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Tsuneo Sasuga^a; Masaaki Takehisa^a

^a Takasaki Radiation Chemistry Research Establishment Japan Atomic Energy Research Institute, Takasaki, Japan

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Radiation-Induced Polymerization of n-Butyl and n-Hexyl Methacrylates at High Pressure and Pressure-Volume Behavior of Polymer-Monomer Coexistence System as Polymerized

TSUNEO SASUGA and MASAOKI TAKEHISA

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

ABSTRACT

Radiation-induced polymerization of n-butyl and n-hexyl methacrylates (BMA, HMA) at high pressure (up to 8000 kg/cm²) and pressure-volume (P-V) behavior of the polymer-monomer coexistence systems at various pressures were studied by dilatometric method. The Van't Hoff plot of the rate of polymerizations broke at 3500 and 4500 kg/cm² for BMA and HMA, respectively. (first breaks). The activation volumes were about -24 cm³/mole for both monomers below the pressure giving the first breaks. The pressure dependences on the rate of polymerizations were small in the pressure ranges of the first break pressures to 4500 kg/cm² for BMA and 5500 kg/cm² for HMA (second breaks), and above the second break pressures the rate of polymerizations increased with constant activation volumes with increasing pressure. The P-V isotherms of the coexistence systems polymerized below 3000 kg/cm² were the same as those of the monomers, and the coexistence systems polymerized at 3800 (BMA) and 4200 kg/cm² (HMA) showed solidlike features in the pressure range of 3000 kg/cm² to the

polymerization pressures. The coexistence systems polymerized at 5500 (BMA) and 6500 kg/cm² (HMA) showed solidlike features in the range of 4500 kg/cm² to the polymerization pressure and 5500 kg/cm² to the polymerization pressure, respectively. The pressure of 4500 kg/cm² for BMA and 5500 kg/cm² for HMA corresponded to the pressure giving the second break in the Van't Hoff plot. We concluded from these results that the solidlike features were due to a strong interaction between as-polymerized polymer chains and monomer molecules similarly to the case of the PMMA-MMA coexistence system, and that the ester chains of BMA and HMA play an important role in alignment of monomer molecules above 4500 (BMA) and 5500 kg/cm² (HMA).

INTRODUCTION

We have reported the existence of alignment of monomer molecules at high pressure from results of the radiation-induced polymerization of methyl methacrylate (MMA) at high pressure and of the pressure-volume (P-V) measurements of PMMA-MMA coexistence system as polymerized [1, 2]. The monomer alignment induced by compression is considered to be due to the planar units of MMA ($\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{R}$;

>C=O). On the other hand, the large n-alkyl ester chains have more freedom in their conformation than the planar units. If these planar units play an important role in the alignment of monomer molecules at high pressure, the mode of alignment under pressure may be altered by introducing long ester chains. The polymerization and P-V behavior of the coexistence systems are expected to be changed by substituent ester groups of methacrylates.

In this paper, we report the radiation-induced polymerization of n-butyl and n-hexyl methacrylates (BMA, HMA) at high pressure and the P-V behavior of the polymer-monomer coexistence systems as polymerized to reveal the effect of ester chains on the alignment of monomer molecules at high pressure.

EXPERIMENTAL

Commercially obtained extra pure grade BMA and HMA (Tokyo Kasei Co., Ltd.) were used after passage through a column containing activated aluminum oxide (Activity grade I, ICN Pharmaceuticals GmbH & Co.) in order to remove polymerization inhibitor.

A glass dilatometer as described in the previous paper [1] was

used for polymerizations and P-V measurements. The high pressure apparatus was the same as described elsewhere [3]. The volume change on polymerization and pressurization was detected electrically from the height of mercury in the capillary of the dilatometer. The calibration of the specific volume from dilatometric reading was carried out by the same method as in the previous paper [4].

The monomers were degassed in the dilatometer by the freeze-thaw method ($\sim 10^{-3}$ Torr) several times. The dilatometer filled with monomer and mercury was pressurized, and polymerization was carried out at 20°C under Co-60 γ -rays at a dose rate of 7×10^3 rad/hr. The rate of polymerization was obtained from the dilatometric reading during polymerization and final polymer yield, which was obtained gravimetrically after vacuum drying of the product.

The P-V isotherms of polymer-monomer coexistence systems as polymerized, which never received thermal treatment, were obtained in a series of successive measurements at increasing and decreasing pressures.

RESULTS

The two monomers were not crystallized by pressurization up to 9000 kg/cm² at 20°C and no peculiar change is observed in the P-V isotherms.

Time-conversion curves for BMA at various pressures are shown in Fig. 1. Polymerization proceeds after an induction period. The rate of polymerization increases and the induction period decreases with increasing pressure. The polymerization of HMA at various pressures proceeds similarly as that of BMA. The rate of polymerization was obtained from the linear part of the time-conversion curves just after the induction period.

Figure 2 shows Van't Hoff plots for BMA and HMA together with that for methyl methacrylate (MMA) reported previously [1]. The Van't Hoff plots break at different pressures for each monomer (first breaks), and the rate of polymerization hardly increases with increasing pressure in the pressure range of the pressure giving the first break to 3700 for MMA [1], 4500 for BMA, and 5500 kg/cm² for HMA (second breaks). Above the pressure giving the second break, the rate of polymerization increases at constant activation volumes with increasing pressure.

The activation volumes calculated from the linear part of the Van't Hoff plots below the first breaks are about -24 cm³/mole for these three monomers. Asai and Imoto have studied polymerizations of methacrylates at 1 to 1000 kg/cm², and reported that the activation volume at atmospheric pressure decreases with increasing ester

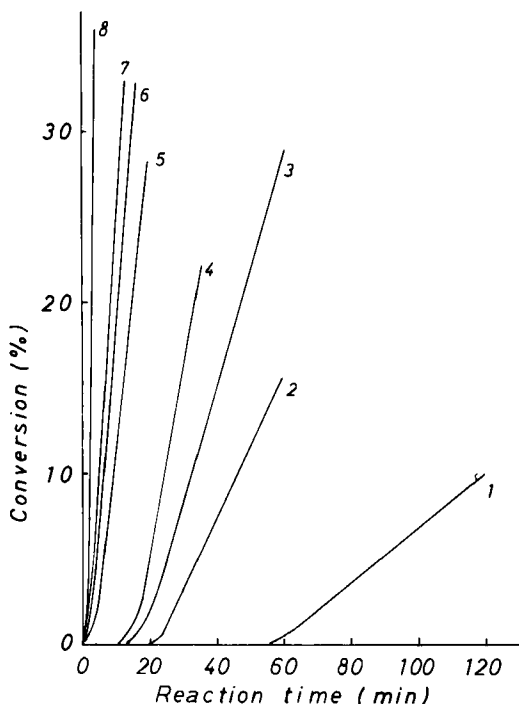


FIG. 1. Time-conversion curves of the polymerization of BMA at 20°C at various pressures: (1) 1100; (2) 2100; (3) 2800; (4) 3400; (5) 4100; (6) 4500; (7) 5000; (8) 7100 kg/cm².

chain length, and the activation entropy becomes similar in value, regardless of the ester chain length at 1000 kg/cm² in the polymerization of methacrylates initiated by AIBN [5]. The similar activation volume below the first break regardless of the ester chain length in this work may be due to higher polymerization pressure, absence of reaction solvent, and correction of rate of polymerization by specific volume of polymeric system.

The activation volume above the second breaks tends to decrease with increasing ester chain length. The activation volumes are -13.7, -14.4, and -17.4 cm³/mole for MMA, BMA, and HMA, respectively.

Figure 3 shows the P-V isotherms for the PBMA-BMA coexistence systems polymerized at 2500, 3800, and 5500 kg/cm². The monomer conversions are indicated. The solid line shows compression curves of BMA monomer, the vertical solid line with the arrow is volume

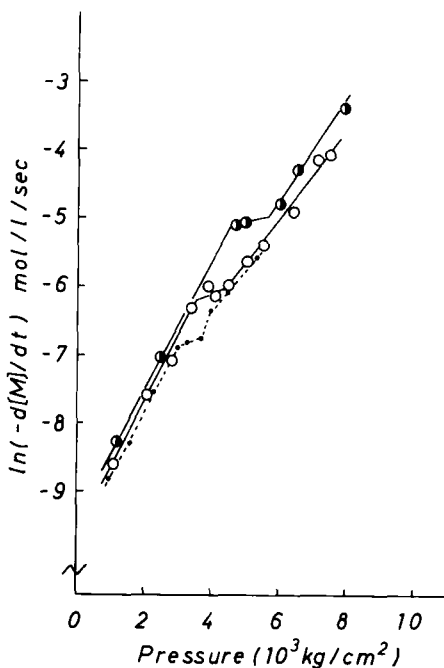


FIG. 2. Van't Hoff plots of (●) MMA, (○) BMA, and (◐) HMA.

contraction by polymerization, the filled circles show the specific volume in the measurement with pressure decreasing from the polymerization pressure, and the open circles show the specific volume in the measurement with pressure increasing from atmospheric pressure again.

Figure 4 shows the P-V isotherms for the PHMA-HMA coexistence systems polymerized at 2500, 4200, and 6500 kg/cm^2 .

The P-V isotherms for the both coexistence systems polymerized at 2500 kg/cm^2 are smooth as are those of the monomers, except for a slight change in compressibility at the polymerization pressure. The coexistence systems polymerized at 3800 kg/cm^2 for BMA and at 4200 kg/cm^2 for HMA show liquid-to-solid like transitions at 3000 kg/cm^2 for BMA and 3500 kg/cm^2 for HMA. In the pressure ranges of 3000 kg/cm^2 to the polymerization pressure for BMA and of 3500 kg/cm^2 to the polymerization pressure for HMA, the compressibilities are of the order of $10^{-6} (\text{kg/cm}^2)^{-1}$, indicating that the coexistence systems show a solidlike behavior in these pressure ranges. Below and above the pressure ranges, the compressibilities are of the order of $10^{-5} (\text{kg/cm}^2)^{-1}$.

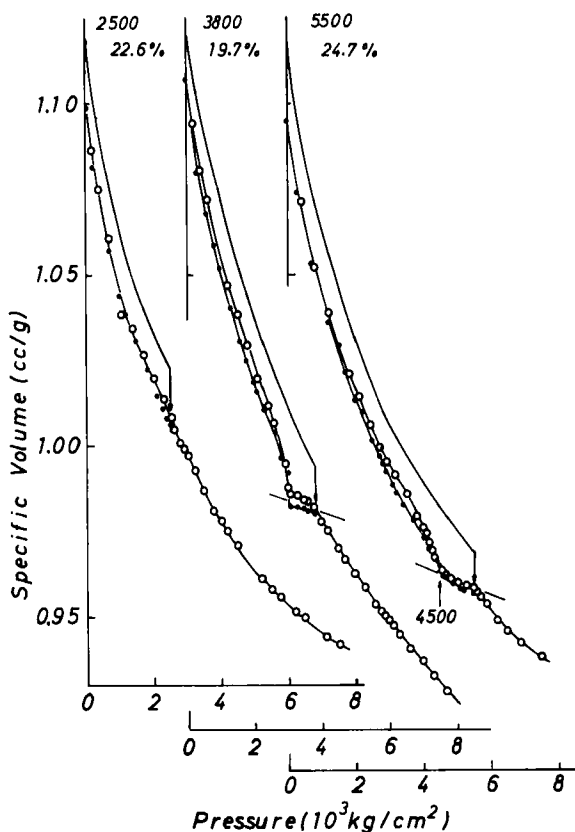


FIG. 3. P-V isotherms of coexistence system of BMA: (—) monomer compression; (—) volume contraction by polymerization; (●) specific volumes in measurements with lowering pressure; (○) specific volume in measurements with elevating pressure.

As seen in the P-V isotherms for the coexistence systems polymerized at 5500 kg/cm² for BMA and 6500 kg/cm² for HMA, the coexistence systems polymerized at these high pressures do not show the liquid-to-solid transitions about 3000 kg/cm². Instead of the transition about 3000 kg/cm², these coexistence systems show liquid-to-solid transitions at 4500 kg/cm² for BMA and 5500 kg/cm² for HMA, and behave like a solid in the pressure range of 4500 kg/cm² to the polymerization pressure for BMA and 5500 kg/cm² to the polymerization pressure for HMA, respectively. Above the

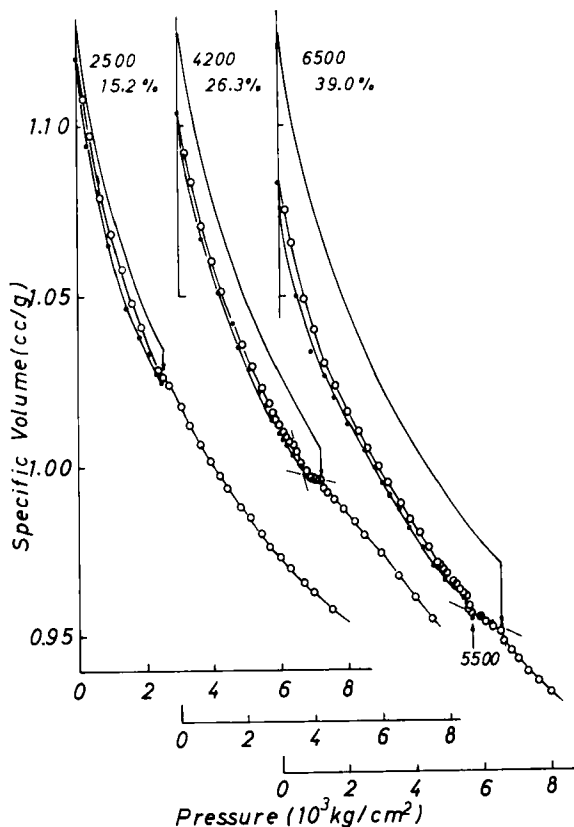


FIG. 4. P-V isotherms of coexistence system of HMA; symbols are the same in Fig. 3.

polymerization pressure, the compressibilities increase to the order of $10^{-5} \text{ (kg/cm}^2\text{)}^{-1}$, indicating that the coexistence systems behave as a liquid. The liquid-to-solid transitions at 3500 and 5500 kg/cm^2 for HMA are broader than those for BMA.

DISCUSSION

The abrupt change in the activation volumes indicates that the physical state of polymeric system changes with pressure. The shift of the pressures giving an abrupt change in activation volume to

higher pressure with increasing ester chain length indicates that the ester chains affect the physical state of the polymeric systems. The fact that activation volumes for these three monomers are the same below the pressure giving the first break in Van't Hoff plots suggests that the physical states of monomers are the same. Below the pressure giving the first break, monomer molecules have a random conformation independent of the ester chain lengths.

The P-V behavior of the mixed system with PMMA dissolved in MMA is similar to the P-V behavior of MMA and gradually changes with the polymer content up to 20% [2]. This means that P-V behavior of MMA is not essentially affected by the presence of polymer chains at a low polymer content.

The coexistence systems polymerized at 3800 kg/cm^2 for BMA and 4200 kg/cm^2 for HMA show a liquid-to-solid transition about 3000 kg/cm^2 to the polymerization pressures. Above the polymerization pressure, the coexistence systems again behave as liquids. Thus, the coexistence system behaves differently upon pressure from the monomer in spite of the fact that the polymer content is similar to that of the mixed system. The difference in P-V behavior in the coexistence and mixed systems is considered due to an interaction between polymer chains and monomer molecules and the conformation of polymer chains in the monomer.

We have proposed that alignment of monomer molecules occurs at suitable pressure from the polymerization behavior of MMA at high pressure and P-V behaviors of the coexistence systems polymerized at high pressure [1, 2]. When the polymerization proceeds in clusters of aligned monomer molecules, a strong interaction takes place between as-polymerized polymer chains and surrounding monomer molecules, because propagation proceeds with preservation of the interaction between monomer units in as-polymerized polymer chains and the surrounding monomer molecules. The liquid-to-solid transition and solidlike behavior in the coexistence systems polymerized at 3800 kg/cm^2 for BMA and 4200 kg/cm^2 for HMA are brought about by the strong interaction.

For BMA, the pressure giving liquid-to-solid transition about 3000 kg/cm^2 agree well with the one for MMA, but the transition pressure for HMA shifts upward to 3500 kg/cm^2 . This may be due to the effect of the long ester chain in HMA on alignment of the monomer molecules.

The disappearance of the solidlike behavior at about 3000 kg/cm^2 and the appearance of the solidlike behavior at higher pressure in P-V isotherms of the coexistence system polymerized at 5500 kg/cm^2 for BMA and at 6500 kg/cm^2 for HMA indicates that the alignment of monomer molecules at about 3000 kg/cm^2 is destroyed, and a new alignment of monomer molecules occurs at higher pressure. It can be considered that the newly formed alignments of these monomer

molecules are alignments in which the ester chains play an important role, because pressure range giving a liquid-to-solid transition is affected by the length of the esters. The pressures of 4500 kg/cm² for BMA and 5500 kg/cm² for HMA which give the liquid-to-solid transitions agree with the second break in the Van't Hoff plots. Activation volumes above the second break pressures change with ester chain length. This fact shows that the conformation of the ester chains plays an important role in molecular alignment, and consequently polymerization behavior is affected by the monomer alignment realized at 4500 kg/cm² for BMA and 5500 kg/cm² for HMA.

The above discussion is based on the concept that clusters of aligned monomer molecules are produced above a suitable pressure. If the monomer molecules align in short range even at atmospheric pressure, another concept can be derived. The transportation rate of disordering is fast in liquid consisting of molecules having short-range order [6]. If the rate of propagation becomes faster than the transportation rate of disordering above a suitable pressure due to fast propagation at high pressure, an interaction between as-polymerized polymer chains and monomer molecules would also be established due to monomer coordination to as-polymerized polymer chains within a time scale of molecular transportation. The occurrence of the interaction may be interpreted by the ratio of the rate of propagation and a relaxation time in ordering-disordering of monomer alignment.

The polymerization behavior, however, cannot be interpreted by this concept. The transportation rate of molecules in liquid may be decreased with increasing size of molecules, so that the relaxation time in ordering-disordering of aligned molecules may be lengthened with increasing size of molecules. This means that pressure at which the rate of propagation becomes comparable to the relaxation time is lowered with increasing size of molecules. However, the pressure giving the break in Van't Hoff plots shifts to higher pressure with increasing size of molecules.

From a comparison of the three monomers, the following conclusions are derived. The liquid-to-solid transition of coexistence systems at about 3000 kg/cm² exists in MMA, BMA, and HMA, so that the alignment of monomer molecules at about 3000 kg/cm² is an alignment which is mainly concerned with the main chain. The alignment at higher pressure is an alignment that concerns the ester chain. Solidlike behavior at higher pressure was not observed in MMA, because the ester chain in MMA is too small to align by itself.

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