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Radiation-Induced Polymerization of Acrylic Esters at High Pressure and Pressure-Volume Behavior of Polymer-Monomer Coexistence System as Polymerized

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ABSTRACT

Pressure-volume (P-V) behavior and radiation-induced polymerization of methyl and n-butyl acrylic esters (MA and BA, respectively) were studied up to 7000 kg/cm^2 at 20°C . The P-V isotherms broke at 1900 and 1200 kg/cm^2 for MA and BA, respectively. The P-V isotherm for MA was not smooth in the pressure range between 3500 and 4000 kg/cm^2 . The polymerization behavior varied with change in the P-V behavior; the polymerization rates were maximum at 1800 kg/cm^2 for MA and 1000 kg/cm^2 for BA, and then minimum at 1900 kg/cm^2 for MA and 1100 kg/cm^2 for BA. The polymerization rates increased again above the pressures giving the minimum rates up to about 3000 kg/cm^2 . Above 3000 kg/cm^2 the pressure dependence of the rates decreased up to 4000 and 4500 kg/cm^2 for MA and BA, respectively. Above these pressures, the pressure dependence of polymerization rates increased again. The P-V isotherms of as-polymerized polymer-monomer coexistence systems showed characteristic behavior near the polymerization pressure. From a comparison of these polymerizations and P-V behavior with those of methacrylic esters, we propose that

acrylic esters align at high pressure and that freedom of rotation of ester group plays an important role in the mode of pressure-induced alignment of monomer molecules.

INTRODUCTION

We have studied the radiation-induced polymerization at high pressure and pressure-volume (P-V) behavior of monomers and as-polymerized polymer-monomer coexistence systems of methacrylic esters [1-3] and acrylonitrile [4]. The P-V isotherms of methacrylic esters are monotonically smooth curves, but the pressure dependence of the polymerization rates and the P-V isotherms of the coexistence systems show characteristic behavior in specific pressure regions. From these results, we proposed that such monomer molecules align at high pressure even in a liquid state and that the planar structure of the vinyl group plays an important role in pressure-induced alignment. On the other hand, the P-V isotherms of acrylonitrile show characteristic features at specific pressure regions, and the pressure dependence of the rate changes, corresponding to the change in P-V behavior of the monomer. The result shows that not only the planar structure of the vinyl group but also the structure of the substituent group plays an important role in pressure-induced alignment of monomer molecules.

We have studied the effect of size of substituent ester groups of methacrylates on pressure-induced alignment [3]. In this paper we report the effect of the α -methyl group on pressure-induced alignment.

EXPERIMENTAL

Extra pure grade methyl acrylate (MA) and n-butyl acrylate (BA) were used after passage through a column containing activated aluminum oxide in order to remove polymerization inhibitor. A glass dilatometer, reported in a previous paper [1], was used for P-V measurement and polymerization. The purified monomer was degassed in the dilatometer by the freeze-thaw method ($\sim 10^{-3}$ Torr) several times, and then mercury was introduced under vacuum.

The application of pressure to the dilatometer was performed hydrostatically by using a high pressure apparatus described elsewhere [5]. The change of mercury level in the capillary caused by a change in volume of sample due to pressurization and polymerization was detected electrically as reported previously [1, 6]. The calculation of specific volume from the dilatometric reading was performed by the same method reported previously [6]. The rate of pressurization for P-V measurement was about 50 kg/cm²-min.

Polymerization was carried out at 20°C with γ -rays from a ^{60}Co source at a dose rate of 7×10^3 rad/hr (for Fricke solution). Polymerization was started after temperature and pressure became constant. Because post-polymerization was not negligible at high pressure, the sample was allowed to stand for about 1 hr at the polymerization conditions. A time-conversion curve was obtained from the time-dilatometric reading curve and the final polymer yield after drying under vacuum. The rate of polymerization was calculated from linear part of the time-conversion curves.

RESULTS

Polymerization Behavior

Figure 1 shows the P-V isotherm of MA and Van't Hoff plot of the polymerization rates at 20°C. The specific volume decreases smoothly with increasing pressure up to 1600 kg/cm², and the compressibility increases slightly up to 1900 kg/cm². Then the compressibility becomes very small in the pressure range between 1900 and 2100 kg/cm² [9.6×10^{-6} (kg/cm²)⁻¹]. Above 2100 kg/cm² the compressibility increases to the order of 10^{-5} (kg/cm²)⁻¹ again and changes slightly in the pressure range between 3400 and 4000 kg/cm².

The rate of polymerization increases with pressure up to 1800 kg/cm² with activation volume ΔV^\ddagger of -21.4 cm³/mole and then decreases sharply at 1900 kg/cm². The pressures giving the maximum and minimum rates correspond to the pressure giving a break in the P-V isotherm. Above 1900 kg/cm² the rate increases with pressure up to 2700 kg/cm² with ΔV^\ddagger of -22.9 cm³/mole. The rate of polymerization hardly depends on pressure in the pressure range of 2700 to 4000 kg/cm². In this pressure range ΔV^\ddagger is -3.6 cm³/mole. A large pressure dependence of rate is observed again above 4000 kg/cm² ($\Delta V^\ddagger = -12.8$ cm³/mole).

Thus, pressure region can be divided based on the P-V and polymerization behavior. We termed these pressure regions as regions 1, 2, 3, and 4 from low to high pressure for convenience and indicate these regions in Fig. 1.

Figure 2 shows the P-V isotherm of BA and Van't Hoff plot of the polymerization rates at 20°C. The isotherm changes in the same manner for MA, but the pressure range giving compressibility of the order of 10^{-6} (kg/cm²)⁻¹ is 1200 to 1500 kg/cm². The Van't Hoff plot shows a shape similar to that of MA. The rate of polymerization becomes maximum at 1000 kg/cm²; the rate increases with increasing pressure in the pressure range of 1200 to 3000 kg/cm². The pressure dependence of the rate decreases in the pressure range between 3000 and 4600 kg/cm², and the pressure dependence increases again above 4600 kg/cm². The values of ΔV^\ddagger are -21.0 cm³/mole in the pressure range of 1 to 1000 kg/cm², -21.2 cm³/mole in the

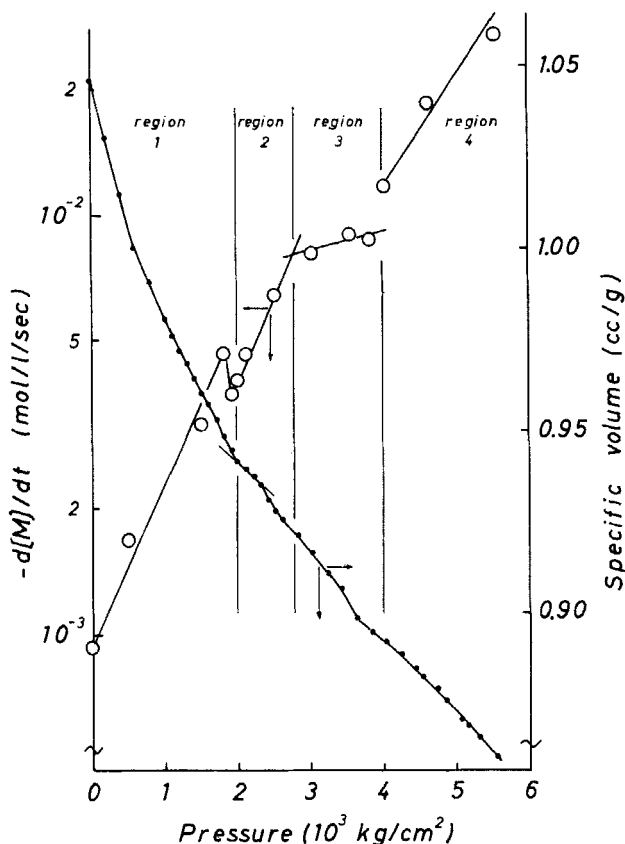


FIG. 1. P-V isotherms of the monomer and Van't Hoff plot of the polymerization rate for MA.

pressure range of 1200 to 3000 kg/cm^2 , $-5.7 \text{ cm}^3/\text{mole}$ in the pressure range of 3000 to 4600 kg/cm^2 , and $-11.4 \text{ cm}^3/\text{mole}$ above 4600 kg/cm^2 . The pressures giving the maximum and minimum rates shift to lower pressure and the pressure range giving low pressure dependence on the rate shifts to higher pressure than those of MA. Pressure regions giving change on P-V and polymerization behavior are divided as regions 1, 2, 3, and 4 in the same manner for MA.

P-V Behavior of the Coexistence System

P-V measurements of "coexistence system" which consists of as-polymerized polymer and residual monomer were carried out as follows: (1) the P-V isotherm for the monomer was measured up to

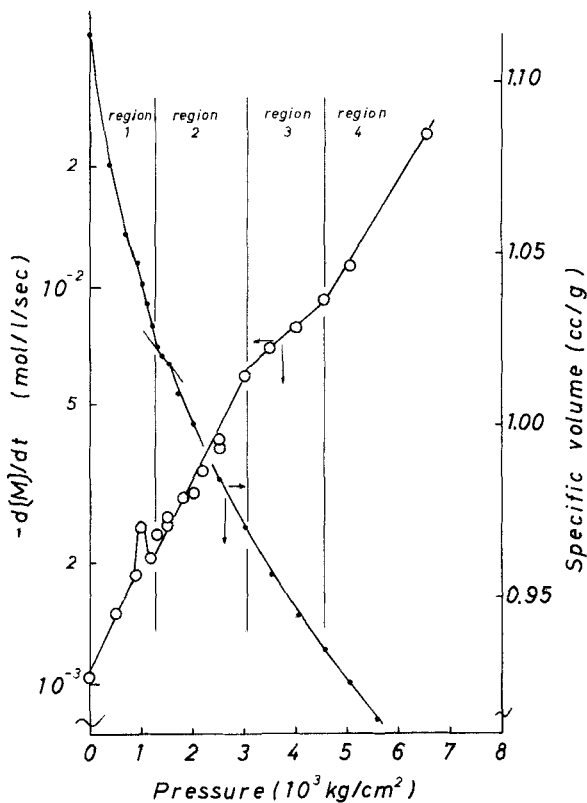


FIG. 2. P-V isotherm of the monomer and Van't Hoff plot of the polymerization rate for BA.

polymerization pressure (solid line in Figs. 3-7); (2) at the polymerization pressure, the sample was irradiated for a suitable time to obtain 10 to 20% conversion (solid line with arrow); (3) after post-polymerization was completed, the P-V isotherm was measured during decreasing pressure to atmospheric pressure (open circles in Figs. 3-7); (4) the P-V isotherm was measured during increasing pressure (filled circles in Figs. 3-7).

Figure 3 shows P-V isotherms of the coexistence systems polymerized at 2000, 2500, and 3000 kg/cm² for MA. The P-V isotherm polymerized at 2000 kg/cm² is smooth throughout the experimental pressure range. The P-V isotherms polymerized at 2500 and 3000 kg/cm² show a characteristic feature at the pressure between the polymerization pressure and 500 kg/cm² lower than that; in this pressure range, compressibilities are of the order of 10⁻⁶ (kg/cm²)⁻¹.

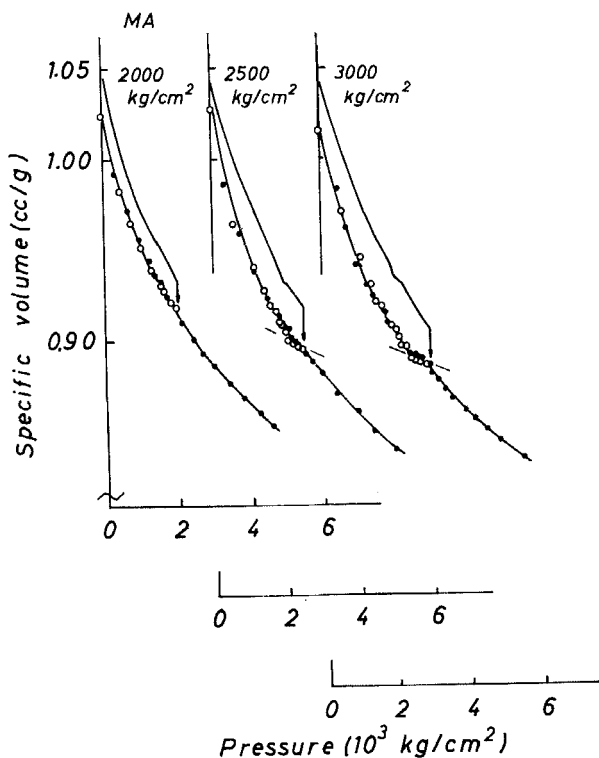


FIG. 3. P-V isotherms of the coexistence systems as polymerized at 2000, 2500, and 3000 kg/cm^2 for MA. (—) monomer compression; (→) volume contraction by polymerization; (○) specific volume during decompression, (●) specific volume during compression.

Above the polymerization pressure, compressibilities are of the order of $10^{-5} (\text{kg/cm}^2)^{-1}$ again. Polymerization pressures of 2500 and 3000 kg/cm^2 correspond to region 2 in Fig. 1.

Figure 4 shows P-V isotherms of the coexistence systems polymerized at 3300, 3700, and 4000 kg/cm^2 for MA. The P-V isotherms of the coexistence systems polymerized at 3300 and 3700 kg/cm^2 are smooth again. The pressures of 3300 and 3700 kg/cm^2 correspond to region 3 in which the pressure dependence on the rate is very low.

The P-V isotherm of the coexistence system polymerized at 4000 kg/cm^2 shows characteristic feature again in the pressure range between the polymerization pressure and 500 kg/cm^2 lower than that. The pressure of 4000 kg/cm^2 is in the region 4 in Fig. 1.

Figures 5, 6, and 7 show the P-V isotherms of the coexistence

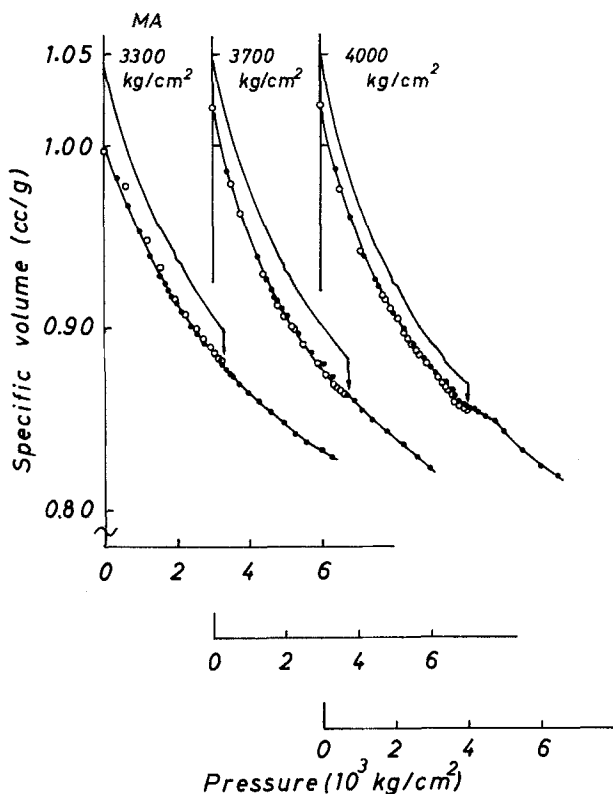


FIG. 4. P-V isotherms of the coexistence systems as polymerized at 3300, 3700, and 4000 kg/cm^2 for MA. Symbols are the same as in Fig. 3.

systems for BA. The correlations between P-V behavior and each pressure region agree with those for MA. The P-V isotherm of the coexistence system polymerized at 700 kg/cm^2 (region 1) is smooth, but the specific volume of the coexistence system polymerized at 1500 kg/cm^2 (region 2) tends to scatter around the polymerization pressure. The P-V isotherms of the coexistence systems polymerized at 2000, 2500, and 3000 kg/cm^2 (region 2) clearly show characteristic features. A characteristic feature disappears in the P-V isotherm of the coexistence system polymerized at 3900 kg/cm^2 (region 3) and appears again in the P-V isotherm polymerized at 5500 kg/cm^2 (region 4).

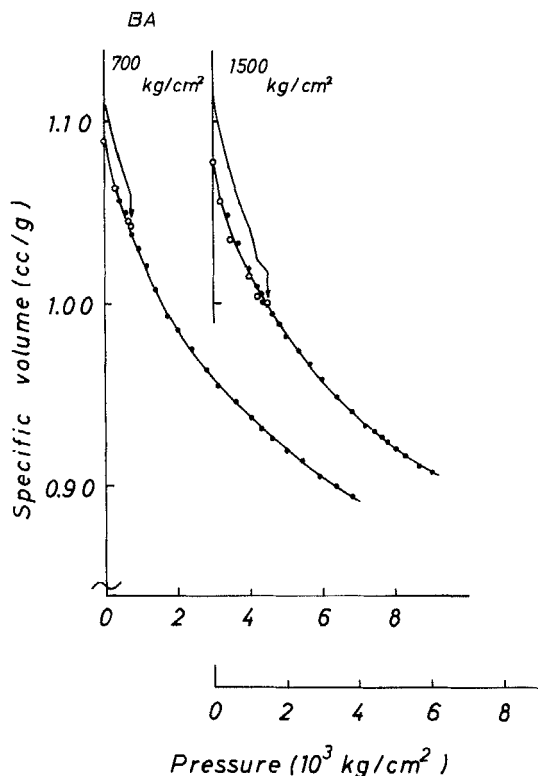


FIG. 5. P-V isotherms of the coexistence systems as polymerized at 700 and 1500 kg/cm^2 for BA. Symbols are the same as in Fig. 3.

DISCUSSION

As mentioned above, polymerization and P-V behavior of the monomer and the coexistence system are characteristic in each pressure region. This indicates that the physical state of the monomer system varies in each pressure region. A difference in physical state may be a difference in packing of monomer molecules in liquid state, because other physical states such as electronic state and molecular structure may not be changed by pressure in this work. The abrupt change in compressibility of monomer directly reflects a change in molecular packing. Low compressibilities about 2000 and 1200 kg/cm^2 for MA and BA, however, are not attributable to solidification of the monomer system, because compressibilities increase above these pressures again and polymerization proceeds at these pressures.

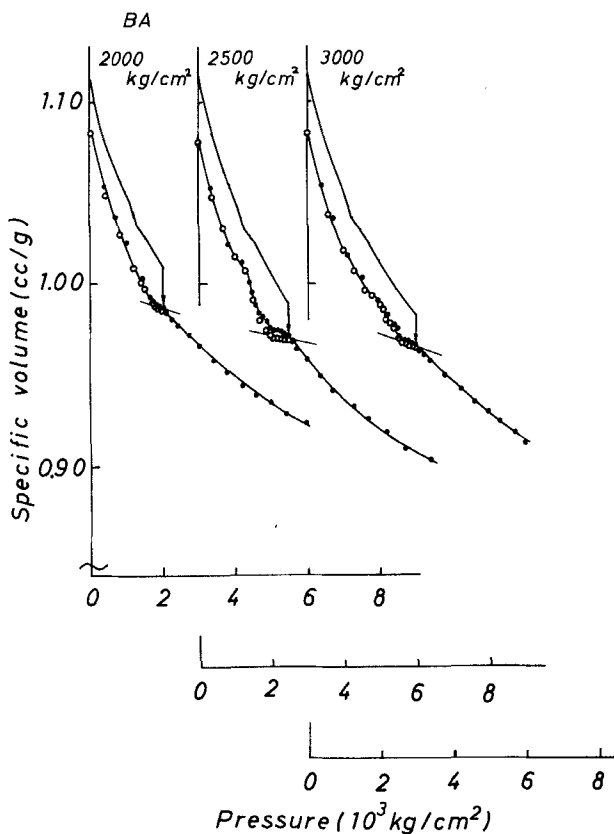


FIG. 6. P-V isotherms of the coexistence systems as polymerized at 2000, 2500, and 3000 kg/cm^2 . Symbols are the same as in Fig. 3.

Abrupt changes in compressibility and polymerization rate were not observed at the same pressure region in the case of methacrylic esters [1-3], indicating that molecular packing of methacrylic esters does not change in this pressure region. Molecular packing which appears in this pressure region may be influenced by molecular structure. The α -methyl group may influence molecular packing in this region, because the difference between the structure of the methacrylic ester and the acrylic ester is the presence of an α -methyl group.

The rates of polymerization change at the boundary between regions 1 and 2, also suggesting that molecular packing of the monomer differs in the two regions. Polymerization and P-V behavior suggest that an alignment of monomer molecules occurs in region 2. The activation

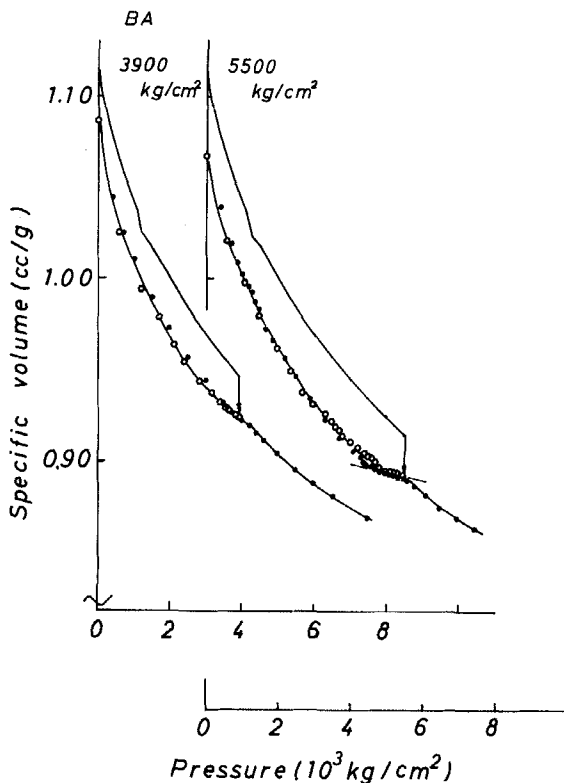


FIG. 7. P-V isotherms of the coexistence systems as polymerized at 3900 and 5500 kg/cm^2 . Symbols are the same as in Fig. 3.

volume, however, does not change greatly in the two regions. Because activation volume corresponds to volume contraction in the transition from original to activated states, volume contractions required in the transition are the same in regions 1 and 2. This result suggests that the vinyl group which is responsible for polymerization is independent of molecular alignment in pressure region 2.

The P-V isotherms of the coexistence systems polymerized in the region 2 show a characteristic feature. This characteristic feature in P-V isotherms may involve alignment of monomer molecules. As reported in the preceding papers [1-4], when propagation proceeds with preservation of an alignment of monomer molecules, the interaction among monomer molecules is converted to a strong interaction between as-polymerized polymer chains and surrounding monomer molecules. As a result of the strong interaction between as-polymerized polymer chains and monomer molecules, a structure with low compressibility arises about the polymerization pressure.

The absolute value of activation volume for acrylic esters in region 3 are very small. Those for methacrylic esters were also very small in the pressure region corresponded to the region termed region 3 in this paper. These results indicate that a volume contraction required in the transition to activated state hardly exists in the pressure region 3 for both esters. If vinyl group is involved in an alignment of monomer molecules in region 3, the volume contraction resulting from the transition to activated state may be hardly changed by compression until the alignment is destroyed by compression. The absolute value of activation volume increases again in pressure region 4. On the boundary between regions 3 and 4, alignment of monomer molecules with vinyl group may be destroyed by compression.

The coexistence system for methacrylic esters polymerized in the pressure range corresponding to region 3 showed characteristic P-V feature [2, 3]. On the other hand, the coexistence systems for acrylic esters polymerized in region 3 do not show a characteristic P-V feature, in spite of the existence of a strong interaction between as-polymerized polymer chains and surrounding monomer molecules. This may be because the coexistence systems for acrylic esters do not form a rigid structure due to the freedom of rotation of the ester group. On the other hand, coexistence systems of methacrylic esters form a rigid structure under suitable condition, because the ester group cannot rotate freely due to structural hindrance of the α -methyl group.

P-V and polymerization behavior are similar in pattern in methacrylic and acrylic esters but differ in detail. We now consider that the difference between the two esters is due to the ability of the ester group to rotate.

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