Thermodynamic analysis of the phase transition of polyethylene under high pressure

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Mechanism of emergence of high pressure phase of polyethylene is analysed on the thermodynamic stand point: The change in free energy due to pressure increase is calculated for each phase on the basis of the experimental data. The transition temperature and melting point under the increased pressures are estimated and the results obtained are consistent with the observed values.

Keywords Analysis; thermodynamics; polyethylene; free energy; transition temperature; pressure

INTRODUCTION

Since the discovery of the growth of chain-extended crystals in polyethylene under high pressure, many experiments have been done. Among the important ones is the observation of the phase change from the ordinary orthorhombic crystal to the hexagonal one[1]. However, the correlation between growth of chain-extended crystals and occurrence of the hexagonal phase is not clear. Takemura *et al.*[2] observed growth of chain-extended crystals directly from the melt through pressure quenching. This implies that the existence of the hexagonal phase is not a 'necessary condition' for formation of chain-extended crystals. They can also be formed by annealing chain-folded crystals under conditions in which the hexagonal phase could be present, so that these conditions themselves may be sufficient for formation of chain-extended crystals.

It has been known for some time that some kinds of long chain hydrocarbons and their derivatives exhibit a phase change under atmospheric pressure in a narrow temperature range below their respective melting points. An interesting question is whether this kind of hexagonal phase has any correlation with the hexagonal phase of polyethylene, even though the former does not appear, for example, in paraffin with more than ~40 carbon atoms[3]. Hoffman[4] proposed a rotational phase model for the hexagonal phase of long chain molecules. On the other hand, the hexagonal phase of polyethylene has a structure with disturbed molecular conformation and is considered similar to that of liquid crystals[5]. Takamizawa reported that oligomers of polyethylene with about 100 carbon atoms still do not exhibit a hexagonal phase[6]. This suggests that the length of the molecular chain may play an important role in the appearance of a hexagonal phase, but this is not clear as yet. Another question is why the hexagonal phase does not appear under pressures lower than about 3.3 kbar. On the basis of the X-ray results[7], we conclude that the phase transformation of polyethylene under high pressure is of the first kind, and we will attempt to analyse its mechanism from the view point of thermodynamics.

FREE ENERGY DIAGRAM

Bassett[8] gave a schematic phase diagram in which the curves of the respective phases (orthorhombic, hexagonal and melt phases) took the relative positions shown in *Figure 1(a)*. If this is the case, the relation between free energy curves under atmospheric pressure should be as illustrated in *Figure 1(b)*. Any detailed discussion on the effect of pressure was not in his paper, therefore, the actual phase diagram should be given on the basis of physical properties of polyethylene and it is necessary to explain why the hexagonal phase becomes observable in the limited physical conditions; the change of diagram with pressure is shown according to the experimental results on polyethylene in the following.

The Gibbs free energy and other thermodynamic quantities of each phase are expressed as a function of pressure, P, with a superscript o, h or m corresponding to ortho-, hexa- or melt phase respectively; for instance,

$$G^o(P) = U^o(P) + P \cdot V^o(P) - S^o(P)T \qquad (1)$$

and so on. As seen from *Figure 1(a)*, the relations

$$H^o < H^h < H^m \qquad (2)$$

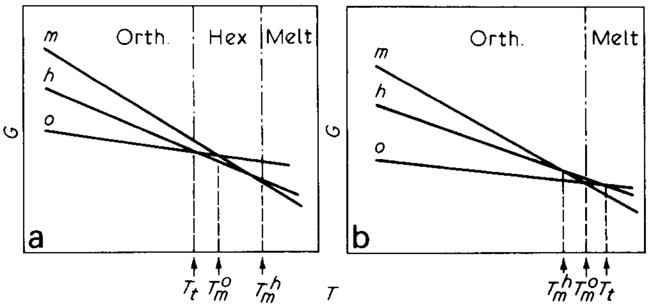

Figure 1 Schematic free energy diagrams under high pressure, (a), and under atmospheric pressure, (b). Transition temperature, T_t, and melting point, T_m, are given as the intersections between corresponding free energy lines. The hexagonal phase becomes observable only in the case of (a). *o*: ortho., *h*: hexa., *m*: melt

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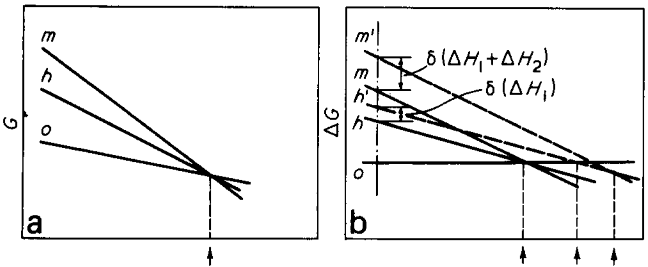

Figure 2 Free energy relation between ortho-, hexa- and melt phases under critical condition, P_oT_o, (a), and its modified diagram, (b). Free energy lines shift to the positions indicated by broken lines with pressure increase

$$S^o < S^h < S^m \qquad (3)$$

must hold for enthalpy, H, and entropy, S, when the hexagonal phase becomes observable.

Since an endothermic peak and an increase in volume are observed at each phase change by measurements made while heating proceeds under high pressure, equation (2) is verified. In studies by X-ray diffraction, the cross section per molecular chain is observed to increase, for instance, from ~35 to ~40 Å^2 as a result of the change from ortho- to hexa- phase under a pressure of 7 kbar; so that considerable increase in internal energy will be expected also: $U^o < U^h < U^m$. Besides the increment of entropy due to volume change, a contribution from the conformational change must be included: More conformational disorders are introduced in the hexagonal phase[7]. Therefore, equation (3) is also verified.

However, quantitative analysis is necessary in terms of thermodynamic quantities of polyethylene, especially under high pressure. This must be investigated if it is possible to come to realize the relation given in *Figure 1(a)*, adding the free energy changes, $\Delta G^i(i{:}o, h, m)$, corresponding to the given pressure on each curve of *Figure 1(b)*.

The transition temperature, T_t, and the melting point, T_m^h, are given by:

$$T_t = (\Delta U_1 + P\Delta V_1)/\Delta S_1 \qquad (4a)$$

$$T_m^h = (\Delta U_2 + P\Delta V_2)/\Delta S_2 \qquad (4b)$$

where:

$$\Delta U_1 = U^h - U^o \qquad \Delta V_1 = V^h - V^o \qquad \Delta S_1 = S^h - S^o$$

$$\Delta U_2 = U^m - U^h \qquad \Delta V_2 = V^m - V^h \qquad \Delta S_2 = S^m - S^h$$

If $T_t < T_m^h$, the hexagonal phase will emerge but in case of $T_t > T_m^h$ it will not be observed. According to the experimental results, the critical condition for the hexagonal phase to emerge is the point of $P = 3.3$ kbar and $T = 491$ K (218°C); i.e., $T_t = T_m^h \equiv T_o$ at this point as illustrated in *Figure 2(a)*.

In equation (4), T_t and T_m are determined only by the differences between thermodynamic quantities within each phase. In *Figure 2(b)*, we show free energy differences referred to the free energy of the orthorhombic phase in the pressure range under consideration.

ESTIMATION OF THERMODYNAMIC QUANTITIES

The experimental data on thermodynamic properties of the high temperature phase of polyethylene are few; for instance, existence of the hexagonal phase is ignored in the work by Gupta *et al.*[9], so that their results are not applicable directly in the present case. Therefore, only semi-quantitative estimation is possible in the following. According to Takemura[10]

$$\Delta S_1 = 0.506 \text{ J/g.K} \qquad \Delta V_1 = 0.075 \text{ cm}^3 \text{ g}^{-1}$$

$$\Delta S_2 = 0.163 \text{ J/g.K} \qquad \Delta V_2 = 0.030 \text{ cm}^3 \text{ g}^{-1}$$

at $P = 5$ kbar. ΔV_1 and ΔV_2 are difficult to determine independently by dilatometric measurement because of the lack of discrete volume steps in the range of phase change, especially from hexa- to melt. Using Takemura's results we obtain $\Delta V \equiv \Delta V_1 + \Delta V_2 = 0.105$ cm^3 g^{-1}. This value is almost the same as that of Kanetsuna[11], 0.102 cm^3 g^{-1}, and that of Gupta *et al.*[9], 0.115 cm^3 g^{-1}. The available data on $\Delta S(= \Delta S_1 + \Delta S_2)$[8,9] disperse around 0.7 J/g.K and take minimum value at 2~4 kbar[9]. Therefore, at the present stage of discussion, ΔS_1 and ΔS_2 are assumed constant in the pressure range 3–5 kbar for rough estimation.

The free energy of the orthorhombic phase under pressure P_o is chosen as the reference energy for the diagram in *Figure 4*, and the points x and y on the ordinate corresponding to hexagonal and melt phases at $T = 200$°C under pressure P_o are obtained using ΔS_1 and ΔS_2. Starting from the point P_o, $T_o(T_t = T_m)$ in *Figure 3*, we try to obtain the free energy line under pressure $P(P > P_o)$ and temperature T:

$$\delta(\Delta G_1)(P) = \{\Delta U_1(P) - \Delta U_1(P_0)\} + \{P\Delta V_1(P) - P_0\Delta V_1(P_0)\} - \Delta S_1(T - T_0)$$

$$\delta G_2)(P) = \{\Delta U_2(P) - \Delta U_2(P_0)\} + \{P\Delta V_2(P) - P_0\Delta V_2(P_0)\} - \Delta S_2(T - T_0) \qquad (6)$$

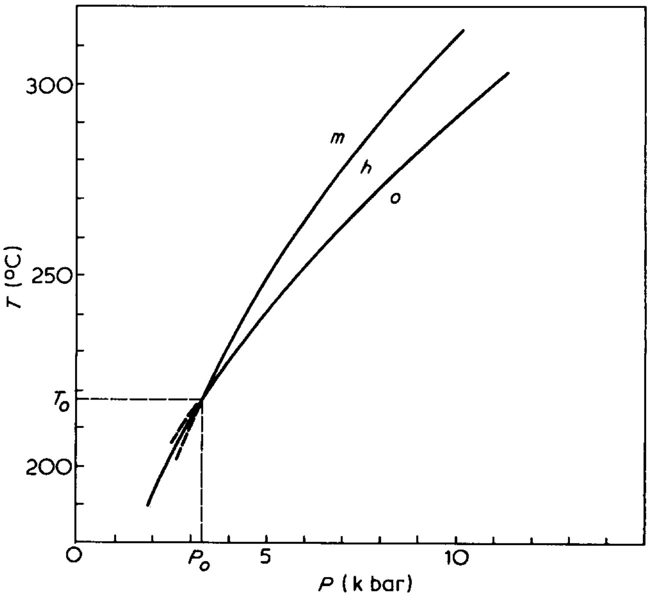

Figure 3 Phase diagram of polyethylene

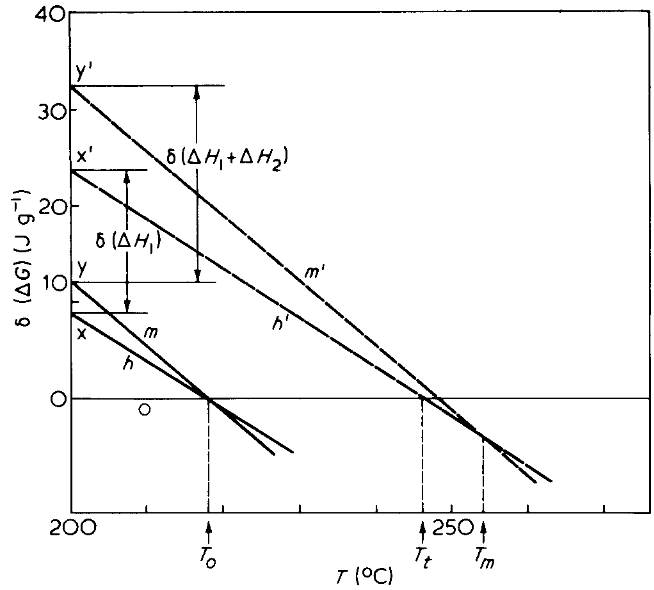

Figure 4 Variation of free energy relation of polyethylene with pressure change from 3.3 kbar (——) to 5 kbar (— — —)

As stated in the textbook of thermodynamics[12], the internal energy of a crystal under a certain hydrostatic pressure consists of lattice energy and stress energy; therefore, the change of internal energy per unit mass of a sample by phase change from ortho- to hexa- phases can be expressed as follows:

$$\Delta U_1(P) = U_0^h(P) - U_0^o(P) + \int_o^T (c_v^h - c_v^o)\mathrm{d}T + \tfrac{1}{2}P^2(V^h\beta^h - V^o\beta^o) \tag{7}$$

The similar expression holds for ΔU_2.

The first term in the right side of equation (7) is the difference in lattice energy between ortho- and hexa-phases, and the second term comes from contribution of thermal energy. These two components will not change very much in the rather narrow pressure range 3-5 kbar, so they are neglected in calculating $\Delta U_j(P) - \Delta U_j(P_0)$ ($j = 1,2$). Consequently,

$$\begin{aligned} \Delta U_1(P) - \Delta U_1(P_0) &= \tfrac{1}{2}(P^2 - P_0^2)(V^h\beta^h - V^o\beta^o) \\ \Delta U_2(P) - \Delta U_2(P_0) &= \tfrac{1}{2}(P^2 - P_0^2)(V^m\beta^m - V^h\beta^h) \end{aligned} \tag{8}$$

Compressibilities of ortho- and hexa- phases, β^o and β^h, are estimated from the X-ray observation[7], where the contraction in c-direction of crystallites is neglected: $\beta^o = 0.86 \times 10^{-2}$/kbar and $\beta^h = 1.18 \times 10^{-2}$/kbar. These values increase gradually with decreasing pressure, but they are assumed constant in the pressure range under consideration, because only the difference between these quantities is important as is shown in equation (8).

The compressibility of the melt, β^m, is estimated from the change of specific volume between ortho- and melt states under pressure P_1 and P_2: $\Delta V(P_1)$ and $\Delta VV(P_2)$[11]. Namely

$$V^m(P_1)\beta^m = V^o(P_1)\beta^o + \frac{\Delta V(P_1) - \Delta V(P_2)}{\Delta P}$$

where $\Delta P = P_2 - P_1$. The specific volume of the melt for P_1, $V^m(P_1)$, is deduced from the specific volume of the ortho-phase at the same pressure, $V^o(P_1)$, by $V^m = V^o + \Delta V(P_1)$. If we take $P_1 = 4$ kbar and $P_2 = 5$ kbar:

$$\begin{aligned} &V^m(P_1) = 1.103\ \mathrm{cm^3\,g^{-1}}, \qquad V^o(P_1) = 0.984\ \mathrm{cm^3\,g^{-1}} \\ &(\Delta V(P_1) - \Delta V(P_2))/\Delta P = 0.021\ \mathrm{cm^3/g.kbar} \end{aligned} \tag{9}$$

Therefore, we get $\beta^m = 2.67 \times 10^{-2}$/kbar.

The free energy change with pressure is calculated using equations (6) and (8).

$$\begin{aligned} \Delta U(P = 5\,\mathrm{kbar}) - \Delta U_1(P_0 = 3.3\,\mathrm{kbar}) &\equiv \delta(\Delta U_1) \\ &= 2.42\,\mathrm{J\,g^{-1}} \end{aligned}$$

$$\begin{aligned} P\Delta V_1(P = 5\,\mathrm{kbar}) - P_0\Delta V_1(P_0 = 3.3\,\mathrm{kbar}) &\equiv \delta(P\Delta V_1) \\ &= 12.1\,\mathrm{J\,g^{-1}} \end{aligned}$$

therefore, $\delta(\Delta H_1) = 14.5$ J g^{-1}. In the same way $\delta(\Delta U_1 + \Delta U_2) = 14$ J g^{-1}, $\delta(P\Delta V) = 6.4$ J g^{-1} and $\delta(\Delta H_1 + \Delta H_2) = 20.4$ J g^{-1}. Thus the enthalpy differences of hexagonal and melt phases, referred to the orthorhombic phase, increase by 14.5 J g^{-1} and 20.4 J g^{-1} respectively as a result of increasing the pressure of the sample cell from 3.3 to 5 kbar.

Assuming the entropy differences between phases do not depend on pressure, we can draw the free energy lines as illustrated by broken lines in *Figure 4* and can determine T_t and T_m as the intersection points of two pairs of curves: ortho–hexa and hexa–melt. The agreement between observed and calculated values is good as shown in *Table 1*.

PRESSURE DEPENDENCE OF T_t

Due to lack of enough experimental data for the transition from hexa- to melt phase, investigation in this section is confined to the pressure dependence of T_t. The variation of a and b spacings have been measured under high pressure for the ortho- and hexa- phases in the pressure range 4–10 kbar[7]. Those of the hexa-phase at 3.3 kbar are obtained by extrapolation. The mean value of the c-spacing of the hexagonal phase has been estimated as 2.43 Å from the analysis of its diffuse pattern[5]. The variation of c-spacing with pressure is small and is neglected; the volume change is calculated for 3.3, 5, 6.5 and 8 kbars. The resulting value of ΔV_1 is 0.098 cm^3 g^{-1} for 5 kbar, which is about 30% greater than the 0.075 cm^3 g^{-1} obtained by Takemura. The former value is estimated for the perfect crystal lattice, but the crystallinity of the actual sample is not 1; rather it contains various defective parts: chain fold, dislocation, etc. Therefore all X-ray values are reduced by the factor of 0.075/0.098 and the modified values of ΔV_1 are listed in *Table 2*. On the bases of Clausius–Clapyron equation ($\mathrm{d}P/\mathrm{d}T = \Delta S_1/\Delta V_1$), ΔS_1 for respective pressures are deduced from P–T phase diagram (*Figure 3*) and ΔU_1 and $P\Delta V_1$ are calculated for these pressure values as before.

Table 1 Comparison of the calculated values of T_t and T_m with the observed ones under 5 kbar

	T_t (°C)	T_m (°C)
obs.	240	252
cal.	247	254

Table 2 Thermodynamical quantities used for the construction of *Figure 5*

P (kbar)	3.3	5	6.5	8
dP/dT (J/K)	9	9	10	11
ΔV_1 (cm^3 g^{-1})	0.077	0.075	0.072	0.071
ΔS_1 (J/g. K)	0.69	0.675	0.72	0.78
$P\Delta V_1$ (J g^{-1})	25.4	37.5	48.8	56.8
$\delta(P\Delta V_1)$ (J g^{-1})	–	12.1	23.4	31.4
$\delta(\Delta U_1)$ (J g^{-1})	–	2.42	5.42	9.16
$\delta(\Delta H_1)$ (J g^{-1})	–	14.5	28.8	40.6
T_t' (cal.) (°C)	(218)	240	257	268
T_t (obs.) (°C)	(218)	240	256	271

Consequently, increments of ΔH_1 over the state of 3.3 kbar, $\delta(\Delta H_1)$, are calculated for 5, 6.5 and 8 kbars and the corresponding transition points are graphically obtained using each entropy increment under the respective pressures. The values obtained are remarkably consistent with the observed ones (*Table 2* and *Figure 5*). This coincidence is not always to be expected, because ΔU_1 is obtained independently from the experimental data though ΔV_1 and ΔS_1 are derived from Clausius–Clapeyron equation; in other words, this result implies the adequacy of calculation of ΔU according to equation (8).

The condition to be fulfilled for the existence of some definite critical pressure above which the hexagonal phase becomes observable, is expressed by equation (4): Critical pressure P_0 is given by:

$$P_0=\left(\left\{\frac{\Delta U_1}{\Delta S_1}-\frac{\Delta U_2}{\Delta S_2}\right\}\Big/\left\{\frac{\Delta V_2}{\Delta S_2}-\frac{\Delta V_1}{\Delta S_1}\right\}\right)_{P=P_0} \quad (10)$$

For the low pressure values:

$$P\approx 0,\ (\Delta U_1/\Delta S_1)_{P=0}\approx T_{to}>T^h_{mo}\approx(\Delta U_2/\Delta S_2)_{P=0} \quad (11)$$

As seen in *Figure 3:*

$$(\Delta V_1/\Delta S_1)=(\partial T/\partial P)_{o-h}<(\partial T\partial P)_{h-m}=(\Delta V_2/\Delta S_2) \quad (12)$$

The quantities, ΔU_j, ΔV_j, ΔS_j ($j=1{,}2$), depend on pressure but the effect on ΔS is assumed to be small, only the stress energy is used to obtain $\Delta U(P)$ as explained in the above discussion. If Takemura's data are used for ΔS, $\Delta U_1=223$ J g^{-1} and $\Delta U_2=60.9$ J g^{-1} at 3.3 kbar are obtained from equation (4). As the contributions from stress energy to these are 2.3 and 9.3 J g^{-1} respectively, $\Delta U_{01}(=\Delta U_1-\frac{1}{2}P^2(V^h\beta^h-V^0\beta^0))$ and ΔU_{02} become 221 and 51.6 J g^{-1}. enthalpy of fusion reported for high density polyethylene under atmospheric pressure is 270~280 J g^{-1} and it is almost the same as $\Delta U_{01}+\Delta U_{02}\approx 270$ J g^{-1}. Consequently, $T_{to}\approx(\Delta U_{01}/\Delta S_1)\approx 441$ K and T_{mo} $\sim(\Delta U_{02}/\Delta S_2)\approx 316$ K. These values express the relation (11) quantitatively.

As the hexagonal phase does not exist under atmospheric pressure, T_{to} and T_{mo} (the melting point of 'hexagonal phase' at $P=0$) cannot be observed and results of equation (11) are difficult to examine directly by experimental facts. However, the melting point of the orthorhombic phase of high density polyethylene is usually ~130°C (~400 K) which lies between T_{mo} and T_{to}. This is reasonable in view of the phase relation illustrated in *Figure 3.*

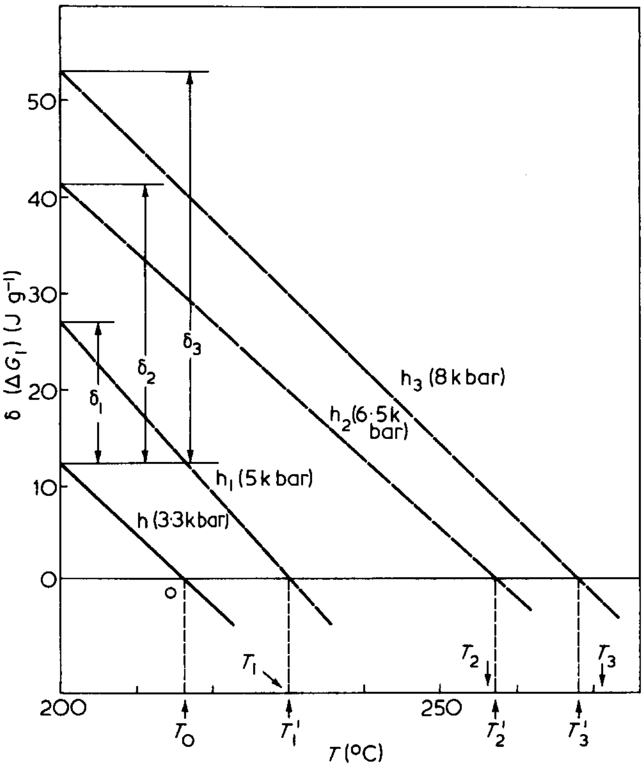

Figure 5 Pressure dependence of transition point of polyethylene. T_i (i = 1, 2, 3) are the observed transition points for the respective pressures and T_i' are the calculated ones

Thus the phase change of polyethylene under high pressure has been analysed in terms of thermodynamic quantities: Emergence of the hexagonal phase under high pressure is closely related with the thermodynamic characteristics of polyethylene. Further accurate experimental data are necessary if the analysis is to be improved. Although, another investigation from the view point of molecular theory is essential in order to clarify the mechanism of this phase change, the present work will give some general analysis of this problem.

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