When the rate of pressurization is faster than the required relaxation time to a quasi-equilibrium state, the material is superheated. If a long relaxation time is required to reach the quasi-equilibrium state after each pressurization, the volume change does not entirely follow each pressurization. Consequently, the free volume is trapped, and the measured value is larger than its quasi-equilibrium volume. When the trapped volume is released at the glass transition pressure, the P-V relation shows an apparently abrupt change at the glass transi-tion pressure. Therefore, we conclude that the abrupt volume change at 5600 kg/cm^2 is attributable to the glass transition, and the AA-FA mixture is in glassy state above 5600 kg/cm^2 at 20°C. A change in slope of the P-V curve at 4900 kg/cm^2 during depression indicates that a glass-to-liquid transition occurs at this pressure. Therefore, the actual glass transition pressure is about 5200 kg/cm^2, and the system would be highly viscous even below glass transition pressure.

The specific volume of an AA-FA binary system at atmospheric pressure at 20°C increases from 0.952 to 0.994 cc/g on addition of 25 vol % of FA. Since the specific volume of FA is 0.882 cc/g, an increase in the specific volume on mixing indicates that intermolecu-lar interactions among AA-AA, AA-FA, and FA-FA is weakened. As a result of weak intermolecular interaction, the AA-FA mixture does not crystallize and attains the glassy state on compression.

Figure 2 shows the P-V isotherms of AA-FA mixture containing 25 vol % FA at 20, 35, and 50°C. The glass transition pressure shifts to higher pressure with increasing temperature. The P-V isotherm at 50°C is smooth over the whole experimental pressure range; when
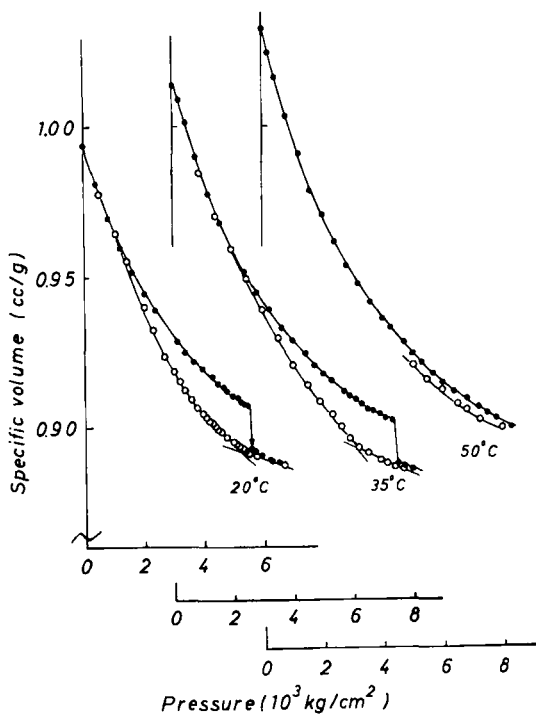
FIG. 2. P-V relations of acrylic acid-formamide 75/25 vol %
binary system at various temperatures: (•) during pressurization
and (○) during depression at 20°C.

the pressure decreases, the specific volume increases with similar
shape during increasing pressure. This result shows that the AA-FA
mixture at 50°C is in the liquid state up to 8000 kg/cm^2 .

Polymerization Behavior

Figure 3 shows the typical time-conversion curves at 20°C.
Polymerization proceeds linearly with time after a short induction
period. The irradiation was stopped at the time indicated by arrows.
Post-polymerization proceeds slowly. The time-conversion curves
at 1000 and 3800 kg/cm^2 are results where the polymerization pro-
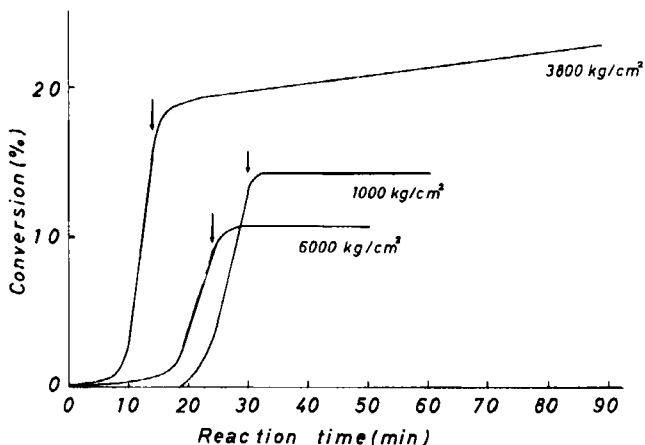ceeds in the liquid state. In the liquid state, the induction period

FIG. 3.   Typical time-conversion curves at 20°C.

shortens, and rates of in-source polymerization and post-polymerization increase with pressure. It is noticeable that polymerization proceeds even in the glassy state. The time-conversion curve at 6000 kg/cm^2 shown in Fig. 3 is typical of those in the glassy state.

Figure 4 shows the logarithm of rate of polymerization calculated from the linear part of the time-conversion curves against pressure (Van't Hoff plot). The relation between volume contraction resulting from polymerization and pressure is also shown in Fig. 4. The rate of polymerization increases with increasing pressure up to 3800 kg/cm^2 and abruptly decreases above 4000 kg/cm^2. The relation between logarithmic rate and pressure is not linear; though the overall activation volume $\Delta V^{\ddagger}$ changes with pressure, no abrupt change in the activation volume as in the polymerization of methacrylates [7-9] is observed up to 3800 kg/cm^2. We proposed that the abrupt change in activation volume is due to pressure-induced short-range alignment of monomer molecules [7-9]. It is concluded from the polymerization behavior in this work that short-range alignment of AA molecules in this system is not realized up to 3800 kg/cm^2.

The rate of polymerization of glass-forming monomers is maximum at somewhat higher than the glass transition temperature, and the rate extremely decreases or polymerization does not proceed below the glass transition temperature [3-6]. This is due to a balance between the retardation of the termination reaction with increasing viscosity and a decrease in rate of propagation with decreasing temperature [3-6].

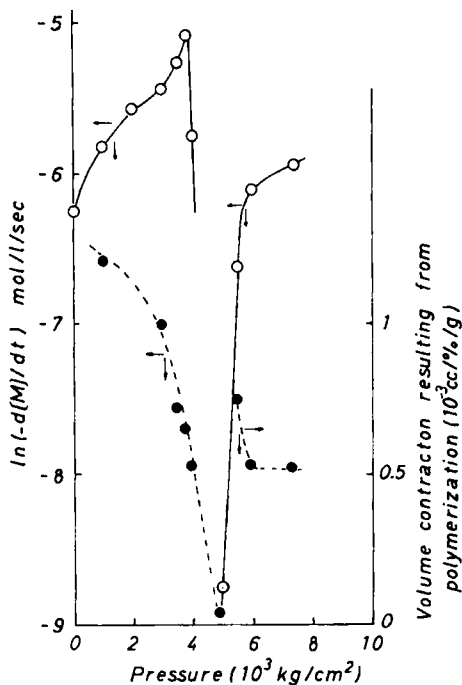On the other hand, the rate constant of propagation does not decrease

FIG. 4. Van't Hoff plot (o) and volume contraction resulting from polymerization (•) at 20°C.

energetically by isothermal compression. Therefore, the rate of polymerization does not decrease on compression. Preferably, the rate of polymerization is accelerated by retardation of the termination reaction due to the increase in viscosity by compression. The decrease in the rate above 4000 kg/cm^2 is considered to be due to a decrease in the rate of propagation by lowering of molecular mobility such as diffusion and geometry change of the monomer molecules required to addition to glowing radicals. The physical meaning differs, in spite of the fact that the apparent polymerization behavior is similar in both cases of lowering temperature and increasing pressure.

The pressure at which the rate of polymerization is minimum corresponds to the pressure giving an abrupt change in the P-V isotherms. The agreement of both pressures adds an evidence that AA-FA binary system becomes glassy state at 5000 kg/cm^2 and 20°C.
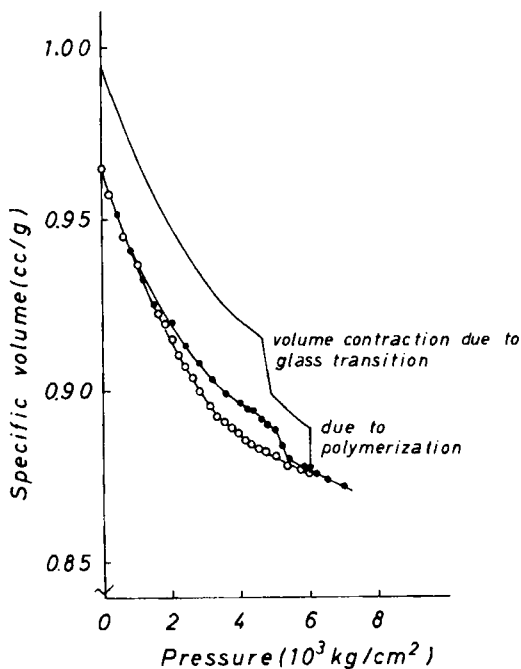
FIG. 5. P-V relations of monomer system (—) and product: (○) during depression and (●) during pressurization at 20°C.

Above the glass transition pressure, polymerization proceeds as shown in Fig. 3. In this experiment, there is a probability that the polymerization is also initiated by trapped radicals in the glass after the glass was changed to liquid by depression. The P-V measurement of the product formed by glassy-state polymerization was carried out in order to make sure that the polymerization does not proceed during depression from the glass.

Figure 5 shows the P-V isotherms of the monomer and the product formed by glassy-state polymerization at 20°C. The P-V measurements were carried out as follows: (1) the P-V isotherm of the monomer was measured up to 6000 kg/cm^2 (solid line); (2) polymerization was performed by γ-ray irradiation and then post polymerization was completed (solid line with arrow; conversion, 25.11%); (3) the P-V isotherm was measured in the course of pressure decreasing to atmospheric pressure (open circles); and (4) the P-V isotherm was measured in the course of pressure increasing up to 7000 kg/cm^2
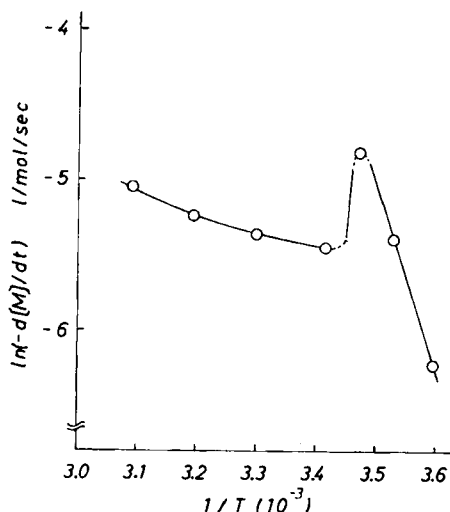
FIG. 6.   Arrhenius plot of acrylic acid-formamide 75/25 vol %
binary system at 3000 kg/cm^2.

(filled circles). The specific volume of the product increases
smoothly without marked change in the shape during depression.
During compression, the specific volume decreases abruptly at about
5000 kg/cm^2, but the specific volume at the polymerization pressure
is the same as the value before depression. If the polymerization is
initiated by trapped radicals in the course of transition from glass
to liquid, the P-V isotherm during depression is not smooth at the
transition from glass to liquid and the specific volume at the polym-
erization pressure after the second compression differs from the
value before depression. Therefore, the P-V data shown in Fig. 5
are proof of the absence of polymerization induced by trapped radical
in the course of depression.

As shown in Fig. 4, the rate of polymerization increases with
pressure even in the glassy state. In the glassy state attained by
lowering temperature, the propagation reaction which has an activa-
tion energy is retarded strongly, while in the glassy state reached
by isothermal compression, the propagation reaction is not retarded
energetically because enough thermal energy is supplied to activate
the molecules. Therefore, polymerization can proceed in the glassy
state by compression. The increase in the rate with pressure in the
glassy state would involve extreme retardation of the termination
reaction.

The volume contraction resulting from polymerization decreases with increasing pressure in the liquid state. The real volume contraction during propagation may be represented as follows: $A(l_{VW} - l_{C-C} + l_{C=C})$ where A, l_{VW}, l_{C-C}, and $l_{C=C}$ are the real cross section of the monomer, the van der Waals' radii, the C–C bond length, and the C=C bond length, respectively. Because the real volume contraction is hardly changed by compression in this work, the apparent volume contraction resulting from polymerization is due to decrease in free volume of monomer system.

The volume contraction resulting from polymerization in glassy state increases again. This cannot be interpreted by a decrease in free volume of monomer system, since free volume does not exist in glassy state. This phenomenon is not clearly interpreted now.

Figure 6 shows an Arrhenius plot of the rate of polymerization of the mixture containing 25 vol % of FA at 3000 kg/cm^2. The rate gradually decreases with decreasing temperature and is a maximum at 15°C. Below the temperature giving the maximum, the rate markedly decreases with decreasing temperature. This polymerization behavior resembles that of glass-forming monomers at atmospheric pressure [5, 6] and is interpreted on the basis of the balance of decrease in rates between propagation and termination with decreasing temperature. The glass transition temperature at 3000 kg/cm^2 extrapolated from the data in Fig. 2 is about 0°C and the activation energy below 15°C is 24.6 kcal/mole.

REFERENCES

[1] G. Y. Hardy, K. Nyitray, G. Kevacs, N. Federova, and I. Varga, Proceedings on Tihany Symposium on Radiation Chemistry, Hungary, 1962.

[2] I. M. Barkalov, V. I. Goldanskii, N. S. Enikolopov, S. F. Trekhova, and G. M. Trofimova, Dokl. Akad. Nauk SSSR, 147, 395 (1962).

[3] J. B. Lando and H. Morawetz, J. Polym. Sci., C4, 789 (1962).

[4] I. Kaetsu, K. Hayashi, and S. Okamura, J. Appl. Polym. Sci., 11, 1101 (1967).

[5] A. Chapiro, L. Perec, and S. Russo, Eur. Polym. J., 10, 71 (1974).

[6] A. Chapiro and R. Gouloubandi, Eur. Polym. J., 10, 1159 (1974).

[7] T. Sasuga and M. Takehisa, J. Macromol. Sci.–Chem., A12, 1307 (1978).

[8] T. Sasuga and M. Takehisa, J. Macromol. Sci.–Chem., A12, 1321 (1978).

[9] T. Sasuga and M. Takehisa, J. Macromol. Sci.–Chem., A12, 1333 (1978).

[10] T. Sasuga, N. Morishita, A. Udagawa, Y. Kusama and M. Takehisa, J. Polym. Sci. Polym. Chem. Ed., 14, 2575 (1976).

[11] K. E. Weale, Chemical Reaction at High Pressure, E. and F. N. Spon, London, 1967.

[12] T. Sasuga and M. Takehisa, J. Macromol. Sci.–Phys., B13, 215 (1977).