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HIGH-PRESSURE MELTING IN POLYETHYLENE

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The melting point of polyethylene has been determined at high pressures up to 30,000 atm by the volume-discontinuity method and differential thermal analysis. The effect of increasing the pressure up to 5,000 atm is to reduce the volume of fusion. Suitable values for the parameters of the Simon equation, a and c , have been obtained from the melting curve.

Introduction

Knowledge of melting properties at high pressures is important because many thermodynamic informations, which experiments at atmospheric pressure do not yield directly, can be obtained. Most previous investigations of the effect of pressure on the melting points have largely been concerned with elements, semiconductors, ionic compounds, and simple organic compounds. In early works elements, especially metals were widely studied and they were reported by Strong¹⁾, Bundy and Strong²⁾, and others. Recently there are many investigations about inorganic compounds, such as alkali halides (Clark, 1959)³⁾, II-VI compounds (Jayaraman, Kennedy *et al.*, 1963, 1964)⁴⁾, nitrates (Owen, 1963, 1965)⁵⁾, potassium halides (Pistorius, 1965)⁶⁾, silver halides (Deaton, 1965)⁷⁾, and so on. Nelson *et al.*⁸⁾ have studied the melting of *n*-paraffins under pressure up to 10 kb. But few works about polymers have been done because of many difficulties.

Polyethylene has high crystallinity among various polymers and shows sharp melting phenomena analogous to that of the substances which have low molecular weight. The melting curve of polyethylene as a function of pressure was reported over the pressure range of 0 to 3,000 atm⁹⁾, but no other previous investigation of the effect of high pressure on the melting point has been reported. Since polyethylene is widely employed as a solid pressure container, the determination of the pressure dependence of its

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- 9) S. Matsuoka, *J. Polymer Sci.*, **57**, 569 (1962)

melting is of special importance. The present work was carried out to study the high pressure melting of polyethylene up to 30,000 atm. The melting curve has been analysed if it can be fit with the Simon equation and by comparing the heat of fusion calculated by using the Clapeyron equation with the value reported in literature. The melting points estimated from the change of folded chain length of single crystal in the previous paper¹⁰⁾ were found to agree well with those of the direct measurement of this work.

The density has been measured for the samples crystallized from the melt under pressure.

Experimental

The sample used for this investigation was high density linear polyethylene, Marlex 50. The melting point at atmospheric pressure agreed with the best value obtained from literature, i. e. 136°C. The phase transition up to 5,000 atm was investigated with the volume-discontinuity method. The piston-cylinder type high pressure vessel and high pressure press used are the same as those in the previous paper¹⁰⁾. Only the vessel was illustrated in Fig. 1. Heating was carried out with an electric furnace, whose temperature was constant within $\pm 0.5^\circ\text{C}$. The sample leakage was prevented by the use of Bridgman's unsupported area gaskets of fluorinated rubber and Teflon. The back-up-ring of copper was used at high temperature. The vertical piston displacement was measured with a dialmicrometer, the sensitivity of which was 10^{-3} mm. The values of the changes of volume on melting were obtained from the compressing curves at constant temperature. The isothermal compressing curve at 178°C is shown in Fig. 2.

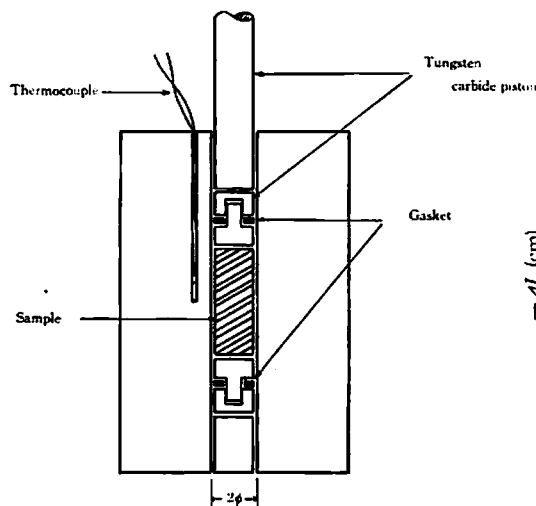


Fig. 1 Piston-cylinder type high pressure vessel

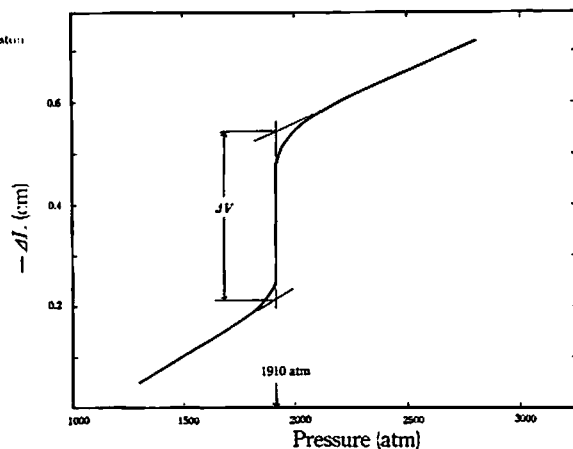


Fig. 2 Isothermal compressing curve at 178°C

Pressures up to 30,000 atm were generated in a compact cubic anvil device, which consists of six carbonyl anvils. The sample is held inside a cubic block of pyrophyllite whose sides are initially 25 per cent larger than the sides of the square anvil faces. As the anvils advance to compress the sample volume,

10) J. Osugi, K. Hara, N. Hirai, and J. Hikasa, *This Journal*, 34, 59 (1964)

some of the pyrophyllite is extended into the gap between the anvil sides, and this extended material provides compressive support for the high pressure ends. The pressure calibration techniques have been already described in detail¹¹⁾. A cylindrical specimen, 3 mm in diameter and 6 mm in length, was placed inside the pyrophyllite cube. As shown in Fig. 3, the specimen was enclosed in a pyrophyllite tube and placed inside a carbon heater tube. The phase transition was detected by differential thermal analysis (DTA). Iron-constantan thermocouples were used, where one junction was placed near the heater and another was kept at the center of the specimen. This technique yielded barely detectable signals for the melting. Thermocouple leads were placed between the anvils. The carbon served as a heat source due to the passage of high alternating current at low voltage from the two opposing anvils.

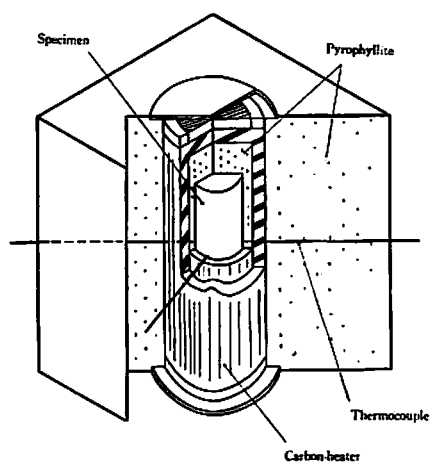


Fig. 3 Schematic view showing the internal construction of the pyrophyllite pressure-transmitting cube for DTA measurements

A density gradient column of ethanol-water mixture was used for the density measurement. This column covered a density range of $0.900\sim 1.000\text{ g/cm}^3$ with an accuracy of $\pm 0.003\text{ g/cm}^3$. The specimen cut into small pellets, 3 mm in diameter, was investigated.

Results and Discussion

The melting P - T curve of polyethylene is shown in Fig. 4. Fig. 4(a) was obtained from the volume discontinuity method and Fig. 4(b) was obtained from DTA measurement. It has an initial slope of 0.025°K/atm and shows a concavity toward the pressure axis; it means $(dT_m/dP) > 0$ and $(d^2T_m/dP^2) < 0$.

No polymorphic transition was observed in the pressure range of this work, and there is no indication of irregularity in the melting curve.

As shown in Fig. 5, ΔV decreases with pressure, and it amounts to $\Delta V_{400\text{atm}} = 0.06\text{ cc/g}$, while $\Delta V_{0\text{atm}} = 0.17\text{ cc/g}$.

The melting points are predicted from the Clapeyron equation

11) J. Osugi, K. Shimizu, K. Inoue, and K. Yasunami, *This Journal*, **34**, 1 (1964)

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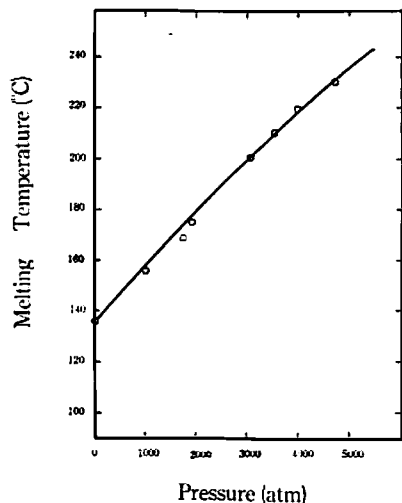


Fig. 4. (a) Melting curve of polyethylene up to 5,000 atm

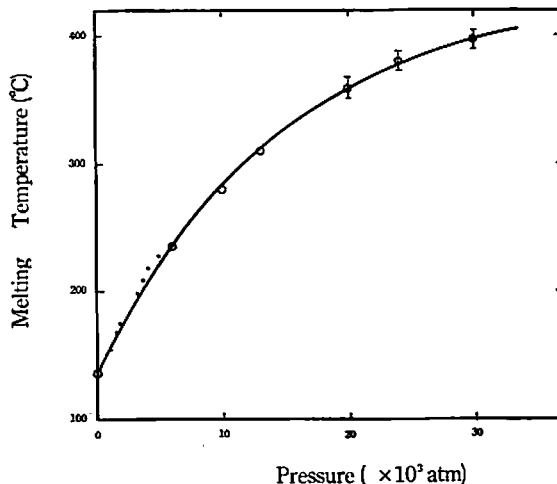


Fig. 4. (b) Melting curve of polyethylene up to 30,000 atm. Small points show the results in Fig. 4(a)

$$\frac{dP}{dT_m} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T_m \Delta V} \quad (1)$$

where T_m and P are the temperature and pressure at the melting, and ΔH and ΔS are the changes of enthalpy and entropy on melting respectively. Table 1 contains the enthalpy on melting obtained from $(dP/dT_m)_{P=0}$ and the value of ΔV extrapolated to zero pressure, and the value reported in literature for comparison.

Table 1 Melting parameters at zero pressure

$(dP/dT_m)_{P=0}$	ΔV	ΔH	ΔH (literature value*)
40 atm/°K	0.17 cc/g	69 cal/g	66.5 cal/g (calorimetrically)

(*) M. Dole and B. Wunderlich, *Makromol. Chem.*, **34**, 29 (1959)

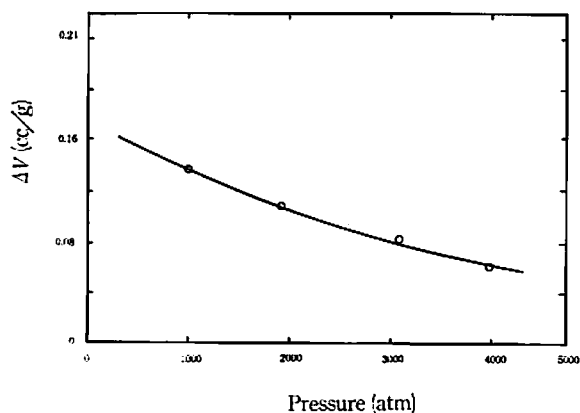


Fig. 5 Variation of ΔV with pressure

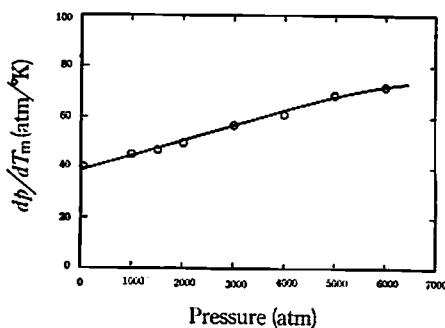
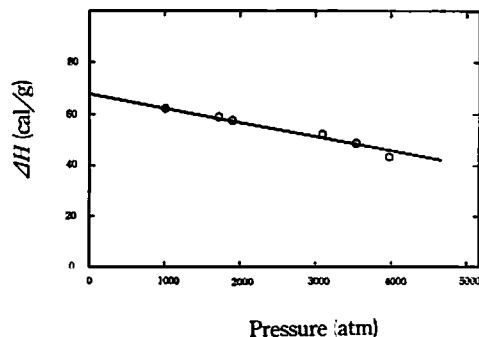
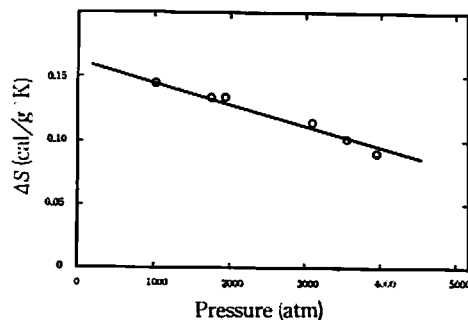


Fig. 6 Variation of dP/dT_m with pressure

Fig. 7 Variation of ΔH with pressureFig. 8 Variation of ΔS with pressure

The slope of the melting curve increases with pressure (Fig. 6). Thus knowledge of dP/dT_m and ΔV permits the calculation of the change of ΔH and ΔS with pressure from the equation (1). They are shown in Figs. 7 and 8. Both tend to decrease slightly with pressure.

The melting curve can be represented quite well by the Simon equation

$$P_m - P_0 = a[(T_m/T_0)^c - 1] \quad (2)$$

where P_m and T_m are the pressure and absolute temperature at the melting point. T_0 is the melting point at pressure P_0 , and a and c are adjustable constants. The Simon parameters have been determined so that S in the following equation may be minimized.

$$S = \sum_i [P_m - P_0 - ax_i]^2 \quad (3)$$

where $x_i = (T_i/T_0)^c - 1$. The parameters of the Simon equation are given in Table 2.

Table 2 Parameters of the Simon equation

T_0	c	a
409°K	4.5	3.1×10^3 atm

They agree well with the melting curve over all the studied pressure range. The initial slope of the melting curve, $(dT_m/dP)_{P=0}$, is T_0/ac by differentiation of the Simon equation. Substituting a and c with the obtained values, we have 0.028°K/atm , which agrees well with the value described above, 0.025°K/atm . This is also an evidence that these parameters express well the experimental results. Considerable effort has been made in fitting high pressure melting curves to the Simon equation, and Babb¹²⁾ has estimated the values of the parameters for many substances. The values obtained above seem favorable in comparison with those found for other materials. For comparison the Simon parameters of the substances from recent papers are given in Table 3. At present no satisfactory theoretical explanation of the Simon parameters exists, but it is probable that the quantity a is related to the internal pressure. As for the value of a , organic crystals have smaller values than most of the inorganic ionic crystals.

The folded chain length in polyethylene single crystal increases rapidly as it approaches the melting

12) S. E. Babb, Jr., *J. Chem. Phys.*, **38**, 2743 (1963)
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Table 3 Parameters of the Simon equation for various substances from recent literatures

Substance	a (kb)	c	Literature
LiCl	14.5	2.5	(3)
NaF	14.3	5.5	(3)
NaCl	16.7	2.7	(6)
NaBr	12.2	2.9	(3)
NaI	10.1	2.8	(3)
KCl	6.9	5.7	(3)
	5.98	5.99	(6)
KBr	3.57	3.57	(6)
AgCl	55.0	1.7	(7)
AgBr	28.0	2.5	(7)
AgI	9.5	8.5	(7)
n-C ₁₈ (Octadecane)	3.45	3.39	(8)
n-C ₂₄ (Tetracosane)	4.5	2.84	(8)

point. This is correct at elevated pressures¹⁰⁾. The melting points estimated from the changes of folded period (161°C at 1,010 atm, 185°C at 1,970 atm) are found to be suitable in the present paper.

The density crystallinity was determined by use of the average of Nielson's¹³⁾ and Gubler and Kovacs'¹⁴⁾ value for V_a (1.173 cm³/g) and Swan's¹⁵⁾ value for V_c (1.001 cm³/g). As seen in Table 4, the crystallinity of polyethylene crystallized from the melt under high pressure increases. But in the case of non-melting no appreciable change was observed even under 30,000 atm. When polyethylene was crystallized from the melt under high pressure, the extended-chain lamellae were observed¹⁰⁾. This increase in crystallinity means the effect of the occurrence of the structure. It is conceivable that this quantity exceeds the possible change of voids. X-ray diffraction indicates no change of the structure in every case, as may be expected.

Table 4 Density and crystallinity

Crystallization conditions Pressure (atm)	Density (g/cm ³)	Crystallinity (%)
1	0.975	87
1,010 (Cryst. from melting)	0.973	91
1,900 (Cryst. from melting)	0.990	95
3,100 (Cryst. from melting)	0.990	95
30,000 (Non-melting)	0.977	89

It is possible to conclude from the results given above that the extended-chain lamella structure crystallized from the melt under high pressure is not the change of crystal structure, but the change of morphology of the molecular chain.

13) L. E. Nielson, *J. Appl. Phys.*, **25**, 1209 (1954)14) M. G. Gubler and A. J. Kovacs, *J. Polymer Sci.*, **35**, (1959)15) P. R. Swan, *J. Polymer Sci.*, **56**, 403 (1962)

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