

A Study on the Orientation Effects in Polyethylene in the Light of Crystalline Texture

Part 3 *On the Effect of Applied Stress on the Molecular and Textural Orientation*

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Special sample types established and characterised in Parts 1 and 2 [1,2] were examined systematically under different modes of external deformation at constant temperatures. The structural changes recorded by means of wide- and low-angle X-ray patterns fully substantiated the bodily rotation of the otherwise unaltered crystallites in accordance with the interlamellar slip mechanism postulated in Parts 1 and 2, both in tension and under two modes of compression. Dimensional changes, however, were significantly in excess of those expected from the rotation of crystallites, but were uniquely correlated with this relation in the different samples under different conditions of deformation. This points to a unique structural and mechanistic interrelation between the crystallites and more compliant amorphous regions. As the X-ray long periods were unaffected by the deformation, the more extensible material cannot be identical to that associated with the lamellar periodicity, a fact which points to a previously unsuspected superlamellar regularity in the texture. A simple structural suggestion is made.

1. Preliminary

Preceding parts of this series [1, 2] (1 and 2) described orientation changes which occurred when low-density polyethylene was drawn, rolled, and subsequently annealed, and in one experiment this annealed material was again redrawn. These orientation changes were followed by recording and correlating the wide- and low-angle X-ray patterns both at room temperature and at the annealing temperature itself. Subsidiary information on dimensional changes, on swelling and oxiditive degradation was also obtained. In our view the main significance of these experiments lies in revealing interactions and interrelations between crystals and amorphous material which is a determining factor in deformation behaviour of semicrystalline poly-

mers. It is for this reason that the low-density polyethylene with its substantial amorphous content is most suited for the examination in question.

It was described that after draw-roll and slight anneal ($\sim 70^\circ$ C stage A) a single texture establishes itself where by wide-angle evidence the molecular direction c is along the draw-roll direction (y in fig. 2 of Part 1), a is perpendicular to the rolling plane (x) and b is perpendicular to both these directions (z). The direction of the periodicities responsible for the low-angle reflexions could be uniquely related to the macroscopic sample directions, hence to the crystallographic axes. The planes responsible for these low-angle reflexions were found to form a double texture with normals in the ac (hence xy)

plane at $\pm 45^\circ$ to y thus corresponding to $\{301\}$ surfaces indexed in terms of the orthorhombic polyethylene cell. These planes were identified with interfaces of lamellae. It needs bearing in mind, however, that the interpretation of the X-ray reflexions while consistent with this picture need not be unique, and the above identification relies on the additional information that polymers in general and oriented and subsequently annealed materials in particular are known to have a lamellar morphology. Further, the $\{h0l\}$ type lamellar surface is the one expected in bulk polyethylene from a different line of morphological study [3].

Information on the lateral extent of the morphological units and on their interconnection (e.g. spatial relation between the components of the double texture) has not been available and is still outstanding at the time of writing. For convenience in discussion they have been presented as in fig. 2 of this paper. The low-angle reflexions themselves are spread along layer lines perpendicular to c with recognisable maxima. While not stated explicitly in part 2, the interpretation presented there implied crystals with a range of obliquities all of the $\{h0l\}$ kind so that each portion of the spread is due to a set of crystals with a particular $\{h0l\}$ value, $\{301\}$ (or $\{201\}$ at more advanced stages of annealing – see Part 2) corresponding to the maximum. The further implication of this picture is that each type of crystal is of sufficient extent laterally (say 1000 Å or more) not to cause an appreciable spread in the diffraction pattern, the spread observed being due to different crystals of differing obliquities. Work in progress thanks to the contribution by J. J. Point leads strong support to the correctness of this view (unpublished).

The annealing phenomena of interest to the present paper are those observed at the lowest annealing temperatures. The basic observation here was, that on shrinkage caused by annealing the texture units changed their orientation by the same amount as the unit cell, established from the movement of the low-angle reflexions and the 200 arcs respectively, which implies that the texture units rotate bodily with unaltered molecular structure (obliquity). This is consistent with the picture of interlamellar slip under compression which finally aligns the lamellar surfaces normal to the compression – i.e. shrinkage direction (y). Redrawing – particularly at the annealing temperature – reverses this

orientation process which again is consistent with interlamellar slip but now under tensile conditions. In the annealing experiments, the pressure was not applied directly, the compressive forces having been released by raising the temperature. In the redrawing case, however, the forces could be controlled externally. Also in the latter case the experiments could be carried out isothermally which eliminated the temperature variable. In addition, while confined to a specially simple model sample, such redrawing experiments also represent one aspect of the more complex general phenomenon of drawing of unoriented polymers. The present paper will be concerned with a more detailed study of such isothermal, externally-controlled reorientation effects in the special samples in question within the temperature range whereby previous evidence interlamellar slip is operating.

In Part 2 the dimensional changes were also followed. Qualitatively they were in agreement with the picture of interlamellar slip in as far as changes along z were found to be small during the orientation. The fit, however, was not quantitative: the changes along y were substantially larger than expected from rotation of lamellae alone. (Changes along x were not measured.) These excess changes in dimension just referred to were tentatively associated with rubberlike extensions of amorphous material considered to be the seat of the stored energy responsible for the compression when released by annealing. In the present paper these dimensional changes will receive more detailed attention.

2. Experimental

2.1. Experimental Procedure

The starting material was melt-pressed sheets of branched polyethylene (ICI Alkathene type WJG 11) which were 1 mm thick. Strips cut from the sheets were drawn $\times 4$ in length and rolled to a thickness reduction $\times 0.7$ at room temperature, the rolling direction being parallel to the draw direction. The material was then annealed between mica sheets in a silicone oil bath at a temperature chosen to give the required orientation. Specimens cut from this material were deformed, at the same temperature as was used for annealing, in various ways to be detailed below. After deformation each specimen was cooled to room temperature, unloaded and low- and wide-angle X-ray diffraction pictures were recorded in a Rigaku-Denki point-collima-

tion goniometer which was adapted so that low- and wide-angle pictures could be obtained at the same time. The specimen dimensions were measured before and after the deformation.

2.2. Results

2.2.1. Sample Orientations and Applied Stress Systems

The sample dimensions are defined again by x , y , and z , where the y axis is in the draw

direction, the x axis perpendicular to the sheet, and the z axis in the plane of the sheet and perpendicular to the draw direction. To determine the orientations of the molecular and textural elements, wide- and low-angle X-ray diffraction photographs were taken with the X-ray beam along the x , y , and z axes.

Two annealing temperatures were used, namely 78 and 98° C. Figs. 1 show some of the wide- and low-angle X-ray pictures taken with

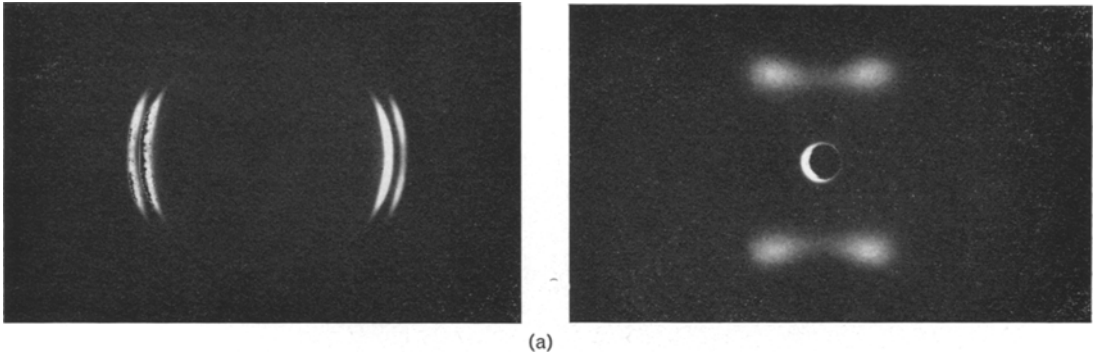


Figure 1a Orientation A1; obtained by annealing at 78° C.

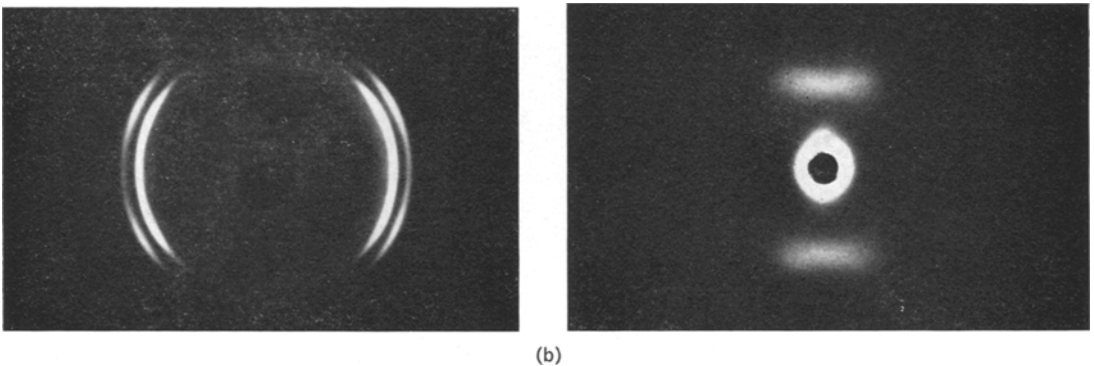


Figure 1b After compressing A1 in the y direction at 78° C. Compression ratio $y/y_0 = 0.74$.

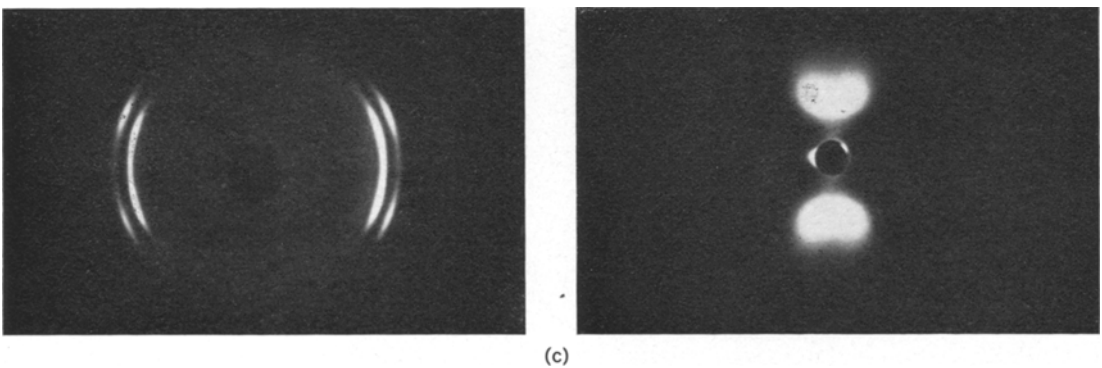
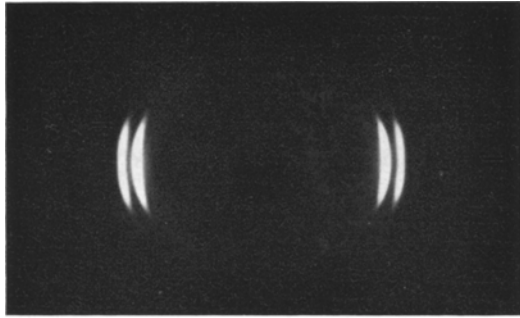
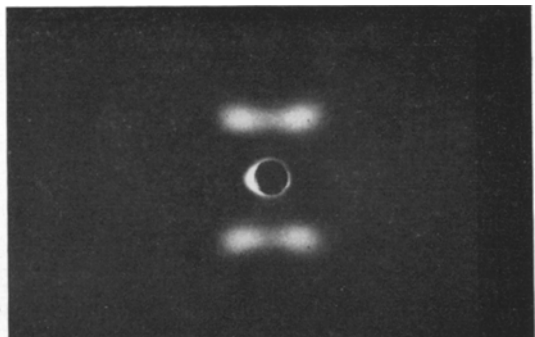
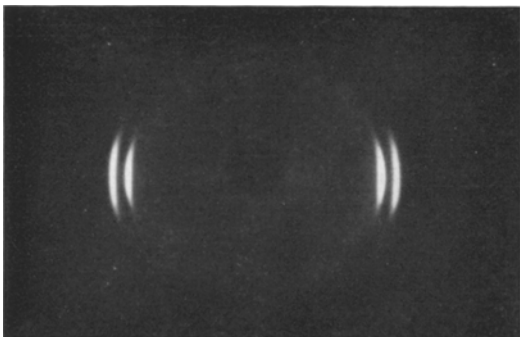


Figure 1c Orientation A2; obtained by annealing at 98° C.



(d)

Figure 1d After extending A2 in the y direction at 98°C . Extension ratio $y/y_0 = 1.46$.



(e)

Figure 2 After compressing A2 in the x direction at 98°C . Compression ratio $x/x_0 = 0.68$.

z is parallel to the X-ray beam and y is vertical in the present mounting throughout fig. 1. y is the original draw direction and z perpendicular to it in the plane of the sheet.

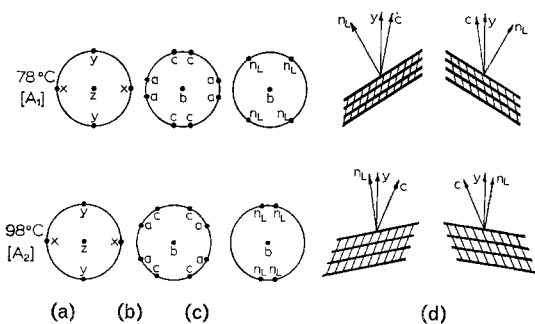


Figure 2 Simplified pole figures for orientation A1 produced by annealing at 78°C and for orientation A2 produced by annealing at 98°C . (a) Macroscopic sample axes: y = original draw-roll direction; x = perpendicular to rolling plane; z = in the plane of the film perpendicular to y and x ; (b) crystal axes a , b and c ; (c) lamella normals n_L ; (d) schematic diagrams of lamellae.

the X-ray beam along z which according to Parts 1 and 2 are the most informative for the present purpose. As established from the full set

of photographs, the b axis is again along, and the lamellar normals are perpendicular to z . Accordingly, diffraction patterns taken along z give direct information on the orientation both of the unit cell, hence the chain, and that of the lamellae about z . With a small correction accounting for the curvature of the Ewald sphere the former is given directly by the angular split of the 200 arcs (2θ) and the latter by the angular split of the low-angle maxima (2ϕ). Thus θ is the inclination of the chains and ϕ that of the lamellar normals with respect to y .

The pole figures corresponding to the samples in the as-annealed condition at 78 and 98°C are shown in fig. 2 both for the unit cell (a , b , and c poles) and for defining the sheet axes. Pictorially the corresponding textures are represented in fig. 2d by means of the scheme adopted in Part 2. It will be seen that stages denoted by A1 (as-annealed at 78°C) and A2 (as-annealed at 98°C) are intermediate between those of Stage A and B defined previously (figs. 2 and

4 in Part 2) i.e. between the four-point patterns of the starting stage and the two-point pattern when referred to the low-angle diagrams. As already stated, it is within this range that reversible interlamellar slip is expected to operate according to the conclusions of Part 2.

The following combinations of starting orientation, deformation mode and temperature were chosen for further experiments. (i) Orientation A2, extension in the y direction at 98°C ; (ii) orientation A1, compression in the y direction at 78°C ; (iii) orientation A2, compression in the x direction at 98°C . The results of these experiments are given in this order in sections 2.2.2., 2.2.3, and 2.2.4.

In all the deformation experiments, wide- and low-angle X-ray diffraction photographs were taken with the X-ray beam along the z direction at a number of successive stages of the deformation. In addition, photographs of the material before deformation and after the largest deformation were taken with the beam along the x and y directions. In all cases deformation produced a slight loss in definition in the low-angle patterns.

2.2.2. Orientation A2 Extended in the y Direction at 98°C

This investigation is a continuation of the experiments represented by table III in Part 2. The wide- and low-angle X-ray photographs showed that with increasing extension the orientation changed continuously from A2 to A1, and went beyond A1 to stage A (see Parts 1 and 2). With increasing extension, b remained along z while c and n_L rotated about z , c towards y and n_L away from y . The angles between n_L and y ($=\phi$) and between c and y ($=\theta$) as functions of the extension ratio y/y_0 are shown in fig. 3.

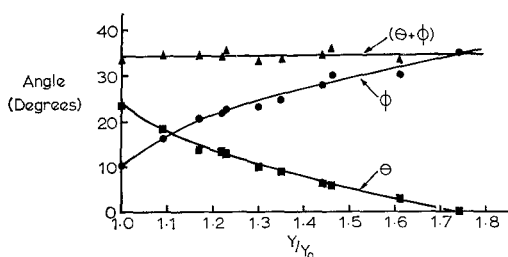


Figure 3 Angles ϕ , θ and $\phi + \theta$ plotted against the extension ratio y/y_0 for orientation A2 extended in the y direction at 98°C . ϕ is the angle between y and the lamella normal; θ is the angle between c and y . $\phi + \theta$ is the angle between the lamella normal and c .

Also plotted in this figure is the angle between n_L and c ; it can be seen that this angle ($\theta + \phi$) remained constant. In fig. 1d are reproduced the X-ray photographs obtained after an extension ratio of 1.46, in which $\phi = 30^\circ$ and $\theta = 6^\circ$; this orientation is just slightly beyond A1.

The long spacing (that is the perpendicular spacing between the reflecting planes deduced from the low-angle photographs by applying Bragg's law) was found to be 186 \AA and this was unchanged by the deformation. (The accuracy of measurement of the long spacing was $\pm 5\%$.)

The contraction ratios of width z/z_0 and thickness x/x_0 are plotted against the extension ratio y/y_0 in fig. 4. It can be seen that the deformation perpendicular to the tensile axis was far from isotropic, the fractional change in the width being significantly less than the fractional change in the thickness. The product of the three ratios was found to be equal to unity (within the experimental error of 5%) for all extensions, indicating a constant volume deformation.

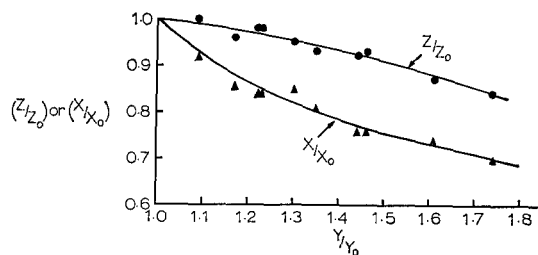


Figure 4 z/z_0 and x/x_0 plotted against y/y_0 for orientation A2 extended in the y direction at 98°C .

2.2.3. Orientation A1, Compressed in the y Direction at 78°C

With increasing compression the orientation changed continuously from A1 to A2 and went rather beyond A2 towards stage B (Parts 1 and 2). The b axis remained parallel to z while c and n_L rotated about z , c away from y and n_L towards y . The angles between n_L and y ($=\phi$) and between c and y ($=\theta$) as functions of the compression ratio y/y_0 are shown in fig. 5. Also shown in this figure is the constancy of the angle between n_L and c . In fig. 1b are reproduced the X-ray photographs obtained after a compression ratio of 0.74, in which $\phi = 15^\circ$ and $\theta = 26^\circ$; at this

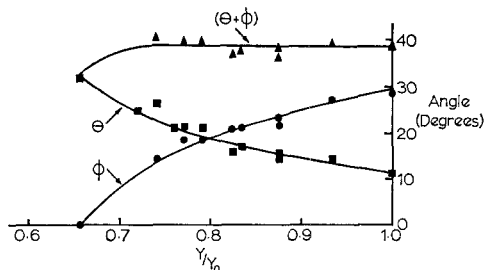


Figure 5 Angles ϕ , θ and $\phi + \theta$ plotted against compression ratio y/y_0 for orientation A1 compressed in the y direction at 78°C . (Angles defined in text and in caption to fig. 3.)

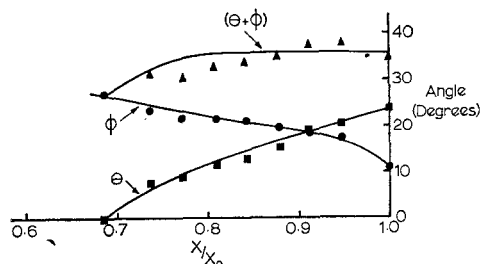


Figure 7 Angles ϕ , θ and $\phi + \theta$ plotted against compression ratio x/x_0 for orientation A2 compressed in the x direction at 98°C . (Angles defined in text and in caption to fig. 3.)

stage orientation A2 has not quite been reached.

The long spacing of the material was found to be 115 \AA , and this remained unchanged by the compression. That the long spacing is shorter than that of the material extended at 98°C is due to the higher temperature used to prepare the latter.

The ratios z/z_0 and x/x_0 are plotted against y/y_0 in fig. 6. Again the fractional change in width (z), was significantly less than that in thickness (x) and again the deformation was at constant volume.

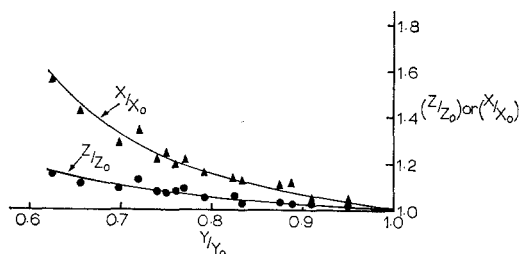


Figure 6 z/z_0 and x/x_0 plotted against y/y_0 for orientation A1 compressed in the y direction at 78°C .

2.2.4. Orientation A2, Compressed in the x Direction at 98°C

The applied compression in this experiment had essentially the same effect as that of the applied tension in the y direction, described in section 2.2.2, as regards orientation changes. The orientation changed from A2 to A1; b remained parallel to z while c and n_L rotated about z , c turning towards y and n_L away from y . The angles between n_L and y ($=\phi$), between c and y ($=\theta$), and between n_L and c are shown as functions of compression ratio x/x_0 in fig. 7. The angle between n_L and c remained constant

over most of the range, only decreasing a little at the highest compression ratios. Fig. 1e shows X-ray photographs obtained after a compression ratio of 0.68; the orientation approximates to A1.

The long spacing remained constant at 169 \AA , unaffected by the amount of compression. The slight difference from the long spacing reported in section 2.2.2 is thought to be due to an unintentional slight difference in the temperature at which the experiment was carried out.

Width and thickness changes were not measured in this experiment.

2.2.5. Some Further Observations

The reversibility of the dimensional and molecular orientation changes with reference to the original drawn and rolled material were examined separately. Two experiments were carried out. In the first, the drawn and rolled samples were relaxed at 100°C . This resulted in a tilt of the c axes through 40° with respect to y . Redrawing at 100°C progressively re-established the orientation of c along y , but on subsequent stress-removal at the same temperature only a small fraction of the extension was recoverable.

In contrast, a sample relaxed at 95°C showed a different behaviour. Here θ ($\sphericalangle cy$) was 20° , and the sample contracted to half of its original length. When redrawn to its original length at 95°C , there was progressive alignment of the c axis to y . c alignment to y was complete at 100% extension, i.e. extension to its original length. When tension was removed at the same temperature the sample contracted by 100%, i.e. to its original relaxed length with c being inclined at 18° to y . It is apparent therefore that the extension-relaxation is completely reversible even in relation to the original unannealed dimensions. This is even more

remarkable when considering that the sample was under tension for several days, the time taken to complete the series of X-ray photographs. Full reversibility of dimensions with associated near-reversibility of chain orientation was ascertained also during intermediate stages of extension.

3. Discussion

3.1. Orientation Effects

The present experiments fully confirmed the relaxation and redrawing results in Part 2 in as far as there is a correlated rotation of unit cell and texture element both on contraction and extension. In view of the complexity of the phenomenon and the possible associated structures involved, the consistent recurrence of this effect in different experiments is very satisfactory and points to a general underlying mechanism. In particular, the experiment under tension (experiment 1) was now carried out in greater detail with many more stages of measurements, thus fully establishing the point made in Part 2.

In addition to confirming the previous results, the present experiments have further information to convey. They demonstrate that the same correlated rotations can be induced also in the reverse sense when applying compression along y (experiment 2). Such compression has been invoked previously as being released internally by the increase in temperature during the annealing treatment. It is very satisfactory therefore that the same effect could now be produced isothermally by applying compression from outside. This clearly supports the contention that the reorientation effects during annealing are caused by compressive stresses on the crystallites. Both types of experiments are fully consistent with the model of interlamellar slip, demonstrating that this can be activated both by tension and compression, the latter being either internally released or externally applied.

Experiment 2 (compression along y) together with the complementary evidence of experiment 3 (compression along x) have further confirmatory strength. Tension is expected to align the chains in the direction of the tension, while

compression is expected to produce an isotropic transverse orientation with the chains perpendicular to the compression direction. The fact that *one particular* transverse direction along the corresponding shortest route is preferred in the absence of lattice deformation, points to the fact that the orientation corresponds neither to an affine deformation of a network nor to a plastic deformation of the crystals and hence must be controlled by the texture*.

3.2. Dimensions

In contrast to contraction on increasing temperature, the present isothermal deformation experiments did not affect the long spacing values. We interpret the long spacing as being the thickness of a lamella plus that of the amorphous layer between two adjacent lamellae, and so conclude that during the deformation the amorphous layers between the lamellae did not change in thickness as the lamellae slipped over one another.

It is therefore possible to calculate the extension (or compression) ratio of the specimen as a function of the angle between n_L and y supposing that the whole length change is due to interlamellar slip. For stress applied in the y direction,

$$y/y_0 = \cos\phi_0/\cos\phi$$

where y is the specimen length in the y direction, ϕ is the angle between n_L and y , and the subscripts refer to the initial state. So, if the whole of the length change is due to slip, a straight line through (1, 1) and of slope unity should be obtained when y/y_0 is plotted against $\cos\phi_0/\cos\phi$. The data for extension along y at 98° C and for compression along y at 78° C are shown plotted in this way in fig. 8. Although both plots are linear, the slopes are significantly smaller than unity, showing that the measured length changes are much greater than can be accounted for by interlamellar slip alone. The ratio of the measured fractional change in length $(y - y_0)/y_0$ to the fractional change in length which would be caused by interlamellar slip is about 3.7 for the tension experiment at 98° C, and about 2.8 for

*It will be seen that in fig. 1d the lobes of the low-angle reflexions are inclined. In Part 2 these lobes were interpreted as layer line streaks which are always perpendicular to the chains, consequently their inclination should be a measure of the chain orientation in the same way as the angular position of the 200 reflexions. Indeed within the accuracy of the measurement, there was agreement between the chain tilt as assessed by these two methods. However, in fig. 1d the lobe inclination is larger than expected from the spread of the 200 reflexion by the above argument. The origin of these departures from the expected lobe orientation is not known. The simplest explanation would be in terms of a range of layer line spacings (large periods along the chain directions) each with a different well-defined orientation. Whatever the reason, we see that the lobe orientation need not always give a direct measure of the chain inclination as it did in the samples of Part 2.

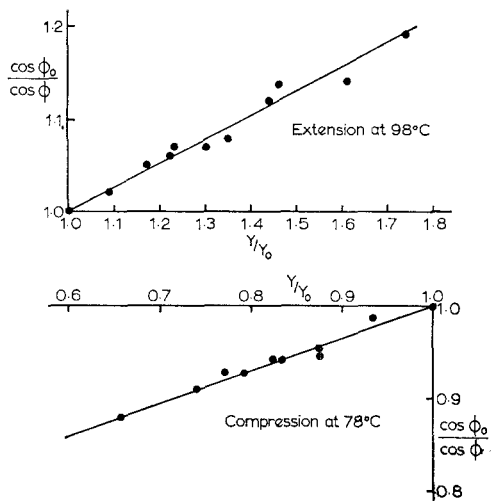


Figure 8 y/y_0 plotted against $\cos \phi_0/\cos \phi$ for orientation A2 extended in the y direction at 98°C and for orientation A1 compressed in the y direction at 78°C .

the compression experiment at 78°C . This suggests that at least 75% of the fractional length change cannot be accounted for by interlamellar slip. Furthermore, dimensional changes in the z direction are not expected to result from lamellar rotation perpendicular to b . As seen from figs. 4 and 6, changes along z while small are nevertheless noticeable.

It is an interesting fact that the curve obtained by plotting ϕ against y/y_0 for compression in the y direction at 78°C (fig. 5) can be made to coincide with the curve of ϕ against y/y_0 for extension in the y direction at 98°C (fig. 3) in the following way. The initial value of ϕ in the compression experiment was 28.5° . This same value of ϕ was achieved in the tension experiment with an extension ratio y/y_0 of 1.45. In order to refer tension and compression ratio measurements to the same initial length at the same orientation, each recorded compression ratio in the compression experiment was multiplied by 1.45 and the product plotted against its corresponding value of ϕ on the same axes as the recorded data from the tension experiment. The result is shown in fig. 9, in which it can be seen that the sets of points from the two experiments lie on the same curve.

The same kind of reversibility was found in the relationships between z/z_0 and y/y_0 and between x/x_0 and y/y_0 . The values of z/z_0 and x/x_0 at $\phi = 28.5^\circ$ in the tension experiment were 0.92 and 0.77. Each recorded z/z_0 and x/x_0 ratio of the 78°C compression experiment was

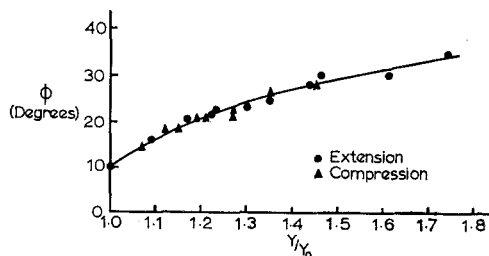


Figure 9 ϕ against y/y_0 for A2 extended in the y direction at 98°C and against 1.45 y/y_0 for A1 compressed in the y direction at 78°C , plotted on the same axes.

multiplied by 0.92 and 0.77 respectively and the product was plotted against the corresponding product of y/y_0 with 1.45 on the same axes as the recorded data from the tension experiment. The result is shown in fig. 10, where it is seen that coincidence is again attained between the sets of points from the two experiments.

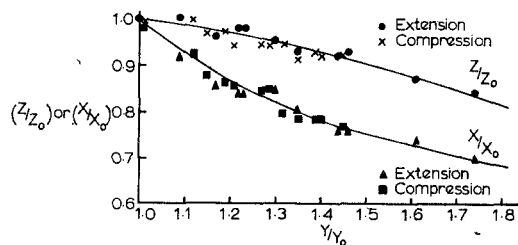


Figure 10 z/z_0 and x/x_0 against y/y_0 for orientation A2 extended in the y direction at 98°C ; 0.92 z/z_0 and 0.77 x/x_0 against 1.45 y/y_0 for orientation A1 compressed in the y direction at 78°C ; all plotted on the same axes.

Both effects, length changes along y in excess of those expected from the lamellar rotation, and small but not inappreciable dimensional changes along z , have been noted previously in Part 2. These deviations from the expected behaviour were attributed to the presence of deformable amorphous material. The presently reported results strengthen this inference with further important additions.

Firstly, the constancy of the long periods is a sure indication of the fact that the excess dimensional changes are not associated with amorphous material seated between the lamellae. Indeed the existence of amorphous material located *outside* the lamellar packets giving rise to the low angle reflexions has been invoked, previously, as responsible for the compression causing the lamellae to slip. In the light of new

results we can state with certainty that it is this extralamellar amorphous material which is responsible for about 75% of the observed dimensional changes.

Secondly, the present results reveal that the dimensional changes, even if larger than required by lamellar rotation, are nevertheless uniquely related to it. Not only are they reproducible in the same kind of experiment, but they are identical in experiments under compression and tension and are not even influenced by a 20° C difference in temperature. The superposability of the extension and the compression results is truly striking. Accordingly, it is unlikely that this extralamellar amorphous material coexists in a fortuitous manner with the crystallites. The consistency of the results rather suggests that it is in an intimate and well-defined relation to the crystals, being part of a superlamellar texture so far unexplained and even unsuspected.

Obviously there is much scope for speculation on the nature of such an amorphous-crystalline superstructure. Here just one, possibly the simplest model, will be mentioned. Consider that packets of layers form individual blocks, and consider that these blocks alternate with regions of more extensible material along the draw direction. This model would suggest a series coupling of two kinds of units. The blocks of layers could then slip and rotate, and produce the orientation effects observed, while the more compliant regions which connect or interrupt them could be responsible for the larger portion of the extensibility. In terms of this model the unique relation between crystal rotation and specimen extension would mean that the stress required to produce a given extension in the more compliant material would always give rise to the same amount of slip in the lamellar packet, provided the proportions of material in blocks and in more compliant regions remain the same at the temperatures considered here. If this softer material between the packets, and the material which ties the layers together, and thus provides the resistance to slip, were both of amorphous material whose behaviour changes with temperature in the same way, the observed interrelation between the two effects would be accounted for. Even if this model held, the origin and amount of the extensible component would still remain an open question. It may be amorphous material which failed to be incorpor-

ated in the lamellar packet structure on crystallisation. It might not even be material of a fixed amount: it could arise through reversible pulling out or disruption of crystals during extension. Recalling some of the subsidiary observations in Part 2 raises still further possibilities and problems which, however, will not be pursued further.

The complete reversibility of dimensional changes below the annealing temperature of 100° C deserves a comment. In the first place, it is remarkable that the material is entirely of a rubbery nature, particularly that no stress relaxation should be noticeable in a chemically uncrosslinked material on being kept under prolonged extension. From the preceding argument, the reversibility means that the extensibility figures used in the superposition of the data in figs. 9 and 10 should be related also to the unrelaxed starting length.

Two further points deserve noting at this stage. Firstly, there is no longer significant dimensional reversibility at the relaxation temperature which leads to a molecular tilt of 40°. This is the range of the two-point pattern (figs. 4, 5 in Part 2) where the postulated interlamellar slip ceases to operate. This is another indication that the reversibility effects in this paper are associated with orientation changes of crystallites themselves (in contrast to deformation within crystallites) which is in line with the general picture. Secondly, even in the temperature range for interlamellar slip the reversibility of molecular orientation on release of tension is not quite complete in contrast to the complete reversibility of the dimensions. The significance and origin of this small difference in angles (18° compared to 20° in the second experiment in section 2.2.5) would require further attention.

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