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Pressure-Volume Behavior of PMMA-MMA Coexistence System as Polymerized at High Pressure

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ABSTRACT

The pressure-volume (P-V) isotherms were measured for the poly(methyl methacrylate) (PMMA)-methyl methacrylate (MMA) coexistence system polymerized by γ -ray irradiation at various pressures. The P-V isotherm of the coexistence system polymerized below 3000 kg/cm^2 was similar to that of the monomer. The specific volume of the coexistence system polymerized above 3000 kg/cm^2 hardly changes in the pressure range between 3000 kg/cm^2 and the polymerization pressure when measurements are made with successively decreasing or successively increasing pressures. The compressibility was of the order of $10^{-6} (\text{kg/cm}^2)^{-1}$ in this pressure range. This indicated that the coexistence system polymerized above 3000 kg/cm^2 behaves like a solid in this pressure range. Above the polymerization pressure, the compressibility was of the order of $10^{-5} (\text{kg/cm}^2)^{-1}$, indicating that the coexistence system behaves as liquid. We concluded that the solid-like behavior of the coexistence system polymerized above 3000 kg/cm^2 is caused by a strong interaction between as-polymerized polymer chains and monomer molecules due to propagation through monomer clusters having short-range order. The present results support that MMA is aligned in short-range order at suitable pressure and temperature as reported in the preceding paper.

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INTRODUCTION

We have proposed, from the study of the radiation-induced polymerization of MMA at high pressure [1], that monomer molecules take a certain alignment above 3000 kg/cm^2 at 20°C . The alignment of reactant molecules is believed to play an important role in chemical reaction [2, 3]. There have been, however, few experimental data on liquid-liquid transition at high pressure.

If the polymerization proceeds in aligned monomer molecules, evolution of a strong interaction between as-polymerized polymer chains and monomer molecules can be expected, because propagation proceeds with preservation of the monomer alignment. On the basis of this viewpoint, we studied the P-V relations of MMA, PMMA dissolved in MMA, and the PMMA-MMA system as polymerized at various pressures by γ -irradiation.

EXPERIMENTAL

Pressure-volume (P-V) isotherms were measured for polymer solution in a monomer "mixed system" and a polymer-monomer system (as-polymerized coexistence system). The PMMA for P-V measurements of the mixed system was commercially obtained PMMA (Wako Junyaku Co., Ltd., $\bar{M}_n = 4.0 \times 10^4$) and radiation-induced polymerized PMMA at atmospheric pressure ($\bar{M}_n = 3.4 \times 10^5$).

Two types of glass dilatometer were employed for P-V measurements; the one used for measurement of mixed system was the same as reported previously [4], and the other for P-V measurements of the coexistence system was the same as reported in the preceding paper [1].

The dilatometers were pressurized in the high pressure apparatus as reported elsewhere [5].

The volume change was detected from the height of mercury in a capillary of the dilatometer. The height of mercury was detected electrically, and calibration of specific volume from dilatometric data was carried out by the same method as in a previous paper [4].

Sample preparations for the P-V measurement of the coexistence systems were the same as reported in the preceding paper [1]. Polymerization and P-V measurements were carried out at 20°C .

The procedure of P-V measurement of the coexistence system was as follows: (1) The P-V isotherm for the monomer was measured up to polymerization pressure. (2) At the polymerization pressure, the sample was irradiated by Co-60 γ -rays (dose rate $7 \times 10^3 \text{ rad/hr}$) for a suitable time (usually 6 to 20 min) to obtain 10 to 20% conversion.

After the irradiation the samples were allowed to stand for about 1 hr at the polymerization pressure to complete the post-polymerization (ca. 2 to 3%). (3) The P-V isotherm for the coexistence system was measured by lowering the pressure to atmospheric pressure at 100 kg/cm² intervals.

(4) The P-V isotherm was measured by elevating pressure up to 8000 kg/cm².

RESULTS

Mixed System

Figure 1 shows the P-V isotherms for MMA and PMMA-MMA mixed systems with different polymer contents and different molecular weights of the polymers. The specific volume decreases smoothly with increasing pressure and abruptly decreases at 5500 to 6000 kg/cm². This abrupt decrease in the specific volume is due to crystallization of MMA, indicating that the mixed system also crystallizes in spite of the presence of the polymer.

When two P-V isotherms for the mixed system containing about 5% polymer are compared, the P-V isotherms are similar. This shows that a difference in molecular weight of the polymer does not affect the P-V isotherms. Compressibility does not change with the polymer content, but the volume contraction at crystallization pressure decreases with increasing polymer content. The compressibility of the mixed system is larger than that of monomer in the high pressure region.

It is proved from Fig. 1 that the P-V isotherms for the mixed system are similar to the P-V isotherm of MMA, except for the slight change in compressibility and volume contraction at crystallization pressure from that for MMA.

Coexistence System

Figures 2-4 show the P-V isotherms of the PMMA-MMA coexistence system polymerized at various pressures. The solid line shows monomer compression, the vertical line with arrow shows volume contraction by polymerization, the filled circles show specific volumes in lowering pressure from the polymerization pressure to atmospheric pressure, and the open circles show specific volume in elevating pressure from atmospheric pressure again. The monomer conversions are indicated.

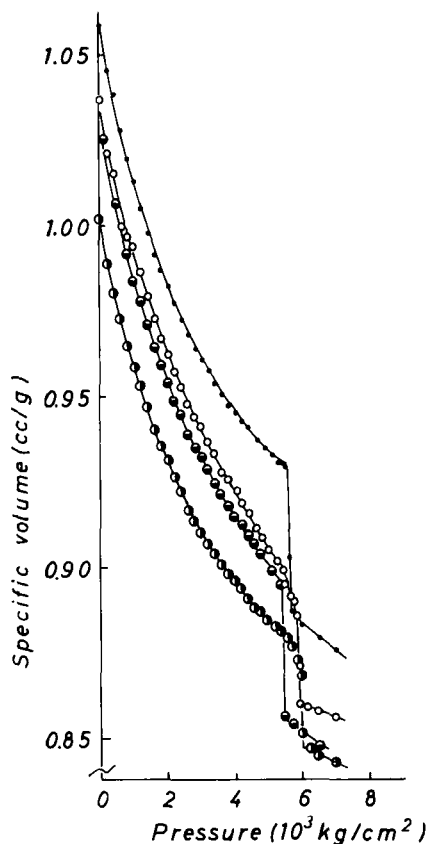


FIG. 1. P-V isotherms of the mixed system: (●) monomer; (○) polymer content 5% ($\bar{M}_n = 4.0 \times 10^4$); (◐) polymer content 5% ($\bar{M}_n = 3.4 \times 10^5$); (◑) polymer content 17% ($\bar{M}_n = 4.0 \times 10^4$).

The P-V isotherms for the coexistence system polymerized at 1000 and 2300 kg/cm^2 (Fig. 2) show a slight change in compressibility at the polymerization pressure in measurement by elevating pressure, but the P-V isotherms are regarded as smooth up to the pressure giving crystallization of the monomer.

In the case of the coexistence system polymerized at 3300 and

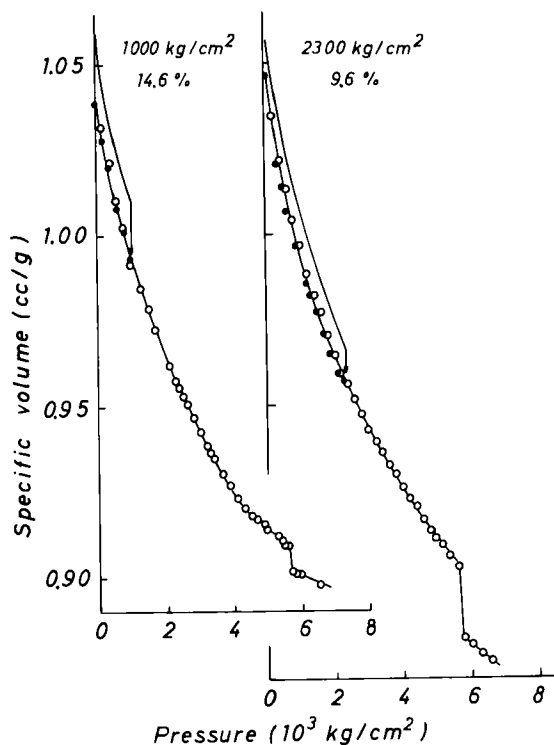


FIG. 2. P-V isotherms of the coexistence systems polymerized at 1000 and 2300 kg/cm^2 : (—) monomer compression; (\downarrow) volume contraction by polymerization; (\bullet) specific volume on measurement with lowering pressure; (\circ) specific volume on measurement with increasing pressure.

4000 kg/cm^2 (Fig. 3), the specific volume changes unusually in the pressure range between 3000 kg/cm^2 and the polymerization pressure in measurement with lowering pressure. The compressibilities just below this pressure range are about 2.4×10^{-5} and 2.7×10^{-5} $(\text{kg}/\text{cm}^2)^{-1}$, but those for the pressure range between 3000 kg/cm^2 and the polymerization pressure are 3.9×10^{-6} and 4.8×10^{-6} $(\text{kg}/\text{cm}^2)^{-1}$ for the coexistence systems polymerized at 3300 and 4000 kg/cm^2 , respectively. A compressibility of the order of 10^{-6} $(\text{kg}/\text{cm}^2)^{-1}$ means that the coexistence system polymerized at 3300 and 4000 kg/cm^2 shows solid-like behavior in the pressure range between 3000 kg/cm^2 and the polymerization pressure.

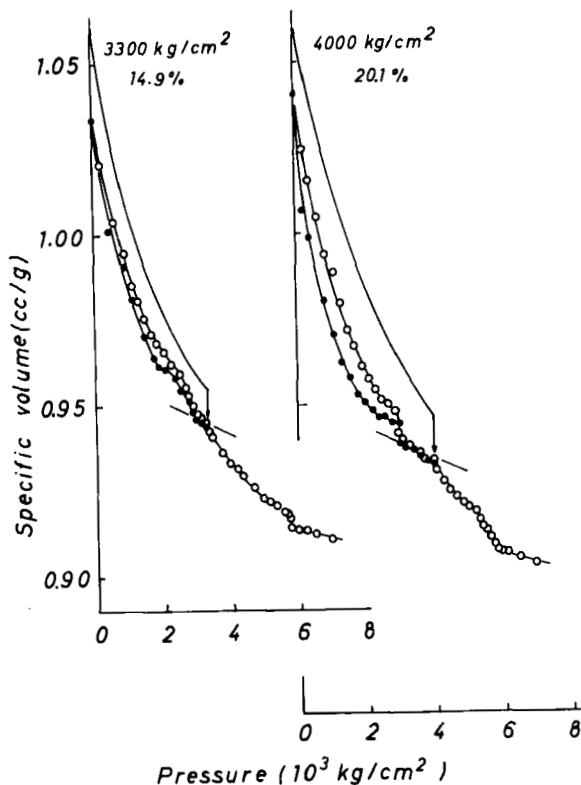


FIG. 3. P-V isotherms of the coexistence systems polymerized at 3300 and 4000 kg/cm^2 ; symbols are the same as in Fig. 2.

The compressibility increases to the order of $10^{-5} (\text{kg/cm}^2)^{-1}$ again above the polymerization pressure in the measurement with elevating pressure, indicating that the coexistence system behaves as liquid to the crystallization pressure of the monomer.

The volume contraction near the pressure range giving crystallization of the monomer is also observed in all the coexistence systems. The magnitude of the volume contraction seems to be related to the polymer content, but the magnitude is somewhat smaller than that for the mixed system.

The P-V isotherm in the case of the PMMA-MMA coexistence system polymerized at 5200 kg/cm^2 (Fig. 4), which is just below crystallization pressure of the monomer, shows different behavior from the others in measurement at lowering and elevating pressures.

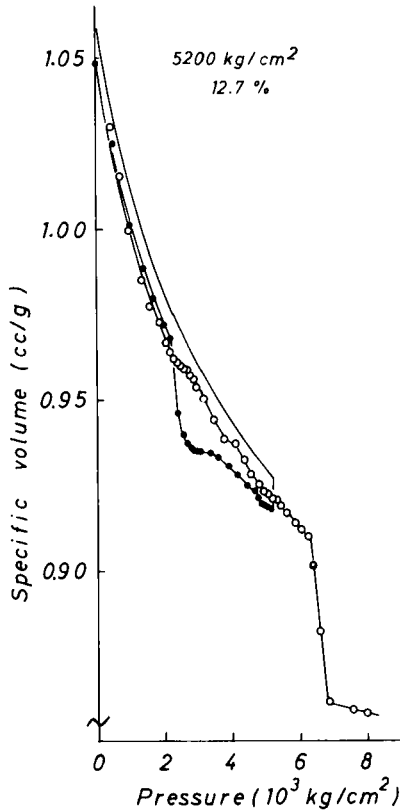


FIG. 4. P-V isotherm of the coexistence system polymerized at 5200 kg/cm^2 ; symbols are the same as in Fig. 2.

Volume expansion in the measurement with lowering pressure is relatively large in the pressure range of 5200 to 3400 kg/cm^2 and is very small in the pressure range of 3400 to 2700 kg/cm^2 . The volume increases abruptly at a pressure of 2500 to 2200 kg/cm^2 .

With the elevating pressure measurement series, the P-V isotherm shows behavior different from that in measurement with lowering pressure. The overall feature of the P-V isotherm in measurement at elevating pressure is smooth and resembles that for the mixed system.

The volume contraction at the crystallization pressure of the monomer is noticeable. The volume contraction is large as is the

one for the mixed system in spite of similar conversions with other coexistence systems.

DISCUSSION

Coexistence System Polymerized below 3000 kg/cm²

The overall feature of the P-V isotherm for the coexistence system polymerized below 3000 kg/cm² resembles that for the mixed system, except for the magnitude of the volume contraction around the crystallization pressure of the monomer. This magnitude is smaller than that for the mixed system containing 17% polymer (cf. Fig. 1). The difference in the magnitude of the volume contraction is due to difference in conformation of polymer chains in the monomer and the difference in interaction between polymer chains and monomer molecules. The interaction between polymer chains and monomer molecules in the coexistence system is considered to be stronger than that in the mixed system. The conformation of as-polymerized polymer chains is shaped during propagation by preserving the interaction between the monomer units in as-polymerized polymer chains and the surrounding monomer molecules, with the result that the polymer chains may be more extended in monomer than in the mixed system.

The interaction between as-polymerized polymer chains and the monomer molecules in the coexistence system prevents crystallization of the system; on the contrary, the mixed system crystallizes easily, and the monomer molecules rarely interact with polymer chains.

The slight change in compressibility with the polymerization pressure may also show an interaction between polymer chains and monomer molecules.

Coexistence System Polymerized at 3300 and 4000 kg/cm²

These two coexistence systems show a solid-like behavior in the pressure range between 3000 kg/cm² and the polymerization pressure. The feature of P-V isotherms at 3000 kg/cm² seems to be the liquid-solid transition of the monocomponent liquid. The fact that the system consisted of as-polymerized polymer and monomer behaves as a monocomponent system indicates the existence of a strong interaction between as-polymerized polymer chains and monomer molecules.

The pressure of 3000 kg/cm² agrees well with the pressure giving

the break in the Van't Hoff plot for polymerization of MMA [1]. In the preceding paper, we proposed that polymerization above 3000 kg/cm^2 must proceed with fairly limited aligned monomer molecules from the difference in activation volume below and above 3000 kg/cm^2 . If the propagation proceeds with preservation of alignment of monomer molecules, the interaction among monomer molecules is converted to a strong interaction between as-polymerized polymer chains and monomer molecules. Due to this strong interaction, the coexistence system behaves as a monocomponent system from 3000 kg/cm^2 up to the polymerization pressure.

A compressibility of the order of $10^{-5} (\text{kg/cm}^2)^{-1}$ above the polymerization pressure means that the strong interaction is destroyed by compression. The interaction in the coexistence system polymerized above 3000 kg/cm^2 , however, remains above the polymerization pressure, since the magnitude of volume contraction near the crystallization pressure of monomer is smaller than that for the mixed system (cf. Fig. 1).

Coexistence System Polymerized at 5200 kg/cm^2

The P-V isotherm of the coexistence system polymerized at 5200 kg/cm^2 behaves differently when the measurements are made by a series of decreasing or increasing pressures. The hysteresis in P-V measurement of MMA indicates that MMA molecules are in a supercooled state in the pressure range between 5000 and 5600 kg/cm^2 [1]. Since the supercooled state is thermodynamically a nonequilibrium state, aggregation of monomer molecules may differ from that at 3300 or 4000 kg/cm^2 . The P-V feature in measurement with lowering pressures from the polymerization pressure is a reflection of an interaction between as-polymerized polymer chains and monomer molecules which brought about the polymerization in the supercooled liquid state.

The large volume expansion at a pressure of 2500 to 2200 kg/cm^2 in lowering pressure and the large magnitude of volume contraction above the crystallization pressure of the monomer indicate that the interaction existing between as-polymerized polymer chains and monomer molecules at the polymerization pressure is destroyed at 2500 to 2200 kg/cm^2 with lowering pressure. The conformation of as-polymerized polymer chains after lowering pressure to atmospheric pressure is considered as same as that for the mixed system. These considerations indicate that the alignment of monomer molecules in a supercooled state differs from that at 3300 and 4000 kg/cm^2 .

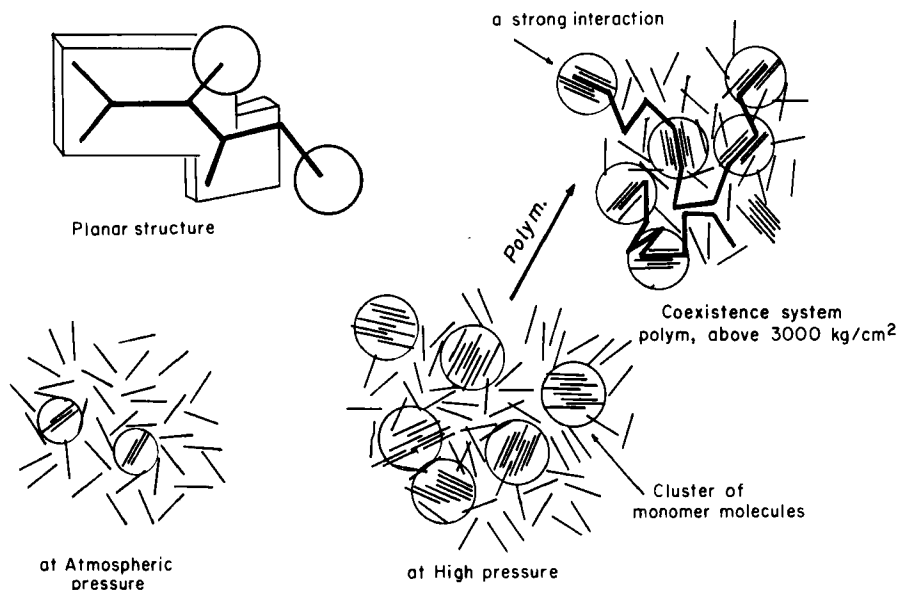


FIG. 5. Illustration of the concept of aligned monomer molecules and interaction in the coexistence system polymerized above 3000 kg/cm² at 20°C.

Concept of Alignment of Monomer Molecules

It is known that liquids of monoatomic molecules such as mercury have statistically clear order in very short range and the transportation rate of disordering is large [6]. It may be possible for MMA monomer to align due to its planar units ($\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{R}$, $>\text{C}=\text{O}$) of MMA under suitable conditions. The P-V behavior for the coexistence system polymerized above 3000 kg/cm² indicates the existence of an alignment of monomer molecules.

It is concluded from the P-V isotherms for the coexistence system that pressure enlarges the domain of alignment of monomer molecules or causes a slowdown of the transportation rate of disordering. In other words, pressure lengthens the relaxation time of ordering-disordering in the monomer system, so that a short-range alignment of monomer molecules is stabilized statistically at high pressure.

Figure 5 illustrates this concept. The stability is shown as numbers of clusters. If the polymerization proceeds in the polymeric system, which consists of a cluster of aligned monomer in a "sea" of

random monomer molecules, the monomer units in as-polymerized polymer chains keep interaction to monomer molecules in clusters. The alignment of monomer molecules in the supercooled state differs from the illustration in Fig. 5.

REFERENCES

- [1] T. Sasuga and M. Takehisa, J. Macromol. Sci.-Chem., **A12**, 1307 (1978).
- [2] J. B. Conant and W. R. Peterson, J. Am. Chem. Soc., **54**, 628 (1932).
- [3] K. Kinkel, Ber Bunsenges. Phys. Chem., **70**, 1030 (1966).
- [4] T. Sasuga and M. Takehisa, J. Macromol. Sci.-Phys., **B13**, 215 (1977).
- [5] T. Sasuga, N. Morishita, A. Udagawa, Y. Kusama, and M. Takehisa, J. Polym. Sci. Polym. Chem. Ed., **14**, 2575 (1976).
- [6] J. G. Kirkwood, Science in Progress, Vol. III, The Structure of Liquid, Yale Univ. Press, New Haven, 1942, pp. 208-221.

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