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Radiation-Induced Polymerization and Pressure-Volume Behavior of Acrylonitrile at High Pressure

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ABSTRACT

Radiation-induced polymerization and pressure-volume (P-V) measurements of acrylonitrile (AN) were studied up to 8000 kg/cm² in the temperature range of 6-72°C. P-V isotherms of AN have several small breaks. A phase diagram of AN was obtained from the breaking pressures and temperatures. Liquid phases were named L_I, L_{II} and L_{III} from low to high pressure.

The polymerization behavior and volume contraction on polymerization changed in L_I, L_{II} and L_{III}. The difference in entropy between original and activated states decreased with increasing pressure at the same phase, but increased with phase change in L_I to L_{II} and L_{II} to L_{III}. It was concluded from these results and from IR data on PAN that molecular packing of AN in liquid changed in L_I, L_{II} and L_{III}. In L_{II} and L_{III} AN molecules aligned in a less suitable geometry for polymerization than in L_I.

INTRODUCTION

It has been reported that bulk polymerization of acrylonitrile (AN) at high pressure showed unusual behavior; the rate of polymerization at 50°C decreased with increasing pressure up to 4000 kg/cm², the rate increased at 5000 kg/cm², and explosion occurred at 6000 kg/cm² leading to carbonization of material [1]. The reasons for these facts were not sufficiently explained.

We have studied radiation-induced polymerization and the pressure-volume measurement of the coexistence system of methacrylates with different substituent ester chains [2-4]. It has been revealed from the studies that monomer molecules are aligned in short-range order at high pressure, and that planar units H₂C=C(CH₃)R and ester chain in methacrylates play an important role on pressure-induced alignment of monomer molecules.

Because AN consists of a planar unit H₂C=CHR and a rodlike unit (-C≡N), an alignment of AN can be expected at high pressure. Therefore, we considered that the unusual behavior in the bulk polymerization of AN at high pressure is due to pressure-induced alignment of AN molecules.

The effect of alignment of monomer molecules on polymerization of AN may be apparent, because interaction between as-polymerized polymer chains and monomer molecules in the system is weaker than that in the methacrylate systems due to heterogeneous polymerization of AN.

In this paper, we studied radiation-induced polymerization and the pressure-volume behavior of AN at high pressure from the viewpoint of pressure-induced alignment of monomer molecules.

EXPERIMENTAL

Polymerization was carried out in a dilatometer described previously [2] up to 7500 kg/cm² in the temperature range from 6 to 72°C. Freshly distilled AN was degassed in the dilatometer by the freeze-thaw method (~10⁻³ Torr) several times on a vacuum line, and then mercury was introduced under vacuum. Pressure was applied hydrostatically to the dilatometer in the high pressure apparatus described elsewhere [5]. After polymerization conditions were established, the sample was irradiated by Co-60 γ-rays (dose rate 7 × 10³ rad/hr). The volume contraction during polymerization was measured from the height of the mercury level in the capillary of the dilatometer as described previously [2].

The rate of polymerization was obtained from the dilatometric reading and the conversion obtained gravimetrically from polymer after drying under vacuum.

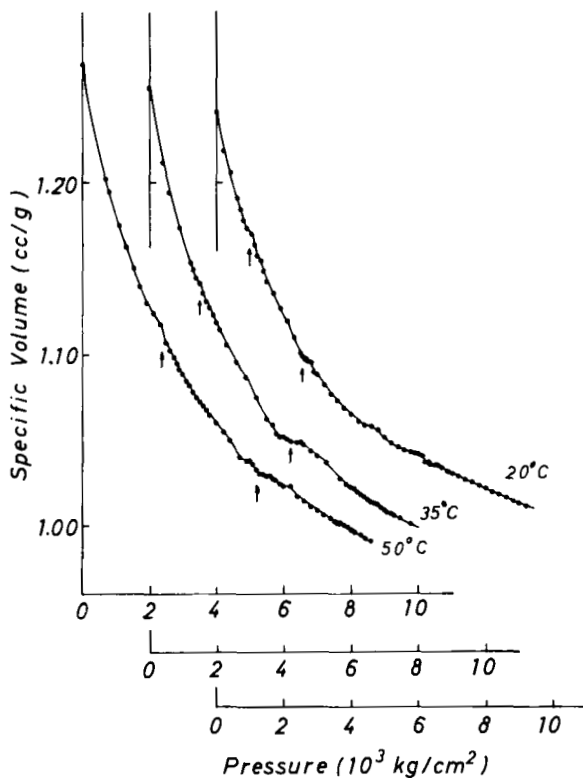


FIG. 1. P-V isotherms of AN without moisture at 20, 35, and 50°C.

The dilatometer for P-V measurement of AN and calculation of specific volume from dilatometric data were the same as described [6]. The rate of pressurization was about 50 kg/cm²/min in the isothermal measurements, and the heating rate was 0.4°C/min in the isobaric measurement.

RESULTS

Figure 1 shows pressure-volume (P-V) isotherms measured at 20, 35 and 50°C. All isotherms have several small breaks, and compressibilities change at the pressures marked by arrows. The

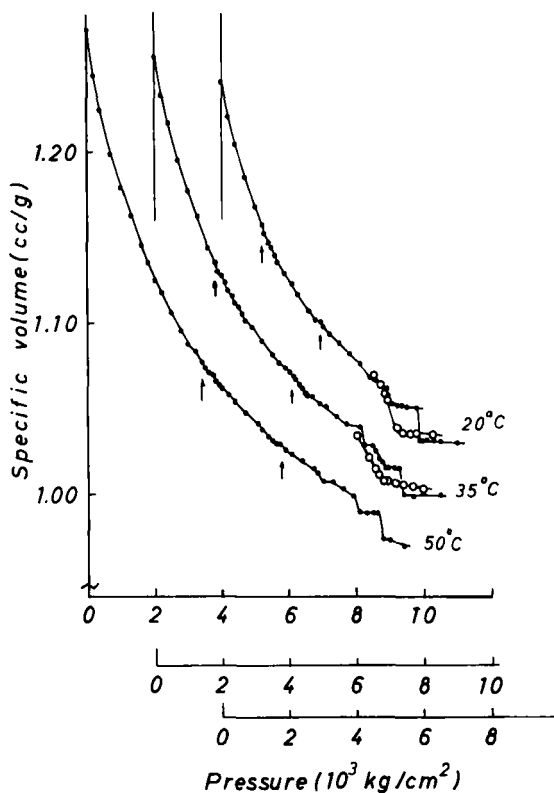


FIG. 2. P-V isotherms of AN with small amount of moisture at 20, 35, 50°C.

reproducibility in P-V isotherms is less perfect than that of methacrylates; the specific volume changes within $\pm 2\%$ between isotherms measured independently. Moisture in the monomer may cause poor reproducibility in P-V isotherms. The P-V isotherms in Fig. 1 are typical of those in the absence of moisture. Figure 2 shows P-V isotherms of AN containing a small amount of moisture. The change in compressibility shown by arrows in Fig. 2 are less than in Fig. 1, and the specific volume change at high pressure (ca. 5000 kg/cm² at 20°C) is like a liquid-to-solid transition.

Figure 3 shows temperature shift curves of the pressure giving the breaks. Regions divided by the curves are named liquid I, II, and III (L_I , L_{II} , L_{III}).

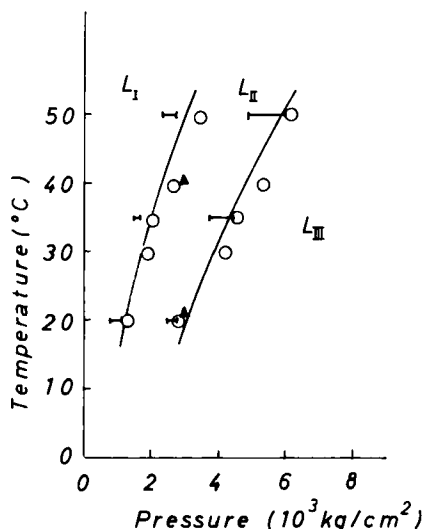


FIG. 3. Temperature shift curves of AN: (◻) obtained from Fig. 1; (○) obtained from Fig. 2 and others; (▲) obtained from isobaric measurement.

Figure 4 shows an isobaric temperature-volume curve (isobar) at 3000 kg/cm^2 together with the specific volume obtained by isothermal measurements. The specific volume in the isobar increases with increasing temperature above 22°C , and increases abruptly at 21°C and 41°C . The pressure and temperature giving an abrupt change in specific volume (breaking point) is also plotted in Fig. 3. Since the breaking points agree in isobaric and isothermal measurements, the changes in slope reflect the same mechanism. As shown in Fig. 4, the specific volume by isothermal measurement decreases with increasing temperature. This is partly due to the result of large volume decrease by compression in low pressure side at high temperature. Though the P-V behavior of AN is not entirely reproducible, the pressure and temperature giving the change in slope are fairly reproducible.

Figure 5 shows typical time-conversion curves at L_I , L_{II} , and L_{III} . Acceleration of the rate of polymerization is observed at an early stage in all time-conversion curves. After the acceleration, the rate of polymerization becomes constant immediately in L_I but in L_{II} and L_{III} the rate of polymerization decreases with time and then

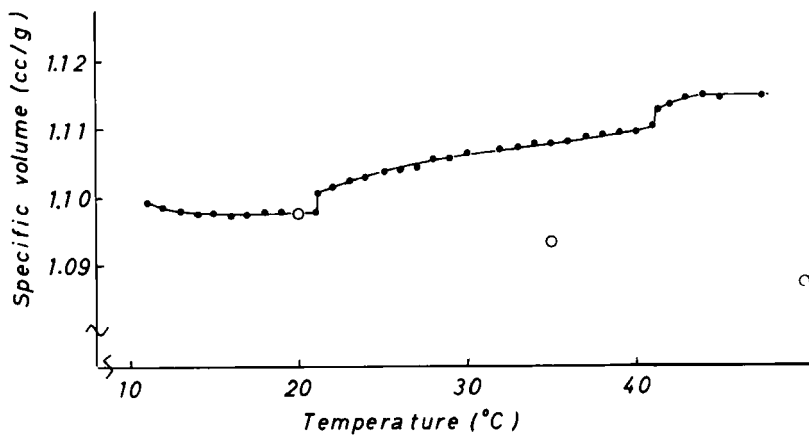


FIG. 4. Isobar of AN at 3000 kg/cm^2 normalized specific volume at 20°C obtained by isothermal measurements; (\bullet) isobar; (\circ) from isotherms.

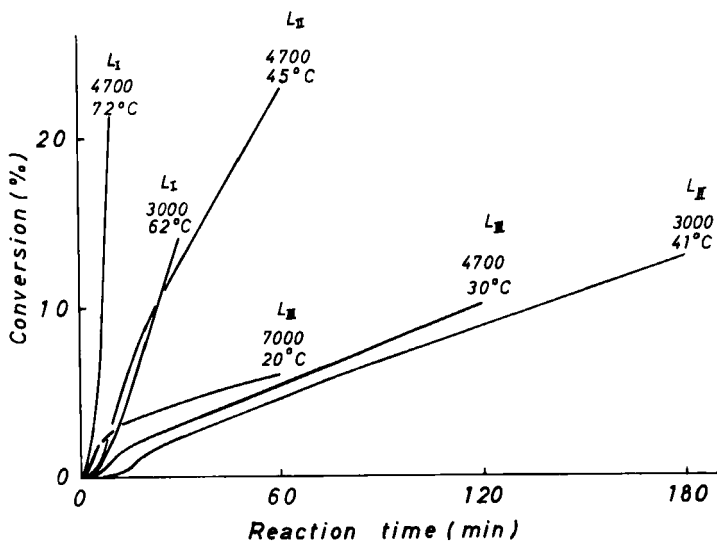


FIG. 5. Typical time conversion curves in L_I , L_{II} , and L_{III} .

becomes constant in a later stage. One of the authors has reported [7] that the rate of polymerization accelerates with time at the initial stage in radiation-induced heterogeneous polymerization of AN at atmospheric pressure, and explained the acceleration to be due to accumulation of growing radicals. Therefore, we define the initial rate of polymerization from the slope of the time-conversion curves just after the acceleration and that at the later stage from the slope of the linear part of the time-conversion curves in L_{II} and L_{III}.

Polymerization at 20°C proceeds up to 7000 kg/cm², but the polymerization does not proceed within the time scale in this work above 7000 kg/cm². The logarithm of rate of polymerization in initial and later stages at 20°C is plotted against pressure in Fig. 6 (Van't Hoff plot). The rate of polymerization increases up to 1000 kg/cm² with increasing pressure and decreases abruptly at 1100 kg/cm². Above 1100 kg/cm² the rate of polymerization increases with pressure up to 3000 kg/cm². Above 3000 kg/cm² the rate of polymerization in the initial and later stages shows different behavior with pressure. The rate of polymerization at initial stage increases abruptly at 3000 kg/cm²,

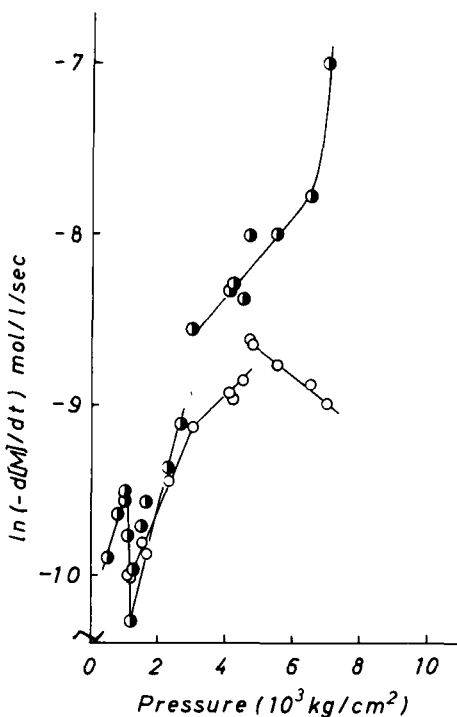


FIG. 6. Van't Hoff plot at 20°C; (●) initial stage; (○) later stage.

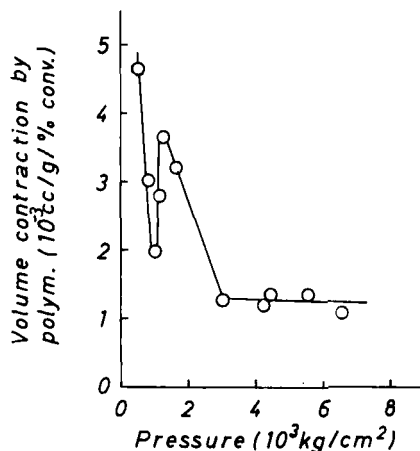


FIG. 7. Volume contraction by polymerization upon pressure at 20°C .

increases with pressure up to 6000 kg/cm^2 , and markedly increases above 6000 kg/cm^2 . On the other hand, the rate of polymerization in the later stage increases up to 4700 kg/cm^2 and decreases with increasing pressure above 4700 kg/cm^2 .

Volume contraction by polymerization is shown against pressure in Fig. 7. The volume contraction changes correspondingly with change in the rate of polymerization with pressure. The volume contraction decreases with increasing pressure, and increases abruptly at 1100 kg/cm^2 , where the rate of polymerization is minimum. The volume contraction decreases with pressure up to 3000 kg/cm^2 and become constant above 3000 kg/cm^2 .

IR spectra of PAN polymerized at various pressures have an absorption peak at 1640 cm^{-1} . The IR absorption peak at 1690 to 1640 cm^{-1} is generally assigned to the $-\text{C}=\text{N}-$ bond [8]. Figure 8 shows the change in ratio of absorbance at 1640 cm^{-1} and 1460 cm^{-1} ($-\text{C}=\text{N}-/\text{CH}_2$) and at 2300 cm^{-1} and 1460 cm^{-1} ($-\text{C}\equiv\text{N}/\text{CH}_2$) upon pressure. $-\text{C}\equiv\text{N}$ and $-\text{C}=\text{N}-$ increase abruptly at 1100 kg/cm^2 . Increase in both absorbances is due to a change in the content of the CH_2 group on addition at $-\text{C}\equiv\text{N}$.

Figure 9 shows time-conversion curves at various temperatures at 4700 kg/cm^2 . Typical polymerization features in L_I , L_{II} , and L_{III} are well realized; the rate of polymerization at 72 and 65°C (L_I) becomes constant with time after short acceleration, but the rates below 55°C (L_{II} , L_{III}) decrease with time in the initial stage.

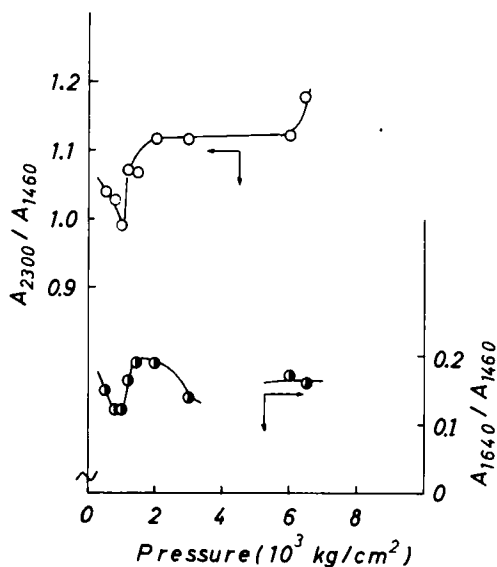


FIG. 8. Absorbance ratios of PAN polymerized at 20°C upon pressure.

Figure 10 shows Arrhenius plots in the initial and later stages at 3000 and 4700 kg/cm^2 . Arrhenius plots at 3000 and 4700 kg/cm^2 break at two temperatures. The temperatures giving breaks in Arrhenius plots agree with the temperatures of the L_I to L_{II} and L_{III} transitions obtained by P-V measurements of AN.

DISCUSSION

Transition of L_I to L_{II}

As shown in Fig. 5, the features of time-conversion curves differ in L_I and L_{II} . The time-conversion curves in L_I show typical feature in heterogeneous polymerization [7], but the one in L_{II} differs from typical heterogeneous polymerizations. This may indicate that physical properties of AN monomer system differ in L_I and L_{II} .

The discontinuous change in specific volume at the transition point

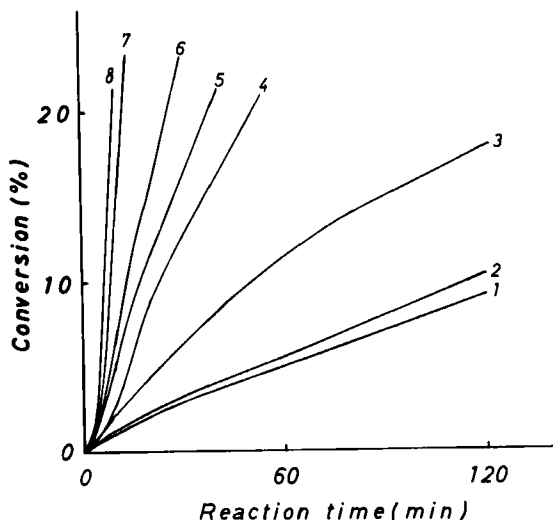


FIG. 9. Time-conversion curves at 4700 kg/cm^2 at various temperatures: (1) 20°C ; (2) 30°C ; (3) 40°C ; (4) 45°C ; (5) 50°C ; (6) 55°C ; (7) 65°C ; (8) 72°C .

of L_I to L_{II} and the low compressibility following the discontinuous volume change indicate that hardly any compressible structure is introduced at this pressure. The structure does not have long-range order such as a crystalline structure, since compressibility increases again above the pressure.

L_{II} exists at higher pressures than L_I at a given temperature, and exists at lower temperatures at a given pressure; therefore, the freedom of AN molecules in L_{II} is less than in L_I .

The above discussion lead to the conclusion that the character of the time-conversion curve differs from that in typical heterogeneous polymerization when polymerization proceeds in a monomer system with little freedom. It is presupposed from this that the field in which the propagation proceeds differs in L_I and L_{II} .

A decrease in the rate of polymerization with time at the initial stage in L_{II} and L_{III} can be considered to be due to the existence of two propagation fields with different monomer alignments and to different interactions of monomer molecules with as-polymerized polymer chains.

We propose the following hypothesis on the basis of the P-V data.

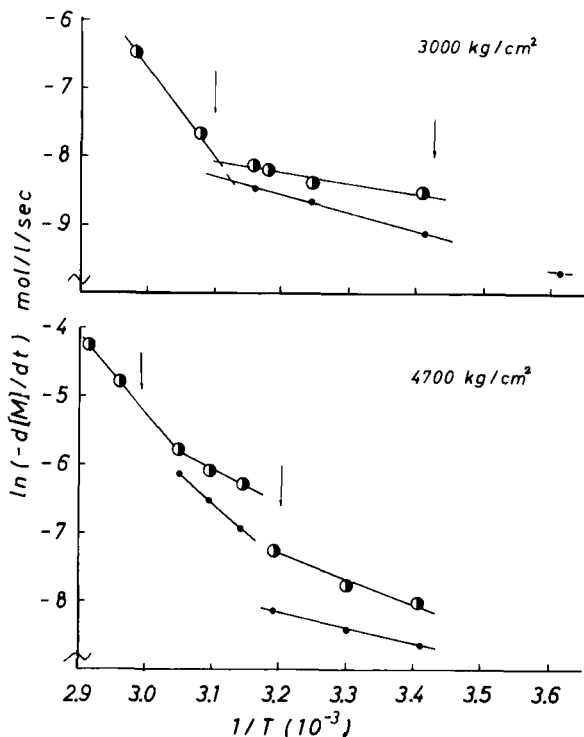


FIG. 10. Arrhenius plots at 3000 and 4700 kg/cm²: (○) initial stage, (●) later, stage; arrows show transition temperatures.

Monomer molecules in L_I are in random alignment, and in L_{II} the monomer system consists of clusters of aligned AN molecules and random AN molecules. If AN molecules are aligned in an unsuitable geometrical position for propagation in the cluster, the rate of polymerization in the cluster may be retarded because aligned AN molecules are required to change the geometrical position for propagation. A decrease in the rate of polymerization with time in L_{II} may be interpreted as due to a shift of the propagation field in the "sea" at random AN molecules to the cluster of aligned AN molecules. An abrupt change in the rate of polymerization at the transition of L_I to L_{II} may be interpreted similarly by a change in the propagation field.

An abrupt increase in volume contraction by polymerization at the transition of L_I to L_{II} (1100 kg/cm² at 20°C, Fig. 7) may indicate

that a change in geometrical position of aligned AN molecules is required for propagation, because volume contraction occurs for aligned AN molecules on rearrangement to a geometrical position suitable for propagation. The activation volume at up to 1000 kg/cm² is -10.8 cm³/mole and that in the pressure range of 1100 to 3000 kg/cm² is -12.6 cm³/mole, indicating that the difference of volumes in the original and activated states becomes larger in L_{II} than in L_I. This also shows that a geometrical change is required for propagation in L_{II}.

Since dynamic equilibrium exists between AN molecules in the clusters and the random AN molecules, the polymerization behavior cannot be explained only by existence of a cluster of aligned AN molecules. We consider also that interactions between as-polymerized polymer chains and AN molecules play an important role in the polymerization at high pressure. The rate of polymerization should be retarded by the interaction, because AN monomer interacting with as-polymerized polymer chains is required to change the geometrical position for propagation as for AN molecules in the clusters.

The activation entropy ΔS^\ddagger can be calculated from the frequency factor A in the Arrhenius equation and the activation energy ΔE . The frequency factor A is divided into the following terms;

$$A = kT/h \exp \{ \Delta S^\ddagger / R \} \quad (1)$$

where k, T, h, and R are Boltzman constant, absolute temperature, Plank constant, and gas constant, respectively.

A steady-state rate equation in radiation-induced unimolecular terminated heterogeneous polymerization is defined as follows:

$$R_p = k_p/k_t [M][G_R \cdot I] \quad (2)$$

where R_p , k_p , k_t , $[M]$, and $[G_R \cdot I]$ are rate of polymerization (mole/liter-sec), rate constant for propagation (liter/mole-sec), overall rate constant of termination (liter/sec), monomer concentration (mole/liter), and rate of initiation (mole/liter-sec); G_R is the G-value for radical formation and I is the dose rate. Generally k_p and k_t cannot be obtained independently, but a complex rate constant k_p/k_t can be defined. Therefore, an absolute value of ΔS^\ddagger cannot be calculated by using Eqs. (1) and (2), but a tendency of change in ΔS^\ddagger can be estimated. Table 1 gives the activation entropy ΔS^\ddagger as calculated by using the complex rate constant. The case giving positive activation

TABLE 1. Activation Energy and Entropy^a

Pressure (kg/cm ²)	Activation energy (kcal/mole)			Activation entropy (relative)		
	L _I	L _{II}	L _{III}	L _I	L _{II}	L _{III}
1	11	-	-	-6	-	-
3000	24	3	-	+34	-32	-
4700	26	12	7	+42	-1	-17

^aCalculated from the frequency factor of the complex rate constant (k_p/k_t , liter/mole), extrapolated to 50°C.

entropy exists. Since the positive value is due to use of the complex rate constant, the positive value does not imply that the entropy of the activated complex is larger than that in the original state.

The data in Table 1 indicate that the difference in entropy between the original and activated complex decreases with increasing pressure within the same phase and increases with transition from L_I to L_{II}. A decrease in the difference in entropy with pressure in the same phase is considered to be due to decreasing entropy of the monomer system by compression. An increase in the difference in entropy with transition from L_I to L_{II} indicates the existence of a larger entropy change for formation of activated complex in L_{II} than L_I. From changes in polymerization features and volume contraction by polymerization in transition of L_I to L_{II}, this increase of difference in entropy may be introduced by a change in the geometrical position required to form the activated complex for aligned AN molecules in the clusters and interaction between AN molecules and as-polymerized polymer chains.

Consequently, AN molecules have a conformation in L_{II} which requires a change in geometrical position to form activated complex.

Transition of L_{II} to L_{III}

The change in specific volume at the transition of L_{II} to L_{III} resembles that at the transition of L_I to L_{II}, but the compressibility in L_{III} becomes less than those in L_I and L_{II}, as shown in Fig. 1. The physical state in L_{III} is considered to be different from that in L_{II}.

The polymerization behavior changes markedly in L_{III} , as shown in Fig. 6. The logarithmic rate of polymerization changes with pressure in the same manner in the initial and later stages in L_I and L_{II} , but the rate in L_{III} shows different manner of variation with pressure in the initial and later stages.

If the monomer system consists of clusters of aligned AN molecules in a sea of random AN molecules, an increase in the rate of polymerization at the initial stage with increasing pressure is due to increase of the rate of polymerization in random AN. The rate of polymerization in the later stage increases to 4700 kg/cm^2 and decreases with increasing pressure above 4700 kg/cm^2 . If the propagation in the later stage proceeds in a cluster and AN molecules interact with as-polymerized polymer chains, it is concluded that AN molecules are aligned in more unsuitable geometrical position for propagation above 4700 kg/cm^2 .

The pressure giving the break at 4700 kg/cm^2 in the Van't Hoff plot agrees with the pressure giving the liquid-to-solid transition in the P-V isotherm with small amount of moisture (20°C , 5000 kg/cm^2). These facts suggest the probability of the existence of a liquid-to-liquid transition (L_{III} to L_{IV}) in this pressure range.

The volume contraction by polymerization is constant above 3000 kg/cm^2 . This means that the compressibility of the polymeric system with small amount (ca. 10%) of as-polymerized PAN is the same as the compressibility of AN molecules above 3000 kg/cm^2 at 20°C . The polymeric system with a small amount of PAN may be in fairly similar physical state to AN due to coordination of AN molecules to as-polymerized PAN. The interaction between as-polymerized PAN and AN molecules may play a more important role in changing polymerization behavior than in L_{II} .

The pressure producing a change in the IR data of PAN does not entirely agree with the pressure giving changes in polymerization and P-V behavior of AN, but these pressures seem to be related to each other. It is certain at least that the $-\text{C}\equiv\text{N}$ group is involved in propagation. Therefore, we consider that the relation of the polymerization and P-V behavior is attributable to molecular packing of $\text{C}=\text{C}$ and $-\text{C}\equiv\text{N}$ units in liquid phase.

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