

On hexagonal phases of paraffins and polyethylenes

A. S. Vaughan and G. Ungar*

J. J. Thomson Physical Laboratory, University of Reading, Whiteknights, Reading RG6 2AF, UK

and D. C. Bassett and A. Keller

*H. H. Wills Physics Laboratory, University of Bristol, Bristol, UK
(Received 11 September 1984)*

Polyethylene, when irradiated to doses exceeding ca500 Mrad forms a hexagonal structure before melting at atmospheric pressure. The phase diagrams of irradiated polyethylenes have been studied as a function of pressure to 5 kbar, and used as a basis for comparing the radiation-induced hexagonal phase with the hexagonal and pseudo-hexagonal rotator phases of n-paraffins and with the disordered hexagonal (anabarc) structure formed by linear polyethylene at high pressure. At atmospheric pressure, the radiation-induced hexagonal phase is intermediate in character between the other two. It is, nevertheless, a high entropy phase whose temperature interval of existence widens, and whose nature moves towards that of the anabarc phase, with increasing pressure.

(Keywords: paraffins; polyethylene; hexagonal phases; rotator phases; high pressure)

INTRODUCTION

The common crystal structure of polyethylene is orthorhombic but at high pressures ($> \approx 3$ kbar) the linear polymer transforms to a disordered hexagonal structure¹ before melting, with the parameters of the transition sensitive to molecular mass². We refer to this hexagonal modification as the anabarc phase³. Certain orthorhombic n-paraffins also form less ordered structures, known as 'rotator' phases, before they melt⁴. Recent works (see for example ref. 5) have shown that there is a number of different but closely related rotator phases, only one of which has a truly hexagonal subcell. Nevertheless, the term 'hexagonal' phase will be used in this text as a synonym for rotator phase when referring to n-paraffins.

There are major differences between the rotator and the anabarc structures. The rotator phases are three-dimensionally ordered solids and their specific volumes, v_h , and specific entropies, s_h , are closer to corresponding values v_o and s_o for the orthorhombic structures than they are to those for the melt, v_m and s_m . In contrast, the high pressure (or anabarc³) phase of polyethylene is ordered only in two dimensions and, like many liquid crystals, is closer to the melt in volume and entropy than to the orthorhombic solid. Indeed it is the low entropy of fusion of this phase which is believed to be responsible for the very thick lamellae produced by crystallization from the melt².

The two hexagonal phases respond quite differently to the application of pressure. Whereas the temperature interval of existence of the anabarc polyethylene structure widens with pressure⁶ (Figure 1a), that for the rotator phase decreases⁷ (Figure 1b) and rotator phases are not found at pressures exceeding 3 kbar⁸. This difference

implies that anabarc polyethylene is a *high entropy phase*² which satisfies the inequality:

$$\frac{s_h - s_o}{s_m - s_o} > \frac{v_h - v_o}{v_m - v_o} \quad (1)$$

Conversely, rotator phases are *high volume* phases for which the inequality of equation (1) is reversed.

Initially linear polyethylene can also be induced to form a hexagonal modification at atmospheric pressure when its structure had been modified by irradiation⁹. Recent work by two of us has shown that for absorbed doses in excess of ≈ 500 Mrad, an irradiated polyethylene which has an orthorhombic structure at room temperature will transform to a hexagonal phase before melting¹⁰. In this paper we compare the properties of this radiation-induced hexagonal phase with those of paraffin rotator phases on the one hand and with the anabarc polyethylene phase on the other. We find that, at atmospheric pressure, the radiation-induced phase is intermediate in nature between the other two, but that the application of pressure brings a progressive move towards the character of the anabarc structure.

EXPERIMENTAL

The principal new data described in this paper are melting endotherms of irradiated polyethylene recorded at pressures to 5 kbar. These were measured in one of two differential thermal analysis (d.t.a.) cells in conjunction with the piston-cylinder apparatus of previous work¹¹.

The design of the more recent cell is drawn in Figure 2. It attempts to provide nearly identical thermal environments for the sample and a reference material and to record both the absolute temperature of the sample and its difference from that of the reference. Two holes drilled in PTFE rod accommodate sample and reference. Ch-

* Permanent address: Ruder Bosovic Institute, Zagreb, Yugoslavia.

romel and alumel leads pass into these chambers and, once completed, the delicate connections and wiring are embedded in Loctite resin. The temperature difference signal is fed via a non-inverting chopper amplifier (Analog Devices 261K) to one channel of a twin-channel chart recorder. The other channel records the output from the sample arm of the opposed pair of thermocouples, thus enabling the temperature of the sample to be measured without loss of symmetry in the design.

The samples used were of linear polyethylene (Marlex 6002, Philips Petroleum) in the form of 0.8 mm thick sheets prepared by melt-pressing and cooling at *ca.* 0.5 K min^{-1} .¹⁰ They had been irradiated (courtesy of Prof A. Charlesby and Dr P. J. Fydelor, RMCS, Shrivenham) at $85.0 \pm 0.5^\circ\text{C}$ *in vacuo* in a ^{60}Co source. Experiments show irradiation at 85°C to be about 50% more effective in producing lattice changes than room temperature treatment.

The atmospheric melting endotherms of these irradiated polyethylenes were recorded using a differential scanning calorimeter (Perkin-Elmer DSC1B) programmed at 8 K min^{-1} and calibrated against the melting of high-purity indium. These all showed, as in *Figure 3a*, that the lower temperature peak indicating the orthorhombic hexagonal transition is smaller, involving smaller entropy and enthalpy changes, than the succeeding change from hexagonal to melt. It is estimated, for the sample of *Figure 3a* that $(s_h - s_0) = 0.44(s_m - s_0)$, a similar proportion to that for paraffin rotator phases. However, the relative magnitude of the two peaks changes smoothly with pressure.

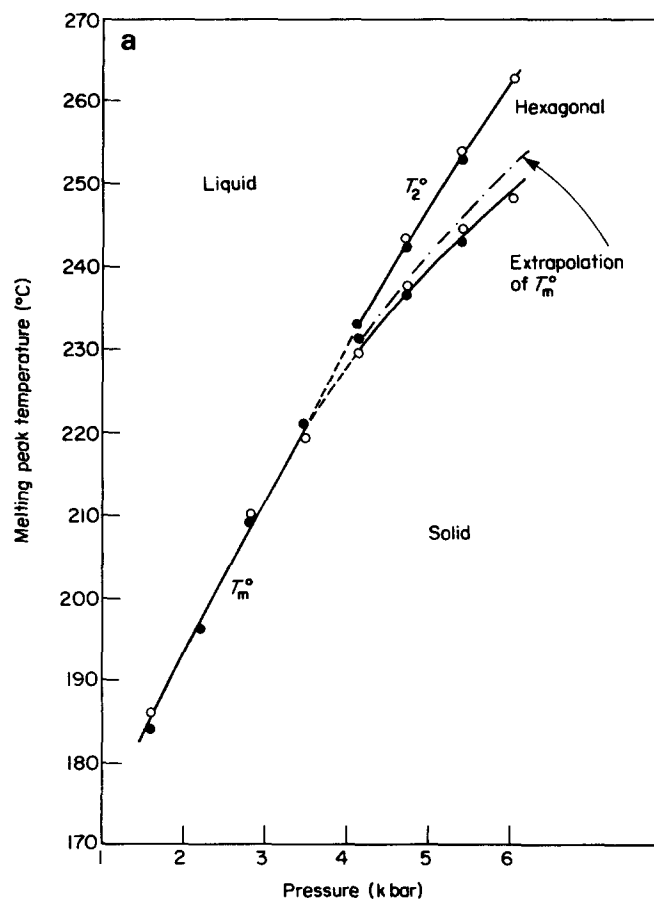


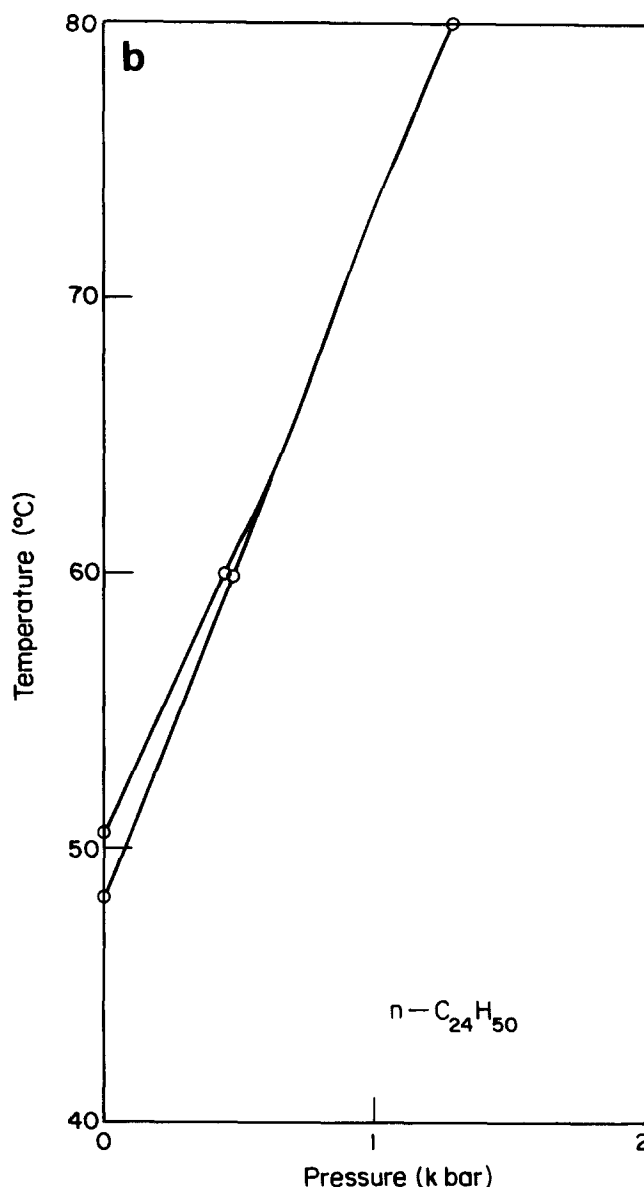
Figure 1 (a) Phase diagram of linear polyethylene (50 000 mass) after Bassett and Turner⁵. (b) Phase diagram of normal tetracosane, $n\text{-C}_{24}\text{H}_{50}$ after Nelson, Webb and Dixon⁶

Figure 3b shows that already at 2.20 kbar the earlier peak in the melting endotherm has become larger. This is now more akin to the behaviour of the anabarc phase or to various liquid crystals.

The high-pressure d.t.a. measurements also show that the temperature interval of existence of the radiation-induced hexagonal structure widens with increasing pressure, i.e. that it is a high-entropy phase (*Figure 4*). Materials with absorbed doses $< 500 \text{ Mrad}$, which do not transform to a hexagonal structure at atmospheric pressure¹⁰, do show a transition at higher pressure (*Figure 5*). The triple point falls with increasing dose and there is a continuous change of the phase diagram from that of the unirradiated linear material (*Figure 1a*), through that of *Figure 5* to that of *Figure 4* and beyond. For highly irradiated specimens at high pressure, however, the second d.t.a. peak, representing melting of the hexagonal structure tends to become so small and broad that it is difficult to detect.

DISCUSSION

When a hexagonal modification is stable, in phase diagrams of the type shown in *Figure 1*, its specific free



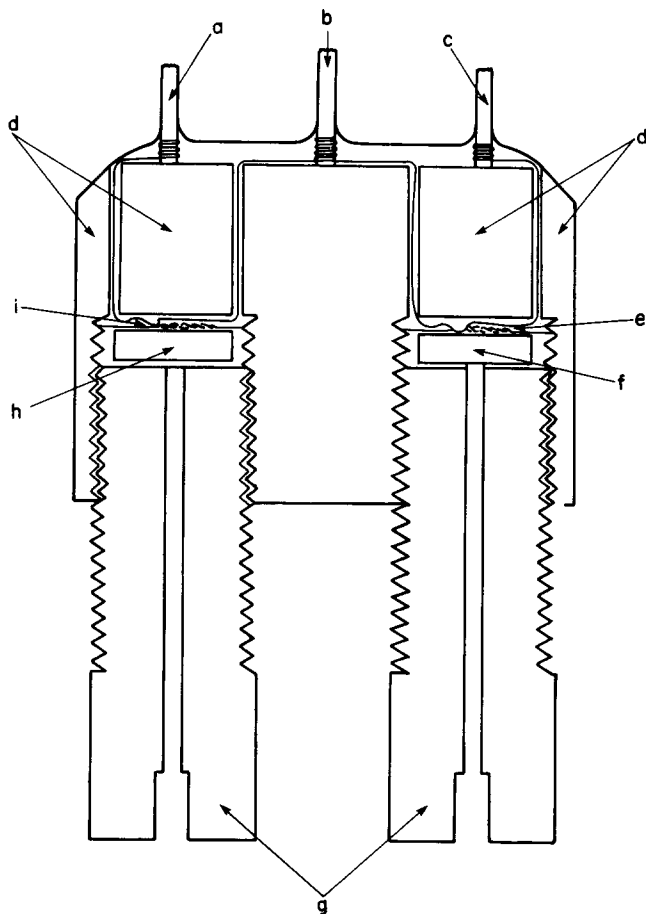


Figure 2 High pressure d.t.a. cell. (a, b, c) Temperature difference and sample temperature signal leads, (d) d.t.a. cell body, (e) sample thermocouple junction, (f) sample material, (g) threaded plugs, (h) reference material, (i) reference thermocouple junction

enthalpy g_h (Gibbs function per unit mass) will be less than the corresponding quantities g_m , for the melt, and g_o for the orthorhombic form¹². This condition is sketched in Figure 7, with the approximation that curvature of the free enthalpy surfaces is neglected. After irradiation the disorder wrought in the structure can be confidently expected to increase the enthalpies of both the orthorhombic and the hexagonal phase. On the other hand, there is experimental evidence, both from radiation-induced melting point elevation^{13,14} and volume contraction of the melt¹⁵, that the entropy of the melt is reduced by introduction of crosslinks. The above enthalpy and entropy effects would increase g_o and g_m relative to g_h under the following conditions: (a) that the enthalpy of the orthorhombic phase is raised more than that of the hexagonal phase, and (b) that the entropy of melt is lowered less than that of the hexagonal phase. The fulfilment of both conditions can be expected *a priori*. Either the enthalpy or the entropy effects alone could quantitatively explain the appearance and the widening temperature interval of the hexagonal phase with increasing radiation dose. We believe that the two effects act in tandem.

The added dimension of increasing pressure enables us to gain further information on the nature of a hexagonal phase. We consider changes in free enthalpies in $g(p, T)$ space along the orthorhombic-melt equilibrium line l , given by $T = T_{om}(p)$, which is derived from the condition $g_o = g_m$.

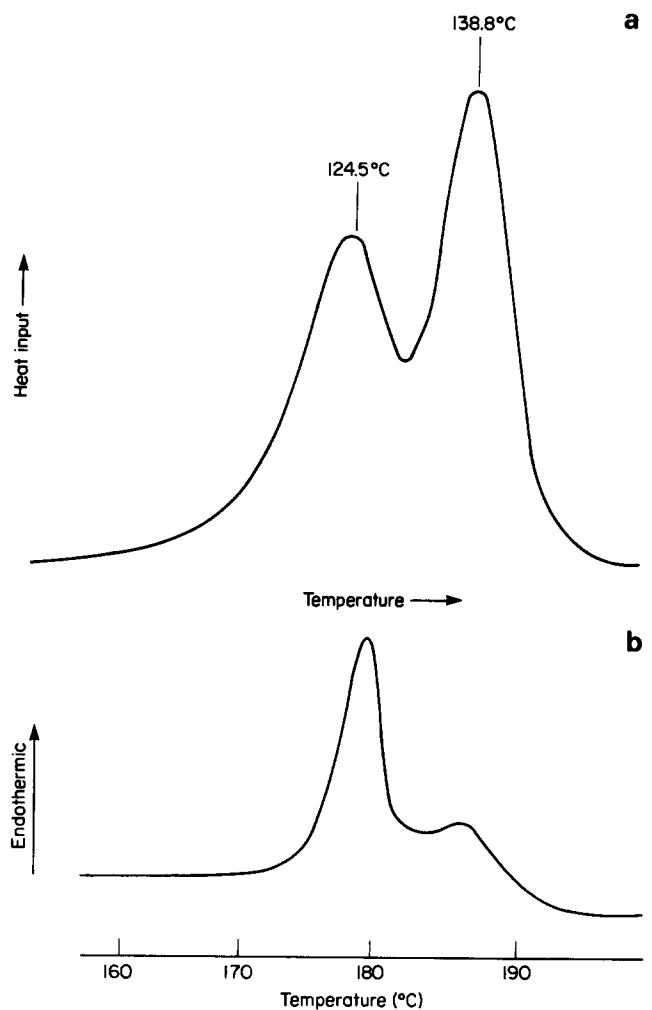


Figure 3 (a) Melting endotherm of polyethylene irradiated to 800 Mrad measured at atmospheric pressure. (b) High pressure, d.t.a. trace of polyethylene irradiated to 225 Mrad, melting at 2.20 kbar

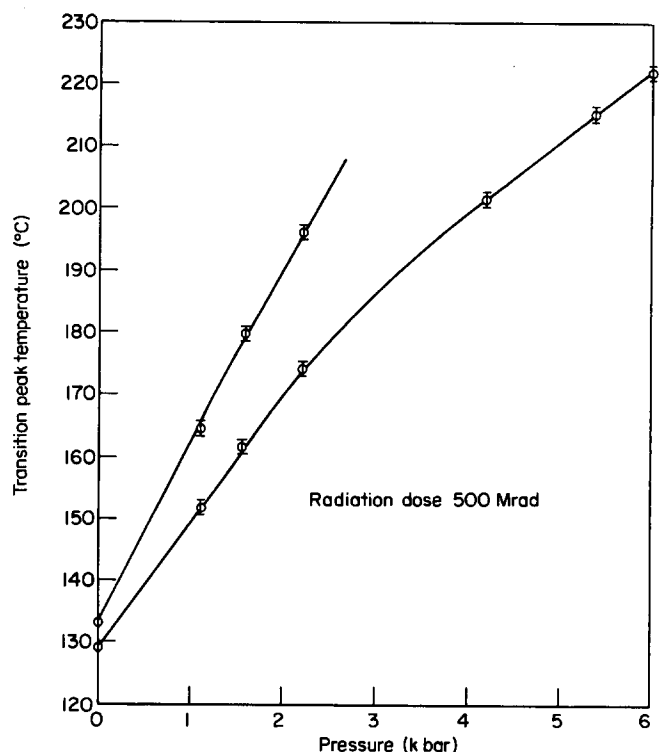


Figure 4 Phase diagram of polyethylene irradiated to 500 Mrad

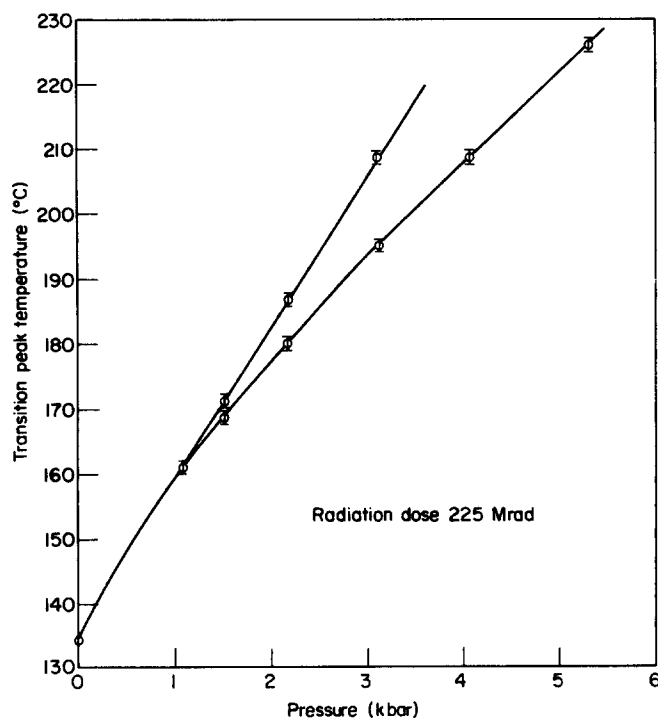


Figure 5 Phase diagram of polyethylene irradiated to 225 Mrad

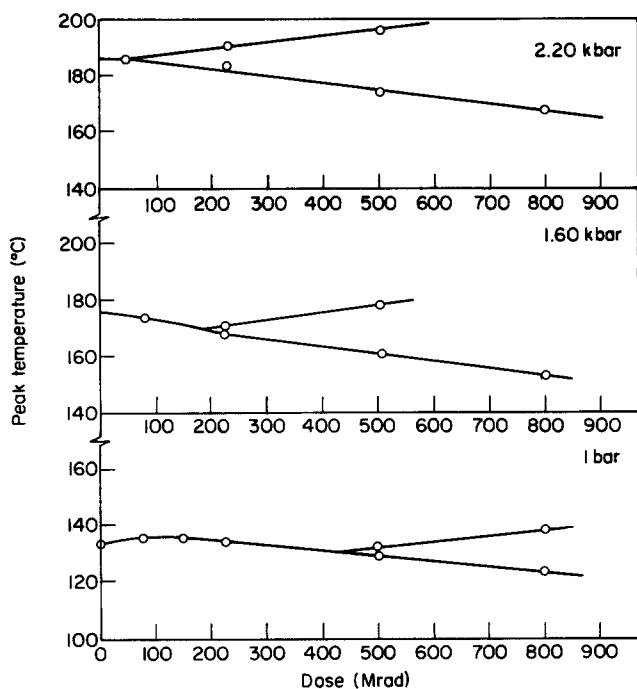


Figure 6 Transition temperatures at three pressures of irradiated polyethylenes as a function of radiation dose

The slope of l is given by the Clausius–Clapeyron equation¹¹

$$\frac{dT_{om}}{dp} = \frac{v_m - v_o}{s_m - s_o}$$

which can be written as

$$\frac{dT_{om}}{dl} = \lambda(v_m - v_o) \text{ and } \frac{dp}{dl} = \lambda(s_m - s_o)$$

where λ depends on the unit chosen for the distance l along the phase line, but is independent of i .

As the general expression for the differential of free enthalpy is

$$dg_i = v_i dp - s_i dT \quad (2)$$

the rate of increase of g_i along l , which we denote by dg_i/dl , is given by

$$\begin{aligned} \frac{dg_i}{dl} &= \left(\frac{\partial g_i}{\partial p} \right)_T (s_m - s_o) \lambda + \left(\frac{\partial g_i}{\partial T} \right)_p (v_m - v_o) \lambda \\ &= \lambda [v_i (s_m - s_o) - s_i (v_m - v_o)] \end{aligned} \quad (3)$$

The relation

$$\frac{dg_h}{dl} < \frac{dg_o}{dl} \left(= \frac{dg_m}{dl} \right) \quad (4)$$

thus represents the condition for a widening temperature interval of existence of the hexagonal phase with pressure; using equation (3) it gives directly inequality (1). This inequality is exact for parameters measured along the metastable equilibrium line. Otherwise it holds to the approximation that changes in v_i and s_i off this line can be neglected. This is equivalent to ignoring curvature and drawing straight lines for the free enthalpy variations in Figure 7. To this approximation, equation (1) is readily derived by application of the Clausius–Clapeyron equation to the transition lines of the phase diagram.

The essential new information provided by this work is that the radiation-induced hexagonal structure is also one of high entropy. This is evident from Figure 4 in which, for a sample of 500 Mrad dose, the small temperature interval of hexagonal stability at 1 bar immediately widens with application of pressure. In consequence, the free enthalpy changes brought by the combined increases of pressure and temperature are in the same sense as those produced by irradiation, a fact confirmed by the observed changes in the triple point. This occurs at lower pressure for a high radiation dose (compare Figures 1b and 5) or, equiva-

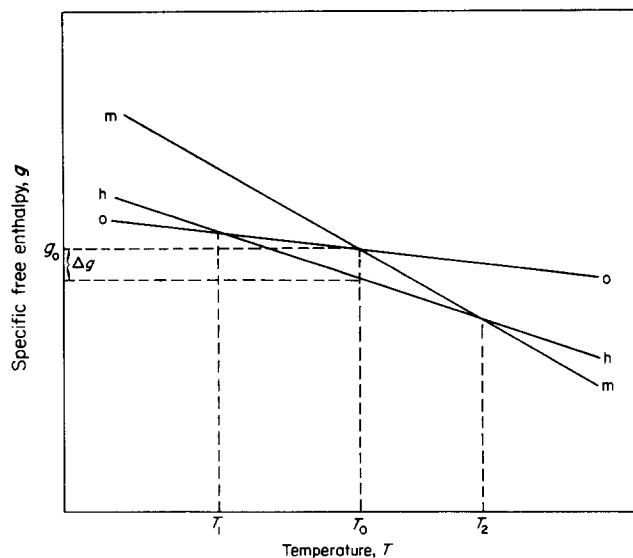


Figure 7 Sketch of the free enthalpy–temperature relationships for a stable hexagonal phase

lently, at a lower dose for a higher pressure (Figure 6). (Observations by Takamizawa and co-workers¹⁶, reported in ref. 17, recording a lowered hexagonal transition temperature for irradiated polyethylene crystals are in agreement with our findings.) It is this positive addition of the free enthalpy changes which provides the basis of continuity of the phase diagrams between unirradiated and irradiated polyethylene.

The evidence provided allows a comparison of the radiation-induced phase with paraffin rotator phases and the anabaric polyethylene phase on three counts: the relative values of specific entropies and volumes, the high entropy/high volume distinction and chain configuration. With regard to this, it would be advantageous to compare the specific volume of the hexagonal phase in irradiated polyethylene with the available values for volumes of the rotator and the anabaric phases. In the absence of direct volume data, we resort to a calculation of v_h based on our p - T diagrams.

As mentioned in the previous section, from the thermogram in Figure 3a we estimate the following entropy ratio:

$$\frac{s_h - s_o}{s_m - s_o} = 0.44$$

Through equation (1) this gives the inequality

$$\frac{v_h - v_o}{v_m - v_o} < 0.44 \quad (5)$$

By equating the two sides of inequality (5) we first calculate the upper limit for the specific volume of the hexagonal phase, v'_h , i.e. that value of v_h for which the orthorhombic-hexagonal and the hexagonal-melt equilibrium lines would be parallel in the p - T diagram. We take the necessary crystallographic, calorimetric and volumetric data at atmospheric pressure for the 800 Mrad sample as they are the most reliable. The crystal lattice parameters were measured with a high-temperature diffractometer; the density of the melt was determined by measuring the buoyancy in silicone oil at desired temperatures using a modified thermobalance. The full results of these measurements will be reported elsewhere.

We choose the temperature of 131°C, midway between the hexagonal and melt transition temperatures, as being close to the metastable o-m equilibrium temperature for the 800 Mrad sample. The extrapolated values for v_o and v_m at this temperature, as obtained from X-ray and density measurements, respectively, are $v_o = 1.088 \text{ cm}^3/\text{g}$ and $v_m = 1.243 \text{ cm}^3/\text{g}$. v'_h , the upper limit of v_h , as obtained from equation (5) is $v'_h = 1.156 \text{ cm}^3/\text{g}$.

We now go one step further and calculate the actual magnitude of v_h from the divergence of T_{o-h} and T_{h-m} with increasing pressure, $d(\Delta T)/dp$. We only have limited data about $d(\Delta T)/dp$ for the 800 Mrad sample, so we use the value for the 500 Mrad sample which we know with better accuracy. We have ascertained, however, that the two do not differ significantly. At zero pressure $d(\Delta T)/dp = 9.5 \text{ K/kbar}$ (Figure 6). Applying the Clausius-Clapeyron equation to $d(\Delta T)/dp = dT_{h-m}/dp - dT_{o-h}/dp$ we get

$$v_h = \frac{v_m(s_h - s_o) + v_o(s_m - s_h)}{s_m - s_o} - \frac{d(\Delta T)}{dp} \frac{(s_m - s_h)(s_h - s_o)}{s_m - s_o} \quad (6)$$

The first term in this equation is equal to v'_h while the second term takes account of the divergence of $T_{o-h}(p)$ and $T_{h-m}(p)$ lines. When the experimental values $(s_h - s_o)/(s_m - s_o) = 0.44$ and $s_m - s_h = 0.32 \text{ J/K per gram}$ ¹⁰ of crystalline phase are inserted it is found that

$$v_h = 1.156 - 0.014 = 1.142 \text{ cm}^3/\text{g}$$

at 131°C.

The characteristic entropy and volume ratios for the hexagonal phase in irradiated polyethylene are thus

$$\frac{s_h - s_o}{s_m - s_o} = 0.44 > \frac{v_h - v_o}{v_m - v_o} = 0.35 \quad (7)$$

Comparable values are:

$$\frac{\text{n-C}_{24}\text{H}_{50} \text{ rotator phase}}{\text{(ref. 7)}} \frac{s_h - s_o}{s_m - s_o} = 0.36 < \frac{v_h - v_o}{v_m - v_o} = 0.404 \quad (8)$$

$$\frac{\text{Linear polyethylene at 5 kbar}}{\text{(ref. 17)}} \frac{s_h - s_o}{s_m - s_o} = 0.72 > \frac{v_h - v_o}{v_m - v_o} = 0.64 \quad (9)$$

A comparison of this kind is admittedly somewhat ambiguous in that the reference points, i.e. the states of the o and m phases, are not the same in all three cases. In particular, v_m and s_m are markedly higher in highly irradiated polyethylene (equation (7)) as compared to those for unirradiated material. Ideally, all thermodynamic quantities should be extrapolated to zero pressure and radiation dose, but there is insufficient data at present to achieve this. The second best alternative, giving a more realistic comparison between the hexagonal phase in irradiated polyethylene and the rotator phase in paraffins, is obtained if the v_o , s_o and v_m values in equation (7) are substituted by those for unirradiated polyethylene. At 131°C the crystallographic data of Swan¹⁸ yield $v_o = 1.033 \text{ cm}^3/\text{g}$, while our density measurements give $v_m = 1.272 \text{ cm}^3/\text{g}$. Furthermore, when the value of $s_m - s_o = 0.73 \text{ J/gK}$ for pure crystalline polyethylene is inserted and the value of $0.44 \text{ J/K per gram}$ of crystalline polymer taken for $s_h - s_o$, since $s_m - s_h = 0.32 \text{ J/gK}$ ¹⁰ (for this purpose we neglect the effect of irradiation on s_m), we obtain the following relation:

$$\frac{\text{irradiated polyethylene}}{\text{(unirradiated o and m phases as reference)}} \frac{s_h - s_o}{s_m - s_o} = 0.56 > \frac{v_h - v_o}{v_m - v_o} = 0.46 \quad (10)$$

At atmospheric pressure, the radiation-induced phase is thus clearly intermediate in character between the rotator and the anabaric phase. On the other hand, it resembles the anabaric phase in being a high entropy phase.

At pressures exceeding 1 kbar, the first peak in the melting endotherm has become the larger (Figure 3b) so that on both the above criteria, the radiation-induced phase has become more akin to the high pressure phase of linear polyethylene than to the paraffin rotator phases. This is far from saying, however, that the two have the same, or even closely similar crystallographies making due allowance for the variation with pressure. It is

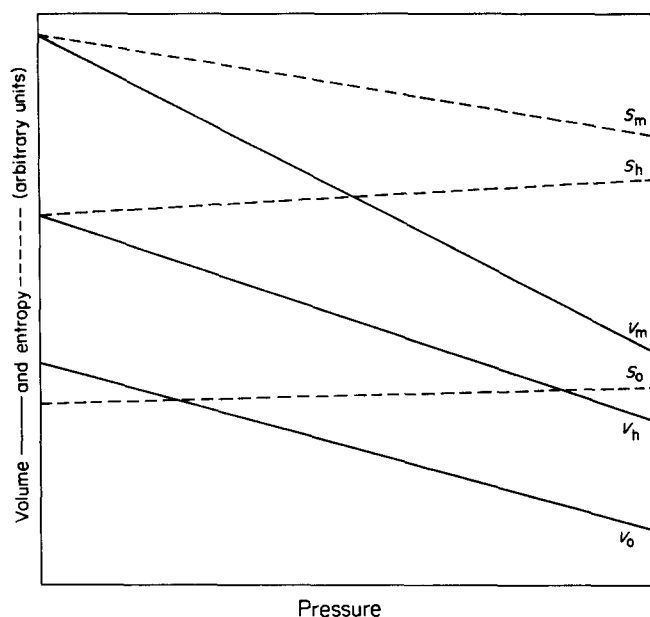


Figure 8 Schematic variation of specific volumes (solid lines) and specific entropies (broken) for orthorhombic, hexagonal and molten phases of highly irradiated polyethylene as functions of pressure.

relevant to this point to discuss the type of chain configuration in the various hexagonal modifications.

According to Muller⁴ and subsequent workers¹⁹, the all-*trans* configuration is transferred from orthorhombic to rotator phase in the *n*-paraffins. This is not true of the anabaric polyethylene phase. For this, the expansion of cross-section per chain at 5 kbar on making the orthorhombic to hexagonal transition exceeds the total volume increase by 6.7%^{1,17}. In consequence the all-*trans* configuration is lost, *gauche* bonds are introduced into the crystalline chain¹ and there is no precise spatial repetition (and hence no sharp X-ray reflections²⁰) along the *c* axis. Incidentally, even in the rotator phase of longer *n*-alkanes more recent works^{21,22} suggest the presence of a certain amount of *gauche* bonds.

There are no X-ray data showing the presence of *hkl* (*l* ≠ 0) reflections for the hexagonal phase in irradiated polyethylene. Nevertheless, we can calculate the average $-(\text{CH}_2-\text{CH}_2)-$ repeat distance in the chain direction (referred to as *c*) from the measured lateral unit cell dimensions and the specific volume v_h obtained above. At 131°C X-ray diffraction gives a cross-section area of 21.6 Å² per chain in the hexagonal phase of the 800 Mrad sample. With $v_h = 1.142 \text{ cm}^3/\text{g}$ we obtain

$$c = 2.46 \text{ \AA}$$

This is substantially smaller than 2.53 Å, the value for the all *trans* conformation in the orthorhombic phase. It indicates the presence of *gauche* bonds in the hexagonal phase of irradiated polyethylene. The above value for *c* may be compared to that of 2.38 Å determined from the position of the first X-ray layer line as quoted by Yamamoto²³ for the anabaric phase in linear polyethylene at 9 kbar and 285°C. If there is continuity between the radiation-induced and the anabaric hexagonal phase, this further contraction of the chain with the application of pressure would be explained as an adjustment of chain conformation to increasing pressure and

temperature. This is, however, a marginal point to the present work and would need special investigation to prove or disprove.

In general thermodynamic terms the changing properties of the three phases for irradiated material are sketched in Figure 8. This is only schematic and makes no attempt to describe the situation exactly. Indeed there are insufficient data available to do so. The lines in Figure 8 represent the specific volumes and entropies of the three phases along the metastable orthorhombic-melt equilibrium line *l* in the phase diagram as functions of pressure. Formally these may be derived by noting that

$$dv = [\partial v/\partial T]_p dT + [\partial v/\partial p]_T dp$$

for an arbitrary change. Along the specified line, therefore,

$$\begin{aligned} \frac{dv}{dl} &= [\partial v/\partial T]_p [dT/dp] + [\partial v/\partial p]_T \\ &= v\beta dT/dp - v\kappa \end{aligned} \quad (11)$$

where $\beta = 1/v[\partial v/\partial T]_p$ is the isobaric volume expansion coefficient and $\kappa = -1/v[\partial v/\partial p]_T$ is the isothermal compressibility. Similarly,

$$ds/dl = [\partial s/\partial T]_p [dT/dp] + [\partial s/\partial p]_T = \frac{c_p}{T} [dT/dp] - v\beta \quad (12)$$

where c_p is the isobaric specific heat capacity and the Maxwell relation $(\partial s/\partial p)_T = -(\partial v/\partial T)_p$ has been used. There are sufficient data to show that the specific volumes of all phases decrease with increase of melting pressure^{10,17,24}. Accordingly the second term in equation (11) will outweigh the first for all phases, in agreement with expected values of $\beta (\approx 5.10^{-4} \kappa^{-1})^{17,18}$ and $\kappa \geq \approx 10^{-2} \text{ kbar}^{-1}$ ²⁵. Furthermore, the coefficients of equations (11) and (12) are interrelated, involving second derivatives of free enthalpy. It is well known that, for a system obeying simple thermodynamics¹²,

$$c_p - c_v = \frac{v\beta^2 T}{\kappa}$$

so that

$$c_p = \left[\frac{\gamma}{\gamma - 1} \right] (c_p - c_v) = \frac{\gamma}{\gamma - 1} \frac{v\beta^2 T}{\kappa} \quad \text{where } \gamma = c_p/c_v$$

and

$$\left[\frac{c_p}{T} \right] \left[\frac{dT}{dp} \right] \frac{1}{v\beta} = \left[\frac{\gamma}{\gamma - 1} \right] \frac{v\beta dT}{v\kappa dp} \quad (13)$$

Equation (13) relates the comparative magnitudes of the two terms on the right of each of equations (11) and (12). Their ratio is $\gamma/\gamma - 1$ which always exceeds unity.

If it were unity then ds/dl would be dominated by the expansion coefficient in the identical way that dv/dl is dominated by the compressibility. As it does exceed unity (its value for molten polyethylene at 1 bar and 140°C is 3.5²⁴) then the contribution of the heat capacity term will be enhanced and is likely to equal or exceed the magnitude of the second term in equation (5) except, perhaps, for

the melt. Thus while it is to be expected that $\beta_m > \beta_h > \beta_o$, the combined effect of both terms depends sensitively upon exact numerical values which are not available for our samples. Nevertheless, *Figure 8* is believed to be a reasonable representation of how pressure alters the relative properties of the three phases in the region of the melting point. Its principal feature is that the specific volume and entropy of the hexagonal structure move smoothly with pressure from values nearer to the orthorhombic parameters towards melt conditions. We conclude that while at atmospheric pressure the radiation-induced hexagonal phase of polyethylene is intermediate in character between the rotator phase of n-paraffins and the disordered high-pressure phase, it moves towards the condition of the latter with application of pressure.

REFERENCES

- 1 Bassett, D. C., Block, S. and Piermarini, G. J. *J. Appl. Phys.* 1974, **45**, 4146
- 2 Bassett, D. C. in 'Developments in Crystalline Polymers I', (Ed. D. C. Bassett), Applied Science Publishers, London, 1982
- 3 Bassett, D. C. *High Temp. High Press.* 1977, **9**, 553
- 4 Muller, A. *Proc. Roy. Soc. A* 1932, **138**, 514
- 5 Ungar, G. *J. Phys. Chem.* 1983, **87**, 689
- 6 Bassett, D. C. and Turner, B. *Nature (Phys. Sci.)* 1972, **240**, 146
- 7 Nelson, R. R., Webb, W. and Dixon, J. A. *J. Chem. Phys.* 1960, **33**, 1756
- 8 Wurfliinger, A. and Schneider, G. M. *Ber. Bunsenges.* 1973, **77**, 121
- 9 Grubb, D. T. *J. Mater. Sci.* 1974, **9**, 1715
- 10 Ungar, G. and Keller, A. *Polymer* 1980, **21**, 1273
- 11 Bassett, D. C. and Carder, D. R. *Phil. Mag.* 1973, **28**, 513
- 12 Pippard, A. B. 'The Elements of Classical Thermodynamics', Cambridge University Press, 1957
- 13 Takamizawa, T., Fukahori, Y. and Urabe, Y. *Makromol. Chem.* 1969, **128**, 236
- 14 Jenkins, H. and Keller, A. *J. Macromol. Sci.-Phys.* 1975, **B11**, 301
- 15 Charlesby, A. and Ross, M. *Proc. Roy. Soc. A* 1953, **217**, 122
- 16 Takamizawa, K., Hasegawa, H. and Urabe, Y. *Polym. Prepr. Jpn.* 1978, **27**, 493
- 17 Leute, V. and Dollhopf, W. *Colloid Polym. Sci.* 1980, **258**, 353
- 18 Swan, P. R. *J. Polym. Sci.* 1962, **56**, 403
- 19 Barnes, J. D. and Fanconi, B. M. *J. Chem. Phys.* 1972, **56**, 5190
- 20 Yamamoto, T., Miyaji, H. and Asai, K. *Jpn. J. Appl. Phys.* 1977, **16**, 1891
- 21 Strobl, G., Ewen, B., Fischer, E. W. and Piesczek, W. *J. Chem. Phys.* 1974, **61**, 5257
- 22 Maroncelli, M., Qi, S. P., Strauss, H. L. and Snyder, R. G. *J. Am. Chem. Soc.* 1982, **104**, 6237
- 23 Yamamoto, T. *J. Macromol. Sci.-Phys.* 1979, **B16**, 487
- 24 Matsuoka, S. *J. Polym. Sci.* 1962, **57**, 569
- 25 Asai, K. *Polymer* 1982, **23**, 391
- 26 Wunderlich, B. *J. Polym. Sci. C* 1963, **1**, 41