A high-pressure phase of polyethylene and chain-extended growth

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Optical and x-ray observations of polyethylene have been made at high pressures and temperatures using a gasketed diamond-anvil cell. The experiments confirm the existence of the high-pressure phase previously postulated by Bassett and Turner. The new phase is hexagonal, with orthohexagonal lattice parameters of $a = 8.4_6$ Å and $b = 4.8_8$ Å. Comparison with the previously measured volume change indicates that there is a decrease in the c dimension to 2.4_5 Å per ethylene unit in transforming from orthorhombic to hexagonal structures. The likely implication is that the molecules in the hexagonal phase do not have an all-trans conformation. Chain-extended growth is the result of crystallization from the melt into the hexagonal phase, whereas chain-folded growth is the familiar process of melt crystallization into the orthorhombic phase. Chain-extended lamellae are observed to grow outwards behind a growing edge with a permanent narrowed profile, showing that the lamellar thickness is determined in a region extending several microns behind the growth front.

INTRODUCTION

The existence of a high-pressure phase of polyethylene, intermediate in properties between orthorhombic solid and melt, was postulated by Bassett and Turner on the basis of volumetric and thermal measurements of melting and crystallization in the range 0–6 kbar.[1] These authors proposed, further, that the characteristic product of high-pressure crystallization, which we shall call chain-extended polyethylene, resulted from crystallization via the intermediate phase, whereas direct crystallization into the orthorhombic phase resulted in chain-folded polymers. Most of the known facts concerning chain-extended crystallization can be readily accounted for using these two postulates.[2] We now report optical and x-ray studies made on polyethylene at high temperatures and pressures using the gasketed diamond-anvil cell which confirm both of these hypotheses and identify the new phase as hexagonal, with the molecules probably no longer in an all-trans conformation. Direct observation of growing chain-extended lamellae also shows that the determination of lamellar thickness in melt growth takes place over a region which can extend several microns behind the growing edge.

EXPERIMENTAL

All experiments have been carried out using the gasketed diamond-anvil cell described previously.[3] The polyethylene sample was contained within it in an Inconel metal gasket and compressed between two parallel-sided diamonds. The cell could be mounted either on the stage of an optical polarizing microscope, allowing transmission microscopy, or on an x-ray powder diffraction camera. Forward transmission photographs could then be taken within the range of the suitably enlarged exit aperture using Mo K radiation.

The diamonds were each approximately 2 mm thick and were found to scatter x rays incoherently throughout the range of the strongest polyethylene reflections. The first photographs taken with a normal-size gasket hole (0.35 mm in diameter by 0.15 mm thick) showed that the three strongest reflections (110, 200, and 020) of orthorhombic polyethylene could barely be distinguished above this incoherent scatter at room temperature. Closer to the melting point under pressure, where the new phase was expected to form, the signal decreased so much that only a single very weak ring could be discerned. Here a considerable portion of the polymer was seen to be molten. The reason for this is that the sample in the gasketed cell is constrained to be essentially at constant volume, so that as the proportion of two phases alters with changing temperature the pressure in the system must readjust. In consequence, the temperature interval over which transitions occur will be broadened in comparison with isobaric conditions. It was evident from optical microscopy, e.g., that crystallization which started around 250 °C was not completed until about 200 °C and that the reverse process of melting covered a similar interval. Moreover, with the pressure in the system being lowered towards or

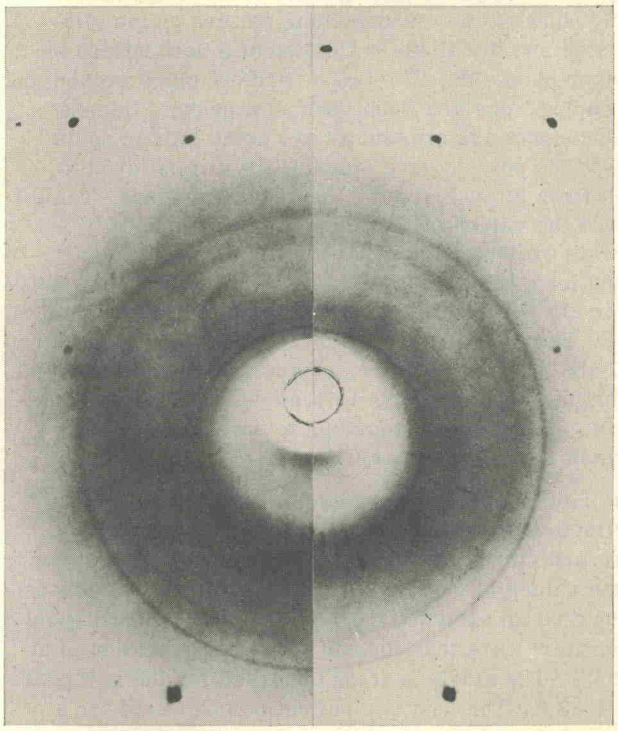


FIG. 1. Composite x-ray pattern showing the 110 and 200 orthorhombic lines of polyethylene on the left-hand side and a single line of the hexagonal phase on the right-hand side.

TABLE I. Crystallographic data.

Reference conditions	d_{obs} (Å)	a (Å)	b (Å)	a/b	$\frac{1}{2}ab$ (Å^2)	Specific volume (ml g^{-1})
20 °C 1 bar	4.10[a] 3.70	7.40	4.93	1.50	18.2	1.00_5
200 °C[b]	4.07 3.80	7.61	4.82	1.58	18.3	1.00_5
210 °C[b]	4.06 3.79	7.58	4.81	1.58	18.2	1.00_5
220 °C[b]	4.06 3.79	7.58	4.81	1.58	18.2	1.00_5
	4.23	8.46	4.88	1.73	20.6	
230 °C[b]	Orthorhombic spacings but very weak					
	4.22	8.44	4.87	1.73	20.6	
240 °C[b]	4.24	8.48	4.90	1.73	20.8	
250 °C[b]	4.24	8.48	4.90	1.73	20.8	

[a] Assumed for calibration purposes.

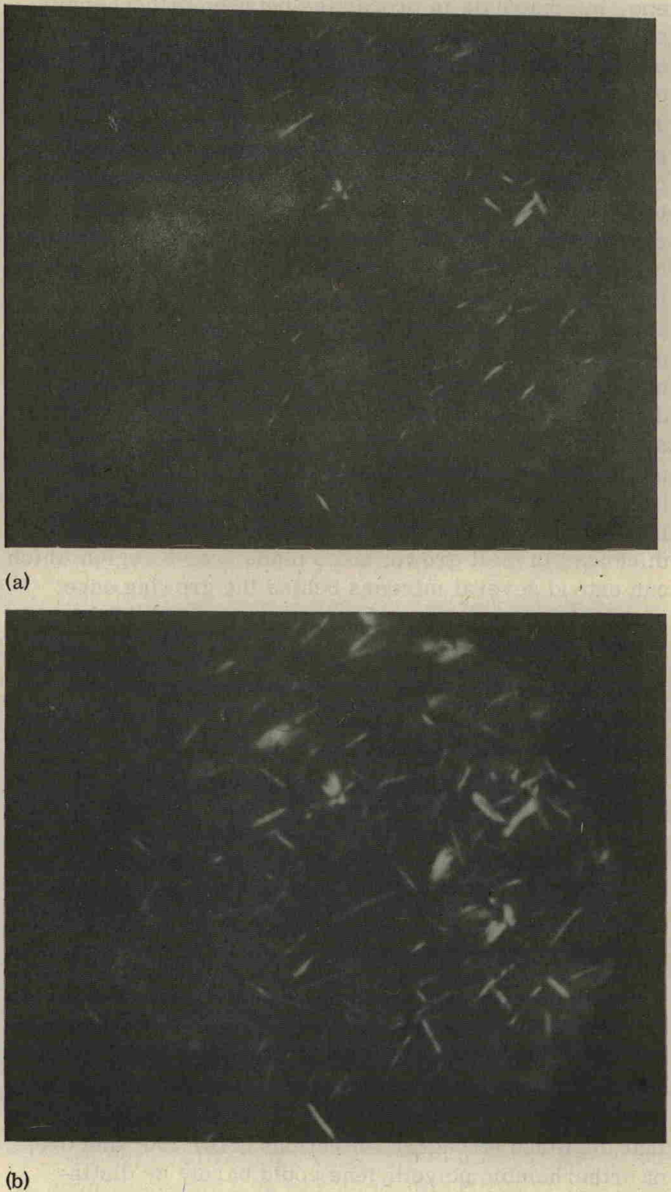
[b] A constant load was maintained resulting in a pressure of approximately 6 kbar at 270 °C and dropped to approximately 3 kbar at 200 °C as explained in the text.

even beyond the triple point, the low-molecular-weight component of the sample could be expected not to form the new phase but to transform directly from orthorhombic crystal to melt.[4] Nevertheless, by increasing the size of the sample (using a hole 0.64 mm in diameter by 0.25 mm thick in the gasket) and by using a fractionated polymer ($\overline{M}_w = 112\,000$ and $\overline{M}_n = 89\,000$) with only a small low-molecular-weight tail, it was possible to improve the diffraction signal and confirm the existence of the new phase.

Figure 1 compares photographs taken in the same setting showing the orthorhombic pattern on the left-hand side and the single reflection of a new pattern on the right-hand side. The two outermost rings present on both photographs are from the metal gasket. Intense diamond spots are present as are some fainter spots close to the polyethylene rings which are believed to result from an inclusion in one of the diamonds. Table I records the values of d spacings measured at 10 °C intervals over the range 200–250 °C for a constant applied load which was set to give the last trace of melting for chain-extended polymers to an isotropic liquid at 272 °C. The temperature referred to was controlled to ±1 °C and is that of a thermocouple situated in the metal support at a similar depth to, and within a few millimeters of, the sample. According to earlier data,[2] this indicates a pressure near 6 kbar.

The ring diameters were each measured at every 60° of azimuth with a standard error of ~1%. The mean values are more repeatable than this (Table I), however, and the values of crystal spacings, obtained by calibration against an assumed $d_{110} = 4.10$ Å at 1 bar and room temperature, are thus thought to have a precision of at least 1%. The single spacing observed for the new phase is at 4.23 Å. The next two reflections expected for a hexagonal structure would be close to the two metal gasket lines and have not been resolved.

Very similar behavior has been observed for a sample of the whole polymer Rigidex 9 (B.P. Chemicals Ltd.) which was initially part of a cold-drawn sheet and preserved a weak fiber orientation around c in the diamond-anvil cell. In this case the single reflection of the new phase showed the same orientation as its orthorhombic predecessor, confirming that it has an index hk0. Here, too, the reflections were less well resolved for the same sample size, apparently because the extensive low-molecular-weight component of this material is either incapable or less capable of forming the new phase, as has been observed in previous work,[4] and tends to remain molten under the conditions of the experiment. In both cases the change of structure was reversible with temperature. There was also an interval where the two orthorhombic lines and the new spacing were observed at the same time. No spacings intermediate between these two values were ever observed. At higher temperatures the new reflection weakened and disappeared above the final melting point.


(a)

(b)

FIG. 2. (a) and (b) Successive stages in the growth of chain-extended polyethylene lamellae.