A STUDY OF ORDER IN POLYMERS

BY X-RAY DIFFRACTION

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in fulfilment of the requirements for the degree of

Doctor of Philosophy

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REFERENCES
X-ray diffraction methods have been employed to determine order parameters in polymeric materials (mainly polyethylene). Two types of order have been defined; structural order, (i.e. crystallinity, unit cell dimensions, crystallite size and perfection) and alignment order (preferred orientation).

Existing methods of analysis have been examined, modified and compared for a range of polymer types. The effect of molecular weight, molecular weight distribution, branching and conditions of crystallisation have been shown to alter the order parameters.

The parameters of structural order have been examined over a range of temperatures up to the melting point of the polymers. These reveal changes in order due to recrystallisation above about 110°C, and a further change a few degrees below the melting point.

Computer data processing techniques have been developed to produce pole figure plots and to determine orientation functions. These enable both qualitative and quantitative characterisation of preferred orientation in deformed and processed material. (310) twinning has been identified in both cold drawn and rolled polyethylene. (110) twinning is observed in polyethylene sheet after rolling, annealing and then further drawing. The operative twinning mode has been explained in terms of the fold geometry of the crystalline regions. Cold rolled polyoxymethylene has been shown to undergo a phase transformation from the hexagonal to orthorhombic phase.

Films of polyethylene produced by the commercial process of extrusion blow moulding have been examined. The orientation results from a stress crystallisation procedure and the actual orientation may be related to the machine variable. The molecular chain axis distribution is defined by means of the $\langle \cos^2 \theta \rangle$ orientation functions. These enable a quantitative correlation of the orientation with film properties to be made.
The aim of this work is to determine the degree of order in polymers, mainly polyethylene, by x-ray diffraction techniques. The parameters of order have been divided into 'structural' order and 'alignment' order.

'Structural' order includes the parameters of crystallinity, unit cell dimensions, crystallite size and perfection. 'Alignment' order is preferred orientation.

**Structural order**

1) To examine and compare existing methods for determining crystallinity, unit cell dimensions, crystallite size and perfection.

2) To make improvements to the existing methods.

3) To relate the structural order parameters to changes in molecular chain characteristics and to processing conditions.

4) To demonstrate the relationship between structural order and various properties of the material.

5) To study the behaviour of these parameters at elevated temperatures.

**Alignment order**

1) To develop methods which enable both qualitative and quantitative determination of preferred orientation in polymers.

2) To use these methods to study the deformation process of drawing, rolling and annealing.

3) To examine the orientation which occurs in the commercial process of extrusion blown films of polyethylene. Also to demonstrate that the molecular alignment in such film may be correlated with the film properties.
1.1. General Introduction

The polymerisation of small monomeric units to form long chain polymeric materials on a commercial scale has developed in importance since its beginnings during the second world war. Today, probably all the simple, cheap organic molecules which are capable of undergoing polymerisation reactions are used to produce various quantities of polymer material. Of these, there are only a few which are made in very large tonnages. See Table 1. The selection of a particular polymer for use in the manufacture of a certain article depends on the material having properties which are required in that article. Since these properties may not coincide with those of the large tonnage polymers, it is commercially desirable to be able to modify the properties of these large tonnage polymers rather than to develop new polymers.

In any polymer type the properties, such as tensile strength, tear strength, stress crack resistance, thermal characteristics, are largely determined by the overall structure of the solid phase i.e. molecular weight, crystallinity, chain perfection, orientation etc. There are two methods of modifying the structure and hence the properties of the material. Firstly, by altering the molecular chains, for example configuration, inclusion of branches, changes in molecular weight distribution. Secondly, changes in processing conditions will alter the bulk structure. Thus thermal history leads to changes in crystallinity and perfection of ordering; commercial moulding processes give rise to orientation of the crystalline regions which results in anisotropy in properties.

It is essential to characterise changes in the bulk structure brought about by such modifications. This aspect has engaged a large number of researches over the past 30 years, using a number of physical and mechanical techniques, for example spectroscopy, thermal methods,
TABLE 1

1972 British production of synthetic resins

<table>
<thead>
<tr>
<th>Thermoplastics</th>
<th>TONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyolefins</td>
<td>556,000</td>
</tr>
<tr>
<td>Polyvinyl chloride</td>
<td>370,000</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>165,000</td>
</tr>
<tr>
<td>ABS</td>
<td>32,000</td>
</tr>
<tr>
<td>Polyvinyl acetate</td>
<td>42,000</td>
</tr>
<tr>
<td>Cellulosics</td>
<td>10,000</td>
</tr>
<tr>
<td>Acrylics</td>
<td>20,500</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Thermosetting</th>
<th>TONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aminos</td>
<td>185,000</td>
</tr>
<tr>
<td>Alkyds</td>
<td>63,000</td>
</tr>
<tr>
<td>Phenolics</td>
<td>68,000</td>
</tr>
<tr>
<td>Epoxides</td>
<td>14,000</td>
</tr>
<tr>
<td>Polyesters</td>
<td>38,000</td>
</tr>
<tr>
<td>Polyurethanes</td>
<td>58,000</td>
</tr>
</tbody>
</table>
such is the complexity of the subject that all these methods have to be brought to bear for the full understanding of order in polymers. In this work, which is on a collaborative basis between BP and the University of Surrey, these problems have been studied using the technique of wide angle x-ray diffraction. This approach limits the scope of the study to the crystalline phase of polymers, but x-ray diffraction is sufficiently versatile to give information on a number of structural parameters which are considered together in relation to the effect of such structural features on the properties.

1.2. Commercial process for polymerisation

Since the bulk of this work considers polymers of ethylene and ethylene/\alpha-olefine mixtures, it is useful to consider the commercial development of their polymerisation. This is relevant since the various methods do, in fact, produce material having different molecular arrangements and therefore give rise to materials of differing properties.

The first process for polymerising ethylene was operated by ICI in 1942. This was a high pressure, free radical process using peroxides as initiator (A').

The steps are as follows:

\[ \text{Initiation: } \text{A}^* + \text{CH}_2 \rightarrow \text{A}\cdot\text{CH}_2 = \text{CH}^* \]

\[ \text{Propagation: } \text{A}\cdot\text{CH}_2 - \text{CH}^* \xrightarrow{\text{CH}_2 = \text{CH}^*} \text{A}\cdot\text{CH}_2 = \text{CH} - \text{CH}^* \xrightarrow{\text{CH}_2 = \text{CH}^*} \]

Due to the random nature of the propagation steps, chain branches are frequently formed. This occurs by transfer reactions between radical and radical or radical and product, i.e.

\[ \text{A}\cdot\text{CH}_2 - \text{CH}^* + \text{A}\cdot\text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} - \text{A} \rightarrow \text{A}\cdot\text{CH}_2 - \text{CH}_2 \]

\[ + \text{A}\cdot\text{CH}_2 = \text{CH} - \text{CH}^* \]

\[ + \text{A}\cdot\text{CH}_2 - \text{CH} - \text{A} \]
Due to the relatively large number of branches the product has a low density and crystallinity.

In 1954 Ziegler presented a route to linear polyethylene by a low pressure process in the presence of various complex organometallic catalysts. A typical catalyst combination is triethyl aluminium with titanium tetrachloride as a promoter.

\[
\text{Et}_3\text{Al} + \text{TiCl}_4 \xrightarrow{\text{Pentane}} (\text{CH}_2 - \text{CH}_2)_n
\]

The mechanism of the reaction is that each ethylene molecule attaches itself directly to the base of the growing polymer one unit at a time.

The importance of Ziegler's findings to polyolefin development lies in the uniqueness of his catalyst systems, which resulted in the manufacture of linear, as opposed to the branched homo-polymers obtained by the ICI high pressure process. These catalysts are now used for the manufacture of other linear polyolefins, such as polybutene and polypropylene.
This uses a metal oxide on silica aluminium base at moderate pressures. Typically, the metal oxide is chromium. The mechanism of the reaction is as yet unknown but involves bonding between the base chromium ions and reaction gas. The product is a linear high molecular weight material.

Modification to the catalyst system, e.g. using two metal oxides, gives rise to polymers having differing ranges of molecular weight. If the reaction mixture is ethylene + some higher olefin the resulting polymer has certain amounts of branching. This results in a wide range of materials. The total 1972 British production of high and low density polyethylene are given in table 2.

Obviously, individual production articles require material having prescribed characteristics, i.e. flexibility, tensile strength, thermal properties, tear resistance, etc. These depend on the bulk structure resulting from the molecular chain characteristics, and, in addition how they are processed (orientation and thermal history). Thus, the process of injection moulding causes preferred orientation of the crystallites. Such ordering gives rise to anisotropic properties which may or may not be desirable. Thus the study of the bulk structure is an essential step in correlating the properties of a polymer to various aspects of the polymer, such as the manufacturing procedures.

1.3. Application of x-ray diffraction to the study of polymers

The application of x-ray diffraction methods to study the structure of polymers has taken place since the early developments in polymers. The special usefulness of x-ray diffraction in the study of solid substances lies in its ability to distinguish ordered from disordered states, and to characterise more fully the nature of the ordered state. Thus, liquids or glasses produce x-ray patterns of a diffuse nature consisting of one or more halos, whereas well-crystallised substances yield patterns of numerous sharp circles or spots. This capacity to reveal the degree of ordering in solid substances makes x-ray
<table>
<thead>
<tr>
<th></th>
<th>Production</th>
<th>Total 1972 British production of polylefins^1</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Low density polyethylene</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Production</td>
<td>375,000</td>
<td></td>
</tr>
<tr>
<td>Consumption</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Film and sheet</td>
<td>211,000</td>
<td></td>
</tr>
<tr>
<td>Injection moulding</td>
<td>38,000</td>
<td></td>
</tr>
<tr>
<td>Wire and cable</td>
<td>23,000</td>
<td></td>
</tr>
<tr>
<td>Blow moulding</td>
<td>25,000</td>
<td></td>
</tr>
<tr>
<td>Pipe</td>
<td>7,000</td>
<td></td>
</tr>
<tr>
<td>Extrusion coating</td>
<td>13,000</td>
<td></td>
</tr>
<tr>
<td>Powder</td>
<td>8,000</td>
<td></td>
</tr>
<tr>
<td><strong>High density polyethylene</strong></td>
<td>66,000</td>
<td></td>
</tr>
<tr>
<td>Production</td>
<td>66,000</td>
<td></td>
</tr>
<tr>
<td>Consumption</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Injection moulding</td>
<td>19,000</td>
<td></td>
</tr>
<tr>
<td>Blow moulding</td>
<td>34,000</td>
<td></td>
</tr>
<tr>
<td>Monofilament</td>
<td>3,000</td>
<td></td>
</tr>
<tr>
<td>Pipe</td>
<td>3,000</td>
<td></td>
</tr>
<tr>
<td>Wire and cable</td>
<td>800</td>
<td></td>
</tr>
<tr>
<td>Film and sheet</td>
<td>7,000</td>
<td></td>
</tr>
<tr>
<td><strong>Polypropylene</strong></td>
<td>115,000</td>
<td></td>
</tr>
<tr>
<td>Production</td>
<td>115,000</td>
<td></td>
</tr>
<tr>
<td>Consumption</td>
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<td></td>
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<tr>
<td>Injection and Blow moulding</td>
<td>60,000</td>
<td></td>
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<tr>
<td>Fibres</td>
<td>43,000</td>
<td></td>
</tr>
<tr>
<td>Sheet</td>
<td>3,500</td>
<td></td>
</tr>
<tr>
<td>Film</td>
<td>17,000</td>
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diffraction well suited to the investigation of polymers, which compared with simple chemical compounds, either crystallise more poorly, or can be crystallised only under carefully controlled experimental conditions.

Compared with the customary ease with which simple ionic and molecular compounds can be crystallised, the great length and often appreciable irregularity of polymer molecules presents formidable hindrances to the attainment of the three dimensional regularity that is required for the growth of a crystal. Those polymers which do crystallise do so only partially, as shown by their x-ray diffraction patterns, which contain relatively sharp spots or lines and one or more amorphous halos.

1.3.1. Two phase model

The initial interpretation of such features was by a two phase model of the polymer structure. Such a model is the fringed micelle concept.\(^3/4\) The molecular chains meander through many crystalline and amorphous regions, the crystalline regions being those where a number of chains are aligned in a regular crystallographic manner. A useful picture of such a structure is Statton’s string model of this concept\(^5\), fig.1.

In 1957, single crystals of polyethylene were first reported; these were grown from very dilute solutions of xylene\(^6\), fig.2. They consist of lamellae with thicknesses of the order of 100 Å and lateral measurements of one to several hundred microns. Electron diffraction studies showed that the molecular axes were perpendicular to the plane of the lamellae. This means that the chains, whose lengths are considerably in excess of 100 Å, must be folded. It was noted that mats of these single crystals still showed sharp Bragg reflections and broad halos, and estimated as 80 to 85% crystalline.

In the light of such observations the simple two phase model in single crystals and bulk material begins to fail. The model may be
Fig. 1. Statton's string model of the fringed micelle concept.

Fig. 2. Single crystals of polyethylene.
Defects may result from the effect of chain ends, branches (when present), dislocations etc. A further problem is presented by the interface, where there must be regions of intermediate order between the substantially crystalline and amorphous regions, see fig. 3. Recent works by Vonk suggest that even in co-polymers of low comonomer content, the interfacial region accounts for about 5 to 10% of the material. These factors have led researchers to consider a second model.

1.3.2. Single phase paracrystalline model

The other polymer model is based on Hosemann's mathematical concept of paracrystallinity. This makes use of a 'sloppy lattice' instead of a perfect one. That such an arrangement can produce sharp and diffuse diffraction effects is illustrated by the optical analogue, fig. 4. The usefulness of the paracrystalline view is that there are a number of different ways in which degrees of disorder can be put into the lattice. Thus chain ends, branches, irregularities in the molecular chain can induce defects in the arrangement.

Lindenmayer has shown the applicability of the paracrystallinity model to polymers by his study of polyacrylonitrile (PAN). Single crystals of PAN can be grown under suitable conditions, but, in spite of the fact that the crystals were large (4 - 5 μ), no non-equatorial reflections were observed, and the non-equatorial scattering maxima remained almost as diffuse in well-annealed and orientated PAN filaments. Thus, the polymer is completely crystalline by the usual definition, i.e. a material bounded by plane surfaces which meet in fixed angles, but which is apparently highly disordered in some fashion, since it produces sharp diffraction maxima in two directions, and only diffuse scattering maxima in the third direction. Thus it must be described in terms of the paracrystalline model.
Fig. 3. Systematic representation of varying degrees of order.

Fig. 4. Paracrystalline lattice and its optical analog diffraction pattern.
1.3.3. Criterion for distinguishing between single and two phase materials

Ruland\textsuperscript{13} has presented a clear criterion for distinguishing between x-ray patterns caused by single-phase systems, and two-phase disordered crystalline and amorphous systems. His approach was to use the diffraction peak breadth to define the maximum paracrystalline disorder present. It is known that any paracrystalline disorder will contribute to the amorphous type scatter. Thus, if the amorphous type scatter observed in the diffraction pattern is greater than that calculated to arise from the deduced paracrystalline disorder, then a second phase of low order is required to account for the total amorphous scatter.

Specifically, he showed that a two phase structure must exist if the degree of crystallinity satisfies the inequality

\[ \phi \, Cr < \frac{(1-2d \delta \beta)}{(1-d \delta \beta)} \]

where \( \phi \, Cr \) is the measured fractional degree of crystallinity, \( d \) is the Bragg spacing for the particular reflection and \( \delta \beta \) is the integral breadth of the peak in reciprocal space, corrected for instrumental broadening. This inequality is drawn out in fig.5, where it is applied to the 110 diffraction peak of polyethylene. For a crystallinity of 80\%, which is a typical figure for high density polymer, the integral breadth of the peak would have to be greater than 1.6\(^0\) for a single phase paracrystalline model. Since this is much greater than the peak widths observed in practice, it may be assumed that the polymer has two phases, although the crystalline phases may still have paracrystalline type distortions.

1.4. Uses to which x-ray diffraction is applied in this work

In this work x-ray diffraction has been employed in two main fields. Firstly, to measure 'structural order'. This includes measurement of
At any crystallinity, if the peak width is less than that given by the plotted curve, then the polymer must be two phase in nature.

Fig. 5. Plot for Ruland's criterion of polyethylene; 110 reflection.
crystallinity, unit cell dimensions and crystalline perfection and size. These parameters come from an examination of the overall diffraction pattern, the positions of the peak maxima and the peak profile respectively. They give a reasonably comprehensive description of the ordered phase, but provide only a small amount of information on the disordered phase. However these parameters are useful in understanding the properties of the material. The second is the measurement of 'alignment order' of preferred orientation, which arises during preparative conditions of machine forming from the molten state, or by subsequent deformation (e.g. rolling) in the solid state. Here, both the manner in which the crystalline regions become aligned with respect to the external axes, and the degree to which they align, may be measured. Alignment causes an anisotropy in properties in the material. Such anisotropy may be desirable (as in fibres) or undesirable.

The first type, that of 'structural order', is considered in Part I, and that of 'alignment order' in Part II.
2.1. Crystallinity in polymers

Although the actual meaning of crystallinity in polymers is being reconsidered in the light of crystalline defects, the measurement of the amount of ordered material is useful. Thus, the overall amount of order may be related to a number of the properties, and therefore applications of that material. In applications where properties such as strength, stiffness, hardness, heat tolerance or shrinkage are important, the highly crystalline polymers are employed. Low crystallinity materials are used mainly where the above properties are not essential, and where ease of moulding is required. Low crystallinity, however, does impart properties of high elongation, impact strength and toughness. Polymers of crystallinities intermediate between these two cases are the most important from the point of this study. The mechanism by which the crystallinity is reduced will affect whether the polymer has properties intermediate to those mentioned above, or whether certain properties of the highly crystalline materials may be kept while, at the same time, enhancing the desirable properties of the lower crystalline content materials.

2.2. Measurement of crystallinity

The measurement of crystallinity in polymers is a slightly special case of the quantitative analysis of a two component mixture, one component being the ordered the other the disordered. In a mixture the total intensity of x-rays diffracted by the $i^{th}$ component of the mixture by some selected plane $(hkl)$ is given by

$$I_i = \frac{k_i f_i}{\nu}$$
where \( K_1 \) depends upon the nature of component \( i \) and the geometry of the apparatus, \( f_i \) is the volume fraction of the \( i \).th component, and \( \mu \) is the linear absorption coefficient of the mixture. If \( x_i \) is the weight fraction and \( \rho_i \) the density of the \( i \).th component then

\[
f_i = \frac{x_i/\rho_i}{\sum (x_i/\rho_i)}
\]

Likewise, \( \mu \) is

\[
\mu = \frac{\sum x_i (\mu_i/\rho_i)}{\sum (x_i/\rho_i)} = \frac{\sum x_i (\mu_i^s)}{\sum (x_i/\rho_i)}
\]

with \( \mu_i \) the linear absorption coefficient of the \( i \).th component and

\( \mu_i/\rho_i = \mu_i^s \) its corresponding mass absorption coefficient substituting

\[
I_i = K_i x_i \frac{x_i/\rho_i}{\sum \mu_i^s x_i}
\]

For a two component mixture with both phases having the same mass absorption coefficient,

\[
\sum \mu_i^s x_i = \mu_M^s
\]

where \( \mu_M^s \) is the mass absorption coefficient of the polymer.

\[
I_i = \left( \frac{K_i}{\rho_i \mu_M^s} \right) x_i \quad \ldots \ldots \quad (2.1)
\]

Thus, the intensity of a peak in one of the phases is directly proportional to the concentration. A comparison with a pure standard should lead to an absolute measure of the crystallinity.

Another method is to consider the ratio

\[
I_i = \frac{K_i}{\rho_i \mu_M} x_i \quad \ldots \ldots \quad (2.2)
\]

\[
I_2 = \frac{K_i}{\rho_i \mu_M} (1-x_i)
\]

where \( I_i \) and \( I_2 \) are the areas from the crystalline and amorphous regions respectively. From which \( x_1 \), the fractional crystallinity, is given by
A number of practical problems arise in the application of this theory to measurements of the amount of crystalline phase in polymers. The most important of these are listed below.

1. No pure standard of the crystalline component is available.

2. Only in a few exceptional cases are the pure standards of the amorphous component available.

3. The Bragg diffraction peaks often occur in the same position as the maximum of the diffuse scatter, presenting problems in separating one from the other.

4. It is known that distortions within the ordered phase generate a certain amount of diffuse scatter. Thus the observed amorphous halo in fact over-estimates the true amount of the amorphous phase.

These problems have led to a number of methods which seek to overcome or minimise their effect.

2.2.1. Methods

Basically, the methods for determining crystalline order in polymers fall into one of three groups.

Group 1. Those which examine the diffraction pattern as a whole, estimating disorder from the Bragg peak profiles and correcting for its effect on the 'amorphous' halo.

Group 2. Those which make measurements on only one of the phases.

Group 3. Those which separate the diffraction pattern into crystalline and amorphous regions and ratio their areas.

2.2.2. Group 1 methods

The first group are based on the work by Ruland.\(^\text{14}\)

Rewriting equation 2.3

\[
x_c = \frac{\int_0^\infty s^2 I_c(s) \, ds}{\int_0^\infty s^2 I(s) \, ds}
\]

where \(s = 2\sin\theta/\lambda\), and \(I(s)\) and \(I_c(s)\) are respectively the intensity of coherent x-ray scatter from a specimen at \(s\), and the part of the
intensity at the same point that is concentrated in the crystalline peaks. Now $x_c$ tends to be smaller than the true crystalline fraction because part of the x-ray intensity that is scattered by the crystalline regions is lost from the peaks, and appears as diffuse scatter. Allowance for this can be made by including in the intensity expression a lattice imperfection factor $D$. The weighted mean-square atomic-scattering factor of the polymer is defined as

$$\bar{f}^2 = \frac{\sum N_i f_i^2}{\sum N_i}$$

where $N_i$ is the number of atoms of type $i$ in the stoichiometric formula.

Equation 2.4 is modified to take account of the lattice imperfection.

$$\bar{x}_c = \frac{\int_0^\infty s^2 I_c ds \int_0^\infty s^2 f^2 ds}{\int_0^\infty s^2 I ds \int_0^\infty s^2 f^2 D ds} \quad \ldots \quad (2.5)$$

Since the implementation of the method requires a detailed analysis of the whole diffraction pattern it is very time-consuming, and cannot be readily adapted to routine use. This limits the use of this method to studies where absolute values of crystallinity are required. It is not considered further in this work.

2.2.3. Group 2 methods

This group includes methods which have been developed for determining the crystalline portion in rubbers. Rubbers can be obtained in their amorphous state from which they may be crystallised by thermal treatment or under deformation. In such cases, the fully amorphous phase may be used as the standard for use in equation 2.1. This method has been developed for use with any polymer which may be obtained in the purely amorphous form. An example is polyethylene terephthalate. In polyolefins, as with most polymers, it is not possible to obtain the polymer in the amorphous state. However Corradini et al have considered the study of the crystalline phase alone. This is considered further since it provides a measure of
crystallinity by a method which has some mathematical basis, and is relatively easy to perform.

2.2.3. (1) Corradini's method

The general relation of the integrated intensity $I_i$ of a diffraction line of a substance is

$$I_i = m A P L \left| F_i \right|^2 \frac{n_i}{V_{oi}}$$

where
- $m$ = the multiplicity
- $A$ = the absorption factor
- $P$ = the polarisation factor
- $L$ = the Lorentz factor
- $n_i$ = the number of unit cells in the irradiated volume
- $V_{oi}$ = the volume of a unit cell

Replacing $n_i$ by

$$n_i = \frac{M_i}{M_{oi} \rho \Omega V_{oi}}$$

where
- $M_i$ = total weight
- $M_{oi}$ = weight of the unit cell content
- $\rho$ = density one obtains for the ratio of two integrated intensities $I_i$ and $I_2$

$$\frac{I_2}{I_1} = \frac{m_1 A_1 L_1 P_1 \rho_1^2 V_{oi}^2}{m_2 A_2 L_2 P_2 \rho_2^2 V_{oi}^2} \left| \frac{F_1^2}{F_2^2} \right| \frac{M_1}{M_2}$$

provided that the general conditions of measurement (primary beam intensity, slit system etc.) are kept constant. For the mixture of two substances, the absorption factors of both components are equal to that of the whole mixture. Using expressions for polarisation factor and monochromatic Lorentz factor for powder method, one obtains

$$\frac{I_1}{I_2} = \frac{m_1 V_{oi}^2}{m_2 V_{oi}^2} \left| \frac{F_1^2}{F_2^2} \right| \frac{\left(1 + \cos^2 2\theta\right)}{\sin^2 \theta \cos \theta} \frac{1}{\rho_2 W_1}$$

$$\frac{I_2}{I_1} = \frac{m_2 V_{oi}^2}{m_1 V_{oi}^2} \left| \frac{F_2^2}{F_1^2} \right| \frac{\left(1 + \cos^2 2\theta\right)}{\sin^2 \theta \cos \theta} \frac{\rho_1 W_2}{\rho_2 W_1}$$
where $W_1$, $W_2$ = weight fractions of components in mixture.

For a mixture of a partially crystalline polymer and a completely crystalline standard substance, the difference between the ratio of the absolute intensities of any diffraction maximum calculated as above and that obtained by experiment must be proportional to the $\%$ crystalline order of the polymer.

If $p$ and $s$ indicate polymer and standard substances respectively and $x$ is the crystalline order of the polymer then

\[
\frac{I_p}{I_s} = \frac{m_p V_p^2}{m_s V_s^2} \left(\frac{1 + \cos^2 \theta}{\sin^2 \theta \cos \theta}\right)_p \cdot \frac{\rho_s W_p}{\rho_p W_s} \cdot x
\]

The standard is chosen so that its pattern is clear of the pattern from the amorphous component of the sample under investigation. The standard should have few diffracting lines, and an absorption coefficient resembling that of the sample. In this work hexamine is used as the standard.

Since the polymer sample is required in the form of a powder, so that it may be mixed with the standard, only two polyethylenes were examined. These are a high density and a low density powders. Weighed amounts of the polymer were mixed together and then compacted into a disc.

The following data were used in the calculation of crystallinity.

**Polyethylene data:**

| Indices of Plane | $^\circ \theta$ | $j$ | $V_o$ | $\rho$ | $\frac{1 + \cos^2 \theta}{\sin^2 \theta \cos \theta}$ | $|F|$ |
|------------------|---------------|-----|-------|-------|---------------------------------|------|
| 110              | 21.5          | 4   | 93    | 1.0   | 57.20                           | 16   |
| 200              | 24.0          | 2   | 93    | 1.0   | 44.05                           | 14.86|

$|F|$ values obtained from Corradini et al.
Crystallinity ($x_c$) was calculated from

\[
\frac{I_p}{I_s} = \frac{J_p V_p^2 \cos^2 (L_p) \rho_p W_p}{J_s V_s^2 \cos^2 (L_s) \rho_s W_s} x
\]

For each mixture two measurements of the crystallinity were obtained by comparing the 110 and 200 peaks separately with the standard.

### 2.2.4. Group 3 methods

There are a large number of methods based on equation

\[
x_c = \frac{I_c}{I_c + I_a}
\]

These methods all have the advantage that they are, in general, relatively easy to carry out, may be applied to any semi-crystalline polymer over a wide range of crystalline orders and they do not require any special sample treatment such as mixing with a standard. Unfortunately the simplicity of the methods imposes a limitation on the validity of the determined value expressed on an absolute scale. In a series of polyethylenes, the crystallinities determined by a particular method, will be meaningful, and reveal any differences between the polymers.

A number of methods are considered here. The reason for this is to compare the performance of any particular method with others, and to obtain some reference by which literature values, using these methods, may be placed on a similar scale.

In essence the methods represent the different ways of separating and comparing the two phases of the diffraction pattern, represented by the Bragg peaks and amorphous background. The methods are outlined as follows:

| Indices of plane | $\theta$ | $j$ | $V_0$ | $\rho$ | $\frac{1+\cos^22\theta}{\sin^2\theta \cos\theta}$ | $|F|$ |
|------------------|---------|-----|-------|-------|-----------------------------------------------|------|
| 110              | 17.9    | 12  | 346   | 1.345 | 86.07                                         | 44.55|
| 200              | 25.5    | 6   | 346   | 1.345 | 39.94                                         | 19.4 |
The method consists of drawing a smooth line through the upper limit of the amorphous scattering. The base line, in the case of polyethylene, is drawn by joining the background at 15.5°2θ and 26°2θ. The process is shown in fig 6. The areas of the crystalline peaks (I_{110} and I_{200}) and the amorphous scatter A, are measured and used direct in the equation

\[ \text{Crystallinity } x_c = \frac{I_{110} + I_{200}}{I_{110} + I_{200} + A} \times 100\% \]

2.2.4.2 The Matthews, Peiser & Richards method

The amorphous scatter is divided off by a procedure which takes into account the actual shape of the amorphous scattering pattern. In polyethylene, the maximum of the amorphous scatter is at 19.7°. A line drawn from the point on the trace at 19.7°2θ to a tangent to the curve at 26°2θ is used to set the upper limit of the amorphous region. The crystalline peak and amorphous scatter are then multiplied by a factor which corrects it for Lorentz polarisation and takes into account the fact that the scattering factor changes with angle.

\[ f(2\theta) = \frac{(L_p)^{-1}}{\sum f_n^2} \]

\[ C_i = \int_A \frac{I(2\theta)(L_p)^{-1}d2\theta}{\sum f_n^2} \]

Where

- \( C_i \) = correction factor for crystalline peaks.
- \( C_A \) = correction factor for amorphous band
- \( A \) = Area of the amorphous band
- \( I(2\theta) \) = Intensity of the amorphous band at various 2
- \( A_i \) = Area of crystalline peaks

The % crystalline order is given by:

\[ \text{Crystalline order } = \frac{\sum C_i A_i \times 100}{C_A A + \sum C_i A_i} \% \]
Fig. 6. Straight ratio method.
In the case of polyethylene the correction factors are as follows:

\[
\text{Crystallinity} = \frac{I_{110} + 1.36I_{200}}{I_{110} + 1.36I_{200} + 0.316A} \times 100\%
\]

2.2.4.(3) The Hermans & Weidinger method

This method requires at least two samples of appreciably differing crystalline orders.

The method is to take two measurement parameters from the diffraction pattern, one of which is associated with the amorphous region, and the other with the crystalline region for each sample. The two parameters are then plotted against each other for each sample and a straight line drawn through the points, fig 7. This line then represents the calibration curve for all samples.

A more accurate calibration may be drawn if a number of samples are available of widely differing crystallinities.

This method has the advantage over the previous two in that it is not necessary to estimate where to put in the amorphous background. Instead of taking the amorphous area as a measurement parameter, it is possible to take the height of the background \( a_p \) at any particular 2\( \theta \) position, fig 8. This height \( a_p \) must be clear of the region of the profile in which appreciable diffraction from the crystalline component occurs.

The crystalline measurement parameter is best taken as an area. The boundary of this measurement parameter may be chosen so that it does not represent the total crystalline area but a proportion of it. Therefore, as long as the boundary is the same in all profiles, it will include the same proportion of the total crystalline area, and so it is not necessary to know the total crystalline area, or the exact division between the two phases.
Crystalline measurement parameter.

The line represents the calibration for the method.

Amorphous measurement parameter.

Fig. 7. Calibration curve for Hermans and Wiedinger method.

Fig. 8. Crystalline and amorphous measurement parameters for Hermans and Wiedinger method.
2.3. Results and Discussion

The crystallinity values determined using Corradini's method, the straightforward ratio method, the Matthews, Peiser and Richards method and the Hermans & Weidinger's method are given in tables 3 to 6 respectively. The calibration graph used in the Hermans & Weidinger method is shown in fig 7. The results are summarised in table 7.

From the summary it is apparent that all the methods rank the series of polyethylenes on the same relative scale. The straightforward ratio method gives values which are consistently below those of the other methods. The reason for this is that, by making no assumptions as to the shape of the amorphous hump, on drawing a smooth line through the background, one ignores the tails of the peaks. Thus the amorphous region is over estimated by this method.

The method of Matthews et al gives values of the crystallinity which, compared with the other two methods, appear to be on the high side. This probably comes from an incorrect value for the correction factor for the amorphous band. In the calculation of the correction factor, the amorphous hump is assumed to be symmetrical about the maximum at $19.7^\circ 2\theta$. At high amorphous contents it is apparent that the hump is unsymmetrical and should be more heavily weighted on the high $2\theta$ side. The Hermans & Weidinger and the Corradini methods give similar results, although the former are slightly lower over the whole range.

Since all the methods, excepting the straightforward ratio method, give substantially similar results, other than the minor variations mentioned above, the Matthews method was chosen for use in subsequent studies in this work. The reason for this choice was the simplicity and applicability to a wide range of crystalline orders.
TABLE 3

Results using the Corradini method

<table>
<thead>
<tr>
<th>Mixture Polyethylene: Hexamine</th>
<th>Area of 110 peak</th>
<th>Area of 200 peak</th>
<th>Area of Standard peak 17.9°2</th>
<th>Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>6.2 sq.cm.</td>
<td>14.85 sq.cm.</td>
<td></td>
<td>78.6%</td>
</tr>
<tr>
<td></td>
<td>2.1 sq.cm.</td>
<td></td>
<td></td>
<td>80.2%</td>
</tr>
<tr>
<td>4:1</td>
<td>11.1 sq.cm.</td>
<td>6.5 sq.cm.</td>
<td></td>
<td>80.4%</td>
</tr>
<tr>
<td></td>
<td>3.6 sq.cm.</td>
<td></td>
<td></td>
<td>78.5%</td>
</tr>
</tbody>
</table>

Low density powder

| 2:1                           | 19.4 sq.cm.     | 33.3 sq.cm.     |                             | 55.9%         |
|                              | 6.8 sq.cm.      |                 |                             | 56.9%         |

TABLE 4

Results using the straight ratio method

<table>
<thead>
<tr>
<th>Polymer</th>
<th>I_{110} sq.cm.</th>
<th>I_{200} sq.cm.</th>
<th>A sq.cm.</th>
<th>% crystalline order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Homopolymer</td>
<td>21.7</td>
<td>7.3</td>
<td>5.6</td>
<td>83.8</td>
</tr>
<tr>
<td>Copolymer 1</td>
<td>20.65</td>
<td>5.5</td>
<td>7.2</td>
<td>78.4</td>
</tr>
<tr>
<td>High density powder</td>
<td>14.65</td>
<td>8.00</td>
<td>12.6</td>
<td>64.4</td>
</tr>
<tr>
<td>Copolymer 2</td>
<td>18.05</td>
<td>5.45</td>
<td>10.15</td>
<td>69.4</td>
</tr>
<tr>
<td>Low density pe</td>
<td>13.7</td>
<td>2.95</td>
<td>16.35</td>
<td>50.4</td>
</tr>
<tr>
<td>Low density powder</td>
<td>13.25</td>
<td>2.5</td>
<td>15.55</td>
<td>50.2</td>
</tr>
</tbody>
</table>
### TABLE 5
Results using the Matthews, Peiser and Richards Method

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$I_{110}^{sq. cm.}$</th>
<th>$I_{200}^{sq. cm.}$</th>
<th>$A^{sq. cm.}$</th>
<th>Crystalline order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Homopolymer</td>
<td>21.9</td>
<td>7.65</td>
<td>4.95</td>
<td>88.9</td>
</tr>
<tr>
<td>Copolymer 1</td>
<td>21.4</td>
<td>6.05</td>
<td>6.45</td>
<td>84.9</td>
</tr>
<tr>
<td>High density powder</td>
<td>15.8</td>
<td>9.85</td>
<td>9.75</td>
<td>78.6</td>
</tr>
<tr>
<td>Copolymer 2</td>
<td>18.85</td>
<td>6.1</td>
<td>8.90</td>
<td>78.9</td>
</tr>
<tr>
<td>Low density pe</td>
<td>14.45</td>
<td>3.4</td>
<td>15.15</td>
<td>60.7</td>
</tr>
<tr>
<td>Low density powder</td>
<td>14.3</td>
<td>2.9</td>
<td>14.0</td>
<td>61.5</td>
</tr>
</tbody>
</table>

### TABLE 6
Results using the Hermans & Weidinger Method

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Amorphous parameter counts/16 sec at 18°2 less background</th>
<th>Crystalline parameter $I_{110} + I_{200}^{sq. cm.}$</th>
<th>Crystalline order using calibration from graph</th>
</tr>
</thead>
<tbody>
<tr>
<td>Homopolymer</td>
<td>1150</td>
<td>29.55</td>
<td>89.4</td>
</tr>
<tr>
<td>Copolymer 1</td>
<td>1700</td>
<td>27.45</td>
<td>83.6</td>
</tr>
<tr>
<td>High density powder</td>
<td>2364</td>
<td>25.65</td>
<td>76.6</td>
</tr>
<tr>
<td>Copolymer 2</td>
<td>2779</td>
<td>24.95</td>
<td>74.2</td>
</tr>
<tr>
<td>Low density pe</td>
<td>4441</td>
<td>17.85</td>
<td>45.7</td>
</tr>
<tr>
<td>Low density powder</td>
<td>4975</td>
<td>17.2</td>
<td>52.9</td>
</tr>
<tr>
<td>Polymer</td>
<td>Straight ratio method</td>
<td>Matthews Peiser &amp; Richards method</td>
<td>Hermans &amp; Wiedinger method</td>
</tr>
<tr>
<td>--------------------</td>
<td>-----------------------</td>
<td>----------------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>Homopolymer</td>
<td>83.8%</td>
<td>88.9%</td>
<td>89.4%</td>
</tr>
<tr>
<td>Copolymer 1</td>
<td>78.4%</td>
<td>84.9%</td>
<td>83.6%</td>
</tr>
<tr>
<td>High density powder</td>
<td>64.4%</td>
<td>78.6%</td>
<td>77.6% Mean value 79.4%</td>
</tr>
<tr>
<td>Copolymer 2</td>
<td>69.4%</td>
<td>77.9%</td>
<td>74.2%</td>
</tr>
<tr>
<td>Low density pe</td>
<td>50.4%</td>
<td>60.7%</td>
<td>56.7%</td>
</tr>
<tr>
<td>Low density powder</td>
<td>50.2%</td>
<td>61.5%</td>
<td>52.9% Mean value 56.4%</td>
</tr>
</tbody>
</table>
3.1. Unit cell dimensions of polymers

The unit cell dimensions serve to define the average repeating unit, which extends in three dimensions to make up the crystalline region. Their knowledge leads to the density of the crystalline phase, and if the bulk density is known some information on the density of the amorphous phase is available. In a given polyethylene, the orthorhombic unit cell dimensions are not unique, but vary systematically with the processing conditions of crystallisation, annealing and deformation, or by changes in the molecular chain, for example branding and molecular weight. The characterisation of the unit cell dimensions is therefore considered useful in the fuller understanding of structure and properties in polymers.

3.2. Methods

There are a number of recommended procedures for the determination of accurate unit cell dimensions in solids. Usually these involve the measurement of the peak positions of a large number of reflections, followed by the correction of various instrumental effects, and least squares refinement of the unit cell dimensions. An alternative method is to use an internal standard. Since the positions of the standard peaks are known, their actual positions may be used to correct the unknown peaks in a near range of 2θ values.

Unfortunately, these methods cannot be applied to polymers without modification. The diffraction pattern of semi-crystalline polymers, for example polyethylene, shows a few strong peaks and a number of much weaker peaks. In highly crystalline material it is possible to measure up to about 20 resolved peaks. However, in less crystalline material the weaker peaks cannot be so easily resolved from the background. Thus, for a method which may be applied over
the widest range of crystalline orders, one can only make use of the polyethylene's two strongest peaks, i.e. 110 and 200. From these one can obtain the unit cell a- and b-dimensions. Although the c-dimension is not obtained this is not too drastic a loss since, to the first approximation, it is little affected by conditions or changes in the backbone chain.

With only two peaks, the correction and least squares extrapolation methods must be rejected, and instead, use made of the internal standard method. Since the method must work on the widest range of material forms, we must consider a method which is applicable to both sheet and powder material. It is not desirable to mix the standard prior to processing into a form suitable for examination, for example, sheet, since its presence may influence the crystallisation behaviour. The procedure that has been adopted in this work is to brush a very small quantity of a characterised graphite on to the surface of the sheet. The quantity is so small, less than 0.001g, that it does not interfere with the alignment of the specimen, but because the graphite packs preferentially with the 002 planes perpendicular to the polymer surface, it gives a very strong 002 reflection. This 002 reflection is sufficiently close to the 110 and 200 polyethylene reflections to serve as a useful angular standard. Any possible variation in the spacing of the graphite is overcome by using a single, characterised, source of the material.

From the diffractometer trace, the angular spacing of the 110 and 200 polyethylene reflections may be determined accurately with reference to the graphite. The unit cell a- and b-dimensions of the polymer are then calculated from the equation

\[
\left( \frac{2\sin \Theta}{\lambda} \right)^2 = \frac{h^2}{a^2} + \frac{k^2}{b^2} \quad \ldots \ldots \quad 3.1
\]
Before the results of this method are considered, the effect of the special property of the low absorption coefficient in polymers must be considered.

### 3.3. Effect of low absorption in polymers

In the usual reflection diffractometry technique the sample face is flat, the primary and diffracted beams make equal angles with the sample face, the distances from source to sample and from sample to receiving slit are equal and the absorption in the sample is so high that diffraction takes place essentially in the surface layer of the sample, fig. 9. When the absorption in the sample is low, as in polymers, diffraction also takes place in the interior of the sample, and there is both an asymmetric broadening and a shift of the measured peak position to lower $2\theta$ values.

A method for correcting both peak shape and position is given by Keating and Warren. If $A$ is the cross sectional area of the primary beam, the effective volume between depths $t$ and $t+dt$ is $dV = A dt / \sin \theta$, see fig. 9. Let $g/2\theta$ represent the internal distribution which would be measured at the receiving slit if the absorption in the sample were high. Let $I(2\theta_m)$ represent the intensity distribution measured at the receiving slit, where $2\theta_m$ is the measured scattering angle.

\[
I(2\theta_m) = \int_{t=0}^{t=T} \exp \left[-\frac{2\mu t}{\sin \theta}\right] \frac{A}{\sin \theta} \, dt \ldots \ldots \ldots \ldots 3.2.
\]

Since

\[
2\theta = 2\theta_m + \frac{2t\cos \theta}{R}
\]

\[
h(2\theta_m) = \int_{2\theta = 2\theta_m + U}^{2\theta = 2\theta_m + V} \exp \left[-\frac{(2\theta - 2\theta_m)}{2\theta_m - 2\theta_m}\right] g(2\theta) \, d(2\theta) \ldots \ldots \ldots 3.3.
\]

where

\[
h(2\theta)_m = \frac{\sin 2\theta}{AR} \cdot I(2\theta_m)
\]

\[
\alpha = \frac{2\mu R}{\sin 2\theta_m}
\]

\[
U = 2T\cos \theta_m
\]

\[
R
\]
Writing $3.3$ in a more convenient form for differentiation with respect to $2\Theta_m$

$$h(2\Theta_m) = \exp\left[\alpha(2\Theta_m)\right] \int_{2\Theta = 2\Theta_m}^{2\Theta = 2\Theta_m + \nu} \exp\left[-\alpha 2\Theta\right] g(2\Theta) d(2\Theta) \quad 3.4.$$ 

Differentiating and combining with $3.4$

$$g(2\Theta_m) = \alpha h(2\Theta_m) - \frac{dH(2\Theta_m)}{d(2\Theta_m)} + \exp\left[-\alpha \nu\right] g(2\Theta_m + \nu)$$

This leads to a series expression for $g(2\Theta_m)$

$$\frac{1}{\alpha} g(2\Theta_m) = (h - \frac{1}{\alpha} h') 2\Theta_m + (h - \frac{1}{\alpha} h') 2\Theta_m + \nu \exp\left[-\alpha \nu\right] + ..$$

where $\nu = 2\mu \tau / \sin \Theta$, $h' = dh/d(\Theta_m)$ and $g(2\Theta_m)$ is expressed in radians for large $\alpha U$ the series converges rapidly. An example of the peak profile correction by this method is given in fig. 10.

Since the above method requires considerable effort in its execution, simpler methods have been considered. Wilchinsky has suggested that the problem may be overcome to some extent by examination of the sample in a transmission mode. Here some broadening occurs due to the beam divergence. This is kept to a minimum by keeping the slit controlling the beam divergence reasonably narrow. Wilchinsky suggests the use of a $1/6^\circ$ divergence slit.

In this present study a third method has been considered, that of using a thin sample. If the sample thickness is of the order of $0.0025 \text{ cm}$, very little defocussing will result from the sample thickness. The sample may be mounted on an aluminium plate which does not give rise to x-ray scattering over the range $19^\circ$ to $27^\circ$. 
Fig. 9. Arrangement of flat sample in a normal diffractometer.
Fig. 10  110 peak of polyethylene using CuKα and a sample T = 1.0mm, before and after correction for low absorption.
The variation in unit cell a- and b-dimensions with thickness of the polymer film are given in table 8. The a- and b-dimensions of a homopolymer and two copolymers of polyethylene, determined by the methods discussed above, are given in table 9. Also included in the table are the results for polymer samples 1 mm in thickness, where no correction for absorption has been made.

The results show just how much the absorption effect can increase the unit cell dimensions. The fact that the unit cell dimensions depend on the method of measurement and correction is important, especially if one attempts to make use of the data published by others. The dependence of the unit cell dimensions on the sample thickness is clearly shown. The observation that the unit cell dimensions for the thin specimen with no correction are less than those of the thick sample, after applying the mathematical correction, suggests that the former are the more 'absolute'. If such 'absolute' values are desired it is probably easiest in fact to prepare very thin specimens. However, the use of this type of specimen has some disadvantages. The preparation of the thin sample probably induces some orientation. This is the most likely reason for the erratic variation in the crystallinity of the two thinnest samples (see table 8).

Another objection which arises from this is that the crystallinity would have to be measured on a second thicker sample, and thus precludes data collection from a single sample.

In many cases the 'absolute' values of the unit cell dimension are not required. Relative changes in both unit cell dimension and crystallinity can then best be followed using a thick sample with no correction. This is the method adopted in this work.
TABLE 8
The effect of thickness on the measured unit cell dimensions of polyethylene

POLYMER RIGIDEX 25

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Crystallinity</th>
<th>Unit Cell Å</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a</td>
</tr>
<tr>
<td>0.001&quot;</td>
<td>92%</td>
<td>7.3883</td>
</tr>
<tr>
<td>0.002&quot;</td>
<td>72%</td>
<td>7.399</td>
</tr>
<tr>
<td>0.004&quot;</td>
<td>79.8%</td>
<td>7.403</td>
</tr>
<tr>
<td>0.008&quot;</td>
<td>81.3%</td>
<td>7.424</td>
</tr>
<tr>
<td>0.016&quot;</td>
<td>80.4%</td>
<td>7.426</td>
</tr>
<tr>
<td>0.040&quot;</td>
<td>82.0%</td>
<td>7.433</td>
</tr>
</tbody>
</table>
### Table 9

Unit Cell a- and b- dimensions obtained by the Various Methods

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thick sample corrected by Warren's method</th>
<th>Thick sample examined in transmission (Wäschinsky's method)</th>
<th>Uncorrected Thin sample 0.025 cm</th>
<th>Uncorrected Thick sample 0.1 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rigidex 25</td>
<td>a = 7.402</td>
<td>a = 7.418</td>
<td>a = 7.388</td>
<td>a = 7.432</td>
</tr>
<tr>
<td></td>
<td>b = 4.940</td>
<td>b = 4.947</td>
<td>b = 4.933</td>
<td>b = 4.953</td>
</tr>
<tr>
<td>Ethylene/propylene copolymer</td>
<td>a = 7.465</td>
<td>a = 7.478</td>
<td>a = 7.450</td>
<td>a = 7.498</td>
</tr>
<tr>
<td></td>
<td>b = 4.947</td>
<td>b = 4.955</td>
<td>b = 4.940</td>
<td>b = 4.962</td>
</tr>
<tr>
<td>Ethylene/butene-1 copolymer</td>
<td>a = 7.464</td>
<td>a = 7.480</td>
<td>a = 7.448</td>
<td>a = 7.494</td>
</tr>
<tr>
<td></td>
<td>b = 4.948</td>
<td>b = 4.956</td>
<td>b = 4.942</td>
<td>b = 4.964</td>
</tr>
</tbody>
</table>
CRYSsTALLITE SIZE AND PERFECTION

4.1. Crystallite size and perfection

It is well established in metals that both the size of the diffracting region (crystallite size) and the perfection (micro-strain) both influence the breadth of the diffraction peaks.

The breadth of the diffraction peak $\beta$, due to crystallite size, is given by

$$\beta = \frac{k \lambda}{L \cos \Theta}$$

where $k$ is a constant, $\lambda$ is the wavelength of the x-rays and $\Theta$ the diffraction angle.

The breadth of the diffraction peak due to micro-strain, $\varepsilon$, is given by

$$\beta = k' \tan \Theta \varepsilon$$

These two factors may be combined, assuming a Gaussian peak shape, in the equation

$$\left(\frac{B_0 \cos \Theta}{\lambda}\right)^2 = \frac{k_1}{L^2} + k_2 \varepsilon^2 \left(\frac{\sin \Theta}{\lambda}\right)^2 \ldots \ldots \ (4.1)$$

where $B_0$ is the peak breadth after correction for instrumental effects.

In the analysis of metals, there are a number of methods which use the above type of equation to interpret the peak breadth in terms of crystallite size and micro-strain. The basis of them is that the crystallite size is independent of the order of the diffraction peak, i.e. 110, 220, whereas micro-strain is dependent on order. One of the simpler methods to apply is the Integral breadth method in which a plot of $(B_0 \cos \Theta/\lambda)^2$ vs $(\sin \Theta/\lambda)^2$ is drawn. The slope of the line is proportional to the micro-strain $\varepsilon^2$ and the intercept proportional to $1/L^2$.

4.2. Crystallite size and perfection in polymers

In principle the above ideas are applicable to polymers; however there are both theoretical and practical limitations to their applicability.
4.2.1. Paracrystalline Distortion

There is the possibility in crystalline polymer of a second type of distortion apart from micro-strain. This is paracrystalline distortions. If micro-strains are present, the lattice constants are distributed around an average value with any elastically distorted crystallite. With paracrystalline distortions any fluctuation between successive atoms is transmitted from neighbour to neighbour and thus influences the whole of the lattice. The fluctuation of distances between n-th neighbours increases with \( \sqrt{n} \). The two types of disorder are shown diagramatically in figure 11. In the case of paracrystalline distortion, the line broadening of the diffraction peak is determined by the relative distance fluctuations between adjacent lattice planes, and is expressed in Hosemann's \( \varepsilon \)-value,\(^{29}\)

\[
\varepsilon_{hkl} = \frac{\sqrt{\Delta^2 d_{hkl}}}{d_{hkl}} \quad \ldots \ldots \quad (4.2)
\]

\[
\Delta^2 d_{hkl} = \bar{d}_{hkl}^2 - d_{hkl}^2 \quad \ldots \ldots \quad (4.3)
\]

and

\[
\beta_s^2 = \frac{1}{d_{hkl}^2} \left( \prod \varepsilon_{hkl}^h \right)^4 \quad \ldots \ldots (4.4)
\]

where \( \beta_s \) is the peak breadth with \( S = 2 \sin \theta / \lambda \), and \( h \) is the order of the reflection.

As shown previously, the term for distortion must be combined with the term for crystallite size. Again, assuming a Gaussian combination,

\[
\beta_s^2 = \frac{1}{L^2} + \frac{1}{d_{hkl}^2} \left( \prod \varepsilon_{hkl}^h \right)^4 \quad (4.5)
\]

This may be compared with the similar equation but taking the distortion as micro-strain,

\[
\beta_s^2 = \frac{1}{L^2} + \frac{16}{d_{hkl}^2} \varepsilon^2 h^2 \quad \ldots \ldots (4.6)
\]
Fig. 11. Distortions of first and second order.
There are two problems to solve in polymers. One, to determine the nature of the distortion (i.e. paracrystalline or micro-strain) and two, to quantify that distortion. The separation of the two effects require the study of at least three diffraction orders, from which plots of $\delta \beta^2$ vs $h^2$ and $h^4$ can be used to determine the type of distortion. A number of such studies have been reported. However, in most cases rather special polymeric material has been examined. These include orientated fibrous material; either natural or drawn fibres. Orientation serves either to separate the $(hko)$ reflections, or gives rise to a large number of orders along the chain direction. Whether the conclusion reached in these studies, i.e. that the plot of $\delta \beta^2$ vs $h^4$ does give a straight line, indicating paracrystalline distortion, can be taken as confirmation that this is the state in truly bulk material, is open to question.

One such study on bulk material is that on isotactic polystyrene. Since isotactic polystyrene has a high crystal symmetry ($\text{trigonal}$), it gives numerous $(hko)$ reflections which are well resolved. The study showed that, at relatively low value of distortion in the bulk state, it was not possible unequivocally to confirm the presence of micro-strain or paracrystallite distortions. The actual results tended towards the former.

In bulk polyolefins, and polyethylene in particular, it is not possible to observe three diffraction orders, and so determination of the nature of the disorder in the crystalline regions is out of the question. However, in order to proceed in this present study the assumption that the disorders are paracrystalline in nature has been made. This model intuitively appears to fit the situation the better of the two models. Even with this assumption the actual quantitative determination of the level of disorder still presents considerable difficulties.

These difficulties include:
1. Absence of higher orders of reflection.
2. Presence of a diffuse, structured background.
3. Overlapping reflections.
4. Lack of reliable crystalline standards to measure instrumental broadening.

Any method adopted must overcome or minimise such problems.

In this study two methods are considered.

4.3. Experimental methods

4.3.1. Integral breadth method

This method makes direct use of the equation (4.5)

\[ \beta_\delta^2 = \frac{1}{L^2} + \frac{1}{d^2} \]

and requires the study of at least two diffraction orders.

The working details of the method are given in the following steps.

1. Collection of data on a diffractometer trace. In this study the 110, 220 and 200, 400 peaks have been examined.

2. The peaks are separated from the background. The 110 and 200 peaks are separated in a similar manner to that described in the section on crystallinity. In general, this involves drawing the baseline between the two lowest points at each end of the peak tail. The 220 peak has to be resolved, by hand, from its partially overlapping neighbour. The intensity at step intervals of 0.05°2θ are measured from the trace.

3. The instrumental peak profile is obtained from a graphite standard, run under similar conditions to the polymer sample.

4. Correction of the peak profile for instrumental broadening using the Stoke's deconvolution procedure. 34

5. Calculation of the integral breadth from the corrected profile.

\[
\text{Integral breadth} = \frac{\text{Peak area}}{\text{Maximum peak height}}
\]

6. Plot of \( \beta_\delta^2 \) against \( h^4 \) (an example is shown in fig. 12).

7. Calculation of the crystallite size from the intercept and paracrystalline distortion from the slope.
Slope $\propto$ paracrystalline distortion.

Intercept $\propto$ reciprocal of the crystallite size.

Fig. 12. Plot of $\beta_s^2$ vs $h^4$. 
4.3.2. The variance/range, fourth moment/range method

Another method considered is one which makes use of a single peak to obtain size and distortion terms. It therefore, in principle, offers important advantages in use with polymers. The method considers the variance and fourth moment/ranges of the peak.

Let \( \psi \) and \( \psi \) represent the fourth central moment and the variance respectively. If the line broadening (corrected for instrumental broadening) is attributed to finite crystallite size and paracrystalline distortions, the specimen line profile would then be a convolution of the line profiles which are obtained when each of these effects is separately considered. The additivity property of the cumulants gives the following relation for the fourth central moment of the pure diffraction profile,

\[ U_{PD} = U_P + U_D + 6 \psi P \psi D \]  

where the suffixes P, D indicate the components for crystallite size and paracrystalline distortion respectively.

Kulshreshtha et al have shown that the fourth central moment is made up from the series

\[ U_{PD} = \frac{(\alpha + \beta)\sigma^3}{2^4 \pi^2} + \frac{3\alpha \beta \sigma^2}{2^4 \pi^4} - \frac{(\alpha^3 + \beta^3 + 6\alpha^2 \beta + 6\alpha \beta^2)\sigma}{8 \pi^4} 
+ \frac{\alpha^4 + \beta^4 + 6\alpha^2 \beta^2}{16 \pi^4} \]  

where \( \alpha = \frac{2\pi^2 g^2 k^2}{b} \) and \( \beta = \frac{1}{M} \)

is the range over which the variance and fourth central moments are considered.

In the expression, only the terms containing \( \sigma^3 \) and \( \sigma^2 \) will have appreciable magnitudes. The moment range function may be represented by means of the polynomial
\[ U_{PD}(\sigma) = \sum_{n=3}^{\infty} a_n \sigma^n \quad \ldots \ldots \quad (4.9) \]

with the coefficient of interest

\[ a_2 = \frac{3\alpha^2}{2\pi^4}, \quad a_3 = \frac{(\alpha+\beta)}{24\pi^2} \]

The value of \((\alpha + \beta)\) can be obtained either from the slope of the variance range function or from the coefficient \(a_3\).

Knowing the values

\[(\alpha + \beta) = y \quad \text{and} \quad \alpha \beta = z\]

one can calculate

\[ \alpha = y + \sqrt{y^2 - 4z} \quad \text{and} \quad \beta = y - \sqrt{y^2 - 4z} \]

or

\[ g^2 = \frac{b}{2\pi^2k^2} \left[ y + \sqrt{y^2 - 4z} \right] \quad \ldots \ldots \quad (4.10) \]

and

\[ K = \frac{2}{y + \sqrt{y^2 - 4z}} \quad \ldots \ldots \quad (4.11) \]

The special feature of the variance range function is that the true background level can be determined accurately. The true background gives a linear portion over a large range. The difficulty with polymeric x-ray diffraction is that the background has a curved shape due to the presence of the amorphous type scatter. If an arbitrary background is selected, this may be modified by addition of or subtraction of further components until the corresponding variance-range function shows a large linear portion, see fig. 13. The background giving such a portion may be used in the subsequent calculations.

The details of the method are given in the following steps.

(1) Collection of intensity data over 110 and 200 peak profiles and the graphite standard in a similar manner to that for the integral breadth method.
Fig. 13. 110 polyethylene peak profile with three different backgrounds and corresponding variance-range curves.
(1) Computation of the peak variance/range functions using a number of positions for the peak base line (see fig.13).

(3) Selection of the best linear fit for the variance/range function. In practice, this is found to occur when the base line is taken as about 85% of that obtained using the line joining the two lowest portions, either end of the peak (fig.13). The base line giving the linear portion is used in subsequent stages.

(4) Correction of the intensity data for Lorentz polarisation and absorption.

(5) Computation of the variance/range and fourth moment/range functions.

(6) Summation of the two corrected functions using the equation

\[ U'_{p0} (\sigma) = (U_b - U_i) - 6W_i (W_b - W_i) \]

where the subscripts b and i refer to the polymer sample and instrumental standard sample respectively.

(7) Fitting the polynomial \[ \sum_{n=2}^{n=3} a_n \sigma^n \] to the calculated function \( \mu_{PD}(\sigma) \).

(8) Use of the coefficients \( a_2 \) and \( a_3 \) to obtain \( q \) and \( \bar{N} \) as shown in equation.

4.3.3. Polymer samples examined

A number of ethylene homo-and co-polymers have been examined by the means of these two methods. The details of the polymers are included, with the determined values for crystallite size and distortion, in table 10. The polymer sheets were prepared, for this examination, by compression moulding, followed by an annealing treatment.

4.4.4. Results and discussion

From table 10 it is evident that the integral breadth method gives larger values for the crystallite size, and smaller values for the distortion, than the variance-fourth-moment method. This is most probably due, in part at least, to the selection of the base
line. Because the base line in the variance-fourth-moment method is set below the 'observed' base line, as used in the integral breadth method, it will have a larger component of intensity in the peak tails. Since the contribution from the tails represents the diffraction effect of the smaller crystallites, i.e. broad peak profile, inclusion of these smaller crystallites will reduce the average size as measured by the variance-fourth-moment method.

The determined values show good agreement between the methods. Unfortunately, part of this agreement may be the fact that the resulting values from the variance-fourth-moment method depend on the base line correction. Given the choice of a number of base line positions, which all give reasonably linear variance range functions, it is perhaps easy to take the one which gives values for size and perfection in a predefined range. Thus, having previously determined the size and distortion values using the integral breadth method, some subconscious matching of results from the second method may have occurred. In this respect the integral breadth method has the advantage that it is straightforward and is non-subjective, although it suffers the disadvantage of requiring two orders of reflection.

Some consideration may be given to the actual results. The results may be summarised as follows:

(1) The crystallite sizes, normal to the 110 planes, are larger than those normal to the 200 planes.

(2) Paracrystalline distortions are largest in the direction normal to the 200 planes.

(3) Quenching the sample results in a reduction of the crystallite size. The distortion remains relatively unchanged.

(4) Methyl and ethyl branches cause a large decrease in crystallite size.
### Table 10
Determination of crystallite size and paracrystalline distortion in ethylene homo and co polymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Integral breadth</th>
<th>Single peak variance method</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Size Å D</td>
<td>Paracrystalline Distortion %</td>
<td>Size Å M</td>
</tr>
<tr>
<td>Rigidex Homopolymer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annealed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cryst = 86.4%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(110) plane</td>
<td>670</td>
<td>1.43</td>
<td>570</td>
</tr>
<tr>
<td>(200) plane</td>
<td>380</td>
<td>1.65</td>
<td>350</td>
</tr>
<tr>
<td>Rigidex Homopolymer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rapidly cooled</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cryst = 81.4%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(110) plane</td>
<td>500</td>
<td>1.38</td>
<td>520</td>
</tr>
<tr>
<td>(200) plane</td>
<td>320</td>
<td>1.76</td>
<td>300</td>
</tr>
<tr>
<td>Ethylene/Propylene Copolymer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.6 Me/1000C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cryst = 72%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(110) plane</td>
<td>420</td>
<td>1.84</td>
<td>390</td>
</tr>
<tr>
<td>(200) plane</td>
<td>260</td>
<td>2.02</td>
<td>270</td>
</tr>
<tr>
<td>Ethylene/Butene-1 Copolymer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.1 Et/1000C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cryst = 70%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(110) plane</td>
<td>360</td>
<td>1.68</td>
<td>360</td>
</tr>
<tr>
<td>(200) plane</td>
<td>320</td>
<td>2.43</td>
<td>330</td>
</tr>
<tr>
<td>Ethylene/Hexene-1 Copolymer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.7 Bu/1000C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cryst = 70%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(110) plane</td>
<td>405</td>
<td>1.54</td>
<td>390</td>
</tr>
<tr>
<td>(200) plane</td>
<td>330</td>
<td>1.96</td>
<td>350</td>
</tr>
</tbody>
</table>
size and an increase in distortion. Butyl branches do not affect the size and distortion to the same degree.

In general, these results show that the factors thermal history and branching influence the crystallite size to a greater extent than the paracrystalline distortion. Further consideration of these results is left to section 5.2.2, where the influence of branches on the structure is examined in more detail.
5.1. Structure and properties of polymers

The parameters of structural order discussed in the previous chapters may be altered by two separate mechanisms. Firstly, by altering the polymerisation conditions so as to change the characteristics of the molecular chain. Secondly, by altering the processing conditions under which the chains crystallise. Since the resulting structural arrangements influence the properties of the material, any change in the structure will cause changes in the properties.

Characterisation of the structural order serves two purposes. One, to monitor and quantify the effect on the structure and relate it to the properties. Two, to use the knowledge of the structure to predict the molecular chain characteristics and processing conditions required to give certain properties in future polymers.

5.2. Variation in molecular chain characteristics

5.2.1. Molecular weight and molecular weight distribution

The molecular weight and molecular weight distribution of polymers form one of the basic descriptions of the polymer chains and have a marked effect on the processability and properties of the material. Their effect on structure is demonstrated by the study of a series of molecular weight fractions of Marlex 50.

5.2.1.1. Experimental

Marlex 50 was fractionated at 140°C using a solvent/no solvent technique. Each fraction was weighed and expressed as a percentage of the total polymer; and the molecular weight determined. These are shown in table 11. The fractions and a sample of the unfractionated bulk polymer were compression moulded into sheets and annealed by the procedure described in Chapter 3. The crystallinity of each fraction was determined by the method of Matthews et al.
<table>
<thead>
<tr>
<th>Fr No.</th>
<th>Weight % of fraction</th>
<th>MW</th>
<th>Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D</td>
<td>36.95</td>
<td>3,640</td>
<td>91.7%</td>
</tr>
<tr>
<td>2D</td>
<td>0.90</td>
<td>12,900</td>
<td>90.4%</td>
</tr>
<tr>
<td>3D</td>
<td>7.32</td>
<td>13,200</td>
<td>90.0%</td>
</tr>
<tr>
<td>4D</td>
<td>8.02</td>
<td>20,000</td>
<td>87.6%</td>
</tr>
<tr>
<td>5D</td>
<td>8.08</td>
<td>28,200</td>
<td>81.3%</td>
</tr>
<tr>
<td>6D</td>
<td>9.12</td>
<td>38,100</td>
<td>78.5%</td>
</tr>
<tr>
<td>7D</td>
<td>10.71</td>
<td>92,100</td>
<td>76.1%</td>
</tr>
<tr>
<td>8D</td>
<td>11.60</td>
<td>139,000</td>
<td>76.5%</td>
</tr>
<tr>
<td>9D</td>
<td>5.18</td>
<td>478,000</td>
<td>76.7%</td>
</tr>
<tr>
<td>10D</td>
<td>2.14</td>
<td>473,000</td>
<td>76.2%</td>
</tr>
<tr>
<td></td>
<td>Unfractionated Polymers</td>
<td></td>
<td>88.9%</td>
</tr>
</tbody>
</table>

\[ \sum \text{Crystallinity} \times \text{weight of fraction} = 84.6\% \]
The results show that the crystallinity decreases with increasing molecular weight. Up to a molecular weight of between 30,000 and 40,000 the fall off is rapid, but at higher molecular weights the decrease is gradual, see fig 14. These results may be compared with the work of Tung, who examined the relationship between density and molecular weight in a series of compression moulded molecular weight fractions and unfractionated polymers. The results of Tung, shown in fig. 15, also show levelling off in density above a molecular weight of 40,000.

These results reflect the fact that, under the compression moulding conditions of a relatively rapid crystallisation, the longer chains are not able to move into crystallographic register before the system becomes solid as easily as the shorter chains.

The results show a second effect. If the crystallinity times the weight of each fraction is summed, the value obtained is 84.6%. This value is 4.3% lower than the crystallinity of the unfractionated polymer. This means that each particular fraction crystallises to a greater extent when present in the unfractionated material than when it is crystallised as a separate component. Again, the density values of Tung show a similar behaviour, see fig. 15.

This effect has been examined further by studying a number of melt blends of pairs of the polyethylene fractions. The results are given in table 12. Again, the calculated value of (crystallinity x weight) for the pairs differs from the measured value. However, even with this limited series of samples, it is possible to see that the 'enhancement' in crystallinity in the blend varies between the pairs. The level of the interaction is thus somewhat dependent on the molecular weights of the fractions.

The enhancement in crystallinity could arise in two ways. Firstly, the process of crystallisation may be considered as taking
Fig. 14. Fractionated Marlex 50, % Crystallinity vs Molecular Weight.

Fig. 15. Density vs Molecular Weight Data from Tung.
### TABLE 12

**Blends of the Molecular Weight Fractions**

<table>
<thead>
<tr>
<th>1:1 Mixture</th>
<th>Crystallinity Observed</th>
<th>Crystallinity Calculated</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D + 3D</td>
<td>92.2%</td>
<td>90.8%</td>
<td>+ 1.4%</td>
</tr>
<tr>
<td>1D + 5D</td>
<td>87.8%</td>
<td>86.5%</td>
<td>+ 1.3%</td>
</tr>
<tr>
<td>1D + 10D</td>
<td>83.8%</td>
<td>83.9%</td>
<td>- .1%</td>
</tr>
<tr>
<td>3D + 10D</td>
<td>83.5%</td>
<td>83.1%</td>
<td>+ 0.4%</td>
</tr>
<tr>
<td>5D + 10D</td>
<td>82.2%</td>
<td>78.8%</td>
<td>+ 3.4%</td>
</tr>
<tr>
<td>7D + 10D</td>
<td>75.2%</td>
<td>76.15%</td>
<td>+ 1.05%</td>
</tr>
</tbody>
</table>

**NB.**

The calculated crystallinities were determined by taking the average of the crystallinities for the two separate components in the mixture.
place in a series of steps with decreasing temperature, the high molecular weight chains having the higher melting points crystallising first. As already shown in table 10, the higher molecular weight chains crystallise least easily, the large amorphous content arising from the fact that, in the fractionated form, the material becomes solid before all the remaining amorphous chains can form into the crystalline lattice. In the bulk form more of these remaining amorphous high molecular weight chains can move into the crystalline lattice, since there is a large amount of molten uncrystallised material (i.e. the lower molecular weight) present. This move of any particular molecular weight fraction present in the bulk may crystallise before the melt becomes rigid.

A second possible reason for the enhancement could be that the smaller chains actually fill in the spaces between the crystalline portion of the larger chains and so give an overall higher crystallinity.

5.2.1.3. Effect in commercial polymers

In bulk polymer the crystallinity obtained under any particular crystallisation conditions will depend on the molecular weight and molecular weight distribution. This may be seen in the series of commercial grades of polyethylene homopolymer shown in table 13.

5.2.2. Effect of branching

The formation of branch groups in the molecular chains is achieved by co-polymerising an ethylene/α-olefin feed. Thus the co monomer feeds of propylene, butene - 1 and hexene - 1 give rise to methyl, ethyl and butyl branches respectively.

As previously mentioned, the orthorhombic unit cell dimensions and the degree of crystallinity of a given polyethylene are not unique, but vary with crystallisation and annealing conditions. However, under specific conditions of crystallisation and annealing, it is possible to obtain reproducible unit cell dimensions and crystallinities.
### TABLE 13

**Crystallinity of a series of commercial grades of polyethylene**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Rigidex 9</th>
<th>Rigidex 25</th>
<th>Rigidex 50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mw</td>
<td>179000</td>
<td>134000</td>
<td>96000</td>
</tr>
<tr>
<td>Mn</td>
<td>9800</td>
<td>8200</td>
<td>74000</td>
</tr>
<tr>
<td>Crystallinity</td>
<td>82.4%</td>
<td>83.5%</td>
<td>84.3%</td>
</tr>
<tr>
<td>Density</td>
<td>0.9618</td>
<td>0.9644</td>
<td>0.9662</td>
</tr>
</tbody>
</table>
In such cases any differences in the measured values between polymer samples then reflect differences in structure rather than the thermal or mechanical history. Branching is one such structural feature which can alter the unit cell dimensions and crystallinities in polyethylene. It has been studied by a number of authors who, unfortunately, have used a wide range of crystallisation conditions to prepare their samples. This leads to a variation in their results; however, the various studies do tend to fall into one of two types. Those whose samples have been rapidly cooled or quenched (as in normal compression moulding), and those who use isothermal crystallisation conditions.

Swan, Cole and Holmes, Reding and Lovell, and Shrayama et al., using the first type of crystallisation condition, found a range of branches, even up to C_{10} in size, all caused an expansion in the unit cell dimensions, predominantly of the a-axis dimension, and a decrease in crystallinity. This was taken to arise from the accommodation of the branches within the crystalline lattice. On the other hand, Richardson et al. and Baker and Mandelkern using isothermal crystallisation conditions found only methyl branches expanded the lattice whereas larger branches, such as propyl, did not. It was found that as the crystallisation condition moved away from the ideal, the propyl branches caused an increasingly larger expansion of the lattice, presumably as more were accommodated.

In this work it is demonstrated that, between the extremes of the quenched and isothermally crystallised states, there is a semi-equilibrium state. Short branches (methyl and ethyl) may be accommodated in this state within the crystalline lattice, whereas other branches, butyl and larger, are rejected from the lattice.

5.2.2.1. Experimental

A number of ethylene/\alpha-olefine copolymers, having known levels of branching, were crystallised by moulding into flat sheets.
at a temperature some 20°C above their melting points, and then cooling slowly to room temperature over a period of about one hour. All samples were subsequently annealed by immersion in a silicone oil bath, maintained at a temperature 5°C below their melting points, for a period of three minutes.

The crystallinities and unit cell dimension have been determined by the methods outlined in chapters 2 and 3.

5.2.2.2. Results and discussion

The effect of various crystallisation and annealing treatments on a single polymer sample containing ethyl branches is shown in table 14. It is clear that the conditions of slow cooling from 150°C, followed by an annealing treatment at a temperature of 115°C, give rise to reproducible unit cell dimensions and crystallinities, which are obviously far removed from those of the rapidly cooled sample. It is believed that, if isothermal crystallisation conditions had been employed (the facilities were not available), the unit cell dimensions would have decreased even more, to approach those of a homopolymer.

The indications are that the state achieved using the described conditions of slow cooling and annealing represents a reproducible semi-equilibrium state, some way between the true equilibrium state, achieved under isothermal crystallisation conditions, and the quenched state.

Table 15 gives the unit cell a- and b-dimensions and crystallinities for a number of copolymers having a range of branch types and levels, together with those of a homopolymer. It is evident that, in samples having methyl and ethyl branches, the unit cell a-dimension is expanded with respect to the homopolymer, whereas those containing butyl branches have similar unit cell dimension to the homopolymer. The interpretation placed upon these results is that the shorter branches, methyl and ethyl, are accommodated within the
Crystallinity and unit cell dimensions of ethylene/butene-1 copolymer containing 9.1 Et branches/1000C, crystallised under a range of conditions

<table>
<thead>
<tr>
<th>Crystallisation conditions</th>
<th>% Crystallinity</th>
<th>Unit cell dimensions aÅ</th>
<th>bÅ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moulded 150°C/5 min Quenched</td>
<td>62.6%</td>
<td>7.512</td>
<td>4.980</td>
</tr>
<tr>
<td>Moulded 150°C/5 min Slow cooled</td>
<td>69.0%</td>
<td>7.499</td>
<td>4.971</td>
</tr>
<tr>
<td>Moulded 150°C/5 min Slow cooled, Annealed 115°C in silicone oil bath 5 min 1st sample</td>
<td>70.2%</td>
<td>7.494</td>
<td>4.964</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2nd sample</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3rd sample</td>
<td></td>
</tr>
<tr>
<td>Moulded 150°C/5 min Slow cooled, Annealed 115°C in silicone oil bath 1 hr.</td>
<td>70.4%</td>
<td>7.493</td>
<td>4.963</td>
</tr>
</tbody>
</table>
TABLE 15

Crystallinity and unit cell dimensions for a number of branched polyethylenes

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Branching Measured by IR</th>
<th>% Crystallinity</th>
<th>Unit cell dimensions Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene homopolymer</td>
<td>0.1 Me/1000C</td>
<td>90%</td>
<td>7.421</td>
</tr>
<tr>
<td>Ethylene/propylene copolymers</td>
<td>5.1 Me/1000C</td>
<td>80.6%</td>
<td>7.457</td>
</tr>
<tr>
<td></td>
<td>6.8 Me/1000C</td>
<td>76.8%</td>
<td>7.472</td>
</tr>
<tr>
<td></td>
<td>9.6 Me/1000C</td>
<td>71.6%</td>
<td>7.498</td>
</tr>
<tr>
<td>Ethylene/butene-1 copolymers</td>
<td>4.0 Et/1000C</td>
<td>83%</td>
<td>7.445</td>
</tr>
<tr>
<td></td>
<td>9.1 Et/1000C</td>
<td>70.2%</td>
<td>7.494</td>
</tr>
<tr>
<td></td>
<td>14.0 Et/1000C</td>
<td>61.6%</td>
<td>7.536</td>
</tr>
<tr>
<td>Ethylene/hexene-1 copolymers</td>
<td>2.5 Bu/1000C</td>
<td>78%</td>
<td>7.420</td>
</tr>
<tr>
<td></td>
<td>4.7 Bu/1000C</td>
<td>69.5%</td>
<td>7.428</td>
</tr>
</tbody>
</table>
Fig. 16  Graph of the number of branches/10000C vs unit cell a-dimension.
Fig. 17. Graph of % crystallinity vs unit cell a-dimension for a number of branched polyethylenes.
crystalline lattice, whereas the larger butyl branch is rejected into the amorphous phase. In the case of the shorter branches the expansion of the a-dimension is proportional to the number of branches and is independent of the nature of the branch, fig. 16. Also, the decrease in the crystallinity per branch is similar for the methyl and ethyl branches but is much larger for the butyl branch, fig. 17.

In the crystallisation process the crystalline regions form by successive layers of folded chains packing side by side to form a three dimensional structure. In a single layer of folds the b-direction is the growth direction, fig. 18a. During the formation of a single folded layer any imperfections, such as branches, are likely to be positioned normal to the folding layer so as to minimise even if this involves distortion of the main chain, their effect on the folding process, fig. 18a. This will mean that, when the next plane grows side by side with the first, the branches will tend to hinder the close approach of the planes. This will result in an expansion of the lattice in this direction (a-direction), thus accounting for the large expansion of the a-dimension with methyl and ethyl branches.

It is now possible to return to the results for the crystallite size and distortion in branched materials given in Chapter 4. These showed that the distortion is larger normal to the 200 planes than normal to 110 planes. Also the results indicated that the distortion is larger in the case of methyl and ethyl branched materials compared to butyl branched and homopolymer. This observation agrees with the postulation that when branches are accommodated within the crystal lattice, the branches are positioned normal to the growth plane. The distortion measured in the butyl branched material is not too different from that measured in the homopolymer. This would support the suggestion that butyl branches can be accommodated within the
Imperfection (branches) positioned normal to fold plane.

Large branches excluded from lattice.

end view of fold plane.

Fig. 18. Position of branches in polymer structure.
lattice. Although the lattice is similar in perfection to that of the homopolymer, the fact that the butyl branches are rejected means that they generate a large amount of amorphous material (fig.18.b) which reduces the size of the crystalline region.

The variation in the behaviour of both crystallinity and unit cell dimensions, with the type of branching present shows that the technique may be used to characterise the behaviour of the various branches and hence their influence on the properties. This is considered further in Section 5.2.2.3. Alternatively, the results provide a method for distinguishing between methyl and ethyl branches and the larger butyl branches, and for determining the level of these shorter branches. The method has been used on a number of co-polymer systems, and also to determine the nature of branches in PVC by the study of the polyethylene obtained on reduction of the PVC with LiAlH₄. As the present work has been concerned only with copolymers in which the branches are believed to be randomly situated along the polymer backbone, and with less than 20 branches/1000 carbon atoms, it would be unwise to use the method on polymers having higher levels of branching until the validity at such levels has been confirmed.

It is not possible to compare the actual effect per branch on the crystallinity and unit cell dimensions as reported in this paper with other such studies, because of the lack of uniformity in the determination of the level of branching which is carried out by infrared methods. For example, Cole and Holmes have used the method described by Haslam and Willis, in which all branches are determined as methyls at the end of butyl branches. The ASTM method D2238 estimates the branching in terms of methyls at the ends of long branches. In reality, different infrared absorbance values should be used for each type of branch, as has been done in our studies. The Haslam and Willis method will underestimate the level of branching smaller than butyl,
and overestimate those larger than butyl. In the work of Shrayama et al no correction was made for the fact that, with the lower molecular weight fractions, there is an appreciable contribution to the apparent branching from the chain ends. With narrow molecular weight fractions, the crystallinity is dependent on the molecular weight and so changes in crystallinity could be due to variation in molecular weight rather than in the presence of branches. Unless the appropriate data are available, this factor also cannot be presumed to be negligible.

5.2.2.3. Effect in commercial polymers

The structure and properties of a series of commercial ethylene copolymers is given in table 16. The fact that branching reduces the crystallinity is reflected in the decrease in tensile strength at yield. Tensile tests are conducted relatively rapidly and so the actual result measures the strength of the whole sample. As the crystalline material is stronger, by virtue of the crystalline lattice, highly crystalline polymers have tensile strengths.

Some properties are influenced by the amorphous phase. One such property is environmental stress cracking. Under stress the cracks form slowly in the structure. Because of the large time scale over which cracking occurs, the crack has time to form and grow in the weakest part of the structure, i.e. the amorphous phase. Any structural feature which changes the makeup of the amorphous phase would therefore influence stress cracking. An increase in stress crack resistance would be expected if the chains in the amorphous phase were made less mobile.

From the work on branching it has been shown that butyl branches are situated in the amorphous phase whereas methyl and ethyl branches can be largely accommodated within the crystalline lattice. Branching affects the stress crack resistance as follows:
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Branch level/1000C</td>
<td></td>
<td>less 1 Me</td>
<td>6.5 Me</td>
<td>1.5 Et</td>
<td>2 Bu</td>
</tr>
<tr>
<td>Crystallinity</td>
<td>%</td>
<td>83.9</td>
<td>78.9</td>
<td>83.2</td>
<td>78.0</td>
</tr>
<tr>
<td>Unit Cell dimensions</td>
<td>Å</td>
<td>7.430</td>
<td>7.472</td>
<td>7.438</td>
<td>7.428</td>
</tr>
<tr>
<td>Density</td>
<td></td>
<td>0.964</td>
<td>0.946</td>
<td>0.954</td>
<td>0.947</td>
</tr>
<tr>
<td>Tensile strength at yield</td>
<td>MN/m²</td>
<td>29</td>
<td>21</td>
<td>27</td>
<td>22</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>%</td>
<td>200</td>
<td>&gt;300</td>
<td>&gt;300</td>
<td>&gt;300</td>
</tr>
<tr>
<td>Stress crack resistance</td>
<td>hrs</td>
<td>8</td>
<td>100</td>
<td>180</td>
<td>&gt;500</td>
</tr>
<tr>
<td>Time to 50% failure</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Me branching - small effect
Et branching - slightly more effect than Me
Bu branching - very large improvement in stress crack resistance.

5.3. Effect of annealing on structure and properties

One of the easiest ways of changing the structure of the bulk polymer (assuming fixed chain characteristics such as molecular weight and level of branching) is by thermal treatments. There is a large change in structural ordering if slow crystallisation procedures are adopted. Commercial production methods involve a relatively rapid rate of cooling and crystallisation. However, important changes in structure and properties may be brought about by annealing after fabrication. These are illustrated in table 17. In general the material becomes tougher as the percentage crystallinity increases with annealing. Stress crack resistance studies show how the amorphous regions are changing on annealing (see table 18). In this series the amorphous content is decreasing, the fraction which decreases being the more mobile of the amorphous chains. After prolonged annealing, the remaining amorphous chains will be those which are less capable of ordering, i.e. those which are heavily entangled or contain irregularities. The increase in stress crack resistance is brought about both by a decrease in the amorphous fraction, and that the fraction which is then left is intrinsically less mobile and so resists crack propagation.
### TABLE 17

Rigidex 9. Annealed at 120°C

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>0 hrs</th>
<th>24 hrs</th>
<th>48 hrs</th>
<th>96 hrs</th>
<th>192 hrs</th>
<th>384 hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength yield</td>
<td>MN/m²</td>
<td>25.9</td>
<td>28.5</td>
<td>28.2</td>
<td>29.1</td>
<td>29.8</td>
<td>30.4</td>
</tr>
<tr>
<td>Elongation at yield</td>
<td>%</td>
<td>11.2</td>
<td>9.2</td>
<td>10.4</td>
<td>8.4</td>
<td>8.4</td>
<td>8.0</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>%</td>
<td>709</td>
<td>200</td>
<td>254</td>
<td>274</td>
<td>125</td>
<td>104</td>
</tr>
<tr>
<td>Tensile modulus</td>
<td>MN/m²</td>
<td>458</td>
<td>555</td>
<td>614</td>
<td>428</td>
<td>505</td>
<td>520</td>
</tr>
<tr>
<td>Crystallinity</td>
<td>%</td>
<td>82.9</td>
<td>86.7</td>
<td>87.8</td>
<td>87.7</td>
<td>88.3</td>
<td>89.0</td>
</tr>
<tr>
<td>Unit cell a dimensions b</td>
<td>Å</td>
<td>7.432</td>
<td>7.429</td>
<td>7.424</td>
<td>7.428</td>
<td>7.417</td>
<td>7.418</td>
</tr>
<tr>
<td>Density</td>
<td></td>
<td>0.9615</td>
<td>0.9728</td>
<td>0.9731</td>
<td>0.9725</td>
<td>0.9733</td>
<td>0.9716</td>
</tr>
<tr>
<td></td>
<td>Annealed</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>----------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0 hrs</td>
<td>4 hrs</td>
<td>4 days</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystallinity</td>
<td>82.9</td>
<td>85.2</td>
<td>87.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stress crack</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>resistance</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>time to 50% failure</td>
<td>29 hrs</td>
<td>53 hrs</td>
<td>94 hrs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6.1. Studies on polymers at elevated temperatures

A number of studies of various aspects of structural order determined at elevated temperatures have been reported. The largest number of these have been concerned with the change in unit cell dimensions at high temperature. These have shown that the unit cell a-dimension increases much more rapidly than the b-dimension. Other studies have examined the decrease in crystallinity with increasing temperature. Kavesh and Schultz have determined these parameters together with crystallite size and perfection on a high density polyethylene (Marlex 6002). In the work report here such studies have been made on both homo- and co-polymers of polyethylene.

6.2. Experimental

6.2.1. Heated diffractometer holder.

In order to obtain the diffractometer traces at elevated temperatures a heating device was constructed to fit the standard Philips goniometer. The essential features of the furnace are shown in the working drawing in fig 19. Heat is supplied to the furnace from an electrically heated nichrome heating coil around the furnace. The desired temperature is maintained by the balance of the thermal loss from the furnace body and the input of heat from the heating coil. The sample is in the form of a 1 mm. thick sheet which fits into the sample holder. The essential feature of the sample holder is that it allows lateral expansion of the sample (fig 20). Any expansion is taken up by the sample sliding under the clip, thereby eliminating any distortion of the sheet. In practice the sample showed no tendency to buckle providing the heating and cooling rates are kept low, i.e. a maximum heating of 30 to 40°C/hr. At faster heating rates the sample showed a tendency to buckle at the edges.
Fig. 20. Details of the sample holder.
The temperature of the sample is measured by one of two thermocouples. One is mounted in the air space immediately above the surface of the sample, and the other is mounted in a cavity of the sample holder, in contact with the underside of the sample.

6.2.2. Samples examined

The samples examined are as follows:

a) Rigidex 25 homopolymer
b) Ethylene/butene-1 copolymer (9.1 Et/1000C)
c) Ethylene/butene-1 copolymer (14 Et/1000C)
d) Ethylene/hexene-1 copolymer (4.7 Bu/10000)

These were compression moulded into sheets 1 mm. thick and annealed by heating in silicone oil at 125°C for 1 hour.

6.2.3. Mode of operation

The mode of operation may be summarised as follows:

(1) The samples were allowed to stabilise at the required temperatures for a period of 30 minutes before each diffractometer trace was recorded.
(2) The temperature was increased at a rate less than 30 to 40°C/hr to avoid buckling of the sample.
(3) The diffractometer traces were analysed for crystallinity, unit cell dimensions, crystallite size and distortion by the methods described in chapters 2 to 4.

6.3. Results and Discussion

The change in crystallinity and unit cell dimensions with temperature are shown in figures 21 and 22 respectively. The values for the crystallite size and distortion are given in table 19. The effect of temperature is more clearly illustrated by plotting crystallinity, unit cell a-dimension and crystallite size together against temperature for individual polymers. Figures 23 and 24 are such plots of the Rigidex 25 homopolymer and of ethylene/butene-1 copolymer(b). These are further discussed at some length. In both the change in unit cell a-dimension shows three regions of separate behaviour. All the sets of plotted data may be divided into these regions, for convenience labelled
Fig. 21. Variation of crystallinity with temperature.
Fig. 22. Variation of unit cell a- and b-dimension with temperature.
### TABLE 19
Crystallite Size and Perfection at Elevated Temperatures

<table>
<thead>
<tr>
<th>Rigidex 25</th>
<th>RT</th>
<th>115°C</th>
<th>125°C</th>
<th>135°C</th>
<th>140°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>110 Size Å</td>
<td>570</td>
<td>600</td>
<td>650</td>
<td>730</td>
<td>780</td>
</tr>
<tr>
<td>distortion %</td>
<td>1.62</td>
<td>1.69</td>
<td>1.63</td>
<td>1.68</td>
<td>1.73</td>
</tr>
<tr>
<td>200 Size Å</td>
<td>350</td>
<td>365</td>
<td>380</td>
<td>410</td>
<td>425</td>
</tr>
<tr>
<td>distortion %</td>
<td>1.88</td>
<td>1.83</td>
<td>1.89</td>
<td>1.93</td>
<td>1.94</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ethylene/butene-1 copolymer</th>
<th>RT</th>
<th>100°C</th>
<th>110°C</th>
<th>120°C</th>
<th>130°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>110 Size Å</td>
<td>360</td>
<td>375</td>
<td>400</td>
<td>430</td>
<td>470</td>
</tr>
<tr>
<td>distortion %</td>
<td>1.89</td>
<td>1.87</td>
<td>1.85</td>
<td>1.94</td>
<td>1.96</td>
</tr>
<tr>
<td>200 Size Å</td>
<td>330</td>
<td>330</td>
<td>350</td>
<td>385</td>
<td>390</td>
</tr>
<tr>
<td>distortion %</td>
<td>2.85</td>
<td>2.85</td>
<td>2.97</td>
<td>2.93</td>
<td>2.95</td>
</tr>
</tbody>
</table>
Fig. 23. Variation of crystallinity, unit cell a-dimension and crystallite size with temperature for Rigidex 25.
Fig. 24. Variation of crystallinity, unit cell a-dimension and crystallite size with temperature for Et branched copolymer (9.1 Et/1000C).
The polymer region A extends from 115°C to about 115°C, B from 120°C to 140°C, and C above 140°C, fig.23. In the region A there is little change in crystallinity or crystallite size and a linear expansion in a-dimension. In the region B the crystallinity decreases rapidly, the crystallite size increases, and the unit cell a-dimension shows a much less marked expansion than in region A. Lastly, above 140°C, where the crystallinity is less 20%, there is a rapid increase in the unit cell a-dimension. A similar behaviour of these parameters is found with the ethyl branched copolymer (fig 24) except that the changes occur at lower temperatures.

The behaviour of both polymers in region A is similar to previous findings. The change in unit cell a-dimension is brought about by a small rotation of the planar zigzag polymer chain backbone. This region is not considered further. The changes in the parameters in region B may be accounted for by a melting and recrystallisation procedure. Such recrystallisation, above the crystallisation temperature of 110°C, was postulated by Kavesh and Schultz. This is the reason for the increase in crystallite size above about 110°C. It also explains the virtual decrease in expansion in the unit cell a-dimension if, upon recrystallisation, any imperfections such as branches or chain ends are rejected from the reformed lattice. The change in rate of expansion is discernible more easily on the ethyl branched copolymer. Since the a-dimension is already considerably expanded by the inclusion of some of the ethyl branches in the lattice, the rejection of even a small portion of these, under the high temperature recrystallisation process, would cause a decrease in the a-dimension.

This only leaves the very rapid rise in unit cell a-dimension, in region C, to be explained. This observation can only be the subject of speculation. It occurs when there is only a small amount of crystalline material left. It is therefore at a point just before the
complete breakdown of the crystalline lattice. It is possible that
it is tending to the hexagonal form of polyethylene. The hexagonal
form would occur when \( b = \frac{a}{\sqrt{3}} \) which for a \( b \)-dimension of 4.25\( \AA \)
requires an \( a \)-dimension of 8.6\( \AA \). Clearly if the linear expansion over
the region A were followed an \( a \)-dimension value of the order of 8.6\( \AA \)
would not occur until a temperature some 100° C above the melting
temperature was reached. However, under conditions where only a small
amount of crystalline material remains, it is possible that the ortho-
rhombic lattice breaks down and forms a non-three-dimensional hexagonal
packed structure.
7.1. Preferred Orientation in Polycrystalline Materials

A polycrystalline aggregate is composed of a number of individual crystallites, which are usually of microscopic size. Each crystallite has a different crystallographic orientation from that of its neighbours considered as a whole; these orientations may be randomly distributed with respect to some frame of reference, or they may tend to cluster about some particular orientation or orientations. The extent to which this clustering occurs will depend on the material and the treatment it has received. An aggregate in which clustering has occurred is said to have preferred orientation or texture.

Examples of preferred orientation are numerous, especially in metallurgy, where the effect is extremely important, and has been extensively studied. In a cold drawn wire, for example, the crystallites are orientated such that the same crystallographic direction \([uvw]\) in most of the crystallites lies parallel, or nearly parallel, to the axis of the wire. In cold rolled sheet most of the crystallites are orientated with a certain plane \((hkl)\) parallel to the sheet surface, and a certain crystallographic direction \([UWV]\) parallel to the direction in which rolling occurred. These are deformation textures and result from the tendency of the crystallite to orientate during plastic deformation, by the mechanism of slip twinning and phase deformation.

The existence of preferred orientation is of industrial importance because of the effect it has on the physical properties of the material. Whereas a random aggregate will be isotropic in its properties, an aggregate possessing preferred orientation will be anisotropic, the
extent of the anisotropy depending on the degree of orientation. This anisotropy is often undesirable, leading to unpredictability in such physical properties as yield strength, modulus of elasticity and thermal expansion coefficients, although for certain specific uses of polymers orientation may be deliberately induced. Preferred orientation may also be desirable in metals occasionally, as in the case of transformer cores, where high permeability in the direction of the applied field is required. Since single crystals of iron are more easily magnetized in the \( \langle 100 \rangle \) direction, the thermal and mechanical treatments are chosen to produce a high degree of \( \langle 100 \rangle \) orientation in the sheet.

When a material that possesses a deformation texture is annealed, recrystallisation occurs, and the new crystallite structure usually possesses a new texture, which is an annealing texture. This texture generally differs from that of the cold-worked material, and is due to the influence of the texture of the matrix on the nucleation and growth of new grains in the matrix.

7.2. Preferred orientation in Polymers

The morphology of polymers is intrinsically more complicated than in metals because they are essentially two phase materials, partially crystalline and partially amorphous.

In general the crystallites are separated by the amorphous phase; however, unlike the case of metal crystallites, there is some interaction between crystalline and amorphous regions, and between the crystallites themselves. This arises because the crystallising chains may grow with large open folds and also the chains may crystallise in more than one crystallite.

The most important feature of polymers is the long molecular chain. Since this is relatively unbreakable, it gives rise to high tensile strengths along the chain. Binding between chains is relatively
This means that any preferred orientation in the polymer will give rise to anisotropic properties. The process of drawing is used to induce alignment of the polymer chains in the manufacture of fibres.

However, the processes such as cold drawing and rolling polymers are less common than in fabrication of metals. Most polymer processing does involve some deformation in the molten state, as in extrusion, blow moulding and film blowing, where preferred orientation results from a crystallisation in the orientated state. In these processes, the machine variables are often chosen as those which give maximum through-put of the finished article, rather than to induce particular orientation effects. The preferred orientation which does result may then be to the detriment of the mechanical properties of the manufactured article.

There are two ways in which a study of preferred orientation in polymers may be used. Firstly, an examination of the deformation and annealing textures which result from the processes of drawing, rolling and heat treatments, gives information on the modes of deformation within the crystalline regions and on the interaction between the crystalline and amorphous sections.

Secondly, a study of the orientation in process articles can lead to a greater understanding of the way the machine variables affect the resulting polymer morphology, and ultimately, to induce orientations which enhance the mechanical properties of such articles.

7.3 Pole Figures

Preferred orientation is studied by means of a set of pole figures for the material. A pole figure is a stereographic projection which shows the variation of pole density with pole orientation for a selected set of crystal planes. A stereographic projection allows a three-dimensional crystal to be drawn in two dimensions. In this the crystal
is considered to be at the centre of a sphere and normals are projected from each of the crystal’s planes to the surface of the sphere; the point of intersection is a pole and fig. 25 shows a typical example. An equatorial plane passing horizontally through the centre of the spherical projection is taken and the upper poles on the sphere are projected on to this plane by joining it to the lowermost point \( P' \) on the sphere; the lower poles are projected to \( P \), the highest point of the sphere.

The equatorial plane showing these points of intersection is the stereographic projection. The stereographic projection for polyethylene is given in fig 26.

A particular material which has the crystallites orientated in a preferred way will approach the single crystal case. In a single crystal each pole has a definite position whereas in an orientated sample the individual poles from each crystallite will tend to be gathered about the single crystal pole. The pole figure of an orientated material is a contoured map, the maxima representing a concentration of certain poles in a particular direction. Each pole figure shows the direction of a particular set of planes (hkl) in the crystals. Hence by taking at least two different directions in the crystals it is possible to define the crystals’ orientation in three dimensions.

Pole figures may be obtained by photographic or by counter methods. The advantage of obtaining pole figures using a texture goniometer instead of flat plate photographs have been discussed in detail by Lindenmeyer and Lustig. The photographic method is very laborious in that a large number of photographs must be produced, and information obtained from them is rather vague. Counter methods allow the intensities to be measured rapidly and quantitatively. This gives a much more detailed pole figure, which is essential for studying the behaviour of polymers.
Fig. 25. The principle of stereographic projection

\[ a = 7.436 \text{Å} \]
\[ b = 4.950 \text{Å} \]
\[ c = 2.54 \text{Å} \]

Fig. 26. Stereographic projection for polyethylene.
The texture goniometer used in this work is the commercial Philips equipment based on the original work of Schulz (see fig. 27). The position of the goniometer and the counter arm are adjusted to make angles of $\theta$ and $2\theta$ respectively with the incident beam, where $2\theta$ is the Bragg angle corresponding to the particular crystal plane being investigated.

The goniometer head allows rotation of the sample such that the sheet normal can have any direction in space, whilst the angle of incidence is held at $\theta$. This is achieved by rotation of the two rings $Q$ and $I$, see fig. 28. $Q$, the large ring, is mounted on the axis of the goniometer and allows rotation of the specimen about the axis $F-G$. This is the angle of tilt $\phi$, and is defined as $90^\circ$ when the plane of the specimen is in the plane of the divergence of the beam. Attached to $Q$ is the inner ring $I$ which contains the plane of the specimen. $I$ allows rotation of the sample about an axis normal to its surface. This angle is known as $\delta$ and is generally taken to be $90^\circ$ when a pre-defined axis of the sheet, for example, the draw or rolling direction is in the plane of divergence of the beam.

The texture goniometer operates on the basis of simultaneous rotation of both the outer and inner rings. The geometry of reflection is given in fig. 29. If the outer ring is rotated, the projection of the reflecting plane normal moves across a diameter of the stereogram. If the inner ring is rotated, the reflecting plane normal moves on a small circle radius $\phi$ centred about the projection of the sheet normal. When both rings are rotating simultaneously the path traced is a spiral, and covers the stereogram. This rotation is synchronized with the motion of the chart in the recorder. Hence a continuous trace is produced, any point on which defines an intensity and a point on the spiral of the stereogram.

Because of the low absorption of polymer materials there is a high
Fig. 27. Schulz Texture Goniometer.
2.8

Ring I rotates in plane F-G.
Ring rotates about axis F-G.

Fig. 28. Geometry of the Schulz reflection method.

Fig. 29. Position of the reflecting plane normal on the pole figure for the Reflection Method.
penetration of the incident X-ray beam, and this causes a large amount of defocusing, and loss of intensity. This occurs as it approaches 90°. In this position the sample surface is parallel to the x-ray beam and so the beam only just glances on the sample. As the angle moves to lower angle the sample surface becomes at right angles to the beam thus utilising the full diffracted intensity. One way of overcoming the fall-off in intensity in the outer part of the pole figure is to remount the sample and examine it in the transmission mode. This procedure requires considerable effort in scaling the overlapping sets of data. In this work it has been found more satisfactory to take a continuous scan form \( \phi = 90° \) to 0° and make some correction for the intensity loss.

The nature of the correction is two-fold. Firstly, the data must be scaled so that pole density is equally represented over the whole of the pole figure. Secondly, only intensity from the particular (hkl) plane should be included in the pole figure. This requires subtraction of any background scattering from the intensity data before it is used in the formation of the pole figure. Since both these factors are dependent on the sample thickness, it has been found desirable to use the actual sample under investigation to formulate the correction data, on a sample of random orientation. In practice this may be effected by examining the sample at angles some way removed from the Bragg reflections. The procedure may be illustrated for correction of (110) pole figures.

From the wide angle diffractometer trace, as used in crystallinity measurements, it may be seen that the background and amorphous scatter at the Bragg angle of the 110 reflection is the same as at angle 18°20. The intensity at 18°20 is sufficiently far removed from the 110 Bragg reflection for it not to contain orientated diffracted intensity. Also, to a first approximation, the amorphous scatter at 18°20 can be considered as that from an unorientated sample. The trace of \( \phi = 90° \) to 0° without \( \beta \) motion is shown in fig 30. The intensity every 5° is taken and used both
Correcting factor is

\[ \frac{I_\phi A_\phi}{A_\phi} - A_0 \]

where \( I_\phi \) is the intensity on the pole figure chart trace at position \( \phi \).

Fig. 30. Correction for absorption and background.
to scale the data and to make a background correction according to the equation.

7.5. Computer Drawn Pole Figures

The data comes from the counter in the form of a continuous trace, any point on which defines an intensity and a point on the spiral, and thus a point on the pole diagram. Therefore, by knowing $\phi$ and $\delta$ the intensities can be plotted and intensity contours drawn. When this is done by hand it is more convenient to measure $\phi$ and $\delta$ at given values of intensity. These points can be plotted as dots on the stereogram, and joined to produce a contour line. This process can be very time consuming and the pole figure never contains the detail which is available from the counting system. To make use of the accuracy of the data collected by the counting system, it is necessary to plot the pole figure by means of a computer.

A programme has been devised in conjunction with the Mathematics and Computer Services Section, Epsom Division, B.P. In this the intensity is measured at $10^0$ intervals of $\delta$ round the spiral, together with values of the scaling and background correction data. These are then presented to the computer, which draws the various contour levels by joining points of equal intensity. The actual values of the contour levels are chosen so that there are about a dozen equal increments up the maximum intensity observed. For further details of the computer programme see Appendix 1.

7.5.1. The advantages of computer drawn pole figures

For a detailed study of the preferred orientation in polymers, it is necessary to be able to have pole figures showing high resolution due to the possibility of complex orientations. These can result from the mobility of the crystalline regions relative to the amorphous regions, in addition to the deformation within the crystalline regions. In order to analyse these effects it is essential to be able to determine the
pole maxima to within 1° or 2°. Computerized pole figures obtained using a Picker single-crystal analyser have been reported but estimates of possible resolving power were not made.

The advantages of drawing the pole figures obtained from the Schulz texture goniometer using a computer instead of hand drawing are:

(a) the ability to utilize very much more data, with a resulting increase in accuracy,

(b) the interpolation process involved in drawing the contour lines is performed with mathematical accuracy,

(c) the elimination of human error.

The effect of these points is greatly to improve the resolution of strong adjacent pole maxima and the accurate delineation of regions with diffuse maxima.

The overall texture, or textures, present in orientated samples may be determined from the position of the maxima in the pole figures. This may be illustrated by the (110) and (020) pole figures from a sample of high density polyethylene, cold rolled to half the original thickness. These are shown in figs.31&32. In all the pole figures included in this work the machine direction and transverse directions of the samples are respectively the north-south and east-west directions in the pole figures. The method by which the orientation of the crystallographic axes may be determined from such pole figures is outlined in fig 33.

7.6. **Degree of orientation**

The pole figures represent the distribution of the particular poles over the whole of space. Therefore it is wasteful of the information contained in the pole figures to take only the position of the maximum intensity. The distribution of the intensity about a particular maximum in fact represents the degree to which the poles are aligned with respect to the direction given by that maximum. It is clearly useful to be able to extend the method to determine quantitatively the degree of orientation in addition to the overall crystallite orientation.
RIGIDEX 25 HEAVILY ROLLED 110 POLE FIGURE

KEY

1  1.1
2  7.1
3 11.9
4 17.6
5 23.7
6 29.5
7 36.3
8 42.6
9 48.6
10 53.1

\[ \langle \cos^2 \hat{\theta}_{110} \rangle = 0.336 \]
\[ \langle \cos^2 \hat{\theta}_{211} \rangle = 0.580 \]
\[ \langle \cos^2 \hat{\theta}_{400} \rangle = 0.102 \]
Fig. 33. Method of interpreting pole figures

Example. Rolled polyethylene

For polyethylene
\[ a = 7.42 \, \text{Å} \]
\[ b = 4.95 \, \text{Å} \]

Basal plane of polyethylene

Observed pole figures showing position of the \{110\} and \{020\} pole maxima

From these we may infer the full pole figure diagram and the crystallite orientation

i.e. the 100 planes are 57° from the 110 planes and the 001 planes is perpendicular to both the 100 and 010 planes. Thus the c-axis is parallel to the rolling direction.
This is particularly important if one is to compare orientation effects in a range of polymer samples. The method for quantifying the degree of orientation is a mathematical description which uses the concept of an orientation function.

7.6.1. Orientation functions

The concept of an orientation function to specify quantitatively the degree of axial orientation in crystalline fibres was originated by Hermans. Such a function takes the form,

$$ f_{\phi} = \frac{1}{2} (3 \langle \cos^2 \phi \rangle - 1) $$

where $\langle \cos^2 \phi \rangle$ represents the mean square cosine, averaged over all crystallites, of the angle between a given crystal axis and the fibre axis. This may be extended to cover all the crystal axes with respect to a reference direction ($z$)

$$ f_{a, z} = \frac{1}{2} (3 \langle \cos^2 \phi_{a, z} \rangle - 1) $$

for the a-direction, with similar equations for the b- and c-directions.

If the crystallographic axes are orthogonal, as is the case with the orthorhombic unit cell of polyethylene, there is the additional relationship that

$$ \cos^2 \phi_{a, z} + \cos^2 \phi_{b, z} + \cos^2 \phi_{c, z} = 1 $$

A given crystallographic axis $\langle \cos^2 \phi \rangle$ will be 1 for perfect alignment with $z$ and $1/3$ for random orientation, i.e. equal orientation in the three directions. The quantitative determination of the degree of orientation therefore involves the measurement of the $\langle \cos^2 \phi \rangle$ parameters. These may be calculated from the distribution of the plane normals in the appropriate pole figure, or directly from the fully corrected intensity distribution from which the pole figure is derived.

In a pole figure the intensity distribution is defined by $I(\phi, \psi)$. In fig 34 it may be seen that for orientation about $z$ the total number of (hkl) plane normals orientated at a given $\phi$ is proportional to the circumference of the circle of radius $r$, of which $\sin \phi$ is a measure.
Fig. 34. Intensity distribution $I(\varphi, \lambda)$ used to derive pole figure.
Therefore, in order to obtain $\langle \cos^2 \phi_{hk1,z} \rangle$ averaged over the entire surface of the orientation sphere, it is necessary to weight $I_{hk1}(\phi, \delta)$ by $\sin \phi$. Thus

$$\cos^2 \phi_{hk1,z} = \frac{\int_0^{\pi/2} I(\phi) \sin \phi \cos^2 \phi d\phi}{\int_0^{\pi/2} I(\phi) \sin \phi d\phi}$$

where

$$I_\phi = \int_0^{2\pi} I(\phi, \delta) d\delta$$

In the present instance it has proved convenient to extend the computer programme used for plotting the pole figures to provide, additionally, values for the various $\langle \cos^2 \phi_{hk1,z} \rangle$ terms.

With sheet samples there are three reference directions; the machine direction (MD), the transverse direction (TD) and the sheet normal (SN). The orientation of the sheet can be fully characterised by calculating the nine quantities $\langle \cos^2 \phi_{a,SN} \rangle$, $\langle \cos^2 \phi_{a,TD} \rangle$, $\langle \cos^2 \phi_{a,MD} \rangle$, $\langle \cos^2 \phi_{b,SN} \rangle$, $\langle \cos^2 \phi_{b,TD} \rangle$, $\langle \cos^2 \phi_{b,MD} \rangle$, $\langle \cos^2 \phi_{c,SN} \rangle$, $\langle \cos^2 \phi_{c,TD} \rangle$, and $\langle \cos^2 \phi_{c,MD} \rangle$. Ideally, these are obtained from the (h00), (0k0) and (001) pole figures respectively, although only two poles are required because of the orthogonality relationship. It is not always convenient in practice, or possible, to obtain the (h00), (0k0) and (001) pole figures because of the absence of the appropriate reflections; however, the axial orientation functions may be calculated from any two independent reflections. In polyethylene, where the two strongest reflections are (110) and (200), the mean square cosines are calculated from equations of the general type

$$\langle \cos^2 \phi_{c,MD} \rangle = 1 + \frac{\cos^2 \phi_{110,MD} - (2e_1^2 - 1)\cos^2 \phi_{200,MD}}{(e_1^2 - 1)}$$

where $e_1$ is the cosine of the angle between the (110) and the (200) planes.

In the example of the cold rolled polyethylene the $\langle \cos^2 \phi_{hk1,z} \rangle$ terms for the (110) and (020) poles are given along with their pole
### TABLE 20
Orientation functions for cold rolled high density polyethylene

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<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>$\cos^2 \theta_{a,\text{MD}}$</td>
<td>=</td>
<td>0.05</td>
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<tr>
<td>$\cos^2 \theta_{a,\text{TD}}$</td>
<td>=</td>
<td>0.31</td>
</tr>
<tr>
<td>$\cos^2 \theta_{a,\text{SN}}$</td>
<td>=</td>
<td>0.64</td>
</tr>
<tr>
<td>$\cos^2 \theta_{b,\text{MD}}$</td>
<td>=</td>
<td>0.16</td>
</tr>
<tr>
<td>$\cos^2 \theta_{b,\text{TD}}$</td>
<td>=</td>
<td>0.62</td>
</tr>
<tr>
<td>$\cos^2 \theta_{b,\text{SN}}$</td>
<td>=</td>
<td>0.22</td>
</tr>
<tr>
<td>$\cos^2 \theta_{c,\text{MD}}$</td>
<td>=</td>
<td>0.81</td>
</tr>
<tr>
<td>$\cos^2 \theta_{c,\text{TD}}$</td>
<td>=</td>
<td>0.06</td>
</tr>
<tr>
<td>$\cos^2 \theta_{c,\text{SN}}$</td>
<td>=</td>
<td>0.13</td>
</tr>
</tbody>
</table>

### TABLE 21
$c$-axis orientation functions derived from the estimated distribution of the $c$-axes

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
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<td>$\cos^2 \theta_{c,\text{MD}}$</td>
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</tr>
<tr>
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</tr>
<tr>
<td>$\cos^2 \theta_{c,\text{SN}}$</td>
<td>=</td>
<td>0.124</td>
</tr>
</tbody>
</table>
figures in figs.31, 32. From these the nine $\langle \cos^2 \phi \rangle$ terms for the a-, b- and c- axes are calculated and are given in table 20. The values may be conveniently displayed in terms of triangular plots, shown in fig.35. This clearly demonstrates that the a-axes are preferentially orientated parallel to the sheet normal, the b-axes parallel to the transverse direction, and the c-axes parallel to the machine direction. It is also evident that, of the polymer chains not along the machine direction, there are more than twice as many with their c-axes parallel to the sheet normal than those parallel to the transverse direction.

The use of this completely mathematical approach of interpreting the pole figures has a serious limitation. The intensity data over the whole of the pole figure is used in the calculation of the $\langle \cos^2 \phi_{hkl,z} \rangle$ terms. Any error in the intensity values will therefore be incorporated in the determined $\langle \cos^2 \phi \rangle$ values. The most serious of the errors arises from the imprecise knowledge of the background intensity. The method described in Section 7.4 attempts to deduct any background scattered intensity, to leave only the diffracted intensity from the planes under consideration. If the corrected intensity values still retain some background scatter, this background scatter will be incorporated in the summations which lead to the $\langle \cos^2 \phi \rangle$ terms. The process of correction is relatively easy in highly orientated samples, which show sharp maxima above a very low background. In less well orientated samples the pole maxima are not so well defined and merge with the background, making the correct separation of that background difficult. In the mathematical procedure which combines $\langle \cos^2 \phi \rangle$ terms to give the orientation function in other directions, the use of imprecise data leads to an incorrect answer. Therefore a second method is considered here.

7.6.2. Estimation of c-axis distribution from visual inspection of the pole figures

As already discussed, the c-axes may be positioned with reference.
Fig. 35. Orientation function diagram for rolled Rigidex 25 sheet.

\[ \cos^2 \phi_{c_{1\text{ND}}} = 0.8 \]
to the position of the maxima in the pole figures. It is also possible to estimate the spread of the distribution from the pole figures. An inspection of the (020) pole figure for the cold rolled polyethylene shows the maxima to be elongated more in the machine direction than in the transverse direction. A convenient measure of the spread is the width of the maxima at half the maximum intensity. From the (020) pole figure the spread is then about 55° in the machine direction and 38° in the transverse direction. A similar spread is obtained from the (110) pole figure. To a first approximation it is possible to assume that the c-axis distribution about the machine direction is similar, i.e. with a spread of 27° either side of the machine direction towards the sheet normal, and 19° either side of the machine direction towards the transverse direction. This is shown in fig. 36. The c-axis orientation functions may be calculated for this visually derived pole figure and are given in table 21. Reasonable agreement is shown with the values derived mathematically.

7.7. Uses of the study of orientation in polymers

Basically there are two ways in which orientation studies in polymers may be used. The first is in the study of the deformation behaviour of characterised material, deformation being by drawing, rolling or thermal treatment. Here the deformation causes changes to the structural elements and characterisation of such changes yield information on the interrelation of such elements. The second use is the characterisation of the orientation produced under commercial production methods. Fabrication methods, such as blowing, induce preferred orientation which gives rise to an anisotropy in properties of the article. These two aspects are considered separately in the two subsequent chapters.
Fig. 36 The c-axis distribution derived from a visual inspection of the pole figures.
8.1. Deformation in polymers

The crystalline portion of polymers has been found to deform by slip, twinning or phase transformation. This work is confined to the occurrence of twinning in deformed polyethylene and of phase transformation in deformed polyoxymethylene.

8.2. Studies of deformed polyethylene

The textures produced in polyethylene by the deformation processes of drawing and rolling, and also that of subsequent annealing, have been examined by a number of authors. In particular Hay and Keller have studied their effect on low density polyethylene. Two main features emerge from the work of these authors. Firstly, that the resulting orientation of the crystalline regions occurs by the mechanism of slip, twinning and phase transformation, in many ways analogous to the processes observed in metals. Secondly, much of the energy of deformation is stored in the amorphous phase, and on annealing such energy is released. The way in which this alters the crystalline texture gives information on the actual amorphous phase, and how it interacts with the crystalline phase.

In this work both of these features have been improved. The greater resolving power obtained by using computer drawn pole figures gives a better description of the resulting texture. This enables a detailed analysis of the deformation mechanisms to be made. By comparing the effect of the deformation processes on polymer having a range of amorphous contents (i.e. high and low density polyethylene), a greater insight into the amorphous-crystalline interaction is obtained. A complete study of the processes of deformation would only duplicate previous work, therefore, only certain aspects are reported here.
0.2.1. Experimental

Samples of high density polyethylene (Rigidex 25) and low density polyethylene (Alkathene WJG11) are the polymers examined in this work. The polymer was compression moulded, at $170^\circ$C, into sheets 1 mm thickness. The sheets were cut into strips 3 cm wide and treated in the following ways.

a) Drawing and subsequent annealing

Samples of the high density polyethylene strip were drawn slowly, at about 2 cm/min, at room temperature so as to produce a 'necked' region. The actual shape after 'necking' is dependent on the method of drawing. Straight forward drawing results in a thickness reduction of about 80% and a width reduction of about 15%. McCrum has described a method which results in no width reduction. In this, after the neck has been formed, the jaws of the drawing device are reclamped against the neck in the region where the width is the same size as the un-necked portion. On further drawing the polymer is physically restrained from decreasing widthways by the jaws. This process is shown diagrammatically in fig 37. Since the textures produced by drawing are dependent on the shape of the starting material, a third sample was prepared having dimensions 2 cm by 0.3 mm. Drawing again resulted in the formation of a necked region, but with a thickness reduction of about 60% and a width reduction of 50%. Appropriate pole figures were obtained from these samples. The sample of straight drawn material was annealed at $115^\circ$C and $130^\circ$C. Annealing was achieved by immersing the samples for three minutes in a silicon oil bath maintained at the desired temperatures.

b) Rolling and subsequent annealing

Strips of both high and low density polyethylene were rolled, at room temperature, to thickness reductions of 50% and 80%. These
Fig. 37. Specimens of drawn high density polyethylene.
samples were subsequently annealed at a range of temperatures in a silicon oil bath.

c) Drawing of sample previously rolled and annealed

A sample was prepared in such a way that it had a (001) [100] texture by the method outlined by Hay and Keller. This was achieved by rolling a sheet of low density polyethylene to 50% thickness and annealing it at 107°C for 1 minute. It was then drawn by 60% along the original rolling direction (a-axis).

8.2.2. Results and Discussion

8.2.2.1. Drawing and subsequent annealing

The (110) and (020) pole figures of the lightly drawn high density polyethylene are shown in fig 38. The (110), (020) and (211) pole figures for the necked material are shown in fig 39. These are considered in detail.

The (020) pole figure for the lightly drawn polyethylene shows maxima along the transverse direction, and the (110) pole figure maxima along a great circle passing through the transverse direction making an angle of 50° to the drawing direction. Along this great circle the maxima are at positions 35° from the transverse direction. This implies that the b-axis is along the transverse direction, and that the a-axis is in the sheet normal/machine direction plane at 50° to the machine direction. Since the c-axis is at right angles to both these it must be in the sheet normal/machine direction plane at an angle of 40° to the machine direction. Such a texture is similar to the initial orientation observed in low density polyethylene at low drawn ratio described by Hay and Keller.

The (110), (020) and (211) pole figures for the straight forward 'necked' high density polyethylene are shown in fig 39.
Fig. 38. Lightly drawn high density polyethylene.
Fig. 39. Necked high density polyethylene.
The (110) pole figure shows three elongated maxima along the transverse direction, two at angles of 64° either side of the perpendicular direction. The (020) pole figure shows four maxima along the transverse direction, two at an angle of 90° and two at an angle of 36° either side of the perpendicular. The (211) pole figure confirms that the c-axis is along the draw direction. An initial interpretation of these pole figures suggests an alignment of the c-axis along the draw direction, with (100) planes and (110) planes parallel to the sheet surface.

Hence, from such textures, the (020) pole figure should have maxima along the transverse direction at 90° either side of the perpendicular when the (100) planes are parallel to the surface, and at 33° either side of the perpendicular when the (110) planes are parallel to the surface. These results show that the second (020) pole maxima occur at an angle of 36° either side of the perpendicular. Also, a careful study of the (110) pole figure in greater detail in fig 40, shows that the (110) plane normals are not along the perpendicular direction, but are at about 2 to 3° on either side of the perpendicular.

The (110) and (020) pole figures for the samples annealed at 115° and 130°C are shown in figs 41, 42 respectively. The sample annealed at the highest temperature shows the simplest texture; the (020) pole figure having two maxima along the transverse direction at 90° either side of the perpendicular direction, the (110) pole figure having two maxima along the transverse direction at 57° either side of the perpendicular direction. These are accounted for by a (100) [001] texture as shown in fig 33.

The interpretation of these pole figures can be made in terms of the crystallographic modes of deformation of the polyethylene and
Fig. 40. Enlarged (110) pole figure of necked high density polyethylene.
Fig. 41. Necked sample annealed at 115°C.

Fig. 42. Necked sample annealed at 130°C.
are in many ways analogous to those observed in metals. In close packed metals, the action of rolling, which is essentially a process of causing thickness reductions with little effect on the width of the sample and so may be compared with the drawn samples, results in a biaxial orientation. Here, the close packed slip planes align parallel to the rolling plane, and the slip direction becomes parallel to the rolling direction. In polymers, slip on (hk0) crystal planes is encouraged by the weak van der Waal's forces between molecular chains, whereas the chain direction [001] orientates parallel to the rolling direction. The shortest lattice translation in polyethylene (other than that along the c-axis) is b [010]. From the analogy with metals one would expect this to become sheet surface on rolling, see fig 43. Deformations which cause elongation with little width reduction in the sample would be expected to have a (100) [001] texture. The actual mechanism by which the crystallites become orientated in this manner has been discussed by Frank, Keller and O'Connor.

It is obvious from the pole figures that the necked polyethylene has a (100) [001] texture, together with a second superposed texture. This second texture reverts to the pure (100) [001] texture on annealing. From the pole figures it may be seen that the second texture is at an angle of 54° to the (100) [001] texture. To account for this the twinning modes of polyethylene must be investigated. These have been listed by Frank, Keller and O'Connor and by Bevis and Crellin. The modes with the smallest shear are as follows:

<table>
<thead>
<tr>
<th>Composition plane</th>
<th>Conjugate plane</th>
<th>Shear direction</th>
<th>Conjugate axis</th>
<th>Shear</th>
</tr>
</thead>
<tbody>
<tr>
<td>(110)</td>
<td>(310)</td>
<td>[110]</td>
<td>[130]</td>
<td>0.249</td>
</tr>
<tr>
<td>(310)</td>
<td>(110)</td>
<td>[130]</td>
<td>[110]</td>
<td>0.249</td>
</tr>
</tbody>
</table>

The appropriate stresses to operate any of these modes are rather similar, namely compressive stresses in a range of directions.
Fig. 43. (100)[001] texture.
twinning modes are drawn out, in fig. 44. It may be seen that in (310) twinning the twinned portion is at an angle of 54° to the parent lattice whereas with (110) twinning the twinned portion is at an angle of 69° to the parent. Since the angle of 54° corresponds exactly with that observed, this appears to be good evidence for the occurrence of (310) twinning in necked polyethylene. The alternative interpretation that drawing in the necked region causes (100) and (110) planes to orientate parallel with the surface may be ruled out for two reasons. Firstly, the fact that the (110) planes are not exactly parallel with the sheet surface; secondly, if (110) planes did orientate parallel to the surface, together with (100) planes, what would be the driving force to make the (110) planes parallel rather than the (100)? In the case of the (100)[001] texture twinning on the (310) planes there would be some distortion and elongation of the amorphous chains around the twinned regions. On annealing, the elastic energy stored in such chains would be able to operate and so cause the twinned portion to 'de-twin' back to the pure (100)[001] texture.

Before considering the nature of the driving force which causes the twinning, it is useful to compare the results for the other drawn samples. The (110) and (020) pole figures for the necked sample with no width reduction, (fig. 45), shows only a (100)[001] texture. The sample which has a higher thickness to width ratio than the previous samples, and in which, after necking, the width reduction is of the order of 50%, shows from the (110) and (020) pole figures in fig. 46 a random arrangement of a- and b- axes perpendicular to the draw direction.

The example of twinning is thus closely connected with the observation of a width reduction. From consideration of the twinning modes the stresses to operate twinning is a compressive stress along the b direction. The compressive stresses are associated with width reduction.

In the sample with a large width reduction
Fig. 44. (110) and (310) twinning in polyethylene.
Fig. 45. Necked sample - no width reduction.

Fig. 46. Necked sample - large width reduction.
multiple twinning can presumably result in a randomisation of the a- and b-axes perpendicular to the draw direction.

The whole process of drawing may be considered in the light of the model proposed by Ishikawa, Miyasaka and Maeda for drawn single-crystal mats of polyethylene. The initial effect of drawing is to orientate the b-axis along the transverse direction with the c-axis at the same angle to the drawing direction, due to tilting of the lamellae (fig 47). The only change of orientation of the crystal axes during necking is a rotation of the chain axes about the b-axis. Since lamellae are composed of continuous chains, it is difficult to imagine a 90° tilt of the chains without collapse of the lamellae; therefore the tilting angle must be much less than 90°. In the necked region, some process like melting and recrystallisation must occur. In the single crystal case some process such as complete unfolding into a two-dimensional crystal followed by a restacking procedure occurs to give a (100) [001] texture. In the drawn single crystal mats no width reduction was reported, and so the resulting structure is exactly analogous to the drawn bulk polymer with no width reduction. If a small amount of width reduction occurs there is a compressive force parallel to the transverse direction (b-direction), which causes (310) twinning. In samples having a much larger width reduction, multiple twinning would cause a randomisation of the a- and b-axis giving rise to a fibre type orientation.

8.2.2.2. Rolling and subsequent annealing

The (110) and (020) pole figures of low density polyethylene lightly and heavily rolled are shown in figs 48,49. These may be interpreted in the light of our findings for necked polyethylene. Light rolling results in a (100) [001] texture; heavy rolling in a (100) [001] texture together with (310) twinning. These results confirm the work of Hay and Keller, who found the action of heavy rolling produced a
Fig. 47. Schematic representation of the drawing of LPE single-crystal mats: (A) regular unfolding (thin ribbons indicate the two-dimensional crystals); (B) irregular unfolding with (d) a slightly strained chain and (s) a highly strained chain.
Fig. 48. Lightly rolled low density polyethylene.

Fig. 49. Heavily rolled low density polyethylene.
Their explanation of this was that the $(100) \{001\}$ texture was the primary consequence of the rolling (as observed in the lightly rolled material). On heavy rolling, the material is elongated along the transverse direction, while the rollers are actually in contact with the material. This causes some elongation of the amorphous chains parallel to the rollers. On removal of the rollers, the elastic energy stored in the elongated amorphous chains is released, and causes a compressive force in the transverse direction, (i.e. along $b$). This provides the driving force for the twinning. In the present work the greater resolving power of the computer drawn pole figures enables a positive identification of the twinning mode as $(310)$.

The $(110)$ and $(020)$ pole figures of high density polyethylene lightly and heavily rolled are shown in figs 50 & 51 respectively. These only show a $(100) \{001\}$ texture. However the pole figures of the heavily rolled polymer after annealing at $110^\circ C$ (fig 52) shows the presence of a small amount of twinning.

The results for the high density polyethylene may be interpreted in terms of the actual process of rolling as proposed by Hay and Keller. Thus, in the low density material, the relatively large amount of amorphous material, $(39\%$ amorphous, $61\%$ crystalline), generates sufficient compressive forces to cause twinning. In the high density polyethylene there is only a small amount of amorphous material $(14\%$ amorphous and $86\%$ crystalline), which presumably does not generate sufficient force at room temperatures to cause twinning. As the polymer is heated the crystalline lattice becomes less rigid, at some point the compressive forces, present in the small amount of amorphous material, become sufficient to give rise to a certain amount of twinning.

The pole figures of annealed heavily rolled low density material show first a reversion to a pure $(100) \{001\}$ texture for
Fig. 50. Lightly rolled high density polyethylene.

Fig. 51. Heavily rolled high density polyethylene.
Fig. 52. Heavily rolled high density polyethylene.
annealing temperatures of 100 °C, fig. 53. On increasing the temperature the (110) pole figure shows a separation of 110 maxima from a position along the SN/TD plane, and rotate about the TD plane. Annealing at 107° results in the pole figures shown in fig 54. Here the (020) pole maxima are along the transverse direction, and the (110) pole maxima are in the transverse direction/machine direction plane 33° from the transverse direction. The arrangement of the axes is that the b-axis is along the transverse direction, the a-axis along machine direction and the c-axis along the sheet normal. This process of rotation of the a- and c-axes about the b-axis has been described in the work of Hay and Keller. Their explanation of the procedure, based both on wide and small angle diffraction, is as follows.

Small angle x-ray diffraction studies show that, although the c-axis is parallel to the machine direction, the lamellar surfaces are not perpendicular to this direction, but make an angle of approximately 45° to it. When the sheet is annealed, just below the melting point of the polymer, the sheet shrinks macroscopically. This causes a rotation of the a- and c-axes about the transverse direction (b-axis). The reason for this is that the compressive forces stored in the extended amorphous chains are released as the molecular mobility is increased at the elevated temperature. Because of the relatively large amount of shrinkage such forces act mainly along the machine direction. The stages of the rotation are as follows. The material consists of stacks of lamellae (fig 55). In stage I the orientation is unfavourable for [001] intralamellar slip but will favour slip on the lamellar interfaces. This interlamellar slip occurs until the lamellae become parallel with the transverse direction. At this stage (II) the orientation is favourable for intralamellar [001] slip on (100) planes. This increases the molecular inclination within the lamellae (III). With increasing tilt the identity of the lamellae can
Fig. 53. Heavily rolled low density polyethylene, annealed at 100°C.

Fig. 54. Heavily rolled low density polyethylene, annealed at 107°C.
Stage I. Sample shrinks macroscopically generating compressive forces along original machine direction.

Stage II. Rotation of chains and lamellae, by interlamellar slip, brings lamellae surface at right angles to machine direction.

Stage III. Further rotation of chains by intralamellar slip.

Stage IV. Disruption of lamellae and reestablishment of molecular chains at right angles to machine direction.

Strong lines represent lamellae surface and weak lines the molecular chains.

Fig. 55. The rotation of the molecular chains on annealing.
be lost, and when the chains have turned through nearly 90° they re-establish themselves by straight chain segments, originally in consecutive lamellae, coming in register to form new lamellae (IV). In practice the amount of rotation of the a- and c-axes is dependent on the level of the heat treatment.

8.2.2.3. Drawing polyethylene along the a-axis

The sample of low density polyethylene heavily rolled and annealed at 107°C in the previous section, was the starting point in this work. As already shown the sample is orientated in a (001) [100] texture. Thus, drawing along the original rolling direction is equivalent to drawing along the crystallographic a-axis of the (001) [100] texture. The (110) and (020) pole figures for the drawn material are given in fig.56. In the (110) pole figures there are two new pairs of maxima around the machine direction/transverse direction, 10° either side of the rolling direction. The (010) pole figures also show four new maxima around the machine direction/transverse direction, 20° either side of the rolling direction. These indicate that a portion of the crystalline lattice has moved through an angle of about 70° with respect to the parent (001) [100] texture. From the previous arguments discussed in section 8.2.2.1, a rotation of 68° will occur if twinning on the 110 plane takes place, see fig.44. Since this corresponds to the observed movement, it is concluded that drawing along the a-axis in a (001)[100] texture causes (110) twinning.

8.2.2.4. Twinning in deformed polyethylene

The occurrence of deformation twinning in this study may be summarised as follows:

When high density polyethylene is drawn so that it 'necks' there is a thickness reduction of about 80% and a width reduction of about 15%. The resulting texture has been shown to be of (100)[001]
Fig. 56. Heavily rolled high density polyethylene, annealed at 1070°C, drawn along the a-axis.
the polyethylene is drawn in such a manner that no width reduction occurs, then the result is a pure (100) [001] texture. This suggests that the contraction along the transverse direction (which is the b-direction in the (100) [001] texture) may be a factor in causing the (310) twinning.

Similarly it has been shown that heavily rolled low density polyethylene, involving a thickness reduction of about 80%, also produces a (100) [001] texture together with (310) twinning. The explanation for this, as proposed by Hay and Keller, is that the (100) [001] texture is the primary consequence of the rolling. However, as the roller pressure is acting, the amorphous chains in the polymer are extended, and this elastic energy is released as the roller passes. This results in compressive forces in the transverse direction (b-direction), which provide the driving force for the twinning.

By a suitable treatment of rolling and annealing it is possible to orientate polyethylene sheet into a (001) [100] texture. Subsequent drawing along the a-axis direction causes (110) twinning.

Thus the evidence suggests that compressive forces along the b-axis produce (310) twinning, whereas tensile forces along the a-axis produce (110) twinning.

Such observations may be compared with the reported studies on the deformation made in single crystals.

Kiho, Peterlin and Geil have studied twinning and phase transformations in drawn single crystals of polyethylene. The crystals were deposited on a Mylar film and deformation of the crystals was achieved by drawing the film. When the drawing was along the crystallographic a-axis, (110) twinning occurred; drawing in other directions caused phase changes to the monoclinic form. Bevis
has carried out a more detailed study of twinning and phase transformations in polyethylene single crystals which essentially confirms Kiho's work. When the crystal is drawn along the a-direction (110) twinning initially occurs, but there is evidence to suggest that the twinned portion can retwin on the (310) plane, and that further (110) twinning may then occur. Drawing in directions other than along the a-axis gives rise to phase transformations. These are not considered in this work.

In the original argument for (310) and (110) twinning, Frank et al (1958), considered only the magnitude of the shear strain, this being equal for the conjugate pairs. Current theories of the crystallography of deformation twinning have shown that, in addition to the magnitude of the shear strain, the ease of twinning is also dependent on the magnitude of molecular shuffles which are required to restore the correct crystal structure. In the case of polyethylene, these shuffles may be described as rotations about the [001] axis of the planar zig-zag molecular chains, there being no rearrangement along the molecular chains. It is also convenient to consider these rotations to occur formally after the macroscopic twinning shear, which is assumed to translate the molecular chains as rigid bodies. These stages are shown in fig 57a to 57c, and fig 57d to 57f for (110) and (310) twinning respectively. The first stage shows the initial structure before deformation, the second stage shows the structure after the shear, and the third stage shows the rotation of the molecular chains which restore the crystal structure. Four different rotations of the molecular chains are involved in each type of twinning. These rotations are all equally represented and, as shown in fig 57, for (110) twinning have magnitudes -16°, -30°, +66° and +66°. The corresponding angles for (310) twinning are +28°, +43°, -55° and -55°. A convenient measure of the energies associated with the shuffles which these rotations imply is the average
Fig. 57.

SHEAR AND MOLECULAR SHUFFLE REQUIRED TO PRODUCE

(110) AND (310) TWINNING IN POLYETHYLENE
of the square of the molecular displacement, see table 22. Using this hypothesis the above rotations indicate that the shuffle energy for (310) twinning is about 10% less than that for (110) twinning, suggesting that, in practice, the former should be marginally favoured. However it does not show the observed orientation dependence of the twinning modes. In order to account for this the applied stresses and strains must be considered.

Processes which cause plastic deformation involve the mechanisms of slip and sometimes twinning. Most experimental evidence suggests that metal single crystals start to twin, or to deform by slip, when the resolved shear stress in the appropriate direction exceeds some critical value. This law of a critical resolved shear stress has been found adequate for the description of slip in metals, and exists because all plastic crystals contain dislocation sources. The critical shear stress activates the weakest source, so that slip may begin and then propagate through the crystal. It is not entirely clear whether the law applies to deformation by twinning. Bell and Cahn, for example, have shown from their study on twinning in zinc crystals that no single reproducible critical shear stress exists for the creation of twinned lamellae.

The resolved shear stresses parallel to the \(K_1\) planes for (110) and (310) twinning in polyethylene obtained, using Mohr's circle construction are respectively 0.46 and 0.40 of the applied tensile stress along the \(a\)-axis or compressive stress along the \(b\)-axis, fig 58. It has been recently reported that a critical shear strain criterion should be used rather than a stress criterion in order to explain the deformation behaviour of crystalline mercury at 77°K (Abell, Crocker and Guynancourt 1971). This results from the fact that mercury is elastically very anisotropic and so the relationship between stress and strain will be a sensitive function of orientation. Orientated
<table>
<thead>
<tr>
<th>(310) Twinning</th>
<th>(110) Twinning</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of Chains N</td>
<td>Rotation</td>
</tr>
<tr>
<td>2</td>
<td>28°</td>
</tr>
<tr>
<td>2</td>
<td>43°</td>
</tr>
<tr>
<td>4</td>
<td>55°</td>
</tr>
<tr>
<td>Sum</td>
<td></td>
</tr>
</tbody>
</table>
Resolved shear stress.

\[ \varepsilon_2 = 0.1177 \sigma_z \]
\[ \varepsilon_1 = -0.0398 \sigma_z \]

Resolved shear strain \( \parallel \) to \( \mathbf{k}_1 \) for 310 twinning
\[ = 0.031 \sigma_z \]

Resolved shear strain \( \parallel \) to \( \mathbf{k}_1 \) for 110 twinning
\[ = 0.036 \sigma_z \]

Resolved shear strain. Compressive force along b.

\[ \varepsilon_1 = 0.1735 \sigma_1 \]
\[ \varepsilon_2 = -0.0398 \sigma_1 \]

Resolved shear strain \( \parallel \) to \( \mathbf{k}_1 \) for 310 twinning
\[ = 0.054 \sigma_1 \]

Resolved shear strain \( \parallel \) to \( \mathbf{k}_1 \) for 110 twinning
\[ = 0.063 \sigma_1 \]

Resolved shear strain. Tensile force along a.

Fig. 58. Mohr's circle construction.
polyethylene is known to be anisotropic and the elastic constants have been calculated for polyethylene single crystals by Odajuma and Maeda. The compliance values are as follows:

<table>
<thead>
<tr>
<th>Compliance x 10^-10 cm^2/dynes</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{11}$ = 0.1735</td>
</tr>
<tr>
<td>$S_{12}$ = -0.0398</td>
</tr>
<tr>
<td>$S_{13}$ = -0.00102</td>
</tr>
<tr>
<td>$S_{22}$ = 0.1177</td>
</tr>
<tr>
<td>$S_{23}$ = -0.00233</td>
</tr>
<tr>
<td>$S_{33}$ = 0.003954</td>
</tr>
<tr>
<td>$S_{44}$ = 0.3413</td>
</tr>
<tr>
<td>$S_{55}$ = 0.1136</td>
</tr>
<tr>
<td>$S_{66}$ = 0.3367</td>
</tr>
</tbody>
</table>

Taking the case of a compressive force applied along the $b$-axis:

The stress

$$\sigma = \begin{bmatrix} \sigma_1 & 0 & 0 \\ 0 & \sigma_2 & 0 \\ 0 & 0 & \sigma_3 \end{bmatrix}$$

The strain along $a$ is given by

$$\varepsilon_{11} = S_{1122} \sigma_2$$

or

$$\varepsilon_1 = S_{12} \sigma_2$$

The strain along $b$ is given by

$$\varepsilon_2 = S_{22} \sigma_2$$

The values of $\varepsilon_1$ and $\varepsilon_2$, calculated from the compliance figures are then used in the Mohr's circle construction to obtain the resolved shear strains parallel to the $K_1$ planes for (110) and (310) twinning. The same procedure is adopted for the case of a tensile force applied along the $a$-axis. Both constructions are shown in fig.58. Although the numerical values for the two cases are different as given overleaf,
Resolved shear strain 11 to $K_1$ for 110 twinning

<table>
<thead>
<tr>
<th>Resolved shear strain 11 to $K_1$ for 110 twinning</th>
<th>Compressive force along b</th>
<th>Tensile force along a</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.036\sigma$</td>
<td>$0.063\sigma$</td>
<td></td>
</tr>
</tbody>
</table>

the resolved shear stress and strain parallel to the $K_1$ plane for (110) twinning is always about 10% larger than for (310) twinning.

If the mechanism of twinning is considered, then the relative energy of the molecular shuffle for the two modes may be taken as representing the critical energy barrier for twinning to occur. The shuffle energy for (310) twinning is less than that for (110) twinning, whereas the resolved shear stress or strain is greater along the (110) twinning direction compared to the (310). The result is that the two effects counteract one another as shown diagramatically in fig 58.

From this it must be concluded that the difference in observed twinning mode cannot be accounted for by the difference in direction of the applied stress.

In order to account for this difference some other effect must be invoked. Recent work by Allen, Crellin and Bevis shows that the operative twinning mode in deformed single crystals is dependent on the geometry of the fold surface.

Normally, single crystals of polyethylene grown from xylene solution have diamond shapes. These diamonds may be divided into sectors having (110) and (110) fold surfaces, see fig 59. Allen et al have examined the deformation behaviour within these two separate sectors. In one sector (110) twinning occurs and the twinned portion then retwins on the (310) plane. In the other sector only (110) twinning occurs. Their explanation for this difference in the deformation behaviour of the (110) and (110) sectors arises from the difference in the (110) twin in the two sectors. As a result of the twinning
(1\overline{1}0) twinning in this sector induces a (100) fold surface. Further retwining in the (310) plane is observed.

(110) fold sector

(1\overline{1}0) fold sector

(1\overline{1}0) twinning in this sector induces a (1\overline{1}0) fold surface. Only (110) twinning is observed.

Fig. 59. Schematic diagram showing the twinning behaviour observed in the (110) and (1\overline{1}0) fold sectors.
process the fold planes within the \((\overline{1}10)\) twin in the \((\overline{1}10)\) and \((110)\) sectors become \((\overline{1}10)\) and \((100)\) respectively. Thus their examination of the deformed crystals shows that \((310)\) twinning occurs only in portions where the fold structure is of the \([100]\) type. The \([110]\) fold structure giving rise to \((110)\) twinning.

These observations may be applied to the results reported in this work. Krimm has shown by IR spectroscopy on a deuterated/hydrogenated mixture of polyethylene that, in normal bulk crystallised material, the fold surface is predominantly of the \((100)\) type. On the above grounds the twinning mode from such a fold surfaced crystallite would be \((310)\). At the moment it must be postulated that, during the process of forming the \((001)\) \([100]\) texture by annealing the rolled sheet, one produces predominantly \((110)\) fold. That a change in fold surface may take place is not improbable, since in the stage IV of the rotation of \(a-\) and \(c-\) axis, the identity of the lamellae is lost and then re-establishes itself to form the new lamellae.

Such a process could easily cause a change in fold surface to the \((110)\) type. The \((110)\) fold surface would then give rise to \((110)\) twinning. Positive identification of the fold surface in the rolled and annealed polyethylene would require an analysis similar to that of Krimm. What is surprising is that the fold surfaces can play an important part in the mechanism of crystallites in the bulk material. It is easier to see how the regular folds in single crystals have some influence on the interior. These findings suggest that the regularity of the folds in bulk polyethylene are not dissimilar to those in single crystals.

8.3. Studies of deformed polyoxymethylene

It is well known that, in close-packed hexagonal metals, rolling results in a biaxial orientation, in which the close-packed slip planes align parallel to the rolling plane, and the slip direction becomes
parallel to the rolling direction. As previously discussed in polymers, slip on (hk0) crystal planes is encouraged by the weak van der Waals forces between molecular chains, whereas it is the chain direction [001] that is found to orientate parallel to the rolling direction. This alignment of the chain direction of polyoxymethylene has been observed by Gezovich and Geil, using cold rolled material, and by Grey and McCrum using hot rolled material. However, only in the case of hot rolling did the most densely packed hexagonal planes of the polyoxymethylene (1010) lie in the surface as expected. Gezovich and Geil found a complex texture in the cold rolled material which was not satisfactorily explained. Their work suggested that on annealing a (1120) [001] texture resulted. The research reported here both confirms the work of these authors and due to the greater resolving power of our technique explains this difference of behaviour in terms of a phase transformation of the hexagonal to orthorhombic form of polyoxymethylene.

8.3.1. Experimental

The polyoxymethylene, Delrin, was compression moulded into a sheet 2 mm thick. The sheet was cut into strips 3 cm wide. The strips were rolled as follows:

1. Sample rolled, at 150°C, to a thickness reduction of 50% of the starting thickness; (1010) & (1015) pole figures in fig.60.

2. Sample rolled, at 150°C, to a thickness reduction of 80%; (1010) pole figure in fig.61.

3. Sample rolled, at low temperature, to a thickness reduction of 60%; (1010) pole figure in fig.62.

The low temperature rolling was achieved by plunging the sample into a solid CO2/acetone mixture, between rolling passes. Although the actual temperature of the sample, while rolling was in progress, was not determined, it is safe to assume that it is certainly less than ambient. The cold rolled sample was subsequently annealed at 150°C, the (1010) pole figure is shown in fig.63.
Fig. 60. Polyoxymethylene lightly rolled at 150°C.

Fig. 61. Polyoxymethylene heavily rolled at 150°C.
Fig. 62. Polyoxymethylene, rolled at low temperature.

Fig. 63. Polyoxymethylene, rolled at low temperature, annealed at 150°C.
The process of annealing was carried out in a similar manner to that previously described for polyethylene.

8.3.2. Results and Discussion

The general features of the (1010) pole figures is the general elongated maxima about the sheet normal/transverse direction plane, making an angle of about 30° with the sheet normal in the sheet normal/machine direction plane at low deformation; and about the sheet normal/transverse direction plane at high deformation. This confirms the observations of Gezovich and Geil, who found that the molecular chains initially became orientated at an angle of about 40° to the machine direction at low deformation. As the degree of orientation increases, this angle decreases to about 28°. The rotation is achieved by a tilt within the lamellae. At high deformation the lamellae break up, and the molecular chains reform parallel to the machine direction. The schematic model of this process is reproduced in fig 64. The alignment of the c-axis along the rolling direction is confirmed by the (1015) pole figure. The molecular chain alignment is not considered further.

Returning to the (1010) pole figures, it is obvious that the rolling process has not produced a pure fibre type orientation in which the (hk10) reflections are randomly arranged at right angles to the molecular chain, since there are discrete maxima within the elongated maxima. The higher deformation produces a more biaxially orientated texture.

The (1010) pole figure of hot rolled polyoxymethylene shows three maxima in the sheet normal/transverse direction plane, one along the sheet normal, and two at 60° either side of the sheet normal. This is consistent with the formation of the (1010) [0001] texture, see fig 65. This is as expected, and so requires no further explanation. The (1010) pole figure of cold rolled polyoxymethylene has four maxima,
Fig. 64. Schematic model indicating the effect of rolling on lamellar and chain tilt. Lamellar breakup is predominant at extents of roll less than 0.5.
Fig. 65. (10\overline{1}0)[0001] texture produced in hot rolled polyoxymethylene.

Fig. 66. (11\overline{2}0)[0001] texture produced in cold rolled and annealed polyoxymethylene.
two strong maxima along the transverse direction and two weak maxima either side of the sheet normal. The maxima no longer show hexagonal symmetry. When the cold rolled sample is annealed at 150°C the resulting pole figure shows six maxima, two along the transverse direction, and four at 30° either side of the sheet normal. This pole figure clearly shows hexagonal symmetry, but with the \( \{11\bar{2}0\} \) planes parallel to the surface, as shown in fig 66.

The observed features of the pole figures may be explained in terms of a phase transformation of the hexagonal to the orthorhombic form.

The method of preparation of orthorhombic polyoxymethylene is carried out at low temperature. The details are described in a patent application, D176, 27th January, 1961. Garazzol and Mammi have found it to have unit cell dimension \( a = 4.77\AA, b = 7.65\AA \) and \( c = 17.80\AA \). This compares with the unit cell dimensions of the hexagonal form of \( a = 4.46\AA \) and \( c = 17.3\AA \). Since the two forms have similar molecular chain arrangements, only variation in the \( (hk0) \) plane may be considered; the relationship between the forms is shown in fig 67. The orthorhombic structure may thus be formed from the hexagonal by an expansion along the \( a \)-axis and a contraction along the \( b \)-axis. It is known that orthorhombic polyoxymethylene transforms to hexagonal polyoxymethylene at 60°C or above.

The \( (10\bar{1}0) \) pole figure of material rolled at sub-ambient temperatures does not show hexagonal symmetry. This can be explained by the action of rolling causing a phase transformation to the orthorhombic form. The pole figure may then be considered as the \((020)\) pole figure of orthorhombic polyoxymethylene. The \( (10\bar{1}0) \) hexagonal and \( (020) \) orthorhombic planes having similar spacings and hence similar Bragg diffraction angles. The strong maxima along the TD arise from a large number of orthorhombic units having a
Fig. 67. Relationships between the hexagonal and orthorhombic forms in the ab plane.

Fig. 68. Phase transformation of (100)[001] orthorhombic to (1120)[0001] hexagonal on annealing.
(100) [001] texture and the weaker maxima along the SN from a (010) [001]. Annealing the sample above the transition temperature of 60°C results in a reversion to the hexagonal form. The orthorhombic (100) [001] texture transforms to the hexagonal (1120) [0001] texture as shown diagramatically in fig 68.

Obviously hot rolling at 150°C ensures that the material will only be present in the hexagonal form and so form a texture in which the (1010) planes are aligned in the sheet surface.

Zerbi suggests that the orthorhombic structure is 'chemically' held in this configuration by constraints in the preparation and therefore the transformation to the hexagonal form should be irreversible. Further evidence for the transformation of hexagonal to orthorhombic forms is required before such a mechanism can be confirmed. In its pure state the orthorhombic form shows both distinctive x-ray diffraction powder, see fig 69, and infra red patterns. The material formed by deformation contains a mixture of forms, and in the case of the x-ray powder patterns, deformation causes broadening of the peaks such that they overlap both forms as shown in fig 69. This makes identification of the particular form impossible.

Bevis and Harris have recently reported studies of deformed single crystals of polyoxymethylene. Deformation was by drawing along the a-axis. The phase transformation to the orthorhombic form was observed in a number of the single crystals. This then confirms that transformation to the orthorhombic form is possible during deformation procedures.
Fig. 69. Diffraction patterns of polyoxymethylene.
The production of finished or semi-finished articles requires moulding from the molten state. The flow in the molten state gives rise to orientation in the article. The orientation may be desirable or not, in that it may enhance or detract from the useful properties required in the article. It may be that any anisotropy in properties will be overshadowed by other factors, for example in blown bottles the wall thickness is usually large enough to give the overall strength required and any variation in properties is unimportant. This is not true of very thin extrusion blown films of high density polyethylene. Here anisotropy in properties will affect the usefulness of the film. An important property in these films is the tear strength. This may be simply related to the molecular structure by the criterion that high molecular axis alignment in a particular direction will give rise to a high tear strength, at right angles to that direction. In other words the tear will not easily cut across the molecular chains.

The molecular alignment present in the films is the result of the machine variables in the extrusion blow moulding equipment. Obviously the overall properties of the film are some function of the molecular properties of the polymer and will therefore vary between polymer grades. The characterisation of the orientation in blown films is useful as a bridge in understanding how the various machine variables give rise to anisotropy in the film properties. It is therefore useful to examine film made from the same polymer grade, but produced under different conditions.

The commercial objective is to produce a film which is tough and has good tear resistance, and to ensure that these properties are reasonably balanced in all directions of the film. Until recent times most
film produced in this way has been made from low density polymer into films of several hundred microns thickness. The relatively large thickness and the large amorphous content mean the film has reasonably similar properties in all directions. Much consideration has been given to the use of high density polyethylene film as a substitute for paper in packaging. Such film is of the order of 20 microns thick and, because it is highly crystalline, can be very highly orientated. In such thin film it becomes much more critical to have balanced properties. It is therefore necessary to understand how the various machine variables affect the morphology of the film and thus ultimately influence the properties of the film.

9.2. Machine Variables

In the process, shown in fig. 70, the molten polymer is extruded as a tube from an annular ring die; the extruded tube is inflated by an internal air bubble, and drawn away from the die by a pair of nip rollers. The molten polymer therefore experiences stresses in two directions, parallel to the machine direction (MD), from the drawing process, and parallel to the transverse direction (TD), as a result of the blowing-up effect of the bubble. The machine variables in such a process are; speed of extrusion, blow-up and draw ratio, and amount of cooling. The cooling is achieved by blowing cool air on to the outer surface of the bubble. A measure of the cooling is the vertical distance above the extruder die where crystallisation first occurs; this is known as the freeze line height. In the production of film these machine variables are not altered independently of each other since a film of constant thickness is required.

High density polyethylene films produced on two types of equipment are discussed in this work. These machines are the commercial Demag equipment which has a fast rate of output, and the smaller experimental Brabender equipment. The Brabender allows a much more flexible arrangement of machine conditions and so is used to study the effect of the machine variables on film properties. In both cases the temperature of the extruded molten polymer is in excess of 220°C.
Fig. 70. The production of extrusion blown film.
9.3. Measurement of film properties

The film properties may be characterised by the measurement of the tear strength parallel to the machine and transverse directions. The force in millinewtons required to propagate tearing across the film is measured using a precisely calibrated pendulum device (Elmendorf Tear Tester). Acting by gravity, the pendulum swings through an arc, tearing the specimen from a pre-cut slit. The specimen is held on one side by the pendulum and on the other side by a stationary member. The loss in energy by the pendulum is indicated by a pointer. The scale reading is taken as the force required to tear the specimen.

9.4. Films examined

Polymer 1 run on the commercial Demag film blowing equipment.

Polymer 2 run on the experimental Brabender film blowing unit under a range of different machine conditions.

The film produced on the Demag is included in this study because it gives a relatively more highly orientated film than that produced on the Brabender. Unfortunately it was not possible to obtain film made from the same polymer type in both. The value of the film from the Demag is that the overall texture present is much more clearly defined than in second series film. It may therefore be used to identify the manner in which orientation is induced in the film, which then leads to a clearer understanding of the orientation in the second series of film. The second series of films produced on the Brabender are made under a range of machine conditions. The machine variables and properties are given in table 23.

9.5. Results and discussion

9.5.1. Film made on the Demag equipment

Since the film was relatively highly orientated (110), (200), (020) and (011) pole figures were recorded and are shown in fig 71. These are discussed in detail.

The (020) pole figure shows two maxima along the TD with a spread of some 40° to 50° towards the SN and about 10° towards the MD. This
### DEMAG FILM

<table>
<thead>
<tr>
<th>Film Reference No.</th>
<th>Draw Ratio</th>
<th>Blow-up Ratio</th>
<th>Tear Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>D.1</td>
<td>not available</td>
<td></td>
<td>300 900</td>
</tr>
</tbody>
</table>

### BRAHÖNDER FILMS

<table>
<thead>
<tr>
<th>Film Reference No.</th>
<th>Draw Ratio</th>
<th>Blow-up Ratio</th>
<th>Freeze Line Height (mm)</th>
<th>Tear Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Machine Direction (millinewtons)</td>
</tr>
<tr>
<td>B.1</td>
<td>10.6</td>
<td>3.9</td>
<td>150</td>
<td>270</td>
</tr>
<tr>
<td>B.2</td>
<td>6.7</td>
<td>5.2</td>
<td>150</td>
<td>248</td>
</tr>
<tr>
<td>B.3</td>
<td>10.6</td>
<td>3.9</td>
<td>20</td>
<td>193</td>
</tr>
<tr>
<td>B.4</td>
<td>8.4</td>
<td>4.7</td>
<td>90</td>
<td>295</td>
</tr>
<tr>
<td>B.5</td>
<td>6.7</td>
<td>5.2</td>
<td>160</td>
<td>322</td>
</tr>
</tbody>
</table>
Fig. 71. Pole figures for Demag film, D1.
then fixes the position of the b-axis. The (110) pole figures show maxima occur on the great circle passing through the transverse direction and having an angle of about 40° with the sheet normal. The actual maxima come about 32° from the transverse direction along the great circle. It is obvious that the maxima elongate in the sheet normal/TD plane. From these two pole figures the a-axis (90° from the b-axis) is concluded to be between the sheet normal and the MD, making an angle of about 40° with the sheet normal. This may be confirmed from the (200) pole figure which shows the maxima to occur at 38° from the sheet normal.

Some information on the position of the c-axis is obtained from consideration of the (011) pole figure. The (011) poles lie between the (020) (b-axis) and the (002) (c-axis) and make an angle of 26° with the c-axis. In the pole figure the maxima along the great circle pass through the transverse direction having an angle of 50° to the SN. The maxima are about 25° either side of the SN/MD plane. Again the maxima elongate in the SN/TD plane.

From the (020) and (011) pole figures it is concluded that the c-axis maxima lie between the machine direction and the sheet normal, at about 50° to the sheet normal. The arrangement of the axes is shown diagrammatically in fig 72.

Previous work on the orientation of high density blown film by Lindenmeyer and Lustig has suggested that the a- and c-axes can orientate in the same direction. In their case both the a- and c-axes were observed to be along the MD (the reason for the a-axis being along the MD is considered later). In the present results, although there is a considerable spread on the maxima, the resolving power is sufficient to show that the a- and c-axes are arranged at right angles to each other, as illustrated in fig 72. The Lindenmeyer and Lustig results may be interpreted in terms of two separate components, one of a relatively small amount of material having a very high c-axis orientation along the MD (as in drawn material), and a second much larger component having the a-axis orientated
Fig. 72. Arrangement of axes in Demag film, D1
Along the MD. The c-axis from such a component is not highly orientated and so its effect merges with the background and it is not visible. Such a film is indicated by the very unbalanced properties reported by the authors.

In order to account for the actual orientation present in the film, some consideration must be given to the row-orientation model proposed by Keller. This model is a result of work carried out on polyethylene which is crystallised in the stressed state. This is achieved by cross-linking the polymer with a small dose of \( \gamma \) rays. The polymer is then drawn in the molten state and allowed to crystallise. Under conditions of stress in the melt, the high molecular weight polymer has been shown to crystallise in an extended chain form with the c-axis parallel to the machine direction. Since such an extended chain form has an inherently higher melting point than normal polyethylene, and it is also of higher molecular weight, it can exist in the melt. As the melt cools the extended chains then act as the nucleating points for the bulk crystallisation. Because nucleation takes place along the length of the extended chain the new crystallisation can take place only in a radial direction. This results in the preferential orientation of \( b \), the growth direction, perpendicular to the machine direction. In the case of thin film this will be along the transverse direction.

The bulk crystallisation occurs in the usual chain folded lamellar growth. Under conditions of high stress the molecular chains are lined up along the stress direction in the molten state. Consequently lamellae crystallise such that they are flat and orientated with normals parallel to the stress direction fig 73b. With conditions of very low stress, the lamellae twist. These conditions are not dissimilar to those of normal bulk crystallisation from the melt as spherulites, where the lamellae twist in growth, see fig 73a. Under conditions of intermediate stress Keller has observed some non-uniform twisting. This is shown
Stress direction

Fig. 73a & b. Schematic diagram illustrating crystallisation under (a) low stress and (b) high stress in polyethylene.

Fig. 73c. Sketch of the types of ribbon twists: (a) Uniform twist, (b) Non-uniform twist with large flat-on-view portions.
The twist of the material is rather abrupt and there is a comparatively long distance between twists. This will give rise to discrete concentrations of a- and c-axes at some angle to the stress direction. The actual amount that the c-axis moves away from the stress direction is a function of the degree to which relaxation of the polymer occurs. Such a process has similarities to the rotation of the a- and c-axes in annealed rolled polyethylene described in chapter

The way in which the crystalline orientation is brought about in the model may be used to describe the behaviour in the blown film.

The effects of draw and blow-up may be considered separately. Since the drawing effect is the larger of the two it is expected to have the greater influence. The process of drawing causes some high degree of molecular chain alignment with the machine direction in the molten state. The blow-up stress will cause the chains to spread out towards the transverse direction. The molten polymer does not crystallise immediately so the stresses in the film can relax. Since the machine direction drawing causes the largest amount of stress it is in the machine direction/sheet normal plane that the relaxation occurs. The actual amount of rotation is dependent on the rate at which cooling occurs. The slower the cooling the greater the relaxation and so the greater the amount of rotation. This process is shown diagrammatically in fig 74.

The orientation functions for the c-axis have been determined by the two methods outlined in Chapter 7. The values are compared with the tear strength values in Table 24.

It may be seen that both show approximately 3 times the amount of compared with the transverse direction. molecular axes along the machine direction/ This is in agreement with the expected criteria that the tear strength in any direction is proportional to the number of molecular axes at right angles to that direction. It may be seen that the results from the estimated position of the c-axis
Orientation under uniaxial stress (draw)

Orientation under biaxial stress (draw and blow up).

Film

Pole diagram

a) Orientation resulting from high stress conditions

b) Orientation resulting if stress condition is allowed to relax, i.e. with slow cooling.

Fig. 74. Arrangement of axes during processing.
<table>
<thead>
<tr>
<th>Direction</th>
<th>C-Axis Orientation function</th>
<th>Tear strength values millinewtons</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD</td>
<td>Mathematically calculated from pole figures</td>
<td>0.493</td>
</tr>
<tr>
<td>TD</td>
<td>Estimated from a visual inspection of pole figures</td>
<td>0.170</td>
</tr>
<tr>
<td>SN</td>
<td></td>
<td>0.337</td>
</tr>
<tr>
<td>Ratio of MD/TD</td>
<td></td>
<td>2.90</td>
</tr>
</tbody>
</table>
This is probably due to the fact that, in the pole figures, unless there is a complete separation of pole intensity from background intensity at the particular Bragg reflection then the pole figures include some intensity due to the background, as discussed in Chapter 7.

9.5.2. Films from Brabender

The films in general show less well defined orientations and so only (110) (200) and in some cases (020) pole figures were recorded, figs 75 to 79.

In all the (200) pole figures the maxima are situated in the sheet normal/machine direction plane and are elongated to a certain extent towards the transverse direction. The position of the maxima along the sheet normal/machine direction plane is given in table 25. This position appears to be dependent on the rate at which the film is cooled, as measured by the freeze line height. The greater the rate of cooling, the closer the maxima become to the sheet normal direction. For similar draw and blow-up conditions film B.3 gives maxima 46° from the sheet normal, whereas film B.1 gives maxima 60° from the sheet normal. It is also evident that, for similar cooling conditions, the films with the higher draw ratios tend to have their maxima closer to the sheet normal.

The films having a high draw ratio show elongated (110) maxima 20° to 30° along the MD extending outwards to the edge of the pole figure. This effect is enhanced by rapid cooling and is particularly noticeable in the case of B.3 (this in fact being similar to the (110) pole figure observed in the Demag film). The maxima do not extend to the edge of the pole figures in the case of the films with a lower draw ratio; the maxima spread to 20° to 30° around the sheet normal. More generally, films obtained under more rapid cooling conditions e.g. B.3 show a higher degree of orientation, which is easily discernible from both pole figures.
Fig. 75. Pole figures for Brabender film, B1.
Fig. 76. Pole figures for Brabender film, B2
Fig. 77. Pole figures for Brabender film, B3
Fig. 78. Pole figures for Brabender film, B4
Fig. 79. Pole figures for Brabender film, B5
In B.3 the maxima are along the transverse direction but spread towards the sheet normal/transverse direction with a slight preference for the maxima at the sheet normal and transverse direction.

### TABLE 25

**Position of 002 Pole Maxima from the Sheet Normal**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.1</td>
<td>59°</td>
</tr>
<tr>
<td>B.2</td>
<td>78°</td>
</tr>
<tr>
<td>B.3</td>
<td>46°</td>
</tr>
<tr>
<td>B.4</td>
<td>62°</td>
</tr>
<tr>
<td>B.5</td>
<td>80°</td>
</tr>
</tbody>
</table>

The (020) pole figure of film B.5 shows an extra weak maximum about the sheet normal. This is probably the result of the slow cooling rate, i.e. largest freeze line height, which allows some transcrystalline growth.

All crystallisation processes are initiated at some nucleating centre, which may consist of impurities or unmelted material. However, nucleation may also take place from the surface. As a result of impingement of the crystallites growing from the surface upon each other, they are forced to grow mainly in the film normal direction, other avenues being blocked. The growing crystallites advance into the interior of the film on a planar front. Since growth is in the crystallographic b-direction the net result is an orientation of the b-axis towards the sheet normal. Conditions of slow cooling favour the formation of this transcrystalline layer. Since the c-axes in such a structure are randomly arranged in the plane of the sheet, it would be expected to give rise to an increase in tear strengths in both machine and transverse directions. This appears to be so as shown by the difference in properties between films B.2 and B.5.
highly orientated Demag film. It is apparent that the slower the rate of cooling, the greater the rotation of the a- and c- axes about the transverse direction. The actual draw and blow-up values have a much smaller effect on the orientation, although high values of draw do give rise to an overall higher orientation. The effect of blow up appears to be fairly constant and, as discussed with the Demag film, tend to elongate the c-axis distribution towards the transverse direction.

9.5.3. Correlation of c-axis orientation function with properties

The c-axis orientation functions have been determined by the two methods outlined in chapter 7. The estimated position and spread of the c-axis distribution are as follows:

<table>
<thead>
<tr>
<th>Film</th>
<th>Position of the c-axis in the SN/MD plane from the MD.</th>
<th>Spread a) in TD/SN plane</th>
<th>b) in MD/SN plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.1</td>
<td>60°</td>
<td>55°</td>
<td>35°</td>
</tr>
<tr>
<td>B.2</td>
<td>80°</td>
<td>60°</td>
<td>40°</td>
</tr>
<tr>
<td>B.3</td>
<td>50°</td>
<td>40°</td>
<td>30°</td>
</tr>
<tr>
<td>B.4</td>
<td>60°</td>
<td>45°</td>
<td>35°</td>
</tr>
<tr>
<td>B.5</td>
<td>80°</td>
<td>65°</td>
<td>40°</td>
</tr>
</tbody>
</table>

The values for the orientation functions are compared with the tear strength measurements in table 26.

The results show that the film properties may be correlated with the c-axis orientation functions obtained from estimated positions. No such correlation appears in the case of mathematically deduced functions. Since the films are not very orientated this finding was to be expected.

9.6. Conclusions

The study of orientation in blown high density polyethylene film leads to an understanding of the way in which the machine variable affects the crystalline orientation. In thin films the crystalline orientation may be directly related to properties of the film such as tear strength.
### TABLE 26

<table>
<thead>
<tr>
<th>Film</th>
<th>Direction</th>
<th>C-axis Orientation function</th>
<th>Tear strength (millinewtons)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mathematically calculated</td>
<td>Estimated from visual inspection</td>
</tr>
<tr>
<td>B.1</td>
<td>MD</td>
<td>0.383</td>
<td>0.098</td>
</tr>
<tr>
<td></td>
<td>TD</td>
<td>0.366</td>
<td>0.272</td>
</tr>
<tr>
<td>B.2</td>
<td>MD</td>
<td>0.292</td>
<td>0.082</td>
</tr>
<tr>
<td></td>
<td>TD</td>
<td>0.408</td>
<td>0.269</td>
</tr>
<tr>
<td>B.3</td>
<td>MD</td>
<td>0.308</td>
<td>0.303</td>
</tr>
<tr>
<td></td>
<td>TD</td>
<td>0.429</td>
<td>0.211</td>
</tr>
<tr>
<td>B.4</td>
<td>MD</td>
<td>0.339</td>
<td>0.142</td>
</tr>
<tr>
<td></td>
<td>TD</td>
<td>0.398</td>
<td>0.276</td>
</tr>
<tr>
<td>B.5</td>
<td>MD</td>
<td>0.306</td>
<td>0.085</td>
</tr>
<tr>
<td></td>
<td>TD</td>
<td>0.395</td>
<td>0.278</td>
</tr>
</tbody>
</table>
The determination of the orientation of the crystallites then becomes the intermediate step in relating film properties to the processing conditions. In this work, it has been shown that the most important factor is the cooling condition (as measured by freeze line height). The faster the rate of cooling, the greater the stress at the point of crystallisation. This results in the $c$-axis being close to the machine direction. Under slower conditions of cooling, the stresses within the melt can relax. This allows the $c$-axis to rotate about the direction, away from the machine direction. The resolved component of the $c$-axis along the machine direction therefore decreases with decreasing cooling rate. This is the reason for the observed variability in transverse direction tear strength with cooling conditions.

The effect of draw ratio only serves to give a more orientated film on which the above process may operate. The effect of blow up only has a secondary effect, that of spreading the $c$-axis distribution towards the transverse direction. When such a distribution rotates about the transverse direction, the actual resolved component along the transverse direction remains approximately the same. This is reflected by only small changes in machine direction tear strength with machine variables. There is some evidence for some trans-crystallisation from the surface of the film when the film is at very slow cooling rates.

The tear strength properties of the films relate to the number of molecular axes aligned at right angles to the direction of tear. The results show that the film properties may be correlated with the $c$-axis orientation functions obtained from the estimated position.
CONCLUSIONS

A large number of x-ray diffraction methods have been described for the study of various structural parameters in polymeric materials. It has been the aim of this work to examine and develop a number of these methods and to compare their relative performance. It has been found useful to divide order into two types; structural order and alignment order. Structural order includes the parameters of crystallinity, unit cell dimensions, crystallite size and perfection. Alignment order is the degree of preferred orientation.

Structural order

The measured value of a chosen structural order parameter, e.g. crystallinity, depends not only upon the method, but also upon the way in which the method is applied. Of particular importance are the assumptions adopted in the interpretation of the x-ray data, for example, where to place the background. The absolute value of a parameter cannot be obtained by any method, but the methods which tend to give the most acceptable values are those in which attempts are made to surmount the problems of x-ray data interpretation.

The methods adopted in this work are as follows:

1) Crystallinity - The Matthews, Païzer & Richards method.
2) Unit cell dimensions - Internal standard method. A small quantity of graphite brushed on to the surface of the sample serves as the reference standard. Where comparative results are required, thick samples are employed with no correction for sample absorption. For more 'absolute' results thin samples are recommended, the thin specimen requiring no correction for absorption effects.
3) Crystallite size and perfection - If two diffraction orders are available, the Integral Breadth method may be used. With only one
The parameters of structural order are used to study the effect of molecular chain characteristics on structure. A series of molecular weight fractions have been examined. Increasing molecular weight causes a decrease in crystallinity. The summation of the product of crystallinity and percentage of the weight fraction gives a considerably reduced figure for crystallinity than is observed in the bulk unfractionated material. This means that there is an interaction between chains of various lengths during the crystallisation process. It is proposed that the presence of the lower molecular weight fractions, in which the longer chains are crystallising, increases the mobility of the system. This enables more of the high molecular weight fraction to crystallise than is possible when that fraction crystallises on its own.

A series of branched copolymers have been studied. By slow cooling and annealing polyethylene, a semi-equilibrium crystallisation state is obtained. Under such crystallisation conditions, changes in unit cell dimensions and crystallinities may be related to the size and number of the branch groups. With methyl and ethyl branches the unit cell 'a' dimension is substantially increased, and is the result of accommodation of the branches within the crystalline lattice. Butyl branches are rejected from the lattice with no consequent increase in unit cell 'a' dimension.

The effect of prolonged annealing has been shown to result in increases in crystallinity of the sample.

The changes of the structural order parameters, brought about by modification to the molecular chain characteristics and processing conditions, have been related to the properties of the material.
The study of the parameters of structural order at elevated temperatures shows three types of behaviour. In the first region, up to about 110°C, the unit cell a-dimension increases linearly, the crystallinity and crystallite size remain approximately constant. The increase in the a-dimension has been explained in terms of a twisting of the planar zig-zag chain backbone. The second region extends from 110°C up to a temperature of about 5 to 10°C below that where the crystalline diffraction peaks completely disappear. In this region the rate of increase in the a-dimension decreases markedly; the crystallinity falls rapidly and the crystallite size increases. These observations are explained by partial recrystallisation. The new crystalline regions incorporate less of the features, such as branches and chain ends, which, if present, cause an increase in a-dimension. Their rejection results in a smaller average unit cell a-dimension. The high temperature recrystallisation causes an increase in crystallite size. The third region occurs just below the point where no crystalline diffraction peaks are observed. In this region, where less than 20% of the polymer remains crystalline, the unit cell a-dimension increases very rapidly. It is proposed that, where only a small amount of crystalline material remains, the normal orthorhombic structure can break down and tend towards the hexagonal form.

**Alignment order**

The determination of preferred orientation has been greatly improved by the use of computing methods to draw up the pole figures and to calculate the \( \langle \cos^2\phi \rangle \) orientation functions. The pole figures may be used qualitatively to examine the textures resulting from deformations, such as rolling and drawing, and from the crystallisation processes.
The use of the increased resolving power of computer drawn pole figures is clearly demonstrated in the studies of the twinning modes in deformed polyethylene. This work has confirmed that a (100) [001] texture, which further undergoes (310) twinning, occurs in both rolled and certain cold drawn samples. The observation of (310) twinning occurs when the material experiences a compressive force parallel to the [010]. If the sheet of polyethylene is orientated such that it is possible to draw parallel to the [100], then the drawing results in (110) twinning. Several mechanisms have been examined to explain the orientation dependence of the twinning mode. These include critical resolved stress and strain criteria for twinning. These ideas have failed to explain the observed twinning features. A likely alternative explanation is that the morphology of the material in the two cases is different. Bevis has shown that the twinning behaviour of the (110) and (110) sectors of a polyethylene single crystal is different. (110) twinning occurs from 110 fold regions and (310) twinning from 200 folds. In compression moulded bulk polyethylene, the fold surface is (200). By analogy with the single crystal case, this would give rise to (310) twinning. The observation of (110) twinning after drawing the (001) [100] texture implies the mechanism by which the (001) [100] texture is formed results in the reformation of the fold surface to a (110) type.

The difference in deformation behaviour between high and low density polyethylenes permits examination of the interaction of amorphous and crystalline phases to be made. In heavily rolled low density polyethylene (310) twinning is observed, whereas in high density material (310) twinning is observed only after the rolled sheet has been annealed at 110°C. The twinning arises from the
rolling procedure. The amorphous chains are extended by the pressure of the rollers. The stored elastic energy may be released on removal of the rollers, giving a compressive force parallel to the rollers. In the low density polymer the relatively large amount of amorphous material generates sufficient compressive forces to cause twinning. In the high density polymer there is only a small amount of amorphous material, and this does not generate sufficient forces to effect twinning. At elevated temperatures the crystalline lattice is not held so rigidly and, on annealing, the compressive forces present in the high density sample become sufficient to give rise to twinning.

Geil and Gezovich, and Grey and McCrum, have pointed out the difference in texture resulting from cold and hot rolling polyoxymethylene, but were unable to explain their observation. The present work has demonstrated that cold rolling results in a phase transformation from the hexagonal to orthorhombic forms, the resulting texture being (100) [001]. Since the transition temperature of the orthorhombic to the hexagonal form is about 60°C, when the sheet is annealed above this temperature the sample reverts to the hexagonal form. The texture changes from the (100) [001] to (1120) [0001]. Hot rolling polyoxymethylene results in a (1010) [0001] texture.

The study of orientation in extrusion blown high density polyethylene film leads to an understanding of the way in which the machine variables affect the crystalline orientation. The orientation results from stress crystallisation, in which the molecular axis (c-axis) is positioned between the machine direction and the sheet normal. The actual position is a function of the rate of cooling; the faster the cooling, the closer the c-axis is to the machine direction. Slow cooling enables the stress state to relax and allows the c-axis to rotate about the transverse direction, towards
the sheet normal. The variables of draw and blow-up have only secondary effects. The effect of draw is to set up the stress state; blow-up causes a spread of the c-axis towards the transverse direction.

The movement of the molecular axis away from the machine direction with changes in the rate of cooling is the main reason for the change in properties. The property of tear strength may be taken as being proportional to the number of molecular chains at right angles to the tearing direction. The distribution of the c-axes along the machine and transverse directions have been quantitatively estimated by means of $\langle \cos^2 \phi \rangle$ orientation functions. These have been shown to correlate with the observed tear strengths of the films.

In general, this study confirms the wide applicability of x-ray diffraction methods in the characterisation of order in semi-crystalline polymers.
APPENDIX I

CONSTRUCTION THE POLE DIAGRAMS ON THE
GRAPH-PLOTTER

A general contour mapping programme is available. This takes
a rectangular grid of points and interpolates between adjacent pairs
of these points to find the positions of equal intensity on the grid
lines. These points are then joined by a smooth curve. This pro­
gramme has been modified to draw pole figures.

The data from the pole figures are intensity values at points
at 10° intervals round a spiral of the reflection method (see chapter
7). The data may be round the circles of equation \( r = a \tan \frac{1}{2} \theta \)
if \( \theta > 70 \) if the transmission method is employed.

The points can be denoted by

\[
(r_i, \delta_j) \quad i = 1, 19 \quad j = 1, 36 \quad \text{and} \quad (r_{20}, \Theta_1)
\]

where

\[
r_i = a \tan \frac{1}{2} \left[ 90 - 5(i - 1) \right] \quad i = 1 \quad \text{for circle at } \theta = 90^\circ
\]

\[
a \tan \frac{1}{2} \left[ 90 - 5(i - 2) - \frac{5 \delta_j}{360} \right] \quad i = 2, 19 \quad \text{for spiral } \theta = 90^\circ
\]

\[
\delta_j = (j - 1) \times 10^\circ \quad j = 1, 36
\]

The measured intensity values \( I_\varphi \) must be corrected both for
fall-off due to the samples low absorption and for background scatter.

The correction applied is as follows:

\[
I_\varphi' = \frac{A}{A_0} I_\varphi - A_0
\]

Where \( A_\varphi \) is the intensity from a non-crystalline sample at
angle \( \varphi \) and \( A_0 \) is the intensity of the sample at the centre of the
pole figure \( \varphi = 0^\circ \).

The data is transformed into a rectangular grid by

\[
(r_i, \delta_j) \rightarrow (i, j) \quad i = 1, 19 \quad j = 1, 36
\]

and also

\[
(r_i, \delta_i) \rightarrow (i, 37) \quad i = 1, 5
\]

\[
(r_i, \delta_i) \rightarrow (i - 1, 37) \quad i = 7, 20
\]
The method of the general contour mapping programme can now be used to determine, on the rectangular grid, points of equal intensity. These are then transformed by the inverse of the above transformation, by naturally extending the definition of $r_i$ and $\delta_j$ for non-integer $i$ and $j$. The transformed points are then joined by a smooth curve to produce a contour of the required intensity on the pole figure.

The programme is written in I.C.L. 1900 Fortran and uses the I.C.L. graph plotting routines.

Output is to an on-line graph plotter

Cone size 13 K

Overlays are not used

Data Layout

These lines which are preceded by NL must be written on a new line.

NL 1. Parameter: 1

NL 2. Scale: Diameter of diagram = scale x 20 cm

NL 3. Parameter: 2 all contours numbered; 3 contour numbers at edge of pole figure only.

4. Starting angle for spiral.

NL 5. Starting angle for

6. Pitch per 360° rotation.

NL 7. Title

NL 8. Number of characters in title above.

NL 9. Number of rotations, $M$

10. Number of readings per rotation, $N$

NL 11. $(M \times N) + 1$, intensity values.

NL 12. Parameter: 0 subtract background readings

1 correct for absorption and subtract background

NL 13. Intensity values for non-crystalline sample; one value corresponding to each value of $M$. 
14. Number of contour levels required, \( k(k \geq 20) \)

15. \( K \) contour values.
   Numbers 1 - 12 repeated as required.

16. All data must end with parameter 0.
|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
| 1 | 0.8 | 2 | 90 | 90 | 5 |
| RIGIDEX 25 HEAVILY ROLLED 110 POLE FIGURE |
| 41 |
| 19 | 36 |
| 20 | 9 | 4 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 8 | 14 |
| 25 | 11 | 5 | 4 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 7 | 12 |
| 25 | 10 | 5 | 2 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 6 | 16 |
| 30 | 13 | 6 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 14 |
| 30 | 12 | 5 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 6 | 18 |
| 35 | 15 | 6 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 5 | 16 |
| 37 | 15 | 7 | 5 | 4 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 6 | 10 | 22 |
| 42 | 20 | 7 | 5 | 4 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 6 | 10 | 20 |
| 44 | 14 | 6 | 5 | 4 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 5 | 6 | 10 | 26 |
| 50 | 24 | 6 | 5 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 5 | 9 | 24 |
| 44 | 14 | 6 | 5 | 4 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 5 | 7 | 12 | 30 |
| 52 | 25 | 9 | 6 | 5 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 6 | 10 | 28 |
| 45 | 20 | 7 | 6 | 5 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 5 | 7 | 12 | 31 |
| 54 | 27 | 10 | 7 | 5 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 5 | 7 | 12 | 28 |
| 47 | 24 | 6 | 5 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 5 | 6 | 12 | 29 |
| 56 | 29 | 11 | 8 | 5 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 5 | 6 | 11 | 26 |
| 44 | 23 | 8 | 6 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 5 | 6 | 11 | 28 |
| 49 | 28 | 11 | 6 | 5 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 5 | 6 | 11 | 25 |
| 33 | 22 | 10 | 6 | 5 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 5 | 7 | 11 | 28 |
| 38 | 25 | 14 | 8 | 5 | 4 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 5 | 7 | 13 | 24 |
| 30 | 23 | 11 | 7 | 5 | 4 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 5 | 8 | 14 | 24 |
| 29 | 25 | 16 | 9 | 4 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 6 | 13 | 20 |
| 23 | 20 | 11 | 7 | 5 | 4 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 6 | 9 | 15 | 21 |
| 23 | 20 | 15 | 9 | 6 | 4 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 6 | 10 | 14 | 17 |
| 23 | 17 | 12 | 8 | 5 | 4 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 6 | 15 | 18 |
| 18 | 17 | 15 | 10 | 6 | 4 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 6 | 8 | 11 | 14 | 15 |
| 15 | 15 | 13 | 9 | 6 | 4 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 6 | 8 | 11 | 14 | 15 |
| 15 | 15 | 14 | 10 | 7 | 5 | 4 | 3 | 3 | 3 | 3 | 4 | 5 | 7 | 10 | 13 | 13 |
| 13 | 14 | 13 | 10 | 7 | 6 | 5 | 4 | 3 | 3 | 3 | 3 | 4 | 6 | 9 | 11 | 14 | 14 |
| 14 | 14 | 14 | 14 | 9 | 6 | 5 | 4 | 3 | 3 | 3 | 3 | 5 | 6 | 7 | 10 | 12 | 12 |
| 12 | 12 | 12 | 11 | 8 | 6 | 5 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 6 | 8 | 10 | 10 |
| 10 | 10 | 9 | 7 | 5 | 4 | 4 | 4 | 4 | 4 | 4 | 5 | 6 | 8 | 9 | 10 | 10 |
| 10 | 10 | 10 | 10 | 8 | 6 | 5 | 5 | 5 | 5 | 5 | 5 | 6 | 7 | 8 | 9 | 9 | 9 |
| 9 | 9 | 9 | 9 | 8 | 8 | 7 | 6 | 5 | 5 | 5 | 5 | 6 | 7 | 7 | 8 | 8 | 8 |
| 8 | 8 | 8 | 8 | 7 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 7 | 7 | 8 | 8 | 8 |
| 8 | 8 | 8 | 8 | 7 | 7 | 6 | 6 | 6 | 6 | 6 | 6 | 7 | 7 | 7 | 7 | 7 |
| 7 | 7 | 7 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
| 6 | 1 |
| 1 |
| 1.1 | 7.1 | 11.9 | 17.6 | 23.7 | 29.5 |
| 36.3 | 42.6 | 48.8 | 53.1 |
APPENDIX II

Papers Published:

1. Study of Twinning in Heavily-Drawn High-Density Polyethylene.  
2. Comparison of Twinning Produced by Rolling and Annealing in 
   10, 369.
3. Phase Transformations in Cold Rolled Polyoxymethylene, Nature 
   Physical Science, 1972, 236, 60.
4. A Study of Branching in Ethylene Copolymers by X-ray Diffraction. 

Papers presented at Conferences:

1. 'A Study of Order in Polymers by X-ray Diffraction'. SCI Polymers 
2. 'The Use of the Schulz X-ray Texture Coniometer to observe 
   Deformation Twinning and Phase Transformations in Polymers'. 
   European Physical Society Conference 'Radiation Scattering 
3. 'The Orientated Structure of Extrusion Blown High Density 
   Polyethylene Films'. Symposium on 'Supramolecular Structure 

Presentation of work at University Research Colloquia

University of Surrey - Physics Department
University of Surrey - Chemistry Department
University of Oxford - Department of Engineering Science
University of Liverpool - Metallurgy & Material Science 
                          Department
University of Reading - Physics Department
University of Bristol - Physics Department
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Phase Transformations in Cold Rolled Polyoxymethylene

Gray and McCrum have pointed out the difference between the textures produced by cold and hot rolling polyoxymethylene (POM)\textsuperscript{1}. They found that rolling POM at a temperature close to the melting point produced a (10\textit{T}0) [0001] texture, that is, with the most densely packed planes (10\textit{T}0) aligned parallel to the rolling plane. Such behaviour is normally expected in rolling\textsuperscript{2}, but Gezovitch and Geil\textsuperscript{3}, who studied the effect of rolling POM at ambient temperatures, obtained textures which tended towards a fibre-type orientation but with a concentration of the (10\textit{T}0) poles along the transverse direction. Annealing this sample produced an orientation in which the (11\textit{T}0) planes tended to align parallel to the rolling plane. We believe that these differences may be accounted for by a phase transformation to the orthorhombic form of polyoxymethylene when rolled at low temperature.

Normally polyoxymethylene is hexagonal (H-POM) having a unit cell \(a=4.46\ \text{Å}\) and \(c=17.3\ \text{Å}\). The preparation of polyoxymethylene with an orthorhombic structure (O-POM) has, however, been described\textsuperscript{4}, the unit cell dimensions being \(a=4.77\ \text{Å}, b=7.65\ \text{Å}\) and \(c=17.80\ \text{Å}\). As the two forms have similar chain backbone arrangements, only variations in the \(ab\) plane may be considered; the relationship between the two
forms is shown in Fig. 1. The orthorhombic structure may be formed from the hexagonal by an expansion along the $a$ axis and a contraction along the $b$ axis. It is known that O-POM irreversibly transforms to H-POM on annealing at 60° C or above.5.
In the reported work on cold rolled POM, Gezovitch and Geil started with an injection moulded sample which almost certainly was orientated, probably approaching the (10T0) [001] texture. In their rolling procedure the authors went to considerable lengths to prevent the sample from heating under the action of rolling. This they achieved by rolling very slowly and allowing the sample to cool between passes. Thus during the rolling the sample would have been well below the transition temperature of 60°C.

In our present work we have examined the effect of rolling POM at sub-ambient temperatures. This was achieved by immersing the injection moulded sheet of POM in a CO2 acetone mixture between each rolling pass. The sample was rolled to 40% of the starting thickness.

A wide angle diffraction pattern was taken and, because of deformation, this showed a broad maximum which covers the orthorhombic (110) and (020) peaks and the hexagonal (10T0) peak. The Schulz texture goniometer on which the sample was examined was set at an angular position which approximated to the orthorhombic (020) and/or the hexagonal (10T0) peaks.

The pole figure was obtained by a previously reported method6, and is given in Fig. 2. The pole figure shows some weak fibre-type orientation in which the fibre axis makes an angle of about 30° with the rolling direction, a fact which has been reported by others3. The chief features of the pole figure are, however, strong maxima along the transverse direction together with weaker maxima about the sheet normal direction. The pole figure may be interpreted in terms of a phase change.

![Diagram](image)

Fig. 3 Phase transformation of (100)[001] O-POM to (1120) [001] H-POM on annealing.
to O-POM under the compressive action of rolling, which produces a large number of orthorhombic units having a (100) [001] texture. These give rise to the strong maxima along the transverse direction. There are also a smaller number of units having a (010) [001] texture which give rise to the weaker maxima along the sheet normal direction.

On annealing the cold rolled specimen at 150° C the pole figure obtained is similar to Fig. 16 of Gezovitch and Geil, showing maxima along the transverse direction and at 30° on either side of the sheet normal direction, at right angles to the fibre axis. As the temperature is well above the transition point of orthorhombic to hexagonal this may be explained as a change from the predominant (100) [001] texture to the hexagonal (1120) [0001] texture as shown diagrammatically in Fig. 3.

Thus phase change from hexagonal to orthorhombic form adequately explains the difference between the texture of cold rolled and hot rolled POM. More details of this work with a fuller discussion of the mechanism of the phase transformation will be reported elsewhere.

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Comparison of Twinning Produced by Rolling and Annealing in High- and Low-Density Polyethylene

A number of authors have studied the effect of drawing, rolling and annealing on the structure of polyethylene. In particular, Hay and Keller have studied, in detail, the effect of these processes on low-density polyethylene. They found the action of drawing, followed by rolling, produced a (100) [001] texture together with (310) and/or (110) twinning. Their explanation of this was that the (100) [001] texture was the primary consequence of the rolling, and twinning arose on removal of the roller pressure. The elastic energy, stored in the amorphous component while the roller pressure is acting, is released as the roller passes on. This results in compressive forces in the transverse direction, which provide the driving force for the twinning.

We have previously described a method of studying orientation in polymers using the Schulz texture goniometer linked with the ability to plot the pole figures by means of a computer program. Among the advantages of this technique are the fact, that the whole pole figure may be studied in detail, that the position of the pole maxima may be determined to 1 or 2 degrees, and that it is possible accurately to delineate the weaker maxima in the pole figure. These facilities are often essential when studying the orientations produced in deformed polyethylene. Here we report our studies of the comparisons of orientations produced in rolled and annealed high and low density polyethylene using computer drawn pole figures.

The materials studied were low-density Alkathene WJG 11, made by ICI Ltd. and high-density Rigidex 25, made by BP Chemicals International Ltd. The polymer chips were compression-molded at 160°C into sheets of 1 mm thickness. Strips 3 cm wide were cut from the sheets and rolled at room temperature. We have defined light rolling as reducing the sheet thickness by about 50% and heavy rolling as a reduction of about 80%. Annealing was carried out by immersing the sheets in a silicone oil bath, maintained at a given temperature, for three minutes.

The x-ray crystallinities were determined by a method based on that of Matthews et al., the Alkathene being 61% crystalline and the Rigidex 86% crystalline. Although such crystallinities cannot be regarded as absolute, the values may be taken as indicative of the amounts of crystalline material present on a relative scale. The texture measurements were made by using a Schulz texture goniometer as previously described.

For the purpose of this work we have examined only the (110) and (020) poles in order to define the texture present. The pole figures for the low- and high-density polyethylenes are given in Figures 1–3. The rolling and transverse directions are defined as the north-south and east-west directions respectively. The contour levels were chosen to give ten contours at equal levels, between the minimum and maximum intensities.

The (110) and (020) pole figures for the lightly rolled Alkathene and Rigidex and the heavily rolled Rigidex all show the same general features (only the latter being illustrated in Fig. 1). The (110) pole figure shows two maxima along the transverse direction at angles of 59° either side of the perpendicular direction. The (020) pole figure has two maxima along the transverse direction at angles of 90° either side of the perpendicular. These are interpreted as a (100) [001] texture. In such a texture the calculated position of the (110) maxima would be along the transverse direction at angles of 59° either side of the perpendicular. Thus, the maxima at 59° are in good agreement with this figure.

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The (110) and (020) pole figures for the heavily rolled Alkathene show extra maxima (Fig. 2). The (110) pole figure shows three elongated maxima along the transverse direction, two at angles of 65° on either side of the sheet normal direction, the third about the normal. The (020) pole figure shows four maxima along the transverse direction, two at angles of 90° and two at angles of 36° on either side of the perpendicular.

We have shown previously with drawn and annealed Rigidex that such pole figures are due to the (100) [001] texture with twinning on the 310 plane. It can be calculated from the cell parameters, that, for (310) twinning, the twinned lattice should be at an angle of 54° to the original lattice (Fig. 4). Thus, where (310) twinning occurs on the (100) [001] texture, the (110) pole figure would have four new maxima along the transverse direction at angles of 70° and 3° on either side of the perpendicular, the one at 70° merging with the original maxima at 57° to give an elongated maximum at 65°; and the (020) pole figure would have new maxima along the transverse direction at an angle of 37° on either side of the perpendicular.
Examination of the (110) and (020) pole figures for the Rigidex sheet, which had previously been heavily rolled and then annealed at 110°C (Fig. 3), shows that the extra maxima caused by 310 twinning are present, although of lower intensity; i.e., new 110 maxima 3° on either side of the perpendicular, and 020 maxima along the transverse direction, 36° on either side of the perpendicular. Thus, although in heavily rolled high-density polyethylene no twinning is observed, a small amount of twinning is detected after the rolled sheet has been annealed.

The observations for the rolled low-density polyethylene are in agreement with the work of Hay and Keller,\(^3,4\) however, by using more accurate pole figures, it is possible to confirm the twinning plane as the (310). Our results for the high-density polyethylene may be interpreted in terms of their model of the actual process of rolling: i.e., elastic energy being stored as the amorphous chains are extended by the roller pressure, which gives rise to compressive forces in the transverse direction. In the low-density polyethylene the relatively large amount of amorphous material (39%) generates sufficient compressive forces to cause twinning. In the high-density polyethylene there is only a
small amount of amorphous material (14%) and presumably this does not generate sufficient force to cause twinning. As the high-density polyethylene is heated, the crystalline lattice will not be held so rigidly and thus, at elevated temperatures, the compressive forces present become sufficient to cause a certain amount of twinning.

This work was carried out on a collaborative basis between the University of Surrey and BP Chemicals International Ltd. The texture measurements were made at the University of Surrey and the computing carried out at BP Chemicals International Ltd.

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Fig. 4. Relationship between (100) [001] texture and 310 twinned lattice in polyethylene.


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A Study of Branching in Ethylene Copolymers by X-ray Diffraction

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By slow cooling and annealing polyethylene a semiequilibrium crystallisation state is obtained. Under such crystallisation conditions changes in unit cell dimensions and crystallinities, as measured by X-ray diffraction, may be related to the size and number of branch groups in polyethylene copolymers. Thus methyl and ethyl groups may be accommodated within the crystalline lattice whereas butyl groups are not. The method may be used to determine the type and extent of branching in unknown ethylene copolymers.

1. Introduction

It is known that the orthorhombic unit cell dimensions and the degree of crystallinity of a given polyethylene are not unique, but vary systematically with crystallisation conditions, annealing and deformation. However, under specific conditions of crystallisation and annealing it is possible to obtain reproducible unit cell dimensions and crystallinities. In such cases any differences in the measured values between polymer samples then reflect differences in structure rather than in the thermal or mechanical history. Branching is one such structural feature which can alter the unit cell dimensions and crystallinities in polyethylene. This has been studied by a number of authors who, unfortunately, have used a wide range of crystallisation conditions to prepare their samples. This leads to a variation in their results; however the various studies do tend to fall into one of two types. Firstly, those whose samples have been rapidly cooled or quenched (as in normal compression moulding), and secondly those who use isothermal crystallisation conditions.

Thus Swann, Cole and Holmes, Reding and Lovell, and Shrayama et al., using the first type of crystallisation condition, found a range of branches, even up to C_{10} in size, all caused an expansion in the unit cell dimensions, predominantly of the a-axis dimension, and a decrease in crystallinity. This was taken to arise from the accommodation of the branches within the crystalline lattice. On the other hand, Richardson et al., and Baker and Mandelkern using isothermal crystallisation conditions found only methyl branches expanded the lattice whereas larger branches, such as propyl, did not. It was found that as the crystallisation condition moved away from the ideal, the propyl branches caused an increasingly larger expansion of the lattice, presumably as more were accommodated.
We believe that between the extremes of the quenched and isothermally crystallised states there is a semi-equilibrium state where short branches (methyl and ethyl) may be accommodated within the crystalline lattice, whereas other branches, butyl and larger, are rejected from the lattice. Such a semi-equilibrium state may be used to determine the type of branch and the level to which it is present in the polymer.

2. Experimental

2.1. Crystallisation procedure

A number of ethylene/α-olefin copolymers, having known levels of branching, were crystallised by moulding into flat sheets at a temperature some 20°C above their melting points and then cooling slowly to room temperature over a period of about one hour. All samples were subsequently annealed by immersion in a silicone oil bath, maintained at a temperature 5 deg. C below their melting points, for a period of 3 min.

2.2. Unit cell dimensions

The diffraction pattern of polyethylene exhibits two strong reflections, the 110 and 200, and a number of very weak reflections. In samples of low crystallinity these weaker reflections become lost in the background. Thus extrapolation procedures for determining the unit cell dimensions are not applicable. Instead we have used an internal standard to calibrate the angular position of the two strong peaks. From these the a- and b-axis dimensions may be obtained, and since it is these which show any expansion in the lattice they suffice to characterise the unit cell.

In the case of a moulded sheet it is not possible to mix in the internal standard before pressing since it might influence the crystallisation behaviour. We, therefore, brush a very small quantity of graphite onto the surface of the sheet. The quantity is so small, less than 0.001 g, that it does not interfere with the alignment of the specimen, but because the graphite packs preferentially with the 002 planes perpendicular to the sheet’s surface it gives a very strong 002 reflection. This 002 reflection is close enough to the 110 and 200 polyethylene reflections to serve as a useful angular standard. Any possible variation in the spacing of the graphite is overcome by using a single, characterised, source of the material.

Thus, from the diffractometer trace the angular spacing of the 110 and 200 polyethylene reflections may be accurately determined with reference to the graphite. The unit cell a- and b-dimensions of the polymer are then calculated from the equation

\[
\left( \frac{2 \sin \theta}{\lambda} \right)^2 = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}
\]

to an accuracy of about 0.003 Å.

2.3. Degree of crystallinity

A number of authors have proposed X-ray methods for the determination of the degree of crystallinity in polymers. All are essentially methods based on the division of the diffraction pattern into two regions, one associated with the crystalline phase and...
A study of branching in ethylene copolymers by X-ray diffraction

the other with the amorphous phase, the ratio of their areas giving a measure of the degree of crystallinity. The short-comings of such methods are well documented; however it has been shown that all the methods are useful when used on a relative basis, i.e. for ranking changes in the degree of crystallinity.

The method used in the present work is based on that of Matthews et al. and is shown in Figure 1. The diffractometer trace is obtained using Ni filtered Cu Kα radiation. The division on the trace of the scattering into amorphous and crystalline areas is facilitated by knowing the shape and position of the amorphous pattern. This may be obtained by examination of the polymer above its melting point. The degree of crystallinity is given by the equation

\[
\text{Degree of crystallinity} = \frac{I_{110} + 1.36I_{200}}{I_{110} + 1.36I_{200} + 0.816A} \times 100\%
\]

where \(I_{110}\) and \(I_{200}\) are the areas of the 110 and 200 diffraction peaks respectively and \(A\) is the area of the amorphous scatter. The correction factors take into account the Lorentz polarisation factor and changes in scattering factor with angle.

It has already been shown that with narrow molecular weight fractions of polyethylene the crystallinity is somewhat dependent on the molecular weight. Low molecular weight material gives a particularly high crystallinity; with increasing molecular weight the crystallinity falls off and remains approximately constant above a molecular weight of about 30000. Thus where one is correlating changes in crystallinity with branching it is essential to use polyethylene samples having a relatively high molecular weight. Taking into account such considerations it is possible to determine the crystallinity to a relative accuracy of about 0.5% by the method outlined above.

3. Results and Discussion

The effect of various crystallisation and annealing treatments on a single polymer
Table 1. Crystallinity and unit cell dimension of ethylene-butene-1 copolymer containing 9.1 Et branches/1000 C, crystallised under a range of conditions

<table>
<thead>
<tr>
<th>Crystallisation conditions</th>
<th>Crystallinity (%)</th>
<th>Unit cell dimensions (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moulded 150 °C/5 min, quenched</td>
<td>62.6</td>
<td>7.512 4.980</td>
</tr>
<tr>
<td>Moulded 150 °C/5 min, slow cooled</td>
<td>69.0</td>
<td>7.499 4.971</td>
</tr>
<tr>
<td>Moulded 150 °C/5 min, slow cooled</td>
<td>70.4</td>
<td>7.493 4.962</td>
</tr>
<tr>
<td>Annealed 115 °C in silicone oil bath 5 min:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1st sample</td>
<td>70.2</td>
<td>7.494 4.964</td>
</tr>
<tr>
<td>2nd sample</td>
<td>70.4</td>
<td>7.493 4.962</td>
</tr>
<tr>
<td>3rd sample</td>
<td>70.0</td>
<td>7.494 4.965</td>
</tr>
<tr>
<td>Moulded 150 °C/5 min, slow cooled</td>
<td>70.4</td>
<td>7.493 4.963</td>
</tr>
</tbody>
</table>

The indications are that the state achieved using the described conditions of slow cooling and annealing represents a reproducible semi-equilibrium state some way between the true equilibrium state, achieved under isothermal crystallisation conditions, and the quenched state.

Table 2 gives the unit cell a- and b-dimensions and crystallinities for a number of copolymers having a range of branch types and levels, together with those of a homopolymer. It is evident that in samples having methyl and ethyl branches the unit cell a-dimension is expanded with respect to the homopolymer, whereas those containing butyl branches have similar unit cell dimension to the homopolymer. The interpreta-

Table 2. Crystallinity and unit cell dimensions for a number of branched polyethylenes

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Branching measured by i.r.</th>
<th>Crystallinity (%)</th>
<th>Unit cell dimensions (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene homopolymer</td>
<td>~0.1 Me/1000 C</td>
<td>90</td>
<td>7.421 4.950</td>
</tr>
<tr>
<td>Ethylene-propylene</td>
<td>5.1 Me/1000 C</td>
<td>80.6</td>
<td>7.457 4.954</td>
</tr>
<tr>
<td></td>
<td>6.8 Me/1000 C</td>
<td>76.8</td>
<td>7.472 4.955</td>
</tr>
<tr>
<td></td>
<td>9.6 Me/1000 C</td>
<td>71.6</td>
<td>7.498 4.962</td>
</tr>
<tr>
<td>Ethylene-butene-1</td>
<td>4.0 Et/1000 C</td>
<td>83</td>
<td>7.445 4.951</td>
</tr>
<tr>
<td></td>
<td>9.1 Et/1000 C</td>
<td>70.2</td>
<td>7.494 4.964</td>
</tr>
<tr>
<td></td>
<td>14.0 Et/1000 C</td>
<td>61.6</td>
<td>7.536 4.977</td>
</tr>
<tr>
<td>Ethylene-hexene-1</td>
<td>~2.5 Bu/1000 C</td>
<td>78</td>
<td>7.420 4.950</td>
</tr>
<tr>
<td></td>
<td>4.7 Bu/1000 C</td>
<td>69.5</td>
<td>7.428 4.948</td>
</tr>
</tbody>
</table>
A study of branching in ethylene copolymers by X-ray diffraction

Figure 2. Graph of the number of branches /1000 C vs. unit cell a-dimension: (O) Me branches; (x) Et branches.

The conclusion placed upon these results is that the shorter branches, methyl and ethyl, are accommodated within the crystalline lattice whereas the larger butyl branch is rejected into the amorphous phase. In the case of the shorter branches the expansion of the a-dimension is proportional to the number of branches and is independent of the nature of the branch, Figure 2. Also, the decrease in the crystallinity per branch is similar for the methyl and ethyl branches but is much larger for the butyl branch, Figure 3.

Figure 3. Graph of % crystallinity vs. unit cell a-dimension for a number of branched polyethylenes: (□) Homopolymer; (O) Me branches; (x) Et branches; (△) Bu branches.
The above results provide a method for distinguishing between methyl and ethyl branches and the larger butyl branches, and for determining the level of these shorter branches. The method has been used on a number of co-polymer systems, and also to determine the nature of branches in PVC by the study of the polyethylene obtained on reduction of the PVC with LiAlH$_4$. As the present work has been concerned only with copolymers in which the branches are believed to be randomly situated along the polymer backbone and with less than 20 branches/1000 carbon atoms it would be unwise to use the method on polymers having higher levels of branching until the validity at such levels has been confirmed.

It is not possible to compare the actual effect per branch on the crystallinity and unit cell dimension as reported in this paper with other such studies because of the lack of uniformity in the determination of the level of branching by infrared methods. Thus, for example, Cole and Holmes have used the method described by Haslam and Willis, in which all branches are determined as methyls at the end of butyl branches. Again, ASTM method D2238 estimates the branching in terms of methyls at the ends of long branches. In reality different infrared absorbance values should be used for each type of branch, as has been done in our studies. The Haslam and Willis method will underestimate the level of branching smaller than butyl and overestimate those larger than butyl. In the work of Shrayama et al., no correction was made for the fact that with the lower molecular weight fractions there is an appreciable contribution to the apparent branching from the chain ends. Additionally, there is the extra problem that with narrow molecular weight fractions the crystallinity is somewhat dependent on the molecular weight and so changes in crystallinity could be due to variation in molecular weight rather than in the presence of branches. Unless the appropriate data are available this factor cannot be presumed to be negligible.

Acknowledgments

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Study of Twinning in Heavily-Drawn High-Density Polyethylene

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Preferred orientation produced by heavily drawing high-density polyethylene sheet has been studied by means of computer drawn pole figures, using a Schulz texture goniometer. A resolving power of the order of one degree was obtained, and this revealed that the heavy drawing caused a (100) [001] texture, and twinning on (310). Annealing at temperatures near the melting point produced relaxation of the residual twinning stresses and restoration of the (100) [001] texture.

Introduction

A number of studies have been reported on the orientation of deformed low-density polyethylene. These show that, during the initial stages of drawing, the (100) planes align preferentially with the first detectable chain orientation, corresponding to a chain inclination of about 55° to the draw direction (Hay & Keller, 1966). On further extension, the chains approach their final alignment by a gradual decrease of this angle of inclination. By following other deformation processes, such as rolling and annealing, it has been possible to gain information about the manner in which the crystalline lamellae and the amorphous chains make up the bulk structure. Phase transformations and deformation processes have been studied in high density polyethylene (Seto, Hara & Tanaka, 1968), but less detailed crystallographic work has been reported on this material than on low-density polyethylene. In this paper an investigation of the texture of heavily-drawn ('necked') high-density polyethylene is reported. The distribution of the a, b and c axes has been determined by computer-drawn pole figures, with a consequent increase in resolving power.

Experimental

Materials

The material studied was a high-density polyethylene, Rigidex 25, made by BP Chemicals Ltd. The polymer chips were compression moulded at 160°C into sheets of 1 mm thickness. Strips 3 cm wide were cut from the sheets and were drawn at room temperature so that a 'necked' region was produced in each specimen. This width was chosen to suit the Schulz goniometer. Necking caused the thickness to be reduced by about 70% and the lateral width by about 20%. Annealing was carried out by immersing the necked sheet for three minutes in a silicon oil bath maintained at a given temperature.

X-ray measurements

The X-ray measurements were made using a Schulz Texture Goniometer (made by Philips, Model PW 1078) employing nickel-filtered Cu Kα radiation. Although this instrument and its use have been described in the literature, (Schulz, 1949; Cullity, 1956), the use of computer drawn pole figures is rare in polymer studies.

For reflexion from a given (hkl) plane, the surface of the sheet specimen is set to be at the appropriate Bragg angle (θ) with respect to the incident beam. In this position, only those (hkl) planes which are parallel to the surface will reflect. For reflexions from other (hkl) planes, which are inclined to the surfaces, the texture goniometer allows the sheet to be rotated about two axes. The first axis is parallel to the intersection of the specimen surface, and the plane defined by the incident and diffracted beams. The second axis is the normal to
the surface. Suitable rotations about these two axes will bring any of these \((hkl)\) planes in the specimen to the reflecting position. Rotation about the two axes are measured in terms of \(\varphi\), the angle of tilt about the first axis and \(\delta\), the angle of rotation about the second axis. As the angle of tilt is changed, the projection of the reflecting plane normal moves across a diameter of the stereogram. Change in the angle of rotation causes the reflecting plane normal to move on a small circle, radius \(\varphi\), centred about the projection of the sheet normal. When both rotations occur simultaneously, the path traced is a spiral and covers the stereogram. This rotation is synchronized with the motion of the chart in the recorder. Hence a continuous trace is produced, any point on which defines an intensity at a point on the spiral of the stereogram.

Because of the low absorption of polymer materials, there is a high penetration of the incident X-ray beam into the sample and this causes a large amount of defocusing, which produces an intensity reduction of high values of \(\varphi\). The simplest way to allow for this effect is to obtain the profile for a randomly orientated (powder) specimen of the same material and correct the recorded intensities from the sheet. The outer portion of the pole figure \((\varphi = 10^\circ \text{ to } 90^\circ)\), where the reduction is greatest, is covered by the transmission method.

Intensity measurements were made, at 10° intervals round \(\delta\), from the continuous trace. These measurements are put into the computer together with the required contour levels. The computer then joins up points of equal intensity at the various contour levels. In the pole figures the contour levels are arbitrarily chosen to give about twelve contours, at equal levels between the maximum and minimum intensities.

### Texture

A pole figure is the stereographic projection of the normals or 'poles' of crystal planes. Normally, for a single crystal, several different crystal planes may be shown on a single pole figure. However, to show the effect of preferred orientation, only poles from a given crystal plane are plotted, the pole density being indicated by the contour lines.

In considering the pole figures of a sheet sample it is customary to orient the sample so that the drawing direction is represented on the pole figure as the north–south direction, and the transverse direction as the east–west direction.

**The advantages of computer drawn pole figures**

The advantages of obtaining pole figures using texture goniometers instead of flat plate photographs have previously been reported (Lindenmeyer & Lustig, 1965). However, for a detailed study of the preferred orientation in polymers, it is necessary to be able to have pole figures showing high resolution due to the possibility of complex orientations. These can result from the mobility of the crystalline regions relative to the amorphous regions, in addition to the deformation within the crystalline regions. In order to analyse these effects it is essential to be able to determine the pole maxima to within 1° or 2°. Computerized pole figures obtained using a Picker single-crystal analyser have been reported (Point, Homès, Gezovich & Keller, 1969) but estimates of possible resolving power were not made.

The advantages of drawing the pole figures obtained from the Schulz texture goniometer using a computer instead of hand drawing are:
(a) the ability to utilize very much more data, with a resulting increase in accuracy,
(b) the interpolation process involved in drawing the contour lines is performed with mathematical accuracy,
(c) the elimination of human error.

The effect of these points is greatly to improve the resolution of strong adjacent pole maxima and the accurate delineation of regions with diffuse maxima.

We feel that the study of twinning in high-density polyethylene reported in this paper demonstrates the value of the method.

**Polyethylene**

In studying crystalline orientations in polymers it is necessary to understand the basic crystallography of the polymer. In the past, some authors have used the (110) and (020) poles to obtain the orientation of the crystalline axes. As has been pointed out, this can lead to erroneous conclusions about the c-axis orientation (Lindenmeyer & Lustig, 1965). The use of the (200), (020) and (002) poles may also lead to incorrect conclusions. Firstly, there is some overlap of the 200 reflexion by the much stronger 110 reflexion. Secondly, the 520 reflexion occurs at the same Bragg angle as the 002 reflexion. However, while it is desirable to have the orientation of the three separate axes, it is not essential to the interpretation.

Since it is not possible to choose planes which directly give the orientation of each axis, one must use planes which give separate diffraction maxima and from which the orientation of each axis may be derived. In this work we have studied the (110), (020) and (211) poles.

**Results**

The (110), (020) and (211) pole figures for ‘necked’ high-density polyethylene are shown in Figs. 1 to 3 respectively. The (110) pole figure shows three elongated maxima along the transverse direction, two at angles of 64° either side of the perpendicular direction, the other about the perpendicular direction. The (020) pole figure shows four maxima along the transverse direction, two at an angle of 90° and two at an angle of 36° either side of the perpendicular. The (211) pole figure confirms that the c axis is along the draw direction. An initial interpretation of these pole figures suggests an alignment of the c axis along the draw direction with (100) planes and (110) planes parallel to the sheet surface.

However, from such textures, the (020) pole figure should have maxima along the transverse direction at 90° either side of the perpendicular when the (100) planes are parallel to the surface, and at 33° either side of the perpendicular when the (110) planes are parallel to the surface. These results show that the second (020) pole maxima occur at an angle of 36° either side of the perpendicular. Again, a careful study of the (110) pole figure shows that the (110) plane normals are not along the perpendicular direction but are at about 2° to 3° either side of the perpendicular. Therefore, although during the action of drawing it would be quite reasonable to expect the most densely-packed planes, (100) and (110), to align themselves with the sheet surface, the pole maxima suggest that the (110) planes are not exactly parallel with the surface, but make angles of ±3° with the surface.
The (110) and (020) pole figures for the sample annealed at 115°C are shown in Figs. 4 and 5, and the samples annealed at 130°C are shown in Figs. 6 and 7. These may be interpreted as a reversion to a pure (100) [001] texture, for which, one would expect the (110) pole figure to have two maxima along the transverse direction at 57° either side of the perpendicular direction, and the (020) pole figure to have two maxima along the transverse direction at 90° either side of the perpendicular direction. The texture obtained may have been affected by the experimental conditions, such as the dimensions of the specimen, temperature etc. In particular the effect of lateral contraction may be important in influencing the deformation mode. Some of these points are being further investigated.

Discussion

Interpretation of these pole figures can be made in terms of crystal rotation, slip and twinning. The expected slip and twinning modes of deformed polyethylene can be predicted from consideration of the crystal structure. From work on low-density polyethylene which had been drawn and subsequently rolled, it has been shown that, on heavy rolling, twinning causes the (110) planes to come near the surface of the sheet (Frank, Keller & O'Connor, 1958; Hay & Keller, 1966; Clayton, 1969). Our pole figures suggested that (110) planes became parallel to the sheet surface when drawing high-density polyethylene without rolling, and thus twinning was suspected.

Here, only the twinning modes are considered (Frank, Keller & O'Connor, 1958). The plane across which twinning occurs must be parallel to the c axis, since any other plane would involve a change in direction of the chains. The structure of polyethylene is orthorhombic, showing pseudo-hexagonal symmetry. The planes with hexagonal symmetry that are lost by the consequent reduction of symmetry are in orthorhombic indices, (110), (1T0), (310) and (3T0). From the work of Frank (1953) there can be expected to be twinning modes of the first kind, where the twin and the original structure are reflections of each other across the plane. The four modes make two conjugate pairs, (310) with (110) and (3T0) with (110). In full, the twinning elements are:

<table>
<thead>
<tr>
<th>Composition</th>
<th>Conjugate plane</th>
<th>Shear direction</th>
<th>Conjugate axis</th>
</tr>
</thead>
<tbody>
<tr>
<td>(110)</td>
<td>(3T0)</td>
<td>[1T0]</td>
<td>[130]</td>
</tr>
<tr>
<td>(310)</td>
<td>(110)</td>
<td>[130]</td>
<td>[110]</td>
</tr>
</tbody>
</table>

The stresses needed to operate either of these modes are similar, being either compressive stresses in a range of directions near the [100] direction, or tensile stresses in a range of directions near the [010] direction. In our case compressive stresses could arise from the lateral contraction associated with necking.

It is possible to distinguish between the two possible modes of twinning by pole figure studies. It can be calculated from the cell parameters that, for (310) twinning, the twinned lattice should be at an angle of 54° to the original lattice, and, for (110) twinning, the twinned lattice should be at an angle of 69° to the original lattice. Therefore, if the (310) twinning occurs with the texture (100) [001], the (110) pole figure would have four new maxima along the transverse direction at angles of 70° and 3° either side of the perpendicular, and the (020) pole figure would have the new maxima along the transverse direction at an angle of 37° either side of...
the perpendicular (see Fig. 8). The maxima fit exactly those observed in our pole figures.

These results suggest that the action of heavy drawing is to produce a (100) [001] texture which then twins on the (310) plane (Fig. 9), rather than that some of the crystallites align themselves with their (100) planes in the sheet surface and other crystallites with their (110) planes in the sheet surface.

The fact that twinning has occurred is confirmed by the study of the annealed sheet. Since it has been observed that annealing causes a reversion to the pure (100) [001] texture, this may be interpreted as arising from the relaxation of the twinning shear at elevated temperature. If the orientations observed came purely from alignment of (100) and (110) planes with the sheet surface, there would be no driving force to restore crystallites back to the (100) [001] alignment.

Conclusions

The (110), (020) and (211) pole figures of the heavily drawn, high-density polyethylene confirm that the c axis is along the draw direction, with some (100) planes parallel to the sheet’s surface, and some (110) planes nearly parallel to the surface. The accuracy of the computer drawn pole figures enables us to demonstrate that these (110) planes make an angle of about 3° with the sheet surface. This shows that the action of drawing is to cause twinning and not to orientate individual crystallites with the most densely packed planes, i.e. (100) and (110), parallel with the sheet surface. We have confirmed that the orientation is that of a (100) [001] texture, together with twinning on the (310) plane.

As confirmation of this we have observed a reversion to the pure (100) [001] texture on annealing the drawn sheet, just below the melting point. If the original structure arose from separate crystallite orientation, there would be no driving force to rotate the (110) oriented crystallites. However, if twinning has occurred, there will be stresses round the boundaries of the twinning regions, and it is the relaxation of these stresses which

Fig. 7. Rigidex 25 020 heavily drawn, annealed 130°C.

Fig. 8. Stereograms to show (a) the (100) [001] texture in drawn and annealed polyethylene and (b) (310) twinning (see smaller type) in drawn polyethylene.
would provide the driving force to convert the twinning structure to a pure (100) [001] texture.

This work has been carried out on a collaborative basis between the University of Surrey and BP Chemicals Ltd. The experimental work was performed at the University of Surrey and the computing at BP Chemicals Ltd.

References
