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PHYSICO-CHEMICAL STUDIES ON ACETALDEHYDE POLYMERIZATION AT HIGH PRESSURE AND LOW TEMPERATURE

I. Liquid-Solid Transition and Polymerization of Acetaldehyde

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Acetaldehyde polymer is obtained with no catalyst at low temperature by applying high pressure to acetaldehyde. In order to obtain the acetaldehyde polymer, there is the limiting pressure at each reaction temperature, and the acetaldehyde polymer is not obtained by the pressure lower than this limiting pressure. In the experimental range, plotting the limiting pressure against reaction temperature, the linear relation is obtained.

At the pressures above and below this limiting pressure, the volume change of acetaldehyde is measured. Since the discontinuity of the volume change of acetaldehyde is found at the limiting pressure, the temperature and the limiting pressure are identified as the transition temperature and pressure of acetaldehyde.

The values of -3.53, -3.84, -4.27 and -4.58 ml/mole are obtained as the volume decreases of acetaldehyde of the liquid-solid transition at temperatures -50, -60, -70 and -78°C, respectively. Using the Clausius-Clapeyron equation ΔH_T and ΔS_T are calculated from the ΔV_T as $-2.40\sim-2.11$ kcal/mole, and $-12.3\sim-9.47$ cal/deg. mole, respectively. The ΔH_T and the ΔS_T increase with temperature and pressure.

The acetaldehyde polymer formed by this polymerization is found as the atactic polyether type polymer by the infrared spectrum and the solubility in the solvents.

The values of $-13.2\sim-12.1$ ml/mole are obtained as the volume decreases of the polymerization of acetaldehyde at temperature $-50\sim-78$°C. The values are in good agreement with the value obtained from the calculation.

Introduction

The liquid-solid transition of organic compound at high pressure had been studied for many substances. Especially P. W. Bridgman[1] had studied on a number of substances in this field. But there are no reports on the liquid-solid transition of acetaldehyde at high pressure.

It was discovered that there was the limiting pressure for the formation of the acetaldehyde polymer with no catalysts by applying high pressure at low temperature. If acetaldehyde monomer was compressed at the pressure lower than this limiting pressure even for long period, the acetaldehyde polymer was not formed.

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[1] P. W. Bridgman, *Proc. Amer. Acad. Arts Sci.*, **49**, 1 (1913), **59**, 141 (1923), **67**, 1 (1931), **68**, 1 (1932), **74**, 399 (1941), **77**, 129 (1949), etc.

On the other hand, the polymer obtained by this polymerization is found as the atactic polyether type polymer by the infrared spectrum and the solubility in the solvents, and this polymer is the same polymer as produced during the solidification of acetaldehyde at its freezing point with no catalysts, and then the solidification of acetaldehyde is necessary for the polymerization of acetaldehyde with no catalysts. From this standpoint, the limiting pressures were supposed to be the liquid-solid transition pressures at those temperatures. In order to retard the polymerization of acetaldehyde, a small amount of impurity was added to the sample and this sample was compressed at the pressures above and below this limiting pressure.

The discontinuity of the volume change of acetaldehyde was found at the limiting pressure. From this fact, the limiting pressure is identified as the liquid-solid transition pressure at the temperature.

On the other hand, the volume decrease of the polymerization of acetaldehyde was obtained by correcting the volume decrease of the liquid-solid transition.

This paper reports the results obtained from the studies of the liquid-solid transition and polymerization of acetaldehyde at low temperature and high pressure.

Experimentals

Acetaldehyde

Acetaldehyde is prepared by the thermal decomposition, in the presence of sulfuric acid, of paraldehyde commercially offered and treated with sodium carbonate and anhydrous sodium sulfate, distilled for several times and the distillate between 20.8~21.0°C is used as a sample.

Apparatus

The schematic layout of the apparatus is shown in Fig. 1. This apparatus consists of the press, the pressure intensifier and the high pressure vessel. The press can be used up to 210kg/cm^2 at an ordinary condition and the ram diameter is 150mm. The pressure intensifier is composed of the piston and the cylinder made of SNCM 8, 20mm in inner diameter, 70mm in outer diameter and 210mm in

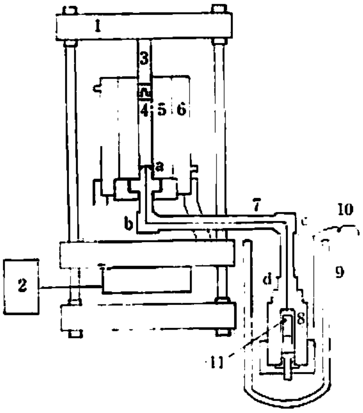

Fig. 1 Apparatus

1. press
2. hand pump
3. piston
4. Bridgman seal
5. cylinder
6. jacket
7. connecting pipe
8. high pressure vessel
9. Dewar vessel
10. thermocouple
11. syringe

length having a jacket and some accesaries. As shown in Fig. 2 the high pressure vessel is the cylinder made of SNCM 8, 20 mm in inner diameter and 70 mm in outer diameter and is sealed at one side with modified Bridgman seal using packing of ABB 3 and rubber which is applied to seal the initial pressure, and the other side 2 mm in inner diameter is connected with the pipe using double cone sealing. The connecting pipe between the pressure intensifier and the high pressure vessel is SNCM 8 pipe of 20 mm in outer diameter and 1.6 mm in inner diameter.

The connecting methods are O-ring at (a) part and double cone sealing at (b), (c) and (d) parts.

Operations

Acetaldehyde prepared is distilled under reduced pressure before use, and sampled into the syringe of glass, 15 mm in inner diameter, and 18 mm in outer diameter. In order to obtain the volume change of acetaldehyde, the thin lead rod which is deformed by the movement of piston is set in the syringe, and the difference of the lengths of the lead rod between those before and after compression is measured. The volume change of acetaldehyde is calculated from the difference of the lengths of the lead rod. Preventing the temperature effect for the volume change of acetaldehyde, before setting the syringe into the high pressure vessel, the lead rod length is measured carefully at a given temperature. The syringe is placed in the high pressure vessel as shown in Fig. 2 and the apparatus is set as shown in Fig. 1. The high pressure vessel is immersed into the Dewar vessel being kept at a definite temperature. The syringe is compressed by introducing the pressure medium from the pressure intensifier into the high pressure vessel. Releasing the pressure, the polymer obtained is dried under reduced pressure at room temperature and is weighed.

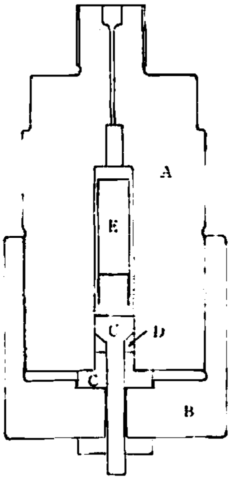

Fig. 2 High pressure vessel (scale 1/4)

A. cylinder	D. packing
B. nut	E. syringe
C. modified Bridgman seal	

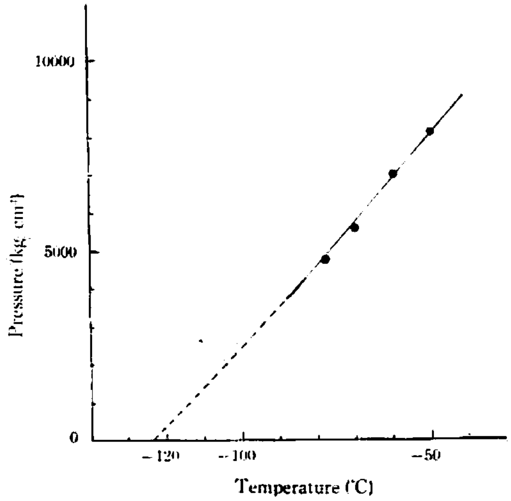

Fig. 3 The limiting pressure for the polymerization

Results

The limiting pressure for the polymerization

There is the limiting pressure for the formation of the polymer of acetaldehyde at each reaction temperature. If acetaldehyde monomer is compressed to the pressure lower than this limiting pressure, even if maintained under the pressure for long period, the polymer of acetaldehyde is not obtained. For example, when acetaldehyde is compressed to the pressure of 4,000 kg/cm^2 at −78°C for 24 hours, the polymerization does not occur. Plotting the limiting pressure against reaction temperature, the linear relation is obtained in this experimental range as shown in Fig. 3. Fawcett and Gibson[2] had reported that acetaldehyde was unchanged at 40°C and 9,000 atm for periods up to 100 hours. This fact is explained from the view that the pressure of 9,000 atm is lower than the limiting pressure for the polymerization.

Table 1 The limiting pressure for the polymerization

Temperature (°C)	−78	−70	−60	−50
Pressure (kg/cm^2)	4780	5525	7000	8100

Determination of the liquid-solid transition

Unfortunately, if the polymerization of acetaldehyde takes place, the discontinuity of the volume change of acetaldehyde is found also in this case as well as the liquid-solid transition. Retarding the polymerization of acetaldehyde, 1 per cent paraldehyde is added to acetaldehyde. The sample of 7 g added paraldehyde is compressed for 3 hours at the pressures above and below this limiting pressure at the intervals of 56 kg/cm^2 and the difference of the lead rod lengths before and after compression is measured at each experiment.

When the sample is compressed at the limiting pressure, the differences of the lead rod lengths are changeable in a wide range, so the measurement at the limiting pressure is omitted. As shown in Fig. 4 the difference of the lead rod length is discontinuous at the limiting pressure. The volume decrease of the liquid-solid transition of acetaldehyde is calculated from the difference of the lead rod length. The results obtained are shown in Table 2.

Table 2 Volume decrease of the liquid-solid transition

Temperature (°C)	−78	−70	−60	−50
ΔV_T (ml/mole)	−4.58	−4.27	−3.84	−3.53

Volume decrease of the polymerization of acetaldehyde

For the measurement of the volume decrease of the polymerization of acetaldehyde, the polymerization of acetaldehyde is performed by the same method as described above and the typical example is shown in Fig. 5. As the yields of the polymer are 25.3%, 24.0%, 21.5% and 20.0% at reaction temperatures, −78°C, −70°C, −60°C and −50°C, respectively, the volume decreases of the polymerization of acetaldehyde at these temperatures are obtained with the correction of the volume

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[2] E. W. Fawcett and R. O. Gibson, *J. Chem. Soc.*, 386 (1934)

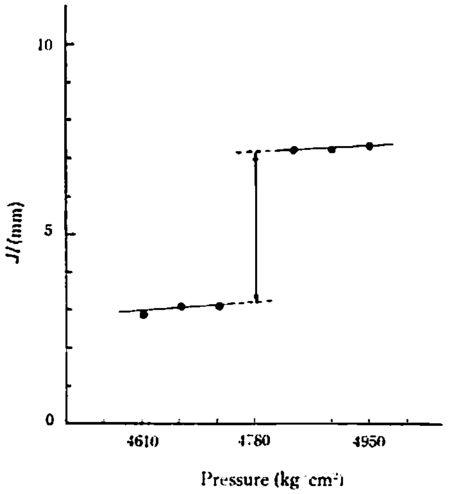

Fig. 4. Volume change of the liquid-solid transition at −78°C
Δl is the difference of the leadrod length between those before and after compression.

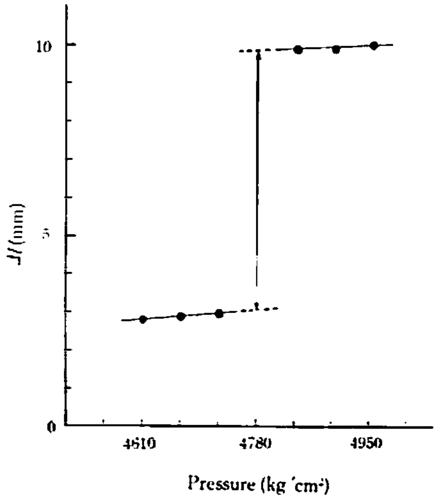

Fig. 5. Volume change of the polymerization and the liquid-solid transition at −78°C
Δl is the same as Fig. 4.

Table 3 Volume decrease of the polymerization

Temperature (°C)	−78	−70	−60	−50
ΔV_p (ml/mole)	−12.1	−12.4	−12.9	−13·2

decreases of the liquid-solid transition of acetaldehyde. The results obtained are shown in Table 3.

The nature of the polymer of acetaldehyde

The polymer obtained is a colorless, non-viscous and elastic solid. and soluble in ordinary organic solvent such as acetone, methyl ethyl ketone, methyl alcohol, ethyl alcohol, ethyl acetate, carbon tetrachloride etc., but insoluble in water, *n*-hexane, *n*-pentane, petroleum ether etc. The infrared spectrum of the polymer is shown in Fig. 6. This infrared spectrum is identical to the infrared spectrum of atactic polyether type polymer which was reported by Furukawa and others.[3] Therefore, from those facts of the solubility in the solvents. the infrared spectrum. and the polymerization at the liquid-solid transition at high pressure, this polymer is confirmed as the atactic polyether type polymer which was prepared by the method of the solidification of acetaldehyde at its freezing point discovered by Letort and Travers[4], and by the alumina catalyst polymerization of acetaldehyde discovered by Furukawa and others.[5]

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3) J. Furukawa, T. Saegusa, M. Kurakano, H. Hirono, T. Iwata and T. Wasai, *J. Chem. Soc. Japan, Industrial Chemistry Section* (*Kogyo Kagaku Zasshi*), **67**, 1920 (1964)

4) M. Letort, *Compt. rend.*, **202**, 767 (1936)
M. S. Travers, *Trans. Faraday Soc.*, **32**, 246 (1936)

5) J. Furukawa, T. Saegusa, T. Tsuruta, H. Fujii, A. Kawasaki and T. Tatano, *J. Chem. Soc. Japan, Industrial Chmistry Section* (*Kogyo Kagaku Zasshi*), **62**, 1962 (1959)

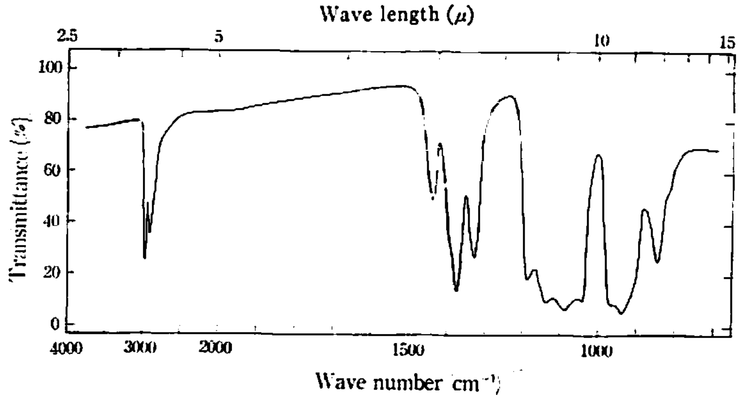

Fig. 6. Infrared spectrum of polymer

Considerations

Volume decrease of the liquid-solid transition

The pressure and temperature dependences of the ΔV_T are shown in Figs. 7 and 8. The ΔV_T decreases with increasing pressure and temperature. This tendency to pressure and temperature can be explained by the following equation given by Zhokhowskii[6],

$$\Delta V = \Delta V_0 \exp[-\kappa(T-T_0)] \qquad (1)$$

where κ is the dimensionless parameter, T_0 and ΔV_0 is the corresponding values at the triple point. Osugi, Shimizu and Onodera[7] found this tendency in the liquid-solid transition of benzene, toluene and monochlorobenzene.

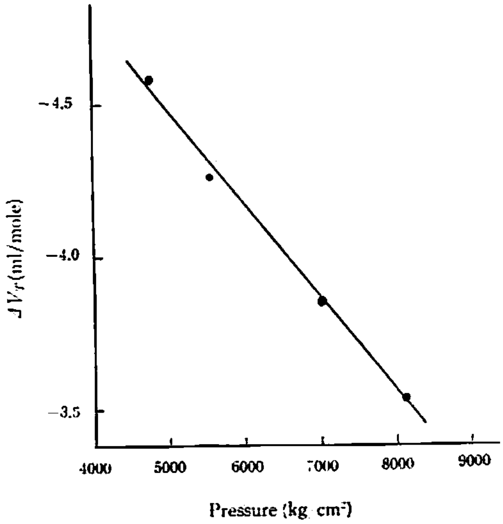

Fig. 7. Effect of pressure on the volume decrease of the liquid-solid transition

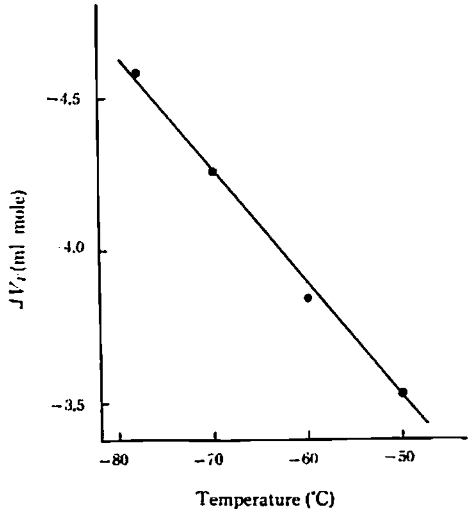

Fig. 8. Effect of temperature on the volume decrease of the liquid-solid transition

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6) M. K. Zhokhowskii, *J. Phys. Chem. U. S. S. R.*, 17 (1964)

7) J. Osugi, K. Shimizu and A. Onodera, *This Journal*, 34, 97 (1964)

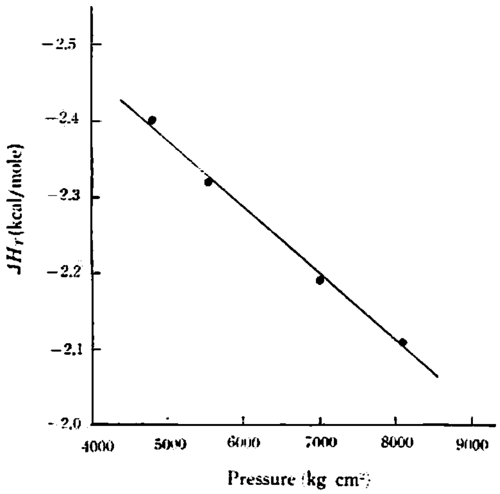


Fig. 9. Effect of pressure on the ΔH_T of the liquid-solid transition

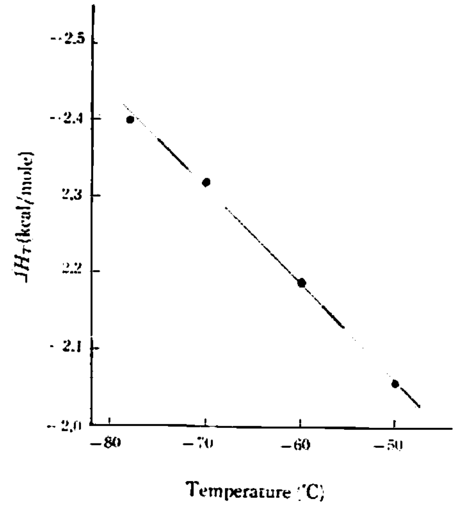


Fig. 10. Effect of temperature on the ΔH_T of the liquid-solid transition

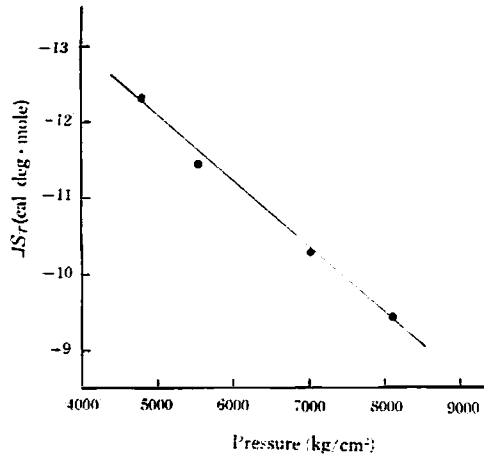


Fig. 11. Effect of pressure on the ΔS_T of the liquid-solid transition

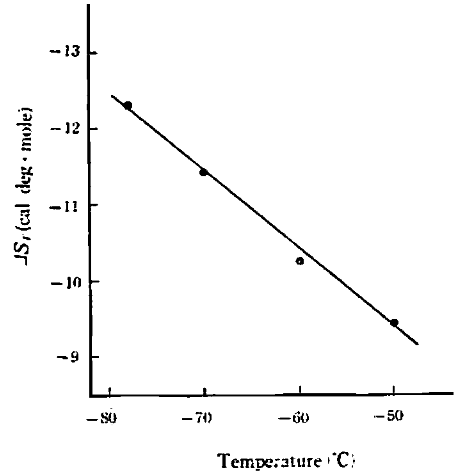


Fig. 12. Effect of temperature on the ΔS_T of the liquid-solid transition

In the measurement of the ΔV_T of the liquid-solid transition of acetaldehyde, in order to retard the polymerization of acetaldehyde, 1 per cent paraldehyde is added to the sample. Therefore, strictly speaking, the obtained value of the ΔV_T does not indicate the volume decrease of the liquid-solid transition of pure acetaldehyde. However, as shown in Fig. 4, the discontinuity of the volume change of acetaldehyde is found evidently at the limiting pressure, the volume changes of pure acetaldehyde and acetaldehyde added 1 per cent paraldehyde at the pressures lower than the limiting pressure are essentially equal as shown in Figs. 4 and 5, and the volume decrease at the limiting pressure is obtained by the extrapolation of the pressures above and below the limiting pressure. In view of the above facts, it seems most reasonable to conclude that for the measurement of the ΔV_T, the presence of 1 per cent paraldehyde in the sample is negligible.

The $\varDelta H_T$ and the $\varDelta S_T$ of the liquid-solid transition

Using the Clausius-Clapeyron equation (2) the $\varDelta H_T$ and the $\varDelta S_T$ of the liquid-solid transition are calculated from the value of the $\varDelta V_T$.

$$\frac{dP}{dT}=\frac{\varDelta H}{T\varDelta V}=\frac{\varDelta S}{\varDelta V} \qquad (2)$$

Plotting the $\varDelta H_T$ and the $\varDelta S_T$ against temperature and pressure, the linear relation is obtained as shown in Figs. 9~12. The $\varDelta H_T$ and the $\varDelta S_T$ increase with temperature and pressure.

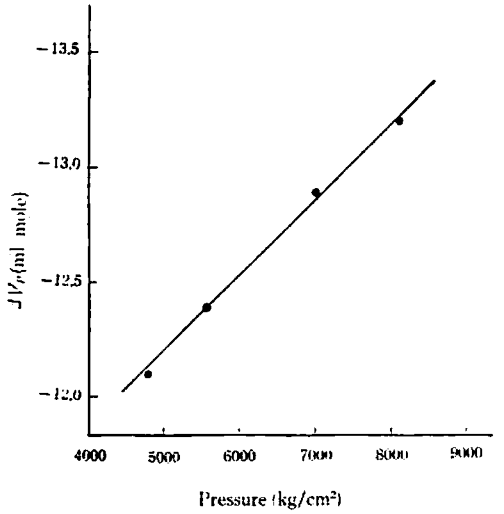


Fig. 13. Effect of pressure on the volume decrease of the polymerization

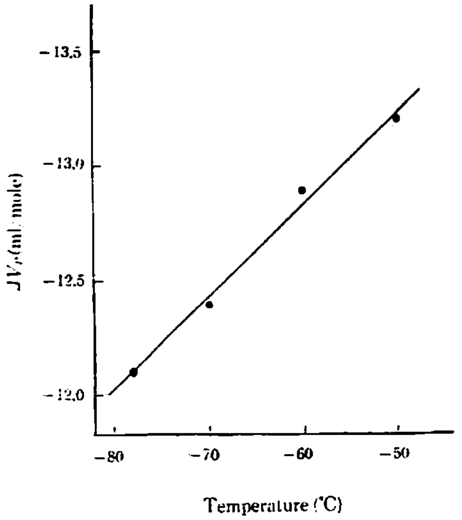
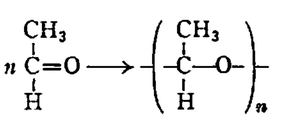


Fig. 14. Effect of temperature on the volume decrease of the polymerization

Volume decrease of the polymerization of acetaldehyde

The acetaldehyde polymer formed is confirmed as the atactic polyether type polymer. Accordingly, this polymerization may be performed by opening the carbonyl group of acetaldehyde as shown in (3). On the relation of the structure between the monomer and the polymer of acetaldehyde, it can be



$$n\,\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}{=}O \longrightarrow \left(-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}-O-\right)_n \qquad (3)$$

assumed that the change of the bond angle between CH_3—C=O and CH_3—C—O is negligible, because the methyl group is spread out with 2Å radius and there is no regularity for the position of the methyl group in the polymer structure since the polymer is atactic one. Accordingly, the cross-sectional area of CH_3—C—H is not changed by the polymerization and the change occurred by the polymerization is the difference of the bond lengths between C=O and C—O. In acetaldehyde, the bond length of C—C is 1.54Å, that of C=O 1.29Å and that of C—H 1.09Å, while van der Waals radius of carbon atom is 1.67Å, that of oxygen atom 1.4Å and that of hydrogen atom 1.2Å. The value of $16.95\times10^{-16}\mathrm{cm}^2$ is calculated as the cross sectional area of CH_3—C—H from those bond lengths and van der Waals radius.

Considering the polymer, the bond length of C—O is 1.43Å. So the value of $-25.4\times10^{-24}\,\mathrm{m}l$ is calculated as the volume decrease for which one molecule of acetaldehyde comes to be the polymer. Then, the value of $-15.3\,\mathrm{m}l/\mathrm{mole}$ is calculated as the volume decrease of the polymerization of acetaldehyde. This value is in good agreement with the values obtained from the experiments.

The effects of temperature and pressure on the ΔV_P are shown in Figs. 13 and 14. The ΔV_P decreases with pressure and temperature, while the ΔV_T increases with temperature and pressure as shown in Figs. 7 and 8. It is considered that this phenomenon may result in the state of alignment of acetaldehyde.

The values of ΔV, ΔH and ΔS will be discussed and used in the next paper.

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