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Mechanical and Structural Studies of Low Density Polyethylene

Part 1: *Lamellar and Crystalline Textures During Hot-Drawing*

B. H. McCONKEY*, M. W. DARLINGTON, D. W. SAUNDERS
Materials Department, Cranfield Institute of Technology, Cranfield, Beds, UK

C. G. CANNON
Research Department, ICI Fibres Limited, Pontypool, Mon., UK

During uniaxial orientation of low density polyethylene (LDPE) at 90 to 95° C some unusual structural changes occur, as revealed by wide and low angle X-ray diffraction. Quantitative measurements of diffracted intensity distributions have been made. At low draw ratios a novel 6-point low angle pattern appears which persists to extensions of over 300%. Cone distributions are present in all the crystal axis orientations, and these are superimposed on transverse components to give complex wide angle diffracted intensity profiles. A spherulite deformation model is proposed to explain these observations. At high draw ratios uniaxial crystal alignment obtains, but we find that the lamellar orientations differ between specimens annealed after drawing at room temperature and those drawn directly at the higher temperature. The implications of this observation are considered.

1. Introduction

The close dependence of mechanical properties of semi-crystalline polymers upon molecular organisation at both molecular and supra-molecular levels is well recognised. In LDPE in particular, Keller, Ward and co-workers [1-7] have applied successfully an extensive structural understanding of specially oriented sheets to the interpretation of their mechanical behaviour.

Complex behaviour occurs during the actual drawing process, which is imposing order on a largely disordered material. Various X-ray studies of cold-drawing of LDPE have been reported [4, 8, 9] from which a satisfactory structural picture has emerged, well supported by optical observations [10] on spherulite deformation. This model will be referred to subsequently. On the other hand, apart from an isolated observation [4] the only previous structural study of the hot-drawing process has been some electron microscope observations of lamellar and spherulitic textures [11].

For comparison with mechanical properties (see Part II) we have carried out quantitative wide angle and low angle X-ray observations of hot-drawn LDPE over a range of draw ratios, and also have compared the effects of hot-drawing with those of annealing the polymer previously drawn at room temperature. There emerge some interesting and unsuspected effects from these different thermal treatments.

2. Experimental

Sheets of LDPE ("Alkathene" grade WJG-11) were prepared by melt pressing at 160°C in a 2 mm thick former and then quenching in cold water. Sections of the sheets were ruled with a 1 cm square grid and were drawn at 6 cm per min in an air oven providing temperature control to within ± 2°C throughout the draw zone. Owing to the sensitivity of tearing to temperature, the draw ratios attainable at the highest temperatures were limited to approximately 3.7 at 95°C, 2.4 at 98°C and 1.3 at 100°C.

*Permanent address: Fibremakers Limited, Bayswater, Victoria, Australia.

After cooling and release of the load all drawn sheets relaxed to some extent, so they were allowed to stabilise unloaded at room temperature for at least three weeks. The draw ratio of each stabilised sheet was then determined from the measured grid dimensions. X-ray measurements proved that transverse isotropy was obtained over the range of draw ratios investigated, namely 1.2 to 4.2.

Some specimens were also prepared by other methods for comparison with the drawing procedure. These were:
(1) Annealing cold-drawn specimens at constant length for 30 min at 55 or 90°C.
(2) Relaxing cold-drawn specimens under zero load at 55°C. Sheets drawn to draw ratios of 3.4 and 4.0 relaxed freely to stable draw ratios of 3.0 and 3.5 respectively.

Low angle photographs were obtained with 30 kV Ni-filtered Cu Kα radiation using pin hole collimation at a specimen to film distance of 40 cm and exposure times of 5 to 17 h. All photographs were scanned by microdensitometer in directions parallel to the equator and meridian, through the individual reflections. Particularly in 4-point patterns, considerable overlap of the peaks occurred. The individual peaks were separated approximately by assuming symmetrical triangular profiles for each peak such that their sum approximates the observed intensity distribution. This yields slightly greater peak separations than the directly observed intensity maxima.

To assist in distinguishing between the various low angle patterns from the high draw ratio materials, some microdensitometer scans are given in fig. 8. The scans were made from left to right along the centre line of one of the reflections from each of the plates indicated. The scale of the horizontal axis is the same in each case but there is no connection between the vertical axis scales.

Wide angle X-ray studies employed similar radiation. Photographs were taken at a specimen to film distance of 3 cm, exposure time 15 min. Quantitative transmission diffraction measurements were made using a Siemens texture diffractometer, scanning 180° of the appropriate Debye ring. The signal from the diffractometer counter was passed, after amplification, to a digitising circuit operating a paper tape punch which permitted a value of diffracted intensity to be recorded at every 0.5° rotation around the Debye ring. The tape was then input to an I.C.L. 1905 computer, programmed to carry out the necessary intensity corrections, to calculate the orientation functions, and to print out a table of corrected intensities relative to an equivalent isotropic sample, I/I_R.

Corrections to measured integrated peak intensities are required for incoherent scattering, Lorentz-polarisation factor, multiplicity, and in LDPE for overlap between adjacent amorphous [110] and [200] peaks. An accurate method of peak separation is available [12], but this would be unsuitable for detailed intensity profile measurement. The approximate approach has been adopted of assuming a linear baseline between Bragg angles of 9° (amorphous peak) and 26° (background or incoherent scattering level) as a correction to the [110] diffraction peak; the amorphous, [200] and [020] peaks have been corrected for background scattering only.

Mean lamellar and chain orientations relative to the draw direction are derived from the maxima of the appropriate X-ray scans (utilising the separation technique, as previously noted, for overlapping double peaks). Thus the (acute) angle ψ is the mean angle between the molecular chains (c-axis) and the draw direction, while $90-\phi$ is the (acute) mean angle between the normal to the lamellar surface and the draw direction. The mean angle between lamellar surface and molecular chains is then $\phi \pm \psi$.

3. Results

3.1. Cold-drawn LDPE

The results obtained for both wide angle and low angle patterns are entirely similar to those reported previously (4, 6, 8, 9] and are reproduced here for purposes of comparison with heat treated material.

At low draw ratios (figs. 1a, 4 and 5) the wide angle pattern shows transverse a-axis orientation and the well known "cone distribution" of [110], b and c-axes which is eliminated upon further drawing at draw ratios above 3.0. In the low angle pattern, the scatter of an isotropic sample is retained in equatorial regions, but in the meridional direction the pattern alters to a diffuse arc of long period 103 Å. With further drawing this arc intensifies at the expense of the equatorial lobes.

In highly drawn samples (figs. 1b, 4 and 5) the a and b-axes are well aligned transversely, indicating high chain orientation. Low angle diffraction gives a relatively ill defined 4-point

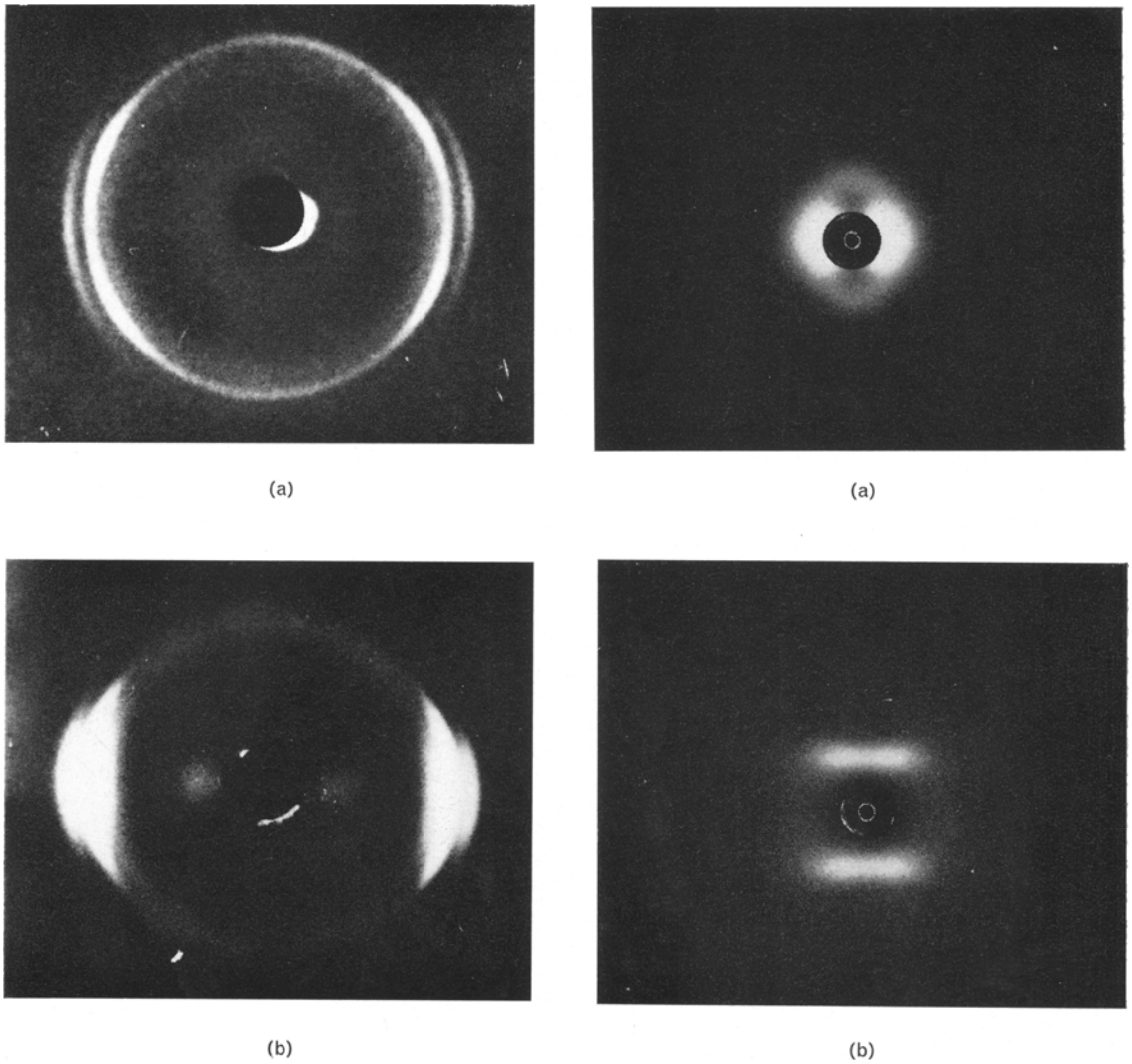


Figure 1 Wide and low angle patterns of cold drawn LDPE
(a) draw ratio 1.5.
(b) draw ratios 2.4 to 3.8.

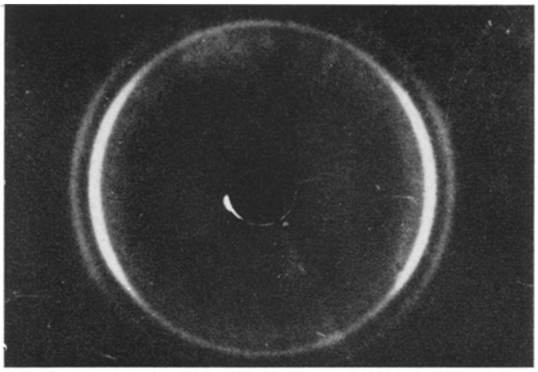
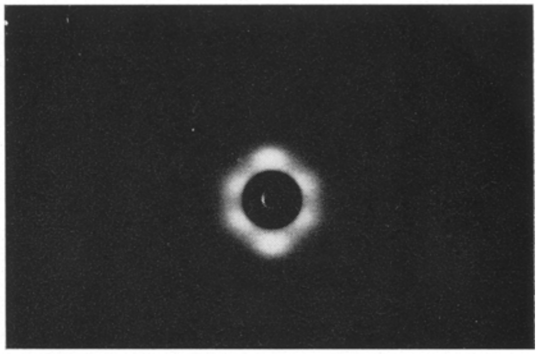
pattern corresponding to lamellar surfaces lying on average at 60° about the draw direction. (i.e. $\phi = 60°$).

3.2. Hot-drawn LDPE

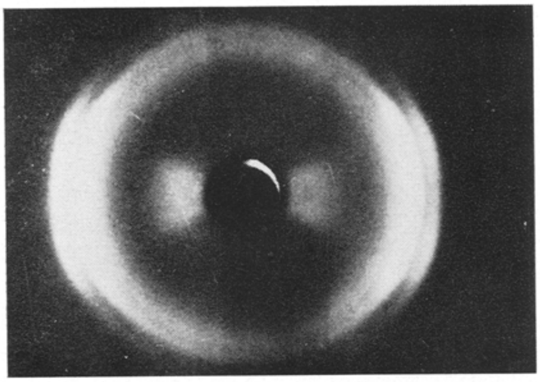
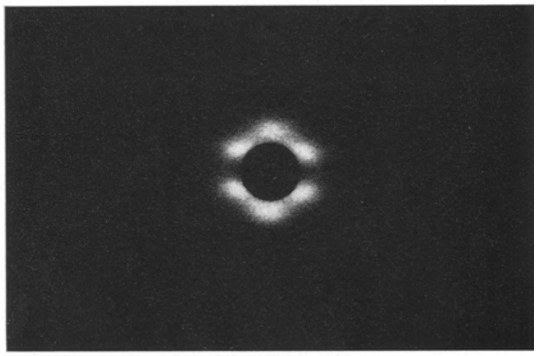
Detailed measurements of chain and lamellar orientations are given in table I, where they are compared with cold-drawing. The corrected X-ray azimuthal scans are compared in figs. 4 and 5.

By drawing at 90 to 95°C rather than 20°C, the characteristic low draw ratio [110] cone distribution is replaced by a curious truncated peak at all draw ratios between 1.3 and 2.4 (fig. 5). However, the overall angular width of the distribution (at half peak height) does not differ significantly from the value for cold-drawn material.

At draw ratio 1.3 the *a*-axis is orienting transversely, as with cold-drawn material, though to a lesser degree. However, above draw ratio 1.6 a narrow cone distribution appears in

(a) (a)

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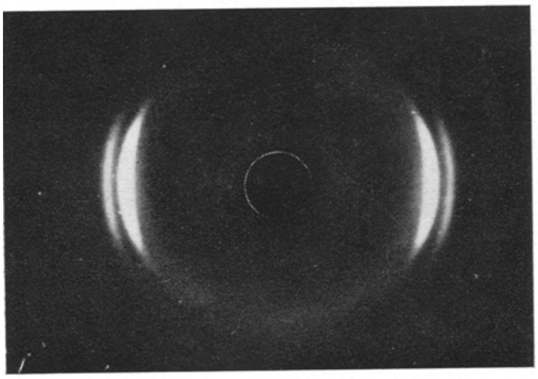
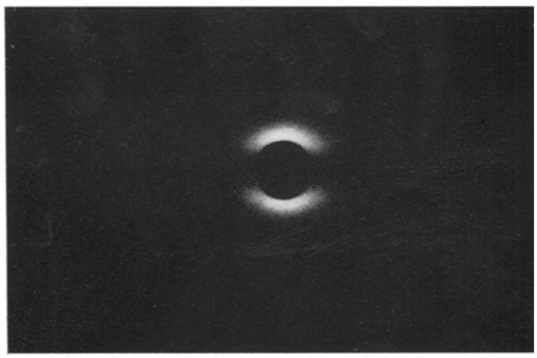
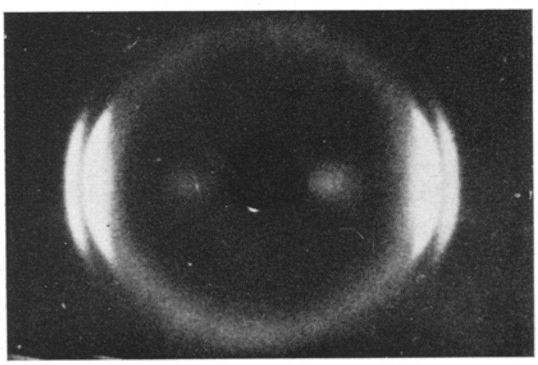
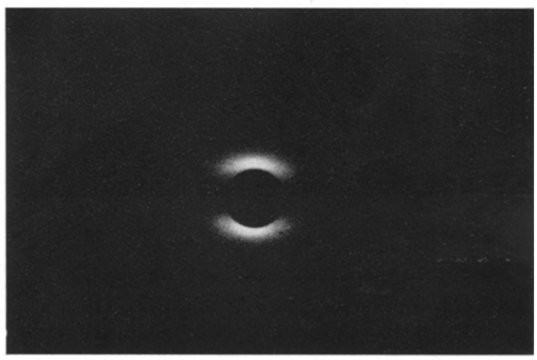
 

(c) (c)

(d) (d)

Figure 2 Wide and low angle patterns of LDPE drawn at 90°C. to draw ratio.
(a) 1.7 (b) 2.4 (c) 3.0 (d) 3.8.

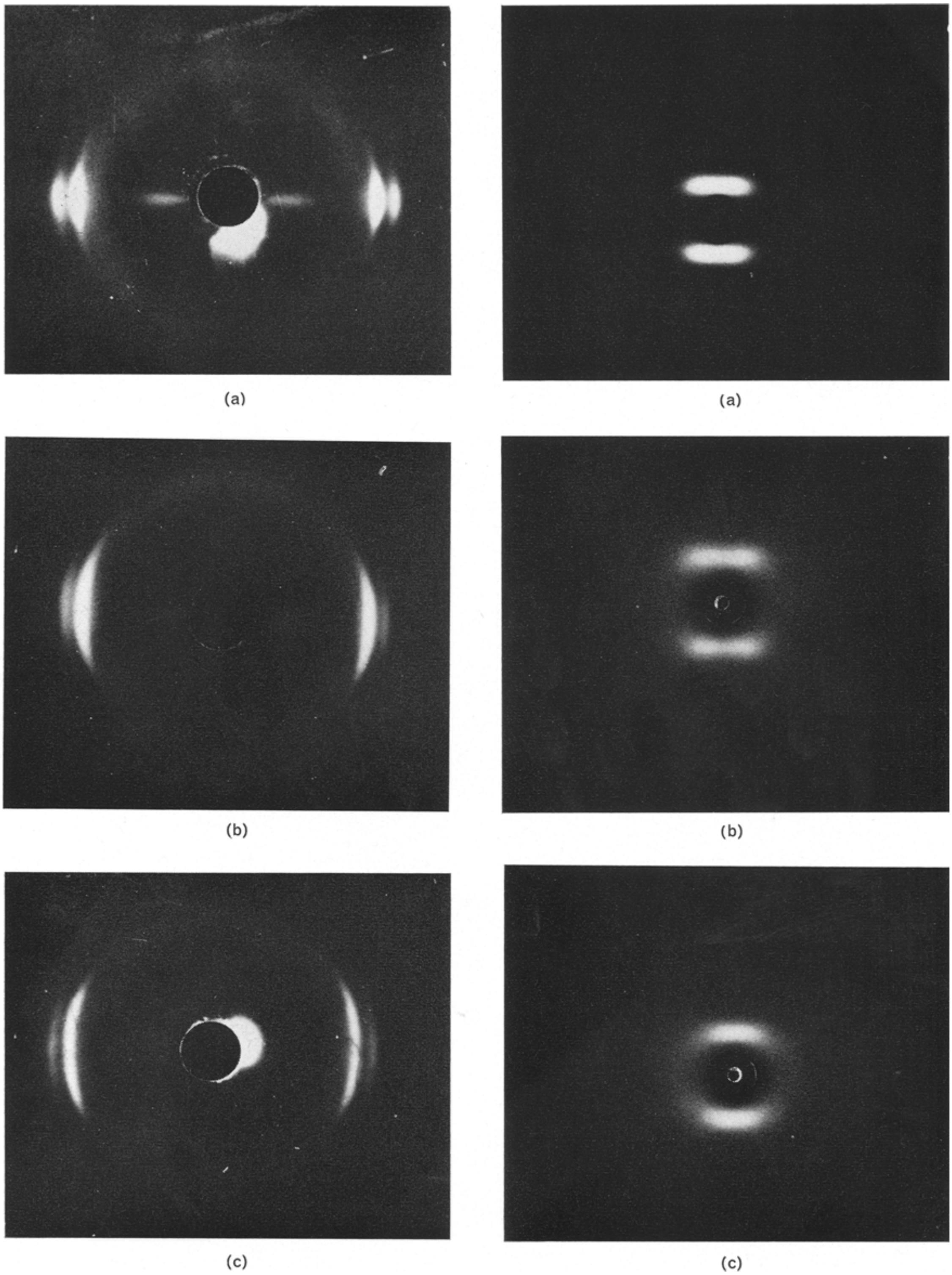


Figure 3 Wide and low angle patterns of LDPE
(a) drawn 20° C, annealed 90° C, draw ratio 3.8.
(b) drawn 20° C, relaxed 55° C, draw ratio 3.0.
(c) drawn 55° C, draw ratio 3.0.

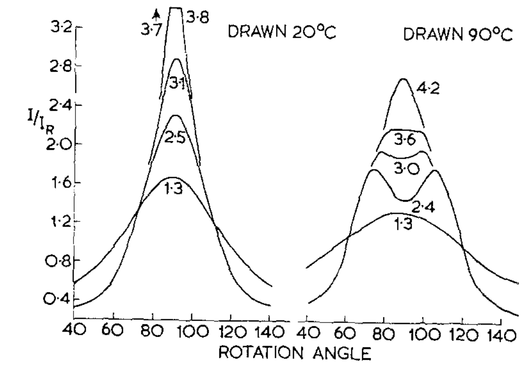


Figure 4 [200] azimuths for LDPE drawn to given draw ratios at 20 and 90° C.

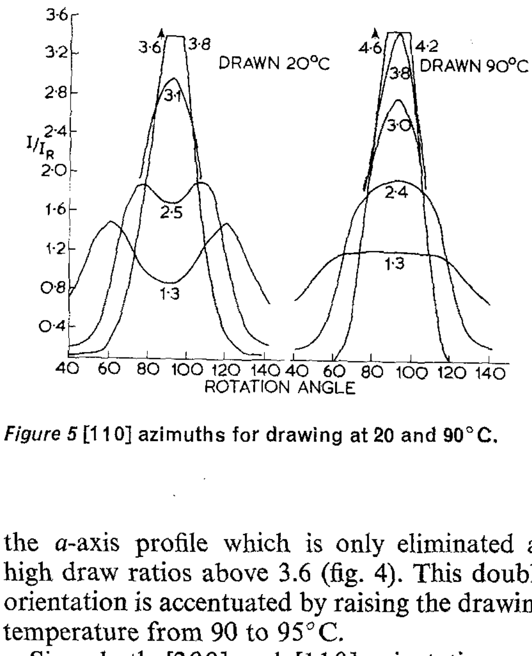


Figure 5 [1 1 0] azimuths for drawing at 20 and 90° C.

the *a*-axis profile which is only eliminated at high draw ratios above 3.6 (fig. 4). This double orientation is accentuated by raising the drawing temperature from 90 to 95° C.

Since both [200] and [1 1 0] orientations are broad and complex, [0 2 0] azimuths have also been recorded, and the direct diffractometer traces are shown in fig. 6. These profiles confirm that at low draw ratio cold-drawing type orientation is initiated; there is some cone distribution of *b*-axes where *a*-axes are aligning transversely. As drawing proceeds the *b*-axis distribution narrows and becomes superimposed on a growing transversely oriented peak, and this alignment precedes the corresponding *a*-axis alignment.

In highly drawn material the same orientation is obtained as with cold-drawing, although with less perfection of alignment.

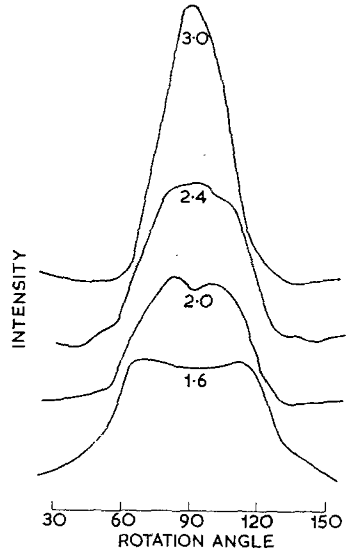


Figure 6 [0 2 0] azimuths (uncorrected) for drawing at 90° C

The low angle patterns are even more interesting and are shown in figs. 2a-2d. At low draw ratios a completely novel 6-point pattern appears which sharpens with further drawing to give near zero equatorial scattering intensity, in complete contrast to the cold-drawn material. The meridional spots of this pattern correspond to a long period of 135 Å, which increases upon drawing as shown in table I. The maxima of the spots at 60° are within the camera backstop, hence their long period is over 160 Å. There is remarkably little change in angular position or relative intensity between the spots until draw ratio of 3.0 to 3.5 when the pattern alters to a simple but broad 2-point pattern with long period of 190 Å. Microdensitometer traces show that each lobe is a single peak, not a superposition of the three spots of the 6-point pattern.

The draw ratio where the low angle pattern alters is similar to that when the double distribution of *a*-axes also disappears. Both these low and wide angle features are accentuated and retained to higher draw ratio by raising the temperature from 90 to 95° C. For instance the 6-point pattern disappears by draw ratio 3.0 when drawing at 90° C, but persists to above draw ratio 3.3 for 95° C drawing.

For comparison a cold-drawn sheet, draw ratio 3.7, was annealed at constant length at 95° C. Its poorly resolved 4-point low angle pattern, shown in fig. 3a, was quite different

TABLE I Crystal and lamellar orientations and long periods

Draw temperature °C	Draw ratio	scan[a]	long period Å	lamellar angle ϕ	chain angle ψ^b	lamellar/ chain angle $\phi + \psi$
20, 90	1.00		> 160	random	random	
20	1.3	—	> 160	random	37	—
	1.5	m	103	approx. random	32	—
		e	> 160			
	2.4	m	94	69	18	87
	3.5	m	91	60	0	60
90/95	1.3		> 160	approx. random	30	—
	1.6	m	140	90		
		m + 60°	> 160	30	17	47
	1.7	m	134	90		
		m + 63°	> 160	27	17	44
	2·2	m	145	90		
		m + 60°	> 160	30	15	45
	3.0	m	158	90		
		m + 46°	186	44	11	55
	3.6	m	195	90	7	97
	3.9	m	190	90	0	90
55	2.9	m	111	90	0	90
20°, relaxed 55°	3.0	m	96	62	0	62

[a]m = meridional scan, e = equatorial scan.
[b]Measured from wide angle patterns. For hot drawn at D.R. 1.6 to 2.2 neither *a*- nor *b*-axes are transverse, and the tilt angle of the *a*-axis is quoted.

from that of the hot-drawn specimens, having a long period of 130 Å and lamellar surface tilts of ± 60°. This is similar to previous reports [2, 6], and is clearly similar to the cold-drawn material.

These differences are reinforced by observations on specimens thermally treated at 55° C. The long period of cold-drawn LDPE only increases appreciably at temperatures above 60° C [1, 2] hence we might expect only slight lamellar "recrystallisation" at lower temperatures. This proves correct for cold-drawn specimens both *relaxed* and *annealed* at 55° C (figs. 3b, 7 and 8) both low angle and wide angle diffractions being essentially identical to cold-drawn polymer. The heat treatment in general causes very slight crystal disorientation, and the long period is scarcely altered; no difference being evident between relaxed and annealed specimens. In specimens *drawn* at 55° C however,

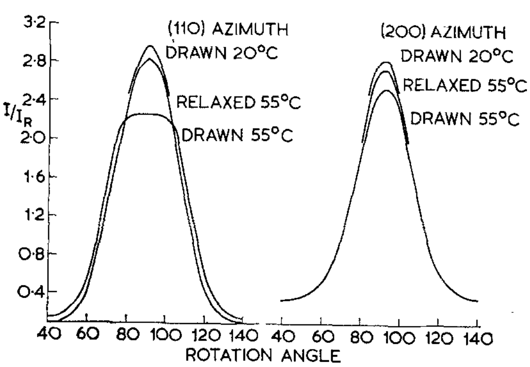


Figure 7 [110] and [200] azimuths comparing specimens relaxed and drawn to draw ratio 3.0 at 55° C with drawing at 20° C.

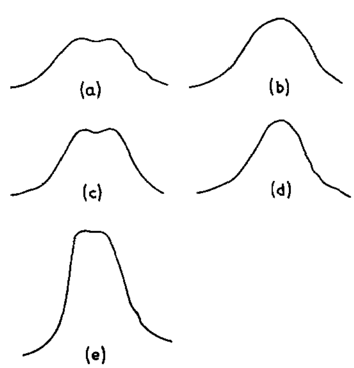


Figure 8 Microdensitometer traces of the low angle X-ray patterns from the following figs.: (a) 1b; (b) 2d; (c) 3b; (d) 3c; (e) 3a. (See section 2 for details.)

while the wide angle pattern remains similar to that from cold-drawing (fig. 7), a 2-point low angle pattern is now obtained (figs. 3c and 8) similar to but less perfect than that of polymer hot-drawn at 90° C.

4. Discussion

The lamellar and crystal rearrangements in polyethylene undergoing cold-drawing are reasonably well characterised. X-ray studies ([9] and this work) and electron microscopy [11] support the model of Hay and Keller [10] that spherulites deform largely inhomogeneously by fracturing transversely and drawing apart from the fracture, giving negligible deformation in quadrants in the draw direction, but fully deformed crystallites in transverse quadrants. The model is sketched in fig. 9. This model provides for the rapid transverse alignment of a-axes. During slip along the boundary of the undeformed regions, the twisted lamellae in the spherulite must unwind partially to allow intracrystalline shear in chain directions; Keller [8] has shown how this unwinding process can produce the cone distribution of b and c-axes. This is said to be the source of the peculiar mechanical properties of LDPE at low draw ratio [4].

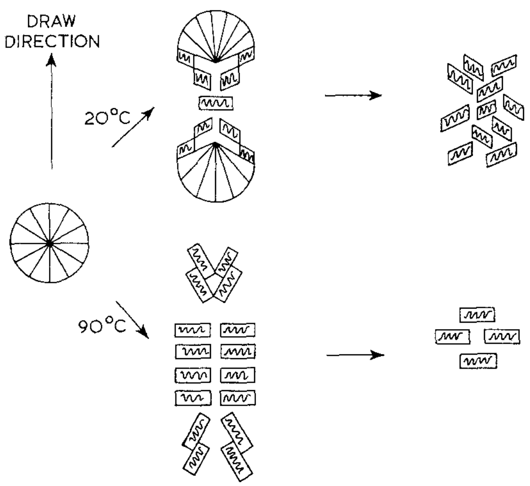


Figure 9 Models for spherulitic deformation and lamellar structure in cold and hot drawing. (Cold drawing model according to Hay and Keller, [1].)

More complex effects have now been observed from hot drawing and from heat treatment of cold drawn material. Clearly thermal relaxations and structural reorientation of the sort observed by Hay and Keller [1-3] could be taking place during the drawing process. The outstanding observations on hot drawn LDPE requiring interpretation by some model are:

(*i*) At draw ratios up to approximately 3.0 a 6-point low angle pattern is observed, having characteristic behaviour with draw ratio and temperature.

(*ii*) In the low angle patterns at draw ratios above say 2.0 there is complete absence of equatorial scatter, implying absence of lamellar surfaces parallel to the draw direction, in direct contrast to the cold drawn case at lower draw ratios.

(*iii*) The wide angle azimuthal scans of all arcs appear to contain both uniaxial and cone orientation components. The cone orientation of a-axes persists to high draw ratio and is most sensitive to temperature changes.

The following conjectural model appears consistent with these observations, but this study has not been sufficiently extensive entirely to eliminate other possibilities, some of which will be mentioned.

We identify the meridional low angle diffraction spots of periodicity 140 Å with lamellar blocks, lying perpendicular to the draw direction ($\phi = 90°$) which have been pulled out of the spherulitic structure (referred to below as "drawn-out" lamellar blocks). The spots at 60° to the meridian are attributed to lamellae which have been rotated whilst remaining within the spherulitic structure. These lamellae have a long period of greater than 160 Å and lie with their surfaces tilted at 30° ($\phi = 30°$) about the draw direction. (Referred to below as "undrawn" lamellae). Thus all lamellae of the original spherulite have first rotated to positions (near 30°) where inter- and intra-crystalline shear stresses are maximised and so permit shearing of whole blocks of crystals following the necessary lamellar unwinding. The lamellar arrangement of this model is also sketched in fig. 9. Similar favoured deformation at an angle to the draw direction (in this case 45°), with retention of lamellar structure, has also been observed in the electron microscope with linear polyethylene [11].

The structure suggested in fig. 9 would be consistent with the wide angle diffraction patterns observed. The diffractions from both [200] and [020] planes would contain overlapping components from the conically disposed undrawn lamellae and from the transversely oriented drawn-out lamellae. Their super-position could produce the kind of profiles observed, however a quantitative dissection of the intensities has not been attempted.

The tilts of *a*-axes are included in table I. If we choose to associate these with the tilted lamellae, then the angle between the lamellar surface and the chains ($\phi \pm \psi$) can be close to 45° if as listed in table I, we choose ($\phi + \psi$) rather than ($\phi - \psi$). This is the angle of a [301] plane which is believed to be the surface plane of a lamella rotating by inter-lamellar shear [2, 3]. Since it is these tilted lamellae which have an unchanged long period, this conclusion also supports the apparently arbitrary assignment of lamellar and chain tilts among drawn-out and undrawn entities. These tilted lamellae appear to be a very characteristic feature of hot-drawing. Their existence over such a wide draw ratio range must be attributed to a balance between the applied stress causing intracrystalline shear, and the opposing thermal relaxation stresses favouring inter-lamellar shear.

It remains to comment on the apparent transition from radial alignment of *b*-axes in the original spherulites to radial alignment of *a*-axes in the cone of tilted lamellae, required by the proposed model. The transition in orientation is clearly seen in the X-ray scans at draw ratios 1.3 to 2.4 in figs. 4-6. This could proceed by rotation around *c*-axes, and would be consistent with [110] or [310] twinning processes. An exact reverse orientation change was observed by Keller [8] at a similar extension of about 60% when re-drawing a thermally relaxed specimen. More recent work by Keller *et al* shows that the necessary twinning processes could certainly occur in our materials [13].

Attention is drawn to the two different types of "cone distribution" of molecular chains in hot drawn (cone of *c* and *a*-axes) and cold drawn LDPE (cone of *c* and *b*-axes) at low draw ratio. Clearly these arise from the characteristic deformation modes of the spherulites under different conditions of temperature and hence of molecular relaxation. These two types of orientation distribution should produce similar low modulus effects in the mechanical properties (as both have a cone distribution of *c*-axes) contrary to earlier conclusions [4], and similar properties may well exist for other spherulitic polymers. This prediction for the case of LDPE is borne out by the results presented in part II.

Other models have been considered but fail to rationalise all the observations. For example, a possible interpretation could involve transverse lamellae with a surface plane, e.g. [111] which gives approximately correct *a* and *b*-axes tilts. There is however no precedent for such a proposed surface, these being generally of the [h, 0, 1] type, and further this model fails to explain the tilted lamellae. Another possibility is that it is the drawn-out lamellae which remain tilted with constant long period, and these finally rotate to transverse alignment under the large applied stresses at high draw ratio. This picture however leaves the meridional spots unexplained. None of the models explain the changes in long spacing with draw ratio given in table I.

A most interesting structural situation has arisen in that we can produce two different lamellar arrangements at a fixed temperature by drawing and by annealing after cold-drawing. The latter retains the cold-drawn structure but increases the long period. Most important, at 55°C we can achieve the different lamellar structures with little or no change in crystal dimensions or orientation. We attribute this difference to the continuous relaxation of the non-crystalline tie molecules permitted at all stages of hot-drawing. These structures can be produced in uniaxially symmetrical material which greatly simplifies quantitative structural studies, in contrast to the biaxially oriented sheets used by other workers [5-7]. The implications for studying mechanical properties scarcely need emphasising.

Obviously further work is needed to substantiate and refine the model of morphological changes proposed. The experiments should be repeated on films thin enough for direct optical observation of the progressive deformation of the spherulites during hot-drawing.

Acknowledgement

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