

High pressure X-ray studies of polymers

Part 3 *Phase transformation of polyethylene*

K. D. PAE, B. A. NEWMAN, T. P. SHAM

High Pressure Research Laboratory and Department of Mechanics and Materials Science, Rutgers University, New Brunswick, New Jersey, USA

A systematic study was made on polyethylene at high pressures and elevated temperatures using X-ray diffraction. Polyethylene with an initial chain-folded morphology and the orthorhombic crystal structure did not transform to any other phase before melting at the temperature and pressure used. Crystallization, however, at high pressures producing extended-chain crystals gave rise to either a new crystal phase, probably hexagonal, or the orthorhombic phase, depending on the crystallization conditions. A reversible solid-state phase transformation was observed between the orthorhombic and hexagonal phases. None of the previous interpretations put forward to account for the high pressure DTA and dilatometric studies of polyethylene, would appear to be appropriate in view of these findings.

1. Introduction

High pressure has been found to be a pertinent variable in the study of structure, morphology, and properties of polymers [1, 2]. With regard to determination of possible structural and morphological changes of polymers at high pressures, several techniques such as differential thermal analysis (DTA) [3, 4], dilatometry [4, 6], and X-ray diffraction methods [7-11] have been employed. X-ray diffraction methods, however, are the only ones that can provide accurate and definitive information concerning structure of polymers if hydrostatic pressure is generated and accurately measured [7].

Several high pressure studies of the crystallization and melting of polyethylene, utilizing high pressure DTA and dilatometry, indicate that experimental data obtained at high pressures are not consistent with the results obtained at atmospheric pressure. Bassett and Turner [3] observed that both whole and fractionated polymers showed two endothermic peaks when heated under pressure through the melting range. Crystallization under pressure was also observed to be a two-step process. In order to account for this behaviour, some evidence was presented that at temperatures near the melting point a transfor-

mation of crystal phase to a new intermediate phase could occur. Bassett and Turner also suggested that chain-extended crystallization is produced via this two-stage process, whereas chain-folded crystals are produced directly from the melt. A later report by Basset *et al.* utilizing high pressure X-ray diffraction [8] confirmed the existence of a new phase in polyethylene at high pressures and temperatures, and a phase transformation from this new phase to the usual orthorhombic phase.

On the other hand Maeda and Kanetsuna [5, 6] who carried out high pressure dilatometric studies which also revealed a two-step process for melting and crystallization at elevated pressures, gave a different interpretation. They suggested, that two kinds of extended-chain crystals can be involved in the melting and crystallization processes: a "highly extended-chain" crystal and an "ordinary extended-chain" crystal. Finally, Yasuniwa *et al.* suggested that a transition to a nematic liquid crystal phase may account for their high pressure DTA data.

It is clear that only high pressure X-ray diffraction methods can provide definitive evidence for a new crystal phase in polyethylene; high pressure DTA or dilatometry can only provide in-

direct evidence. Here, the results of a systematic study made on polyethylene at high pressures and temperatures using X-ray diffraction are presented, and some new findings pertinent to the proposed solid-state phase transformation are described.

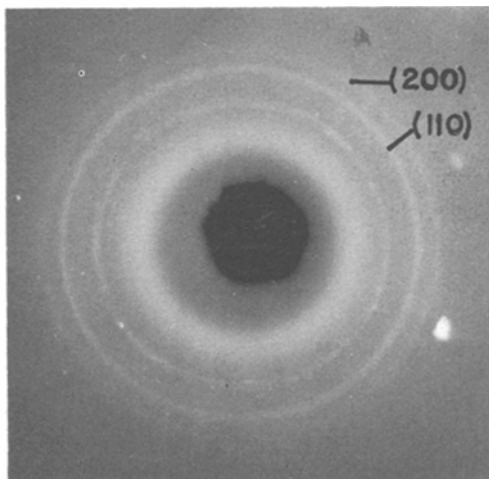
2. Experimental

The diamond-anvil high pressure X-ray camera employed has been described elsewhere in detail [7]. A brass retaining ring 3/8 in in diameter and 1/32 in. thick was used and an axial hold 1/32 in. in diameter was employed to contain the sample. Silicone oil was used as a pressure medium.

Optical observation of the shape of the sample during application of the pressure, for each specimen, ensured that the pressures generated were indeed hydrostatic. Hexamethylene tetramine (HMT) was used as an internal pressure standard as described previously [12, 13], the pressure being measured from the equation of state for HMT.

A Rigaku-Denki rotating anode 6 kW generator was used with a molybdenum target. X-rays traversed both diamonds and the samples were filtered using a zirconium foil to give $\text{MoK}\alpha$ radiation. The diffraction patterns were recorded on flat film, the specimen-to-film distance (approximately 8 cm) being determined from the known spacings of HMT at room pressure.

Figure 1 X-ray diffraction pattern of (a) an original unpressurized PE sample at room temperature, (b) pressurized PE sample at room temperature, showing orthorhombic structure, (c) PE sample at 295°C and 11 kbar.



3. Material

Linear high density polyethylene (Marlex 6009) obtained from Phillips Petroleum Company in powder form was used. A small sample, mixed with HMT, was moulded, and annealed at 100°C for 3 h at atmospheric pressure to increase the extent of crystallinity.

4. Results and discussion

X-ray diffraction photographs obtained from samples at high pressures and high temperatures are shown in Figs. 1–3, the corresponding important d -spacings being tabulated in Table I.

The following three important conclusions were reached:

(1) Polyethylene with an initial chain-folded morphology in the usual orthorhombic phase does not transform to the hexagonal phase before melting at any temperature or pressure. Fig. 1a

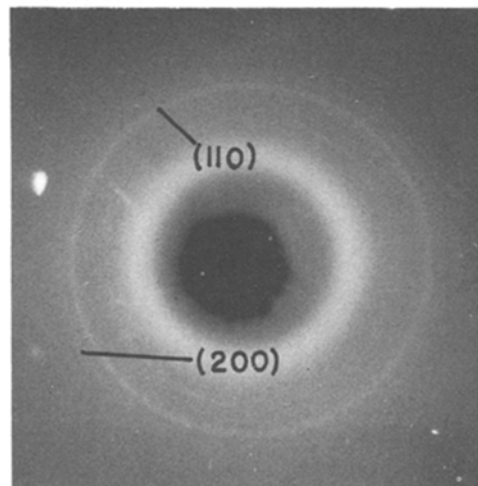
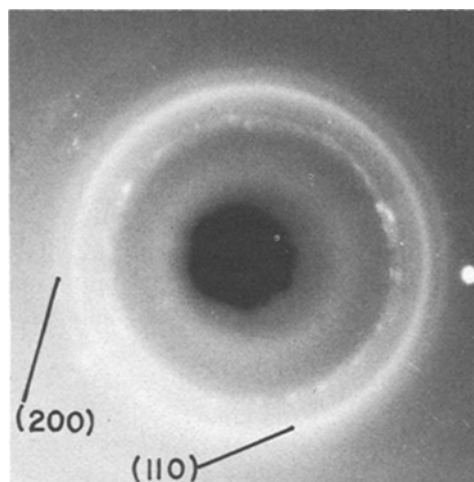


TABLE I

Figure	Temperature (° C)	Pressure (kbar)	ORTHO.		HEX.
			d_{110} (Å)	d_{200} (Å)	d_{100} (Å)
1a	24	atmos.	4.118	3.704	
1b	24	4.1	4.031	3.592	
1c	295	11.0	4.117	3.802	
2a	270	9.6			4.219
2b	180	5.3	4.049	3.703	
3a	24	2.2	4.050	3.627	
3b	228	6.5			4.164

shows the X-ray diffraction pattern of an original unpressurized polyethylene sample at room temperature. The two most intense reflections of the orthorhombic phase, (110) and (200), are present together with a number of reflections from HMT and the gasketed material. Several different samples were pressurized to various pressures (3 to 5 kbar) at room temperature and the original orthorhombic phase was retained as shown in Fig. 1b. The temperature of the pressurized samples was then increased until the samples melted while a large number of X-ray photographs were taken at different temperatures. In all cases no transformation to the hexagonal phase occurred prior to melting. Fig. 1c shows the X-ray diffraction pattern of a sample at 295°C and 11 kbar (this sample melted at 300°C, 11.4 kbar). It is clear that the orthorhombic phase is still present, although the d -spacings of the (110) and (200) planes have changed considerably and are much closer.

It should be noted that a very large number of X-ray photographs were taken during the heating process and several days elapsed before the melting point was reached. It is likely, then, that a considerable fraction of the chain-folded crystals had converted to the extended-chain morphology. No phase transformation associated with this process was detected, however. High pressure DTA and dilatometric data [3, 5, 6] with respect to heating process should not, therefore, be attributed to a phase transition.

(2) Crystallization at high pressures and high temperatures, producing extended-chain crystals, gave rise to either the usual orthorhombic phase or a new crystal phase, depending on the crystallization condition.

Fig. 2a shows the X-ray diffraction pattern taken at 270°C and 9.6 kbar where a sample was isothermally crystallized after melting at 300°C and 11.4 kbar. The two usual reflections of the orthorhombic phase (110) and (200), are not seen. Only one intense reflection corresponding to (110) is seen. This must be characteristic of a new phase, and it is reasonable to attribute this reflection to a hexagonal structure. It also confirms this aspect of studies made by Bassett *et al.* [8].

A second sample crystallized isothermally at 180°C and 5.3 kbar gave rise to the X-ray diffraction pattern at this temperature and pressure as shown in Fig. 2b. The two lines characteristic of the orthorhombic phase are now present. It should be pointed out that this sample was quenched from the melting temperature (250°C and

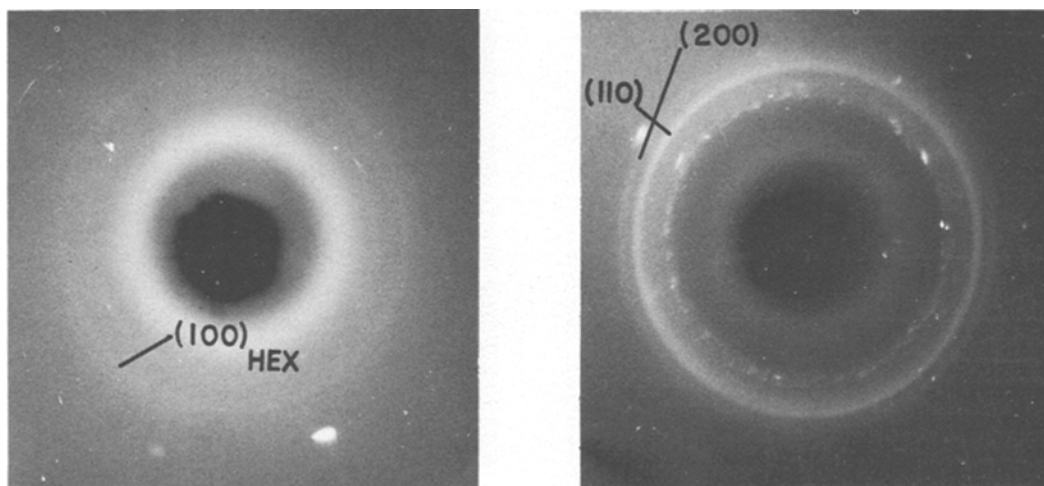


Figure 2 X-ray diffraction pattern of (a) PE sample at 270°C and 9.6 kbar where the sample was isothermally crystallized after melting at 300°C and 11.4 kbar, showing hexagonal structure, (b) PE sample at 180°C and 5.3 kbar where the sample was isothermally crystallized after melting at 250°C and 8.4 kbar, showing orthorhombic structure.

8.4 kbar) to 180°C. It is unlikely that prior crystallization at a higher temperature (during quenching) in the hexagonal phase and a subsequent phase transformation to the orthorhombic phase on further decrease of temperature to 180°C could have occurred. There is no reason to believe that crystallization in the hexagonal phase occurred first in 180°C and then transformed subsequently or the orthorhombic phase at the same temperature and pressure.

The critical crystallization parameters in these experiments are pressure and the degree of supercooling. Since pressure varies with temperature, as previously shown [13], and also with the extent of crystallization, the equilibrium melting point of the sample varies. Consequently, during the course of the crystallization the supercooling varies. However, it can be estimated that in the case of the first sample the supercooling was small ($\Delta T \sim 10^\circ\text{C}$) and in the second sample the supercooling was larger ($\Delta T \sim 30^\circ\text{C}$). Since in both cases there is reason to suppose that extended-chain crystals are formed [14], it would appear that direct crystallization into the orthorhombic phase with an extended-chain morphology can occur.

(3) A reversible solid-state phase transformation can occur between the orthorhombic and hexagonal phases. The sample giving rise to the X-ray diffraction pattern of Fig. 2a was cooled slowly. Fig. 3a is an X-ray photograph of the sample taken at room temperature and 2.2 kbar. The hexagonal

phase transformed to the orthorhombic phase. The sample giving rise to the X-ray diffraction pattern of Fig. 2b was heated slowly to 228°C and 6.5 kbar. The X-ray photograph shown in Fig. 3b was obtained. This shows that the sample has transformed to the hexagonal phase, although a very weak (200) reflection can be seen. This (200) reflection is expected to appear in the X-ray diffraction pattern since some fraction of the sample originally crystallized in the folded-chain crystals retains the orthorhombic phase upon heating, as was shown in conclusion (1).

To summarize the results, polyethylene may crystallize, giving rise to an extended-chain morphology, in either the orthorhombic phase or the hexagonal phase and a reversible phase transformation between these two phases can occur. However, polyethylene in the form of folded-chain morphology retains its orthorhombic structure at any temperature and pressure.

The interpretation put forward by Maeda and Kanetsuna [5, 6] appears to be plausible in the case when a folded-chain polyethylene is heated to melting at high pressures, since no phase transformation is associated with this process (conclusion (1)). But the interpretation of Bassett *et al.* [8] may be consistent when crystallization of polyethylene is carried out at high temperatures since crystallization into a new hexagonal phase and subsequent transformation to the orthorhombic phase can occur (conclusion (3)).

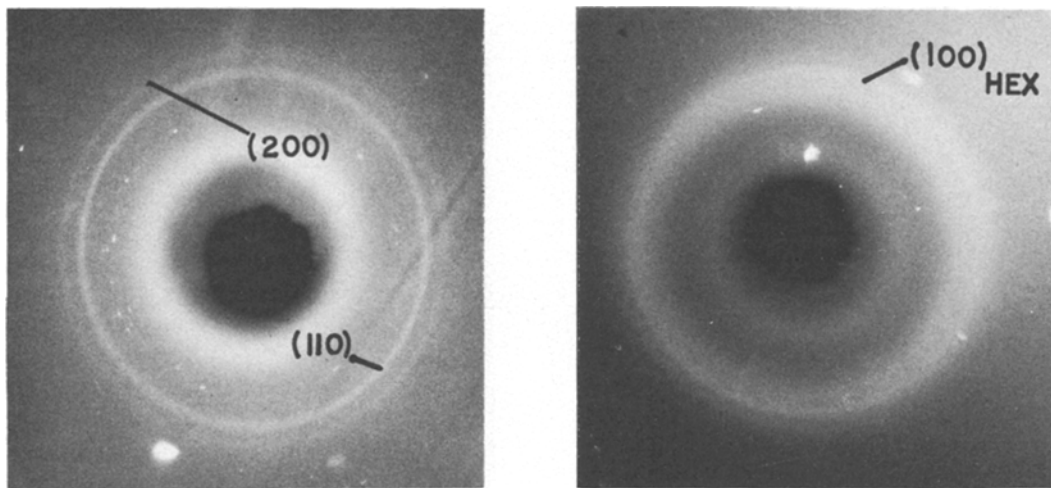


Figure 3 X-ray diffraction pattern of (a) PE sample of Fig. 2a at room temperature and 2.2 kbar, showing orthorhombic structure, (b) PE sample of Fig. 2b at 228°C and 6.5 kbar, showing hexagonal structure.

In view of the results and these considerations, an alternative interpretation to the high pressure DTA and dilatometry data should be sought.

Acknowledgement

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