Effect of radiation on the crystals of polyethylene and paraffins: 1. Formation of the hexagonal lattice and the destruction of crystallinity in polyethylene

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In this, the first of a series of three preliminary papers on the effect of high dose radiation on the paraffinoid crystal lattice, the destruction of crystallinity in polyethylene under the influence of γ-radiation is followed by X-ray diffraction and calorimetry. The principal new finding is the occurrence of an orthorhombic–hexagonal phase transition on heating *subsequent* to irradiation at ambient temperature beyond a certain critical dose. This othorhombic–hexagonal transition temperature is an increasing function of crystal thickness, and for all samples decreases with increasing dose. While the lattice parameters are seen to change gradually with dose (as observed at room temperature) the destruction of crystallinity itself occurs rather catastrophically beyond a certain dose. It is envisaged that this collapse of crystallinity is taking place as the temperature of the orthorhombic–hexagonal transition, which decreases steadily with dose, approaches the irradiation temperature. The above scheme is supported by the higher radiation sensitivity of the hexagonal, or nearly hexagonal, phase as found here in paraffins. As a side-line, the present findings lead to a grading of hexagonal phases in paraffinoid substances as obtained along different routes.

INTRODUCTION

The principal radiochemical effects produced in saturated long-chain hydrocarbons and polyethylene (PE) include crosslinking, main chain scission and double bond formation[1,2]. Crosslinks present potentially the most severe lattice defects if formed inside the crystal. Abundant experimental evidence (see, for example, refs 3–6) has shown that crosslinking takes place primarily in the fold surface of PE single crystals or in the non-crystalline phase of the bulk polymer. The scarcity of crosslinks inside the crystal lattice at relatively low irradiation doses has been ascribed[6] to carbon atoms on adjacent chains being too far apart (4.1 A at least), and to the lattice being too rigid at room temperature, for the interchain C–C bonds (1.54 A) to form easily. However, at high irradiation doses the crystal lattice becomes disrupted and finally destroyed by irradiation[8,9]. In order to understand how this occurs we made a detailed study of the changes in single crystal and bulk PE and a number of n-paraffins exposed to γ-radiation up to a dose of 2–3 Grad. The present series of papers reports the salient results of these studies. This first paper deals with studies on PE and in particular with the role of a radiation-induced hexagonal crystal modification. The findings for γ-irradiated n-paraffins are summarized in the second paper[10]. The third paper[11] will report the changes in paraffin and PE crystals which take place during exposure to an electron microscope beam[†]. A full account of this work will appear later.

EXPERIMENTAL

Linear PE (Marlex 6002) was γ-irradiated *in vacuo* in a ^{60}Co source (by courtesy of Professor A. Charlesby and Dr. P. J. Fydelor at the Royal Military College of Science at Shrivenham). The irradiation temperature was between 40° and 45°C and the dose rate was 2.7 Mrad h^{-1}. PE was in the form of slowly crystallized bulk (denoted *s*), ice-quenched bulk (*q*), single crystals (*SC*) grown from xylene solution at different temperatures, annealed single crystals, etc. Self-seeding and freeze-drying procedures were employed in the preparation of single crystals.

The irradiated polymer was examined by differential scanning calorimetry (d.s.c.) and X-ray diffraction.

RESULTS AND DISCUSSION

A set of d.s.c. melting thermograms for a number of irradiation doses is shown in *Figure* 1 for slowly crystallized bulk PE (sample *s*). The most interesting feature is the splitting of the endotherm for samples irradiated with intermediate and high doses. A new endotherm emerges from the main peak on the low temperature side at a critical dose D_c, which is around 800 Mrad for this particular PE sample. With further irradiation the lower peak greatly broadens and its temperature decreases rather steeply. Other PE samples behave similarly, but D_c depends greatly on the crystal morphology[‡].

X-ray diffraction revealed that the low temperature endotherm represents an orthorhombic–hexagonal ($o \rightarrow h$) crystal transition. In *Figure* 2 the lattice spacings are plotted against temperature for sample *s* irradiated with

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[†] These three papers include material presented as a communication at the Biennial Conference of the Polymer Physics Group, Institute of Physics (London) held at Weybridge September 1979

[‡] While this work was in progress the appearance of an unexplained double melting peak was also reported by Ahmad and Charlesby[12] for highly irradiated bulk PE

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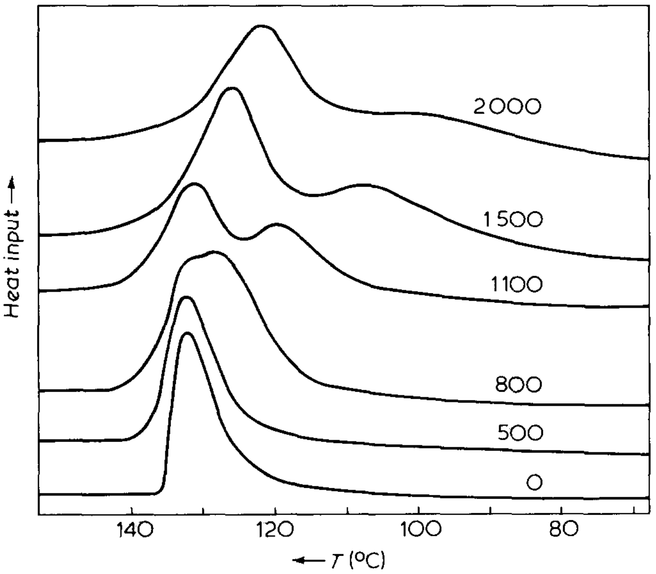

Figure 1 Thermograms of irradiated slowly crystallized (*s*) bulk PE. Dose in Mrad is marked for each curve

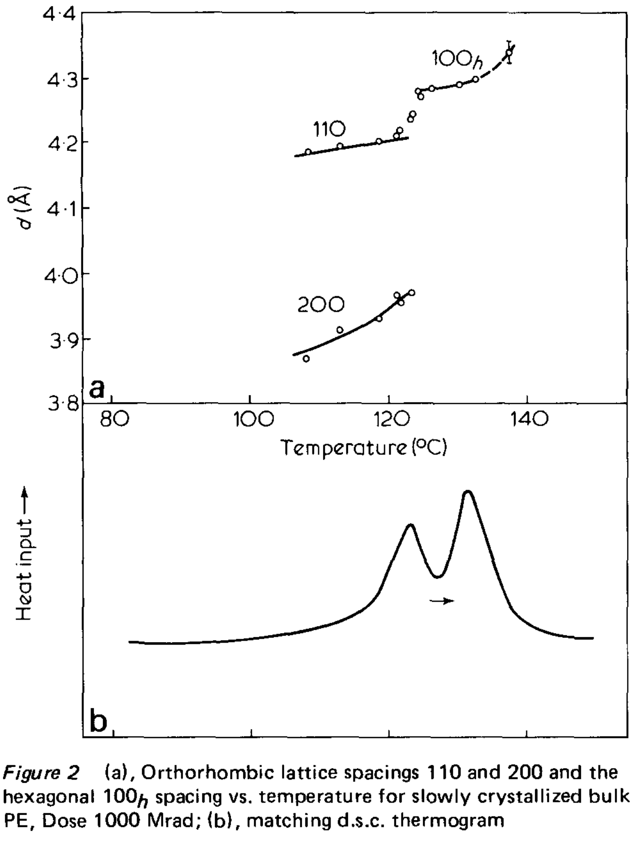

Figure 2 (a), Orthorhombic lattice spacings 110 and 200 and the hexagonal 100_h spacing vs. temperature for slowly crystallized bulk PE, Dose 1000 Mrad; (b), matching d.s.c. thermogram

1000 Mrad. The corresponding d.s.c. curve is shown beneath. At the temperature of the lower d.s.c. peak (~123°C) the orthorhombic 200 and 110 X-ray reflections give way to a single maximum ascribed to the 100 diffraction of a hexagonal lattice. In addition to this strong 100_h reflection a very weak 100_h peak is also observed. The 100_h spacing is 4.3 A and it changes little over a temperature interval of about 10°C. Above ~133°C it increases steeply while the diffraction intensity falls off and disappears completely above 140°C, thus indicating that the hexagonal crystals have melted. Melting is also revealed by the second d.s.c. endotherm.

Melting and $o \rightarrow h$ transition temperatures are plotted against radiation dose in *Figure* 3 for slowly crystallized (*s*) and quenched bulk PE (*q*) and single crystals grown at 85°C (*SC*). The temperature of the $o \rightarrow h$ transition, $T_{o \rightarrow h}$, decreases markedly with increasing dose. $T_{o \rightarrow h}$ depends greatly on the crystal morphology. There is a clear correlation between $T_{o \rightarrow h}$ and the crystal thickness: the thicker the crystals the higher the transition temperature for a given radiation dose, a trend borne out explicitly also by an experimental series on single crystals of different thicknesses. (There is also a corresponding dependence on the crystal thickness of the changes in the a lattice spacing with dose, *Figure* 5.) *Figure* 4 displays this effect on an expanded dose scale in the lower dose range.

The differences in melting points, T_m, for irradiated samples of different morphologies are also pronounced. A similar observation has already been attributed to entropy effects in the melt[13] and will not be dealt with here.

The hexagonal phase features frequently in the literature of paraffinoid substances. The way of obtaining it, as described here, is of some interest from the point of view of its crystallography and mode of ordering. This will be elaborated immediately below. In addition, the hexagonal phase seems to be of special significance for the understanding of how radiation can destroy crystals. A note to this effect will conclude the present paper.

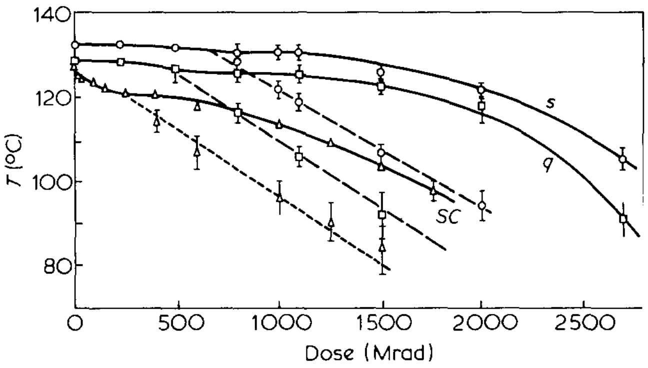

Figure 3 Melting (——) and $o \rightarrow h$ transition temperatures (– – – –) vs. dose for slowly crystallized, (*s*) (o), and quenched bulk (*q*) (□), and single crystals grown at 85°C (*SC*) (△)

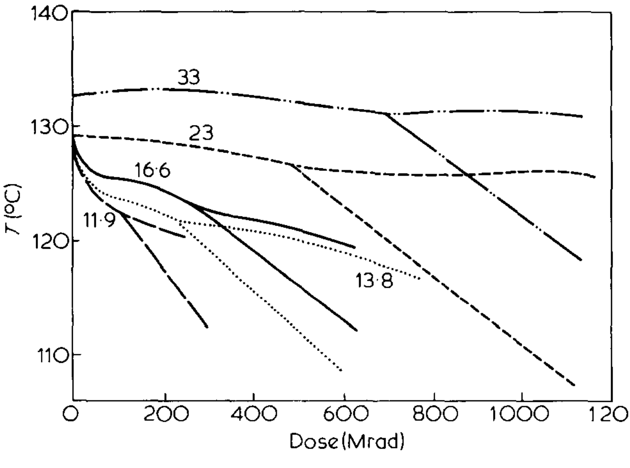

Figure 4 Traces of peak melting and $o \rightarrow h$ transition temperature vs. dose for a number of PE samples of different morphologies: — · · — · · — · ·, bulk *s*; — — — — —, bulk *q*; ———, single crystals (*SC*) grown at 90°C; · · · · · · *SC* grown at 85°C; — —— — —*SC* grown at 70°C. Crystal long periods in nm are indicated

Table 1 Extrapolated $o \to h$ transition temperatures ($T^0_{o\to h}$) and experimental melting points (T^0_m) for unirradiated PE

Sample	Crystal long period (nm)	$T^0_{o\to h}$ (°C)	$T^0_{m(o\to l)}$ (°C)	$T^0_{o\to h}-T^0_m$ (°C)
Single crystals grown at 85°C	13.5[a] 13.8[b]	130	125.5[c]	4.5
Single crystals grown at 90°C	16.6[b]	131	126.5[c]	4.5
Quenched bulk (*q*)	23[b]	142	129	13
Slowly-crystallized bulk (*s*)	33[b]	150	132.7	17

[a] From Raman scattering
[b] From X-ray scattering
[c] Corrected for refolding according to ref 27

Hexagonal phases in paraffinoid substances arise under the following circumstances.

(1) On heating lower n-paraffins a first order transition into a so-called 'rotator' phase occurs a few degrees below the melting point; this is either hexagonal or nearly so[14,15]. This is the earliest recognized example of a hexagonal phase and thus the best known. Such a transition on heating does not occur in higher paraffins and in polyethylene except under special circumstances which will be enumerated next.

(2) Under the application of high hydrostatic pressure (4 kbar and above) polyethylene can be obtained in a hexagonal phase at suitably high temperatures[16].

(3) When highly extended fibres are constrained to a constant length the usual orthorhombic crystal phase transforms into a hexagonal phase above the normal melting temperature[18,19].

(4) The presently recognized case of orthorhombic–hexagonal transformation on heating irradiated polyethylene.

(5) A hexagonal crystalline phase is found at room temperature in some ethylene–propylene copolymers containing a small diene component.[20]

We shall now proceed to discuss the common features and the differences between the hexagonal phases in cases (1)–(5). Regarding case (1) it is known that $T_{o\to h}$ in short alkanes increases with increasing chain length[14], an effect also dealt with by statistical theories[21]. The inability to reach this state in higher alkanes and in PE under ordinary conditions is due to the fact that the melting temperature, T_m, does not increase with increasing chain length (n) as steeply as does $T_{o\to h}$. Thus the $T_{o\to h}$ vs. n and T_m vs. n curves cross over, i.e. for sufficiently long chains the orthorhombic crystals melt directly. The common feature of the special circumstances under (2)–(5) is that they all produce a situation where $T_m > T_{o\to h}$ also for the longer chains. However, in cases (2) and (3) this is achieved in a different manner from that in (4) and (5).

In cases (2) and (3) the melting point is raised beyond the usual T_m value. This occurs with increasing pressure, P, according to the Clausius–Clapeyron equation $dT_m/dP = \Delta V_{o\to l}/\Delta S_{o\to l}$ in case 2. Here $\Delta V_{o\to l}$ and $\Delta S_{o\to l}$ denote respectively the changes in volume and entropy of fusion (orthorhombic→liquid transition). Occurrence of the hexagonal phase at high pressures shows that $(\Delta V_{o\to h}/\Delta S_{o\to h}) < (\Delta V_{o\to l}/\Delta S_{o\to l})$ which means that the h phase is one of high entropy achieved by a comparatively small increase in volume[17]. In the case of constrained fibres (case 3) keeping the polymer chains stretched reduces the configurational entropy of melt. This results in an increase in T_m, since $T_m (\equiv T_{o\to l}) = \Delta H_{o\to l}/\Delta S_{o\to l}$ whereas $T_{o\to h}$ remains practically unaffected. T_m is thus raised above $T_{o\to h}$ enabling the $o\to h$ transition to occur.

In cases (4) and (5) $T_{o\to h}$ is again brought below T_m, but this time primarily by reducing $T_{o\to h}$ due to introduction of defects into the crystal lattice. In irradiated PE (case 4) the main defects are crosslinks, and in the ethylene–propylene copolymer (case 5) they are the methyl branches. The severity of the defects produced by crosslinking in the orthorhombic lattice is manifested by a considerable increase in the a lattice spacing (*Figure* 5) and a decrease in $\Delta H_{o\to l}$, the heat of fusion. To quote some figures: for 800 and 1500 Mrad, $\Delta H_{o\to l}$ is reduced by 28% and 46% respectively, in the case of slowly-crystallized bulk polymer.

Although the chemical defects are primarily responsible for the occurrence of the hexagonal phase in irradiated PE, another effect that favours its appearance is the reduction in the configurational entropy of the melt caused by crosslinking of polymer molecules. Similarly to case (5) this results in a lowering of $\Delta S_{o\to l}$ with the consequence that the melting point remains high. There is direct evidence for the reduction in melt entropy from previous work at lower doses[13,22,23], where a small increase in T_m was observed indicating that the reduction in $\Delta S_{o\to l}$ can exceed that of $\Delta H_{o\to l}$. Thus the constraint imposed on the melt, which is the primary factor in producing the hexagonal phase in cases (2) and (3), is also operative to some extent in irradiated polymer (case 4).

Summing up, an orthorhombic–hexagonal transition appears in PE for the following reasons: in cases (2) and (3), because T_m increases (by constraining the melt) beyond $T_{o\to h}$; and in cases (4) and (5) primarily because $T_{o\to h}$ decreases below T_m (by introduction of lattice defects).

From the measured dose dependence of $T_{o\to h}$, the latter can be extrapolated to zero dose ($T^0_{o\to h}$), where an orthorhombic→hexagonal phase transformation cannot be observed directly. As seen from *Table* 1 these $T^0_{o\to h}$ values, pertaining to the unirradiated samples, are always above T^0_m values and also show a greater rate of increase with increasing crystal thickness (see last column in *Table* 1). This is in line with the behaviour of n-alkanes where $T_{o\to h}$ increases more steeply with chain length than does T_m except that in the case of chain-folded polyethylene the crystal thickness is to be considered in place of chain length.

It needs mentioning at this point that a hexagonal crystal modification in polyethylene has been reported previously by Orth and Fischer[24], obtained by electron irradiation in an electron microscope at elevated temperatures. This hexagonal phase was different from ours, obtained by heating samples irradiated with γ-rays at

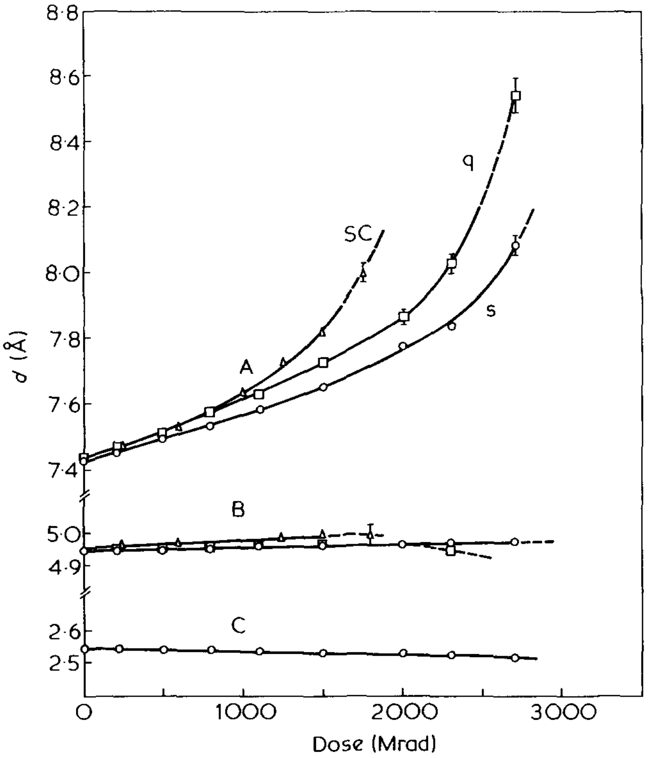

Figure 5 Dose dependence of unit cell parameters *a*, *b* and *c* (curves A, B and C, respectively) measured at room temperature for samples *s* (○), *q* (□) and *SC* (△). Values for *c* refer to sample *s* only (no *hkl* reflections were observed for the others at high doses). Note the crystal thickness dependence (*Table 1*) of the increase in *a*

room temperature, in as far as it did not transform into the orthorhombic phase on cooling and hence did not reveal an $o \rightarrow h$ transition. In our case the transition was always reversible. The relation of the findings in ref 23 to ours has not yet been investigated in sufficient detail.

In what follows the degree of ordering of the hexagonal phases achieved along routes (1)–(5) will be compared, to see whether there are basic differences between them. For this purpose the heat of fusion values for the hexagonal phases ($\Delta H_{h \rightarrow l}$) will be compared together with the lattice parameters.

For sample *s*, irradiated with 1000 Mrad, $\Delta H_{h \rightarrow l}$ is only 20.6 cal per g of polymer, or 20.6/0.70 = 29 cal per g of crystalline phase, as the X-ray crystallinity was 0.70 for this sample. It is of interest to compare this value of 29 cal g^{-1} with the heat of fusion of the 'rotator' phase in n-paraffins which is 38–40 cal g^{-1} [14]. The corresponding value of $\Delta H_{h \rightarrow l}$ for hexagonal PE at high hydrostatic pressure (5 kbar) is only around 15 cal g^{-1}, as calculated by the Clapeyron equation using the published dilatometric data[25]. The reduction in enthalpy of melt at high pressures is of course partly responsible for such a low $\Delta H_{h \rightarrow l}$. Thermograms of constrained PE fibres showed similarly low heats of fusion of the hexagonal modification[18,19].

The cross-sectional area of a chain in the hexagonal lattice of irradiated PE varies between 20.6 and 22.0 A^2 for most samples. It is thus always greater than the cross-sectional area in the 'rotator' structure in paraffins (19.5–20.0 A^2)[15,26] but on average somewhat smaller than that in constrained PE fibres above $T_{o \rightarrow h}$ (21.4–22.7 A^2)[18]. An ethylene–propylene–diene copolymer with approximately 64%, 32% and 4% by wt of each component, respectively (Vistalon 3708, Enjay Chemical Corp.) was found to contain hexagonal crystals with $d_{100_h} = 4.19$ A at room temperature, i.e. with a chain cross-section of 20.3 A^2 [20].

According to the above data the different hexagonal phases in question possess different degrees of ordering. A problem which arises in comparing different hexagonal lattices is that they most often occur at different temperatures and sometimes at different pressures, so that a knowledge of their expansion coefficients and specific heats is desired. By pooling all the present information, the following sequence in ascending degree of ordering emerges for different hexagonal phases: constrained PE fibres and PE at high pressures (cases 2 and 3), irradiated PE (case 4), ethylene–propylene copolymers (case 5), paraffin 'rotator' phase. In spite of the wide span in the degree of order no basic discontinuity appears to exist between various hexagonal PE phases (cases 2–5), but the 'rotator' phase in paraffins may have a special place, being more ordered. Some support for this proposition comes also from our preliminary Raman scattering experiments, but more work on this subject is in progress.

Finally, we revert to the problem of how crystallinity is destroyed by radiation of polyethylene. We see from *Figure* 3 that the melting temperature decreases rapidly at high doses, indicating a rather catastrophic final crystal destruction. The trend suggests that the final break up of crystalline order takes place when $T_{o \rightarrow h}$ approaches the irradiation temperature, which in our case was 40°–45°C. The approach to hexagonal lattice symmetry (i.e. $a/b \rightarrow \sqrt{3}$) shown in *Figure* 5 is accompanied by a large increase in chain motion in the crystalline phase, which should increase the crosslinking efficiency within the lattice.

Evidence for the above suggestion comes from the experiments with shorter paraffins (the corresponding experiments with PE are not yet complete). n-Tricosane ($C_{23}H_{48}$) was irradiated in three states of aggregation: orthorhombic crystals (1°C), 'rotator' phase (42°C) and liquid (53°C). The reduction in the heat of fusion ($\Delta H_f \equiv \Delta H_{o \rightarrow l}$) proved to be a reliable relative measure of the extent of crosslinking. The most significant decrease in ΔH_f occurred when the paraffin was irradiated in the 'rotator' state (*Figure* 6). It even exceeded the decrease

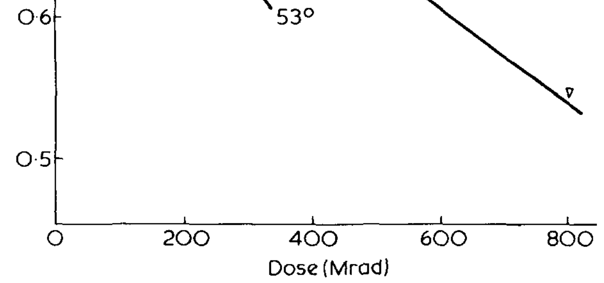

Figure 6 Relative heat of fusion vs. dose for paraffin n–$C_{23}H_{68}$ irradiated at 1°C (orthorhombic), 42°C ('rotator') and 53°C (liquid state)

produced by liquid state irradiation. Accordingly, transition from the more rigid orthorhombic to the highly mobile hexagonal lattice results in a substantial increase in crosslinking for a given radiation dose.

CONCLUSION

The effect of high dose radiation on polyethylene crystals is to produce an orthorhombic→hexagonal ($o \rightarrow h$) phase transition on subsequent heating of the sample. The transition temperature $T_{o \rightarrow h}$ increases with crystal thickness. For all samples $T_{o \rightarrow h}$ decreases with increasing radiation dose. The eventual crystal destruction is catastrophic and is envisaged to take place as $T_{o \rightarrow h}$ approaches the irradiation temperature. The above scheme is supported by the higher radiation sensitivity of the hexagonal or nearly hexagonal phase as found in paraffins. As a sideline to the main theme the present findings lead to a grading of hexagonal phases in paraffinoid substances as obtained along different routes.

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