STUDIES ON THE BULK POLYMERIZATION OF ALIPHATIC ALDEHYDES UNDER HIGH PRESSURE[1]

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The bulk polymerization of propionaldehyde was studied at temperatures of 10-35°C as a function of pressure.

The resulting polymer was amorphous and had a polyacetal structure which depolymerized to the original monomer under normal conditions.

The ceiling temperature for the bulk polymerization was determined by extrapolating the yields under various reaction conditions to zero yield (weight measuring method) and also by measuring the temperature rise due to the heat of polymerization (thermal method). The thermal method could follow the polymerization more sensitively than the weight measuring method.

The thermodynamic quantities of polymerization were determined by the volume change of the polymerization and the pressure coefficient of the ceiling temperature. The volume change was obtained by measuring the molar volumes of the polymer and the monomer at 25°C up to $4000\,kg/cm^2$. At 25°C and $6400\,kg/cm^2$, the heat of polymerization is $-4.7\,kcal/mol$, and the entropy change is $-16\,e.\,u.$

The effect of alkyl groups on the bulk polymerization of aliphatic aldehydes is discussed by comparing the present result with the previous ones on butyraldehyde and isobutyraldehyde. The effect of pressure on the ceiling temperature of monomers with poor polymerizability is also discussed in comparison with that on the melting point of some compounds.

Introduction

It is well known that aliphatic aldehydes can be converted into high polymers by the application of high pressure at room temperature, and that the resulting polymers have polyacetal structures which depolymerize to the original monomers under normal conditions. These phenomena were first found by Bridgman and Conant[2]. Further studies were made by several workers from the view points of the reaction mechanism[3, 4] or the structures of the resulting polymers[5].

There are two problems in the polymerization of aliphatic aldehydes under high pressure. One is the reaction mechanism and the other is the effect of pressure on the ceiling temperature. On the former, Conant and Peterson[3] concluded that the polymerization of butyraldehyde could proceed by free radical

1) Polymerization of Aldehydes under High Pressure III
2) P. W. Bridgman and J. B. Conant. *Proc. Nat. Acad. Sci.*, 15, 680 (1929)
3) J. B. Conant and C. O. Tonberg, *J. Am. Chem. Soc.*, 52, 1659 (1930); J. B. Conant and W. R. Peterson, *ibid.*, 54, 628 (1932)
4) V. M. Zhulin and M. G. Gonikberg. *Vysokomolekul. Soedin.*, 3, 262, 268 (1961) *Chem. Abstr.*, 55, 26506c, 26506d (1961)
5) A. Novak and E. Whalley, *Can. J. Chem.*, 37, 1710, 1718 (1959)

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mechanism because the polymerization was catalyzed by benzoyl peroxide. The radical mechanism was supported by Gonikberg and Zhulin[4]. Walling and Augurt[6], however, reported that the propagation step in the polymerization of butyraldehyde involved a simple acid-catalyzed hemiacetal formation because the polymerization was catalyzed by 2, 4. 6-tri-*t*-butylphenol and traces of carboxylic acids, but neither initiated by di-*t*-butyl peroxyoxalate nor inhibited by galvinoxyl. The author and Osugi carried out the bulk polymerization of butyraldehyde to know the reproducibility of the polymerization yield using various catalysts. It was observed that benzoyl peroxide and 2, 4, 6-tri-*t*-butylphenol gave a poor reproducibility, but 1, 1-diphenyl-2-picryl hydrazyl (DPPH) gave a good one. With respect to the second problem, pressure effects on the monomer-polymer equilibrium for chloral in pyridine[7] and butyraldehyde in hexane[8] have been studied. The effect of pressure on the ceiling temperatures of such bulk monomers as α-methylstyrene[9], tetrahydrofuran[10], butyraldehyde[11] and isobutyraldehyde[12] was also investigated. It was found by the present author *et al.*[11, 12] that the ceiling temperatures of butyraldehyde and isobutyraldehyde increased markedly with increasing pressure.

In the present work, the effect of pressure on the ceiling temperature and the thermodynamic quantities for the bulk polymerization of propionaldehyde were determined. Substituent effects on these quantities for aliphatic aldehydes are discussed.

Experimentals

Materials

Propionaldehyde was purified by drying commercial material with anhydrous calcium sulphate and fractionating several times through a packed column. The final middle fraction was put into a glass ampoule which was attached to a high vacuum line, and then degassed. The degassed monomer was distilled four times successively into ampoules containing calcium sulphate. The purified monomer was stored at liquid nitrogen temperature and distilled in vacuum into a sealable ampoule just before use. This treatment was necessary to obtain reproducibility of yield in bulk polymerization.

DPPH was purified by recrystallization from chloroform-ether, dried in vacuum for 40 hr at 80°C and stored in vacuum.

High pressure apparatus and procedures

The general lay-out of the high pressure apparatus has been described previously[11]. Temperatures were kept constant within ±0.1°C. Pressures were measured by a manganin wire whose pressure coefficient was determined with the Bourdon gauge calibrated by the free piston gauge in Kobe Steel Ltd.,

6) C. Walling and T. A. Augurt, *J. Am. Chem. Soc.*, **88**, 4163 (1966)
7) W. K. Busfield and E. Whalley, *Trans. Faraday Soc.*, **59**, 679 (1963)
8) Y. Ohtsuka and C. Walling, *J. Am. Chem. Soc.*, **88**, 4167 (1966)
9) T. G. Kilroe and K. E. Weale, *J. Chem. Soc.*, **1960**, 2839
10) M. Rahman and K. E. Weale, *Polymer*, **11**, 122 (1970)
11) M. Okamoto and J. Osugi, *Nippon Kagaku Kaishi (J. Chem. Soc. Japan)*, **1974**. 31
12) M. Okamoto and J. Osugi, to be published in *Nippon Kagaku Kaishi*

and was reproducible within ± 20 kg/cm^2.

A reaction cell containing the catalyst was dried in vacuum for several hours, and filled with puri-
fied monomer in a dry box under nitrogen atmosphere. The resulting polymer was precipitated from
methanol, dried in vacuum at room temperature, and weighed to determined the yield of polymer.
The experimental errors were within about $\pm 2\%$ at a yield of 35%.

Measurement of the molar volumes and the viscosity

Compressibilities were measured in a mercury-displacement piezometer[13] up to 4000 kg/cm^2 at
25°C. The compressibility of propionaldehyde was measured directly. That of the polymer was mea-
sured by comparing the compressibility of methanol alone with that observed when a known weight of
the polymer film was placed in the piezometer which was then filled with methanol. The molar volumes
were determined by the densities at 1 atm and the compressibilities.

Viscosity measurements on the polymer were attempted in chloroform at 25°C and 0°C, but were
difficult because of the depolymerization.

Differential temperature measurements

The schematic diagram of Bridgman's unsupported area packing for measurements of the pressure
and the differential temperature is shown in Fig. 1. The differential temperature between the center of
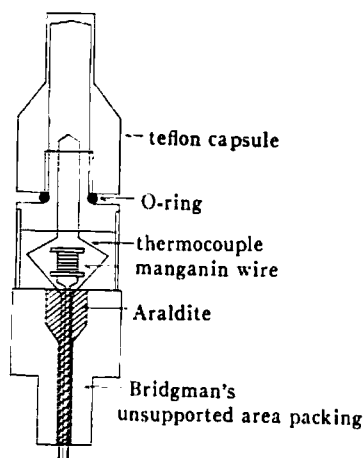

teflon capsule

O-ring

thermocouple
manganin wire

Araldite

Bridgman's
unsupported area packing

Fig. 1. Schematic diagram of Bridman's
unsupported area packing for the
measurements of the pressure and the
differential temperature

a reaction cell and the reference points was measured. The reaction cell was made of Teflon with a thin
wall. Chromel-alumel thermocouples were used to measure the differential temperature. The reference
points were near the inner wall of the high pressure vessel. The signal was amplified by using an am-
plifier (Model PM-16A, TOA Electronics LTD). In the highest sensitivity, the full scale of the recorder
was 40 μV which corresponded to 1°C, and the noise level was ± 0.2 μV.

Infrared spectra

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13) D. M. Newitt and K. E. Weale, *J. Chem. Soc.*, **1951**, 3092

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The polymer was examined as a thin film cast from a chloroform solution. The infrared spectrum was recorded on a Hitati EPI-S2 double beam spectrophotometer.

Results

Properties of the resulting polymer

The resulting polymer is a colourless, non-viscous and elastic solid, and soluble in monomer, chloroform, carbon tetrachloride and ether, but insoluble in methanol. The polymer depolymerizes to the original monomer at the normal condition. The infrared spectrum of the polymer is shown in Fig. 2. This spectrum is identical with that reported by Novak and Whalley[5]. The X-ray diffraction
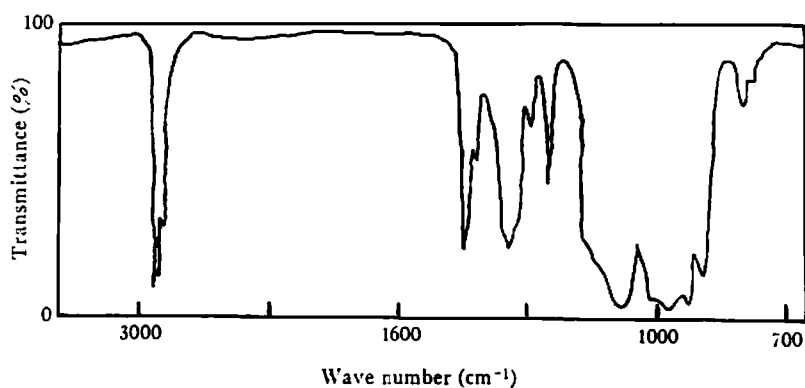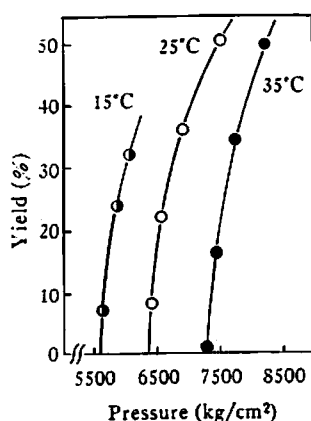
Fig. 2.   Infrared spectrum of polymer

Fig. 3.   Polymerization yield vs.
pressure for propion-
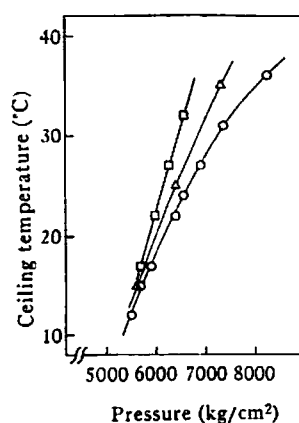aldehyde
Reaction time, 240 min;
[DPPH], 0.2 wt%

Fig. 4.   Pressure vs. ceiling tem-
perature for various ali-
phatic aldehydes
□, isobutyraldehyde;
△, propionaldehyde;
○, butyraldehyde

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pattern showed that the polymer was amorphous. From these results. it was concluded that the polymer has a polyacetal structure.

Effect of pressure on the ceiling temperature of the polymerization

To define that the ceiling temperature is T_c at P_c is to define that the polymerization pressure is P_c at T_c.

The relation between the yield and the pressure is shown in Fig. 3. The pressure which corresponds to zero yield was determined by extrapolation of the curves. These pressures are the polymerization pressures at the temperatures. The ceiling temperatures are shown in Fig. 4 including those of other aliphatic aldehydes (weight measuring method).

Determination of the ceiling temperature in the polymerization by means of the differential temperature measurements

When the heat in the reaction cell changes by the conduction of heat and a chemical reaction, the relaxation of the differential temperature ΔT t sec after compression obeys

$$\frac{d\Delta T}{dt} = -k\Delta T + \alpha R_p, \qquad (1)$$

where the first term on the right hand side shows the Newtonian cooling effect and the second one shows the reaction effect, and k, R_p and α are respectively an overall cooling constant, the rate of the reaction and a proportionality constant.

When a reaction does not occur, that is, there exists no catalyst, the change of ΔT with time was obtained at $25°C$ up to $8000\,kg/cm^2$ by the repetition of compression, and good linearities were observed in the relation between t and $\ln \Delta T$. The values of k were obtained graphically from the slope of above relation, and increased from 1.5×10^{-2} to $2.1 \times 10^{-2}\,sec^{-1}$ with increasing pressure up to $5500\,kg/cm^2$ and were $2.1 \times 10^{-2}\,sec^{-1}$ in the pressure range of $5500-8000\,kg/cm^2$.

When a reaction occurs, the change of ΔT with time was also obtained by the repetition of compression, and a typical example at $25°C$ is shown in Fig. 5. ΔT does not become zero after compression
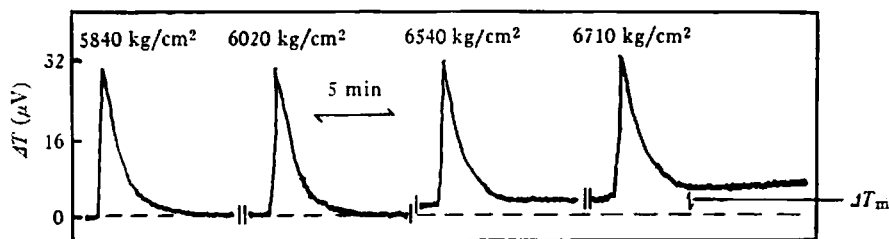

Fig. 5.   A typical example of the change of ΔT with time at $25°C$ and various pressures

at higher pressure than a definite pressure as seen in Fig. 5. The value of this pressure was determined as described in the next paragraph. The sample used for the measurement of ΔT was analyzed immediately after the release of pressure. The volatile fraction was found to be only the parent mono-

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mer by means of gas chromatography and the non-volatile one to be the polymer by means of IR spectrum. So, the temperature rise seems to result from the exothermic polymerization reaction.

At a time when ΔT becomes a minimum, ΔT_m, the term of the left hand side in equation (1) is zero. Then, $\Delta T_m = (\alpha/k) \cdot R_p$ can be used as a measure of the polymerization rate. The relations between ΔT_m and the pressure are shown in Fig. 6. The pressure extrapolated to $\Delta T_m = 0$ corresponds to
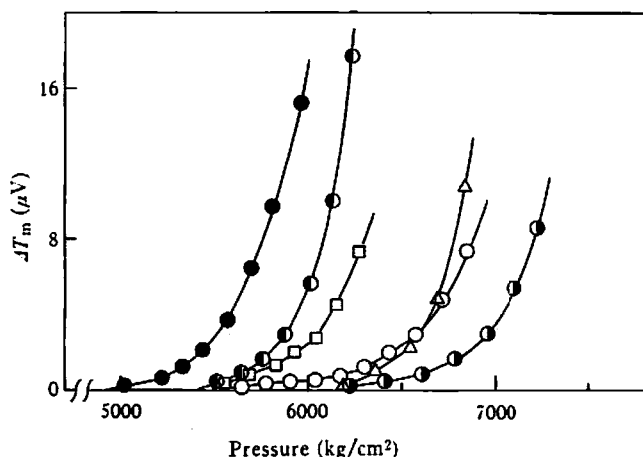

Fig. 6. ΔT_m vs. pressure for propional-
dehyde at various temperatures
and catalyst concentrations
●, [DPPH]=0.15 wt% at 10°C;
◑, [DPPH]=0.35 at 15°C;
□, [DPPH]=0.20 at 15°C;
○, [DPPH]=0.03 at 15°C;
△, [DPPH]=0.10 at 25°C;
◐, [DPPH]=0.02 at 25°C

the polymerization pressure P_c. The relationship between the polymerization pressure and the ceiling temperature is shown in Fig. 7 together with the results obtained by the weight measuring method. The values of the ceiling temperature obtained by both methods are in agreement within 3°C, and their pressure coefficients are also in good agreement.

The volume change of the polymerization

The volume change of the polymerization ΔV $(P, 25°C)$ was determined from the molar volumes of the polymer and the monomer at 25°C. The results are shown in Fig. 8.
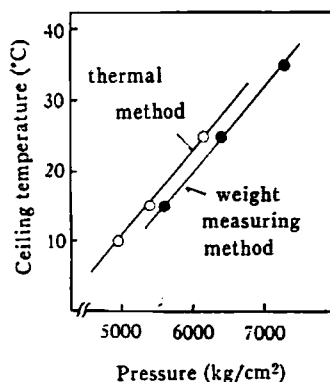

Fig. 7. Ceiling temperature vs.
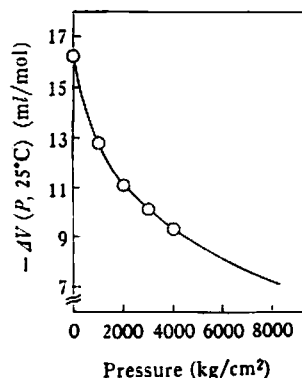pressure for propionalde-
hyde

Fig. 8. ΔV $(P, 25°C)$ vs. pressure
at 25°C

Discussion

A comment on the reaction mechanism

DPPH. which is well known as a radical scavenger, was found by the present author and Osugi to be an effective catalyst for the polymerization of butyraldehyde[11] and isobutyraldehyde[12]. Although the mechanism is still unknown, the catalytic behavior of DPPH seems to suggest, as Augurt and Walling pointed out, that the polymerization of such aliphatic aldehydes as butyraldehyde, isobutyraldehyde and propionaldehyde do not proceed with a radical process.

ΔT increases with time after compression as shown in the case of $6710 \, \mathrm{kg/cm^2}$ in Fig. 5. From equation (1), this result indicates that R_p increases with time and suggests that the active species (M*) is accumulated during the polymerization, since in reversible addition polymerization R_p is equal to $(k_p[M] - k_d)[M*]$. Then, it may be concluded that the polymerization reaction has a slow initiation rate.

The thermodynamic quantities for the polymerization

When polymer and monomer are at equilibrium in addition polymerization, the following relationship is obtained[14];

$$\Delta G_p^\circ / RT = \ln [M]_e / [M]_0 \qquad (2)$$

where $[M]_e$, $[M]_0$ and ΔG_p° are respectively the equilibrium molar concentration of monomer, the molar concentration of pure monomer and the standard free energy change of the polymerization. This relationship is based on the assumptions that the degree of polymerization is very large and the solution is ideal. Equation (2) is expressed by the following equation when $[M]_e = [M]_0$:

$$\Delta G_p^\circ = \Delta H_p^\circ - \Delta S_p^\circ \cdot T_c^{id} = 0$$

and then,
$$T_c^{id} = \Delta H_p^\circ / \Delta S_p^\circ$$

where ΔH_p° and ΔS_p° are the enthalpy change and the entropy change of the polymerization at T_c^{id} under $P \, \mathrm{kg/cm^2}$ in the ideal solution. respectively, and T_c^{id} is the ceiling temperature at $[M]_e = [M]_0$ under $P \, \mathrm{kg/cm^2}$ in the ideal solution.

For solution polymerization, Bywater[15] has studied the monomer-polymer equilibrium in a real solution. A similar treatment was applied to bulk polymerization. According to the Flory-Huggins theory[16], the respective activities of monomer and monomer segments in the polymer are given by the following equations:

$$\ln a_1 = \ln v_1 + v_2 + x v_2^2 \qquad \text{(for monomer)} \qquad (3)$$

$$\ln a_2 = v_2 - 2x v_2 + x v_2^2 \qquad \text{(for polymer)} \qquad (4)$$

14) F. S. Dainton and K. J. Ivin, *Quart. Rev.*, **12**, 61 (1958)

15) S. Bywater, *Makromol. Chem.*, **52**, 120 (1962)

16) P. J. Flory, "Principles of Polymer Chemistry", Chap. 12, Cornell University Press (1953)

where v_1 and v_2 ($=1-v_1$) are respectively the volume fractions of monomer and polymer, and x is the interaction parameter between monomer and polymer. The standard states of the activities for monomer and polymer were chosen as follows:

    (a)   the standard state of monomer is pure liquid,

        and

    (b)   the standard state of polymer is infinite dilution in monomer.

When the monomer and the monomer segments in the polymer are at equilibrium, the standard free energy change of the bulk polymerization ΔG_p^* is given as follows:

$$-\Delta G_p^*/RT=\ln a_2-\ln a_1. \tag{5}$$

From equations (3), (4) and (5), ΔG_p^* is given by the following equation:

$$\Delta G_p^*/RT=\ln v_1+2xv_2. \tag{6}$$

In an ideal solution, equation (6) is identical with equation (2).

    The ceiling temperature (T_c) in the bulk polymerization is a temperature at which ΔG_p^* becomes zero. Then, the pressure coefficient of T_c obeys the following equation:

$$\frac{dT_c}{dP}=\frac{\Delta V_p^*}{\Delta S_p^*}, \tag{7}$$

where ΔV_p^* and ΔS_p^* are the volume change and the entropy change of the polymerization at T_c under P kg/cm^2 in the standard state, respectively.

    Under the assumption that the change of partial molar volume ΔV_p^* is equal to the change of molar volume ΔV, the thermodynamic quantities for the polymerization of propionaldehyde at 25°C were determined by equation (7) using ΔV (P, 25°C) and the pressure coefficient of the ceiling temperature, and are shown in Table 1 together with the results of other aliphatic aldehydes.

Table 1   Thermodynamic quantities for the bulk polymerization of aliphatic aldehydes at 25°C

monomer	pressure (kg/cm^2)	$-\Delta S_p^*$ (e. u.)	$-\Delta H_p^*$ (kca/mol)	reference
propionaldehyde	6400	16	4.7	this work
butyraldehyde	6700	20	6.0	11)
isoburyraldehyde	6160	11	3.3	12)

    The thermodynamic quantities along the equilibrium line determined by the polymerization pressure and the ceiling temperature were estimated as given below. The effects of pressure and temperature on the respective values of ΔV_p^* and ΔS_p^* are shown by the following equations;

$$\Delta S_p^*(P_c, T_c)=\Delta S_{p'}^*(P_c', T_c')+\int_{T'_c}^{T_c}(\Delta C_p^*/T_c)dT_c-\int_{P'_c}^{P_c}(\partial\Delta V_p^*/\partial T_c)_{P_c}dP_c, \tag{8}$$

$$\Delta V_p^*(P_c, T_c)=\Delta V_{p'}^*(P_c', T_c')+\int_{T'_c}^{T_c}(\partial\Delta V_p^*/\partial T_c)_{P_c}dT_c+\int_{P'_c}^{P_c}(\partial\Delta V_p^*/\partial P_c)_{T_c}dP_c, \tag{9}$$

and

$$T_c=T_c(P_c), \tag{10}$$

where $\Delta C_p{}^*$ is the difference in the heat capacity between polymer and monomer in the standard state. A linear relation between T_c and P_c is observed in the polymerization of isobutyraldehyde[12] and propionaldehyde. The conditions for this are given as follows;

$$\Delta V_{p'}{}^*/\Delta S_{p'}{}^*=a \quad \text{and} \quad dT_c/dP_c=a. \tag{11}$$

Then, from equations (7), (8) and (9) one can obtain the following equation:

$$a\int_{T'_c}^{T_c}(\Delta C_p{}^*/T_c)dT_c-2\int_{T'_c}^{T_c}(\partial\Delta V_p{}^*/\partial T_c)_{P_c}dT_c=\int_{P'_c}^{P_c}(\partial\Delta V_p{}^*/\partial P_c)_{T_c}\,dP_c. \tag{12}$$

The ceiling temperature for propionaldehyde increases from 15°C at 5600 kg/cm² to 35°C at 7300 kg/cm², and so the value of a defined above is 0.50 deg·ml/cal. The value of $\Delta C_p{}^*$ for propionaldehyde is assumed to be -2.4 cal/mol·deg at 1 atm, the same as that estimated for butyraldehyde[11] and to be independent of the pressure and the temperature. In the case of the weight measuring method, the following values are obtained approximately;

$$a\int_{288}^{308}(\Delta C_p{}^*/T_c)dT_c\sim-0.1 \text{ ml/mol}.$$

$$\int_{5600}^{7300}(\partial\Delta V_p{}^*/\partial P_c)_{25°C}dP_c\sim+0.8 \text{ ml/mol},$$

and so from equation (12)

$$\int_{288}^{308}(\partial\Delta V_p{}^*/\partial T_c)_{P_c}dT_c\sim-0.4 \text{ ml/mol}. \tag{13}$$

The mean value $\langle\partial\Delta V_p{}^*/\partial T_c\rangle$ was about -0.02 ml/mol·deg in the experimental range. By using this value, equation (9) was rewritten as follows;

$$\Delta V_p{}^*(P_c, T_c)\sim-8.2-0.02(T_c-288)+\int_{5600}^{P_c}(\partial V_p{}^*/\partial P_c)_{25°C}dP_c \tag{14}$$

Then, $\Delta S_p{}^*$ at each pressure is given by the following relation:

$$\Delta S_p{}^*=\text{equation (14)}/a.$$

An equation corresponding to equation (14) was also obtained in the case of the thermal method, and $\Delta S_p{}^*$ was similarly determined. The thermodynamic quantities thus obtained are shown in Table 2. As seen in Table 2, $-\Delta S_p{}^*$ seems to decrease slightly with increasing pressure, while $-\Delta H_p{}^*$ to be almost constant.

As seen in Table 1 and Fig. 4, the values of T_c have not large differences among aldehydes.

Table 2   Thermodynamic quantities for the polymerization of propionaldehyde

pressure (kg/cm²)	T_c (K)	$-\Delta S_p{}^*$ (e. u.)	$-\Delta H_p{}^*$ (kcal/mol)	pressure (kg/cm²)	T_c (K)	$-\Delta S_p{}^*$ (e. u.)	$-\Delta H_p{}^*$ (kcal/mol)
weight measuring method				thermal method			
5600	288	16.4	4.73	4950	283	17.0	4.81
6400	298	16.0	4.76	5400	288	16.6	4.79
7300	308	15.6	4.80	6150	298	16.2	4.83

Nevertheless, $-\Delta H_p{}^*$, $-\Delta S_p{}^*$ and the pressure coefficient of T_c are greatly affected by the alkyl groups of the aldehydes, and $-\Delta H_p{}^*$ is extremely low compared with those of typical ethylene derivatives, which range from 8 (α-methylstyrene) to 21 kcal/mol (vinyl acetate)[14,17].

In the polymerization of ethylene derivatives, Dainton and Ivin have pointed out that groups substituted on the olefinic bond affect the enthalpy change of the polymerization whose variations arise mainly through (i) the steric strain in the polymer and (ii) the differences in the stabilization energy between monomer and polymer[14]. For the various aliphatic aldehydes, the heats of hydrogenation ΔH_h[18] which are a measure of the stabilization energy are shown in Table 3. ΔH_h seems to change in

Table 3   Heat of hydrogenation, ΔH_h, of RCHO in the liquid phase (l) and gas phase (g) at 25°C and 1 atm[18]

R	$-\Delta H_h$ (l) (kcal/mol)	$-\Delta H_h$ (g) (kcal/mol)
C_2H_5	20.25	16.0
n-C_3H_7	22.48	17.9
iso-C_3H_7	20.19	15.8

the same way as $\Delta H_p{}^*$ in the case of propionaldehyde and butyraldehyde, while $\Delta H_p{}^*$ for isobutyraldehyde is much smaller than that expected from ΔH_h. This fact may indicate that the steric strain in the poly (isobutyraldehyde) is larger than those in the other polymers.

The entropy change for the polymerization of ethylene derivatives ranges from -25 to -30 e.u., and is not affected significantly by the steric strain in the polymer[14]. The linear extrapolation of Fig. 7 (weight measuring method) to atmospheric pressure leads to a ceiling temperature of $-50°C$, which gives $\Delta S_0{}^* \sim -21$ e.u. at 1 atm under the assumption that $\Delta H_p{}^*$ is considered to be constant as mentioned above. The values of $\Delta S_0{}^*$ thus estimated for isobutyraldehyde and butyraldehyde are -16 e.u. and -25 e.u., respectively. Mita et al. studied the effect of solvents on the polymerization of chloro- and methyl-substituted acetaldehydes catalyzed by sodium benzylate[21]. They showed that the entropy change ranged from -17.6 e.u. in tetrahydrofuran to -22.4 e.u. in hexane for the polymerization of isobutyraldehyde, and concluded that it was remarkably affected by the solvation of monomer in solution and by the association for monomer itself in bulk. The wide variation in $\Delta S_p{}^*$ or $\Delta S_0{}^*$ for the aliphatic aldehydes may arise from differences in the degree of association for monomers themselves and from those in the solution properties of the polymers.

The effect of pressure on the ceiling temperature

The polymerization would usually occur in the liquid phase which exists between the ceiling temperature and the melting point (T_s). The reaction range for the polymerization increases with increasing

17) G. E. Ham, "Vinyl Polymerization", Vol. 1, Part 1, Chap. 8, Marcel Dekker, Inc. (1967)
18) ΔH_h is obtained from the standard heat of formation of aliphatic aldehydes[19] and that of the corresponding alcohols[20].
19) E. Buckley and J. D. Cox, Trans. Faraday Soc., 63, 895 (1967); J. Tjebbes, Acta Chem. Scand., 16, 953 (1962); G. R. Nicholson. J. Chem. Soc., 1960, 2377
20) J. H. S. Green, Quart. Rev., 15, 125 (1961)
21) I. Mita, I. Imai and H. Kambe, Makromol. Chem., 137, 155 (1970)

pressure when $dT_c/dP > dT_s/dP$, and decreases with increasing pressure when $dT_c/dP < dT_s/dP$. The pressure coefficients of T_c and T_s are shown in Table 4 and 5, respectively. As seen in Table 4, d ln

Table 4 Pressure coefficients of the ceiling temperature of various monomers at 1 atm and 6000 kg/cm²

monomer	pressure (kg/cm²)	$-\Delta V_p$ (ml/mol)	$-\Delta H_p$ (kcal/mol)	$\Delta V_p/\Delta H_p$ $(=d \ln T_c/dP)$ (ml/kcal)	reference
propionaldehyde	1	16.2 (25°C)	—	2.3[a]	this work
	6000	8.1 (25°C)	4.7	1.7	
butyraldehyde	1	16.2 (25°C)	5.07[b]	3.2	11)
	6000	7.9)25°C)	6.0	1.3	
isobutyraldehyhe	1	17.7 (25°C)	—	3.7[a]	12)
	6000	7.7 (25°C)	3.3	2.4	
chloral	1	22 (15°C)	8.0	2.7	7)
α-methylstyrene	1	14.1 (20°C)	8.1	1.7	9)
tetrahydrofuran	1	9.5 (26°C)	4.3	2.2	10)
styrene	1	19.8 (27°C)	17.7	1.1	22)
methyl methacrylate	1	24.5 (27°C)	13.8	1.8	22)

a) These values are obtained from dT_c/dP at high pressure and T_c at 1 atm extrapolated linearly.
b) Value measured at 1 atm and 20°C by Walling et al.[8]

Table 5 Pressure coefficients of the melting point at 1 atm and high pressure.

	pressure (kg/cm²)	$d \ln T_s/dP$ (ml/kcal)	reference
acetaldehyde	1	2.7[a]	23)
	6000	1.6	
carbon dioxide	1	3.2[b]	24)
	6000	1.6	
chloroform	1	3.2[b]	24)
	6000	1.9	
α-methylstyrene	1	4.0[c]	25)
	3790	2.7	
toluene	1	4.5	26)
	6000	1.8	
sulphur dioxide	1	3.3	22)

a) From T_s at 1 atm and 4780 kg/cm².
b) From T_s at 1 atm and 4000 kg/cm².
c) From T_s at 1 atm and 2140 kg/cm².

T_c/dP for the monomers such as ethylene derivatives has smaller values than those for the aliphatic aldehydes. This fact is attributable to extremely low values of $-\Delta H_p{}^*$, that is, low polymerizability

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of aliphatic aldehydes. Comparing Tables 4 and 5, $d \ln T_c/dP$ is smaller than $d\ln T_s/dP$ in the case of the ethylene derivatives, however, in the case of the aliphatic aldehydes $d\ln T_c/dP$ seems to be as large as or larger than $d\ln T_s/dP$. It appears likely that the increase of pressure may increase the ceiling temperature in the case of the bulk polymerization of such monomers with low polymerizability as aliphatic aldehydes more greatly than in that case of ethylene derivatives, and may increase the reaction range between T_c and T_s in the liquid phase polymerization. In particular, the effect of pressure on a polymerization system in which T_c exists near or below T_s would be of interest in connection with this point of view.

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