

Thermodynamic Properties of Polyethylene and Eicosane.

I. P — V — T Relations and Internal Pressure

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ABSTRACT: The P — V — T relations are measured for linear polyethylene over the temperature range from 20 to 230°C and for eicosane from -30 to 120°C under hydrostatic pressures up to 800 kg/cm², using a pressure apparatus which is equipped with pyrex glass windows and a dilatometer. From the results the thermal expansion coefficient, α , compressibility, β , and internal pressure, P_i are obtained and their temperature dependences of polyethylene and eicosane are compared with each other. These quantities show λ -type changes in the melting region which are broad for polyethylene and narrow for eicosane. α is more sensitive than β to the premelting, and as a result P_i begins to increase at a temperature as low as 50°C for polyethylene.

P_i of eicosane in the solid state is smaller than that of polyethylene. P_i of each sample in the liquid state is not proportional to V^{-2} but to V^{-6} for polyethylene and to $V^{-2.45}$ for eicosane.

KEY WORDS P — V — T Relations / Pressure Vessel / Thermodynamic Quantities / Internal Pressure / Polyethylene / Eicosane /

For the purpose of thermodynamic studies of polymers as well as low-molecular-weight substances, it is important to know the P — V — T (pressure—volume—temperature) relations, that is, the equation of state, from which valuable quantities characterizing thermodynamic states can be obtained. For example, internal pressure, P_i , as one of such quantities, represents the intermolecular interactions and is additionally important because cohesive energy density, another measure of the intermolecular interactions, can not be obtained directly by experiments in the case of polymers.

Up to the present, many studies¹⁻¹¹ have been published on the P — V — T relations of polymers, but, for crystalline polymers, at least the data and the analyses do not seem to be adequate to discuss thermodynamic states and the changes in them at melting temperature. In this and the succeeding papers some thermodynamic quantities of linear polyethylene are presented from observed P — V — T relations, being compared with those of n -paraffine (eicosane), which has a more complete crystallinity than polyethylene. Sims¹² has also measured thermal pressure coefficient of polyethylene and eicosane

in the vicinity of melting temperature, but not over a wide range of temperature.

In order to study thermodynamic states of crystalline polymers, it is necessary to measure volume under hydrostatic pressure over a wide range of temperature covering the molten state. A pressure apparatus of piston in cylinder type frequently used in these studies appears not to be adequate for the purpose, because it is doubtful whether or not hydrostatic pressure equilibrium is attained. In this work a pressure apparatus was developed, which is equipped with glass windows through which the height of mercury meniscus in the dilatometer in the pressure vessel can be read directly. Because of strength limitations of the glass window, the available pressure must be restricted to below 1000 kg/cm², but this is high enough to study the behavior near atmospheric pressure.

The thermodynamic quantities discussed here are as follows.

Thermal expansion coefficient

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (1)$$

Compressibility $\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (2)$

Internal pressure

$$\begin{aligned} P_i &= \left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial V} \right)_T - P \\ &= T \left(\frac{\partial P}{\partial T} \right)_V - P \approx T \left(\frac{\partial P}{\partial T} \right)_V \\ &= T \frac{\alpha}{\beta} \end{aligned}$$

where V is volume, T temperature, P pressure, U internal energy, and S entropy.

EXPERIMENTAL

Materials

Unfractionated linear polyethylene of molecular weight $M=34000$ was presented by the Mitsui Petroleum Co.. In order to avoid changes in crystalline structures such as recrystallization and thickening of lamellae during compression or heating, the sample was crystallized for a long time at high temperature, *i.e.*, at 130°C for a month. The crystallinity was calculated as 78.2% from the density measurement by the floatation method with toluene-carbon tetrachloride mixtures.

Eicosane was obtained from the Takachiho Chemical Co.. Its purity was stated to be more than 99.9%.

Apparatus and Procedure

The block diagram of the pressure apparatus is shown in Figure 1 and the container part with pyrex glass windows in Figure 2. A dilato-

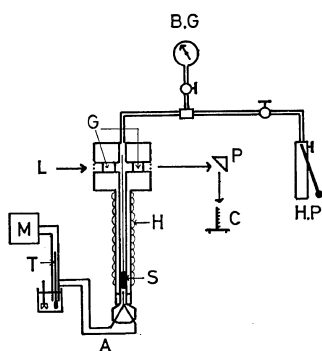


Figure 1. The block diagram of the pressure apparatus:

A, Almel—Chromel thermocouple; B.G., Bourdon gauge; C, cathetometer; G, glass window; H, heater; H.P., hand pump; L, Light source; M, Microvolt meter; P, Prism; S, Specimen; T, Thermometer.

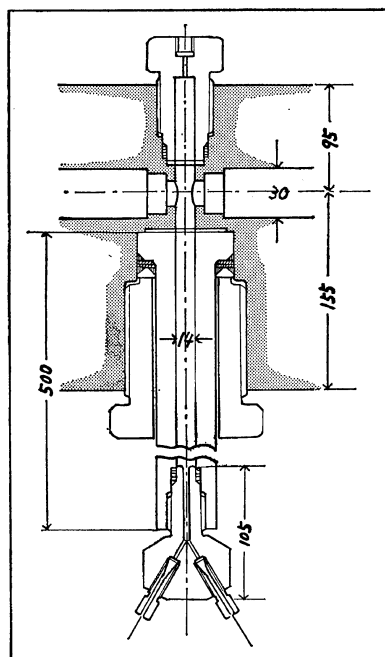


Figure 2. The container part of the pressure vessel.

meter was put into the container which is filled with silicone oil. Measurements of volume were made by reading the height of mercury meniscus through windows, the diameter of which is restricted to 17 mm for strength reasons. As the measurable change of meniscus height is limited to the diameter, it is impossible to observe the full range of volume changes at the set position of the dilatometer and with the constant mass of mercury. Hence, the measurements were carried out separately for the solid state, the liquid state, and a melting region by regulating the mercury mass.

Pressure was read from a Bourdon Gauge manufactured by Heise Bourdon Tube Co. and controlled by a hand pump. Temperature was measured by the thermocouples inserted at the bottom of the dilatometer and regulated by a heater of nickel-chrome wire wound outside the cylindrical container. Experimental errors were within $\pm 0.5 \text{ kg/cm}^2$ for pressure, $\pm 0.3^\circ\text{C}$ for temperature, and $\pm 0.0006 \text{ cc/g}$ for volume.

Temperature variation within the specimen was eliminated by covering a part of the dilatometer near the specimen with a copper capsule.

At the same time, to correct for the effects of temperature gradient along the capillary of the dilatometer, P - V - T relations were measured for the dilatometer containing mercury alone.

The apparatus described here can be used in the following three ways for P - V - T measurements, that is, (1) V - T relations under a constant pressure, (2) V - P relations at a constant temperature, and (3) P - T relations at a constant apparent volume. In each case the net change in volume of the sample ΔV is calculated from the observed change in total volume ΔV_{obs} read from the change in mercury meniscus by the following equations, where the subscripts Hg and g represent mercury and glass respectively.

- (1) Under a constant pressure

$$\Delta V = \Delta V_{\text{obs}} - (\alpha_{\text{Hg}} V_{\text{Hg}} - \alpha_{\text{g}} V_{\text{g}}) \Delta T \quad (4)$$

- (2) At a constant temperature

$$\Delta V = \Delta V_{\text{obs}} - \{V_{\text{Hg}}(\beta_{\text{Hg}} - \beta_{\text{g}}) - V_{\text{g}}\beta_{\text{g}}\} \Delta P \quad (5)$$

- (3) At a constant apparent volume

$$-\Delta V = (\alpha_{\text{Hg}} V_{\text{Hg}} - \alpha_{\text{g}} V_{\text{g}}) \Delta T - \{V_{\text{Hg}}(\beta_{\text{Hg}} - \beta_{\text{g}}) - V_{\text{g}}\beta_{\text{g}}\} \Delta P \quad (6)$$

The measurements were mainly carried out by the second method in this study, except in the vicinity of the melting temperature. In the latter case the melting temperature was determined by the first method.

RESULTS AND DISCUSSION

P - V - T Relations, Thermal Expansion Coefficient, and Compressibility

Using the second method as described above, the pressure was increased at the rate of nearly $10 \text{ kg/cm}^2 \text{ min}$, and the measurements were made at intervals of 30 – 50 kg/cm^2 . In the initial stages (in the range of 0 – 10 kg/cm^2), an abnormal change of volume, that is, an abrupt contraction was sometimes observed, especially for eicosane. It is thought to be due to incomplete contact between the sample and mercury. Therefore in these cases, volume extrapolated from the range of higher pressure to 0 kg/cm^2 is taken as the value at the atmospheric pressure.

The typical V - T curves obtained at 0 , 300 ,

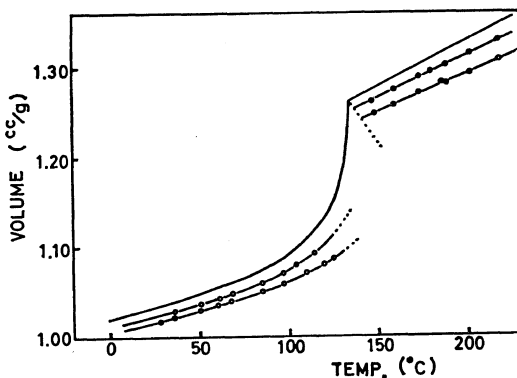


Figure 3. Volume vs. temperature relations under elevated pressures for polyethylene. Pressure is 0 , 300 , 600 kg/cm^2 for the solid state and 0 , 100 , 250 kg/cm^2 for the liquid state.

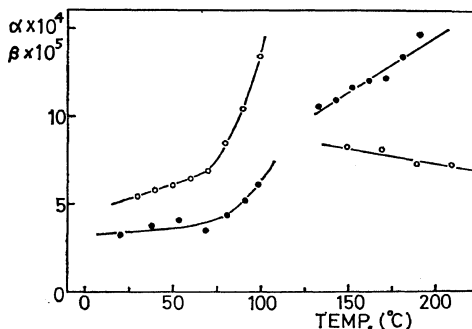


Figure 4. The temperature dependence of thermal expansion coefficient, α , deg^{-1} (\circ) and compressibility, β , $(\text{kg/cm}^2)^{-1}$ (\bullet) of polyethylene.

and 600 kg/cm^2 for the solid polyethylene and those at 0 , 100 , and 250 kg/cm^2 for the liquid one are shown in Figure 3.

It is generally observed that there is a broad region of premelting related to the variation of the thermal expansion coefficient, α , and compressibility, β . The values of α and β under atmospheric pressure are shown in Figure 4. As seen in the figure, both α and β behave like the λ -type transition and the λ shape of α is broader than that of β . It is noteworthy that the premelting phenomena are more sensitively represented by α than by β . As a result, the internal pressure $P_1 \approx T(\alpha/\beta)$ begins to increase from a temperature, as low as 50°C for polyethylene as shown later in Figure 7.

Figures 5 and 6 show the comparable re-

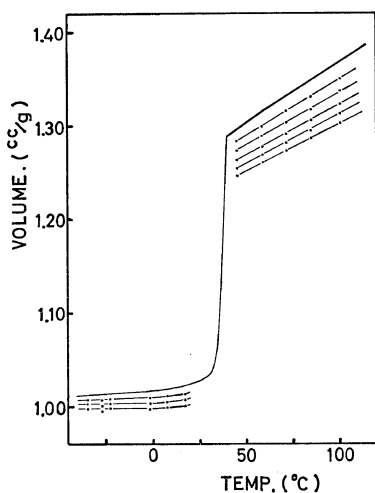


Figure 5. Volume vs. temperature relations under elevated pressures for eicosane. Pressure is 0, 200, 400, 600, kg/cm² for the solid state and 0, 100, 200, 300, 400, 500 kg/cm² for the liquid state.

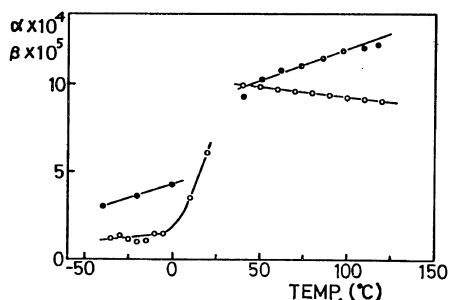


Figure 6. The temperature dependence of thermal expansion coefficient, α , deg⁻¹ (○) and compressibility, β , (kg/cm²)⁻¹ (●) of eicosane.

sults for eicosane, naturally showing a sharper transition than polyethylene. A noteworthy difference between two samples is in the fact that α value of eicosane in the solid state is smaller than that of polyethylene to the extent of one fifth, whilst β shows nearly the same value.

Internal Pressure

Internal pressure, P_i is defined as a volume derivative of internal energy at constant temperature as given by eq 3. It mainly depends on the intermolecular potential energy, but little on the intramolecular one, because the

latter has small volume dependence. Assume any intermolecular potential, e.g., Lennard-Jones potential, P_i initially increases with increasing volume and then decreases through the maximum value which corresponds to the inflexion point of the potential curve. Furthermore, in order to describe a crystalline polymer including its molten state, two different curves of P_i will be needed, because of the different dependencies of intermolecular potential on volume between the crystalline and liquid states.

Two parts of P_i in Figures 7 and 8 represent the behaviors qualitatively mentioned above. In Figures 7 and 8 the data of Sims¹² are also plotted [indicated by cross-point, (×)], which

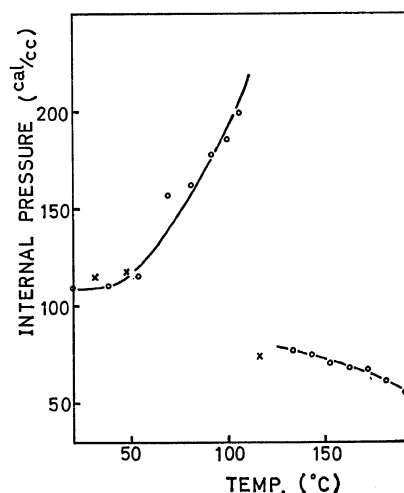


Figure 7. The temperature dependence of internal pressure of polyethylene at atmospheric pressure: ×, Sims's data¹².

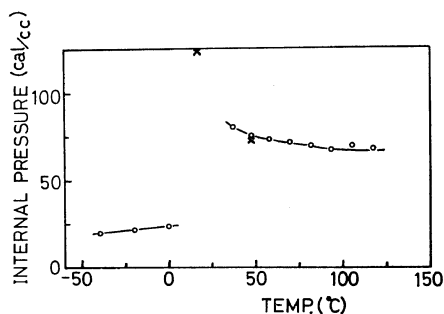


Figure 8. The temperature dependence of internal pressure of eicosane at atmospheric pressure: ×, Sims's data¹².

agree well with the authors'. The value of Sims for eicosane in the crystalline region closely near the melting temperature is much larger than the values in this paper at the lower temperature of the crystalline region. This fact may correspond to the λ -type transition of polyethylene found in the vicinity of the melting temperature. Hence in order to study the behavior of internal pressure in the crystalline state one should measure P_i not only near the melting temperature (as Sims did) but also at the lower temperature of the crystalline region.

Comparing the solid state of polyethylene with that of eicosane in the low temperature regions of the figures, P_i of the former was much larger than that of the latter, although the reasonable comparison must be done at a corresponding state, *i.e.*, at the same reduced temperature or volume (considered in a later paragraph).

The λ -type transition was also found in P_i for both samples. The drastic change in P_i will occur at the point of the abrupt change of volume dependence of the intermolecular interaction energy from crystalline to liquid. The broad shape of the λ -type transition for polyethylene seems to be caused by the broad distribution of crystal sizes and the degrees of perfection, accordingly to melting temperatures. One may also assume the same circumstances in eicosane, considering the data of Sims¹² and examining in detail thermal expansion coefficient α and compressibility β in Figure 6 which relate to internal pressure, *i.e.*, $P_i \approx T\alpha/\beta$.

In the liquid state, P_i decreased gradually with increasing temperature or volume. In comparison with the values in the solid state, it was found that, in the case of polyethylene, P_i (liquid) $<$ P_i (solid), even in the lower temperature region where the premelting is not observed, and the reverse was true in the case of eicosane.

How much of the increase and decrease in P_i occurs on melting depends on the shape of potential energy curves as a function of volume of both crystalline and liquid states and on the location of the melting point. In fact Sims¹² has reported cases of both increases and decreases in P_i for some crystalline polymers.

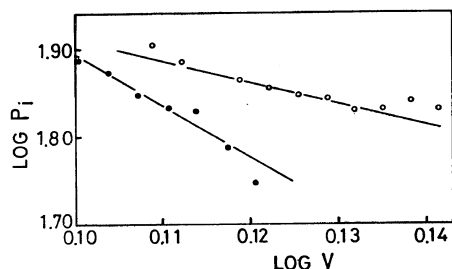


Figure 9. The plot of $\log P_i$ (cal/cc) vs. $\log V$ (cc/g) for polyethylene (●) and for eicosane (○).

Next the dependence of P_i on volume in the liquid region will be examined. Van der Waals' equation assumes P_i to be proportional to V^{-2} . Hildebrand, *et al.*,¹³ and Allen, *et al.*,^{14,15} experimentally proposed that the internal energy U of liquid is proportional to V^{-1} , accordingly $P_i \propto V^{-2}$, Bondi¹⁶ concluded, however, from data for low-molecular-weight liquids that U is not necessarily proportional to V^{-1} .

The relation of P_i to V is examined for liquid polyethylene and eicosane in Figure 9. P_i of polyethylene varies to the minus 6-th power of V in this range of volume, while, that of eicosane to the minus 2.45-th power and internal pressures of neither change with minus second power of volume.

As before mentioned, the reasonable comparison between polyethylene and eicosane must be done in a corresponding state. According to the recent hole theory of polymer liquids proposed by Nose¹⁷, one of the authors, reduced internal pressures in liquid and crystalline states may be expressed as

$$\bar{P}_{i \text{ liquid}} = 0.699s(\bar{V} - 1 + s)^{-2} \quad (7)$$

$$\bar{P}_{i \text{ crystal}} = s\bar{V}^{-3}(2.409 - 2.0218\bar{V}^{-2}) \quad (8)$$

where $\bar{P}_i = P_i/P_i^*$ and $\bar{V} = V/V^*$ are reduced internal pressure and volume respectively and s is a constant related to the coordination number. Here $\bar{P}_{i \text{ crystal}}$ was calculated by assuming that the crystalline state is regarded as the glassy one with no hole.

The characteristic volume V^* is defined as an occupied volume, $\sigma^3 N$, where σ is an intermolecular distance at the zero potential energy and N is the number of segments, related to the volume at 0°K, V_0 , as $V_0 = 0.9161 V^*$. By the

use of volume of the perfect crystal and the temperature dependence of the lattice constant¹⁸ V^* was calculated to be 1.0426 cc/g for polyethylene and 1.0743 cc/g for eicosane.

Secondly the characteristic internal pressure $P_1^* = \varepsilon^* z' / \sigma^3$, where ε^* is the minimum value of the potential energy and z' is coordination number per segment, was evaluated by the superposition of the experimental curve of P_1 vs. \bar{V} on the theoretical curve of eq 7. The values of P_1^* thus obtained are 136 cal/cc and 141 cal/cc for polyethylene and eicosane respectively.

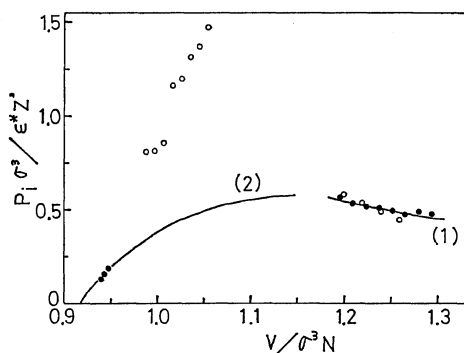


Figure 10. Reduced internal pressure $P_1 \sigma^3 / \varepsilon^* z'$ at atmospheric pressure vs. reduced volume $V / \sigma^3 N$ for polyethylene (○) and for eicosane (●). The solid line (1) indicates the theoretical curve of eq 7 for the liquid state, and the solid line (2) indicates that of eq 8 for the crystalline state.

For the purpose of comparison between two samples, reduced internal pressures in the crystalline state were evaluated with the use of these values of P_1^* and V^* . Figure 10 shows the results of \bar{P}_1 plotted against \bar{V} . Though \bar{P}_1 thus obtained for polyethylene falls for outside

the theoretical curve (the solid line) according to the eq 8, that for eicosane agrees fairly well with the theoretical. It is clear that, in the solid state, the internal pressure of polyethylene is larger than that of eicosane even in a corresponding state.

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