JOURNAL OF MATERIALS SCIENCE 1 (1966) 41–51

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

Part 1 *The Molecular Orientation on Heat Relaxation*

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Received 25 October 1965

This paper, first of a series, maps out the changes in molecular orientation occurring when doubly-oriented polyethylene is heat relaxed as a preliminary to further work on the relation of molecular orientation and crystalline texture. While earlier investigations have dealt with individual aspects of this field, the present results have now brought the previous, in some respects diverging views, into a single, unified scheme. Drawing followed by rolling produces a twinned, double texture which has been shown to result from a single texture (single crystal analogue) present under pressure, in agreement with an earlier hypothesis. The same single crystal analogue is produced by slight annealing. Further annealing leads to progressive molecular tilt around the *b* crystal axis and finally to a texture which is the macroscopic analogue of a solution grown crystal platelet. Beyond this stage, randomisation around *b* sets in, resulting in a texture analogue of a spherulitic fibril (Point's fibre "N"). Some orientation in the non-crystalline position of the material is also indicated, which, however, decays faster than that of the crystals.

The present paper is the first of a series, covering an extensive research programme on oriented polyethlene. The reporting of the new material will be preceded by an historical introduction serving the whole series, in order to bring together a widely-diversified background which provides both the foundation and the motive of the present project.

1. Historical Background

1.1. The Traditional Concept of a Fibre

The structure and properties of fibres have always been central issues in pure and applied polymer science (e.g. [1]). From the earliest days the ability to form fibres has been associated with the long chain nature of the polymer molecules, coherent fibres resulting from the alignment of chains. The properties of these fibres would accordingly depend on the chemical nature and the length of the molecules. It was soon recognised, however, that in addition to these purely chemical factors the modes of molecular aggregation are also relevant. It was found that most technically useful fibres were crystalline, to varying extents, as judged by their X-ray diffraction patterns. This crystallinity arises through parallel chain segments fitting together in crystallographic register, the details of the atomic arrangement being assessable by the usual methods of crystal structure analysis [1]. This crystallinity, however, is never perfect. The imperfections are of two kinds and give rise to two distinct effects in the diffraction patterns. Firstly, there is always some diffuse scatter, mostly in the form of a broad halo, which together with other physical effects (density, mechanical properties, etc.) is indicative of an appreciable amount of randomly-ordered material and is taken as representing a distinct amorphous phase present simultaneously with the crystals. Secondly, the reflections from the crystals are always broadened, which indicates that the coherently scattering regions are either small or imperfect or both. For these reasons fibres have traditionally been visualised as consisting of small crystals, with various degrees of perfection, formed by a regular fitting together of chain segments embedded in an amorphous matrix, there being intimate molecular connectedness between the two phases (the "fringed-micelle" model, see e.g. [1]).

1.2. Unaccounted Features

In the course of time a number of features have been recognised which do not obviously fit into the traditional picture. Here we group them in two main classes: orientation; and texture effects.

1.2.1. Unusual Orientations

It was found that on drawing an unoriented crystalline film or filament ("cold drawing", an important process in industrial practice), the final chain alignment is not attained in a way expected from an affine deformation of a random assembly with a gradually increasing number of chain segments pointing in the draw direction. Instead, certain specific crystallographic planes containing the chain direction become parallel first, the chains themselves taking up some more or less discrete inclination with respect to the draw direction. To quote the most conspicuous case, in certain polyamides the chains may even become perpendicular to the draw direction initially, the hydrogen-bonded planes aligning first [2]. In the case of polyethylene, the subject of the present study (for structure see fig. 1), the (1 0 0) planes align preferentially [3, 4, 5] with the first detectable discrete chain orientation corresponding to a chain inclination of about 55° to the draw direction [6]. On further extension the chains approach their final alignment by a gradual decrease of this discrete angle of inclination [6].

When a fully-oriented fibre is heat treated it shrinks macroscopically and becomes disoriented on the molecular scale. However, again this disorientation is not a statistically random process, but proceeds by the chains tilting gradually (with increasing temperature) to well-defined, inclined positions with one specific set of crystallographic planes remaining parallel to the draw direction. In this way the chains may even turn through 90°, i.e. they may become perpendicular to the original draw direction. The planes retaining their orientation in the drawn fibre are the ones which aligned last in the course of drawing. In polyethylene these are (0 1 0), which means that during the heat relaxation process the *b* axis direction retains the orientation it has in the drawn fibre while *c* and *a* rotate around it [3, 4, 6, 7].

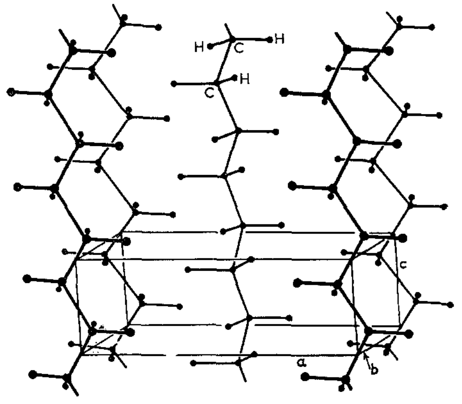

Figure 1 The unit cell of polyethylene: $a = 7.40$ Å; $b = 4.93$ Å; c — 2.54 Å (After Bunn [1]).

Compared with cold drawing, heat relaxation starts from a comparatively well-defined state where all the molecules (*c* axes) are aligned in the draw direction. For this reason the individual stages of the reorientation occurring on relaxation are more distinct. These will be the subject of the present studies.

It needs emphasising that information derivable from X-ray reflections refers to the unit cell, hence to the crystalline phase only. There is no corresponding unique method for assessing the chain orientation in the amorphous phase, which up to the present date remains a problematic subject.

1.2.2. Texture Effects

The traditional model does not imply the existence of any texture beyond that of the fringed micelle. However, textural effects of unsuspected variety and regularity have emerged from two, originally unconnected, lines of observation.

Firstly, X-ray reflections at low angles corresponding to spacings of 80 to 200 Å were detected, most prominently in fibres [8, 9]. Here the spacings correspond to a periodicity along the fibre axis as revealed by more or less extended layer line streaks. In some cases the streaks give off-meridional intensifications [10] (so-called four-point diagrams, as there are four maxima, two on each of the two layer lines normally present) indicating some oblique arrangement of the periodicities with respect to the fibre axis [11]. From the earliest, such low angle X-ray effects were attributed to some periodic arrangement of the crystallites. Concurrently direct morphological observation revealed a whole hierarchy of textural elements observable by light and electron microscopy in unoriented polymers as crystallised from the melt and from solution. It emerged that the primary products of crystallisation are lamellae 100 to 200 Å thick more exactly dependent on the crystallisation temperature. In the solution-crystallised material, these lamellae contain the molecules in a folded configuration, the straight segments normal or at a specified large angle to the lamellar surfaces, the lamellar thickness corresponding or being simply related to the fold length [12, 13, 14]. In the usual melt-crystallised material, the situation as regards the molecular structure is not quite as straightforward, but the observed individuality of the lamellae coupled with other effects strongly suggests that an appreciable amount of chain folding is present in combination with molecules which tie the lamellae together [14, 15, 16]. The nature of the amorphous material is problematic, but it is most likely located between the lamellae either as a separate phase or as part of the lamellar (fold) surface (e.g. [17, 18, 19]).

In the melt-crystallised polymer, the lamellae give rise to complex superstructures, the spherulites; it is these spherulites which become deformed and disrupted in the course of transforming the unoriented material into a fibre on cold drawing (e.g. [20]).

Nothing definitive is known about the texture of a drawn fibre itself, nevertheless there are certain analogies with the more widely explored, unoriented system. Thus, stacks of sedimented solution-crystallised lamellae also give rise to reflections at low angles, which in this case can be identified with the thickness of the layers hence the fold length. It has been pointed out [21, 22] that the analogous low angle X-ray patterns in drawn fibres could be of the same origin, which would mean that a fibre consisted of stacks of chain folded lamellae with the straight chain segments parallel to the draw direction contrary to the usual expectations of fully extended parallel chains. In fact the usual measure of chain orientation by X-rays or birefringence is intrinsically unable to distinguish between these alternatives. A fibre consisting of stacks of lamellae, however, would possess little strength unless the lamellae were connected by reasonably frequent tie molecules. These chains or chain portions tying the layers together could then be one source of the non-crystallographic (amorphous) material, the amount of it depending on the extent of drawing.

Recent morphological observations using the dispersive and etching action of strong oxidising agents indeed showed up lamellae as characteristic units of drawn fibres of polyethylene [17], the lamellae being stacked along the fibre axis [23].

2. Scope of the Present Investigations

The assumption underlying the present work is that the unusual orientation effects are related to the novel textural features now in the process of emerging. The work is aimed at exploring this correlation if such exists. The process of heat relaxation of doubly-oriented polyethylene, obtained by rolling the usual drawn material, was chosen for this study. Such doubly-oriented material is characterised by three reference directions identifiable both in terms of the macroscopic sample and in terms of the unit cell orientation, which enables more information to be extracted from such samples than is possible from the drawn-only material possessing cylindrical symmetry.

The first part of the work will be concerned with the orientation changes of the unit cell. This has not yet been reported in the complete form to be presented here. The origins of this part of the work go back to 1956, when it coincided with, and was partly influenced by, the concurrent work of Point [24, 25] to be referred to more specifically below. In the later parts of the series, the corresponding variation in the low angle X-ray patterns (textural elements) will be reported, together with the effects of further sample treatments relevant to the problem. A preliminary summarising account of some of the principal results has already been presented [26].

3. Experimental

3.1. Samples

The materials used were melt pressed sheets of polyethylene possessing no initial orientation. The relaxation effects to be presented were equally characteristic of low and high density polyethylenes. Nevertheless, the branch containing low density polyethylene (Alkathene) was used for the systematic work, as the orientation effects to be studied occurred over a much larger temperature range (80 to 115° C) than in the linear high density material (130 to 135° C), which enabled the individual stages of the relaxation process to be more clearly separated.

Strips 1 cm wide and several cm long were cut from the films which were about 250 μm thick, and drawn about 5x. Drawing took place by necking as is normally observed. The drawn material was subsequently rolled, the direction of advance being parallel to the drawing direction. The rolling produced an increase in width of about 50% on the drawn width, the change in length being less than 1%.

Pieces about 3 cm long were placed between thin mica sheets coated with silicone oil and annealed by placing on a hot plate for 1 min, a fresh sample being taken for each new annealing treatment. The mica served to stop the specimen distorting and the silicone oil gave better thermal contact. A check was made on the time dependence of annealing and it was found that the changes in orientation were practically complete within about 15 sec.

3.2. Results

3.2.1. X-ray Diffraction

Three sets of prominent hko reflections were utilised in defining the crystal orientation in the various specimens namely 110, 200 and 020 (indicated in fig. 7(*x*)). Their relation to the crystal structure [27] can be read off from perspective drawing of the unit cell in fig. 1. Two of these should be adequate for the purpose, most conveniently 200 and 020. but the conspicuous presence of the third, 110, provides independent confirmation.

In a doubly-oriented specimen, the full exploration of the texture patterns would require the taking of a very large number of X-ray photographs, so as to cover all possible ranges of orientation, in small angular steps. While in a few selected cases this was done partially, it was found in the course of this that, for the purpose of identifying the maxima only, the lengthy procedure could be substituted by taking only three photographs with the beam along the three principal directions, x, y, z, defined in fig. 2, and clearly identifiable in terms of the macroscopic sample shape. As seen, x is normal to the rolling plane, y is parallel to the draw and rolling direction, and z is normal to both x and y, which means that it lies in the film plane perpendicular to the long dimension of the usual specimens.

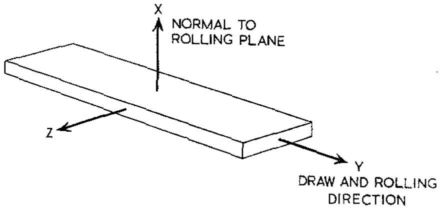

Figure 2 Notation of directions in the macroscopic specimen. (The assignment corresponds to that adopted in [26].)

When taking an X-ray photograph along x, y or z, one samples the distribution along circles in reciprocal space which for any given set of planes corresponds to a particular constant plane inclination – which is the Bragg angle – to the beam direction. This means that the intensity distribution along the Debye-Scherrer rings will not give exactly the distribution of planes which are parallel to x, y or z but of those inclined to these directions through their respective Bragg angles which are 10°49′, 12°1′ and 18°12′ for 110, 200 and 020 respectively when using CuK$_\alpha$ radiation. These angles being small particularly for 110 and 200, we shall take the observed intensity distribution along the rings as measures of the orientation distribution in zones defined by x, y and z as axes. It has been ascertained by taking photographs tilted through the Bragg angles with respect to x, y and z that this simplification does not affect the azimuthal position of the maxima to any appreciable extent.

There is always a comparatively broad distribution of orientations in the type of samples investigated here. The present work was restricted to the identification of the maximum of the distribution in each sample. Owing to the large spread of the orientation distribution more than one of the three sets of reflections – 110, 200, 020 – could be present simultaneously in a given photograph. Their relative intensities, however, are largely variable in photographs taken along x, y or z. In the knowledge of the intrinsic intensities (for 020, 200 and 110 these are in the ratio 1:10:40 [27]), and by observing the intensity distributions along the appropriate circles, the maxima in the orientation distribution could, nevertheless, be identified with sufficient accuracy for the present purpose. In a few selected cases the correctness of the assignment was tested by mapping the distribution itself in small steps around y and z.

Figs. 3 to 10 illustrate the X-ray diffraction patterns of polyethylene as drawn and rolled and annealed in successive stages. The photographs were taken at room temperature. The members of each triplet correspond to diffraction patterns with the beam along y, x or z. A pole figure representation is added as viewed along z to each set of three diffraction patterns. The poles a, b and c are idealised representations based on the photographs; e.g. a and b only correspond to observable reflections (2 0 0, 0 2 0); the c pole in itself is not observed but follows from the geometry. Spread is not indicated unless it is considered to be intrinsic to the texture.

As familiar, drawing aligns the c axes along the draw direction. The additional effects of *strong* rolling are shown by fig. 3. As seen from fig. 3 (y), the principal feature is a double orientation where one set of $\{110\}$ planes is parallel to the rolling plane while two other sets have maxima at equal angles about x. Figs. 3(x) and 3(z) are consistent with this assignment. (The weak innermost ring corresponding to a spacing of 4.5 to 4.6 Å is due to a second triclinic form of polyethylene [28, 29] produced by rolling [29]. It disappears on heating, and will not be commented on further in the present context.)

The series of figs. 4 to 10 shows the progressive changes occurring on heat relaxation. Fig. 4(y) reveals that on slight heat treatment the (1 1 0) plane orientation changes into a (1 0 0) plane orientation. In fig. 4(x), 2 0 0 is weak, while 0 2 0 is pronounced, and the reverse is the case for fig. 4(z), which implies a texture as represented in an idealised form by 4(p), i.e. where a, b and c axes are along x, y and z respectively.

We also obtained diffraction patterns such as fig. 4 when entirely unannealed samples such as giving fig. 3 were held under compression along x while the photograph was taken. This transformation was reversible, the orientation in fig. 3 was regained when the pressure was removed. (In addition there was an increased amount of the second crystalline phase while under pressure, an observation already reported [30].)

Without discussing each following photograph of the annealing series individually it will be noted that on subsequent stages of heat relaxation the b axis remains parallel to z with a and c rotating around it so that c becomes progressively inclined to y. This is immediately obvious from the increased split and shift towards y of the 200 reflections along the series 4(z) to 8(z). In these photographs 0 2 0 is absent which is expected if b is along z. The (0 2 0) planes will be less inclined to the beam if the beam is along x and y, hence, owing to the disorientation present, they may have some chance to reflect. It is observed nevertheless that the (0 2 0) planes are more strongly reflecting in patterns x than in y, i.e. the b axis has a larger angular spread around the y than around the x direction. This means that the orientation with respect to the draw direction is more perfect than with respect to the plane of rolling, a point which in some cases is directly assessable from the spread of the arcs (e.g. fig. 6(y) and (x)).

It will be noticed that there is a small split in the 2 0 0 arcs also in fig. 4(z) and parts of weak 2 0 0 maxima flank the strongest 2 0 0 maxima in 5(y). The origin of these effects is as follows. There are two processes occurring to some extent independently. Firstly a change from the (1 1 0) to (1 0 0) plane orientation with the c axis unaltered, secondly progressive c axis tilt through a rotation of the unit cell around b. The two effects may overlap to varying extents depending on sample preparation conditions. Thus in fig. 4 some c axis inclination has taken place simultaneously with the establishment of the (1 0 0) plane alignment, while in fig. 5 the transition from (1 1 0) to (1 0 0) plane orientation is still incomplete even in a fairly advanced stage of c inclination. (Naturally with c inclined to y the (1 1 0) or (1 0 0) planes will not be parallel to the rolling plane any longer. The "plane" alignment here corresponds to the appropriate plane normal being in the xy plane. Incidentally fig. 5(y) also reveals that the transition between the (1 0 0) and (1 1 0) plane orientations is discontinuous.) In the corresponding pole figures these secondary effects are ignored. Fig. 4(p) represents the idealised case of (1 0 0) plane orientation with c along y (to be denoted stage A) while in fig. 5(p) the (1 0 0) plane normal is drawn as if it were entirely in the xy plane, to emphasise the main features of the patterns.

As annealing progresses further the 2 0 0 arcs become concentrated on the y direction (fig. 8(z)), which in combination with figs. 8(x) and 8(y) clearly signifies that the c axes have rotated through 90° now being parallel to x (to be denoted stage C).

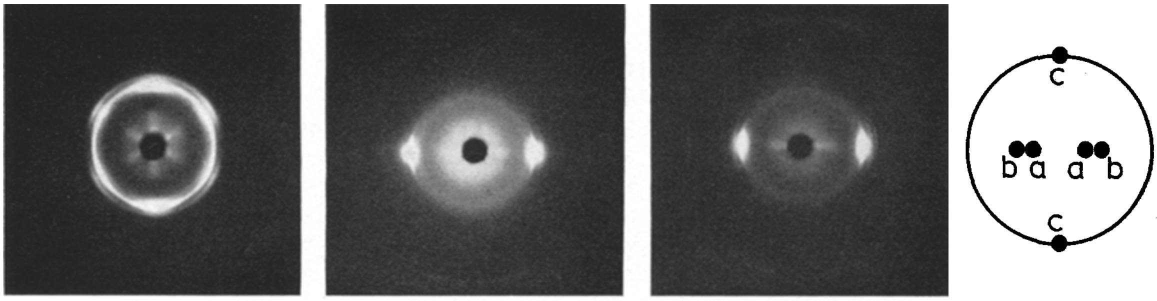

Figure 3 (*y*) (*x*) (*z*) (*p*)

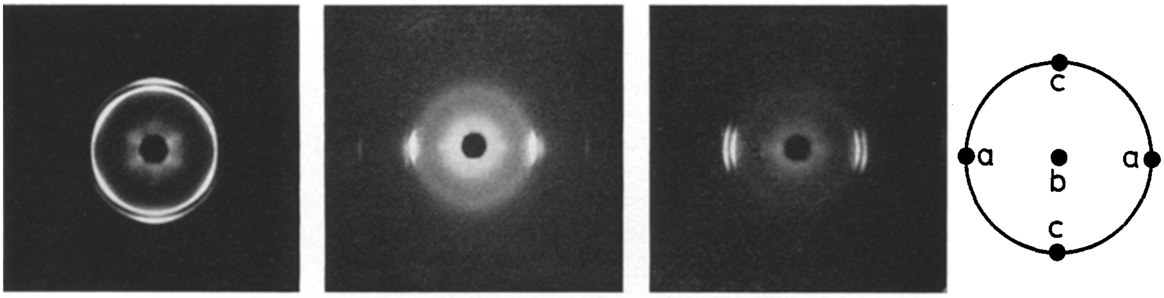

Figure 4 (*y*) (*x*) (*z*) (*p*)

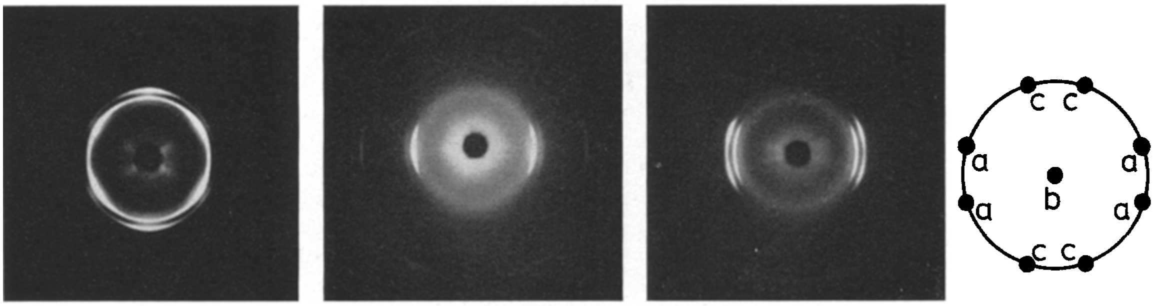

Figure 5 (*y*) (*x*) (*z*) (*p*)

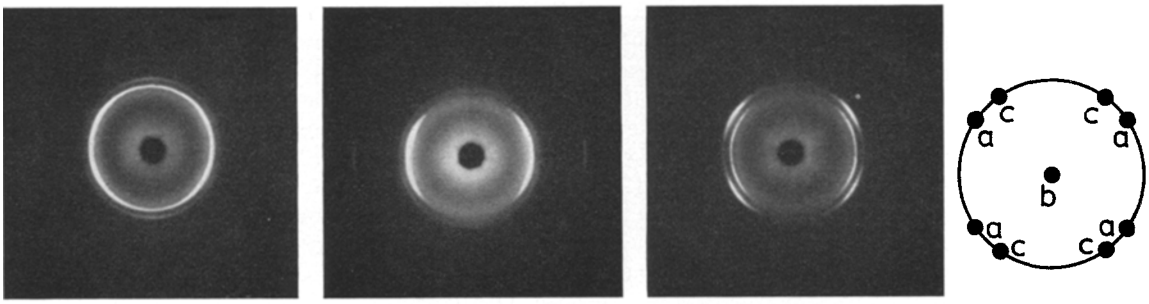

Figure 6 (*y*) (*x*) (*z*) (*p*)

Figures 3 to 10 X-ray patterns of high pressure polyethylene and simplified pole figures for various relaxation temperatures. Figure 3 Unrelaxed, (4) 75° C, (5) 95° C, (6) 105° C, (7) 107° C, (8) 109° C, (9) 111° C, (10) 113° C. The notation

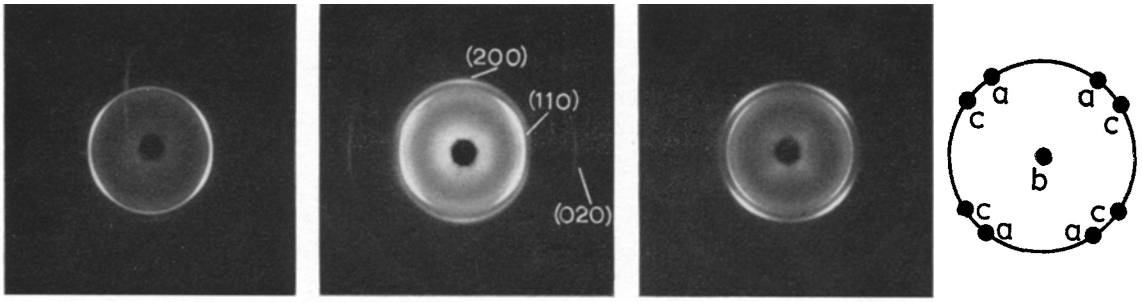

Figure 7 (*y*) (*x*) (*z*) (*p*)

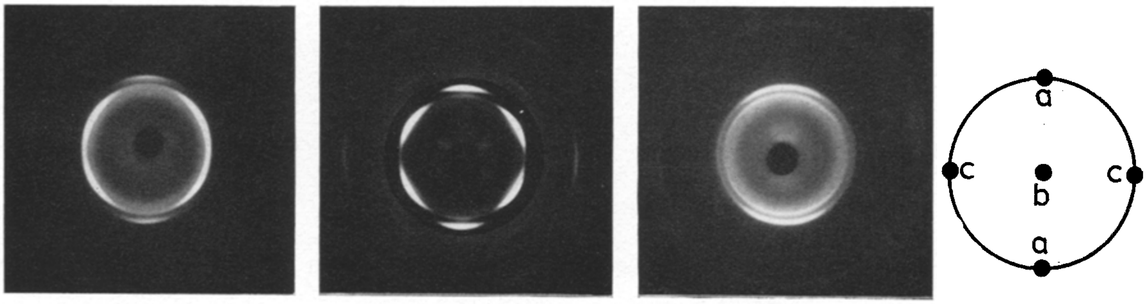

Figure 8 (*y*) (*x*) (*z*) (*p*)

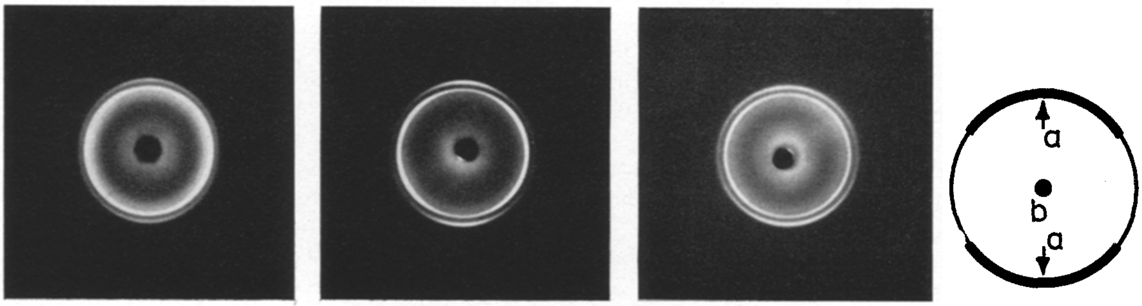

Figure 9 (*y*) (*x*) (*z*) (*p*)

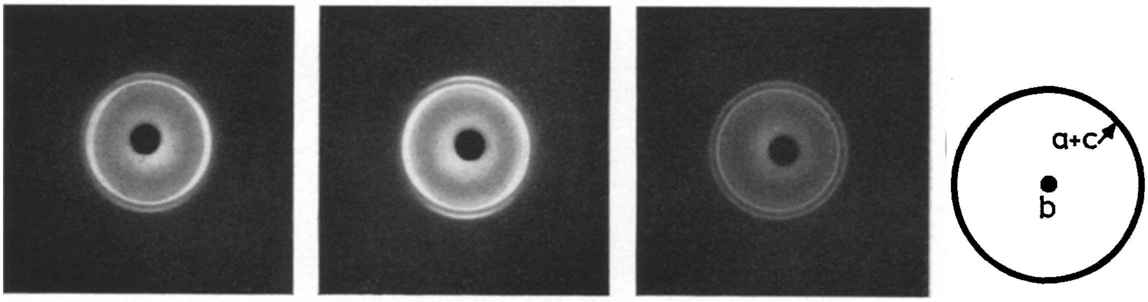

Figure 10 (*y*) (*x*) (*z*) (*p*)

(*y*), (*x*), (*z*) refers to the specimen direction parallel to the X-ray beam. *y* is vertical in (*x*) and (*z*) and *x* is vertical in (*y*). (*p*) refers to pole figures where *z* is normal to the plane of the drawing and *y* is vertical.

The rotation of the unit cell as a function of temperature is shown by fig. 11. There is a sudden increase in the temperature coefficient of the reorientation just below 100° C. It will be apparent in the later parts that the corresponding orientation is distinct and of special significance. It will be denoted as stage B.

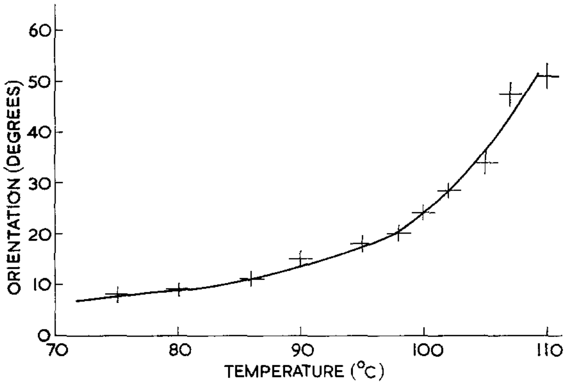

Figure 11 Variation of chain orientation (c axis) with relaxation temperature in high pressure polyethylene.

Annealing beyond stage C results in gradual randomisation about *b* which itself stays unaltered along *z* (fig. 9). In fig. 10 complete randomisation around *b* is achieved (stage D) which is immediately obvious from the fact that the 1 1 0 and 2 0 0 reflections are uniform rings in fig. 10(*z*) while the arced patterns of fig. 10(*x*) and 10(*y*) are practically identical. This stage is followed by complete randomisation probably resulting from melting and recrystallisation at the high temperatures involved.

There is always a broad halo present at about 4.6 Å, i.e. just inside the 1 1 0 ring, which corresponds to the amorphous phase. There is no appreciable amorphous orientation throughout the annealing series as indicated by this halo.

3.2.2. Birefringence

The birefringence of the film samples could conveniently be measured only with the light along *x*. The results are plotted in fig. 12. As expected there is a high positive birefringence in the initial drawn and rolled material which decreases gradually on crystal reorientation. Attempts to measure birefringence with the light along *z* were foiled by the excessive thickness of the sample along this direction while cutting introduces birefringence of its own. Nevertheless, it could be established that in the range of stage A (fig. 4) the maximum refractive index was along *y* (positive birefringence) while around stage C (fig. 8) it was along *x* (negative birefringence).

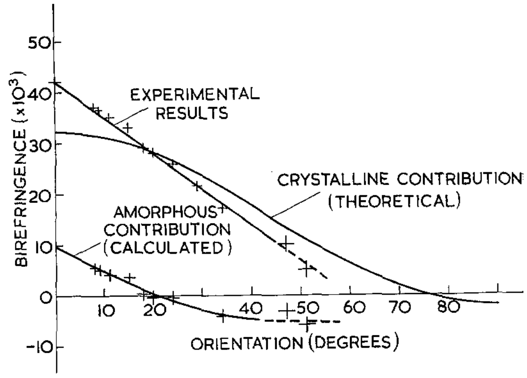

Figure 12 Variation of birefringence with c axis orientation for high pressure polyethylene. Experimental and calculated curves (see text).

4. Discussion

This paper serves to lay out the basic orientation phenomena on which the later material will be based. The discussion of these orientation effects in relation to the crystalline texture will be deferred till all the relevant material has been presented. Nevertheless, a few points can be appropriately raised at this stage.

4.1. Twinning Effects

The (1 1 0) alignment with respect to the rolling plane is the result of strong rolling. As shown earlier, weak rolling can lead to a texture with (1 0 0) in the rolling plane, even if poorly defined [5, 29]. The explanation suggested at the time [29] was that the (1 0 0) plane alignment is the primary consequence of the rolling action due to preference of [0 1 0] (1 0 0) slip over other slip modes perpendicular to *c*, and the (1 1 0) plane orientation would arise only on removal of the roller pressure, provided rolling has been drastic enough. There are plausible reasons for such a process. Thus, it is to be expected that elastic energy will be stored in the amorphous component of the material, which has low modulus but remains elastic to high elongations, while the roller pressure is acting. When the roller pressure is removed there will be a resulting compressive force perpendicular to *c* and parallel to the rolling plane acting on the crystallites. In the (1 0 0) plane, orientation assumed by the crystallites on rolling (3 1 0) and/or (1 1 0) twinning will be activated by this force leading to the observed discontinuous establishment of the double texture with (110) plane orientation. The present finding of a reversible transition between (110) and (100) plane orientations on application and removal of pressure now confirms the original hypothesis. Slight annealing would remove the driving force for this twinning, and the energy stored in the twinned crystals would then cause twinning back to the (100) plane orientation, accounting for the transition from fig. 3 to fig. 4. This picture is purely phenomenological and takes no account of the possible morphological factors involved. It is strongly supported by the discontinuous one-step nature of the transition from (110) to (100) plane orientations (e.g. fig. 5(*x*)).

4.2 Single Crystal and Spherulitic Fibril Analogues

Although the evaluation of the reorientation processes in figs. 4 to 10 is being deferred, three distinct stages A, C and D will be commented on. Double orientation has long been used in crystal structure determinations [31]. However, in the past doubly-oriented structures corresponded to twin orientations. In fact, the structure in fig. 3 represents a pair of (310) and/or (110) twins with the (110) plane about parallel to the plane of rolling [29]. The structure in fig. 4 is the first instance of a macroscopic polymer approximating a single texture. It can be considered as a macroscopic representation of a single crystal with axes *a*, *b* and *c* along the macroscopically identifiable directions of *x*, *z* and *y* respectively. Similarly, stage C can be considered as a single crystal analogue but now with *a*, *b* and *c* corresponding to *y*, *z* and *x* respectively. The existence of these single crystal analogues opens up the possibility of investigating various physical properties resolved along the three crystallographic directions on a macroscopic specimen. As for the measurement of different properties, different macroscopic samples shapes are required, stages A and C may serve complementary purposes. Thus, e.g. stage A should be suitable for a measurement along *c*, where this has to be an extended specimen dimension, and stage C would be the preferred sample type where the specimen extension along *c* needs to be small. Stage C would further be the suitable form for most purposes when a given property along *a* or *b* is to be resolved. In fact stage C is the macroscopic analogue of a solution-grown, tabular, single crystal.

Stage D is the macroscopic analogue of another important micro-structural element, namely the radiating fibril along a spherulite radius, which is known to have a texture pattern as in fig. 10. Consequently, the study of a sample in stage D should be relevant to the exploration of the properties of an isolated spherulite radius, and hence to the behaviour of the spherulitic bulk material in general. This stage D has in fact been obtained by Point [24, 25], who termed it fibre "N" ("fibre normal"), in a work which, as referred to above, partially coincided with the commencement of the present investigations. In his remarkable and comparatively little known investigation, Point relaxed drawn and rolled material and arrived at stage D as an end state. He recognised its analogy with a spherulite radius and carried out preliminary mechanical measurements with this analogy in mind. However, Point missed all the intermediate stages leading from stage A to D, and considered the establishment of stage D as resulting from a gradual randomisation around *b* without the distinct states of orientation represented by figs. 4 to 8. In this respect he was at variance with all other work on the annealing behaviour. We now find that a delicate temperature and specimen handling control is needed to separate the individual stages, particularly C and D. As Point was not aware of the existence of these as distinct stages, the homogeneity of his surprisingly large samples which he claimed to be in stage D, and which he used for his work as such, may well require closer scrutiny. (We now find it practically impossible to obtain sample sizes such as he used in a uniform state of stage D.)

The texture pattern corresponding to stage D is playing an important part also in melt-extruded films. It has been suggested by one of us in 1955 [6] that the diffraction patterns given by such a film can be accounted for by considering a spherulitic fibril, i.e. a texture as in fig. 10, and randomising it around the extrusion direction which in fig. 10 would correspond to *y*. (This structure (row structure) is somewhat difficult to distinguish from the one that corresponds to fig. 8 randomised around *y*, and the matter has been the subject of considerable dispute [32] – see summarising account in [33]. This matter is now in the process of being cleared up in favour of the row structure [34].) The relation between the melt-extruded films and the present samples in stage D is under examination. At this stage it will merely be emphasised that the spherilutic fibril analogue of fig. 10 should provide usefully simplified samples for the exploration of the properties of commercial melt-extruded films.

4.3. Birefringence

It has already been pointed out that wide angle X-ray diffraction only gives information regarding the crystalline orientation, the diffuse scatter due to the amorphous material generally being quite random (figs. 3 to 10). One method by which the amorphous orientation may be characterised is the measurement of birefringence. The total birefringence ($\triangle_T$) is the sum of the amorphous ($\triangle_a$) and crystalline ($\triangle_c$) contributions separately. $\triangle_c$ can be evaluated from knowledge of the orientation (from X-ray measurements), percentage crystallinity (X_c) (from density measurements) and the birefringence ($\triangle$) of an isolated crystalline unit (calculated from bond polarisabilities [35]).

In fig. 12 the measured birefringence is compared with the theoretical crystalline contribution. This latter was obtained assuming perfect orientation (i.e. b parallel to z and c at an angle $\pm\theta$ to y) and $X_c = 52\%$. Polyethylene has a biaxial indicatrix with its principal axes parallel to a, b and c. The values of these axes were taken as $n_c = 1.600$, $n_b = 1.538$ and $n_a = 1.534$ [32].

For viewing normal to the film plane, i.e. along x,

$$\triangle_c = X_c\,(n_y - n_b)$$

where n_y, the refractive index parallel to the y direction, is given by the polar equation for an ellipse

$$n_y = \left[\frac{\cos^2\theta}{n^2_c} + \frac{\sin^2\theta}{n^2_a}\right]^{-\frac{1}{2}}$$

Also plotted is the difference which is $\triangle_s$.

It should be noted here that both the values of X_c and $\triangle$ are not precise enough to attribute any real significance to the crossing of the experimental and theoretical curves, i.e. to the negative $\triangle_a$ values at the higher angles. Only the overall shape of the curves can be taken as giving real information. These show that the measured birefringence falls off more rapidly than the theoretical one throughout. This steeper drop is most conspicuous in the initial stages of heat annealing, levelling off gradually in the later stages. Accordingly there is a comparatively large initial amorphous contribution to the birefringence which diminishes at a decreasing rate. This behaviour would be expected from partially-oriented amorphous material becoming progressively random. Even allowing for the uncertainty in absolute values, the orientation of the amorphous could hardly be more than partial. The linear relation between increased birefringence and angle in fig. 12 is noteworthy and possibly significant. We can offer no explanation at this stage.

Acknowledgements

We are indebted to Professor F. C. Frank, for his contribution to the work on rolling structures from which the present studies originated.

Our thanks are due to Dr T. Kawai, for having stimulated the resumption of this work after several years of abeyance.

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