JOURNAL OF MATERIALS SCIENCE 4 (1969) 1051–1058

On Molecular and Textural Reorientations in Polyethylene Caused by Applied Stress

A. COWKING, J. G. RIDER
Department of Physics, University of Surrey, Guildford, Surrey, UK

Received 5 June 1969

Biaxially oriented branched polyethylene was used as a model material for an investigation of crystalline polymer structure and deformation mechanisms. Within the prepared form of this material were regions with a morphology consisting of alternate crystalline lamellae and amorphous layers. X-ray methods were used to assess the reorientations of the crystalline texture, and also of the chains of which the crystals were composed, when a uniaxial stress was applied at constant temperature. The initial orientation and the compressive stress system were such that rotation of undeformed lamellae took place, in accordance with an interlamellar slip mechanism, as previously observed. A transition to an intralamellar slip mode occurred when the lamellae became normal to the stress axis, and the X-ray long spacing then *decreased* with further compression. With simple geometric assumptions the angular rotation of chain directions is related to the above change in interlamellar separation; a quantitative explanation of the total deformation, however, requires the existence of amorphous polymer other than that between the lamellae, a finding which supports a structural suggestion made earlier.

1. Introduction

If polyethylene is rolled and heat-relaxed following the initial orientation, a stage of double orientation [1] can be achieved where the unit cell axes (*a*, *b*, *c*) for the whole sample are orthogonal. The preparation and the effects of subsequent annealing on the internal structure of such material have been described in detail by Hay and Keller for branched polyethylene "Alkathene" [1, 2]. The ideas put forward by Hay and Keller on the internal structure and annealing behaviour of this material have been used as a basis for the further work carried out here. Their model is that doubly oriented polyethylene contains lamellar crystals, having $\{h0l\}$ basal planes, which are established in the earliest stages of heat-treatment at about 70° C; at higher temperatures of annealing (70 to 105°C, referred to by Hay and Keller as range 2) a progressive lamellar reorientation takes place due to slip between adjacent lamellae, activated by internal forces which are released from non-crystalline regions. This structural model, and its mode of deformation in range 2, have been substantiated by experiments using externally applied forces at constant temperatures, which produce lamellar reorientations in a sense consistent with interlamellar slip [3].

The upper temperature limit of range 2 is referred to as stage B (about 105° C) at which stage the lamellae have rotated into the position where they are perpendicular to the original drawing direction [2]. Here, the shear stress for interlamellar slip becomes zero, and annealing above 105° C (range 3) gives a continued rotation of the chain axes, whilst the lamellar planes remain stationary. The process is interpreted as one where slip occurs along the chain directions *within* the lamellae (intralamellar slip).

Beyond stage B (range 3) the regions of the material responsible for discrete X-ray diffraction appear to consist of alternating crystalline and amorphous layers arranged normal to the draw direction. This simple system facilitates a comparison with changes in the X-ray diffraction patterns as they occur during a deformation. Fig. 2 shows, by means of pole figures and schematic diagrams, the unit cell directions *a*, *b*,

c, the lamellar normal directions n_L, and also the postulated model of crystalline lamellae separated by amorphous layers. Although constructed in reference to the present work, fig. 2 illustrates the essential molecular and textural changes which occur according to the Hay and Keller model; the original draw direction is vertical in the plane of the diagrams, and the axis about which the lamellae and chain axes rotate is perpendicular to the plane of the diagrams. The model of lamellar and amorphous layers in fig. 2 is schematic only. Lamellar spacing is shown as if affected only by intralamellar slip and not by temperature changes as such. In fact when these textures are produced by annealing [2] the long spacing increases with temperature through range 2 to stage B and remains constant in range 3. In the present work the texture shown in fig. 2b, where the lamellae had rotated to the point where they were normal to the draw direction, will be called point B.

Previous work [3] had already shown that the application of external stress to textures obtained in range 2 of the annealing process brings about changes consistent with the interlamellar slip model. However, those experiments were designed to keep the textures both before and after deformation within those of range 2; as a result they gave no information about intralamellar slip. The aim of the experiments described in the present paper was to find out whether the application of an external stress to a texture obtained in range 2 could transform the texture through that obtainable at stage B into the range of textures obtainable in range 3; and if so, to see whether the observations were consistent with the transition from inter- to intra-lamellar slip. Samples were subjected to applied compressive stresses at constant temperature; the advantage of using a constant temperature is that lamellar spacing changes due to temperature changes alone, are avoided, and such changes as are observed are due to the applied stress.

2. Experimental Procedure

Samples of branched polyethylene (ICI Alkathene type WJG11) of initial thickness 4 mm were drawn about 400% and then rolled along the draw direction at room temperature. The material was then annealed in a silicone oil bath at a temperature chosen to give a lamellar orientation in range 2, close to point B. Samples from this sheet were compressed by different amounts in the initial drawing direction at a slightly lower temperature than that used for annealing. After deformation each specimen was cooled to room temperature at constant length before unloading. X-ray diffraction pictures at low and wide angles were taken at each stage of the experiments, using a point collimated beam. A microscope stage and photocell system, measuring light transmitted through the X-ray films, was used to determine the co-ordinates of the diffraction maxima. Specimen dimensions were measured at each stage using a travelling microscope, and with the aid of a 0.2 mm rectangular grid of ink dots, which was stamped onto the sample prior to deformation. All measurements were taken at room temperature with the specimens unloaded.

3. Results

3.1. Initial Orientation and Texture

The principal specimen directions are defined, as in [1], with respect to an orthogonal reference frame. y is taken to be the initial drawing direction, x to be the normal to the specimen plane, and z is in the plane of the specimen and perpendicular to y and x. X-ray photographs taken along these three directions were used to determine the molecular and textural orientations at each stage.

The initial annealing temperature was 103.5°C, and the X-ray photographs taken after annealing at this temperature are shown in fig. 1a, where the directions of the X-ray beam are denoted by subscripts. Fig. 1 shows wide-angle X-ray pictures with the beam parallel to z only, since these give information essential to the present studies. Low-angle pictures taken with the beam parallel to y gave no observable diffraction and are not shown. Conclusions regarding orientation were, however, drawn from the complete set of photographs at each stage of deformation. As in previous work, [2, 3], the form of the low-angle diffraction is attributed to the textural structure of lamellar crystals separated by amorphous layers; the direction of the reciprocal lattice vector associated with such patterns is identified with the lamellar normal n_L, and the magnitude of the reciprocal lattice vector gives the interlamellar separation d. Wide-angle diffraction indicates the unit cell directions a, b, c and the angle 2θ between the directions of the chain (c) axes is given by the angular split of the (200) arcs in the X-ray pictures taken with the beam along z. The picture of initial orientation

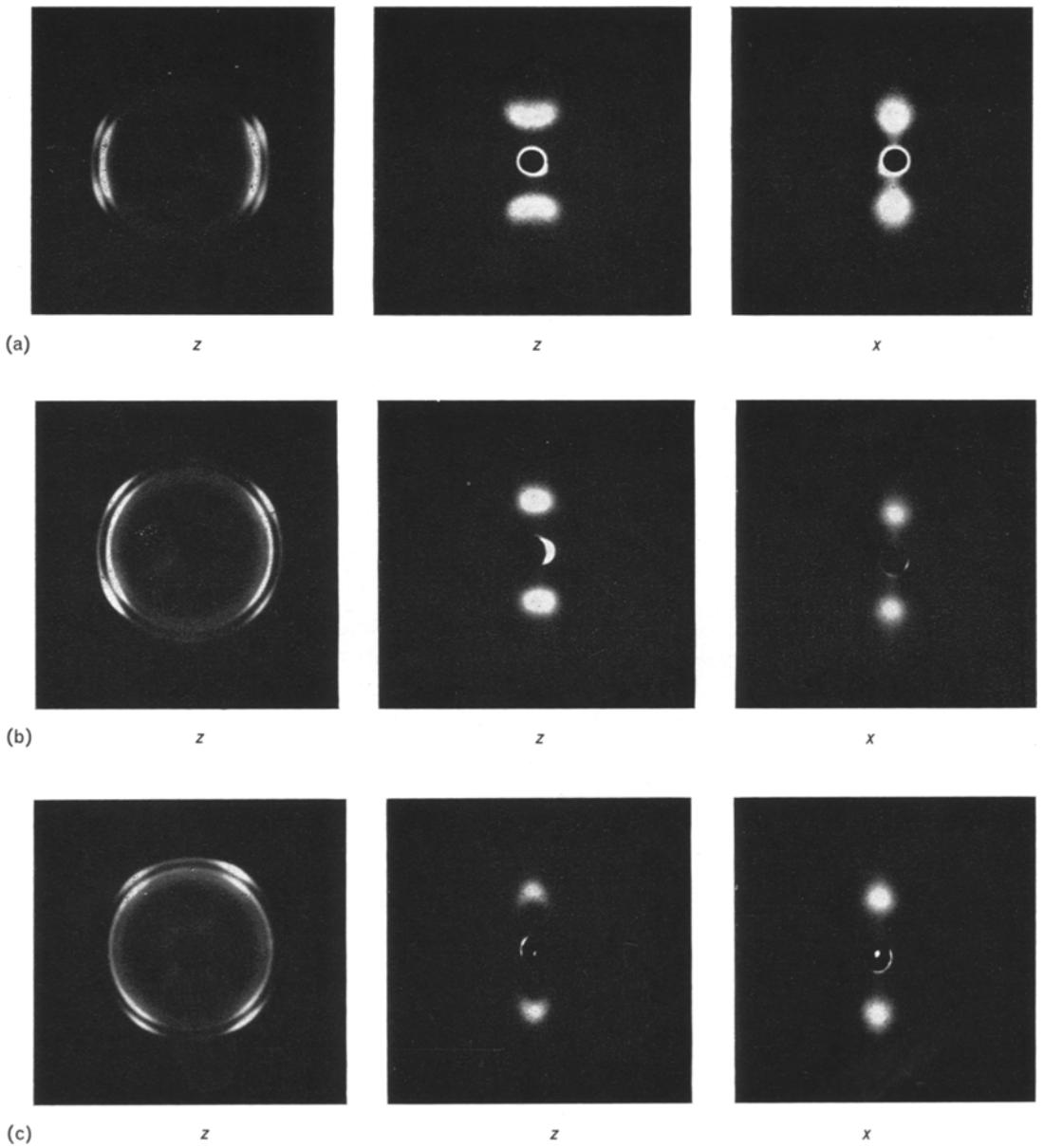

Figure 1 (a) Initial orientation, obtained by annealing at 103.5° C. (b) After compressing in the *y* direction at 97.5° C. Compression ratio $y/y_0 = 0.77$. (c) After compressing in the *y*-direction at 97.5° C. Compression ratio $y/y_0 = 0.49$. The subscript on each photograph denotes which specimen axis was parallel to the X-ray beam. The initial draw direction, *y*, is vertical in all pictures; *x* is perpendicular to the specimen plane, and *z* is in the specimen plane and perpendicular to *x* and *y*.

and texture emerging from the photographs of fig. 1a is shown in fig. 2a by means of pole figures and schematic diagrams; in all cases *z* is perpendicular to the plane of the diagrams. In terms of the unit cell, the lamellar planes were of the form $\{h0l\}$, just as they were in the material annealed at 70° C [2], since *b* still remains in the lamellar plane; however, as *b* is also still along *z* the lamellae have rotated around *b* in the reorientation.

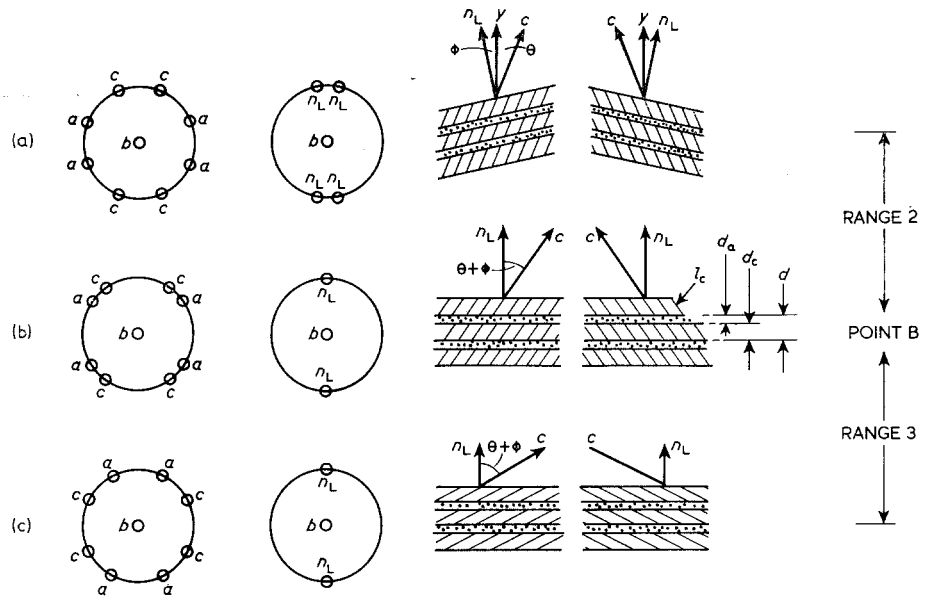

Figure 2 Lamellar models and simplified pole figures for each of the photographs given in fig. 1, taken in turn, showing unit cell axes *a*, *b*, *c*, and lamellar normals n_L. d_c and d_a are the thicknesses of lamellar crystals and interlamellar amorphous layers respectively; the measured long spacing $d = d_a + d_c$. l_c is the length of molecule involved in traversing a single lamellar thickness. *y* is vertical and *x* is horizontal in the plane of the diagrams.

The annealing temperature of 103.5° C was chosen to produce the required small, but measurable, angle ϕ between the lamellar normal and the draw direction *y*. This texture corresponds closely to the texture A2 [3], obtained by annealing at 98° C, but since the samples used in the present work had a greater thickness in the *x* direction, a slightly higher temperature was required. The effect of sample size on the annealing sequence has already been noted in [2] section 2. Since 103.5° C is close to the temperature range for intralamellar slip (105 to 110° C) [2], the experiment of applying compressive stress to the samples was carried out at a slightly lower temperature (97.5° C).

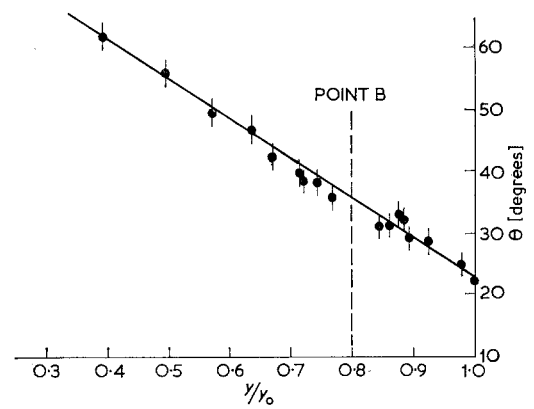

Figure 3 Angle θ plotted against compression ratio y/y_0. θ is the angle between *c* and *y*.

3.2. Compression in the *y*-Direction at 97.5° C

The wide-angle X-ray pictures of fig. 1 show that as the material was compressed, the chain axes moved continuously away from the *y*-direction. The angle θ between *c* and *y* is plotted in fig. 3 as a function of compression ratio y/y_0. Wide-angle X-ray diffraction photographs (including those along *x* and *y*, which are not shown in fig. 1) also established that *b* remained along *z* at all stages of compression, whilst *c* rotated about *z* and away from *y*.

Fig. 4 shows the angle ϕ between lamellar normals and *y*, and also the angle $\theta + \phi$ between lamellar normals and *c*, plotted as functions of the compression ratio y/y_0. It was found that ϕ decreased from its initial value of 12°, to become zero at a y/y_0 value of between 0.85 and 0.80 (it was not possible to locate exactly the y/y_0 value where ϕ became zero since the four point X-ray pattern as seen along *z* at low angles changed continuously to a two point pattern, and the photometer method of determining the positions of the maxima was unable to

resolve the separation for $\phi \leqslant 5°$). During further compression the low-angle X-ray pattern along z continued to show two maxima, which indicates that ϕ remained at zero. The behaviour of the obliquity of the chain direction to the lamellar normal is given in fig. 4 by $\theta + \phi$, which remained at a constant value of 34° until $y/y_0 \simeq 0.85$, and subsequently increased during further compression. Figs. 1a, b and c show respectively the X-ray photographs obtained at compression ratio $y/y_0 = 1.0$ where $\phi = 12°$ and $\theta = 22°$, $y/y_0 = 0.77$ where $\phi = 0°$ and $\theta = 37°$, and $y/y_0 = 0.49$ where $\phi = 0°$ and $\theta = 55°$. The pole figures, and pictorial models of texture, which correspond to the samples of figs. 1a, b and c, are shown respectively in figs. 2a, b and c.

The X-ray low-angle spacing d is plotted against compression ratio in fig. 5. d was essentially constant at 194 to 196 Å until a y/y_0 value of about 0.85 was reached, at which point it began to decrease.

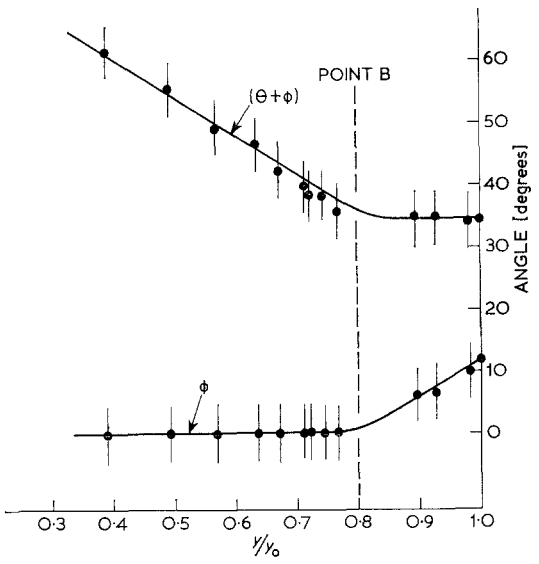

Figure 4 Angles ϕ and $\theta + \phi$ plotted against compression ratio y/y_0. ϕ is the angle between y and the lamellar normal, and $\theta + \phi$ is the angle between c and the lamellar normal.

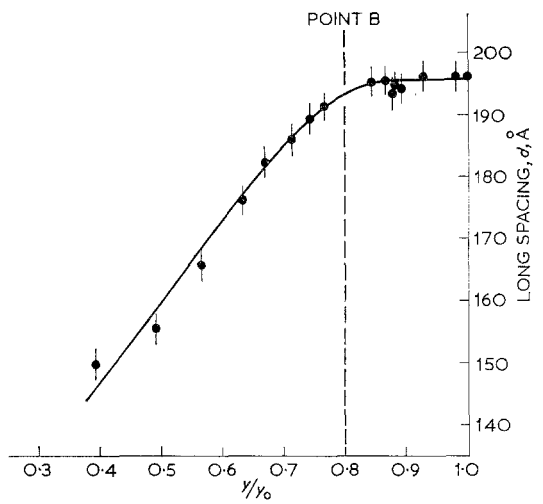

Figure 5 Long spacing d [Å] plotted against compression ratio y/y_0.

4. Discussion

The effects of compression upon molecular and textural orientation fall into two ranges. For compression ratios between 1.0 and 0.8 we see that θ increased and ϕ decreased by equal amounts such that their sum, $(\theta + \phi)$, which represents the obliquity ($\measuredangle\, n_L c$) of chains to lamellae, remained constant at 34°. In this compression range the value of the long spacing, d, also maintained a constant value of 195 Å. From these results we conclude that the lamellar crystals were rotating rigidly, as found in previous work [3] and as would be expected for an interlamellar slip process. On this basis we expect the point where ϕ becomes zero to be reached when $\theta = \phi_0 + \theta_0 = 34°$, where ϕ_0 and θ_0 refer to the angles which n_L and c respectively make with y in the initial state. From fig. 3 we see that θ became 34° at $y/y_0 = 0.83$; this compression ratio is between $y/y_0 = 0.80$ and 0.85 where, within experimental error, ϕ became zero (fig. 4), and hence the lamellae were undeformed even down to small values of ϕ. Since $\theta + \phi$ ($= \measuredangle\, n_L c$) was 34° for the part of range 2 included here, we may observe that the lamellar surface is crystallographically {201}, in terms of the lattice, as the obliquity for {201} planes is 34° 20′. This result is in agreement with the statement of Hay and Keller [2], that the faces of lamellae in doubly oriented polyethylene annealed just below stage B are {201}, following a discontinuous transition from {301} (obliquity 43°) in range 2. In addition the obliquity angles ($\measuredangle\, n_L c$) were $\simeq$ 34° for the compression (x) and extension (y) experiments in [3] where the annealing temperature was also just below stage B (98° C).

Regarding the interlamellar slip model as applied to compression in the y direction, the resolved shear stress becomes zero for slip on lamellar interfaces when $\phi = 0°$. Hence interlamellar slip would not be expected beyond this

point. Low-angle X-ray photographs taken at and beyond point B (y/y_0 below $\simeq$ 0.8) such as those of figs. 1b and c had only two maxima, which lay on the meridian, showing that n_L remained always along y. Thus, as anticipated, ϕ remained at zero for compression beyond point B, the lamellae did not rotate, and interlamellar slip did not continue. However, since θ continued to rise, so consequently did $(\theta + \phi)$ (fig. 4), which clearly means that the lamellae began to deform internally, causing a decrease in the angle between c and the basal planes of the crystals. The point B, as indicated in figs. 2 to 5 and 7, thus marks a transition from inter- to intra-lamellar slip. Within the crystals the inclination of the chain axes to y gives them a favourable orientation for intralamellar [001] slip, and most effectively on (100) slip planes, which is consistent with the observed rotation of chain axes around b. Preference for (100) slip planes in polyethylene has been noted previously by Frank, Keller and O'Connor [4].

The point where abrupt changes of slope occur in the plots of ϕ and $(\theta + \phi)$ (fig. 4) coincide with the onset of a decrease in long spacing (fig. 5). This is what would be expected for rotation of chain axes about b as a result of chains slipping parallel to c within the crystals. The decrease in long spacing is a new feature to emerge from these experiments at constant temperature, and is important in that it gives new evidence for a lamellar texture in polyethylene which can be identified with the low-angle X-ray diffraction and which is capable of a distinct transition between its modes of deformation.

The annealing experiments of Hay and Keller [2] showed that although d increased continuously within range 2, there was no significant change in d within range 3. The most likely explanation is that the tendency for d to decrease by rotation of the crystalline lattice, as described above, was balanced out by the increase in d spacing which commonly occurs in crystalline polymers as the annealing temperature is raised. The compression experiments in the present work were carried out isothermally in order to avoid the complications both of a long spacing increase and also the action of internal rubber-elastic forces which are usually involved with an increase in temperature.

The long spacing d is taken here to be the thickness of one lamellar crystal together with the interlamellar amorphous layer. If the material at compression ratios beyond point B is composed entirely of such alternate crystalline and amorphous layers stacked perpendicularly to the compression axis, y, then the fractional change in long spacing,

$$\epsilon_d = \frac{d - d_B}{d_B},$$

should equal the fractional change in gauge length of the sample in the y direction,

$$\epsilon = \frac{y - y_B}{y_B},$$

where the fractional changes are measured from point B, the point of transition from inter- to intra-lamellar slip (suffix B indicates measurements made at point B). Fig. 6 shows the relationship between ϵ and ϵ_d, taking the point B at $y/y_0 = 0.8$, where $d_B = 194$ Å. From this almost

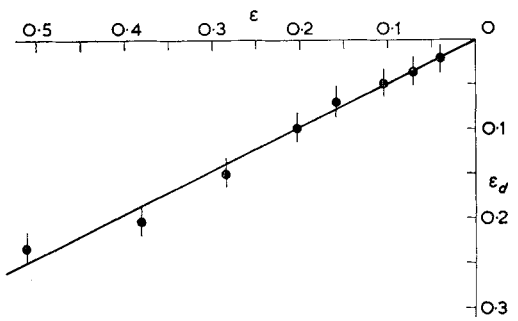

Figure 6 ϵ plotted against ϵ_d; ϵ_d is the fractional change in long spacing measured from point B, and ϵ is the fractional change in specimen length in the y direction measured from point B, where point B marks the transition from inter- to intra- lamellar slip.

linear graph it is found that $\epsilon \simeq 2.2\ \epsilon_d$, or only about one half of the total deformation can be accounted for by decrease in interlamellar spacing. The analysis in the previous work [3] of interlamellar slip within range 2, was based on a model of a material consisting only of lamellar stacks, which deform by slip according to the relation

$$y/y_0 = \frac{\cos \phi_0}{\cos \phi}.$$

Relationships were obtained between the measured strain, $\Delta y/y_0$, and the strain expected for a sample comprised entirely of crystalline lamellae which undergo slip without change in their separation, $(\Delta y/y_0)_{slip}$. It was found that $\Delta y/y_0 = 2.8\ (\Delta y/y_0)_{slip}$ in compression, and

$\Delta y/y_0 = 3.7\,(\Delta y/y_0)_{\text{slip}}$ in extension, so the total deformation was not accounted for by slip alone. The finding in the present paper that the strain in the sample is considerably larger than can be accounted for by the decrease in d, is strong confirmatory evidence in favour of the structural suggestion made already in [3], namely that a significant amount of amorphous polymer is present in the material which does not form a part of the lamellar stacks that give rise to the low-angle diffraction. This evidence is not dependent on a model of deformation, and is therefore much stronger than that of [3], on which the original suggestion was based.

It can be deduced from that part of the data presented in fig. 4 which relates to range 2 (that is from $\phi = 12°$ and $y/y_0 = 1.0$ to $\phi = 0°$ and $y/y_0 \simeq 0.8$), that in this part of the range the mean ratio of $\Delta y/y_0$ to $(\Delta y/y_0)_{\text{slip}}$ is about 8 ± 1. This is much higher than the values of 2.8 and 3.7 quoted from [3] in the previous paragraph. The value of this ratio is difficult to determine with any precision in the neighbourhood of point B, $\phi = 0°$, because measurement errors have a big effect when ϕ is small. Nevertheless a comparison of the results does suggest that interlamellar slip contributes proportionately less to the total strain as point B is approached. This is understandable in terms of the structural picture discussed in the previous paragraph, for as ϕ becomes small so does the resolved shear stress for interlamellar slip, with the result that a relatively larger amount of deformation occurs in the amorphous polymer not forming part of the lamellar stacks.

A further examination of deformation within the lamellar stacks in the intralamellar slip range (range 3, $\theta \geqslant 34°$) is possible, in view of the behaviour of θ and d. By reference to fig. 2 we assume that the measured long spacing is given by

$$d = d_c + d_a = l_c \cos\theta + d_a$$

where d_c is the lamellar thickness measured parallel to n_L, d_a is the thickness of the interlamellar amorphous layer measured along n_L, and l_c is the chain length involved in traversing a single lamella. For isothermal intralamellar slip in the c direction l_c would remain constant.

In fig. 7 we see that a plot of d versus cos θ shows a linear decrease of d with cos θ for values of cos θ less than about 0.83, i.e. θ greater than 34°, that is in the range in which intralamellar slip is expected. This suggests that if l_c is unchanged as postulated, then the interlamellar amorphous layer does not participate in the deformation (constant d_a). This is a property noted in the previous lamellar rotation experiments [3], as evidenced there by the constancy of d, and also of $(\theta + \phi)$, where the mode of deformation was believed to be interlamellar slip. The constancy of d_a in a situation where intralamellar slip takes place is unexpected and hard to explain, because the lamellae must be increasing in lateral width in the x-direction. Fig. 7 gives, from the intercept on the cos $\theta = 0$ axis, that $d_a = 85$ Å and from the slope, that $l_c = 130$ Å throughout the compression range of intralamellar slip. Thus d_a is a substantial fraction of d.

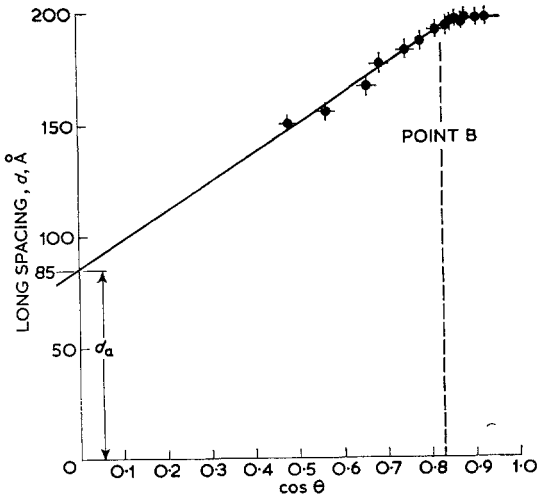

Figure 7 Long spacing d [Å] plotted against cos θ.

5. Conclusions

The experiments have shown that the application of an external stress to a texture obtained in range 2 of the annealing process transformed the texture through that obtainable by annealing alone at stage B into the range of textures obtainable by annealing alone in range 3. The observed changes in the orientation of the chain axis (θ) and of the lamellar normal (ϕ), and in the lamella spacing (d), produced by the application of an external stress, are strikingly in agreement with predictions from the inter- and intra-lamellar slip model of Hay and Keller. The observations provide strong evidence for the existence of a significant amount of amorphous material other than that forming part of the lamellar stacks. The inference is drawn, that the amorphous layers

between lamellae remain of constant thickness during intralamellar slip.

Acknowledgements

The authors wish to thank Dr A. Keller for introducing them to this line of research. The work was supported by a grant from the Science Research Council to the University of Surrey.

References

1. I. L. HAY and A. KELLER, *J. Materials Sci.* **1** (1966) 41.
2. *Idem, ibid* **2** (1967) 538.
3. A. COWKING, J. G. RIDER, I. L. HAY, and A. KELLER, *ibid* **3** (1968) 646.
4. F. C. FRANK, A. KELLER, and A. O'CONNOR, *Phil. Mag.* **3** (1958) 64.