THE TENSILE DEFORMATION OF ORIENTED POLYVINYL CHLORIDE
AND ORIENTED POLYETHYLENE

A Thesis submitted to the Faculty of Mathematical and
Physical Sciences of the University of Surrey for the
Degree of Doctor of Philosophy

by

Edward Hargreaves

February 1970
Abstract

Polyvinyl chloride was oriented by hot drawing. The deformation was investigated under uniaxial tension at room temperature and at 50°C.

The onset of yield was localised in deformation bands of which two kinds, referred to as type 1 and type 2, were observed. Type 2 bands formed before type 1 bands, but only type 1 bands developed into a running neck. The yield behaviour could be satisfactorily accounted for by a yield criterion based on the von Mises criterion, provided that a term representing an internal compressive stress in the molecular alignment direction was included. The internal stress was found to increase from zero with increasing prior extension ratio and birefringence, and was also equal to the true stress acting on the material during the initial hot drawing. The inclusion of a hydrostatic stress term in the criterion, the application to anisotropic materials of the Coulomb criterion and a critical strain form of the von Mises criterion are considered.

Optical anisotropy changes are discussed in terms of an affine deformation model, which was found to apply for deformation at room temperature and 50°C, but not at 71°C and 90°C. The model has also been applied to the deformation, at 50°C, of oriented polyvinyl chloride, the molecular alignment of which was described by three different distribution functions. The agreement between theory and experiment was best for what is referred to as the Kuhn and Grün type 1 distribution.
Stress whitening, which developed during hot stretching, is associated with changes in the room temperature deformation behaviour. There was a yield-fracture transition at $\lambda_0 = 0^\circ$ and a change in ductile fracture behaviour at other values of $\lambda_0$. The ductile fracture direction in stress whitened material has been accounted for by a theory which proposed that the minimum energy was used in propagating the fracture.

Two different kinds of type 1 bands were observed in oriented polyethylene. It is suggested that crystallinity may affect the position of the minimum yield stress.
1. Tables and diagrams appear in that order at the end of each Chapter.

2. The symbol, Y, for the angle between the band boundary and the tensile axis should be read as γ in Chapters 3 and 4.

3. The reference to Darlington and Saunders (1968) in Chapter 4 and References should be Saunders and Darlington (1968).
# CONTENTS

<table>
<thead>
<tr>
<th>Abstract</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>4</td>
</tr>
</tbody>
</table>

## CHAPTER 1  Introduction

1.1 Yielding of Oriented Polymers 10
1.2 Yield Criteria 11
1.3 Optical Anisotropy 12
1.4 Fracture 13
1.5 Outline of Project 13

## CHAPTER 2  Experimental Procedure and Preparation of Oriented Material

2.1 Experimental Procedures 15

2.1.1 Tensile Testing Facilities 15
2.1.2 Optical Microscopy 18
2.1.3 Measurement of the Density of Polyvinyl Chloride 19
2.1.4 X-ray Diffraction and Scattering Studies 19
2.1.5 Electron Microscopy 23
2.1.6 Strain Measurements 23

2.2 Material Specification 25

2.3 Preparation of Oriented Polyvinyl Chloride 27

2.3.1 Stress-Strain Behaviour during Extension at Elevated Temperatures 32
2.3.2 Birefringence of Oriented Polyvinyl Chloride 38
2.3.3 Wide Angle X-Ray Diffraction Studies 39
2.3.4 Stress Whitening of Polyvinyl Chloride 47
2.3.5 Summary 55

2.4 Preparation of Oriented Polyethylene 56

2.5 Tensile Testing of Oriented Material 57
### CHAPTER 3 Observations of the Yielding and Cold Drawing of Oriented Polyvinyl Chloride

3.1 Experimental

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2.1 Load-Extension Curves</td>
<td>92</td>
</tr>
<tr>
<td>3.2.2 Yield and Drawing Stresses</td>
<td>95</td>
</tr>
<tr>
<td>3.2.3 General Features of Deformation Bands</td>
<td>102</td>
</tr>
<tr>
<td>3.2.4 Deformation Band Directions</td>
<td>104</td>
</tr>
<tr>
<td>3.2.5 Appearance of Deformation Bands</td>
<td>105</td>
</tr>
<tr>
<td>3.2.6 Stages in the Development of Deformation Bands</td>
<td>108</td>
</tr>
<tr>
<td>3.2.7 Strains in Deformation Bands and Necked Regions</td>
<td>114</td>
</tr>
<tr>
<td>3.2.8 Geometry of Deformation</td>
<td>119</td>
</tr>
<tr>
<td>3.2.9 Optical Anisotropy in Deformation Bands and Necked Regions</td>
<td>122</td>
</tr>
</tbody>
</table>

3.3 Discussions

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>123</td>
</tr>
</tbody>
</table>

### CHAPTER 4 Evaluation of a Yield Criterion

4.1 Choice of a Suitable Yield Criterion

4.2 The Hill Modification of the von Mises Criterion

4.3 Influence of Internal Stress on Yielding

4.4 The Influence of Molecular Orientation on the Internal Stress and the Hill Theory Parameters

4.5 Comparisons of the Yield Behaviour of Oriented Polyethylene Terephthalate and Oriented Polyethylene with that of Oriented Polyvinyl Chloride

4.6 The Bauschinger Effect and the Influence of Hydrostatic Stress on Yielding

4.7 Possible Modifications of the Coulomb Criterion

4.8 Concluding Remarks

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>168</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>175</td>
</tr>
<tr>
<td>4.3</td>
<td>180</td>
</tr>
<tr>
<td>4.4</td>
<td>190</td>
</tr>
<tr>
<td>4.5</td>
<td>206</td>
</tr>
<tr>
<td>4.6</td>
<td>212</td>
</tr>
<tr>
<td>4.7</td>
<td>225</td>
</tr>
<tr>
<td>4.8</td>
<td>230</td>
</tr>
</tbody>
</table>

### CHAPTER 5 Observations of Optical Anisotropy Changes During Deformation

5.1 Experimental Procedures

5.2 Results

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2.1 First Stage. Extension of the Unoriented Material</td>
<td>263</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>261</td>
</tr>
<tr>
<td>5.2</td>
<td>263</td>
</tr>
<tr>
<td>5.2.1</td>
<td>263</td>
</tr>
</tbody>
</table>
## 5.2.2 Second Stage. Uniform Deformation of Oriented Polyvinyl Chloride

## 5.2.3 Second Stage. Cold Drawing of Oriented Material

## 5.3 Discussion

### 5.3.1 Qualitative Interpretation of Results

### 5.3.2 Optical Anisotropy and Strain History

## CHAPTER 6 Optical Anisotropy in Oriented Polyvinyl Chloride

### 6.1 Theory

#### 6.1.1 Outline of Theory

#### 6.1.2 Optical Anisotropy Due to a Distribution of Units

#### 6.1.3 Evaluation of the Distribution of Units

#### 6.1.4 Alternative Procedure for Averaging Angular Functions

### 6.2 Application of the Theory to the Experimental Results

#### 6.2.1 First Stage of Experiment

#### 6.2.2 Second Stage of Experiment; Choice of Initial Distribution Function

#### 6.2.3 Second Stage of Experiment; Kuhn and Grün Type 1 Distribution Function

#### 6.2.4 Second Stage of Experiment; Kuhn and Grün Type 2 Distribution Function

#### 6.2.5 Second Stage of Experiment; Ratary Distribution Function

### 6.3 Results and Discussion

## CHAPTER 7 Some Observations on the Fracture of Oriented Polyvinyl Chloride

### 7.1 Experimental

### 7.2 Results
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Section</th>
<th>Description</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.2.1</td>
<td>Sudden Fracture at $\lambda_0 = 90^\circ$</td>
<td>339</td>
<td></td>
</tr>
<tr>
<td>7.2.2</td>
<td>Sudden Fracture at $\lambda_0 = 0^\circ$</td>
<td>340</td>
<td></td>
</tr>
<tr>
<td>7.2.3</td>
<td>Ductile Fracture in the Neck Boundary</td>
<td>346</td>
<td></td>
</tr>
<tr>
<td>7.2.4</td>
<td>Ductile Fracture at the Neck Boundary</td>
<td>347</td>
<td></td>
</tr>
<tr>
<td>7.3</td>
<td>Concluding Remarks</td>
<td>355</td>
<td></td>
</tr>
</tbody>
</table>

### CHAPTER 8

**Some Observations on the Plastic Deformation of Oriented Polyethylene**

<table>
<thead>
<tr>
<th>Section</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1</td>
<td>372</td>
</tr>
<tr>
<td>8.2.1 Yield Stress</td>
<td>373</td>
</tr>
<tr>
<td>8.2.2 Deformation Bands</td>
<td>373</td>
</tr>
<tr>
<td>8.3 Discussion</td>
<td>377</td>
</tr>
</tbody>
</table>

### CHAPTER 9

**Summary and Suggestions for Further Work**

Acknowledgements: 388

References: 389
CHAPTER 1

Introduction

In recent years, synthetic polymers have been rapidly replacing traditional materials, such as metals, wood, natural fibres, natural rubber, paper, etc., in such diverse fields as textiles, packaging, paints, household goods, and engineering components. In cases where the polymer is used in the form of film or fibre, use is made of the improvement in mechanical properties which can be achieved by the introduction of some molecular alignment in the material. Also, in some processes, such as injection moulding or blow moulding, molecular alignment is introduced during the fabrication of articles. Thus, it is important to understand how molecular alignment affects the physical properties of the polymer. It is particularly important, when the polymer is used in a load bearing capacity, to determine how the molecular alignment influences the yield, plastic deformation, and fracture behaviour of the polymer. At the initiation of the project to be discussed in this thesis, most investigations of the yielding of oriented polymers had been restricted to highly crystalline polymers, such as nylon and high density polyethylene. Because of this, it was decided to carry out an extensive study of the yield behaviour of oriented polyvinyl chloride, a polymer of low crystallinity which was below its glass transition temperature at room temperature. Before outlining the work carried out in this project, a brief literature survey will be given. This will be brief in order to avoid unnecessary repetition, since it is considered more suitable to discuss the literature in more detail where appropriate in the text. The following survey gives an indication of the fields covered in this work, and the important relevant publications.
1.1 Yielding of Oriented Polymers

The earliest investigation of the anisotropy of the yielding behaviour of oriented polymers appears to be that of Richard and Gaube (1956) who investigated the yielding of high density polyethylene. However, the increased interest in recent years originates with the work of Zaukelies (1962) who investigated the yielding of oriented nylon. Later work on oriented high density polyethylene has been carried out by Kurokawa and Ban (1964), Keller and Rider (1966) and Seto and Tajima (1966). All of these workers observed that the plastic deformation at yield was localised into narrow bands which were in many ways analogous to features observed in metal single crystals. Zaukelies observed kink bands in oriented nylon which had been compressed parallel to the molecular alignment direction; such features have long been recognised in metal single crystals having a hexagonal unit cell (see Orowan (1942)). It was proposed by Zaukelies (1962) that oriented nylon was essentially a single crystal containing vacancies and dislocations, and that the slip systems involved in the kinking were (010) \([1,3,14]\) for nylon 66 and (010) \([1,3,18]\) for nylon 610. Similarly, Kurokawa and Ban (1964) proposed that the (110) \([001]\) slip system, and possibly other slip and twin deformations were involved in the formation of kink bands in polyethylene. Seto and Tajima (1966) proposed that, although kinking necessarily involves slip parallel to the c-axis, the direction of the kink band is parallel to the boundary between lamellar crystals. Features similar to slip bands in metals (see Cottrell (1963), Figure 3) have been observed by Kurokawa and Ban (1964), Seto and Tajima (1966), and Keller and Rider (1966). Keller and Rider pointed out that their results were not consistent with the mode of deformation being slip parallel to the c-axis, and Kurokawa and
Ban proposed that the mode of deformation was a combination of slip and twinning. Hinton and Rider (1968) have since shown that the uniform deformation of oriented polyethylene is by slip parallel to the c-axis only to a first approximation. Further work, by Kurokawa, Konishi, and Sakano (1966) on oriented polyethylene having different amounts of molecular alignment, led these workers to propose that the deformation band did not represent a twin deformation but was more analogous to the necking phenomenon observed in unoriented polymers. It is presumed that, as the molecular alignment increases, a highly crystalline polymer would become more like that of a single crystal, and hence the necking phenomenon would become more analogous to the deformation of a single crystal.

After the initiation of the work on polyvinyl chloride, reports of an extensive investigation into the yielding of oriented polyethylene terephthalate have been published by Brown and Ward (1968 a and b) and Brown, Duckett, and Ward (1968 a and b). Bridle, Buckley, and Scanlan (1968) have also investigated the yielding of oriented polyethylene terephthalate. Since the results obtained by the above workers were similar to those for oriented polyvinyl chloride to be presented in this thesis, detailed discussion of these publications will be left until later in this thesis.

1.2 Yield Criteria

A number of workers have attempted to determine the yield criterion which best describes the yielding of polymers. The yield criterion determines the magnitudes of the stresses necessary for a particular stress system to cause yielding. Those
which have been found to be applicable to actual materials are those of von Mises, Tresca, and Coulomb, and these have been discussed extensively by Hill (1950), Nadai (1950), and Jaeger (1962). Keller and Rider (1966) found that the yield stress results for oriented polyethylene could best be fitted by a form of the Coulomb criterion. Later work, by Whitney and Andrews (1967) on polystyrene, and by Bowden and Jukes (1968) on a number of polymers, has also shown that polymers yield according to the Coulomb criterion. Only the work of Thorkildsen (1964) on polymethylmethacrylate has shown that unoriented polymers yield according to the von Mises criterion. It will be shown in this thesis that oriented polyvinyl chloride yields according to a modified von Mises criterion. Brown, Duckett and Ward (1968a) and Bridle, Buckley, and Scanlan (1968) have obtained similar results for oriented polyethylene terephthalate.

1.3 Optical Anisotropy

The alignment of the anisotropic molecules causes oriented polymers to be both optically and elastically anisotropic. The development of this anisotropy has been related to the macroscopic deformation of the material through two models proposed by Kuhn and Grün (1942). In these models it is considered that the polymer is made up of a large number of rod-like anisotropic units. These units are randomly arranged in the unoriented polymer, but during deformation they become re-arranged in a manner related to the macroscopic dimensions of the material (affine deformation). Kuhn and Grün (1942) proposed two different modes of affine deformation. The first model has been used with some success by Ward (1962) and by Pinnock and Ward (1967) to account for the
optical and mechanical properties of oriented polyethylene and polyethylene terephthalate respectively. Ward (1967) has also used both models to account for the changes in optical and mechanical anisotropy of polyethylene terephthalate which had been first oriented by extrusion at elevated temperatures and then cold drawn. More detailed discussion of this model, and its application to optical anisotropy changes in polyvinyl chloride, are presented later in this thesis.

1.4 Fracture

Some observations of the fracture behaviour of oriented polyvinyl chloride have been made during the course of this investigation. However, although the fracture behaviour of polymers has been extensively studied in recent years, no similar results seem to have been reported previously. For reviews of the fracture behaviour of polymers, the reader is referred to the publications of Andrews (1968) and Rosen (1964).

1.5 Outline of Project

The oriented polyvinyl chloride was prepared by extension of the unoriented material at 71°C and 90°C. The molecular alignment achieved by this extension was "frozen in" by cooling the material to room temperature at constant length. Details of the preparation and structure of the oriented polyvinyl chloride are presented in Chapter 2. Tensile tests were carried out at room temperature on small test pieces which were cut from the strips of oriented polyvinyl chloride. At yield, the plastic deformation was observed to be localised into narrow bands running
obliquely across the test piece, and a detailed investigation has been carried out into the anisotropy of the yield behaviour, both as regards yield stresses and deformation bands. These results are presented in Chapter 3. In Chapter 4, these yield behaviour results are discussed in detail, and it is shown that, in many aspects, the yielding behaviour could be accounted for by a modification of the von Mises criterion. As a result of the introduction of molecular alignment, the oriented polyvinyl chloride was optically anisotropic, i.e. birefringent, and the subsequent plastic deformation at room temperature caused a change in optical anisotropy. These observations necessarily led to a detailed investigation of the optical anisotropy changes during extension at elevated temperatures and at room temperature. The results of this investigation are presented and discussed in Chapters 5 and 6. During the investigation of the yielding behaviour some observations on the cold drawing and fracture behaviour were made. Results for the cold drawing are presented in Chapter 3, but the fracture results are discussed in some detail in Chapter 7. Before the work on oriented polyvinyl chloride was started, some preliminary tests were carried out on oriented polyethylene as an extension of the work carried out by Keller and Rider (1966). Although this investigation was by no means rigorous, the results are considered to be of sufficient interest to be presented in Chapter 8. Finally, a summary of the important results and suggestions for further work are given in Chapter 9.
CHAPTER 2

Experimental Procedures and Preparation of Oriented Material

A description of the equipment and techniques used in the experimental work, together with a detailed account of the preparation of the oriented material, will be given in this Chapter. This will be followed by an account of the investigation into the structure of the oriented material. During the preparation and investigation of the structure of the oriented polyvinyl chloride some interesting results were obtained. These results will be discussed in this Chapter rather than in later Chapters which are largely concerned with results of the deformation of the oriented material.

2.1 Experimental Procedures

2.1.1 Tensile Testing Facilities

The majority of tensile tests were carried out using an E-type Tensometer manufactured by Tensometer Ltd., Croydon, England. In this machine the crosshead was driven by one of two motors, enabling test pieces to be extended at any rate from 0.0003 mm.min⁻¹ to 250 mm.min⁻¹. A load-extension curve was automatically produced on a chart recorder. The speed of the chart was directly related to that of the crosshead and the deflection of the recorder pen gave a direct reading of the load. In all of this work chart speed to crosshead speed ratios of either 1 : 1 or 16 : 1 were used. Two load cells were available with the machine, these being able to record maximum loads of 250 Kg and 25 Kg. A load range selector enabled full scale deflections of the pen to be
achieved for loads of 100%, 40%, 20%, 10%, 4%, 2% and 1% of the maximum load capacity of each load cell; the lower two ranges were not reliable and were never used. The load calibration was checked periodically by static loading of the load cell and was always found to have an accuracy of better than ±1% of the recorded load. Checks on crosshead and chart speeds, and on the chart to crosshead ratio also showed these to be accurate to ±1%.

The E-type Tensometer was fitted with an environmental test chamber, manufactured by Sondes Place Research Laboratories, Dorking, England. This enabled tests to be carried out above or below ambient temperature in the range 250°C to -100°C. Uniform temperature distribution in the chamber was achieved by the forced circulation of hot or cold air. At elevated temperatures, the temperature of the air was controlled by the thermostatic switching of a 350 watt control heater. When this control heater was insufficiently powerful to achieve the higher temperatures, one, two, or all of the three additional 350 watt background heaters could be switched on. At the most frequently used elevated temperatures, 50°C, 71°C, 80°C and 90°C, the temperature at a fixed position in the environmental chamber was constant to ±1°C. Once the operating temperature was reached, the temperature distribution at a given time was uniform to ±1°C. These checks on the accuracy were carried out using a copper-constantan thermocouple, but during tests the temperature was measured using mercury-in-glass thermometers which were calibrated in tenths of a degree. Temperatures below ambient were achieved by the injection of liquid nitrogen into the chamber from a pressurized vessel. The nitrogen vapourised immediately upon entering the chamber and was circulated by the fan. Temperature control was
maintained by the switching on and off of the liquid nitrogen flow by a thermostatically controlled solenoid valve. Tests at temperatures below ambient were carried out at -80°C. This temperature was measured using an alcohol-in-glass thermometer which recorded a temperature fluctuation of ±4°C at -80°C. When testing in the environmental chamber, the grips were attached to the crosshead by means of a long rod, as shown in Figure 2.1. When not required the chamber could be moved back to allow free movement of the crosshead.

Two different sets of grips were used for holding test pieces in the tensile machine. The larger pair shown in Figure 2.1 were used in preparing the oriented material. Small test pieces, which were cut from the oriented material. Small test pieces, which were cut from the oriented material, were extended using the grips shown in Figure 2.2. The grips are held in a small jig which ensured that they were held rigid whilst inserting the test pieces. This prevented any damage to the test piece during mounting. To prevent the test pieces slipping from the small grips during testing, fine emery paper was glued to each face of the grips. When using either set of grips, care was taken to place the test piece centrally in each grip to ensure axial application of the load during testing.

A number of tests were carried out on a small tensile testing machine (shown in Figure 2.3) designed by Dr. T. Hinton. By attaching the machine to an optical microscope, successive stages in the deformation of a test piece could be observed microscopically and photographed. This machine had no load recording facilities but there was a selection of extension rates. However, only polyvinyl chloride test pieces were extended using this machine and,
because of the comparatively high load required to produce yielding, the motor was insufficiently powerful for testing other than at the lowest speeds of 1.1 mm.min\(^{-1}\) and 0.66 mm.min\(^{-1}\).

2.1.2 **Optical Microscopy**

Optical observations and measurements on the test pieces before and after testing were carried out in transmitted light using a Zeiss Pol Photomicroscope. This was a polarizing microscope, the important features of which were special strain free optics, rotatable polarizer and analyser, and an eyepiece fitted with crosshairs. When the analyser was set at zero on its calibrated scale and the polarizer was rotated until it located positively in the 90° position on its scale, the axes of the two were at right angles and no light was transmitted through the system. In addition, in these positions, the axes of polarizer and analyser were parallel to the crosshairs. The technique for checking this latter feature will be discussed in Section 2.5.

Oriented polymers are optically anisotropic and birefringence measurements are useful for characterising the molecular alignment of the material. Birefringence measurements were made with the aid of an Ehringhaus rotating calcite compensator which could be positioned in the optical path of the microscope. From calibration tables the compensator could be used to determine the retardation of the birefringent materials. Over the range used, the retardation could be measured to an accuracy of ±4 nm. In measuring the retardation care was taken to eliminate the effects of backlash and zero error in the compensator. In conjunction with thickness measurements, the birefringence could be calculated.
from the measured retardation. Thickness measurements could be made to ±2 μm using a dial gauge.

Photomicrographs of test pieces were obtained using a 35 mm camera which was built into the microscope.

Some microscopic observations were also made using a Reichart Universal Camera Microscope "MeF". This will be discussed where appropriate in the text.

2.1.3 Measurement of the Density of Polyvinyl Chloride

The density of oriented polyvinyl chloride was measured by hydrostatic weighing in distilled water using a Stanton type S.M.21 balance. With this instrument specimens could be weighed to an accuracy of ±0.02 mg in air and ±0.05 mg when the specimen was suspended in water. The damping effect of the water on the movement of the specimen accounts for the loss of sensitivity of the balance when specimens were weighed in water. For weighing in water, the specimen was fitted into a paper clip which was weighted by a piece of lead. This was suspended into a beaker of water by a wire which was fixed beneath the balance pan. Although no special temperature control was used, all measurements on a particular batch of material were carried out at the same temperature. This temperature will be specified where appropriate in the following text. In taking measurements care was taken to shield the balance from draughts, and the balance was situated in the part of the laboratory in which least disturbance occurred.

2.1.4 X-Ray Diffraction and Scattering Studies

Wide angle X-ray diffraction photographs were obtained using
a Unicam S-25 flat plate camera. A specimen to film distance of approximately 6 cm was used, but, since no precise measurements of lattice spacings were required, this distance was not measured accurately. Care was taken to ensure that the X-ray beam was directed along the axis of the camera by adjustment of the collimator, using the telescope supplied with the instrument. In addition the face of a sheet specimen was carefully aligned to be perpendicular to the beam. In X-ray diffraction investigations of deformation bands it was necessary also to locate accurately the direction of the deformation band relative to the X-ray film. This was achieved by aligning the deformation band parallel to a fine wire which was stretched across the film cassette. This wire left a shadow on the film, and thus defined the direction of the deformation band. Alignment of the deformation band was carried out using the arrangement shown in Figure 2.4. The back was removed from the film cassette so that a travelling microscope could be focussed on the reference wire, or the specimen, or either hole of the collimator. The microscope was first adjusted until it was directed along the axis of the camera. This was achieved by adjusting the microscope such that, when focussed on the collimator holes, the crosswires were positioned on the centre of each hole. The microscope was then focussed on the reference wire on the cassette, and the crosswires were rotated until one crosswire was parallel to the reference wire. The specimen was then brought into focus and adjusted until the deformation band was parallel to the crosswire, and hence parallel to the reference wire on the cassette. Finally, all of the previous alignment procedures were rechecked. Results, obtained by taking a number of X-ray photographs of one test piece, which was realigned for each photograph, suggest that the alignment procedure was accurate to ±0.5°.
Low angle X-ray scattering photographs were obtained using a Rigaku-Denki low angle goniometer. This instrument produced an approximately parallel beam of X-rays by using two widely spaced pinholes. In this investigation two pinholes, of diameter 0.5 mm and 0.3 mm separated by a distance of 240 mm, were used, the pinhole of 0.5 mm diameter being nearest the X-ray source. A specimen to film distance of 319 mm was used, approximately 280 mm of this being in vacuum. The overall length from the first pinhole to the film was 600 mm. With these dimensions, and ignoring any effects due to scattering from the pinholes, the diameter of the beam at the film was calculated to be 1.5 mm. Low angle X-ray scattering studies were only carried out on polyvinyl chloride.

Nickel-filtered CuKα radiation was used at all times with the equipment discussed above. For polyethylene, exposure times of the order of 2 or 3 hours were found satisfactory. However, in obtaining wide angle X-ray diffraction photographs of polyvinyl chloride exposure times were inconveniently lengthy, being of the order of 70 hours. A difficulty similar to that of long exposure times was experienced by D'Amato and Strella (1969) who carried out diffractometer investigations on polyvinyl chloride. They suggested that the use of Mo Kα radiation would overcome this problem since the absorption coefficient of polyvinyl chloride at this wavelength is a factor of nine less than that for Cu Kα radiation. Unfortunately no facilities were available for producing Mo Kα radiation. Exposure times of between 12 and 20 hours were used in obtaining low angle scattering photographs from polyvinyl chloride.
In analysing some of the wide angle diffraction and low angle scattering photographs, it was necessary to measure the intensity of diffracted or scattered X-rays. This was carried out by measuring the optical density of the photographic emulsion using a Wooster Microdensitometer. This was a double beam instrument which operated by comparing the intensity of the beam passing through the X-ray film with the intensity of a reference beam passing through an optical wedge. This comparison was carried out by alternately recording the intensity of the beams using a photomultiplier. Any difference in intensity resulted in a phase change in the photomultiplier output, which activated a phase sensitive motor. The motor drove the optical wedge in such a direction as to equalise the intensity of the two beams. The pen of the chart recorder was directly geared to the optical wedge, and hence followed the movement of the wedge. Thus the displacement of the pen recorded the optical density of the photographic emulsion. The response time of the pen for full scale deflection was 0.25 s according to the manufacturers. At all times a wedge having optical density from 0-4 D was used. For the purpose of comparison the intensity measurements were accurate to ±1%. The beam could be produced using a number of apertures which gave an image x9 smaller when focussed on the film. In this case the smallest aperture of 0.5 mm diameter was used. The film table could be driven by independent x and y drives. The x drive could be used to rotate the table when required. The coordinates of the film table were recorded by digital counters, calibrated in tenths of a millimetre, which were reported to be accurate to ±0.05 mm. Tests have confirmed the accuracy of these counters. In measuring the intensity variation of the film,
the chart of the chart recorder moved in a direct ratio to the distance moved in the y-direction by the film table. The ratio, which could be varied, was always checked by recording the y-coordinates before and after each traverse of the film. In investigating the intensity distribution of x-ray diffraction photographs of polyvinyl chloride, the y-scan only was used, and care was taken to ensure the scan went through the centre of the photograph. Distances from the centre of the film could be converted to Bragg angle, θ, knowing the specimen to film distance. Another useful facility was the oscillation of the film table in the y-direction through distances of 2, 4 or 6 mm. The use of this facility will be discussed in Section 2.3.4.

2.1.5 Electron Microscopy

Because of the small depth of focus and limited manoeuvrability of specimens when using optical microscopy, it was found useful to obtain micrographs of specimens using a Cambridge Instruments Stereoscan electron microscope. This was used at magnifications ranging from x20 to x6000. Specimens were prepared by coating with gold-palladium using an AEI Rotary Coating Unit. Micrographs were obtained from a small number of polyvinyl chloride test pieces.

It was hoped to investigate structural changes in oriented polyvinyl chloride using transmission electron microscopy. Unfortunately, insufficient time was available for developing suitable techniques for obtaining thin sections of material.

2.1.6 Strain Measurements

Strains in small test pieces, such as that shown in Figure 2.2,
were determined from the dimensions, before and after deformation, of an initially square grid of dots which had been printed on the sheet of material from which the test pieces were cut. The printing technique was that developed by Hinton (unpublished) and used by Hinton and Rider (1968). A viscous, slow drying ink was applied to a half tone plate using a roller. This plate was then fitted into a hand press and was used to print a grid of dots on the material from which test pieces were subsequently cut. Two different size grids were used, having average spacings between nearest-neighbor dots of 0.193 mm and 0.400 mm respectively.

As a result of the extension of the test piece, the square forming the basis of the grid became a parallelogram. This is illustrated in Figure 2.5, in which a test piece is shown before and after extension. The same situation is shown diagramatically in Figure 2.6. By measuring the spacings $a_2$, $c_2$, $a_3$ and $c_3$, and the angles $\beta_0$, $\beta$, and $\omega$, it was possible to determine the strains in the plane of the test piece. A useful measure of the amount of deformation is the extension ratio. The extension ratio in a given direction is here defined as the ratio of distances between the same pair of points after and before extension, the points being such that the line joining them is parallel to the given direction. In test pieces shown in Figures 2.5 and 2.6, lines of dots initially parallel to the tensile axis, $O_t$, remained so after extension. The extension ratio, $R_t$, measured in the tensile direction, $O_t$, is given by

$$R_t = \frac{\lambda}{\lambda_0} = \frac{c_3 \cos \beta_0 \cos \beta + a_3 \sin \beta_0 \cos (\omega - \beta)}{c_2}, \quad (2.1)$$

where $\lambda$ and $\lambda_0$ are the distances, after and before extension, between two points, the line joining which is parallel to the tensile
axis. Spacings and angles were measured from micrographs using ruler and protractor. The distances were not measured between adjacent dots, but were averaged over a number of dots, usually four or five, for which the deformation was considered uniform. Angles were measured between lines which were drawn through the centre of the dots. It was estimated that spacings could be measured to ±1% and angles to ±1°. Shrinkage of the micrographs was negligible since no changes could be found in spacings measured from micrographs immediately after printing and again several weeks after printing.

2.2 Material Specification

Both the polyethylene and polyvinyl chloride used were commercial grades obtained directly from the manufacturers or from wholesale suppliers.

The polyvinyl chloride, of which two grades were used, was received in the form of sheet, approximately 0.5 mm thick. Most of the work was carried out on a rigid polyvinyl chloride, Vybak DVR294, Clear 33, manufactured by Bakelite Ltd. This was a clear sheet of homopolymer containing small amounts of stabiliser and colouring material. The quoted softening temperature was 76°C. More detailed specifications of the material were not available from the manufacturers. In an attempt to determine the glass transition temperature, T_g, of this material, dilatometric measurements were carried out by Dinnewell (1969) in our laboratories. The average value of T_g obtained from two experiments was found to be 61.5 ± 0.5°C. (In another experiment the T_g could not be determined exactly but was thought to be between 54°C and 63°C.
with the possibility of it being at 61.5°C.) By hydrostatic weighing in water at 19°C, the density of the material was found to be 1.344 ± 0.002 gm.cm⁻³. The as-received sheet had a birefringence which was too small to be measured, but was less than 0.002 x 10⁻³.

Since the manufacture of the above material was discontinued during the course of this investigation, some of the later work was carried out on Cobex manufactured by Bakelite-Xylo®ite Ltd. This, too, was a rigid polyvinyl chloride of similar composition to that of the Vybak, in that it was a homopolymer containing small amounts of stabiliser and colouring material. A value of 64.2 ± 2.0°C was obtained for Tg from dilatometric measurements. The density was found to be 1.390 ± 0.001 gm.cm⁻³ by hydrostatic weighing in water at 18.4°C. The birefringence of the as-received sheet was 0.046 x 10⁻³.

Dilatometric measurements, although not particularly accurate, indicate that the Tg of Vybak was less than that of Cobex. Mechanical properties to be discussed in Section 2.3.1 confirm this. Since both the density and glass transition temperature of Cobex were larger than those of Vybak, it would seem that Cobex and Vybak contained different amounts of additives.

The polyethylene, both high and low density, was received in the form of granules which had to be subsequently compression moulded into sheet form. The high density polyethylene, trade name Rigidex, was manufactured by British Hydrocarbon Chemicals Ltd. (now B.P. Chemicals Ltd.). Rigidex of two different molecular weights was used, Rigidex 50 with melt index 50 having a lower average molecular weight than Rigidex 2 with melt index 2.
The low density polyethylenes, Alkathene W.J.G. 11 and Alkathene W.N.F. 15, were manufactured by I.C.I. Ltd. and had melt indexes of 1.1 to 3.0 and 6.1 to 10.0 respectively.

2.3 Preparation of Oriented Polyvinyl Chloride

The purpose of this work was to investigate the deformation behaviour of oriented polymers. However, in the as-received sheets of polyvinyl chloride, molecular alignment, as indicated by birefringence measurements, was largely absent. Only in the case of the Cobex was there any measurable birefringence in the as-received sheet, but, as will become apparent in Section 2.3.2, this was negligible compared with that achieved in the subsequent preparation of the oriented polyvinyl chloride. Alignment of the initially randomly oriented molecules was achieved by extending the unoriented material.

Oriented polyvinyl chloride was prepared by extending parallel sided strips of unoriented material at a strain rate of $100\% \text{ min}^{-1}$, at $71^\circ C$, $80^\circ C$ and $90^\circ C$, using the E-type tensometer with the environmental chamber in position. Before extending the strips care was taken to ensure that the temperature in the environmental chamber had reached the testing temperature and the strip was left for a further ten minutes prior to starting the tensile machine. Once the required amount of extension had been achieved, the tensile machine was stopped and the extended strip was cooled as quickly as possible to below $30^\circ C$ at constant length by blowing air, at room temperature, over it. If the load had been removed from the strip at the stretching temperature, a substantial contraction of the strip would have occurred. Details of the magnitude of this contraction will be given later in this section.
At the temperatures used, the strips, except for regions near the grips, deformed uniformly over their entire gauge length. The strips, which were cut from a larger sheet using a scalpel, were initially between 6 cm and 4 cm wide, approximately 0.5 mm thick, and of gauge length varying from 12 cm to 5 cm such that the ratio of length to width was never less than 5 : 4 in most cases. Varying gauge lengths were used because the environmental chamber restricted the separation of the grips to 27 cm and, hence set an upper limit on the amount of extension which could be achieved for a particular gauge length. If a strip was used with a length to width ratio of less than 5 : 4, the material was constrained by the grips from contracting laterally over a substantial portion of the gauge length. In the constrained regions the strain was not uniform and the sides of the strip were curved. If the ratio of length to width was 5 : 4 or greater, the lateral contraction of the strip, except for regions near the grips, was unconstrained. Where the lateral contraction was unconstrained, the strain in the strip was uniform and the sides of the strip were straight and parallel. Strips, which had length to width ratios of less than 5 : 4, were extended at 90°C to give extension ratios of 6.0 and 7.5. Test pieces for subsequent retesting were only obtained from a small region in the strip of 7.5 extension ratio where the lateral contraction was unconstrained. This was not the case for the strip of 6.0 extension ratio.

The measures used to determine the amount of strain in the deformed material were the extension ratios $R_z$, $R_x$ and $R_y$. In this case the $z$ and $x$-axes are defined to be in the plane of the strip, respectively parallel and perpendicular to the tensile axis. $Oy$ is defined to be perpendicular to the face of the strip. Since
the material was initially isotropic and was deformed under the action of a uniaxial stress in direction Oz, it is reasonable to assume that Oz was a direction of principal strain, and that the lateral contraction perpendicular to Oz was isotropic. Under such circumstances Ox can be taken as being another direction of principal strain, in which case the remaining direction of principal strain is parallel to Oy. The extension ratio, \( R_z \), in the direction of extension was measured from the dimensions before and after extension of a 1 cm square grid of lines which were drawn on the strip parallel and perpendicular to the tensile axis and remained so during the subsequent extension. This is consistent with Ox and Oz being directions of principal strain. \( R_z \) was determined by measuring the distance between lines drawn perpendicular to the tensile axis. Distances were not measured between adjacent lines but between lines at the extremities of the uniformly deformed regions. The region of uniform deformation was here taken as that in which the width of the deformed strip remained constant. Using a ruler calibrated in millimetres the distances could be measured to ±0.5 mm, giving an accuracy of ±2% in measuring the extension ratio. The extension ratio, \( R_x \), of the strip was determined from measurements of the distance, before and after deformation, between lines drawn parallel to the tensile axis. These distances could be measured to ±0.2 mm giving an accuracy of ±3% at \( R_z = 5.0 \). At smaller values of \( R_z \) the accuracy became progressively better. \( R_y \) was calculated from thickness measurements to an accuracy of ±1.5% or better, depending upon the value of \( R_z \). Care was taken in measuring thicknesses before and after extension at the same point on the strip since there were some fluctuations in the thickness of the
as-received sheet. Results of measurements of \( R_x \), \( R_y \), and \( R_z \) for strips of Vybak and Cobex extended at 71°C and 80°C respectively, are presented in Tables 2.1 and 2.2. The product \( R_x R_y R_z \), which should be unity if there is no volume change, is also given in Tables 2.1 and 2.2. No results were obtained for Vybak and Cobex extended at 90°C and 71°C respectively, since appropriate dimensional measurements were not made. No width or thickness measurements were obtained for the strip of Vybak with \( R_z = 4.5 \), which was extended at 71°C. It can be seen from the results presented in Tables 2.1 and 2.2 that, within the limits of experimental error, \( R_x = R_y \) and \( R_x R_y R_z = 1 \). Some results for \( R_x \), \( R_y \), and \( R_z \) were obtained from small dumb-bell shaped test pieces, 10 mm gauge length and 2 mm width, cut from a sheet of unoriented Vybak on which was printed a grid of dots, as discussed in Section 2.1.6. These test pieces were deformed at 71°C and 90°C, and the results are reproduced in Tables 2.3 and 2.4. The accuracies of these measurements were the same as those for the strips. Again it can be seen that, within the limits of experimental error, \( R_x = R_y \) and \( R_x R_y R_z = 1 \).

Because the polyvinyl chloride deformed uniformly at the elevated temperatures discussed here, as opposed to developing a running neck, a range of extension ratios, up to a certain maximum, could be achieved. Beyond this maximum the material usually failed before the tensile machine could be stopped. The Vybak was extended at 71°C and 90°C, maximum extension ratios of 4.5 and 7.5 being achieved at 71°C and 90°C respectively. Maximum extension ratios of 3.9 and 5.0 were obtained for Cobex extended at 71°C and 80°C respectively. The higher extension ratios at each temperature were only obtained if the flaws in the edges of
the unoriented strips were removed by polishing with fine emery cloth. Although the surfaces of the grips were roughened in order to prevent the material slipping from the grips, at the higher extension ratios it was necessary to sandwich those portions of the strips in the grips between pieces of coarse emery cloth, the rough surface being in contact with the poly-vinyl chloride.

It was stated earlier that if the extended strip was unloaded at the stretching temperature a substantial contraction of the strip occurred. Results showing the magnitudes of the contraction are presented in Table 2.5 for Vybak extended at 71°C and 90°C. These results were obtained from small test pieces similar to those used in obtaining some of the results in Tables 2.3 and 2.4. After the test piece had been extended, it was cooled at constant length under load and a micrograph of the test piece was obtained at room temperature. These test pieces were then annealed at the stretching temperature for 30 minutes under zero load. Further annealing at 120°C was carried out on the test pieces originally extended at 90°C. After each stage of the annealing, further micrographs were obtained and $R_z$ was measured from these. It can be seen that annealing at the extension temperature resulted in a considerable recovery of the original extension. At extension ratios of 4.3 or less, the amount of recovery was approximately the same for material extended at either temperature. The largest value of $R_z$ after annealing was 1.7 for material of extension ratio 5.8 prepared by extension at 90°C. It is also apparent that annealing at a temperature above the original extension temperature, i.e. annealing at 120°C, caused further recovery of the extension.
In order to ensure that all material was prepared under standard conditions the strips were extended at a standard strain rate of 100% min⁻¹. The importance of using a fixed strain rate is apparent from results presented by Nielsen and Buchdahl (1950) for mechanical properties of polystyrene oriented by hot stretching. They reported that the mechanical properties of oriented polystyrene are more closely related to the birefringence rather than the amount of hot stretching. It was considered that this might possibly be true for polyvinyl chloride. However, since birefringence measuring facilities were not available when this investigation was initiated, the extension ratio had to be used as a measure of molecular alignment. For extension ratio to be a meaningful measure of molecular alignment, at a particular temperature the strip had to be extended at a standard strain rate since birefringence depends upon both extension ratio, strain rate and temperature.

Details of stress-strain behaviour during hot stretching and characterisation of the structure of the oriented polyvinyl chloride are given in the following sections. More emphasis is placed on the results for Vybak since most of this investigation was carried out using this material.

2.3.1 **Stress-Strain Behaviour During Extension at Elevated Temperatures**

From the load-extension data recorded by the tensometer during extension, and from the initial and final dimensions of the extended test pieces, it was possible to evaluate the nominal stress during extension as a function of extension ratio. The nominal stress is the loaded divided by the initial cross-sectional
area of the test piece. In Figure 2.7 the nominal stress is plotted as a function of extension ratio for Vybak extended at 71°C and 90°C. The results for extension at 71°C were obtained for the extension of the strips as discussed in Section 2.3. However, no measurements of width and thickness were made for strips extended at 90°C, and so the results shown in Figure 2.7 were obtained using small test pieces, for which extension ratio results are presented in Table 2.4. The experimental points in Figure 2.7 indicate the results obtained from the measurements of the dimensions of the strips after they had been extended and then cooled at constant length under load. The nominal yield stress against extension ratio curve was drawn smooth through these points. The part of the curve below extension ratio 2.0 for extension at 71°C was determined from load-extension curve for the strip extended to extension ratio 2.0; this strip had the largest initial gauge length. A similar procedure was used for plotting all of the stress, both nominal and true, against extension ratio curves to be discussed in this section.

The nominal stress curve for Vybak extended at 71°C was similar in shape to that of a rubber (e.g. see Treloar (1958), Figure 5.4). The stress rose slowly at low extension ratios, the slope of the curve decreasing with increasing extension ratio until, at an extension ratio of approximately 1.7, the slope started to increase and the nominal stress increased rapidly with increasing extension. There is a slight decrease of slope at the higher extension ratios. The curve for extension at 90°C was initially similar to that for extension at 71°C, but at no stage did the slope of the curve start to increase, instead, it continued to decrease, eventually becoming negative at high
extension ratios. No report of this type of behaviour occurring in rubbers has been found, and network theories of rubber elasticity predict that the nominal stress should increase with increasing extension ratio (see Treloar (1958) p.86 and Chapter VI). In addition such network theories predict that the stress at a given extension ratio should be larger at the higher temperature; this was not the case for the results shown in Figure 2.7.

The initial moduli for extension at 71°C and 90°C were calculated from the slopes of the load-extension curves and were found to be 20 MN m⁻² and 1.5 MN m⁻², respectively. Treloar (1958) quotes the modulus of rubber to be 10 Kg cm⁻² (i.e. approximately 1.0 MN m⁻²) whilst the modulus of Vybak at room temperature was measured from the load-extension curve and was found to be 1.0 GN m⁻². The above measurements are only approximate and are only intended to give an indication of the order of magnitude. From these results it can be seen that as far as the magnitude of the modulus is concerned, the behaviour of Vybak at 90°C is more rubber-like than is the Vybak extended at 71°C. The network theory of rubber elasticity predicts that the modulus should be larger at the higher temperature, but this was not so for the Vybak.

Another property of rubber is that large extensions, strains of the order of 400%, are recoverable to within 1% of the undeformed dimensions upon removal of the load. Measurements of the recoverability of extension for Vybak are presented in Table 2.5. It can be seen that in most cases the extension was recoverable to within 70% or better. Although this is not quite
as good as the recoverability quoted for rubbers, it is certainly better than that for the rigid polymer, for which only 7 or 8% of extension ratios of the order of 200% is recoverable.

The results discussed above show that, in some respects, the deformation behaviour of polyvinyl chloride, in this case Vybak, at elevated temperatures was similar to that of rubber, although there were some inconsistencies in the effect of temperature on the shape of the nominal stress against extension ratio curves and on the magnitudes of the modulus. Nevertheless the results do suggest that the behaviour can be accounted for by a network model similar to that used for rubbers (see Treloar (1958)). In rubbers the molecular network is maintained by permanent chemical cross-links connecting molecular chains together. However, in the case of polyvinyl chloride, the network is maintained by physical entanglements through which molecules slip and which could be destroyed as a consequence of the deformation. Because of this the material cannot support such high stresses as it could if the entanglements were permanent. Such effects would become more pronounced at elevated temperatures where the molecules are more mobile, or at high extensions when the molecules are highly extended. This would account for the observed negative slope in the curve for extension at 90°C in Figure 2.7, and for the decrease in slope of the curve at high extension ratios for extension at 71°C.

Although the nominal stress decreased at higher extension ratios for Vybak deformed at 90°C, the true stress acting on the material in fact increased with increasing extension ratio. The true stress is obtained by dividing the load by the current cross-sectional area of the strip during deformation and is the actual
stress acting on the material during extension. Plots of true stress as a function of extension ratio for both Vybak and Cobex are presented in Figure 2.8. The curves for Cobex differ from those for Vybak in that the stresses at all stages of the extension were higher than those for Vybak. The curve for Cobex extended at 71°C was different from all other curves in that there was an initial sharp stress rise followed by a stress drop, after which the stress increased with increasing extension ratio. Such a stress drop is characteristic of both Vybak and Cobex deformed at room temperature and at 50°C. That it was still present for Cobex deformed at 71°C, but not for Vybak, suggests that the Cobex was at a lower effective temperature than the Vybak, i.e. the glass transition temperature of Cobex was higher than that of Vybak. In fact Andrews and Whitney (1964) have indicated that his maximum disappears as the material approaches its glass transition temperature. Langford, Whitney and Andrews (1963) have shown how this might be used as a basis for determining a glass transition temperature. The glass transition temperature evaluated would be that appropriate to the strain rate at which the tests were carried out.

Although birefringence results have not as yet been presented (see Section 2.3.2), it is interesting to consider the variation of true stress during extension as a function of birefringence rather than extension ratio. Such plots are shown in Figure 2.9 and Figure 2.10. In these figures the birefringence is the residual birefringence measured at room temperature after the material had been removed from the tensile machine. For Vybak the stress at a given birefringence was higher for the higher extension temperature. Network theories for the photoelastic properties of
rubbers (see Treloar (1958) Chapter X) predict that this should be so. (The birefringence referred to by Treloar (1958) is that measured at the stretching temperature and not the residual birefringence as measured here. However it is reasonable to suppose that, although changing the temperature would change the birefringence, a higher residual birefringence would correspond to a higher birefringence at the extension temperature.)

When the true stress for Cobex is considered as a function of birefringence the curves are different from those of Vybak in that the stress for extension at the higher temperature, 80°C, is lower than that at the lower temperature, 71°C. The curves for Cobex in Figure 2.10 are of the same shape, except in the region of small birefringence, but are displaced by an almost constant stress of approximately 6 MN m⁻². This stress value is in fact the difference in stress between the minimum in the curve for extension at 71°C and the stress at the same birefringence on the curve for extension at 80°C. This displacement of the curves can be accounted for in the following way. Since the material at 71°C was above its glass transition temperature appropriate for the particular strain rate, two factors contributed to the stress-strain behaviour. There was the stress arising from the tendency of the chains in the molecular network to retract back to a random configuration, and there were the viscoelastic forces opposing the movement of the molecular segments relative to one another. At 80°C the viscoelastic effect can be considered to have become negligible and the applied stress was that required to extend the molecules from their random configuration. Since the network theory predicts that the stress should be larger for the higher
temperature, the stress by which the two curves differ can be considered to arise largely from the viscoelastic contribution for deformation at 71°C. In fact, since the material at 80°C was still quite near the glass transition temperature, there was probably some effect due to viscoelastic forces at this temperature. A detailed theory, following the lines discussed above, has been proposed by Haward and Thackray (1968) in accounting for the stress-strain curves of glassy thermoplastics.

From the results discussed in this section it can be concluded that the deformation behaviour of the polyvinyl chloride, at the temperatures discussed, can be accounted for by a molecular network theory similar to that which has been applied to rubbers. However, in the case of polyvinyl chloride consideration must also be taken of relaxation effects, the non-permanent nature of the physical cross-links, and viscoelastic effects when deformation is carried out in the vicinity of the glass transition temperature.

2.3.2 Birefringence of Oriented Polyvinyl Chloride

Birefringence measurements were carried out at room temperature after the material had been removed from the tensile machine. White light was used in making the measurements but the compensator was calibrated for light of wavelength 5893 Å. The variations of birefringence as a function of extension ratio for Vybak and Cobex extended at different temperatures are presented in Figure 2.12. Taking into account errors in the thickness and retardation measurements it was estimated that the birefringence measurements were accurate to ±2% or better. In measuring the retardation it was
necessary to locate the zero order black fringe in the centre of the field of view of the microscope. In the case of Vybak, this zero fringe was dark and hence easily located. However, for Cobex the zero order fringe was coloured and sometimes difficult to distinguish from other fringes.

In all cases the oriented material was found to be positively birefringent, i.e. for plane polarised light the maximum refractive index occurred when the plane of vibration was parallel to the original extension direction. Comparing initially curves for different temperatures in Figure 2.11, it can be seen that for both Cobex and Vybak, the birefringence at a given extension ratio was higher for the lower of the stretching temperatures. If the birefringence is regarded as a measure of the degree of molecular alignment, it would seem that stretching at the lower temperature was more effective in producing molecular alignment. A direct comparison of molecular alignment in Cobex and Vybak on the basis of birefringence may not be justified since differences in composition or structure of the material could give rise to differences in optical anisotropy for the same degree of molecular alignment. Further comments concerning this will be made in Chapter 6 when birefringence results will be discussed in more detail. It is also clear from Figure 2.11 that the birefringence of the as-received Cobex was negligible in comparison to that achieved in the subsequent extension.

2.3.3 Wide Angle X-Ray Diffraction Studies

Possible structural changes, which might occur during the extension of polyvinyl chloride at elevated temperatures, were
investigated using wide angle X-ray diffraction. Details of equipment and techniques have been discussed in Section 2.1.4. Photographs obtained from sheets of oriented polyvinyl chloride of different extension ratios are presented in Figures 2.12, 2.13, and 2.14. The discussion of these photographs will be largely restricted to those for Vybak. It is apparent, however, from Figures 2.12 and 2.14 that the photograph for Cobex of extension ratio 5.0 obtained by extension at 80°C is similar to that for Vybak of extension ratio 4.5 obtained by extension at 71°C. It is presumed that photographs for lower extension ratios would be similar.

It can be seen from Figure 2.12 that for the unoriented material, extension ratio 1.0, there was a large amount of diffuse scatter at the centre of the photograph. The variation in intensity of this scatter was measured from the original negative using the densitometer. The results are reproduced in Figure 2.15, which is a plot of intensity as a function of 2θ, θ being the Bragg angle. It can be seen that the intensity decreased with increasing values of 2θ. Diffuse scatter of this kind has been observed previously by D'Amato and Strella (1969), who suggested that it was caused by the scattering of X-rays by air in the X-ray path and also by the scattering of the white radiation. This air scatter, which could be reduced by using a helium atmosphere or vacuum for the X-ray path, tends to mask any diffraction effects arising from the polyvinyl chloride. In fact on the original negative there appeared to be two diffuse rings. By measuring the diameter of these rings using a ruler calibrated in millimetres, these rings were found to be at 2θ = 24° and 17°. On the densitometer trace in Figure 2.15 no equivalent peaks in the intensity can be
detected. However, although the intensity decreases continuously with increasing \( \theta \), there are some fluctuations in the slope of the curve. In particular, in the vicinity of the arrows in Figure 2.15, the slope increases and then decreases again as \( \theta \) increases. These variations in slope can be considered to arise from contributions to the intensity by diffraction from polyvinyl chloride at specific values of \( \theta \). These contributions are not sufficient to produce peaks in the curve but do cause an increase in slope of the curve. The arrows indicate where it is assumed that the contributions to the intensity, due to diffraction, are at a maximum. The arrows are at \( \theta = 16.4 \) and 24.4, these values agreeing quite well with those obtained by direct measurement from the original negative. The existence of two diffuse rings is characteristic of X-ray diffraction photographs of polyvinyl chloride, and they have been observed by Lebedev, Okladnov and Shylkova (1967), Mammi and Nardi (1963) and D'Amato and Strella (1969). Mammi and Nardi (1963) reported these rings to be at \( \theta = 17.7 \) and 24.6. The slight discrepancy between these and the results presented here probably arise from the uncertainty in the value of the specimen to film distance and the uncertainty in the position of the maximum intensity contribution due to diffraction from the polyvinyl chloride.

Extension at 71°C caused two diffuse equatorial reflections to develop, as can be seen in Figure 2.12. The intensity of these equatorial reflections appeared to increase with increasing extension ratio. This was confirmed from densitometer traces taken along the equator from the negatives for extension ratios 2.6, 3.9 and 4.5. These results are presented in Figure 2.16. Since the specimens were of different thicknesses and since different
exposure times were used for different specimens, the total intensity of X-rays transmitted through each specimen would vary. In order to allow for this in comparing intensities in Figure 2.16, all curves were normalised at $\theta = 7.0^\circ$. In using this procedure, it has been assumed that the scatter at small values of $\theta$ was primarily due to air scatter, and the intensity would therefore depend upon the total intensity of X-rays transmitted through the specimen and would not be affected significantly by structural changes. The position $\theta = 7.0^\circ$ was chosen since this was the only small value of $\theta$ for which data was obtained at all extension ratios. From the normalised curves presented in Figure 2.16, it can be seen that the equatorial arcs, at $\theta = 16.5^\circ$ approximately, increased in intensity with increasing extension ratio. The value of $\theta$ obtained from these curves varied between $16^\circ$ and $17^\circ$. These variations probably arise from variations in the specimen to film distance. The average value of $\theta$, $16.5^\circ$, suggests that this equatorial reflection corresponds to the inner diffuse ring observed for unoriented polyvinyl chloride at $\theta = 16.4^\circ$. In fact for the 2.6 extension ratio, Figure 2.12, the complete ring can be observed with some intensification on the equator. The single equatorial reflection has been observed for oriented polyvinyl chloride by Lebedev et al (1967) and Mammi and Nardi (1963). Lebedev et al (1967) suggested that this reflection is produced by regions in which the axes of the molecular chains are parallel but there is no order in rotations or displacements of the chains. The spacing obtained from the reflection gives the mean distance between molecular chains in these regions and was reported to be $5.2 \, \AA$ by Lebedev et al (1967) and $5.0 \, \AA$ by Mammi and Nardi (1963). The average value
of 2θ obtained from our photographs corresponds to an average spacing of 5.3 Å. The increasing intensity of the equatorial reflection with increasing extension ratio might be expected since the extension would tend to align these regions parallel to the extension direction. Thus, the diffracted X-rays, which are spread evenly round the ring in the unoriented material, became concentrated into arcs with a limited angular spread. Extension might also increase the size or number of regions in which molecules are parallel.

From Figure 2.12 it can be seen that the effect of extension at 71°C on the outer ring at 2θ = 24° was to cause a weakening of intensity on the equator producing two meridional arcs. This weakening of intensity is apparent from Figure 2.17. This shows a plot of intensity against 2θ along the meridian and equator of the negative obtained for material of extension ratio 3.9. The other curve in this figure is a plot of intensity variation along a diagonal and will be discussed later. It can be seen that at 2θ = 24°, corresponding to the outer diffuse ring, the intensity on the meridian is greater than that on the equator.

The photographs for material extended at 90°C are presented in Figure 2.13. It can be seen that for both extension ratios that the diffuse rings observed for the unoriented material remained complete but in each case there was some intensification on the equator of the inner ring, this being more pronounced for the 6.0 extension ratio. There also appears to be some weakening of intensity on the meridian of the outer ring. This latter point can be confirmed from Figure 2.18 by comparing intensities at 2θ = 24° for material of extension ratio 6.0.
It was reported in an earlier paragraph that the equatorial reflection arises from regions in which molecular chains were parallel. If additional lateral order develops, then truly crystalline regions will exist in the polymer. In this case two crystalline reflections appear superimposed upon this inner diffuse ring (see D'Amato and Strella (1969) and Mammi and Nardi (1963)). By assuming that the crystals have an orthorhombic unit cell, Natta and Corradini (1956) suggested that these are (110) and (200) reflections. In addition, for the oriented polymer the outer diffuse ring should split into four arcs, (111) reflections, with a decrease in intensity on both meridian and equator. For the material extended at 71°C, no additional reflections could be detected superimposed on the equatorial reflection for most extension ratios. However, careful study of Figure 2.12(b) for extension ratio 2.6 reveals that, at the extremes of the equatorial reflection, the inner ring appears to be split into two reflections. Densitometer traces did not show these two reflections. In the photographs for material extended at 90°C, shown in Figure 2.13, the splitting of the inner ring into two reflections is more easily detected. However, densitometer traces along the equator of the negative for the 6.0 extension ratio did not show the two peaks superimposed on the inner diffuse peak. Instead, this peak was not a smooth curve but was stepped, as shown in Figure 2.19, curve A. It was thought that the absence of two separate peaks arose from air scatter masking any diffraction effects from the polyvinyl chloride. In order to eliminate the effect of air scatter the following procedure was followed. It was assumed that the intensity at small and large values of 2θ arises largely from air scatter.
The intensity distribution due to air scatter at intermediate values of $\theta$ was assumed to take the form of curve B which connects smoothly with curve A at large and small values of $\theta$. Curve B was then subtracted from curve A to give curve C, which was assumed to be that due to diffraction from the polyvinyl chloride. It can be seen that the stepped peak in curve A becomes two small peaks in curve C. Although curve B is not necessarily the correct one for eliminating the air scatter, the procedure does indicate how the peaks can be masked by other unwanted scattering.

The existence of four arcs on the outer diffuse ring can just be detected in Figures 2.12($d$) and 2.13(b) for material of extension ratios 4.5 and 6.0. This was confirmed by taking densitometer traces along the meridian, equator, and diagonal from each negative. The direction of the diagonal scan was chosen to go through the regions of maximum intensity on the outer ring. This direction is indicated by the arrows in Figures 2.12 and 2.13. The results from the densitometer traces are reproduced in Figures 2.18 and 2.20. It can be seen that, in each case, at $\theta = 24^0$, corresponding to the reported position of the outer ring, the diagonal scan shows a greater intensity than either equatorial or meridional scans. Figure 2.17 shows that similar results were obtained for the material of 3.9 extension ratio obtained by extension at 71°C.

It is clear that, without the use of more sophisticated techniques, such as the use of monochromatic radiation and the elimination of air scatter by using a vacuum X-ray path, quantitative results cannot be obtained from the photographs discussed in this section. However, some conclusions of a qualitative nature have been reached on the basis of the results presented here.
If the inner reflection at \( 2\theta = 17^\circ \) is considered to arise from regions in which the molecules are parallel, the splitting of the inner ring into equatorial arcs, and the increasing intensity of these arcs indicates that extension caused the molecular chains to become aligned in the extension direction. Since these arcs for material extended at 90\(^\circ\)C were not as well developed as those for extension at 71\(^\circ\)C, the extension at 90\(^\circ\)C was not as efficient in producing molecular alignment as extension at 71\(^\circ\)C. This is in agreement with the birefringence results presented in Section 2.3.2.

The existence of (110) and (200) crystalline reflections in material of extension ratio 2.6, prepared by extension at 71\(^\circ\)C, and in material of extension ratios 3.0 and 6.0, prepared by extension at 90\(^\circ\)C, indicates that the material was slightly crystalline. The (111) reflections for material of extension ratios 3.9, 4.5, 3.0 and 6.0 also show this to be so. However, because suitable techniques were not used in obtaining the X-ray diffraction photographs, the magnitudes of the crystallinity of these materials could not be calculated. Lebedev et al (1967) have stated that the crystallinity of commercial grades of polyvinyl chloride is between 0 and 10\%. It can only be assumed that the same applies in this case. Since the crystalline reflections were more easily detected for material extended at 90\(^\circ\)C, it can be concluded that this material was more crystalline than that extended at 71\(^\circ\)C. It was not possible to determine the effects of extension on the crystallinity of the material. The diffuse nature of the reflections suggests that any crystalline regions were small and imperfect.
2.3.4 Stress Whitening of Polyvinyl Chloride

An effect observed during the extension of Vybak at 71°C was the development of a milky appearance, stress whitening, in the material. If the material was cooled under load and removed from the tensile machine, the stress whitening was retained. Material of extension ratio 3.3 was transparent, but some whitening could be observed in material of extension ratio 3.7. This suggests that the stress whitening started to develop in the material at an extension ratio of approximately 3.5. At higher extension ratios the whitening became more pronounced, so much so that it was not possible to obtain birefringence measurements at extension ratios 3.9 and 4.5. If the load was removed from the strip at the stretching temperature, the strip contracted and the stress whitening disappeared. Vybak extended at 90°C became slightly whitened at extension ratios above 7.5 but always failed before the machine could be arrested. The development of stress whitening was also observed during the extension of Cobex at both 71°C and 80°C. In the case of extension at 80°C the stress whitening started to develop at an extension ratios between 3.5 and 3.7. No similar detailed results were obtained for the extension of Cobex at 71°C.

The appearance of stress whitening during the deformation of polyvinyl chloride has previously been observed by Andrews and Yazama (1968). These workers carried out creep experiments at different stress levels in the temperature range 30°C to 140°C. It was reported that whitening developed during creep at 60°C, but it was not made clear whether this also occurred at other temperatures. They found that the birefringence of the stress whitened material was higher than that of the transparent material of the same extension ratio. Similar results could not be obtained for the material used here since both transparent and
stress whitened material of the same extension ratio were not obtained under the same extending conditions. Andrews and Yazama (1968) suggested that the stress whitening was caused by the formation of voids in the material. Both density measurements and low angle X-ray scattering studies carried out on the material used in this investigation indicate that this is indeed the case.

Using the method discussed in Section 2.1.3 the densities of oriented Vybak and oriented Cobex were measured by hydrostatic weighing at temperatures of 19°C and 18.4°C, respectively. These results are reproduced in Figure 2.21. The differences in the accuracies of the density measurements indicated in this figure arose from differences in the mass of samples available for measurement. From Figure 2.21, it can be seen that, for both Vybak and Cobex at low extension ratios, the density was constant within the limits of experimental error. However, in both cases the density started to decrease at an extension ratio of approximately 3.5. Some stress whitening was detectable in most materials which showed a decrease in density. Maximum density changes of 8% and 5% were measured for Vybak of extension ratio 4.5 and Cobex of extension ratio 5.0, respectively. Some of the stress whitened Vybak was rolled parallel to the original extension direction and was observed to become more transparent. The density of the rolled material (indicated by square plotting symbols in Figure 2.21) was found to have increased to values near that of the transparent material at lower extension ratios. Rolling transparent Vybak of extension ratio 2.6 produced no visible changes in the material and no significant change in density was measured. A decrease in density of the stress whitened material is consistent with the
development of voids causing the whitening. The term voids is here used to mean regions having lower density than the surrounding material. A density decrease could arise from either a decrease in mass of the material, or an increase in volume, or a combination of both. Unfortunately the limits of accuracy of the volume measured after deformation, as indicated by the product $R_x R_y R_z$, were greater than the measured change in density. For Vybak of extension ratio 4.5, which showed a density change of 8%, no appropriate dimensional measurements were made. The values of $R_x R_y R_z$ given in Tables 2.1, 2.2, 2.3 and 2.4 showed no particular trend with increasing $R_z$. To check whether a decrease in mass or increase in volume was responsible for the density decrease, test pieces having gauge length 12.5 mm and width 4.0 mm were cut from a sheet of Vybak, and they were weighed before and after extension at 71°C. Three such test pieces were deformed and in each case the change in weight was less than 1 part in 1000. One test piece remained transparent and showed no change in density, but another test piece stress whitened and had a density change of at least 5%. Such a change in density, if due to a change of mass at constant volume, would cause a weight change considerably larger than that measured. These results indicate that the density decrease associated with stress whitening arose from an increase in volume.

Stress whitening during the cold drawing of polyethylene has also been accounted for by the formation of voids. In this case the voids also give rise to scattering of X-rays at low angles (see Geil (1963) p.424). In view of this, low angle scattering photographs were obtained for polyvinyl chloride of
different extension ratios with the intention of obtaining information concerning the shape and size of the voids. These photographs are reproduced in Figure 2.22. It can be seen that, for clear Vybak of extension ratios 2.0 and 3.3, there was a small amount of low angle scattering. However, comparison with Figure 2.22(a), which was obtained with no specimen in the X-ray beam, shows that a significant contribution may have come from parts of the main X-ray beam missing the beam stop. Further comments will be made concerning this contribution when measurements of scattered intensity are discussed later in this section. For extension ratios 3.9 and 4.5 there was a considerable amount of scattering. The shape of the scattering pattern was approximately elliptical, the major axis being perpendicular to the original stretching direction, which was vertical in Figure 2.22. (The term scattering pattern refers to the pattern on the X-ray film produced by the scattered X-rays.) For the rolled material, initially extension ratio 4.5, Figure 2.22(f), the scattering pattern was less intense and was more nearly circular in shape. A detailed study of the shape of the intensity distribution of the scattered X-rays for the 4.5 extension ratio was obtained using the following procedure. The negative was placed at the centre of the rotating table of the densitometer and was successively placed in different positions by rotating through 10° or 15° relative to the y-traverse of the specimen table. For each position a densitometer trace was taken by traversing the negative in the y-direction. From the densitometer traces lines of equal intensity can be plotted as a function of r and θ, where r is the distance from the centre of the film in a given direction θ. Such a plot is presented in Figure 2.23 for two intensities in the ratio 4 : 9. It can be seen that the scattering spot is
approximately elliptical, although the shape cannot be fitted exactly to the equation of an ellipse. That low angle scattering occurs suggests that there are inhomogeneities in the electron density within the material, and these act as scattering centres for the X-rays. The decrease in density of the material, for which a considerable amount of low angle X-ray scattering occurred, indicates that these scattering centres are in fact voids in the material.

It is possible to evaluate the shape and dimensions of the scattering centres, voids in this case, from the variation of intensity of the scattered X-rays as a function of scattering angle, $\epsilon$. Guinier (1952) has discussed size determinations for certain simple cases. In particular, he states that, if the voids are ellipses with their major axes all parallel, the scattering pattern is also an ellipse with its major axis at right angles to that of the voids. Thus the results presented in Figure 2.23 indicate that the voids were elliptical with their major axes parallel to the original extension direction. Guinier (1952) also shows that the intensity distributions, $I_{\text{major}}$ and $I_{\text{minor}}$, along the major and minor axes of the scattering spot, are given as a function of $\epsilon$ by

\[
I_{\text{major}} = N n^2 I_e \exp \left( -\frac{4\pi^2}{5\lambda^2} \frac{a^2}{\epsilon^2} \right),
\]

\[
I_{\text{minor}} = N n^2 I_e \exp \left( -\frac{4\pi^2}{5\lambda^2} \frac{c^2}{\epsilon^2} \right),
\]

where $a$ and $c$ are the minor and major axes respectively of the elliptical voids, $I_e$ is the intensity scattered by an electron
at small angles, N is the number of voids, \( n \) represents the difference between the electron densities of the voids and the surrounding material, and \( \lambda \) is the wavelength of the radiation used. Assumptions made in deriving equation (2.2) are that the voids are all of the same size and are widely spaced. If this latter condition does not hold, there is interference between the X-rays scattered from different particles and the intensity distributions become considerably modified. In particular the scattered intensity at \( \varepsilon = 0 \) is reduced and subsidiary maxima of scattered intensity occur at values of \( \varepsilon \) determined by the spacing between particles.

From equation (2.2) it is apparent that a plot of \( \Delta n I \) vs \( \varepsilon^2 \) should be a straight line of slope \(-4\pi^2 a^2/5\lambda^2\), or \(-4\pi^2 c^2/5\lambda^2\), depending upon which axis of the scattering pattern the intensity variation was measured along. The results obtained from the negatives for the polyvinyl chloride have been treated in this way. The intensity distribution along the major and minor axes was determined using the following procedure. The negative was aligned so that when traversed in the x-direction, the densitometer light beam moved along the major axis of the scattering pattern. In actually measuring the intensity, the negative was traversed in the x-direction and at the same time scanned backwards and forwards in the y-direction through 2 mm. If the intensity had been measured by a straight traverse there was no certainty that the densitometer beam would have followed exactly the major axis of the scattering pattern. Using the scanning technique the densitometer beam did not follow the major axis but always intersected it at regular intervals. A typical trace obtained in this way reproduced in Figure 2.24. The intensity distribution along the major axis is
the envelope of the curve in Figure 2.24. The scattering angle, $\epsilon$, can be evaluated from the distance traversed in the x-direction, knowing the specimen to film distance. In order to evaluate the intensity distribution in the direction of the minor axis, the negative was rotated through $90^\circ$ and the above procedure was repeated. From the results obtained in this way plots of $\ln I$ vs $\epsilon^2$ were obtained and are reproduced in Figures 2.25, 2.26 and 2.27. It can be seen that in all cases the plots were approximately linear. Such linear plots would confirm the validity of the assumption made in deriving equation (2.2) that all the voids are of the same size. If this were not the case there would be a decrease in slope at small values of $\epsilon^2$, the limiting slope of the curve at small values of $\epsilon^2$ giving the dimensions of the largest void. The dimensions of the major and minor axes of the voids derived from the slopes of these curves are plotted as a function of extension ratio in Figure 2.28. There seem to be some inconsistencies in the results reproduced in this figure. It can be seen that as the extension ratio increased the minor axis decreased in size. This might be expected if the voids, when they developed, did so rapidly until they reached a finite size and then deformed in the same way as the strip. However, under such circumstances the length of the major axis would be expected to increase with increasing extension ratio. In fact the opposite occurred, in that the major axis for the 4.5 extension ratio was smaller than that for the 3.9 extension ratio. (The major axis dimensions were not evaluated for smaller extension ratios since the scattering pattern was too small for the intensity distribution to be satisfactorily evaluated.) In view of these inconsistencies it seems worthwhile considering what factors could give rise to errors in the size determinations.
Earlier in this section it was noted that with no specimen present some X-rays were not intercepted by the back stop. The back stop was 1.5 mm in diameter, and since this is the calculated diameter of the main beam at the film, it is thought that the pattern in Figure 2.22(a) arises from scattering from the second pinhole. After correcting for different exposure times and absorptions, this scattering was found to be negligible compared with the scattering from the polyvinyl chloride. (In evaluating the absorption effects, the mass absorption coefficient for polyvinyl chloride was calculated to be $60 \text{ gm cm}^{-2}$ using data supplied by Guinier (1952), Appendix V and equation (1.10) of his book.)

A more serious difficulty could arise from the size of the beam being of the same order as that of the scattering pattern, and also from the divergence of the main beam. In fact the extremities of the beam stop correspond to a value of $\varepsilon^2$ of $0.6 \times 10^{-5}$ radians$^2$, as indicated in Figures 2.26, 2.27 and 2.28. The angle of divergence of the main beam was calculated to be $3.3 \times 10^{-3}$ radians. Thus the scattered X-rays reaching any point on the film could have been scattered through angles differing by as much as $3.3 \times 10^{-3}$ radians. Yudowitch (1949) has analysed such effects in systems where the beam is collimated by slits and has shown how the size of both height and width of the slits can modify the scattering pattern.

Another problem has been pointed out by Shull and Roess (1947) who obtained scattering intensities for the same specimen using unfiltered Cu, nickel-filtered CuKa and monochromated CuKa radiation. They found at low angles, $\varepsilon^2 = 4 \times 10^{-4}$ radians$^2$, that the unfiltered radiation and filtered radiations gave intensities 50% and 20%, respectively, higher than those for the monochromated
radiation. The difference between the results for nickel-filtered and monochromated CuKa radiation arises from the fact that the white radiation is not removed by the filter. Since the results presented here were at smaller values of $\varepsilon^2$ than that mentioned above, it is to be presumed that this might have a serious effect on the results.

In view of the difficulties discussed above the results presented in Figure 2.28 cannot be considered to represent the true variation of void dimensions with extension ratio. However, these results can be considered to give an order of magnitude for the size of the voids. The shape of the scattering pattern indicates that the voids were elliptical in shape with the major axes parallel to the original extension direction.

2.3.5 Summary

In this section a brief summary will be made of the behaviour during the hot stretching of polyvinyl chloride and the properties of the oriented material.

1. The similarity between the stress-strain behaviour of polyvinyl chloride and rubber as discussed in Section 2.3.1 suggests that the behaviour of polyvinyl chloride at temperatures above $T_g$ can be described by a molecular network theory, provided allowance is made for relaxation effects, the non-permanent nature of the physical cross-links, and viscoelastic stress effects.

2. During extension the material deformed such that $R_x = R_y$ and $R_x \cdot R_y \cdot R_z = 1$, within the limits of experimental error.
3. Both oriented Vybak and Cobex were positively birefringent, the birefringence increasing with increasing extension ratio. For a given extension ratio the birefringence was higher for the lower extension temperature.

4. Wide angle X-ray diffraction photographs showed that the molecules became aligned parallel to the extension direction. The polyvinyl chloride was slightly crystalline, the material extended at 90°C being more crystalline than that extended at 71°C.

5. At certain extension ratios both Cobex and Vybak started to stress whiten. Density and low angle scattering studies indicated that this arose from the formation of voids in the material. These voids were elliptical with their major axes parallel to the extension direction and had linear dimensions of the order of 140 Å.

2.4 Preparation of Oriented Polyethylene

Since it was received in the form of granules, the polyethylene had to be compression moulded into the form of sheet. At the initiation of this work no facilities were available for compression moulding, and so the sheets were prepared by Dr. T. Hinton whilst at the H.H. Wills Physics Laboratory, University of Bristol. The sheets, which were approximately 0.5 mm thick, were compression moulded at 160°C and subsequently quenched into water at approximately 20°C.

The oriented material was prepared by extending test pieces, which were of the order of 10 cm long and 5 cm wide, at room
temperature \((20^\circ C \pm 2^\circ C)\). Since there was a tendency for the material to tear at the grips, shoulders were cut on the test pieces. Care was also taken in polishing the sides of the test pieces using fine emery cloth. Extension was carried out at a rate of \(1 \text{ cm.min}^{-1}\), irrespective of gauge length. A fixed extension rate, rather than a fixed strain rate, was used because the material necked. Under these conditions the boundaries of the neck propagated at a constant rate, irrespective of the gauge length.

The structure of the oriented material was not investigated in any detail. Any information available concerning the oriented material will be presented in Chapter 8 when the deformation behaviour is discussed.

2.5 Tensile Testing of Oriented Material

Tensile tests on the oriented material were carried out on small dumb-bell shaped test pieces. These were punched out of the oriented strips using a die fitted into a hand cutting press, as shown in Figure 2.29. Four dies giving test pieces of different dimensions were available. Investigations of the yielding and optical anisotropy changes during deformation were carried out on test pieces of gauge length 6 mm and width 1.5 mm. Some fracture tests were also carried out using test pieces of gauge length 12.5 mm and width 4.0 mm. The thickness of these test pieces varied from 500 \(\mu\)m to 130 \(\mu\)m, depending upon the extension ratio of the oriented strip. The oriented polyethylene was tested using test pieces of gauge length 10 mm, width 2.4 mm and thickness varying from 500 \(\mu\)m to 100 \(\mu\)m.
The test pieces were cut out of the oriented strip at various angles relative to the original extension direction. The angle, $\lambda$, between the original extension direction and the axis of the test piece was measured, using a polarising microscope, by locating the extinction position when the test piece was rotated between crossed polars. In this position the original extension direction, i.e. that in which the molecules were aligned, could be parallel to the axis of either polarizer or analyser. If the axes of polarizer and analyser were parallel to the crosswires, the molecular alignment direction would also be parallel to either wire of the crosswires. To determine which of the wires was actually parallel to the molecular alignment direction, it was noted which of them was parallel to the drawing marks on the oriented sheet. If the drawing marks were not detectable, the extinction direction was taken to be that which was parallel to that of maximum refractive index as indicated by the position of the zero order fringe when using the compensator. All future references to the extinction direction will mean that corresponding to the larger refractive index. When the extinction direction was identified, the reading on the angular scale of the rotating table was noted and the table was rotated until the same crosswire was parallel to the edge of the test piece. The reading on the angular scale was again noted and the difference between the two readings gave the value of $\lambda$. This method of measuring $\lambda$ relies upon the axes of polarizer and analyser being parallel to the crosswires. This can be checked by measuring $\lambda$ as above, then turning the test piece over, so that its other face is uppermost, and remeasuring $\lambda$. If the axes are parallel to the crosswires the two values of
\( \lambda_o \) should be the same within experimental error. Figure 2.30 shows how different values of \( \lambda_o \) arise if the axes of polarizer and analyzer are not parallel to the crosswires. In this case the misalignment is approximately 10°, giving rise to a difference of 20° in the two values of \( \lambda_o \). Figures 2.30(a) and 2.30(b) show the orientation of the test piece at the extinction position before and after turning it over. In each case the original extension direction is parallel to the axis of the polarizer. Using this checking technique, the axes of polarizer and analyser were always found to be parallel to the crosswires. For transparent polyvinyl chloride test pieces \( \lambda_o \) could be measured to an accuracy of ±0.2°. As the material became whitened this accuracy was reduced until it became ±1° for Vybak of extension ratio 3.9. At extension ratios higher than this the extinction position could not be located and so the value of \( \lambda_o \) used was the nominal one at which the test piece had been cut from the oriented strip. Results from transparent material suggests that the values were accurate to ±2°.

Details of testing conditions, such as extension rate and testing temperature, will be given where appropriate in the text.
Table 2.1

Values of $R_z$, $R_x$, $R_y$, and $R_x R_y R_z$ for Strips of Vybak Extended at 71°C.

<table>
<thead>
<tr>
<th>$R_z$</th>
<th>$R_x$</th>
<th>$R_y$</th>
<th>$R_x R_y R_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>0.70</td>
<td>0.72</td>
<td>1.00</td>
</tr>
<tr>
<td>2.6</td>
<td>0.62</td>
<td>0.61</td>
<td>0.99</td>
</tr>
<tr>
<td>3.0</td>
<td>0.58</td>
<td>0.57</td>
<td>1.00</td>
</tr>
<tr>
<td>3.3</td>
<td>0.55</td>
<td>0.55</td>
<td>1.00</td>
</tr>
<tr>
<td>3.7</td>
<td>0.52</td>
<td>0.54</td>
<td>1.03</td>
</tr>
<tr>
<td>3.9</td>
<td>0.51</td>
<td>0.51</td>
<td>1.01</td>
</tr>
</tbody>
</table>

Table 2.2

Values of $R_z$, $R_x$, $R_y$, and $R_x R_y R_z$ for Strips of Cobex Extended at 80°C.

<table>
<thead>
<tr>
<th>$R_z$</th>
<th>$R_x$</th>
<th>$R_y$</th>
<th>$R_x R_y R_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.7</td>
<td>0.60</td>
<td>0.61</td>
<td>1.00</td>
</tr>
<tr>
<td>3.0</td>
<td>0.58</td>
<td>0.56</td>
<td>0.98</td>
</tr>
<tr>
<td>3.2</td>
<td>0.57</td>
<td>0.57</td>
<td>1.05</td>
</tr>
<tr>
<td>3.5</td>
<td>0.54</td>
<td>0.54</td>
<td>1.03</td>
</tr>
<tr>
<td>3.9</td>
<td>0.51</td>
<td>0.51</td>
<td>1.01</td>
</tr>
<tr>
<td>4.3</td>
<td>0.47</td>
<td>0.48</td>
<td>0.97</td>
</tr>
<tr>
<td>5.0</td>
<td>0.44</td>
<td>0.45</td>
<td>1.03</td>
</tr>
</tbody>
</table>
Table 2.3

Values of \( R_z, R_x, R_y, \) and \( R_x R_y R_z \) Obtained From Small Test Pieces of Vybak Extended at 71°C.

<table>
<thead>
<tr>
<th>( R_z )</th>
<th>( R_x )</th>
<th>( R_y )</th>
<th>( R_x R_y R_z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>0.94</td>
<td>0.96</td>
<td>1.01</td>
</tr>
<tr>
<td>2.5</td>
<td>0.63</td>
<td>0.64</td>
<td>1.01</td>
</tr>
<tr>
<td>3.1</td>
<td>0.57</td>
<td>0.57</td>
<td>1.00</td>
</tr>
<tr>
<td>3.3</td>
<td>0.55</td>
<td>0.55</td>
<td>0.99</td>
</tr>
<tr>
<td>3.5</td>
<td>0.54</td>
<td>0.54</td>
<td>1.01</td>
</tr>
<tr>
<td>3.8</td>
<td>0.52</td>
<td>0.52</td>
<td>1.02</td>
</tr>
<tr>
<td>4.3</td>
<td>0.47</td>
<td>0.49</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Table 2.4

Values of \( R_z, R_x, R_y, \) and \( R_x R_y R_z \) Obtained From Small Test Pieces of Vybak Extended at 90°C.

<table>
<thead>
<tr>
<th>( R_z )</th>
<th>( R_x )</th>
<th>( R_y )</th>
<th>( R_x R_y R_z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.7</td>
<td>0.60</td>
<td>0.62</td>
<td>1.00</td>
</tr>
<tr>
<td>3.9</td>
<td>0.49</td>
<td>0.53</td>
<td>1.01</td>
</tr>
<tr>
<td>5.0</td>
<td>0.43</td>
<td>0.47</td>
<td>0.95</td>
</tr>
<tr>
<td>7.1</td>
<td>0.37</td>
<td>0.39</td>
<td>1.03</td>
</tr>
</tbody>
</table>
Table 2.5

Values of $R_z$ for Vybak After Extension and After Subsequent Annealing at the Temperatures Indicated.

<table>
<thead>
<tr>
<th>Extension Temperature, °C</th>
<th>$R_z$ After Extension</th>
<th>$R_z$ After Annealing at the Extension Temperature</th>
<th>$R_z$ After Annealing at 120°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>71</td>
<td>2.52</td>
<td>1.04</td>
<td>-</td>
</tr>
<tr>
<td>71</td>
<td>3.08</td>
<td>1.08</td>
<td>-</td>
</tr>
<tr>
<td>71</td>
<td>3.52</td>
<td>1.13</td>
<td>-</td>
</tr>
<tr>
<td>71</td>
<td>3.79</td>
<td>1.22</td>
<td>-</td>
</tr>
<tr>
<td>71</td>
<td>4.34</td>
<td>1.26</td>
<td>-</td>
</tr>
<tr>
<td>90</td>
<td>3.21</td>
<td>1.12</td>
<td>1.06</td>
</tr>
<tr>
<td>90</td>
<td>4.16</td>
<td>1.19</td>
<td>1.11</td>
</tr>
<tr>
<td>90</td>
<td>5.79</td>
<td>1.70</td>
<td>1.20</td>
</tr>
</tbody>
</table>
environmental chamber in position. The large grips shown in this photograph are those used in preparing the oriented material.

Figure 2.2 Photograph showing the grips used in extending the small test pieces. The grips are shown positioned in the mounting jig.
Photograph of small tensile machine which could be attached to the optical microscope in order to observe stages in the deformation of test pieces.

Diagram showing the arrangement for aligning deformation bands parallel to the reference wire on the film cassette of the X-ray camera. (Not to scale.)
Figure 2.5  Optical micrographs showing the change in dimensions of the grid of dots resulting from deformation.

Figure 2.6  Diagram of grid of dots before and after extension showing the dimensions and angles required in order to evaluate the extension ratio, $R$. 
Figure 2.7. Graph showing the variation of nominal stress as a function of extension ratio, $R_z$, during the extension of Vybak at $71^\circ\text{C}$ and $90^\circ\text{C}$.
Figure 2.8. Graph showing the variation of true stress as a function of extension ratio, $R_z$, during the extension of Cobex and Vybak at elevated temperatures.
Figure 2.9. Graph of true stress vs. birefringence for Vybak extended at 71°C and 90°C.
Figure 2.10. Graph of true stress vs. birefringence for Cobex extended at 71°C and 80°C.
Figure 2.11 Plots of birefringence vs. extension ratio for Vybak and Cobex extended at different elevated temperatures. The birefringence was measured at room temperature.
Figure 2.12  Wide angle X-ray diffraction photographs obtained for Vybak extended at 71°C, having extension ratios (a) 1.0, (b) 2.6, (c) 3.9, and (d) 4.5. Tensile axis is vertical.
**Figure 2.13** Wide angle X-ray diffraction photographs obtained for Vybak extended at 90°C, having extension ratios (a) 3.0 and (b) 6.0.

**Figure 2.14** Wide angle X-ray diffraction photographs obtained for Cobex extended at 80°C, having extension ratio 5.0.
Figure 2.15. Plot of intensity vs. $2\theta$ obtained from the densitometer trace of the X-ray diffraction photograph for Vybak of extension ratio 1.0.
Figure 2.16. Plot of intensity vs. $2\theta$ obtained from the densitometer trace along the equators of the X-ray diffraction photographs for Vybak of extension ratios 2.6, 3.9, and 4.5.
Figure 2.17. Plot of intensity vs. $2\theta$ along the equator, diagonal, and meridian of the X-ray diffraction photograph for Vybak of extension ratio 3.9.
Figure 2.18. Plot of intensity vs. 2θ along the equator, diagonal, and meridian of the X-ray diffraction photograph for Vybak of extension ratio 6.0.
Figure 2.19. Graphs of intensity vs. 2θ showing how the background scattering can mask crystallographic reflections. Curve A is the plot of intensity distribution for the X-ray diffraction photograph for Vybak of extension ratio 6.0. Curve B is the assumed intensity distribution for the background scattering. Curve C is the result of subtracting Curve B from Curve A.
Figure 2.20. Plot of intensity vs. $2\theta$ along the equator, diagonal, and meridian of the X-ray diffraction photograph for Vybak of extension ratio 4.5.
Figure 2.21 Plots of density vs. extension ratio for Vybak and Cobex extended at 71°C and 80°C respectively. The square plotting symbols indicate the results for rolled material, and the arrows indicate the density change due to rolling.
Figure 2.22 Low angle scattering patterns (a) with no specimen in beam, and for Vybak of extension ratios, (b) 2.0, (c) 3.3, (d) 3.9, (e) 4.5, and (f) 4.5 after rolling.
Figure 2.23 Plots of lines of equal intensity for the low angle scattering pattern from Vybak of extension ratio 4.5.
Figure 2.24  Typical trace obtained from a low angle scattering using the densitometer.
Figure 2.25 Plot of ln (Intensity) vs. $\varepsilon^2$ for the intensity distribution along the major axes of the scattering patterns obtained from Vybak of extension ratios 3.3 and 2.0.
Figure 2.26 Plot of $\ln$ (Intensity) vs. $\varepsilon^2$ for the intensity distribution along the minor axes of the scattering patterns obtained from Vybak of extension ratios 3.9 and 4.5.
Figure 2.27 Plot of ln (Intensity) vs. $\varepsilon^2$ for the intensity distribution along the major axes of the scattering patterns obtained from Vybak of extension ratios 3.9 and 4.5.
evaluated from low angle scattering photographs, as a function of extension ratio for Vybak extended at 71°C.
Figure 2.29 Photographs showing the dumb-bell shaped dies and the hand cutting press used in cutting out small test pieces.
Figure 2.30 Diagram showing how errors in $\lambda_0$ arise if the axis of the polariser is not parallel to the crosswire. The test piece is shown at the extinction position before and after being turned over. In each case the original extension direction is parallel to the axis of the polariser.
Observations of the Yielding and Cold Drawing of Oriented Polyvinyl Chloride

In this Chapter a detailed account will be given of the results for the investigation on the yield and cold drawing behaviour of oriented polyvinyl chloride. This will include measurements of yield and drawing stresses, and observations of deformation features formed at yield, and stages in their development. Also to be discussed will be strain measurements and optical anisotropy changes during deformation.

3.1 Experimental

In investigating the yielding and cold drawing of oriented polyvinyl chloride, tensile tests were carried out, using the E-type Tensometer, on test pieces of gauge length 6 mm and width 1.5 mm. These were cut from sheets of oriented Vybok, as discussed in Section 2.6. Tests were carried out at an extension rate of 1 cm.min⁻¹, strain rate 1.7 min⁻¹, on test pieces having $\lambda_0$ ranging from 0° to 90° in approximately 15° steps. For a given extension ratio, the tests were all carried out at the same temperature, and all tests were carried out in the temperature range 19°C to 21°C. (The term extension ratio is used here to mean the extension ratio, $R_x$, for the initial hot stretching. In cases where confusion might arise, this will be referred to as the prior extension ratio.) Those test pieces which were cut from sheets of extension ratios 2.0, 2.6, 3.0 and 3.9, obtained by extension at 71°C, were extended to failure in order to observe the general deformation behaviour and
the ultimate mode of failure. For those test pieces cut from sheets of extension ratios 2.0, 3.3, 3.7 and 4.5, and 3.0 and 6.0, obtained by extension at 71°C and 90°C respectively, the tests were stopped immediately after yield in order to study deformation bands formed at yield. In addition, some tensile tests were carried out on unoriented material after it had been annealed, some at 71°C and some at 90°C. The annealing time was approximately the same as the time for which the oriented material was in the environmental chamber during the original extension. From the load-extension curves obtained from these test pieces, measurements were made of yield and drawing stresses. Some measurements of strains in deformation bands and necked regions were also made.

Stages in the formation and subsequent development of the deformation bands were studied by testing a number of test pieces, in tension, at an extension rate of 0.66 mm.min⁻¹, strain rate 0.11 min⁻¹, using the small tensile machine attached to the microscope. At various stages in the deformation the tensile machine was stopped, and the test piece was photographed whilst in the machine. In addition, a number of test pieces, having the same value of λ₂ and cut from the same sheet of oriented polyvinyl chloride, were tested at an extension rate of 1 mm min⁻¹, strain rate 0.17 min⁻¹, using the E-type Tensometer. These test pieces were stopped at various stages on the load-extension curve, and the existence of any deformation features was investigated by observing the test piece under the optical microscope. In this way, stages in the development of the deformation bands could be correlated with positions on the load-extension curve. These tests were carried out on both oriented Vybak and Cobex.
In order to measure strains in cold drawn test pieces, a grid of dots, of spacing 0.193 mm, was printed on the sheets of extension ratio 2.0 and 2.6, using the technique discussed in Section 2.1.6. The grid was printed such that one line of dots was parallel to the extinction direction. Test pieces, with various values of $\lambda_o$, were cut from these sheets, and were tested at an extension rate of 1.1 mm.min$^{-1}$, strain rate 0.18 min$^{-1}$, using the small tensile machine shown in Figure 2.3. From measurements of the grid of dots before and after extension, the variation of the natural draw ratio was determined as a function of $\lambda_o$ and prior extension ratio.

A detailed study of the geometry of deformation was carried out on test pieces extended at 50°C with a strain rate of 0.17 min$^{-1}$. It had been found that these were the most suitable conditions under which the test pieces deformed uniformly, as opposed to forming a deformation band. In uniformly deformed test pieces the strain could be varied in a controlled manner by varying the amount of extension. Such tests were carried out on test pieces with different values of $\lambda_o$, cut from sheets of extension ratios 1.5, 2.9, 3.0, 4.4, 5.0 and 7.5, obtained by extension at 90°C. A grid of dots was printed on these sheets so that a detailed analysis could be made of the deformation geometry. For a particular value of $\lambda_o$, several test pieces were cut from the same strip, and each was extended by different amounts.

Measurements of changes in both optical extinction direction and birefringence were made in deformation bands, and on cold drawn and uniformly deformed test pieces. Some of these results will be presented in this Chapter, but most of them will be dealt with in Chapter 5.
3.2.1 Load-Extension Curves

A useful guide to the effect of varying extension ratio and \( \lambda_0 \) on the deformation behaviour of oriented polyvinyl chloride can be obtained by considering the load-extension curves presented in Figure 3.1. For the majority of test pieces, the curve had an initial sharp load rise, which was followed by a load drop and a region in which extension occurred at constant load. In some cases the deformation at constant load was followed by a region in which the load rose before failure occurred. The first load rise corresponded to the elastic region in which the test piece deformed uniformly over the entire gauge length. At the first load maximum, and during the subsequent load drop, one or more deformation bands appeared to develop obliquely across the test piece. The continued extension at constant load coincided with the plastic deformation spreading along the gauge length, by the movement apart of the boundaries of the deformation band, i.e. a running neck was formed. Some test pieces failed before the whole of the gauge length had been deformed in this manner. If the entire gauge length was deformed, a second load rise occurred as the boundaries of the neck propagated into the shoulders of the test piece. This type of behaviour is characteristic of cold drawing in both crystalline and some glassy amorphous polymers. A number of workers have investigated this phenomenon and much of this work has been reviewed by Ward and Pinnock (1966).

There were some exceptions to the behaviour discussed above. For the test pieces at \( \lambda_0 = 0^\circ \), extension ratio 3.0, the load rose continuously throughout the test, but there was a point at which the slope of the curve changed abruptly. Test pieces, which
fractured before there was any noticeable change in slope of the load-extension curve, were at $\lambda_0 = 90^\circ$, extension ratio 3.0, and at $\lambda_0 = 0^\circ$ and $15^\circ$, extension ratio 3.9. A load drop did occur for test pieces at $\lambda_0 = 75^\circ$ and $90^\circ$, extension ratio 2.6, and $\lambda_0 = 60^\circ$ and $75^\circ$, extension ratio 3.0, but failure occurred before the neck could start propagating.

Some effects of both extension ratio, and the angle $\lambda_0$, on the load-extension behaviour are apparent from Figure 3.1. For instance, for material of extension ratio 2.0, the second load rise, if it occurred, started at an earlier stage in the deformation as $\lambda_0$ decreased. A similar trend is apparent for other extension ratios in Figure 3.1. For those test pieces which failed before a second load rise occurred, the extension at failure increased as $\lambda_0$ decreased. The stress whitened material, of extension ratio 3.9, did not show any such well defined trends.

Another effect of varying $\lambda_0$ for a particular extension ratio, was that the load at the first load maximum increased with decreasing values of $\lambda_0$.

The effect of the extension ratio on the deformation behaviour is best studied by considering test pieces of fixed $\lambda_0$ but different extension ratios. Again, the stress whitened material of extension ratio 3.9 did not fit the pattern established for the clear materials of extension ratio 2.0, 2.6 and 3.0. For instance at $\lambda_0 = 90^\circ$, the test piece of extension ratio 2.0 was ductile and formed a running neck, but failed before the whole of the gauge length had been deformed. The material of extension
ratio 2.0 failed immediately after the load drop, and the material of extension ratio 3.0 failed suddenly just before the yield point was reached. Following this trend, the material of extension ratio 3.9 would be expected to have failed before the yield point was reached, but it did in fact deform in a ductile manner and formed a running neck. A test piece from the stress whitened material of extension ratio 4.5 and with $\lambda_o = 90^\circ$ also deformed in a ductile manner. For the clear materials of extension ratios 2.0, 2.6 and 3.0, the behaviour, in which the test pieces failed at earlier stages of the extension with increasing extension ratio, is apparent for $\lambda_o = 75^\circ$, 60$^\circ$, and 45$^\circ$. At all these angles the stress whitened material of 3.9 extension ratio extended further than the clear material of extension ratio 3.0.

The absence of a yield point at $\lambda_o = 0^\circ$ for the 3.9 extension ratio does not seem to deviate from the trend established at the lower extension ratios. For these test pieces the yield point became less well defined with increasing extension ratio since the load drop at yield decreased and was in fact non-existent at extension ratio 3.0.

One other aspect in which the load-extension curves for the stress-whitened material of extension ratio 3.9 differed from those of the clear material, is the shape of the load decrease. It is apparent from Figure 3.1 that the slope of the load-extension curve during the load drop is greater than that for the clear materials.

In the following sections a quantitative and more detailed discussion of the deformation behaviour will be given. Details of the mode of fracture of the material will be discussed in Chapter 7.
3.2.2 Yield and Drawing Stresses

From the load-extension curves, the nominal yield stress could be evaluated for each test piece. The nominal yield stress is the load at yield divided by the cross-sectional area measured prior to deformation. For those load-extension curves which showed a load drop, the yield point was taken as the maximum of the load-extension curve, as shown in Figure 3.2(a). For those curves which showed no load drop, as in Figure 3.2(b), the load at yield was taken as the value at the intersections of the extrapolation of the linear portions of the curve before and after the yield point. The curves for test pieces at $\lambda_o = 0^\circ$, extension ratio 3.7, at $\lambda_o = 0^\circ$ and $15^\circ$, extension ratios 3.9 and 4.5, and at $\lambda_o = 90^\circ$, extension ratio 3.0, showed no obvious yield point before the test pieces fractured. In this case the nominal stress, which was evaluated from the maximum recorded load, was taken as a fracture stress. These fracture stresses will not always be differentiated from the yield stress results to be discussed in this section. The load at yield could be measured to $\pm 1\%$. The cross-sectional area of the test piece was evaluated from measurements of thickness and width. The width, which was measured to an accuracy of $\pm 1\%$ using a travelling microscope, was 1.50 mm. The thickness was measured, using a dial gauge, to an accuracy of $\pm 1\mu m$, giving an accuracy of $\pm 1\%$ at extension ratio 6.0; this accuracy improved with decreasing extension ratio. Thus the nominal stress could be evaluated to $\pm 3\%$, or better. Since the test pieces were cut out using the same die, their widths were the same, and thus, for comparison purposes the nominal yield stress was accurate to $\pm 2\%$ or better.
In measuring the thickness of the test pieces, care was taken to check any variations along the gauge length. Within the limits of experimental error, there was no such variation. Most test pieces had a uniform tensile strain of between 6.5% and 10.5% at yield, and so, assuming constant volume deformation, true yield stresses should be between 6.5% and 10.5% higher than the quoted nominal yield stress values. The higher tensile strain was obtained at the smaller values of $\lambda_o$, and thus the true stress at small values of $\lambda_o$ would be larger relative to the nominal yield stress than it would be at large values of $\lambda_o$.

For a given extension ratio, the nominal yield stress had its maximum value at $\lambda_o = 90^\circ$ and decreased to a minimum at $\lambda_o = 0^\circ$. Figure 3.3 shows the typical variation of the nominal yield stress as a function of $\lambda_o$ for a number of extension ratios prepared by extension at 71°C. Similar results for polyvinyl chloride extended at 90°C are presented in Figure 3.4. Gibbs (1966) and Brown et al (1966) have obtained similar results for the variation of yield stress for oriented polyvinyl chloride and oriented polyethylene terephthalate respectively. The results of Keller and Rider (1966) were different in that the minimum yield stress occurred at $\lambda_o = 57^\circ$, approximately.

Since the yield stress vs $\lambda_o$ curves were of approximately the same shape at different extension ratios, the effect of extension ratio on the nominal stress may be usefully illustrated by considering the variation of yield stress, $\sigma_{\lambda}$, at particular values of $\lambda_o$ as a function of extension ratio. In Figure 3.5, $\sigma_{\lambda}$, $\sigma_{15}$, $\sigma_{30}$, $\sigma_{45}$, $\sigma_{60}$, and $\sigma_{90}$ are plotted as a function of extension ratio for material prepared at 71°C. Similar results for material
prepared at 90°C are presented in Figure 3.6. The points plotted in Figure 3.5 and 3.6 are not actual experimental points but are taken from the curves in Figure 3.3 and 3.4; these curves were drawn through the experimental points. It can be seen that, for material extended at 71°C, both $\sigma_{90}$ and $\sigma_{60}$ decreased with increasing extension ratio. At all other values of $\lambda_{0}$, the yield stress initially increased and then decreased with increasing extension ratio. As $\lambda_{0}$ decreased, the position of the maximum in $\sigma_{\lambda}$ occurred at larger values of extension ratio. The results for extension ratio 4.5 suggest that, at large values of extension ratio, the yield stress may start to increase again at $\lambda_{0} = 90^\circ$, $60^\circ$, $45^\circ$ and $30^\circ$. Since this material showed a considerable amount of stress whitening, it is not clear whether the stress whitening or just an increase in extension ratio were responsible for this increase. In Figure 3.5, those points, for which fracture occurred before any yield point could be detected, are marked with a cross plotting symbol. It is thought that the decrease in $\sigma_{\lambda}$ at large extension ratios does not represent the true behaviour of the yield stress, but only comes about because fracture occurred before yielding. The dashed curve indicates the assumed variation of $\sigma_{\lambda}$ if fracture had not intervened. There is no evidence to justify this assumption, but further discussion of this will be presented in Chapter 4. It is also apparent from Figure 3.5 that, at $\lambda_{0} = o^\circ$, those test pieces which fractured were cut from sheets of stress whitened material. It is not clear whether this behaviour is due to stress whitening, or whether it arises as a consequence of the increase in extension ratio. This will be discussed further in Chapter 7. The results for material extended at 90°C are presented in Figure 3.6. It can be seen that
these were similar to the results for material extended at 71°C, in that $\sigma_\lambda$ goes through a maximum for $\lambda_0 = 60^\circ$, $45^\circ$ and $30^\circ$.

Gibbs (1966) presented some of his results for the yield stress of oriented polyvinyl chloride in the same form as Figure 3.5. In this case, he found that $\sigma_{45}$ was constant at all values of extension ratio. For values of $\lambda_0$ less than $45^\circ$, the yield stress increased with increasing extension ratio and at no stage decreased. For values of $\lambda_0$ greater than $45^\circ$, the yield stress decreased with increasing extension ratio. Robertson (1964) and Allison and Ward (1967) have shown that, for oriented polycarbonate and oriented polyethylene terephthalate respectively, $\sigma_0$ increased with increasing extension ratio. Results presented in tabular form by Bridle, Buckley and Scanlan (1958) for oriented polyethylene terephthalate have been plotted as in Figure 3.5. It was found that, at all values of $\lambda_0$ at and below $45^\circ$, the yield stress increased with increasing extension ratio. At $\lambda_0 = 90^\circ$, the yield stress appeared to go through a minimum as the extension ratio increased.

A comparison of the results in Figures 3.5 and 3.6 shows that, for material extended at 71°C and 90°C, the yield stresses differed quite considerably when considered as a function of extension ratio. However, when taken as a function of birefringence in Figure 3.7, the results were in much better agreement. To avoid confusion in Figure 3.7, the results for material prepared at 71°C are represented by the curves, the experimental points having been omitted, and the results for material prepared at 90°C are represented by plotting symbols. In Figure 3.7, the anisotropy, as indicated by the ratio $\sigma_0/\sigma_{90}$, was greater for the
material extended at 90°C, although the optical anisotropy was the same. It is possible that these differences arise from the differences in crystallinity which were indicated by the X-ray diffraction results presented in Section 2.3.3. The improved agreement in results, when considered as a function of birefringence, might be expected if the deformation behaviour is dependant upon molecular alignment and not the amount of prior deformation.

For material annealed at 71°C the value of the yield stress was 10% smaller than the value for the unannealed material. A further reduction of 2% occurred for material annealed at 90°C. The reduction was not due to the removal of any orientation effects since the yield stress of the unannealed material was found to be independent of the direction in which the test pieces were cut from the sheet.

It has been suggested that there is a correlation between tensile modulus and yield stress. Allison and Ward (1967) have discussed this, and they have gathered together results for the modulus and yield stress of a number of oriented polymers. They have shown that, at \( \lambda_0 = 0^\circ \), such a correlation exists for polystyrene, polymethylmethacrylate, polycarbonate, and polyethylene terephthalate. Bridle et al (1968) have shown that, for various values of \( \lambda_0 \) and extension ratio, there is a correlation between modulus and a "corrected" yield stress. In view of these results this correlation was investigated for oriented polyvinyl chloride. In Figure 3.8, the tensile modulus is plotted against yield stress for test pieces having different values of \( \lambda_0 \) and cut from sheets of different extension ratios. The modulus was calculated from the slope of the load-extension curve, which was taken as the tangent of the angle between the curve and the extension axis.
The angle was measured using a protractor, giving rise to errors of ±7° in the slope. In Figure 3.8, for a given extension ratio, the experimental points at small stress values are for test pieces having large values of $\lambda_0$. It is clear from this figure that there is a definite correlation between modulus and yield stress for oriented polyvinyl chloride.

Another important stress measurement, which can be obtained from the load-extension curve, is the nominal drawing stress. This is defined as the constant load, at which cold drawing occurred, divided by the initial cross-sectional area of the test piece. The load during cold drawing was not strictly constant but varied by as much as ±2%. In the results presented here, the average value of this load was taken. The nominal yield stress is the stress required to initiate yielding, and the nominal drawing stress can be considered as the stress required to continue the plastic deformation. The variation of nominal drawing stress as a function of $\lambda_0$ is shown in Figure 3.9 for polyvinyl chloride of different extension ratios. No results are presented at $\lambda_0 = 90^\circ$, extension ratio 2.6, and $\lambda_0 = 90^\circ$ and 75°, extension ratio 3.0, since these test pieces failed before a running neck had become established. The absence of results at $\lambda_0 = 0^\circ$ and 15° is due to there being no load drop, the load rising continuously throughout the test. From Figure 3.9, it can be seen that the drawing stress varied in a manner similar to that of the yield stress, in that it increased as $\lambda_0$ decreased. However, the variation of drawing stress was more pronounced than that of the yield stress, in that the difference between maximum and minimum drawing stresses was larger than that for
the yield stress. This is illustrated in Figure 3.10 for material of extension ratio 2.0.

It is apparent from their definitions that the ratio of nominal yield stress to nominal drawing stress gives a measure of the load drop for the load-extension curves shown in Figure 3.1. By considering the ratio of these stresses, the qualitative discussion of the change in shape of the load-extension curves, given in Section 3.2.1, can be placed on a more quantitative basis. Figure 3.11 is a plot of the ratio of nominal yield stress to nominal drawing stress as a function of \( \lambda_0 \) for four extension ratios. These curves were not plotted from results obtained from individual test pieces, but the experimental points were obtained from the curves of drawing stress and yield stress shown in Figures 3.9 and 3.3. Figure 3.11 also shows another aspect in which the behaviour of the stress whitened material differed from that of the clear material. At large values of \( \lambda_0 \), e.g., \( \lambda_0 = 60^\circ \), the stress ratio increased with increasing extension ratio, but, for the stress whitened material of extension ratio 3.9, the stress ratio was below that of extension ratio 2.0. The curves, other than that for the 3.9 extension ratio, intersect in the vicinity of \( \lambda_0 = 25^\circ \), and for values of \( \lambda_0 \) less than 20\(^\circ\) the stress ratio decreased with increasing extension ratio. Unfortunately, because insufficient results were obtained for the material of extension ratio 3.9, it was not possible to see if it would follow the same trend at small values of \( \lambda_0 \).

Ignoring any slight changes in cross-sectional area due to elastic deformation, the drawing stress, as defined above, is the stress acting on the undeformed material during cold
drawing. The other important stress measurements during cold drawing is the tensile stress acting on the deformed material in the necked region. This stress will be referred to here as the true drawing stress, that is, the constant load during cold drawing divided by the cross-sectional area of the necked material. The cross-sectional area was calculated from width and thickness measurements. The width was measured from micrographs, and the thickness was measured using a dial gauge. It was estimated that the cross-sectional area was accurate to ±4%.

The true drawing stress is plotted as a function of \( \lambda_0 \) for different extension ratios in Figure 3.12. The most striking aspect of these results is that there was little variation of true drawing stress, particularly when compared with the variations of the nominal yield and drawing stresses. There does not appear to be any particular trend in the variation as a function of \( \lambda_0 \). Results have not been presented in Figure 3.12 for the 3.9 extension ratio, but at \( \lambda_0 = 90° \) and 75°, the true drawing stress was 90 MN m\(^{-2}\).

Further discussion of the cold drawing results will be given at the end of this Chapter, and the yield stress results will be dealt with in Chapter 4. It should be noted, with reference to the yielding behaviour, that the tensile strain at yield, which was mentioned earlier in this section, showed much less anisotropy than did the yield stress. The importance of this result will be made apparent in Chapter 4.

3.2.3 General Features of Deformation Bands

It was reported in Section 3.2.1 that, at yield, the plastic deformation of oriented polyvinyl chloride was localised into
narrow deformation bands which were inclined at an angle to the tensile axis, as shown in Figure 3.13. It was observed that two different types of deformation band were formed, and these are here classified as type 1 and type 2 bands, defined as follows. Let a quadrant be formed bounded by the tensile axis and by the direction which is in the plane of the test piece and at right angles to the tensile axis, such that the quadrant includes the extinction direction; then, if the direction of the band also lies in this quadrant, it is of type 1, and if it does not, it is of type 2. The definition is illustrated by Figure 3.14, and micrographs of type 1 and type 2 bands are presented in Figure 3.13. According to this definition, the bands in oriented polyethylene, for which Keller and Rider (1966) presented detailed results, correspond to type 1 bands, and the band shown in Figure 10 by Keller and Rider (1966) is a type 2 band. The slippy and kinky bands observed by Brown and Ward (1968a) in polyethylene terephthalate correspond to type 1 and type 2 bands respectively. For polyvinyl chloride, either one or both types of bands were observed in the majority of test pieces for which the load extension curve showed a load drop (Figure 3.2(a)). In fact, for the test pieces deformed at a strain rate of $1.7 \text{ min}^{-1}$ to yield, in only one out of the thirty six test pieces, in which deformation bands were formed, was a type 1 band observed in the absence of type 2 band. Type 1 bands were observed in all of these test pieces. No bands were observed in test pieces for which the load extension curve did not show a load drop (Figure 3.2(b)), or in test pieces which fractured before yielding occurred. Another important feature of both types of deformation band was that, as a result of the deformation, the extinction direction became inclined at a smaller
angle to the tensile axis. Such changes in extinction direction are illustrated diagramatically in Figure 3.15.

More detailed discussions of measurements and observations on deformation bands are given in the following sections.

3.2.4 Deformation Band Directions

It was stated in Section 3.2.3 that deformation bands were formed obliquely across the test piece. Because of this, the angles $\gamma_1$ and $\gamma_2$, between the tensile axis and the directions of type 1 and type 2 bands respectively (Figure 3.14), were measured. The effect of varying $\lambda_c$ on $\gamma_1$ is shown in Figures 3.16 and 3.17 for material extended at 71°C and 90°C respectively. The results $\gamma_2$ are shown in Figures 3.18 and 3.19. In addition to these results, the angle $\gamma$ for the unoriented material was found to be approximately 55°C. It is estimated that the angles $\gamma_1$ and $\gamma_2$ could be measured to an accuracy of ±2°C, or better.

It is apparent from the definition given in Section 3.2.3 that, for unoriented material and oriented material at $\lambda_c = 0^\circ$ and $\lambda_c = 90^\circ$, type 1 and type 2 bands are indistinguishable.

Considering first type 1 deformation bands formed in material extended at 71°C, it is apparent that the effect of increasing $\lambda_c$ was to cause an increase in $\gamma_1$. This is not strictly correct for material of extension ratio 2.0 since a minimum in $\gamma_1$ appears to be developing at $\lambda_c = 25^\circ$. Increasing the extension ratio caused an increase in the spread of values of $\gamma_1$. In particular, the tendency was for an increase in extension ratio to cause an increase in $\gamma_1$ at large values of $\lambda_c$ and a decrease at small values of $\lambda_c$. As far as type 2 bands are concerned, the effect of varying
\( \lambda_0 \) was to cause \( Y_2 \) to have a minimum between \( \lambda_0 = 60^\circ \) and \( 50^\circ \).

The effect of increasing extension ratio was to cause this minimum to become more pronounced, in that the value of \( Y_2 \) at the minimum became smaller and \( Y_2 \) increased more rapidly on either side of the minimum. The results for material extended at \( 20^\circ \)C, shown in Figures 3.17 and 3.19, were similar to those for material extended at \( 71^\circ \)C. However, the anisotropy in deformation band behaviour for material of extension ratio 6.0 was less pronounced than that for the 3.3 and 3.7 extension ratios, prepared at \( 71^\circ \)C. This is in agreement with the yield stress results discussed in Section 3.2.2.

Similar results for the effect of extension ratio and \( \lambda_0 \) on the directions of type 1 bands have been reported by Bridle et al \( (1968) \) for oriented polyethylene terephthalate. Results, presented by Keller and Rider \( (1966) \) and Brown and Ward \( (1963a) \) for the directions of type 1 bands in oriented polyethylene and oriented polyethylene terephthalate respectively, although presented in a different form, were similar to those of polyvinyl chloride of extension ratio 3.7. No results seem to have been presented previously for the directions of type 2 bands.

3.2.5 Appearance of Deformation Bands

Not only did the deformation band directions vary as a function of extension ratio and \( \lambda_0 \), but so also did the appearance of the deformation bands formed in test pieces which were deformed to yield at room temperature. Since the deformation band was formed at the yield point on the load extension curve and continued to develop during the load drop until it eventually formed a running neck, the appearance of the deformation band would to some extent
depend upon the stage of the deformation at which the tensile machine was stopped and reversed. However, all tests were stopped as soon as the load started to drop, and thus, some comparison of the band appearance would seem justified. In the following discussion it should be realised that extension ratios 2.0, 3.3 and 3.7 were obtained by extension at 71°C, and extension ratios 3.0 and 6.0 were obtained by extension at 90°C.

For all values of $\lambda_0$ and extension ratio, for which deformation bands were formed, both type 1 and type 2 bands were observed, usually, but not always, in the same test piece. The exception to this was the test piece at $\lambda_0 = 75^\circ$, extension ratio 2.0, in which only a type 1 band was observed. This is in contrast to the results of Brown and Ward (1968a) and Keller and Rider (1966) who only observed type 2 bands at large values of $\lambda_0$ in oriented polyethylene terephthalate and oriented polyethylene respectively.

In discussing the appearance of the deformation bands, consideration will be given first to the effect of varying $\lambda_0$ and extension ratio on type 1 deformation bands. At large values of $\lambda_0$, the deformed material inside the band was stress whitened, causing the band to be opaque. An opaque type 1 deformation band is illustrated in Figure 3.20. Such bands were observed at $\lambda_0 = 90^\circ$ and $75^\circ$, for extension ratios 2.0, 3.0, and 6.0, and at $\lambda_0 = 90^\circ$ for extension ratios 3.3 and 3.7 (the material of extension ratio 3.7 was already slightly stress whitened but this became more pronounced in the deformation band). At intermediate values of $\lambda_0$ type 1 bands were still clearly observable, as is apparent from Figures 3.21 and 3.22. In this case, the bands
are clearly observable because of the dark regions bounding the band. The dark appearance of the boundary regions does not arise from the material being opaque. Instead, in these regions the thickness of the test piece changed rapidly causing the surface to be curved. Because of this curvature, light was refracted and reflected out of the cone of rays being received by the microscope objective, causing the region to appear dark. By altering the illumination and changing the microscope objective it was possible to receive transmitted light from this region. Such deformation bands were observed at $\lambda_0 = 60^\circ$, $45^\circ$, $30^\circ$ and $15^\circ$ for extension ratio 3.0, at $\lambda_0 = 60^\circ$, $45^\circ$, and $30^\circ$ for extension ratios 2.0 and 3.0, at $\lambda_0 = 75^\circ$, $60^\circ$ and $45^\circ$ for extension ratio 3.3, and at $\lambda_0 = 75^\circ$ and $60^\circ$ for extension ratio 3.7. At a given extension ratio, decreasing $\lambda_0$ caused the dark regions bounding the bands to become less well developed. This change arose since the thickness change in the deformation band became smaller as $\lambda_0$ decreased. At small values of $\lambda_0$ the thickness changes were insufficiently great to produce dark boundary regions, and deformation bands were only observable using polarised light. As a result of the deformation, the optical extinction direction in the deformation band was rotated towards the tensile axis. Figure 3.23(b) shows how slight changes in the optical extinction direction enable deformation bands to be detected using polarised light. The same test piece is shown in Figure 3.23(a) in unpolarised light. In this figure no deformation bands can be detected. Such deformation bands were observed at $\lambda_0 = 0$ for extension ratio 3.0, at $\lambda_0 = 0^\circ$ and $15^\circ$ for extension ratios 2.0 and 6.0, at $\lambda_0 = 15^\circ$ for extension ratio 3.3, and at $\lambda_0 = 30^\circ$ and $45^\circ$ for extension ratio 3.7. No deformation
bands were observed at \( \lambda_0 = 0^\circ \) for extension ratio 3.3, and at \( \lambda_0 = 0^\circ \) and 15\(^\circ\) for extension ratio 3.7.

As far as type 2 bands are concerned, they were detectable by virtue of their opacity at \( \lambda_0 = 90^\circ \) and 75\(^\circ\) for extension ratio 2.0, and at \( \lambda_0 = 90^\circ \) for extension ratios 3.3 and 3.7. Such a type 2 band is shown in Figure 3.24. At all other values of \( \lambda_0 \) for which deformation bands were observed, type 2 bands could only be detected using polarised light (Figure 3.25). For material of extension ratios 3.0 and 6.0, type 2 bands could only be observed using ordinary light at \( \lambda_0 = 90^\circ \) and 75\(^\circ\).

The above discussion gives some indication of the variation in appearance of the deformation bands. However, this appearance would have depended to some extent upon the stage of deformation at which the test was stopped.

3.2.6 The Stages in the Development of Deformation Bands

In view of the fact that the appearance of deformation bands would depend upon the stage at which tensile tests were stopped, it was thought worthwhile to observe microscopically the stages in the development of deformation bands. This was achieved by extending test pieces at a strain rate of 0.18 min\(^{-1}\), using the small tensile machine attached to the microscope. This low extension rate was useful since it enabled the tensile machine to be stopped before any observed deformation features were destroyed by further extension. When the tensile machine was stopped, the test piece was photographed, and then the machine was restarted. These tests were carried out on test pieces
having \(\lambda_0 = 60^\circ\), extension ratio 2.0, \(\lambda_0 = 54^\circ\) and 52\(^{\circ}\), extension ratios 3.0, and \(\lambda_0 = 65^\circ\) and 69\(^{\circ}\), extension ratio 3.3, all strips having been extended at 71\(^{\circ}\)C. Since, at small deformations, bands were only detectable by virtue of the rotation of the extinction direction, all observations during testing were made using polarised light. In this way very early stages in the development of bands could be detected.

Figures 3.26, 3.27, 3.28, and 3.29, show different test pieces at successive stages of the deformation. The extinction direction is indicated by the double headed arrow, and the tensile axis is parallel to the edge of the test piece. It was found that, in all cases, type 2 bands developed before type 1 bands. This is apparent in Figure 3.26 in which are presented micrographs of a test piece having \(\lambda_0 = 52^\circ\), extension ratio 3.0, at successive stages of the deformation. After a small amount of deformation, a type 2 band was formed, as shown in Figure 3.26(a). This was initially detected in polarised light, but it is detectable in Figure 3.26(a) because of the slight opacity of the deformed regions. There are also narrow dark regions in the type 2 band. These regions are approximately parallel to the extinction direction and may be cracks or crazes. Upon further extension, the type 2 band remained largely unchanged, but a type 1 band developed intersecting the type 2 band. It is apparent from Figures 3.26(b), (c) and (d) that the development of the type 1 band resulted in the deformation associated with it being much greater than that associated with the type 2 band. A similar behaviour was observed at \(\lambda_0 = 40^\circ\), extension ratio 3.0. In this case, the type 2 band could only be detected using polarised light, as shown in Figure 3.27(b). Figure 3.27(a) is a micrograph,
obtained using unpolarised light, at the same stage in the de-
formation as Figure 3.27(b). Subsequently, there developed a
type 1 band, which could only be observed using polarised light.
The intersection of type 1 and type 2 bands resulted in a rather
ill-defined region, which can be seen in Figure 3.27(c). How-
ever, after further extension, the type 1 band became observ-
able using unpolarised light (Figure 3.27(d)), and it eventually
developed into a running neck (Figures 3.27(e) and (f)). In
Figure 3.28 are shown micrographs of a test piece having $\lambda_o = 65^\circ$, extension ratio 3.3, in which the type 1 band developed into a
running neck. In Figure 3.28(a), intersecting type 1 and type 2
bands are shown. It is clear from observations of the surface
markings in Figure 3.28(b), (c), (d), (e) and (f) that, upon
further extension, the boundaries of the type 1 band moved along
the test piece, forming a running neck. At the same time, the
boundary of the type 2 band, indicated by the broken line in
Figures 3.28(d), (e) and (f), did not move. Instead, in the
region bounded by the boundaries of the type 1 and type 2 band,
the extinction direction rotated towards the tensile axis. This
did not occur by the movement of the boundary of the type 2 band,
but seemed to result from the formation of further type 2 bands
in this region. The existence of the region, in which the ex-
tinction direction has rotated, is apparent from the change in
direction of the type 1 band. Similar behaviour, in which the
type 2 band remains stationary but the type 1 band forms a run-
nine neck, is also observable in Figure 3.26.

One other rather interesting feature was observed during
the propagation of the running neck. This is shown in Figure
3.29 for test pieces having $\lambda_o = 60^\circ$ and extension ratio 2.0,
prepared by extension at 71°C. As the boundary of the neck moved along the test piece, spike-like features were observed to develop at the neck boundary, and they gradually grew ahead of the boundary. This is apparent from Figures 3.29(a), (b), and (c), in which the movement of the neck can be detected by observing the large dark region, believed to be a speck of dirt, on the test piece. Since the features grow ahead of the neck, they must be moving at a slightly faster rate than the neck boundary. In polarised light these features show up very sharply (Figures 3.29(d), (e), and (f)). Figures 3.29(e) and (f) correspond to Figures 3.29(a) and (b). Under higher magnification, it can be seen from Figure 3.30 that the features have sharp boundaries and correspond in direction to type 2 deformation bands. The spacing between these features also appears to be quite regular. The arrows in Figure 3.30 show where there appears to be some displacements of scratches crossing these regions, suggesting that there is some shear associated with them. Figure 3.31(a) shows another test piece in which features corresponding in direction to both type 1 and type 2 bands. These are indicated by arrows in Figure 3.31(a). The feature corresponding to the type 2 band appears to be formed ahead of the neck formed by a propagating type 1 band, and the feature corresponding to a type 1 band appears to be formed ahead of the boundary of a type 2 band. The intersecting features are shown at higher magnifications in Figure 3.31(b). Finally, as the neck propagates, the feature becomes deformed in the necked regions of Figures 3.29(c) and Figure 3.30. Insufficient time was available for a detailed study of these features. Since they do not appear until the neck boundary had been propagating for some time, and since they
were not observed in test pieces extended at a strain rate of 1.7 min\(^{-1}\), it appears that a slow rate of movement of the neck is necessary for the formation of these features.

In order to correlate stages in the deformation with positions on the load-extension curve, test pieces, having the same value of \(\lambda_0\) and same extension ratio, were deformed by varying amounts. These tests were only carried out on Cobex of extension ratio 3.9, obtained by extension at 71\(^\circ\)C, and for only one value of \(\lambda_0\), 64\(^\circ\). The load-extension curve for these test pieces is shown in Figure 3.32. The positions, at which the various tests were stopped, are indicated by the plotting symbols in Figure 3.32. The letters adjacent to the symbols indicate which of the micrographs in Figure 3.33 corresponds to each position on the load-extension curves. No deformation features were observed in test pieces for which no micrographs are presented. In those test pieces, for which the tests were stopped before the maximum on the load-extension curve, no deformation bands were observed. A type 2 band was observable, using polarised light (Figure 3.33(a)), in the test piece for which the test was stopped in the vicinity of the load maximum. The band has not propagated across the test piece. When the test was stopped just after the load maximum, a type 2 band was observable using polarised light, and the start of a type 1 band could be observed in the position indicated by the arrow in Figure 3.33(b). At a position further down the load drop (Figures 3.33(c) and (d)) both type 1 and type 2 bands could be observed. The type 1 band was just detectable using unpolarised light, but both types are clearly observed using polarised light.

At subsequent stages in the deformation, the type 1 band, as
shown in Figures 3.33(c), (f) and (g), became sufficiently well developed to be observed in unpolarised light, and it eventually developed into a running neck. From Figure 3.33(g), it is clear that, although the extension is continuing at constant load, the neck has not attained stable dimensions. The above discussions indicate that both type 1 and type 2 bands develop in the vicinity of the maximum of the load-extension curve. Thus, the assumption used in Section 3.2.2, that the maximum load should be taken as the load at yield, would seem justified.

The observations discussed in this section can be summarized as follows:

1. Deformation bands formed in a test piece at, or close to, the same point in time at which the maximum occurred in the load-extension curve.

2. As a result of the extension, type 2 bands developed first, and subsequently, a type 1 band formed intersecting the type 2 band. Since, for material deformed to yield at a strain rate of 1.7 min⁻¹ in only one out of thirty six test pieces, in which bands were formed, was a type 1 band observed in the absence of type 2 bands, this would seem to be the normal mode of deformation.

3. The bands, when they developed, did so at one edge of the test piece, and then they propagated across the test piece.

4. Only type 1 bands were capable of developing into running necks by the movement apart of their boundaries. The boundaries of type 2 bands did not appear to move.
5. During the movement of the neck boundary, a new type of deformation band was observed to grow ahead of the boundary. These bands had much sharper boundaries than the type 1 and type 2 bands discussed in Section 3.2.5. There were two different types of this new band, these corresponding in directions to type 1 and type 2 deformation bands. A slow rate of propagation of the neck boundary appeared necessary in order for this deformation feature to develop.

In above references to differences between type 1 and type 2 deformation bands, it should be realised that they may depend to some extent upon $\lambda_0$ and prior extension ratio, since, at $\lambda_0 = 0^\circ$ and $90^\circ$, and for extension ratio 1.0, the two types of bands became indistinguishable.

3.2.7 Strains in Deformation Bands and Necked Regions

It was suggested in Section 3.2.5 that the change in thickness of the material in the deformation bands became smaller as $\lambda_0$ decreased. This has been verified by thickness measurements. Since deformation bands were narrow, it was not possible to measure thicknesses using a dial gauge. Instead, observations on the test piece were made by reflection, using the Reichart microscope. Using high power objectives, the microscope had a small depth of focus, and so the surfaces of the test pieces in the undeformed regions and in the deformation bands could not be brought into focus at the same position of the specimen table relative to the objective. However, by focussing alternately on undeformed and deformed regions, the thickness change was measured from a micrometer gauge, which recorded the movement of the specimen table in
changing the focus. This was repeated for the other surface of the test piece and the thickness change was found to be symmetrical. The ratio of thicknesses before and after deformation for test pieces cut from material prepared by extension at 90° are presented in Table 3.1. It can be seen that in each case the thickness decrease became smaller as \( \lambda \) decreased. Unfortunately, details of the depth of focus of the objective used were not recorded, and so no estimate of the accuracies of these measurements could be made. However, it is thought that any errors were considerably less than the thickness changes measured. Since the material in the deformation band was constrained from contracting significantly in a direction parallel to the deformation band, the thickness ratios in Table 3.1 give a measure of the extension ratio at right angles to the band direction in the plane of the sheet. Some calculations were made of the shear strain parallel to the deformation band from measurements of the displacement at the edge of the test piece. These measurements were taken from micrographs of the test pieces. Results were obtained from the same test pieces for which thickness changes were measured, and in all cases was found to be approximately 100%. These measurements were insufficiently sensitive to detect any effect of varying \( \lambda \).

Similar results have been presented by Keller and Rider (1966) and Brown and Ward (1968a) for deformation bands in oriented polyethylene and oriented polyethylene terephthalate respectively. In oriented polyethylene terephthalate the thickness ratio was found to be 1.5 at \( \lambda = 60^\circ \), and shear strains of the order of 200% were measured. However, for oriented polyethylene the thickness ratios were between 1.1 and 1.3, but shear strains were
as large as 1000%. Thus, from the point of view of strains, deformation bands in polyvinyl chloride were more like those in polyethylene terephthalate than those in polyethylene.

Since deformation bands eventually develop into necks, it seems likely that the deformation in the neck would be affected in the same way as the strains in deformation bands by changes in both $\lambda_o$ and extension ratio. The load-extension curves presented in Figure 3.1 gave a qualitative indication of the way in which the deformation in the neck varies. In particular, they gave a measure of the natural draw ratio of the test piece, this being the same as the extension ratio, $E_t$, as defined in Section 2.1.6. The position of the second load rise on the load-extension curves gave the extension of the test piece at which the boundaries of the necked region propagated into the shoulders of the test piece. Since all the test pieces had the same gauge length, comparison of the extension, at which the second load rise started, gave a comparison of the natural draw ratios of the test pieces. For instance, for prior extension ratio 2.0, as $\lambda_o$ decreased, the extension at which the second load rise started, also decreased. Thus, the natural draw ratios of test pieces of a particular prior extension ratio decreased with decreasing $\lambda_o$. Similar trends can be observed for prior extension ratios 2.6 and 3.0. The effect of prior extension ratio on the natural draw ratio at small values of $\lambda_o$ can be determined by considering the load-extension curves at either $\lambda_o = 0^\circ$ or $15^\circ$. In each case it is clear that the natural draw ratio decreased with increasing prior extension ratio. Similar comparisons cannot be made at large values of $\lambda_o$ since these test pieces failed before the neck had propagated throughout the gauge length.
More quantitative results were obtained from measurements on the test pieces, the load-extension curves of which are presented in Figure 3.1. Assuming constant volume deformation, the ratio of the cross-sectional area of the necked regions before and after deformation is equal to the natural draw-ratio of the test piece. The cross-sectional areas were measured in the manner discussed in Section 3.2.2. \( A_0 / A_1 \) the ratio of cross-sectional area before and after extension, is plotted in Figure 3.34 as a function of \( \lambda_o \) for prior extension ratios 2.0, 2.6, 3.0, 3.9 and 1.0. These results confirm one of the trends discussed above, in that the natural draw ratio decreased with decreasing \( \lambda_o \). As far as the effect of extension ratio is concerned, at low values of \( \lambda_o \), the natural draw ratio decreased with increasing extension ratio. The results at low values of \( \lambda_o \) are somewhat confused since the ratio \( A_0 / A \) is not a measure of natural draw ratio because these are the test pieces for which the second load rise occurred in Figure 3.1. This second load rise caused the necked region to be extended beyond its natural draw ratio. This was not the case for the test pieces of prior extension ratio 1.0.

At large values of \( \lambda_o \), comparison of results for prior extension ratios 2.0 and 1.0 indicates that the natural draw ratio increased with increasing prior extension ratios. Consideration of results for prior extension ratios 2.6 and 3.0 suggest that these materials would have followed this trend at large values of \( \lambda_o \), but insufficient results were obtained for a valid comparison to be made. Comparison of results for prior extension ratios 1.0, 2.0 and 3.9 at \( \lambda_o = 90^\circ \) indicates that the stress-whitened material of extension ratio 3.9 did not fit the trend established for the clear materials of lower prior extension ratios.
Because of the lack of results at larger values of $\lambda^o$, more accurate measurements were obtained for test pieces cut from sheets of prior extension ratios 2.0 and 2.6. On these sheets a grid of dots was printed as discussed in Section 2.1.6, such that one line of dots was parallel to the molecular alignment direction. From measurements on the grid of dots before and after deformation, the extension ratio, $R_t$, as defined in Section 2.1.6, was determined using equation (2.1). It was estimated that $R_t$ could be measured to an accuracy of $\pm 2\%$. Measurements were made for different values of $\lambda^o$. Care was taken to ensure that the neck spread over most of the gauge length, but it was not allowed to propagate into the shoulders of the test piece. Exceptions were at $\lambda^o = 58.7^0$ and $54.0^0$ for prior extension ratio 2.6. These tests had to be stopped before the neck propagated throughout the gauge length since there were indications that the test pieces were about to fracture. These test pieces were deformed at a strain rate of $0.17 \text{ min}^{-1}$ in the small tensile machine shown in Figure 2.3. From the results presented in Figure 3.35, it can be seen that the natural draw ratio decreased with decreasing $\lambda^o$. The effect of increasing prior extension ratio was to increase the natural draw ratio at large values of $\lambda^o$, and to decrease it at small values of $\lambda^o$.

Similar results have been presented by Allison and Ward (1967). They deformed test pieces at $\lambda^o = 0^0$ and showed that the natural draw ratio decreased with increasing molecular alignment. No reports of results at other values of $\lambda^o$ have been found.
3.2.8. Geometry of Deformation

Hinton and Rider (1968) have shown that, to a first approximation, oriented high density polyethylene deforms by simple shear parallel to the molecular alignment direction (referred to as the c-direction by Hinton and Rider). However, because of differences between deformation bands formed in oriented polyethylene and oriented polyvinyl chloride, it was thought unlikely that oriented polyvinyl chloride would deform by simple shear parallel to the molecular alignment direction. The deformation bands in polyvinyl chloride differed from those in polyethylene in that they were less well defined, had a ratio of shear strain parallel to the band to compressive strain perpendicular to the plane of the specimen which was smaller, and deviated from the extinction direction over a wider range of angles. Because of the localised nature and non-uniformity of the bands, it was not possible to carry out accurate studies of the deformation mode in deformation bands. When the deformation band was allowed to develop into a neck, accurate measurements became possible, but, since the strain was controlled by the natural draw ratio of the test piece, the available range of strain was restricted. In view of these difficulties, studies of the deformation geometry were carried out on test pieces deformed uniformly under the conditions discussed in Section 3.1.

If the polymer deforms by simple shear parallel to the molecular alignment direction, certain conditions must be satisfied. These have been discussed by Hinton and Rider (1968) and are listed below.

1. Lines drawn parallel to the shear direction remain unchanged in length.
2. Lines drawn parallel to the shear direction, remain parallel to it during deformation.

3. The relation between \( \lambda_o \) and \( \lambda \) at extension ratio, \( R_t \), is given by

\[
R_t = \frac{\sin \lambda_o}{\sin \lambda}, \quad (3.1)
\]

where \( \lambda \) is the angle between the extinction direction and the tensile axis after deformation. The molecular alignment direction is here taken as being given by the extinction direction. Since the grid of dots was printed such that one line of dots was parallel to the extinction direction, for the above conditions to be satisfied, this line should remain parallel to the extinction direction, and the spacing between the dots forming this line should remain constant.

Considering first condition 1, a plot of \( c_3/c_2 \) as a function of \( R_t \), as shown in Figure 3.36, indicates that the spacing between dots on the line initially parallel to the extinction direction did not remain constant. For \( \lambda_o = 45^\circ \), prior extension ratio 1.5, and \( \lambda_o = 25^\circ \), prior extension ratio 4.4, the spacing increased, but in all other cases it decreased with increasing \( R_t \). The only results in Figure 3.36 which are strictly comparable with those of Hinton and Rider (1968) are those for test pieces having \( \lambda_o = 64^\circ \). For oriented polyethylene test pieces with \( \lambda_o = 62^\circ \), Hinton and Rider (1968) showed that the spacing decreased. For polyvinyl chloride test pieces with \( \lambda_o = 64^\circ \), the spacing also decreased, but the decrease was greater than that for polyethylene. However, the difference between these results for \( \lambda_o = 64^\circ \) and \( 62^\circ \)
As a result of the deformation, the extinction direction deviated from the line to which it was initially parallel, such that the extinction direction was inclined at a smaller angle to the tensile axis than was the line. In Figure 3.37, \( \alpha \), the angle between the extinction direction and the line to which it was initially parallel, is plotted as a function of \( R_t \). It can be seen that, in all cases, \( \alpha \) initially increased with increasing \( R_t \). For \( \lambda_o = 45^\circ \), extension ratio 1.5, and \( \lambda_o = 25^\circ \), extension ratio 4.4, there was a maximum in \( \alpha \), and, at large extensions, \( \alpha \) decreased as \( R_t \) increased. For oriented polyethylene, \( \alpha \) was reported to increase up to \( 4^\circ \) at \( R_t = 3 \). However, for polyvinyl chloride, values of \( \alpha \) were of the order of \( 20^\circ \). Thus, as far as condition 2 is concerned, the deformation behaviour of oriented polyvinyl chloride in no way approximated to simple shear parallel to the molecular alignment direction.

In order to see if condition 3 was satisfied, \( \sin \lambda_o / \sin \lambda \) is plotted as a function of \( R_t \) in Figure 3.38. The dashed curves in this figure are drawn through the experimental points, and the continuous straight line is that expected if the deformation had been by simple shear parallel to the molecular alignment direction. It is clear from Figure 3.38 that, with the exception of \( \lambda_o = 64^\circ \), extension ratio 7.5, the deformation deviated considerably from simple shear parallel to the molecular alignment direction. The results for \( \lambda_o = 64^\circ \), extension ratio 7.5, seem to agree quite well with the predicted straight line variation. However, if plotted on the same scale as the results of Hinton and Rider (1965) (their Figure 5), the deviation is considerably greater than the
results for oriented polyethylene. The results in Figure 3.38 show that, for a particular value of $\lambda_0$, the deformation behaviour did become nearer to simple shear as the prior extension ratio increased. Thus, it might be that oriented polyethylene deformed by simple shear because the molecular alignment was somewhat greater than that for polyvinyl chloride. However, another factor might be that the polyethylene was considerably more crystalline than the polyvinyl chloride.

All of the results presented here indicate that the deformation behaviour of oriented polyvinyl chloride in no way approximated to that of simple shear. Further discussion of these results will be given in Section 4.5.

3.2.9 Optical Anisotropy in Deformation Bands and Necked Regions

It was reported in Section 3.2.3 that, as a result of the deformation, the extinction direction inside the deformation band rotated towards the tensile axis. Results are presented in Table 3.2 for $\lambda_0$ and $\lambda$, in the undeformed and deformed regions respectively, for type I bands in material of extension ratios 2.0, 3.3 and 3.7, prepared by extension at $71^\circ$C. $\Delta \lambda$ in Table 3.2 is the angle through which the extinction direction has rotated. Insufficient results are presented in Table 3.2 to establish any sort of trend. In any case, the value of $\Delta \lambda$ would depend upon the stage of deformation at which the tests were stopped. The birefringence of the material inside the deformation band was also measured, and these results are presented in Table 3.3. These results are from material originally extended at $90^\circ$C, for which thickness change results were presented in Table 3.1. From these results it is
clear that birefringence changes do occur as a result of deformation.

Since deformation bands ultimately develop into running necks, it is likely that optical anisotropy changes occurred also in the necked regions. Such results are presented in Figures 3.39 and 3.40, which are plots of $\lambda$ and birefringence in the necked region as a function of $\lambda_0$. No clear trends in behaviour are apparent from these results. This, however, is not surprising since these test pieces were not deformed in a particularly controlled manner. More detailed results were obtained from cold drawn and uniformly deformed test pieces for which accurate strain measurements were obtained from grids of dots. These results will be presented and discussed in more detail in Chapters 5 and 6. Brown, Duckett and Ward (1968b) have also carried out studies of optical anisotropy changes in deformation bands in oriented polyethylene terephthalate.

3.2.10 Discussion

In the preceding sections detailed results have been presented for the yielding and cold drawing behaviour of oriented polyvinyl chloride. Most of these results will be discussed further in later chapters. However, although this investigation was not primarily concerned with cold drawing, some aspects of this behaviour will be discussed in this section.

At yield, the plastic deformation of the oriented polyvinyl chloride was localised into narrow bands. These bands subsequently developed into a running neck, and the plastic deformation spread throughout the test piece at constant load. This
phenomenon of cold drawing has been discussed by a number of workers in terms of the true stress-strain curve of the material. One condition necessary for localised plastic deformation and the associated load drop, is that the strain hardening rate of the material should decrease such that the decrease in cross-sectional area during deformation is insufficient to compensate for it, and there is a subsequent decrease in load. This has been illustrated, using Considère's construction, by Vincent (1960) and Ward and Pinnock (1966). Considère's construction is reproduced in Figure 3.41. This is a plot of true stress as a function of extension ratio, \( R_t \). As the material is extended, the nominal stress, measured relative to the original cross-sectional area, is given by the slope of the line drawn from the point \( R_t = 0 \) to the appropriate position on the true stress-extension ratio curve. During the extension, all of the material in the gauge length will deform along the line AB. However, because of inhomogeneities in the material, some small element will reach the yield point, B, before the other material in the gauge length does so. As a consequence of the decrease in strain hardening rate at yield, it is now easier for the yielded material to continue deforming, and the deformation will become localised into a neck. The slope to the tangent to the curve at the point B gives the maximum load, and the load decreases during the continued extension beyond the point B. In order for the neck to stabilise at a fixed strain and form a running neck, the region of decreased strain hardening must be followed by a region in which the strain hardening rate increases rapidly. The material then deforms at a constant load which is given by the slope of the tangent to the point C. The localisation of deformation does not necessarily require a sudden change.
in the slope of the true stress-extension ratio curve at the point B. All that is required is that a tangent can be drawn to the curve from \( R_t = 0 \). However, Brown and Ward (1968b) have discussed the decrease in strain hardening rate at yield and have suggested that strain softening occurs, i.e. the slope of the true stress-strain curve becomes negative. They presented evidence to show that this is so for compressive, tensile, and shear deformation, but, because of the formation of a neck, they were unable to evaluate the true stress-strain curve for tensile deformation. It was possible, however, to evaluate such a curve for oriented polyvinyl chloride deformed in tension at 50°C. These results are reproduced in Figure 3.42 as plots of true stress against extension ratio, \( R_t \), for material of different prior extension ratios and different values of \( \lambda_0 \). Such a decrease in true stress was referred to as intrinsic yielding by Brown and Ward (1968b). Although Considère's construction is useful in understanding how neck formation is initiated, it cannot completely account for all aspects of the cold drawing behaviour. For instance, it might be expected that, once one element of the material had yielded and strain hardened, the load would rise again until a second element yields and deforms along the true stress-strain curve. However, since in polymers, further deformation occurs at constant load, the stress required to initiate yielding is greater than that required to propagate plastic deformation. Thus, the material in the gauge length, other than that which yields initially, will not follow the true stress-strain curve shown in Figure 3.41. A number of proposals have been put forward to account for this behaviour. Marshall and Thompson (1954) have suggested that the localised plastic deformation generates heat,
and hence causes an increase in temperature in the undeformed material adjacent to the neck boundary. This increase in temperature produces a decrease in yield stress, and thus, the stress required to propagate plastic deformation is less than that required to initiate plastic deformation. Vincent (1960), however, has shown that this effect cannot account for cold drawing at very slow extension rates. Instead, he has suggested that, because of the existence of a complex stress system in the necked region, the deformation can no longer be considered to be under the action of a tensile stress, and so the stress-strain curve in Figure 3.41 no longer applies. Another complicating factor, which might modify the stress-strain behaviour, is the non-uniform strain rate distribution during cold drawing. For instance, in the undeformed region, the elastic strain rate, ignoring creep effects is zero, but, in going through the neck, the plastic strain rate increases to a maximum and then decreases to zero again in the necked region. McClintock and Argon (1966) (p. 313) have discussed the situation in which deformation occurs by the formation of a running neck. In particular, they suggest that the stress required to propagate plastic deformation is smaller than the yield stress because plastic deformation in one element spills over into an adjacent element, thus making plastic deformation easier in that element. In metals the mechanism for spreading plastic deformation is the movement of dislocations. However, without a more detailed knowledge of molecular deformation mechanisms in polymers, it is not possible to account for these aspects of cold drawing. Although a decrease in strain hardening rate is necessary for localised deformation to occur, it does not follow that a decrease in strain hardening rate necessarily results in localised deformation. This is apparent from Figure 3.42, in which a fall in true stress was recorded for uniformly deformed test pieces.
If the strain hardening required to stabilise the neck is considered to arise from the alignment of the molecules in the tensile direction, the observed behaviour of the natural draw ratio can be accounted for qualitatively. For instance, at \( \lambda_0 = 90^\circ \) the molecules are aligned at right angles to the tensile direction, and so a large amount of deformation would be required to realign the molecules in the tensile direction. As the prior extension ratio of the material is increased, a larger amount of deformation would be required to realign the molecules. Thus, as the prior extension ratio is increased, the natural draw ratio of test pieces with \( \lambda_0 = 90^\circ \) would increase, as was observed. The amount of strain hardening, and hence the amount of molecular alignment, required to stabilise the neck would depend upon the relative magnitudes of the nominal yield and drawing stresses.

In the above discussion the effect of varying the prior extension ratio on the yield and drawing stresses has been ignored. For a particular prior extension ratio, as \( \lambda_0 \) decreased, the molecules became more nearly aligned in the tensile direction, and hence a smaller amount of deformation would be required to realign the molecules in the tensile direction. Thus, the natural draw ratio would decrease with decreasing \( \lambda_0 \), as was observed. Again the effects of anisotropy in yield and drawing stresses have been ignored.

In spite of its failure to account completely for the cold drawing behaviour, Considère's construction can account qualitatively for some aspects of the cold drawing behaviour. Considère's construction has been applied to the true stress against extension ratio curves in Figure 3.42. For \( \lambda_0 = 0^\circ \), the ratio of nominal yield stress to nominal drawing stress,
evaluated using Considère's construction, were 1.14 and 1.67 for prior extension ratios 3.0 and 1.0 respectively. Similarly, at $\lambda_0 = 64^\circ$, the stress ratios were 1.40 and 1.65 for prior extension ratios 2.9 and 7.5 respectively. These results are in agreement with the trend established at room temperature. In addition, the extension ratio, at which the line giving the nominal drawing stress is tangential to the true stress-extension ratio curve, is a measure of the natural draw ratio. For $\lambda_0 = 0^\circ$, the construction gives draw ratios of 1.08 and 1.30 for material of prior extension ratios 3.0 and 1.0 respectively. Similarly, at $\lambda_0 = 64^\circ$, this construction gives draw ratios of 1.70 and 1.48 for prior extension ratios 7.5 and 2.9 respectively. The above results again exhibit the same trends as those obtained at room temperature. Although these results were obtained for extension at 50°C, it seems likely that the true stress-strain behaviour at room temperature would be of the same shape, only varying in magnitude.

The fact that the ratio of nominal yield stress to nominal drawing stress, and the natural draw ratio results were different for the stress whitened material of prior extension ratio 3.9, as discussed in Sections 3.2.2 and 3.2.7, suggests that the true stress-extension ratio curves for the stress whitened material would be different from those of the clear materials. It is not apparent from the discussion of Considère's construction why the true drawing stress, i.e. the stress acting on the material in the necked region, was constant.

The observation that type 2 bands formed before type 1 bands, can be accounted for by the fact that the yield stress for type 2 bands was smaller than that for type 1 bands. The reason, that type 1 bands formed subsequently, and that the type 2 bands did not develop into a running neck, must be that the strain hardening
characteristics were different for the two bands. In particular, the decrease in strain hardening rate must be more pronounced for type 1 bands, and so they develop into a running neck more readily than do type 2 bands.

The other important aspects of the deformation behaviour will be discussed in the following Chapters. However, the important observations can be summarised as follows:

1. At yield, deformation was localised into narrow bands of plastically deformed material. These bands were inclined at an angle to the tensile axis, and two different types of deformation bands were observed. These bands are here referred to as type 1 and type 2 bands.

2. Deformation bands were formed at the maximum on the load-extension curves, the type 2 band being formed before the type 1 band was formed.

3. The magnitude of the yield stresses and directions of the deformation bands were affected by the anisotropy of the material, as produced by the alignment of the molecules during extension at elevated temperatures. The form of the anisotropy has been discussed in Sections 3.2.2 and 3.2.4.

4. The variation of tensile strain at yield showed much less variation than did the yield stress.

5. As a result of the deformation, optical anisotropy changes occurred in the material within the deformation bands. This will be discussed further in Chapters 5 and 6.
6. The deformation behaviour of oriented polyvinyl chloride in no way approximated to simple shear parallel to the molecular alignment direction. This is in contrast to the results for oriented polyethylene presented by Hinton and Rider (1963).

7. The stress whitened material of extension ratio 3.9 behaved in a different manner to that of the clear material of lower extension ratios. Firstly, at $\lambda_o = 90^\circ$, the stress whitened material was more ductile than the clear material, in that the extension to failure was greater than that of the clear material of extension ratio 3.0. At $\lambda_o = 0^\circ$, the development of stress whitening was associated with a transition from yield to fracture, with an associated decrease in fracture stress. This effect could not be separated from the effect of increasing prior extension ratio, and this will be investigated further in Chapter 7. The ratio of nominal yield stress to nominal drawing stress for the stress whitened material deviated from the pattern established for the clear material of lower extension ratios. Likewise, the natural draw ratio did not fit the pattern established for the clear materials.
Table 3.1

Values of the ratio, $t_o/t$, of the thickness of the material within the deformation band before and after deformation. These results are for deformation bands formed in test pieces cut from sheets of Vybak extended at 90°C. The extension ratios and values of $\lambda_o$ are indicated in the Table.

<table>
<thead>
<tr>
<th>Extension Ratio</th>
<th>$\lambda_o$</th>
<th>$t_o/t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.0</td>
<td>84.0</td>
<td>1.8</td>
</tr>
<tr>
<td>6.0</td>
<td>62.3</td>
<td>1.4</td>
</tr>
<tr>
<td>6.0</td>
<td>52.1</td>
<td>1.3</td>
</tr>
<tr>
<td>3.0</td>
<td>74.2</td>
<td>1.6</td>
</tr>
<tr>
<td>3.0</td>
<td>54.3</td>
<td>1.6</td>
</tr>
<tr>
<td>3.0</td>
<td>43.3</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Table 3.2

Values of $\lambda_o$, $\lambda$, and $\Delta \lambda$ for deformation bands in test pieces cut from sheets of Vybak extended at 71°C. The extension ratios are indicated in the Table.

<table>
<thead>
<tr>
<th>2.0</th>
<th>$\lambda_o$</th>
<th>88.4</th>
<th>73.4</th>
<th>72.5</th>
<th>47.2</th>
<th>47.5</th>
<th>33.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>22.2</td>
<td>32.8</td>
<td>26.9</td>
<td>31.0</td>
<td>41.8</td>
<td>24.6</td>
<td></td>
</tr>
<tr>
<td>$\Delta \lambda$</td>
<td>66.2</td>
<td>40.6</td>
<td>45.6</td>
<td>16.2</td>
<td>5.7</td>
<td>8.8</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>3.3</th>
<th>$\lambda_o$</th>
<th>75.4</th>
<th>61.9</th>
<th>59.3</th>
<th>46.5</th>
<th>-</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>44.7</td>
<td>58.7</td>
<td>54.2</td>
<td>44.5</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$\Delta \lambda$</td>
<td>30.7</td>
<td>3.2</td>
<td>5.1</td>
<td>2.0</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>3.7</th>
<th>$\lambda_o$</th>
<th>60.8</th>
<th>47.8</th>
<th>43.5</th>
<th>-</th>
<th>-</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>50.8</td>
<td>42.6</td>
<td>33.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$\Delta \lambda$</td>
<td>10.0</td>
<td>5.2</td>
<td>9.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.3

Values of birefringence measured prior to deformation and within deformation bands for test pieces of different extension ratios and different values of $\lambda_0$.

<table>
<thead>
<tr>
<th>Extension Ratio</th>
<th>$\lambda_0$</th>
<th>Birefringence in Band $\times 10^3$</th>
<th>Birefringence Prior to Deformation $\times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>54.3°</td>
<td>2.78</td>
<td>1.40</td>
</tr>
<tr>
<td>3.0</td>
<td>43.3°</td>
<td>2.61</td>
<td>1.40</td>
</tr>
<tr>
<td>6.0</td>
<td>62.3°</td>
<td>1.80</td>
<td>2.25</td>
</tr>
<tr>
<td>6.0</td>
<td>52.1°</td>
<td>2.2</td>
<td>2.25</td>
</tr>
</tbody>
</table>
Figure 3.1 Load-extension curves for test pieces having different values of $\lambda_0$ and cut from sheets of Vybak of different extension ratios prepared by extension at $71^\circ C$. The values of $\lambda_0$ are the nominal ones at which the test pieces were cut from the sheet.
Figure 3.2  Load-extension curves for (a) $\lambda_o = 15^\circ$, extension ratio 3.3, and (b) $\lambda_o = 0^\circ$, extension ratio 3.3, showing how the yield point (arrowed) was determined.
Figure 3.3 Plots of nominal yield stress vs. $\lambda_0$ for Vybak of different prior extension ratios prepared by extension at 71°C.
Figure 3.4 Plots of nominal yield stress vs. $\lambda_0$ for Vybak of different prior extension ratios prepared by extension at 90°C.
Figure 3.5 Plots of nominal yield stress, $\sigma_{\lambda}$, at a particular value of $\lambda_0$, as a function of extension ratio for Vybak extended at 71°C.
Figure 3.6 Plots of nominal yield stress, $\sigma_\lambda$, at a particular value of $\lambda_o$, as a function of extension ratio for Vybak extended at 90°C.
Figure 3.7 Plots of nominal yield stress, $\sigma_{\lambda}$, at a particular value of $\lambda_0$, against birefringence for Vybak extended at 71°C (curves) and 90°C (plotting symbols).
Figure 3.8 Plots of nominal yield stress vs. tensile modulus, evaluated from the load-extensive curves, for test pieces of different \( \lambda \) and cut from sheets of Vybak extended at 71°C.
Figure 3.9  Plots of nominal drawing stress vs. $\lambda_0$ for Vybak of different extension ratios prepared by extension at 71°C.
Figure 3.10 Plots of nominal yield stress and drawing stress vs. $\lambda_0$ for Vybak of extension ratio 2.0 prepared by extension at 71°C.
Figure 3.11 Plots of the ratio of nominal yield stress to nominal drawing stress vs. $\lambda_0$ for Vybak extended at $71^\circ C$. 

Stress Ratio

$\lambda_0$ (degrees)
Figure 3.12 Plots of true drawing stress vs. $\lambda_0$ for Vybak of different extension ratios prepared by extension at 71°C.
Figure 3.13  Optical micrographs of (a) type 1 and (b) type 2 bands. In these, and all future micrographs the extinction direction is indicated by the double headed arrows and the single headed arrows indicate deformation features.

Figure 3.14  Diagram illustrating the definitions of type 1 and type 2 bands, and showing the sense in which $\gamma_1$, $\gamma_2$, and $\lambda_0$ are measured.
Figure 3.15 Diagram illustrating type 1 and type 2 bands, and the angles $\gamma_1$, $\gamma_2$ and $\lambda_0$. The diagram shows the re-orientation of the extinction direction in the bands.
Figure 3.16  Plots of $\gamma_1$ vs. $\lambda_0$ for Vybak of different extension ratios prepared by extension at 71°C and 90°C.

Figure 3.17
Figure 3.18 Plots of $\gamma_2$ vs. $\lambda_0$ for Vybak of different extension ratios prepared by extension at 71°C and 90°C.
Figure 3.20 Optical micrographs showing type 1 bands in test pieces with \( \lambda_0 = 74^\circ \), extension ratio 3.0, and \( \lambda_0 = 45^\circ \) extension ratio 3.0, respectively.

Figure 3.21

Figure 3.22 Optical micrographs showing type 1 and type 2 bands, respectively. The type 1 band is in a test piece having \( \lambda_0 = 46^\circ \), extension ratio 3.3, and the type 2 band is in a test piece having \( \lambda_0 = 74^\circ \), extension ratio 2.0.

Figure 3.24
Figure 3.23 Optical micrographs of a test piece with $\lambda_0 = 45^\circ$, extension ratio 3.7, using (a) ordinary light and (b) plane polarised light. The type 1 band can be detected by virtue of the rotation of the extinction direction.

Figure 3.25 Optical micrographs of a test piece with $\lambda_0 = 61^\circ$, extension ratio 3.3, using (a) ordinary light and (b) plane polarised light. The type 2 band can be detected by virtue of the rotation of the extinction direction.
Figure 3.26  Optical micrographs of a test piece with $\lambda_0 = 52^\circ$, extension ratio 3.0, at successive stages of deformation.
Figure 3.27  Optical micrographs of a test piece with \( \lambda_0 = 40^\circ \), extension ratio 3.0, at successive stages of deformation.
Figure 3.28 Optical micrograph of test pieces with $\lambda_o = 65^\circ$ extension ratio 3.3, showing successive stages of deformation. The dashed line indicates the position of the boundary of the type 2 band.
Figure 3.29 Optical micrographs of a test piece with $\lambda_o = 60^\circ$, extension ratio 2.0, showing stages in the development of spike-like features.
Figure 3.30  High magnification optical micrograph of the spike-like features shown in Figure 3.29. The arrows indicate the positions at which scratches cross the features, and also the features deformed in the necked region.
Figure 3.31 Optical micrographs of a test piece with $\lambda_0 = 50^\circ$, extension ratio 2.0, in which spike-like features corresponding in direction to both type 1 and type 2 bands were observed. The arrows indicate where these intersect.
Figure 3.32 Load-extension curve for a test piece having \( \lambda_0 = 64^\circ \) and cut from a sheet of Cobex extended at 80°C to extension ratio. The points at which the various tests were stopped are indicated by the plotting symbols. The letters refer to the micrographs in Figure 3.33.
Figure 3.33 Optical micrographs of Cobex test pieces, having \( \lambda_0 = 64^\circ \) and extension ratio 3.9, at different stages of deformation. The letters refer to positions on the load-extension curve in Figure 3.32.
Figure 3.34 Plots of natural draw ratio vs. $\lambda_0$ for Vybak of different prior extension ratios prepared by extension at 71°C. The draw ratio was measured as discussed in the text.

---

**Figure 3.34**

- Circle: 2.0
- Square: 2.6
- Triangle: 2.0
- X: 3.9

**Figure 3.35**

- Circle: 2.0
- Triangle: 2.6
Figure 3.36  Plots of $c_3/c_2$ vs. $R_t$, for test pieces uniformly deformed at 50°C.
Figure 3.37 Plots of $\phi$ vs. $R_t$, for test pieces deformed uniformly at 50°C.
Figure 3.38 Plots of $\sin \frac{\lambda_0}{\sin \lambda}$ vs. $R_t$ for test pieces deformed uniformly at 50°C.
Figure 3.39 Plots of $\lambda$ and birefringence, respectively, vs. $\lambda_0$ for the necked regions of cold drawn test pieces which had been cut from sheets of Vybak.

**FIG. 3.39**

**FIG. 3.40**
Figure 3.41 Diagram illustrating Considère's construction.
(For details see text.)
Figure 3.42: True stress-extension ratio curves for Vybak deformed uniformly at 50°C.
In early studies of yield and fracture of metals, before failure mechanisms were well understood, a continuum mechanical approach was used in determining under what conditions failure would occur. Since the work to be discussed is concerned with plastic deformation, particular reference will be made to yield as the form of failure, although some of the theories to be discussed were originally formulated with reference to fracture. For an isotropic body, yield can be considered to take place when the principal stresses $\sigma_1$, $\sigma_2$, and $\sigma_3$, acting on the body satisfy the following equation:

$$f(\sigma_1, \sigma_2, \sigma_3) = 0.$$  \hspace{1cm} (4.1)

The stresses are taken positive in tension and, where necessary, the magnitude of the stress will be indicated by $|\sigma|$. Equation (4.1) is a general expression for the yield criterion, which, when plotted in principal stress space gives a surface, which is usually referred to as the yield surface. Whenever the point representing the state of stress in the body lies on this surface, the material will just start to yield. A number of workers have suggested exact forms for the function $f(\sigma_1, \sigma_2, \sigma_3)$ and these have been discussed extensively by Nadai (1950) and Jaeger (1962). Those which have been found to describe the yielding of materials most successfully were proposed by von Mises in 1913 (see Hill (1950) Chapter 2) and Mohr (see Nadai (1950), p. 214).
The von Mises yield criterion, which was derived on purely mathematical grounds, by considering the invariants of the deviatoric stress tensor, takes the following form:

\[(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2 = 6k^2, \quad (4.2)\]

where \(k\) is a constant for the material and is equal to the yield stress in pure shear. In principal stress space, equation (4.2) gives a circular cylinder, the axis of which coincides with the space diagonal \(\sigma_1 = \sigma_2 = \sigma_3\). Although this yield criterion was derived from mathematical considerations, other workers have interpreted or derived this criterion in physical terms. In fact Huber proposed the same criterion earlier than von Mises in 1904 (see Hill (1950) for deformation which involved an elastic decrease in volume. He suggested that yielding occurs when the elastic strain energy of distortion reaches a critical value. (For deformation involving a volume increase, the total elastic energy was assumed to reach a critical value.) Hencky in 1924 reintroduced this interpretation of the von Mises criterion for all types of deformation. An alternative interpretation due to Nadai (1950) was that yielding occurs when the shear stress on the octahedral plane reaches a critical value.

The Mohr criterion is important in that yield criteria suggested earlier by other workers are in fact special cases of the Mohr criterion. Mohr proposed that yield occurs by plastic slip when the shear stress, \(\tau\), on the plane of slip reaches a critical value, which in general, will depend on the normal stress, \(\sigma\), acting on the plane (see Nadai (1950)). This criterion takes the form:

\[\tau = f(\sigma) . \quad (4.3)\]
This criterion is most conveniently represented by a plot of $\tau$ against $\sigma$. The shear stress, $\tau$, and normal stress, $\sigma$, acting on any plane in the body can also be represented on the same plot using the Mohr circle diagram. The plane on which yield will occur is then determined by the point on the Mohr circle at which it is tangential to the plot $\tau = f(\sigma)$, (for details see Nadai (1950). If $f(\sigma) = \text{constant}$ in equation (4.3), the yield criterion reduces to the maximum shear stress criterion, which takes the form:

$$\tau_{\max} = \frac{\sigma_1 - \sigma_3}{2} = \text{constant}, \quad (4.4)$$

where $\sigma_1 > \sigma_2 > \sigma_3$. In principal stress space the yield surface takes the form of a hexagonal cylinder, co-axial with the circular cylinder of the von Mises criterion. This criterion was originally proposed by Tresca (see Nadai (1950), p. 211) as a result of experiments which he carried out on the extrusion of soft metals in 1865. If $f(\sigma) = S_0 - \mu \sigma$, where $S_0$ and $\mu$ are constants, the Mohr criterion becomes the same as that proposed by Coulomb in 1773, and equation (4.3) reduces to

$$\tau = S_0 - \mu \sigma. \quad (4.5)$$

Coulomb originally used this criterion to account for the failure of soils. Jaeger (1962) has suggested that Coulomb originally proposed a criterion similar to that in equation (4.4), which was later modified by Navier to give equation (4.5). However, for present purposes, equations (4.4) and (4.5) will be referred to as the Tresca and Coulomb yield criteria respectively.
Of the yield criteria discussed above, the von Mises criterion has been found to be most suitable in accounting for the yielding of most unoriented polycrystalline metals. However, under some circumstances, the yielding of mild steel is best described by the Tresca criterion. The Coulomb criterion has been found most appropriate for accounting for the fracture of rocks.

As far as polymers are concerned, Bowden and Jukes (1968) and Whitney and Andrews (1967) have shown that a number of unoriented glassy polymers yield according to the Coulomb criterion. The results in both of the above references showed this to be true for polystyrene, and Bowden and Jukes (1968) also reported that polymethylmethacrylate, amorphous polyethylene terephthalate, and rigid polyvinyl chloride obey the Coulomb criterion. Recent unpublished work of Bowden and Jukes has shown that highly crystalline polyethylene also yields according to this criterion. Keller and Rider (1966) and Hinton and Rider (1968) have fitted the tensile yield stress data for oriented polyethylene to a form of the Coulomb criterion given by

\[ \tau_s + k \sigma_n = \sigma_o \],

where \( \tau_s \) and \( \sigma_n \) are the shear and normal stresses acting on the plane containing the molecular alignment direction; \( k \) and \( \sigma_o \) are constants. The only suggestions that polymers obey the von Mises criterion has been made by Thorkilsden (1964) who investigated the yielding of polymethylmethacrylate.

In the present chapter an attempt is made to determine a yield criterion which satisfactorily accounts for the yield behaviour of oriented polyvinyl chloride, the results for which were presented in Chapter 3. In fact it is shown that the
Coulomb criterion, as in equation (4.6), cannot be fitted to the observed yield stress data. Instead, the yielding behaviour could be satisfactorily accounted for by a theory based on the von Mises criterion, provided that an internal stress term is taken into account. This criterion, however, is not completely satisfactory since no account is taken of the effect of hydrostatic stress on yielding. Suggestions are made for modifying the criterion to take account of such effects. Finally, it is indicated that the satisfactory use of the von Mises criterion does not necessarily eliminate the possibility of the Coulomb criterion being the correct criterion. With this in mind a modification is suggested which would enable the Coulomb criterion to be used for oriented polymers; this is considered more suitable than the form of criterion used by Keller and Rider (1966) and Hinton and Rider (1968). Some aspects of this work have been reported elsewhere (Hargreaves and Rider (1967) and Rider and Hargreaves (1969)).

4.1 Choice of Suitable Yield Criterion

From the considerable amount of evidence presented in the previous section, it might be thought likely that the yielding of oriented polyvinyl chloride could be described by a Coulomb type of criterion, of the form used by Keller and Rider (1966) and Hinton and Rider (1968). This criterion predicts that the variation of \( \sigma_\lambda \) with \( \lambda \) should take the following form:

\[
\sigma_\lambda = \sigma_0 \left( \sin \lambda \cos \lambda + k \sin^2 \lambda \right)^{-1}
\]

(4.7)

This form of the yield stress variation was satisfactorily fitted to the yield stress data for oriented polyethylene but the results presented in Figure 4.1 for material of prior extension ratio 3.0
show that it is not possible to fit the yield stress data for oriented polyvinyl chloride to equation (4.7). In Figure 4.1 the continuous curves are plots of equation (4.7). By fitting this equation to the measured yield stress values at two values of $\lambda_o$, the constants $\sigma_o$ and $k$ were evaluated, and then the variation of $\sigma_\lambda$ for all values of $\lambda_o$ was calculated using equation (4.7). For the curves in Figure 4.1, the yield stress at $\lambda_o = 90^\circ$ was always taken as a fitting point, and the other fitting point was taken as the yield stress at $\lambda_o = 75^\circ, 60^\circ, 45^\circ, 30^\circ$, and $15^\circ$ for the different curves. The dashed curve in Figure 4.1 is drawn through the experimental points. It is clear that equation (4.7) cannot satisfactorily account for the observed yield stress variation.

The fit would be even worse for material of lower extension ratios since, as formulated, the criterion cannot account for the behaviour of material with limitingly small anisotropy. Thus it would appear that although Bowden and Jukes (1968) found that unoriented polyvinyl chloride yielded according to the Coulomb criterion, the form of the criterion used here does not satisfactorily account for the yielding behaviour of oriented polyvinyl chloride.

In considering possible alternative yield criteria that might be used, it is useful to follow the course taken by Keller and Rider (1966) in selecting equation (4.6) as an appropriate yield criterion. They observed, in oriented polyethylene, deformation bands (Figure 1 of Keller and Rider (1966)) similar to localised slip steps observed in metal single crystals. These similarities in deformation features suggested that there might also be similarities in yield criteria. In fact equation (4.6) applies to metal single crystals with $k$ equal to zero and to the results of Hinton and Rider (1968) for oriented polyethylene with $k = 0.2$. However, no matter what
value of k is chosen, equation (4.7) does not give a good fit to the oriented polyvinyl chloride data: but then the deformation bands observed in oriented polyvinyl chloride are much less reminiscent of slip bands in single crystals when compared with bands in polyethylene. In addition, as discussed in Chapter 3, the deformation of oriented polyvinyl chloride does not approximate to simple slip in the molecular alignment direction, in contrast to the results for oriented polyethylene presented by Hinton and Rider (1968).

Although the deformation geometry of oriented polyvinyl chloride is not similar to that of metal single crystals, deformation bands other than slip bands also occur in metals. These bands, usually referred to as Lüders bands, are observed to form in thin strips of polycrystalline metals when pulled in tension. They have been described by, among others, Nadai (1950) and are illustrated in Figures 19.25 and 19.26 of his book. There is a clear resemblance to bands formed in oriented polyvinyl chloride (Figure 3.13 of this thesis), which were themselves also formed in thin strips. The similarity between Lüders bands and deformation bands formed in polymers, in this case unoriented nylon, has previously been commented on by Kauffman and George (1951).

The resemblance between deformation features in polycrystalline metals and oriented polyvinyl chloride suggests that one should look for a similarity in yield criteria. The yield criterion which has been found to best describe the yielding of most metals is that of von Mises. This criterion was originally formulated for isotropic metals but has been modified by Hill (1948) to account for both the angles at which these bands were formed in strip specimens cut from anisotropic metal sheets, and
for the variation of tensile yield stress with the direction in which the strips are cut. It is intended in the following sections to attempt to fit this criterion to the observed yielding behaviour of oriented polyvinyl chloride.

4.2 The Hill Modification of the von Mises Yield Criterion

As discussed earlier in this Chapter, the von Mises yield criterion takes the following form:

\[(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2 = 6 k^2 \] (4.8)

This equation can be restated in terms of stress components measured relative to arbitrary Cartesian axes and becomes,

\[(\sigma_x - \sigma_y)^2 + (\sigma_y - \sigma_z)^2 + (\sigma_z - \sigma_x)^2 + \]
\[6(\tau_{yz}^2 + \tau_{zx}^2 + \tau_{xy}^2) = 6 k^2 \] (4.9)

where \(\sigma_x\), \(\sigma_y\) and \(\sigma_z\) are tensile stresses, and \(\tau_{xy}\), \(\tau_{yz}\), and \(\tau_{zx}\) are shear stresses referred to Cartesian axes. It was this form of the yield criterion which Hill (1948) modified to include metals which are anisotropic. The yield criterion then takes the following form:

\[H(\sigma_{xx} - \sigma_{yy})^2 + F(\sigma_{yy} - \sigma_{zz})^2 + G(\sigma_{zz} - \sigma_{xx})^2 +
\]
\[2N\tau_{xy}^2 + 2L\tau_{yz}^2 + 2M\tau_{zx}^2 = 1 \] (4.10)

In this case the Cartesian axes \(x\), \(y\) and \(z\) are taken along the principal axes of anisotropy of the material and \(H\), \(F\), \(G\), \(N\), \(L\) and \(M\) are parameters characterising the state of anisotropy of
the material. The term $6 k^2$ in equation (4.9) has been incorporated into the parameters of equation (4.10). The values of these parameters cannot at the moment be predicted on the basis of the material structure but must be determined experimentally.

This theory can now be applied to the results presented in Sections 3.2.2 and 3.2.4. In these experiments

$$
\begin{align*}
\sigma_{xx} &= \sigma_\lambda \cos^2 \lambda_0, \\
\sigma_{yy} &= \sigma_\lambda \sin^2 \lambda_0, \\
\tau_{xy} &= \sigma_\lambda \sin \lambda_0 \cos \lambda_0, \\
\sigma_{zz} &= \tau_{yz} = \tau_{zx} = 0,
\end{align*}
$$

(4.11)

where $\sigma_\lambda$ is the tensile yield stress for a test piece with angle $\lambda_0$, $\lambda_0$ is the angle between the molecular alignment direction, which is taken as the x-axis in Figure 4.2, and the tensile axis. The y-axis is at right angles to the x-axis in the plane of the sheet and the z-axis is perpendicular to the plane of the sheet.

It should be noted that these axes are not the same as those defined earlier in Chapter 2. Since, during the initial hot stretching, the width and thickness of the strips contracted relatively by the same amount, the oriented material was considered to have rotational symmetry about the x-axis. Under such circumstances equation (4.10) can be modified by putting $G = H$ and the yield criterion becomes,

$$
\sigma_\lambda^2 \left[ 2H \cos^4 \lambda_0 + (H + F) \sin^4 \lambda_0 + 2(N - H) \sin^2 \lambda_0 \cos^2 \lambda_0 \right] = 1
$$

(4.12)
By substituting the measured values of the tensile yield stress, \( \sigma_\lambda \), for three angles, \( \lambda_0 = 0^\circ, 45^\circ \) and \( 90^\circ \), three simultaneous equations were obtained, from which the constants \( H, F \) and \( N \) were derived. This, and all calculations to be discussed in this section and Section 4.3, were computed on an ICL 1905F computer. This was done for each extension ratio obtained at the two hot stretching temperatures. In the case of extension ratio 3.9, for which the measured \( \sigma_0 \) was believed to be a fracture stress, two calculations were carried out, one with \( \sigma_0 \) equal to the measured value, and one with \( \sigma_0 \) obtained from the extrapolated yield stress curve (the dashed curve in Figure 3.5). Having derived \( H, F \) and \( N \), the variation of \( \sigma_\lambda \) with \( \lambda_0 \) was computed from equation (4.12) for the whole range from \( \lambda_0 = 0^\circ \) to \( \lambda_0 = 90^\circ \), and this is compared with the measured values for prior extension ratio 3.3 in Figure 4.3, curve A. The agreement between the results can be seen to be good and, similar good agreement was obtained for the other extension ratios. In fact, with the exception of the material of prior extension ratio 6.0, the largest difference between experimental and predicted results was 2% at \( \lambda_0 = 15^\circ \) and \( 30^\circ \), when the experimental result was always smaller than the predicted result. For material of prior extension ratio 6.0 the error was 4% at these values of \( \lambda_0 \). Thus, the difference between the results was slightly greater than the estimated experimental error of \( \pm 2\% \).

The theory was extended by Hill (1948) in order to determine the angle at which deformation bands would be formed in thin strip test pieces such as the ones used here. (The theory does not concern itself with whether or not deformation bands are formed. This depends only upon the work hardening rate as discussed in
It was postulated that these bands would be formed along the characteristics whose slopes $dy/dx$ are given by

$$
\frac{d\varepsilon_{yy}}{dy/dx} (dy/dx)^2 + 2 \frac{d\varepsilon_{xy}}{dy/dx} (dy/dx) + d\varepsilon_{xx} = 0 .
$$

(4.13)

The directions of the characteristic coincide with the directions of zero plastic extension. The plastic strain increments are obtained from the plastic potential, $f(\sigma_{ij})$, using the Levy-Mises equations which take the following form:

$$
d\varepsilon_{ij} = \left[ \frac{df(\sigma_{ij})}{d\sigma_{ij}} \right] d\Lambda ,
$$

(4.14)

d$\Lambda$ being a constant. The plastic potential is a concept introduced by von Mises and has been discussed by Hill (1950). The plastic potential is in fact the same function as the yield criterion. McClintock and Argon (1966) (p. 287) have derived equation (4.14) from the yield criterion when it takes the form $f(\sigma_{ij}) = \text{constant}$. From equations (4.10), (4.11) and (4.14) the plastic strain increments are given by

$$
\begin{align*}
\frac{d\varepsilon_{xx}}{\sigma_{xx}} & = \left[ 2H_{xx} - H_{yy} \right] d\Lambda = H \left[ 2 \cos^2 \lambda_{o} - \sin^2 \lambda_{o} \right] \sigma_{\lambda} d\Lambda , \\
\frac{d\varepsilon_{xy}}{\sigma_{xy}} & = \left[ -H_{xx} - \sigma_{yy} \right] + F_{xy} \left[ -H \cos^2 \lambda_{o} \\
& \quad + (H + F) \sin^2 \lambda_{o} \right] \sigma_{\lambda} d\Lambda.
\end{align*}
$$

(4.15)

In equation (4.13) $dy/dx = \tan (\lambda_{o} + Y)$ where $\lambda_{o}$ and $Y$ are taken positive in the sense shown in Figure 4.2. Hence, by substituting equation (4.15) in (4.13), $\tan (\lambda_{o} + Y)$ is given by
\[ \left[ (F + H) \sin^2 \lambda_o - H \cos^2 \lambda_o \right] \tan^2 (\lambda_o + Y) + 2N \sin \lambda_o \]
\[ \cos \lambda_o \tan (\lambda_o + Y) + H (2 \cos^2 \lambda_o - \sin^2 \lambda_o) = 0. \quad (4.16) \]

Since \(H, F\) and \(N\) have been determined from the tensile yield stress data, \(Y\) can be evaluated for each value of \(\lambda_o\) by substituting these values in equation (4.16). (This does not require the determination of any more constants, since \(dA\) cancelled in deriving equation (4.16)). Since equation (4.16) is a quadratic, for each value of \(\lambda_o\) there are two roots, one giving a positive value of \(Y\) and the other a negative value. From Figures 4.2 and 3.14 it is apparent that the negative value of \(Y\) corresponds to the type 1 band and the positive value corresponds to the type 2 band. The experimental and predicted values of \(Y_1\) and \(Y_2\) for the materials hot stretched at \(71^\circ C\) are shown in Figure 4.4 (broken lines). It can be seen that the calculated curves are of the right shape qualitatively but for the higher extension ratios the quantitative agreement is not very good. It is apparent from Figures 4.4(c) and (d) that the use of the extrapolated value of \(\sigma_o\) for prior extension ratio 3.7 instead of the measured value made no significant difference to the lack of agreement between experimental and predicted results. The curves for the polyvinyl chloride hot stretched at \(90^\circ C\) are presented in Figure 4.5. The agreement between experimental and predicted results is quite good for prior extension ratio 3.0 but the agreement is not so good for prior extension ratio 6.0. For unoriented (isotropic) material \(N = 3F = 3H\), and the insertion of these values in equation (4.16) gives \(\tan Y = \pm \sqrt{2}\), or \(Y = \pm 54.7^\circ\), with which the measured value of \(55^\circ\) agrees very well.
As a consequence of the qualitative agreement between theory and experiment, consideration was given to possible ways of improving the quantitative agreement. The possibility of varying the parameters H, F and N was rejected since any improvement of the fit to the band angle curve would only be at the expense of the fit to the yield stress data. A more fundamental approach is to consider the applicability of the assumptions on which the theory is based.

4.3 Influence of Internal Stress on Yielding

A fundamental assumption made in formulating the von Mises yield criterion is that, if any stress component is changed in sign, the criterion should be unaltered. This is why the von Mises criterion, and its Hill modification, were formulated to exclude terms linear in stress. In fact pre-stressing polycrystalline metal in tension results in the yield stress in tension becoming greater than that in compression (the Bauschinger effect), and thus, the above assumption does not hold. The physical explanation of this asymmetry in yield stress is that the initial pre-stressing introduces internal stress into the metal (e.g. see Cottrell (1956)). Litt and Koch (1967) have proposed that similarly the mechanical working of polymers also sets up internal stresses, which affect the subsequent deformation behaviour. In this work, they rolled sheets of glassy polymers, polycarbonate and polyvinyl chloride, and showed that, if the reduction in thickness during rolling was sufficiently great, the thickness increased upon subsequently testing the material to yield in tension. They suggested that one would expect a decrease in thickness but internal stresses caused the thickness to increase. In fact, if the rolling is
considered to introduce anisotropy, then the theory proposed by Hill does include the possibility of a thickness increase in the absence of internal stresses. Using the notation introduced in Section 4.2, but replacing the molecular alignment direction by the rolling direction, the plastic strain increment in the $z$-direction is given by

$$\varepsilon_{zz} = - \left[ G \varepsilon_{xx} + F \varepsilon_{yy} \right]. \quad (4.17)$$

Thus, if $\sigma_x$ and $\sigma_y$ are positive tensile stresses, and $G$ and $H$ are positive, the thickness does decrease. However, depending upon the relative magnitudes of $\sigma_x$ and $\sigma_y$, negative values of either $G$ or $F$ could make $\varepsilon_{zz}$ positive, corresponding to a thickness increase. The only condition which need be satisfied is that

$$\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} = 0, \quad (4.18)$$

i.e. the deformation occurs at constant volume. Thus without more information concerning the anisotropy of the material, the results of Litt and Koch cannot be said to be due solely to the effect of internal stress. However, in the light of the results presented by Litt and Koch, it seemed worthwhile considering the possibility that internal stresses affected the plastic strain increments, and hence the deformation band directions, in oriented polyvinyl chloride.

It is proposed that the hot stretching of polyvinyl chloride caused internal stresses to be set up in the material. It is assumed that it is these internal stresses which were responsible for the deviations between experiment and theory described in the previous section. The following molecular picture is proposed to describe how these stresses were set up and the effect they produced.
A tensile stress applied to unoriented polyvinyl chloride tends to extend the molecular chains, which are initially in a random un-stretched configuration, in the direction of the stress. The process of extension occurs by the rotation of molecular chain segments and is hindered by interaction between neighbouring segments. Thus the attempt to extend the chains is resisted by internal stresses which are of a viscoelastic frictional nature, tending to oppose chain movement in any direction. Yielding requires the relative movement of the molecular segments and takes place when the applied stress can overcome these viscoelastic stresses. If the extension is continued beyond yield, the chains become appreciably extended in the tensile direction and the material becomes oriented. The chains tend to contract in order to maximise their entropy. In the stretched material, therefore, there are internal stresses of two kinds: viscoelastic stresses tending to prevent molecular chain movement, in any direction, whether extension or retraction, and rubber-like stresses arising from the tendency of molecular chains to shorten in the line in which they have been extended. The experiments presented here will now be interpreted in terms of this picture.

As discussed in Chapter 2, the deformation behaviour of polyvinyl chloride during hot stretching could be accounted for by a molecular network theory similar to that used in accounting for the behaviour of rubber. The applied stress during hot stretching was, therefore, essentially that required to extend the molecular chains from a random configuration, and only a small effect arose from viscoelastic stresses. Cooling below $T_g$ reduces the free volume available for segments to move in. Thus, the viscoelastic stresses increased to the extent that they could withstand the
stresses exerted by the molecular chains in attempting to shorten to their equilibrium length. This accounts for the fact that, having cooled the stretched material to room temperature at constant length, it was possible to remove the material from the stretching machine without it contracting significantly. Under these conditions (zero applied stress and room temperature), the tensions in the chains were counterbalanced by the viscoelastic stresses. Thus, the repulsive forces between molecular segments opposed the compressive forces due to the stretched network so that the internal stresses summed to zero in the absence of an applied stress.

Reheating the unconstrained material caused it to contract in the original stretching direction. This is because the rise in temperature reduced the viscoelastic stresses to the point where they could no longer withstand the compressive effect of the stretched molecular chains. In the absence of an applied stress, the chains were therefore able to contract, so lowering their tension and shortening the material. This can be regarded as the yielding of the material in compression under its own internal stress at zero applied stress. This model would account for the results of Nielsen and Buchdahl (1950) who observed that the temperature at which oriented polystyrene film started to retract decreased as the birefringence of the film increased. Taking the birefringence as a measure of molecular alignment, increasing birefringence indicates an increase in internal compressive stress. Thus, since the viscoelastic stresses decreased with increasing temperature, as the birefringence increased a lower temperature would have to be reached before the internal compressive stress could
overcome the viscoelastic stresses and cause the film to contract.

Stretching the material at room temperature in the direction of the extended chains did not produce yield until the applied stress was able to overcome the viscoelastic stresses. However, the applied tensile stress was not fully effective in doing this because it was opposed by the molecular chain retractive stresses. Only the difference between the applied tensile stress and the total chain stress was effective in producing yield. In compression in the chain direction, on the other hand, the chain stress would aid the applied stress in producing yield. On these grounds an asymmetry in yield stress as between tension and compression (a Bauschinger effect) in the direction of molecular alignment (the x-direction) is to be expected. We represent this effect very simply by considering the component of the applied tensile stress in the molecular alignment direction, \( \sigma_{xx} \), to be reduced by a constant amount \( a_{xx} \), and thus introduce a Bauschinger effect into the yield criterion. So in the analysis already given above \( \sigma_{xx} \) is replaced by \( (\sigma_{xx} - a_{xx}) \). This method of allowing for the effects of internal stress has been suggested by Olszak, Mroz and Perzyna (1963). Under these circumstances the yield criterion becomes

\[
2f(\sigma_{ij}) = H(\sigma_{xx} - a_{xx} - \sigma_{yy})^2 + F(\sigma_{yy} - \sigma_{zz})^2
+ G(\sigma_{zz} - \sigma_{xx} + a_{xx})^2 + 2N \tau_{xy}^2 + 2L \tau_{yz}^2 + 2M \tau_{zx}^2 = 1.
\]

(4.19)

Still assuming transverse isotropy, so that \( G = H \), and putting the stress components in terms of the applied stress we obtain for the yield criterion:
The expressions for the strain increments are also modified by the presence of the \( a_{xx} \) term, and the quadratic for \( \tan (\lambda_o + Y) \) becomes

\[
[F + H] \sigma_\lambda \sin^2 \lambda_o - H(\sigma_\lambda \cos^2 \lambda_o - a_{xx}) \tan^2 (\lambda_o + Y)
\]

\[
+ 2N \sigma_\lambda \sin \lambda_o \cos \lambda_o \tan (\lambda_o + Y) + H[2(\sigma_\lambda \cos^2 \lambda_o - a_{xx})
\]

\[
- \sigma_\lambda \sin^2 \lambda_o \right] = 0 .
\]

For each extension ratio there were, then, the values of four constants \( F, H, N \) and \( a_{xx} \) to be determined. This was done in the following way. A set of values of \( a_{xx} \), increasing from zero in steps of 4.9 MN m\(^{-2}\) for material of prior extension ratios 3.3, 3.7, and 6.0, and 0.98 MN m\(^{-2}\) for material of prior extension ratios 2.0 and 3.0, was taken. (It should be realised that, when these calculations were originally carried out, the units of stress were taken as Kg mm\(^{-2}\). Thus, the increments in \( a_{xx} \) were 0.5 Kg mm\(^{-2}\) and 0.1 Kg mm\(^{-2}\) respectively.) For each value of \( a_{xx} \), \( F, H, \) and \( N \) were computed from the measured yield stress at \( \lambda_o = 0^\circ, 45^\circ \) and \( 90^\circ \). Then, for each chosen value of \( a_{xx} \), the complete \( \sigma_\lambda \) against \( \lambda_o \) curve was computed, as also were the curves for \( Y_1 \) and \( Y_2 \) against \( \lambda_o \). The set of values for the four constants which gave the best fit to the experimental results for the yield stress and band angle was then selected for each prior extension ratio. This
fitting procedure is illustrated in Figure 4.6 for material of prior extension ratio 3.3. Values of \( Y_1 \) and \( Y_2 \) predicted by the theory are presented for different values of \( a_{xx} \), along with the actual experimental values. The curves are not plotted at low values of \( \lambda_0 \) since they all merge and meet at \( Y_1 = Y_2 = 54.7^\circ \) at \( \lambda_0 = 0^\circ \). It can be seen that the values of \( Y_1 \) are best fitted by \( a_{xx} = 29.4 \text{ MN m}^{-2} \). The curve for \( a_{xx} = 24.5 \text{ MN m}^{-2} \) fits the results at \( \lambda_0 = 89.5^\circ \) but at no other point. The curve for \( a_{xx} = 34.3 \text{ MN m}^{-2} \) deviates from the results at large values of \( \lambda_0 \) but does not improve the agreement in the vicinity of \( \lambda_0 = 27^\circ \).

However, at small values of \( \lambda_0 \) the predicted results are insensitive to changes in \( a_{xx} \), so that the agreement for \( a_{xx} = 34.3 \text{ MN m}^{-2} \) is not significantly better than that for \( a_{xx} = 29.4 \text{ MN m}^{-2} \). Thus, \( a_{xx} = 29.4 \text{ MN m}^{-2} \) was considered the most suitable value of \( a_{xx} \) to give a good fit. In Table 4.1 are shown the values of the parameters \( H, F \) and \( N \) for each value of \( a_{xx} \). Because of the difference in shape of the experimental and predicted curves for \( Y_2 \), it is more difficult to determine the most appropriate value of \( a_{xx} \) which gives the best fit to the experimental results. However, the curve for \( a_{xx} = 29.4 \text{ MN m}^{-2} \) seems to be in closest agreement with the experimental results. This is particularly so when it is realised that at \( \lambda_0 = 90^\circ \), \( Y_1 \) and \( Y_2 \) should be the same, and hence, from Figure 4.6(a), equal to approximately \( 62.5^\circ \). This is indicated by a square plotting symbol in Figure 4.6(b), but this is not strictly an experimental point. Varying the value of \( a_{xx} \) did not significantly affect the fit to the yield stress results. This is apparent from curve A and curve B, for \( a_{xx} = 0 \) and \( a_{xx} = 29.4 \text{ MN m}^{-2} \) respectively, plotted in Figure 4.3. The curves for intermediate values of \( a_{xx} \) were positioned between curve A and curve B.
For $a_{xx} = 29.4 \text{ MN m}^{-2}$ the predicted yield stress results agreed with the experimental results to $\pm 2\%$ or better with exception of the material of prior extension ratio 6.0 for which the difference was $\pm 4\%$.

In Figure 4.4 and 4.5 the predicted values of $Y_1$ and $Y_2$ are plotted for $a_{xx} = 0$ and for the value of $a_{xx}$ which was considered to give the best fit to the experimental results. Experimental results are also presented in Figures 4.4 and 4.5. It should be realised that $Y_1$ and $Y_2$ are taken positive when measured in opposite senses relative to the tensile axis. As far as the results for extension ratio 3.7 are concerned, the fitting procedure was carried out using both the extrapolated and measured values of $\sigma_0$. In fact comparison of band angle results in Figures 4.5(c) and (d) evaluated using measured and extrapolated values of $\sigma_0$, suggested that the values calculated using the extrapolated value gave the closest agreement with the experimental results. However, any differences were too small to be considered significant.

It was originally assumed that, because the transverse contraction during the original hot stretching was isotropic, the parameters $G$ and $H$ were equal. In order to check the validity of this assumption, some calculations were carried out with $G$ not equal to $H$ for material of prior extension ratio 3.3. Under these circumstances the equations for the variations of yield stress, $\sigma_0$, and band angle, $Y$, as a function of $\lambda_0$ are as follows:

$$
(G + H) \left( \sigma_0^2 \cos^4 \lambda - a_{xx} \right)^2 + (H + F) \sigma_0^2 \sin^4 \lambda_0
$$

$$
+ 2 \left[ H \sigma_0^2 \cos^2 \lambda_0 - H_0 (\sigma_0 \cos \lambda_0 - a_{xx}) \right] \sin^2 \lambda_0 = 1,
$$

(4.22)
The fitting procedure was essentially similar to that used previously, but, in this case, an additional piece of experimental information had to be supplied in order to evaluate the additional constant, $G$. Three measured yield stresses were supplied along with the measured values of $Y_1$ at a particular value of $\lambda_0$. The values of the parameters $H$, $G$, $F$, and $N$ were then evaluated for different values of $a_{xx}$. The set of values for the five constants which gave the best fit to the experimental results for both yield stress and band directions was then determined. The three values of yield stress, $\sigma_0$, $\sigma_{45}$, and $\sigma_{90}$, were used as fitting point, as before, but the additional fitting point for $Y_1$ was taken to be at different values of $\lambda_0$. For each fitting position for $Y_1$, $a_{xx}$ was varied from 19.6 MN m$^{-2}$ to 39.2 MN m$^{-2}$ in steps of 4.9 MN m$^{-2}$. This procedure was carried out for prior extension ratio 3.3. The fit of the theory to the yield stress data was found to be uninfluenced by the choice of $a_{xx}$ or the fitting point for $Y_1$. In Figure 4.7 the predicted values of $Y_1$ are plotted for different values of $a_{xx}$ and for different positions of the fitting point. In each case the point at which the theory is fitted to the values of $Y_1$ is indicated in the figures. The interesting feature of these results is that, with the exception of the results fitted to $Y_1$ at $\lambda_0 = 30^\circ$, the predicted results for $Y_1$ agree quite well with the experimental results. Also, the variation of $a_{xx}$ has
no effect on the predicted curves for Y₁ at values of λₒ above 35°. However, at values of λₒ in the vicinity of λₒ = 30°, and below, varying axx did affect the predicted results. In particular, decreasing axx improved the fit between experimental and calculated results. Thus, considering only results for Y₁, it would seem that, with G = H, the experimental results would best be fitted by axx = 0, although no results have been presented for this value of axx in Figure 4.7. Considering now the results for Y₂ in Figure 4.8, it is apparent that, with the exception of results fitted to Y₁ at λₒ = 30°, the variation of axx has little influence upon results at values of λₒ greater than 45°. However, at smaller values of λₒ, increasing axx caused Y₂ to increase. In fact it would appear that Y₂ is best fitted at small values of λₒ by axx = 29.4 MN m⁻². This conclusion is only based on one experimental point at λₒ = 23°, but its position would seem to be confirmed by comparing the variation of Y₂ for prior extension ratios 3.3 and 3.7 in Figure 4.4. Thus, decreasing axx, although improving the fit of predicted and experimental results for Y₁, does not predict correctly the observed large value of Y₂ at λₒ = 23°. In Figure 4.9, G and H are plotted as a function of axx for different fitting positions of the Y₁ results. From these results it can be seen that in most cases G is equal to H in the vicinity of axx = 29.4 MN m⁻², as indicated by the arrows. The exception to this is for the results for Y₁ fitted at λₒ = 30°, which in any case did not agree well with the experimental band directions. Although the evidence is not substantial, the above discussion of the band angle results does suggest that the assumption, that G = H, is correct. The isotropic contraction during prior extension, however, is still considered the most substantial justification for this assumption.
The above discussion does indicate that results for yield stress and the direction of type 1 bands only are insufficient to evaluate the parameters in the Hill theory if it cannot be reasonably assumed that $G = H$. In the case of material of prior extension ratio 6.0, the transverse contraction was not isotropic and, therefore, it cannot be assumed that $G = H$. However, because insufficient experimental results were available, it was not possible to evaluate exactly all the parameters if $G \neq H$, and so it was assumed that $G = H$. The results of Brown, Duckett and Ward (1968a), which will be discussed in more detail in Section 4.5 show that if, during the initial stretching, the width of the material is constrained from contracting, then the Hill theory parameters evaluated from the subsequent yielding behaviour are such that $H > G$.

Although the Hill modification of the von Mises criterion, with an internal stress term, satisfactorily accounts for most aspects of the yielding behaviour of oriented polyvinyl chloride, the theory is not satisfactory in that it gives the correct qualitative, but not quantitative, variation of the directions of the type 2 bands. This perhaps would not be surprising if type 1 bands formed first at yield. However, as discussed in Chapter 3, type 2 bands formed first at yield, and thus should be better fitted to the theory. Further reference will be made to this aspect of the yielding behaviour in later sections.

4.4 The Influence of Molecular Orientation on the Internal Stress and the Hill Theory Parameters

By considering steps of $4.9 \text{ MN m}^{-2}$ or $0.98 \text{ MN m}^{-2}$ in $a_{xx}$ it was possible to find, to an accuracy of $\pm 2.4 \text{ MN m}^{-2}$ or $\pm 0.49 \text{ MN m}^{-2}$...
respectively, the value of $a_{xx}$ which gave a good fit to the experimental data. Figure 4.10(a) shows that, both for material originally extended at 71°C and 90°C, $a_{xx}$ increased from zero with increasing prior extension ratio, although the two sets of results do not in themselves agree. However, prior extension ratio, while used here as a convenient parameter to describe the pretreatment, does not necessarily give a measure of the internal state of the material. As suggested earlier in Chapter 3, birefringence is likely to be a more meaningful parameter in this sense, and, in Figure 4.10(b), $a_{xx}$ is plotted as a function of birefringence. The results for material extended at 90°C and 71°C are in much better agreement when plotted in this way than when plotted against extension ratio.

If the birefringence is regarded as a measure of the degree of molecular alignment, then these results suggest firstly that the internal stress rises from zero as the molecular orientation is increased from the unoriented state, and secondly that the internal stress is approximately the same for the same degree of orientation irrespective of the stretching temperature. This is consistent with the concept of internal stress described in Section 4.3.

Furthermore, the molecular picture presented in Section 4.3 suggests that, for a given prior extension ratio, the internal stress, $a_{xx}$, should be related to the applied true stress at the hot stretching temperature at which the initial extension was carried out. Molecular network theories predict that the stress, arising from the tendency of the molecules to retract back to a random configuration, should be smaller at the lower temperature, i.e. the temperature at which $a_{xx}$ was evaluated. It might
therefore be expected that \( a_{xx} \) and the stress during extension would be proportional but not necessarily equal. In Figure 4.11, both \( a_{xx} \) and the true stress during the original extension at 71°C and 90°C are plotted as a function of prior extension ratio. The experimental points are the values of \( a_{xx} \) and the continuous lines are plots of true stress during extension at 71°C and 90°C. Only in the case of prior extension ratio 6.0 was the difference between true stress and \( a_{xx} \) greater than the experimental errors. However, it was pointed out in Section 4.3 that \( H \) should be greater than \( G \), and Figure 4.9 indicates that under such circumstances \( a_{xx} \) should be smaller than that evaluated using \( G = H \). This would improve the agreement between \( a_{xx} \) and the true stress. Thus the agreement between \( a_{xx} \) and the true drawing stress is remarkably good. It can be considered even more significant since agreement was obtained for material extended at two different temperatures.

The parameters \( H, F \) and \( N \) were also found to vary according to the degree of molecular alignment of the polyvinyl chloride. These variations as a function of both prior extension ratio and birefringence for material originally extended at 90°C and 71°C are shown in Figure 4.12. Two factors affect the accuracy of the values of the parameters, these being the accuracy of the yield stress measurements used as fitting points, and the effect of the uncertainty in the values of \( a_{xx} \) on the values of the parameters. In fact by considering the possible errors in yield stress at the fitting points, the uncertainty in the values of the parameters was found to be greater or equal to that arising from the uncertainty in the appropriate value of \( a_{xx} \). The estimated uncertainties are indicated in Figure 4.12. As might be expected
from previous discussions, when plotted as a function of prior extension ratio, the results for the material extended at the two temperatures do not agree. However, when considered as a function of birefringence, the agreement is considerably improved, although there is still a discrepancy in the results.

It can be seen from Figure 4.12(b) that $H$ decreased and $F$ increased with increasing birefringence. By putting $\lambda_0 = 0^\circ$ and $\lambda_0 = 90^\circ$ in equation (4.20), it is clear that the values of these parameters are determined by the values of $\sigma_0$ and $\sigma_90$, and so, the variation of this form might be expected from the results presented in Figure 3.5. However, one rather interesting feature of the results is that $N$ went through a minimum as the birefringence increased. One implication of this variation of $N$ is that the shear yield stress, $\tau_{xy}$, for shear parallel to the molecular alignment direction went through a maximum as the birefringence increased. This is shown in Figure 4.13 where $\tau_{xy}$ is plotted as a function of prior extension ratio for material originally extended at 71°C. These values of $\tau_{xy}$ were calculated by putting all stress components except $\tau_{xy}$ in equation (4.20) equal to zero to give

$$\tau_{xy}^2 = (1 - 2H a_{xx}^2)(2N)^{-1}.$$  \hspace{1cm} (4.24)

By substituting in equation (4.24) the values of the parameters $H$, $N$ and $a_{xx}$ obtained from the tensile yield data, $\tau_{xy}$ could be calculated. Unfortunately no measurements of shear yield stress have been carried out to confirm experimentally the existence of this maximum in $\tau_{xy}$.
Since Hill included the anisotropy parameters in the von Mises criterion in a quite arbitrary manner, and since in formulating the yield criterion the material is considered as a continuum, taking no account of microstructure, it is difficult to interpret the variation of H, F and N in terms of structural changes. However, in this context it is interesting to note the observed relationship between tensile yield stress and tensile modulus, which was discussed in Section 3.2.2. (The corrected yield stress which was mentioned with reference to the work of Bridle et al (1968) was evaluated in the following way. They determined the Hill theory parameters and $a_{xx}$ from the observed yielding behaviour, and then calculated the corrected yield stress by using these values of the parameters in an equation similar to equation (4.20), but with $a_{xx} = 0$. Other evidence suggests that shear moduli are related to the shear yield stresses. For instance, the existence of a minimum at $\lambda_0 = 57^\circ$ in the plot of $\sigma_\lambda$ vs $\lambda_0$ for oriented polyethylene (see Keller and Rider (1966)) indicates that slip parallel to the molecular alignment direction is the easiest mode of plastic deformation, and Darlington and Saunders (1968) have shown that the equivalent elastic compliance, $s_{55}$, is very much larger than the other compliances. The results presented in Figure 4.13 show that the tensile yield data led to a prediction that, for polyvinyl chloride, the shear yield stress, $\tau_{xy}$, had a maximum value as the prior extension ratio increased. Unfortunately, no information has been obtained concerning a possible maximum in the equivalent modulus of polyvinyl chloride with increasing prior extension ratio. However, it has been shown by Raumann (1963) that, for polyethylene terephthalate, the equivalent compliance, $s_{55}$ ($s_{44}$ using Raumann's notation) had a minimum as
the extension ratio increased. These results indicate that it is not inconceivable that $s_{55}$ for oriented polyvinyl chloride might behave in a similar manner.

It is possible, by considering a physical interpretation, which has been given to the von Mises yield criterion, to relate the yield stress and modulus on the basis of this interpretation. Jaeger (1962) has shown that, if the von Mises criterion is taken as a critical elastic distortional energy criterion, then for isotropic materials, the criterion can be considered as a critical strain, rather than a critical stress criterion. The criterion is then given by

$$ (e_1 - e_2)^2 + (e_2 - e_3)^2 + (e_3 - e_1)^2 = c, \quad (4.25) $$

where $c$ is a constant and $e_1$, $e_2$, and $e_3$ are the principal strains. Robertson (1964) has taken this form of the criterion and has suggested that it applies, with no modifications, to anisotropic materials. In view of the fact that the tensile strain at yield for polyvinyl chloride did not show a large variation for different values of $\lambda_0$ and prior extension ratio (see Section 3.2.2) it was thought worthwhile to consider this proposed criterion in more detail. Robertson (1964) considered only the simple case of tensile deformation with the stress applied parallel to the molecular alignment direction, i.e. $\lambda_0 = 0^\circ$. Equation (4.25) will now be extended to apply to test pieces having any value of $\lambda_0$.

The left-hand side of equation (4.25) is proportional to the square of the shear strain on the octahedral plane expressed in terms of principal strains. Expressed in terms of strain components measured relative to arbitrary Cartesian axes, this becomes
\[
(\varepsilon_{xx} - \varepsilon_{yy})^2 + (\varepsilon_{yy} - \varepsilon_{zz})^2 + (\varepsilon_{zz} - \varepsilon_{xx})^2 + \\
6(\varepsilon_{xy}^2 + \varepsilon_{yz}^2 + \varepsilon_{zx}^2) = c ,
\]

(4.27)

where \( \varepsilon_{ij} \) are the strain components measured relative to the Cartesian axes. The strain components expressed in terms of stress components and elastic compliances are as follows:

\[
\begin{align*}
\varepsilon_{xx} &= s_{11} \sigma_{xx} + s_{12} \sigma_{yy} + s_{13} \sigma_{zz} \\
\varepsilon_{yy} &= s_{12} \sigma_{xx} + s_{22} \sigma_{yy} + s_{23} \sigma_{zz} \\
\varepsilon_{zz} &= s_{13} \sigma_{xx} + s_{23} \sigma_{yy} + s_{33} \sigma_{zz} \\
\varepsilon_{yz} &= s_{44} \tau_{yz} \\
\varepsilon_{xz} &= s_{55} \tau_{xz} \\
\varepsilon_{xy} &= s_{66} \tau_{xy}
\end{align*}
\]

Substituting equation (4.27) in equation (4.28) gives

\[
\begin{align*}
&\left[ (s_{11} \sigma_{xx} + s_{12} \sigma_{yy} + s_{13} \sigma_{zz}) - (s_{12} \sigma_{xx} + s_{22} \sigma_{yy} + s_{23} \sigma_{zz}) \right]^2 \\
&+ \left[ (s_{12} \sigma_{xx} + s_{22} \sigma_{yy} + s_{23} \sigma_{zz}) - (s_{13} \sigma_{xx} + s_{23} \sigma_{yy} + s_{33} \sigma_{zz}) \right]^2 \\
&+ \left[ (s_{13} \sigma_{xx} + s_{23} \sigma_{yy} + s_{33} \sigma_{zz}) - (s_{11} \sigma_{xx} + s_{12} \sigma_{yy} + s_{13} \sigma_{zz}) \right]^2 \\
&+ 6 \left[ (s_{44} \tau_{yz})^2 + (s_{55} \tau_{xz})^2 + (s_{66} \tau_{xy})^2 \right] = c .
\end{align*}
\]

(4.28)
Equation (4.28) is a yield criterion, expressed in terms of stress components, which can be applied to either isotropic or anisotropic materials. The anisotropy will be taken into account in the values of the elastic compliances. In the particular experiments discussed here the material is considered transversely isotropic and thus, \( s_{12} = s_{13}, s_{22} = s_{33}, s_{66} = s_{55}, \) and \( s_{44} = 2(s_{22} - s_{23}). \) Under these circumstances, and taking the stress components as those given in equation (4.11), the yield criterion becomes

\[
\sigma_{\lambda}^2 \left\{ 2(s_{11} - s_{12})^2 \cos^4 \lambda_o + \left[(s_{12} - s_{22})^2 + (s_{22} - s_{23})^2 \right] \sin^4 \lambda_o + \left[2(s_{11} - s_{12}) (2s_{12} - s_{22} - s_{23}) \right] \sin^2 \lambda_o \cos^2 \lambda_o \right\} = c . \tag{4.29}
\]

This criterion takes the same form as that given in equation (4.12) by the Hill modification of the von Mises yield criterion. However, the following discussion shows that, in general, the Hill theory parameters cannot be expressed in terms of the elastic compliances and the constant \( c. \) By putting all stress components, except \( \tau_{xy}, \) equal to zero in equation (4.10) and (4.28) it is easily shown that

\[
\tau_{xy}^{-2} = 2N = 6s_{66}^2 (c)^{-1} . \tag{4.30}
\]

Taking this expression for \( N \) in terms of \( s_{55} \) (transverse isotropy is assumed) and equating coefficients of \( \cos^4 \lambda_o \) and \( \sin^2 \lambda_o \cos^2 \lambda_o \) in equations (4.29) and (4.12) it is apparent that a consistent expression for \( H \) in terms of elastic compliances cannot be obtained.
Since equation (4.29) does have the same form as equation (4.12), it is apparent that it could predict the correct form for the variation of $\sigma_\lambda$ as a function of $\lambda_0$. Unfortunately, no measured values of the elastic compliances were available, and so equation (4.29) could not be applied to the results for oriented polyvinyl chloride. However, Raumann (1963) has carried out extensive experiments and evaluated the variation of elastic compliances of oriented polyethylene terephthalate as a function of birefringence. The results given by Raumann have been used by the present author in equation (4.29) to see if the predicted variation of $\sigma_\lambda$ as a function of $\lambda_0$ and birefringence is the same as that observed for polyvinyl chloride discussed here, or for polyethylene terephthalate, as discussed by Bridle, Buckley and Scanlan (1968). In Figure 4.14 the values $\sigma_\lambda$ evaluated using the values of compliances given by Raumann, are plotted as a function of birefringence. ($s_{11}, s_{12}, s_{13}, s_{66}$ and $s_{66}$ given by Raumann are equivalent to $s_{22}, s_{23}, s_{12}, s_{31}, s_{55}$ and $s_{44}$, respectively, in equation (4.29).) It can be seen from Figure 4.14 that the results are similar to those for polyvinyl chloride in that $\sigma_{90}$ decreased with increasing birefringence, but $\sigma_{45}$ and $\sigma_{30}$ went through a maximum as the birefringence increased. $\sigma_0$ increased with increasing birefringence. The results obtained by Bridle, Buckley and Scanlan were not the same as those in Figure 4.14 in that no maximum was observed in $\sigma_{45}$ and $\sigma_{30}$ and there was a minimum in $\sigma_{90}$. The similarity between the predicted results and the observed results for polyvinyl chloride does confirm that equation (4.29) is capable of accounting for the yielding behaviour of oriented polymers.
The results given in Figure 3.8 indicated that the tensile yield stress, $\sigma$, and the tensile modulus, $E$, are related. Since equation (4.29) gives the yield stress in terms of elastic compliances, it follows that the critical strain criterion will result in the yield stress and tensile modulus being related. $E$ is given in terms of the elastic compliances by

$$E^{-1} = s_{11} \cos^4 \lambda + (2s_{12} + s_{55}) \sin^2 \lambda \cos^2 \lambda_0 + s_{22} \sin^4 \lambda_0.$$  \hspace{1cm} (4.31)

Again using the values of the elastic compliances given by Raumann, $E$ was evaluated for different values of $\lambda_0$ and birefringence. This value of $E$ is plotted against the value of $\sigma$, given by equation (4.29) in Figure 4.15. It can be seen that the two are not linearly related, but there is a slight curvature in the same sense as that for polyvinyl chloride in Figure 3.8. Robertson (1964), in applying this theory, predicted a linear relationship between $E$ and $\sigma$, but his results for oriented polycarbonate were not linearly related. However, in manipulating the equations, he made the assumption of incompressibility. Since the results given by Raumann were actually measured, no such assumption has been made in evaluating the results in Figures 4.14 and Figures 4.15. It has already been shown in equation (4.30) that $\tau_{xy}$, the yield stress for shear parallel to the molecular alignment direction is related to the compliance $s_{66}$ ($s_{66} = s_{55}$ for transverse isotropy). The possibility of the two being related has been discussed earlier in this section.

Unfortunately no yield stress results are available for the polyethylene terephthalate for which Raumann measured the elastic
compliances, but the yielding behaviour, as predicted by the critical strain criterion in equation (4.26), is remarkably similar to that observed for polyvinyl chloride. Similarities exist in the effect of \( \lambda_0 \) and birefringence on \( \sigma_\lambda \), in the relationship between tensile modulus and tensile yield stress, and in the existence of a minimum in \( s_{55} \) for polyethylene terephthalate and a predicted maximum in \( \tau_{xy} \) for polyvinyl chloride, when these are considered as a function of birefringence (or extension ratio).

As far as deformation band directions are concerned, the critical strain criterion does not give the same results as the Hill modification of the von Mises criterion. Using equations (4.13), (4.14) and (4.28) it can be shown that the band directions are given by

\[
\begin{align*}
\{ \sigma_{yy} [ (s_{12}-s_{22})^2 + (s_{22}-s_{23})^2 + (s_{23}-s_{12})^2 ] \\
+ \sigma_{xx} (s_{11}-s_{12}) (2s_{12}-s_{22}-s_{23}) \} \tan^2 (\lambda_0 + Y) \\
+ 2 \# s_{55}^2 \tau_{xy} \tan (\lambda_0 + Y) + [2 \sigma_{xx} (s_{11}-s_{12})^2 \\
+ \sigma_{yy} (s_{11}-s_{12}) (2s_{12}-s_{22}-s_{23}) ] = 0.
\end{align*}
\] (4.32)

For an isotropic material this equation gives the same value for \( Y \) as that given by the Hill theory, namely \( Y = 54.7^\circ \). However, although the Hill theory gives \( Y = 54.7^\circ \) for anisotropic materials with \( \lambda_0 = 0^\circ \), equation (4.32) shows that with \( \lambda_0 = 0^\circ \), the value of \( Y \) is affected by the anisotropy of the material through the variation of the elastic compliances. Similarly at \( \lambda_0 = 90^\circ \) the Hill theory and equation (4.32) give different values of \( Y \) for anisotropic materials. The effect of using equation (4.32)
to evaluate the band angles has not been investigated in any detail, but it may be that using the critical strain criterion would give a more satisfactory fit to results for $Y_2$ than does the Hill theory. It seems likely that an internal stress term would still have to be included in the yield criterion since equation (4.28) cannot account for the observed asymmetry in the anisotropy of the shear yield stress which has been reported by Brown et al (1968a) and Bridle et al (1968).

One other aspect of the critical strain criterion is that it predicts that the yielding of anisotropic materials should be influenced by hydrostatic stresses. This seems reasonable since the application of a hydrostatic stress causes shear strains to be set up in elastically anisotropic material. This hydrostatic stress effect does not lead to a difference in yield stress in tension and compression. This will be discussed further in Section 4.6.

Since the critical strain criterion can predict the correct form for the yield stress variation, and also relates the yield stress to the modulus, it would seem more satisfactory than the Hill theory which was formulated in a quite arbitrary manner. It would also be of considerable practical importance in that the yielding behaviour could be predicted on the basis of compliance measurements. Obviously the ultimate test of the critical strain criterion is to measure both yield stresses and compliances for the same material.

There is another possible approach for relating the yield stress to the modulus on the basis of the critical elastic distortional energy interpretation of the von Mises criterion. If the material
is incompressible, it follows that yield will occur when

$$\sigma_\lambda \varepsilon_\lambda = k_o, \quad (4.33)$$

where $\varepsilon_\lambda$ is the tensile strain in the direction of the applied tensile stress, $\sigma_\lambda$, for a test piece having a particular value of $\varepsilon_o$, and $k_o$ is a constant. By substituting for $\varepsilon_\lambda$ in terms of and the tensile modulus, $E_\lambda$, equation (4.33) becomes

$$\sigma_\lambda = E_\lambda^{1/2} k_o. \quad (4.34)$$

Although both this and the critical strain criterion approach were based on the critical elastic distortional energy interpretation of the von Mises criterion, it should be realised that the elastic energy criterion can only be expressed as a critical strain criterion for isotropic materials. By substituting the expression for $E_\lambda$, as in equation (4.31), into equation (4.34), the following expression is obtained for the tensile yield stress:

$$\sigma_\lambda = k_o \left[ s_{11} \cos^4 \varepsilon_o + (2s_{12} + s_{55}) \sin^2 \varepsilon_o \cos^2 \lambda_o \right. \left. + s_{22} \sin^4 \varepsilon_o \right]^{-1/2}. \quad (4.35)$$

Equation (4.12) can be written in a similar form and it is then possible to relate the Hill theory parameters to the elastic compliances as follows:

$$2H = k_o s_{11};$$

$$N = k_o (2s_{12} + s_{55}); \quad (4.36)$$

$$(H + F) = k_o s_{22}.$$

Although equation (4.35) is much simpler than that obtained using the critical strain criterion, it cannot account for the observed
relationship between \( \sigma_\lambda \) and \( E_\lambda \) shown in Figure 3.8. In Figure 3.8 the dashed curve is the plot of equation (4.34). The discrepancy between the proposed theory and experiment is clearly quite large.

Allison and Ward (1967) have pointed out that, although an experimental correlation exists between yield stress and modulus, it does not necessarily imply that the two are directly related. However, the critical strain criterion discussed earlier shows how the two can be directly related. Since the yield stress was related to the elastic compliances, the anisotropy in the yield behaviour of oriented polymers can be related to molecular alignment indirectly by using a model which satisfactorily accounts for the elastic anisotropy of oriented polymers. In the model it is assumed that the polymer consists of identical anisotropic rod-like units which have a range of spatial orientations. Each unit is considered to be transversely isotropic, five independent elastic constants specifying the elastic properties of the unit. The elastic constants of the bulk polymer are then derived in terms of the elastic constants of the units by suitable averaging procedures. In the unoriented polymer the units are random arranged and the bulk polymer is isotropic. In the limit of perfect molecular alignment, the oriented polymer has elastic properties which are the same as those of the individual unit. This model has been used with some success to account for the mechanical properties of oriented polymers by Pinnock and Ward (1964) and Hadley, Pinnock and Ward (1969). Since the model accounts for the elastic anisotropy of oriented polymers, it can also account indirectly for the yield stress anisotropy if the critical strain criterion is correct. This model will be discussed further in Chapter 6 with reference to optical anisotropy studies.
The yield stress anisotropy of oriented polymers may be accounted for more directly by using a similar aggregate model. Robertson and Joynson (1966) have proposed that a glassy polymer is not structureless but consists of a large number of grains. Each grain consists of a region in which the polymer chains are aligned parallel to one another. No transverse order in the arrangement of the molecules exists. A similar structure has been suggested by Lebedev et al (1967) as a result of X-ray diffraction studies. These grains can be considered as the basic unit of the aggregate model. It was also proposed by Robertson and Joynson (1966) that the deformation of each grain could be described by five independent slip systems. These involve slip in directions parallel and perpendicular to the molecular chains and also kinking of molecular chains. Slip would be easier on some slip systems than on others. For instance, results for oriented polyethylene discussed earlier suggest that slip parallel to molecular chains is very much easier than other modes of deformation. It is assumed that for each slip system a critical shear stress is required to produce plastic deformation. If all of the grains were oriented in the same direction, the problem of predicting the variation of yield stress as a function of \( \lambda_o \) would be simple since, for any particular value of \( \lambda_o \), yield would occur in all grains at the same applied stress and with the same deformation geometry. However, with a spread in orientations of the grains, different shear stresses would be acting on different slip systems in the various grains. Thus, some grains would yield at a lower applied stress than others, and individual grains would be prevented from deforming by the constraints of adjacent grains. Under such conditions it is difficult to specify
what state of yielding on a microscopic scale would constitute macroscopic yielding, particularly in determining what the tensile yield stress would be.

Similar attempts have been made to account for the yielding behaviour of polycrystalline metals in terms of the yielding behaviour of single crystals which constitute the metal. One of the first such attempts was made by Bishop and Hill (1951a) and (1951b). These latter authors discussed the yielding of isotropic, face-centred cubic polycrystalline metals in which they assumed that each slip system of the individual grains required the same critical resolved shear stress, \( \tau \), to produce yielding. They showed that the yield criterion obtained using this model was intermediate between that of Tresca and von Mises although experimental results for aluminium and copper were best fitted by the von Mises criterion. In particular, they predicted that the ratio of yield stress in shear to that in tension should be 0.540. This compares with ratios of 0.500 and 0.577 predicted by the Tresca and von Mises criteria respectively. Further discussions of this theory have been given by Lin (1957) and Hutchinson (1964a) and (1964b), who considered both face-centred cubic and body-centred cubic metals. Although Bishop (1954) has discussed the development of texture during the straining of face-centred cubic metals on the basis of an aggregate model, no attempt has been made to account for the yield stress anisotropy of metals having some texture. The theory used by Bishop and Hill (1951a and b) is rather complicated and, because insufficient time was available, no attempt was made to account for the yielding of oriented polymers in terms of an aggregate model. Nevertheless, it is thought that such an analysis would be worth attempting in the future.
Comparisons of the Yield Behaviour of Oriented Polyethylene Terephthalate and Oriented Polyethylene with that of Oriented Polyvinyl Chloride

During the course of this investigation and after the submission of this work for publication (Rider and Hargreaves (1969)), Brown et al (1968a) and Bridle et al (1966) have published accounts of experiments on the yielding behaviour of oriented polyethylene terephthalate deformed in tension and in shear. As discussed in Chapter 3, both the yield stress and deformation band results in tension were very like those for oriented polyvinyl chloride. In both of the above publications the authors found that yield behaviour could be accounted for by the Hill theory only if an internal stress term was included. The inclusion of the $a_{xx}$ term in the theory as discussed in this thesis was carried out independently of the work of the above authors.

Detailed consideration will be given first to the work of Brown et al. The sheet that they used had been oriented by extension at room temperature to an extension ratio of 5.0 with its width held constant during extension. (The polyvinyl chloride sheet used here was laterally unconstrained and the contraction was isotropic.) Brown et al, too, applied Hill's theory to their results but, because X-ray diffraction photographs showed that their material was not transversely isotropic about the molecular alignment direction, they did not assume $G = H$. They, too, found that better agreement between theory and experiment was achieved by the inclusion of a term corresponding to $a_{xx}$, which they termed $a_i$. However, in their case, the need for this additional term only became apparent in the shear tests; their tensile data were satisfactorily fitted, both as regards yield stress and as regards
the deformation band directions, by putting $a_1 = a_{xx} = 0$, and
the value of $a_{xx}$ which was taken to fit their shear data, did
not significantly affect the fit to their tensile data. In
view of the good fit of the Hill theory to the results for the
yield stress and $Y_1$ for oriented polyvinyl chloride with $G \neq H$
but with $a_{xx} = 0$ as discussed in Section 4.4, it is not surprising
that Brown et al also obtained a good fit with $a_{xx} = 0$. It is
apparent from Table 4.2 that the anisotropy of their material,
as measured by the ratio $\sigma_0/\sigma_{00}$, was more pronounced than that
of the polyvinyl chloride used here, while their internal stress
expressed as a fraction of $\sigma_0$ was lower than that of any of
the polyvinyl chloride. It is presumably also as a consequence
of the small values of $a_{xx}$ in relation to the anisotropy of the material
that caused the inclusion of the internal stress in the yield
criterion to have little effect on the fit of the theory to
the tensile yield data. In an earlier publication, Brown and
Ward (1968a) reported observations of type 2 bands (referred to
as kinky bands by Brown and Ward) in oriented polyethylene tere-
phthalate but Brown et al (1968a) have not compared the directions
of these bands with those predicted by the Hill theory.

The results of Bridle et al, rather than those of Brown et
al, are probably more suitable for comparison with the polyvinyl
chloride results, since the polyethylene terephthalate was pre-
pared by extension at 80°C and a range of extension ratios up to
a maximum of 5.0 was obtained. These workers, too, fitted their
shear stress results to the Hill theory with an internal stress
term included (referred to as $\sigma_0$ by Bridle et al). Bridle et al
assumed that $G = H$, but did not justify this assumption. In
fact, they state that X-ray diffraction evidence showed that there
was no rotational symmetry about the molecular alignment direction. From Table 4.2 it can be seen that although the anisotropy, as indicated by $\sigma_0/\sigma_{90}$, of their polyethylene terephthalate was more pronounced than that of the polyvinyl chloride, the internal stress expressed as a ratio of $\sigma_0$ and $\sigma_{90}$ was of the same order of magnitude as that of the polyvinyl chloride. Since the internal stress was comparatively large in relation to the yield stress at the higher extension ratios, its inclusion in the Hill theory significantly improved the fit of theory and experiment for the type 1 deformation band directions for polyethylene terephthalate. One exception to this was the 2.5 extension ratio, the results of which have been fitted by the present author using the technique discussed in Section 4.3 and found to be best fitted by $a_{xx} = 0$. This could presumably arise from incorrectly assuming that $G = H$. As far as the variation of $a_{xx}$ and the Hill theory parameters are concerned, they found that $a_{xx}$ increased and $H$ decreased with increasing extension ratio. This behaviour is similar to that of polyvinyl chloride. $N,$ with the exception of the material of extension ratio 3.5, decreased with increasing extension ratio, but did not go through a minimum value, as was observed for polyvinyl chloride. The results for the third parameter, $F,$ were rather more scattered and showed no definite trend.

It is also of interest to compare the results of Bridle et al and Brown et al for polyethylene terephthalate of extension ratio 5.0. Despite differences in material preparation, the tensile yield stress results were in very good agreement. However, the anisotropy of the shear yield stress was more pronounced for the results of Bridle et al. It was as a consequence of the difference in shear stress results that the internal stress obtained by Bridle
et al was much larger than that obtained by Brown et al (69 MN m$^{-2}$ as opposed to 12.5 MN m$^{-2}$). For polyvinyl chloride both $\sigma_0$ and $\alpha_{xx}$ were shown to be approximately single valued functions of the birefringence but, although no birefringence results were presented, this cannot be so for oriented polyethylene terephthalate. Assuming that the birefringences were approximately the same, then the difference in internal stress values could be accounted for by the difference in crystallinity reported for the two materials. Bridle et al reported that their material was initially amorphous, although some crystallinity developed during the hot stretching. The polyethylene terephthalate used by Brown et al was reported to be of intermediate crystallinity for this polymer. In Section 4.3 the existence of an internal stress was accounted for by the tendency of the molecules to retract in order to minimise their entropy. However, in crystalline polymers the extended molecules in the crystalline regions are in a minimum energy state. In such cases the tendency of the molecules to be in a minimum entropy condition is outweighed by the minimum energy effect. Thus the molecules no longer tend to retract in crystalline regions, and it might be expected that, for polyethylene terephthalate of higher crystallinity, the internal stress would be smaller, as was the case.

In Section 4.1, it was pointed out that Keller and Rider (1966) based their choice of the Coulomb criterion, equation (4.7), upon the similarities between deformation features in metal single crystals and oriented polyethylene, in that they looked for similarities in yield criteria. However, this argument could be used equally well in selecting the Hill modification of the von Mises criterion as a suitable yield criterion, since
equation (4.10) applies to metal single crystals with all parameters, except \( N \), equal to zero. In fact Rider (unpublished) has attempted to fit the results for oriented polyethylene to the Hill theory but experienced some difficulty in obtaining a good fit. However, he did not attempt to modify the Hill theory to include an internal stress.

Following the success in accounting for the tensile yield behaviour of oriented polyvinyl chloride by using the Hill theory as modified to include an internal stress effect, Rider (private communication) has attempted to fit the results presented by Keller and Rider (1966) to this criterion. It was apparent that this theory could be fitted to both yield stress and band direction results, but, unfortunately, because of lack of data at low values of \( \lambda_0 \), a precise fit of the theory to these results could not be obtained. Nevertheless, sufficient results were obtained to make worthwhile comparisons with the results for oriented polyvinyl chloride, particularly with reference to the geometry of deformation results obtained by Hinton and Rider (1968).

In evaluating the deformation band directions, the plastic strain increments were obtained in terms of the Hill theory parameters and the applied tensile yield stress. The ratios of the shear strain increment, \( \frac{d\varepsilon_{xy}}{d\varepsilon_{xx}} \), to the tensile strain increments, \( \frac{d\varepsilon_{xx}}{d\varepsilon_{yy}} \) and \( \frac{d\varepsilon_{yy}}{d\varepsilon_{xy}} \) are given by

\[
\frac{d\varepsilon_{xy}}{d\varepsilon_{xx}} = \frac{2N \sin \lambda_0 \cos \lambda_0}{H(2 \cos^2 \lambda_0 - \sin^2 \lambda_0)}
\]

\[
\frac{d\varepsilon_{xy}}{d\varepsilon_{yy}} = \frac{2N \sin \lambda_0 \cos \lambda_0}{\left[ -H \cos^2 \lambda_0 + (H + F) \sin^2 \lambda_0 \right]}.
\]

(4.37)
For present purpose the effect of the internal stress has been ignored. At $\lambda_0 = 0^\circ$ and $\lambda_0 = 90^\circ$, it is apparent from equation (4.37) that the ratios become equal to zero, i.e. $d\epsilon_{xy} = 0$, and there is no shear parallel to the molecular alignment. If the Hill theory were applied to the yield stress results for a metal single crystals, all of the parameters except $N$ would be equal to zero. Thus the strain increment ratios in equation (4.37) become infinite i.e. deformation is by simple slip only. In Table 4.3 the ratios of the strain increments are given for all prior extension ratios at $\lambda_0 = 45^\circ$. From these results it can be seen that as far as the ratio $d\epsilon_{xy}/d\epsilon_{yy}$ is concerned the deformation is not affected very much by changing the prior extension ratio. As far as the ratio of $d\epsilon_{xy}/d\epsilon_{xx}$ is concerned, the shear part of the deformation becomes more important. This increase in $d\epsilon_{xy}/d\epsilon_{xx}$ indicates that it becomes more difficult to extend the material in the molecular alignment direction as the prior extension ratio increases. The increasing importance of the shear strain with increasing prior extension ratio is consistent with the results given in Chapter 3 for the deformation geometry of uniformly deformed test pieces. It was shown that, as the prior extension ratio increased, the deformation tended towards simple shear parallel to the molecular alignment direction.

Rider has fitted the results, for the variation of stress as a function of $\lambda_0$, given by Hinton and Rider (1968) to the Hill theory, using the assumption that $G = H$. Since deformation band results were not available, these results could be fitted using a considerable range of values for the parameters. However, the results quoted in Table 4.4 for very different values of $a_{xx}$ indicate that, although the parameters differ in magnitude for
the two values of $a_{xx}$, N was always considerably larger than H or F. Using these values of the parameters the plastic strain increment ratios were calculated for $\lambda_0 = 45^\circ$, and these are quoted in Table 4.4. It can be seen that the values of these ratios are considerably larger than those for oriented polyvinyl chloride. This would be agreement with the observation that the deformation of oriented polyethylene approximates much more closely to simple shear in the molecular alignment direction than does the deformation of oriented polyvinyl chloride. In their paper, Hinton and Rider (1968) attempted to account for the deviation of the molecular alignment direction from the grid of dots, and the change in distance between the dots, by using a shear reorientation model. In this they considered small increments of shear and their effect on the reorientation of the molecular distribution. Their predicted results using this model deviated slightly from those actually measured (see Figure 10 of Hinton and Rider (1968)). Use of the Hill theory suggests that one should also consider increments in tensile as well as shear strains. This might improve the agreement between experimental and predicted results. It seems likely that the Hill theory would fit the results of Hinton and Rider (1968) better than does the Coulomb criterion.

4.6 Bauschinger Effect and the Influence of Hydrostatic Stress on Yielding

One consequence of the inclusion of an internal stress term in the yield criterion is that the material should exhibit a Bauschinger effect i.e. a difference in yield stresses in compression and tension. In fact for test pieces with $\lambda_0 = 0^\circ$ equation (4.20) gives the value of yield stress in tension and compression as:
where \(|\sigma_o^T|\) and \(|\sigma_o^C|\) are the magnitudes of the yield stresses in tension and compression respectively for test pieces with \(\lambda_o = 0^\circ\).

Equation (4.38) predicts that \(|\sigma_o^T| > |\sigma_o^C|\) and Brown et al (1968a) have obtained such results in experiments carried out on oriented polyethylene terephthalate. Similar results for oriented polyvinyl chloride have been obtained by Rawson (private communication). A Bauschinger effect occurs not only for test pieces having \(\lambda_o = 0^\circ\) but also for most other values of \(\lambda_o\). In the particular case of \(\lambda_o = 90^\circ\), the Bauschinger effect is such that

\[
|\sigma_{90}^T| = |\sigma_{90}^C| - \frac{2Ha_{xx}}{(H + F)} \quad (4.39)
\]

Since \(H\), \(F\) and \(a_{xx}\) were always positive (see Figure 4.12), equation (4.39) shows that the compressive yield stress should be larger in magnitude than the tensile yield stress. This is the opposite of the situation at \(\lambda_o = 0^\circ\). No experimental results have been obtained to confirm that \(|\sigma_{90}^C| > |\sigma_{90}^T|\). From the above discussion it is apparent that there must be some value of \(\lambda_o\) at which there is no Bauschinger effect. The precise value of \(\lambda_o\) at which this occurs would depend upon the relative magnitudes of \(H\), \(F\), \(N\) and \(a_{xx}\). If \(a_{xx}\) was zero in equation (4.20), the Bauschinger effect would disappear at all values of \(\lambda_o\).

For unoriented material \(a_{xx} = 0\), and thus, the yield criterion in equation (4.20) predicts that \(|\sigma^C| = |\sigma^T|\). However, it has been shown experimentally by Bauwens (1967) that unoriented
Polyvinyl chloride exhibits an asymmetry in yield stress such that $|\sigma_o^C| > |\sigma_o^T|$. (The term Bauschinger effect is not used to describe this asymmetry since the Bauschinger effect is usually taken to be an asymmetry arising from pre-stressing of the material. The unoriented material would have undergone no such pre-stressing.) The failure of the yield criterion to account for this asymmetry arises from the fact that, in formulating the yield criterion, von Mises, and later Hill, assumed that yielding is unaffected by hydrostatic stresses. In fact Pae and Mears (1968) and Pae et al (1968) have shown that a compressive hydrostatic stress caused an increase in the tensile yield stress of polyethylene, polypropylene, and polytetrafluorethylene. Brown et al (1968a) have also presented evidence that yielding in polymers is affected by hydrostatic stress. It is presumed that this effect still occurs in oriented polymers, and must have been outweighed by the internal stress effect in the results for oriented polyethylene terephthalate and oriented polyvinyl chloride as mentioned earlier. In fact Rawson (private communication) has carried out experiments on oriented polyvinyl chloride in which $|\sigma_o^C| - |\sigma_o^T|$ decreased as the extension ratio increased, until $|\sigma_o^T| > |\sigma_o^C|$ when the internal stress effect outweighed the hydrostatic stress effect.

The following simple picture indicates how the effect of hydrostatic stress gives rise to an asymmetry in yield stresses in the unoriented material. A uniaxial stress can be resolved into a hydrostatic stress and two shear stresses. The hydrostatic stress gives rise to an elastic volume decrease in uniaxial compression and an elastic volume increase in uniaxial tension. The volume change, $\Delta V$, is given by:

$$\Delta V = \frac{(1 - 2\nu)\sigma}{E},$$  \hspace{1cm} (4.40)
where $\sigma$ is the uniaxial stress, taken positive in tension, $E$ is Young's modulus and $\nu$ is Poisson's ratio. As discussed in Section 4.3 yielding occurs by the relative movement of molecular segments which is hindered by interaction between neighbouring segments. In compression the elastic volume decrease causes the molecular segments to be closer together than they would be in tension when there is a volume increase. This closer packing increases the interaction between segments, and hence, a larger applied stress is required to overcome viscoelastic stresses opposing molecular movement. The opposite argument would apply for tensile deformation, and hence, the yield stress would be expected to be larger in compression than in tension. The yielding of metals is not affected to the same extent by hydrostatic stresses.

Whitney and Andrews (1967) have suggested that this is because glassy polymers yield at much higher stresses relative to their bulk moduli than do metals. Thus volume changes at yield would be much greater for polymers than for metals.

If it is assumed that the hydrostatic stresses have the effect of changing the free volume, hence making the relative movement of molecular segments easier or more difficult, the material can be considered to undergo either a softening or hardening. This can be represented by a contraction or expansion of the yield surface in principal stress space, i.e. $k^2$ in equation (4.8) is pressure dependant. Nadai (1950) has interpreted this pressure dependence by saying that the octahedral shearing stress at yield is a function of the normal stress acting on the octahedral plane. He suggested two possible modifications of the von Mises criterion. In one case the yield surface is a circular cone, the axis of which coincides with $\sigma_1 = \sigma_2 = \sigma_3$ and the criterion becomes
\[(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2 = \]

\[
\frac{2}{3} [c_o (\sigma_1 + \sigma_2 + \sigma_3) - c_1]^2 ,
\]  

(4.41)

where \(c_o\) and \(c_1\) are given by

\[
c_o = \frac{-\sqrt{3} \left( |\sigma_C| - |\sigma_T| \right)}{|\sigma_C| + |\sigma_T|} \quad \text{and} \quad c_1 = \frac{-2\sqrt{3} |\sigma_C||\sigma_T|}{|\sigma_C| + |\sigma_T|} .
\]

where \(|\sigma_C|\) and \(|\sigma_T|\) are the magnitudes of the yield stresses in uniaxial tension and uniaxial compression respectively. Another form suggested by Nadai is

\[
\sigma_1 + \sigma_2 + \sigma_3 = 3a_1 + 9a_2 \left[ (\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2 \right],
\]

(4.42)

where

\[
a_1 = \frac{|\sigma_C||\sigma_T|}{3(|\sigma_C| - |\sigma_T|)} \quad \text{and} \quad a_2 = -\frac{1}{18(|\sigma_C| - |\sigma_T|)} .
\]

Equation (4.42) is the equation of a parabola of revolution about \(\sigma_1 = \sigma_2 = \sigma_3\). Schleicher (1926) has also discussed possible modifications of yield criteria along the lines discussed above. He based his discussions on the Beltrami yield criterion. This criterion states that yield occurs when the total elastic energy stored in the material reaches a critical value. This is not the same as the physical interpretation of the von Mises criterion which is concerned only with the elastic energy associated with the change in shape of the material, and not the change in volume. In the case of an incompressible material the two criteria are equivalent. Schleicher effectively assumed that
where $A$ is the total elastic energy stored at yield and $f(\sigma_1 + \sigma_2 + \sigma_3)$ is some function of the mean normal stress. By considering the results of von Kármán and Böker (see Nadai (1950) Chapter 17) for compressive and torsional tests on marble under the influence of a hydrostatic stress, Schleicher showed that these tests fitted equation (4.43) and gave the same form for $f(\sigma_1 + \sigma_2 + \sigma_3)$. When $A$ was taken as the elastic energy associated with the change in shape only, a plot of $f(\sigma_1 + \sigma_2 + \sigma_3)$ for the above results showed rather more scatter than when considering the total elastic energy.

It is interesting that, whilst it is generally accepted that rock, and in particular marble, obeys a Coulomb criterion (see Jaeger (1962) p. 154), Schleicher showed that marble obeys a pressure dependant form of criterion, similar to that of von Mises.

With this in mind, an attempt has been made to see if the results of Bowden and Jukes (1968), which they fitted to a Coulomb criterion, could similarly be fitted to the pressure dependant von Mises criterion in equation (4.41). They applied a tensile stress, $\sigma_2$, to strips of polymethylmethacrylate and then applied a compressive stress, $\sigma_1$ (taken positive in tension), perpendicular to the plane of the strip, and at right angles to $\sigma_2$, by means of two anvils. In analysing the results they recognised that the frictional effects at the anvils would constrain the material, and they made corrections for this effect on $\sigma_1$. However, they ignored any effects arising from the constraints due to such frictional effects on any strains at right angles to $\sigma_1$ and $\sigma_2$. An additional constraining effect would arise from the fact that the adjacent material outside the compressive anvils would be under the action of a tensile stress only and would thus deform elastically in a
different way to the material under the anvils. If it is assumed
that these constraints caused the tensile elastic strain at
right angles to $\sigma_1$ and $\sigma_2$ to be zero, this would give rise to a
third principal stress, $\sigma_3$, given by

$$\sigma_3 = \nu(\sigma_1 + \sigma_2),$$

(4.44)

where $\nu$ is Poisson's ratio. If $\nu = 0.5$, and equation (4.44) is
substituted in equation (4.41), the yield criterion becomes

$$\sigma_1 - \sigma_2 = c_0(\sigma_1 + \sigma_2) - 2c_1/\sigma_3,$$

(4.45)

This gives a linear relationship between $\sigma_1$ and $\sigma_2$, which is exactly
the result obtained by Bowden and Jukes. Thus, in this particular
case the Coulomb and pressure dependent von Mises criterion have a
similar form. For polymers $\nu \neq 0.5$, and hence, equation (4.45) is
not strictly correct. However, if there are no constraints, $\sigma_3 = 0$,
and equation (4.41) gives an ellipse for the plot of $\sigma_1$ against $\sigma_2$.
In fact, over the stress range for which their material yielded, the
linearly related results of Bowden and Jukes were fitted by the pre­
sent author quite closely by equation (4.41) with $\sigma_3 = 0$. Thus, even
if the material is not fully constrained and $\nu \neq 0.5$, the pressure
dependent von Mises criterion would still be fitted quite closely
to the yield stress results for polymethylmethacrylate. Since
Bowden and Jukes (1968) have used similar experiments to show that
polystyrene, amorphous polyethylene terephthalate and rigid
polyvinyl chloride obey the Coulomb criterion, it seems likely that
the yielding behaviour of these materials could also be described
by the pressure dependent von Mises criterion.
The von Mises yield criterion, as originally formulated, along with the assumption of zero tensile strain parallel to the band, predicts that deformation bands formed in strip specimens of isotropic material should be inclined at 54.7° to the stress axis for both uniaxial tension and compression. However, Argon et al. (1968) have reported that, for polystyrene with a small amount of molecular orientation, bands were observed to be formed at $\gamma = 52^\circ$ and $38^\circ$ for uniaxial tensile and compressive deformation respectively. The stress axis was parallel to the molecular alignment direction. Although no compressive tests have been carried out on unoriented polyvinyl chloride, it is not unreasonable to assume that the deformation bands would not be inclined at $\gamma = 55^\circ$, particularly since the results for deformation bands in tensile deformation were very nearly the same for polystyrene and polyvinyl chloride. In view of this, the effect of hydrostatic stress in the yield criterion on the deformation band directions has been investigated.

The procedure used to evaluate the band directions was that used by Nadai (1950) (p. 325). Consider a strip test piece in which a deformation band has formed, as shown in Figure 4.16. The direction of the applied stress, $\sigma$, is indicated and the band is inclined at an angle, $\beta$, to a plane which is perpendicular to the tensile axis. The $x$ and $y$ axes are defined to be respectively parallel and perpendicular to the band direction in the plane of the sheet. The $z$-axis is perpendicular to the plane of the test piece. For plane stress the yield criterion in terms of the stress components measured relative to the Cartesian axes, becomes

\[ \sigma_x^2 - \sigma_x \sigma_y + \sigma_y^2 + 3\tau_{xy}^2 = \left[ c_0 (\sigma_x + \sigma_y) - c_1 \right]^2 / 3 \]  

(4.46)
The plastic tensile strain, $\varepsilon_y$, parallel to the band direction is zero and for small strains is given by

$$\varepsilon_y = \phi \left( \sigma_y - \sigma_x / 2 \right) = 0 \quad (4.47)$$

where $\phi$ is a constant (see Nadai (1950) equation (16.14)). From equation (4.47), it is apparent that $2\sigma_y = \sigma_x$ and equation (4.46) becomes

$$3\sigma_x^2 + 12 \tau_{xy}^2 = 4 \left[ c_o \frac{3\sigma_x}{2} - c_1 \right] / 3 \quad (4.48)$$

$\sigma_x$ and $\tau_{xy}$ are given in terms of $\sigma$ and $\beta$ by

$$\sigma_x = \sigma \cos^2 \beta \quad (4.49)$$

$$\tau_{xy} = \sigma \cos \beta \sin \beta \quad (4.50)$$

Substituting these values in equation (4.48) gives

$$\sigma^2 (3 \cos^4 \beta + 12 \cos^2 \beta \sin^2 \beta - 3c_o^2 \cos^4 \beta) + 4c_o c_1 \cos^2 \beta$$

$$- 4c_1^2 / 3 = 0 \quad (4.50)$$

Solving this quadratic gives

$$|\sigma_T| = 2c_1 \left[ c_o \cos \beta + (4 - 3 \cos^2 \beta)^{1/2} \right] \left[ 12 \cos \beta$$

$$- 3 \cos^3 \beta \left( 3 + c_o^2 \right) \right]^{-1} \quad (4.51)$$

$$|\sigma_c| = 2c_1 \left[ c_o \cos \beta + (4 - 3 \cos^2 \beta)^{1/2} \right] \left[ 12 \cos \beta$$

$$- 3 \cos^3 \beta \left( 3 + c_o^2 \right) \right]^{-1} \quad (4.52)$$

If $c_o = 0$, $|\sigma_c|$ and $|\sigma_T|$ become equal and the same as the value given by the unmodified von Mises criterion. In order to find the value of $\beta$ at which the band will form, it is necessary to find
the value of $\beta$ for which $|\sigma_T|$ and $|\sigma_c|$ are at a minimum, that is at which

$$\frac{d |\sigma_T|}{d\beta} = 0 = \frac{d |\sigma_c|}{d\beta} \quad .$$

(4.53)

In general, the value of $\beta$ will be different in compression and tension. From equation (4.51) and (4.52), $\cos \beta$ must satisfy the following condition if $d |\sigma_T|/d\beta = 0$ and $d |\sigma_c|/d\beta = 0$:

$$\cos^4 \beta 6(c_o^2 + 3) + \cos^3 \beta (4 - 3 \cos^2 \beta) \frac{1}{2} c_o (c_o^2 + 3)
- \cos^2 \beta 12(c_o^2 + 3) + 16 = 0 \quad ,$$

(4.54)

$$\cos^4 \beta 6(c_o^2 + 3) - \cos^3 \beta (4 - 3 \cos^2 \beta) \frac{1}{2} c_o (c_o^2 + 3)
- \cos^2 \beta 12(c_o^2 + 3) + 16 = 0 \quad .$$

(4.55)

Equation (4.54) applies for yielding in tension and equation (4.55) applies to yielding in compression. If $c_o = 0$, the two equations become the same and one of the roots $\frac{2}{3} \cos \beta = (2/3)^{1/4}$, corresponding to the minimum value of $\sigma$. This is the same result as that obtained for the von Mises criterion (see Nadai (1950) p. 325) and gives $\gamma$ to be $54.7^0$. Using the result that $|\sigma_c|/|\sigma_T| = 1.3$ obtained by Bauwens (1967) for unoriented polyvinyl chloride, and using the result that $\sigma_T = 60.7 \text{ MN m}^{-2}$ for the material used here, the following results were obtained:

$$c_o = 0.266 \quad \text{ and } \quad c_1 = 119 \text{ MN m}^{-2} .$$

(4.56)

With these values of the constants, $\beta$ was found to be $29.5^0$ for tensile deformation and $40.5$ for compressive deformation. The
corresponding values of $Y$ are $60.5^\circ$ and $49.5^\circ$ for tension and compression respectively. Thus the hydrostatic stress term causes $Y$ to become larger than $55^\circ$ in tension and to decrease in compression. The result, that $Y = 55^\circ$ for unoriented polyvinyl chloride, is not consistent with this effect of hydrostatic stress on the band direction. The results obtained by Argon et al (1968) are not consistent with this theory since the band direction in tension was $52^\circ$, i.e. smaller than $55^\circ$ rather than larger, but in compression was $38^\circ$, which deviates considerably from the value expected with no hydrostatic stress effect.

In using equation (4.45) to give the plastic strain, $\varepsilon_y$, it was implicitly assumed that there was no plastic volume change, i.e. $\varepsilon_x + \varepsilon_y + \varepsilon_z = 0$. If, however, one writes equation (4.41) in the form $f(\sigma_{ij}) = \text{constant}$ and apply equation (4.14) to evaluate the plastic strain increments, then a plastic volume change is obtained. Dividing both sides of equation (4.41) by 

$$[c_o (\sigma_x + \sigma_y + \sigma_z) - c_1]^2$$

yields

$$\left( \sigma_x^2 + \sigma_y^2 + \sigma_z^2 - \sigma_x \sigma_y - \sigma_y \sigma_z - \sigma_z \sigma_x + 3\tau_{xy}^2 + 3\tau_{yz}^2 + 3\tau_{zx}^2 \right)$$

$$[c_o (\sigma_1 + \sigma_2 + \sigma_3) - c_1]^{-2} = 1/3 .$$

(4.57)

In the experiments discussed here, uniaxial tension or compression only is used, and for an isotropic material the $x$-axis can be chosen to coincide with the stress axis, in which case, $\sigma_y = \sigma_z = \tau_{xy} = \tau_{zy} = 0$. Using this condition and equation (4.14) and (4.57), the plastic strain increments are given by

$$d\varepsilon_{xx} = (2\sigma_x [c_o \sigma_x - c_1]^{-2} - 2c_o \sigma_x^2 [c_o \sigma_x - c_1]^{-3}) dA ,$$

$$d\varepsilon_{yy} = d\varepsilon_{zz} = (- \sigma_x [c_o \sigma_x - c_1]^{-2} - 2c_o \sigma_x^2 [c_o \sigma_x - c_1]^{-3})dA .$$

(4.58)
The relative plastic volume change, \( \text{d}V^P \), is given by
\[
\text{d}V^P = \text{d}e_{xx} + \text{d}e_{yy} + \text{d}e_{zz} = -6c_o \sigma_x^2 |c_o \sigma_x - c_1|^{-3} \text{d}A.
\]

Using the values of \( c_o \) and \( c_1 \) given in equation (4.56) for polyvinyl chloride, the following values are obtained for the plastic strain increments at the tensile yield point:
\[
\text{d}e_{xx} = (0.107 + 0.014)\text{d}A = 0.121 \text{d}A,
\]
\[
\text{d}e_{zz} = \text{d}e_{yy} = (-0.054 + 0.014)\text{d}A = -0.040 \text{d}A,
\]
\[
\text{d}V^P = +0.042 \text{d}A.
\]

In compression the plastic strain increments are
\[
\text{d}e_{xx} = -(0.083 - 0.011) \text{d}A = -0.072 \text{d}A,
\]
\[
\text{d}e_{yy} = +(0.042 + 0.011) \text{d}A = 0.053 \text{d}A,
\]
\[
\text{d}V^P = 0.033 \text{d}A.
\]

One rather interesting feature of these results is that, in both tension and compression, a plastic volume increase is given. This is perhaps not surprising for tensile deformation, but it is unexpected for compressive deformation, for which there is an elastic volume decrease. There is, however, some evidence for a plastic volume increase during compressive deformation. Whitney and Andrews (1967) have measured such a plastic volume increase. They measured the strain in the direction of the applied stress, and also the plastic volume increase. The results for polyvinyl chloride, given in equation (4.61), give the volume change to be approximately 45% of the strain in the direction of the applied stress, whereas
Whitney and Andrews (1967) found this to range from 5% to 15% for a number of polymers, not including polyvinyl chloride. Although the results predicted using equations (4.58) and (4.59) are somewhat larger than those actually measured, the above discussion does indicate the importance of allowing for the plastic volume change in evaluating the band angles.

The strain increments in equation (4.58) have been used in equation (4.13) to evaluate the band angle, $Y$. For polyvinyl chloride deformed in tension and compression, the values of $Y$ were found to be $60.2^\circ$ and $49.6^\circ$, respectively. These values are almost identical with those obtained assuming no plastic volume change, but, since in this case a plastic volume change does occur, this agreement seems likely to be fortuitous. Since these values are the same, the same criticisms can be made about them, as before. It seems likely that any modification of the von Mises criterion, which includes a hydrostatic stress term, is going to cause the values of $Y$ in tension and compression to be different and not equal to $55^\circ$. Thus it will be difficult to account for $Y$ being equal to approximately $55^\circ$ for both polyvinyl chloride and polystyrene, no matter what approach is used. As far as the results for polystyrene are concerned, Argen et al (1968) successfully accounted for differences in both yield stresses and band directions for tensile and compressive deformation by using a Coulomb criterion.

In this section it has been shown that, for a number of polymers, yield stress results, which can be fitted to a Coulomb criterion, can also be fitted by a pressure dependant von Mises criterion. However, it does seem that the band direction results of Argen et al (1968) for polystyrene can only be fitted to the Coulomb criterion. In order to determine which of the criteria is in fact correct, it
is apparent that further investigation should be carried out on the yielding of unoriented polymers under the action of biaxial or triaxial stress systems. If in fact the pressure dependant von Mises yield criterion is the correct one, it is also necessary to evaluate what form the pressure dependence should take. In addition, it would also be necessary to investigate and account for the directions of deformation bands formed in uniaxial tension and compression.

In order to extend the pressure dependant von Mises yield criterion to apply to anisotropic materials, modifications must be made as discussed in sections 4.2 and 4.3. The yield criterion then becomes:

\[
H(\sigma_{xx} - a_{xx} - \sigma_{yy})^2 + F(\sigma_{yy} - \sigma_{zz})^2 + G(\sigma_{zz} - \sigma_{xx} + a_{xx})^2
\]
\[+ 2L\tau_{yz}^2 + 2M\tau_{zx}^2 + 2N\tau_{xy}^2 = 2\left[c_2 (\sigma_{xx} - a_{xx} + \sigma_{yy} + \sigma_{zz})ight]^2 - 1]^{2/3} .
\] (4.62)

The constant \( c_1 \) has been incorporated in the other constants in equation (4.62). Other than for the inclusion of \( a_{xx} \), the right-hand side of equation (4.62) has been assumed to be unaffected by anisotropy. If the critical strain criterion as given in equation (4.28) is considered, a similar modification for the effect of hydrostatic stress would have to be made. It would be interesting to see if the inclusion of pressure dependence in the Hill theory improves the fit of the theory to the measured values of \( Y_2 \).

4.7 Possible Modifications of the Coulomb Criterion

The Hill theory modification of the von Mises yield criterion was fitted quite accurately to the yield stress data for oriented
polyvinyl chloride. It was only as a consequence of its failure to account for the deformation band directions that a further modification was made by including an internal stress term. Similarly the Coulomb criterion could be fitted to the yield stress data of oriented polyethylene but could not account for the band directions. However, instead of considering possible modifications of the Coulomb criterion for polyvinyl chloride, use has been made of the modified Hill theory as discussed in Section 4.5. In view of the considerable amount of evidence, discussed at the beginning of this Chapter and in the previous section, which indicated that unoriented polymers might yield according to the Coulomb criterion, it seems worthwhile considering possible modifications of this criterion.

As discussed earlier, the Coulomb criterion takes the following form,

$$\tau = S_o - \mu \sigma$$  \hspace{1cm} (4.63)

where $S_o$ and $\mu$ are constants for the material, and $\tau$ and $\sigma$ are the shear and normal stresses respectively acting on the plane on which yield occurs. $S_o$ is usually referred to as the shear strength of the material. By suitably altering the magnitudes of the stresses, for a particular stress system, yield can occur on any plane in the isotropic material. However, since they only considered the shear stress and normal stress acting on a particular plane, i.e. that containing the molecular alignment direction and the normal to which was in the plane of the strip test piece, Keller and Rider (1966) implicitly assumed that failure would occur on that plane. This, indeed, was not the case since it was reported that the deformation bands were not parallel to the molecular alignment direction. Since failure could only occur on one plane, the shear strength in all other directions was
effectively considered to be infinite. An alternative approach is that of Jaeger (1960) who considers the case of an isotropic material containing a plane of weakness. It can then be shown that for some stress systems failure will take place in the plane of weakness. For other stress systems failure will take place in directions determined by the Coulomb theory for the isotropic material and these will intersect the plane of weakness. A second suggestion by Jaeger (1960) which seems more realistic for oriented polymers is that the shear strength is anisotropic. In particular, he assumed that, for rocks, the shear strength, $S$, in a plane inclined at an angle $\omega$ to the plane of minimum shear strength, is given by

$$S = S_0 - S_1 \cos 2\omega,$$

where $S_0$ and $S_1$ are constants characterising the anisotropy of the material. Thus the shear strength varies between minimum and maximum values of $S_0 - S_1$ and $S_0 + S_1$ at $\omega = 0^\circ$ and $\omega = 90^\circ$ respectively. However, Brown et al (1968), Bridle et al (1968) and Robertson and Joynson (1969) have shown that for a number of oriented polymers, minima in shear strength occur in directions given by $\omega = 0^\circ$, $90^\circ$ and $180^\circ$, where $\omega = 0^\circ$ and $\omega = 180^\circ$ correspond to the molecular alignment direction. Maxima in shear strength occur at $\omega = 45^\circ$ and $\omega = 135^\circ$. Thus equation (4.64) is not appropriate for describing the shear strength anisotropy of oriented polymers. At this stage one is not in a position to say what form the anisotropy should take and so for the present it will be considered to be some arbitrary function, $S(\omega)$ of $\omega$.

The form of the criterion used by Keller and Rider (1966) for tensile tests is given by
\[ \sigma_\lambda \sin \lambda_o \cos \lambda_o + \mu \sigma_\lambda \sin^2 \lambda_o = S, \quad (4.65) \]

where \( S \) and \( \mu \) are constants. For the anisotropic Coulomb criterion the equivalent equation is

\[ \sigma_\lambda \sin Y \cos Y + \mu \sigma_\lambda \sin^2 Y = S(\lambda_o - Y). \quad (4.66) \]

It should be realised that the shear and normal stresses are those acting on the plane of failure, i.e. in the deformation band direction, hence the use of \( Y \) on the left-hand side of equation (4.66). From symmetry considerations it might be expected that \( S(\omega) = S(-\omega) \). If this is indeed the case, then it is easily shown that equation (4.66) cannot satisfactorily account for the deformation behaviour of oriented polyethylene. In the particular case \( \omega \), the maximum shear stress acts on the plane of minimum shear strength, i.e. the plane containing the molecular alignment direction. Thus, if it were not for the normal stress effect, failure would occur on this plane. Instead, failure will occur on some plane inclined at an angle to the molecular alignment direction. For two planes equally inclined at an angle \( \omega \) on opposite sides of the molecular alignment direction, the shear stress on the plane and the shear strengths will be the same for each of the planes. Thus, it is the normal stress term which will determine on which side of the molecular alignment direction the deformation band will form.

It is apparent from equation (4.66) that yield will occur on the plane for which \( \sigma_\lambda \sin^2 Y \) is the larger. This will occur when \( Y = \lambda_o + \omega \) as opposed to \( Y = \lambda_o - \omega \). Therefore, the deformation band will form such that \( Y > \lambda_o \). However, Keller and Rider (1966) have shown that yield occurs such that \( \lambda_o > Y \), thus indicating that this criterion is still not appropriate. However, it is possible to modify the Coulomb criterion to include an internal
stress term as for the Hill theory. The diagrams in Figure 4.17 indicate that such a modification would favour the formation of deformation bands such that \( \lambda > Y \). For \( Y > \lambda \), as shown in Figure 4.17(a), shear parallel to the band tends to extend the molecules and this is opposed by the internal stress. However, for \( \lambda > Y \), Figure 4.17(b), shear parallel to the band tends to shorten the molecules, this being aided by the internal stress.

The effect of the internal stress has also been used by Brown et al (1968a) and Bridle et al (1968) to account for the inequality of the maximum shear strengths at \( \omega = 45^\circ \) and \( \omega = 135^\circ \). The internal compressive stress can be included in the yield criterion by considering it to be a compressive stress, acting in the molecular alignment direction, which can be resolved into shear and normal stresses acting on the plane of failure. The yield criterion then becomes

\[
\tau + a_{xx} \sin \omega \cos \omega + \mu(\sigma - a_{xx} \sin^2 \omega) = S(\omega) .
\] (4.67)

For tensile tests equation (4.67) gives

\[
\sigma \sin Y \cos Y + a_{xx} \sin (\lambda - Y) \cos (\lambda - Y) + \mu[\sigma \sin^2 Y - a_{xx} \sin^2 (\lambda - Y)] = S(\lambda - Y).
\] (4.68)

At this stage no assumptions will be made concerning the form of the function \( S(\omega) \), but from symmetry considerations it may be reasonably assumed that \( S(\omega) = S(-\omega) \). Any asymmetry in the shear yield stress as measured by Brown et al arises from the effect of the internal stress. The exact form of \( S(\omega) \) and the magnitudes of \( \mu \) and \( a_{xx} \) could be evaluated from shear and tensile tests as carried out by Brown et al and Bridle et al.
In using the angles $Y$ and $\lambda^q$ in equation (4.68) it is assumed that yield will occur on a plane whose normal is in the plane of the sheet test piece. Instead, yield could be considered to occur on any plane in the material. In order to account for the symmetrical thickness decrease in deformation bands discussed in Chapter 3, yield can be considered to occur on two planes, the normals of which are not in the plane of the sheet, but which are in mirror symmetry relative to the plane of the sheet. However, equation (4.68) will no longer be correct since $Y$ will not be related to the direction and plane of failure, but will give the direction of the line of intersection of the failure plane and the plane of the sheet. Thus, $Y$ could not be used in equation (4.68). In addition the shear strength would have to be evaluated for all planes in the material.

In view of the difficulties discussed above no attempt has been made to fit equation (4.68) to the observed yielding behaviour of oriented polyvinyl chloride.

4.8 Concluding Remarks

In this section the important aspects of the results and discussions given in previous sections will be summarized, and suggestions will be made for possible future lines of investigation. The important results were as follows:

1. The tensile yield behaviour of oriented polyvinyl chloride, both as regards yield stresses and the directions of the deformation bands, was fitted by the Hill modification of the von Mises yield criterion, provided an internal stress was taken into account.
This internal stress acted in compression in the molecular alignment direction. Although the inclusion of the internal stress term improved the fit between the measured deformation band directions and those predicted by the Hill theory, there was still some discrepancy between predicted and measured values of $Y_2$. This discrepancy is considered to be of particular significance in view of the fact that, at yield, type 2 bands were observed to form before type 1 bands.

2. The existence of the internal stress has been accounted for by the tendency of the molecules to retract back to a random configuration. The internal stress was set up by the extension of the polymer at elevated temperatures, and was frozen into the material by cooling to below $T_g$ at constant length under load. The results obtained are consistent with this model. The internal stress was uniquely related to the birefringence independent of the temperature at which the extension was carried out. Also, the internal stress, with one exception, was found to be equal, within the limits of experimental error, to the stress applied to the material during hot stretching. Comparison of the results of Brown et al (1968a) and Bridle et al (1968) suggests that crystallinity might have an important effect on the magnitude of the internal stress.

3. The parameters in the Hill theory were found to vary as a function of prior extension ratio and birefringence in the manner shown in Figure 4.12. The variation of these parameters led to the prediction that the shear yield stress, $\tau_{xy}$, for shear parallel to the molecular alignment direction should go through a maximum as the extension ratio increased.
4. It has been shown that the critical strain criterion, as discussed by Robertson (1964) has a number of pleasing features. It can be applied to both isotropic and anisotropic materials without any fundamental alterations, such as the arbitrariness of inclusion of constants. Use of the elastic compliances measured by Raumann (1963) for oriented polyethylene terephthalate has shown that the critical strain criterion can account for the observed variation of yield stress as a function of both birefringence and $\lambda_0$. In addition, the theory gives the correct relationship between yield stress and modulus, and also predicts a maximum in the shear yield stress for shear parallel to the molecular alignment direction. The important practical application of this theory is that the yielding behaviour can be predicted by measuring elastic compliances. In the case of the Hill theory the parameters have to be evaluated by experiments. Since the variation of elastic compliances as a function of birefringence can be predicted on the basis of an affine deformation model, the variation of yield stress can also be predicted indirectly through the variation of the compliances.

5. It has been suggested that the anisotropy of the yield stresses could be predicted more directly using an aggregate model similar to that which has been used by Bishop and Hill (1951a and b) to account for the yield behaviour of polycrystalline metals.

6. The difference in yield stress for unoriented polymers deformed in tension and compression can only be accounted for by the Coulomb criterion or a pressure dependent form of the von Mises criterion. It has been shown that the results of Bowden and Jukes (1968), which these authors fitted to a Coulomb criterion, can also
be accounted for by a pressure dependant form of the von Mises criterion. However, some difficulty has been experienced in attempting to account for the observed deformation and directions using the pressure dependent von Mises criterion. It has been shown how this criterion leads to the prediction of a plastic volume increase for both compressive and tensile deformation. Such a plastic volume increase in compression has been measured by Whitney and Andrews (1967).

7. Finally, if unoriented polymers are found to obey a Coulomb criterion, a method has been discussed for extending this criterion to anisotropic materials. This form of the criterion is considered more suitable than that used by Keller and Rider (1966) and Hinton and Rider (1968).

In view of the results discussed above it is apparent that it is necessary to determine whether unoriented polymers yield according to a Coulomb or pressure dependent von Mises criterion. It is important to decide this before investigating the yielding of oriented polymers with the added complication of anisotropy. The investigation will require the study of yielding under the action of biaxial and triaxial stress systems. If the polymers are found to yield according to a pressure dependent von Mises criterion, it will be necessary to determine the form of the pressure dependence.

If the unoriented polymers are found to obey a Coulomb criterion, then the yielding of the oriented material should be accounted for in terms of the criterion discussed in Section 4.7.

If the pressure dependent form of the von Mises yield criterion is obeyed, it will be necessary to account for the
obscured deformation band directions. In particular, it might be interesting to investigate volume changes which occur during plastic deformation in tension or compression.

In extending the von Mises criterion to account for the yielding of oriented polymers, it would seem worthwhile investigating the relative merits of the Hill theory and the critical strain criterion. In using both of these criteria it would be necessary to modify them to include both internal stress and pressure dependence. In investigating the critical strain criterion, it would be essential to measure the elastic compliances of the material. It would be particularly interesting if the directions of type 2 bands could be accounted for using either of these criteria.

It was suggested earlier that the internal stress was a unique function of both birefringence and true stress during the original extension, for both stretching temperatures. This is to some extent inconsistent since molecular network theories predict that the true stress at a given birefringence should be different for different temperatures. (The birefringence in the molecular network theories is that at the stretching temperature, whereas the birefringence referred to here is the residual birefringence measured at room temperature.) The inconsistency arises from the large errors involved in determining $a_{xx}$. Further investigation into the relationship between $a_{xx}$ and both the birefringence and true stress during stretching would be of interest. The effect of other factors, such as crystallinity, would also be worth further study.

Although the yielding behaviour of oriented polyvinyl chloride has been satisfactorily accounted for using the Hill theory with an internal stress term included, the yielding behaviour, both as
regards the continuum mechanical approach and the molecular mechanisms, is not well understood. There clearly remain many possibilities for further investigation into the yielding of polymers.
Table 4.1

Values of the Hill theory parameters $H$, $F$, and $N$ evaluated from the yield stress results for Vybak of extension ratio 3.3 using different values of $a_{xx}$.

<table>
<thead>
<tr>
<th>$a_{xx}$ MN m$^{-2}$</th>
<th>$H \times 10^4$ mm$^4$ N$^{-2}$</th>
<th>$F \times 10^4$ mm$^4$ N$^{-2}$</th>
<th>$N \times 10^4$ mm$^4$ N$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.30</td>
<td>3.14</td>
<td>3.67</td>
</tr>
<tr>
<td>4.9</td>
<td>0.33</td>
<td>3.06</td>
<td>3.74</td>
</tr>
<tr>
<td>9.8</td>
<td>0.36</td>
<td>2.94</td>
<td>3.82</td>
</tr>
<tr>
<td>14.7</td>
<td>0.39</td>
<td>2.79</td>
<td>3.90</td>
</tr>
<tr>
<td>19.6</td>
<td>0.42</td>
<td>2.60</td>
<td>3.98</td>
</tr>
<tr>
<td>24.5</td>
<td>0.46</td>
<td>2.36</td>
<td>4.04</td>
</tr>
<tr>
<td>29.4</td>
<td>0.51</td>
<td>2.07</td>
<td>4.11</td>
</tr>
<tr>
<td>34.3</td>
<td>0.56</td>
<td>1.71</td>
<td>4.18</td>
</tr>
</tbody>
</table>
Values of stress ratios, $\sigma_0/\sigma_{90}$, $a_{xx}/\sigma_0$, and $a_{xx}/\sigma_{90}$ for oriented polyvinyl chloride and oriented polyethylene terephthalate of different extension ratios. The results for oriented polyethylene terephthalate are those of Bridle, Buckley, and Scanlan (1968) and Brown, Duckett and Ward (1968a).

### Polyvinyl Chloride

<table>
<thead>
<tr>
<th>Extension Ratio</th>
<th>$\sigma_0/\sigma_{90}$</th>
<th>$a_{xx}/\sigma_0$</th>
<th>$a_{xx}/\sigma_{90}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.0</td>
<td>1.4</td>
<td>0.06</td>
<td>0.08</td>
</tr>
<tr>
<td>3.3</td>
<td>2.4</td>
<td>0.23</td>
<td>0.55</td>
</tr>
<tr>
<td>3.7</td>
<td>2.8</td>
<td>0.27</td>
<td>0.8</td>
</tr>
</tbody>
</table>

### Polyethylene Terephthalate

<table>
<thead>
<tr>
<th>Extension Ratio</th>
<th>$\sigma_0/\sigma_{90}$</th>
<th>$a_{xx}/\sigma_0$</th>
<th>$a_{xx}/\sigma_{90}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>1.75</td>
<td>0.051</td>
<td>0.09</td>
</tr>
<tr>
<td>3.5</td>
<td>3.23</td>
<td>0.174</td>
<td>0.56</td>
</tr>
<tr>
<td>4.25</td>
<td>4.14</td>
<td>0.262</td>
<td>1.09</td>
</tr>
<tr>
<td>5.0</td>
<td>6.10</td>
<td>0.192</td>
<td>1.17</td>
</tr>
<tr>
<td>5.0*</td>
<td>6.04</td>
<td>0.036</td>
<td>0.22</td>
</tr>
</tbody>
</table>

*Results of Brown, Duckett and Ward (1968a).
Table 4.3

Values of the strain increment ratios for polyvinyl chloride of different extension ratios and for polyethylene using different values of $a_{xx}$. The strain increments were evaluated from the Hill theory parameters as discussed in the text.

Polyvinyl Chloride

<table>
<thead>
<tr>
<th>Extension Ratio</th>
<th>$\frac{\Delta \varepsilon_{xy}}{\Delta \varepsilon_{xx}}$</th>
<th>$\frac{\Delta \varepsilon_{xy}}{\Delta \varepsilon_{yy}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>6.0</td>
<td>6.0</td>
</tr>
<tr>
<td>2.0</td>
<td>8.6</td>
<td>4.0</td>
</tr>
<tr>
<td>3.3</td>
<td>15.9</td>
<td>3.9</td>
</tr>
<tr>
<td>3.7</td>
<td>23.4</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Polyethylene

<table>
<thead>
<tr>
<th>$a_{xx}$ [Kg mm$^{-2}$]</th>
<th>$\frac{\Delta \varepsilon_{xy}}{\Delta \varepsilon_{xx}}$</th>
<th>$\frac{\Delta \varepsilon_{xy}}{\Delta \varepsilon_{yy}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>60</td>
<td>-85</td>
</tr>
<tr>
<td>20</td>
<td>730</td>
<td>93</td>
</tr>
</tbody>
</table>
Figure 4.1 Graph showing the variation of nominal yield stress as a function of $\lambda_0$, as given by equation (4.1) (continuous curves). The curves are fitted to the experimental results at $\lambda_0 = 90^\circ$ and at one other value of $\lambda_0$, as discussed in the text. The plotting symbols are experimental points, and the dashed curve is drawn smoothly through these.
Figure 4.2 Diagram showing co-ordinate axes x and y and the senses in which γ and λ were taken positive.

Deformation band

X, direction of molecular alignment (extinction direction)

Tensile axis
Figure 4.3. Graph comparing the fit of the Hill theory without $\alpha_{xx}$ (curve A), and with $\alpha_{xx}$ (curve B) to nominal yield stress results for Vybak of extension ratio 3.3 prepared by extension at $71^\circ$C.
Figure 4.4 Graph comparing the predictions of the Hill theory without $a_{xx}$ (dashed curve), and with $a_{xx}$ (continuous curve), to the experimental results (plotting symbols) for band angles in Vybak oriented by extension at 71°C.
Extension Ratio 3.7
Full line using extrapolated values of $\sigma_0$

$\lambda_0$ (degrees)

Extension Ratio 3.7
Full line using measured values of $\sigma_0$

$\lambda_0$ (degrees)
Figure 4.5  Graph comparing the predictions of the Hill theory without \( a_{xx} \) (dashed curve), and with \( a_{xx} \) (continuous curve), to the experimental results (plotting symbols) for band angles in Vybak oriented by extension at 90° C.

(a) Extension Ratio 3.0

(b) Extension Ratio 6.0

\[ \lambda_0 \text{ (degrees)} \]

\[ \chi, \chi_2 \text{ (degrees)} \]
Figure 4.6 Graphs illustrating the determination of the value of \( a_{xx} \) which gave the best fit to the band angle results. The results are for Vybak of extension ratio 3.3.
Figure 4.7  Graph showing how the assumption, that $G \neq H$, affects the fit of the Hill theory to the experimental results for $\gamma_1$. 

(a) $\lambda_0 = 75^\circ$

(b) $\lambda_0 = 60^\circ$
Figure 4.8 Graph showing how the assumption, that $G \neq H$, affects the fit of the Hill theory to the experimental results for $\gamma_2$. 

(a) $\lambda_0 = 75^\circ$

(b) $\lambda_0 = 60^\circ$
Figure 4.9 Plots of $G$ and $H$ against $a_{xx}$ ($G = H$) for different fitting positions of $\chi_i$.

$\chi_i$ fitted at $\lambda_0$: 75°, 60°, 45°, 30°.
Figure 4.10 Plots of $\alpha_{xx}$ vs. (a) extension ratio and (b) birefringence for extension temperatures $71^\circ C$ and $90^\circ C$. 
Figure 4.11 Plots of $a_{xx}$ (plotting symbols) and true stress during hot stretching (curves) vs. extension ratio for material originally extended at 71°C and 90°C.
Figure 4.12 Plots of the Hill theory parameters $H (H = G)$, $F$, and $N$ vs. (a) extension ratio and (b) birefringence.
A graph showing the relationship between birefringence and the properties of substances at different temperatures. The graph includes lines for substances labeled H, F, and N at temperatures 90°C and 71°C. Error bars are present for each data point, indicating variability or uncertainty in the measurements.
Figure 4.13  The variation of (shear yield stress) $\tau_{xy}$, as a function of extension ratio, as predicted by equation (4.24).
Figure 4.14 The variation of tensile yield stress with birefringence for polyethylene terephthalate, as predicted using the critical strain criterion and the results of Raumann (1963).
Figure 4.15  Graph showing the relationship between tensile modulus and tensile yield stress for polyethylene terephthalate, as predicted using the critical strain criterion and the results of Raumann (1963).
Figure 4.16 Diagram showing the co-ordinate axes, x and y, and the sense in which $\beta$ was taken positive.
Figure 4.17  Diagram showing how the existence of an internal stress favours the formation of deformation bands such that $\gamma < \lambda_0$. 
Observations of Optical Anisotropy Charges During Deformation

It was reported in Chapter 3 that changes in optical extinction direction and birefringence occurred when oriented polyvinyl chloride was plastically deformed. Some results for these optical anisotropy changes were presented in Chapter 3, but not in conjunction with accurate deformation measurements. It is intended in this Chapter to investigate more closely the effect of deformation on optical anisotropy by carrying out accurate measurements of both deformation geometry and optical anisotropy.

These measurements were in fact obtained from uniformly deformed and cold drawn test pieces, for which some deformation geometry results have been presented in Chapter 3. No measurements have been made on deformation bands since accurate measurements of strain and optical anisotropy were made difficult by the localised nature and non-uniformity of the bands.

Measurements of birefringence changes reported by other workers appear to be restricted to cases in which the material was initially unoriented. Such experiments have been carried out on polyethylene by Crawford and Kolsky (1951) and Raumann and Saunders (1961) and on polyethylene terephthalate by Pinnock and Ward (1964). Allison and Ward (1967) have also presented results for polyethylene terephthalate which was oriented by extrusion and was then extended at room temperature in the original draw direction. A study of changes in the optical extinction direction in deformation bands in oriented polyethylene terephthalate has been carried out by Brown, Duckett and Ward (1968b).
5.1 Experimental Procedure

Details of experimental procedure have been presented in various sections of previous Chapters. However, for the sake of clarity in the following discussions, it is convenient to repeat briefly some of these details in this section.

The experimental work can be considered in two stages. In the first stage oriented polyvinyl chloride, in this case Vybak, was prepared by uniaxial hot stretching of strips of material at a temperature above the glass transition temperature. In order to obtain material of different degrees of molecular alignment for use in the second stage, these strips were extended to different extension ratios. In the second stage tensile test pieces were cut from the oriented material and were tested in uniaxial tension. These testpieces had a gauge length of 6 mm, width 1.5 mm, and thickness ranging from 0.5 mm to 0.13 mm. As reported in Section 3.1 such test pieces deformed uniformly when extended at 1 mm min$^{-1}$, strain rate 0.17 min$^{-1}$, and 50°C. Uniform deformation was carried out on test pieces having values of $\lambda_o = 0^\circ, 25^\circ, 45^\circ, 56^\circ, 64^\circ$ and $90^\circ$ and cut from material extended at $90^\circ$C in stage 1. For each particular value of $\lambda_o$, several parallel test pieces were cut from the same strip, and each was then extended to a different extension ratio. Cold drawing in stage 2 was carried out at 1 mm min$^{-1}$, strain rate 0.17 min$^{-1}$, and at room temperature on test pieces having $\lambda_o = 26^\circ, 45^\circ, 54^\circ, 58^\circ$ and $66^\circ$ cut from a strip of extension ratio 2.6 and $\lambda_o = 20^\circ, 32^\circ, 47^\circ$ and $70^\circ$ cut from a strip of extension ratio 2.0; both strips were prepared by extension at $71^\circ$C. For comparison purposes test pieces were also cut from the unoriented material and tested, some at room temperature and some at $50^\circ$C. Owing to difficulty in extending large
pieces of material at these temperatures, small test pieces could not be cut from this material and so it was not used as starting material for the second stage.

For extension at 90°C, 71°C and 50°C the E-type Tensometer was used with the environmental chamber in position. In extending the unoriented material at room temperature, the E-type Tensometer was used without the environmental chamber. The small tensile machine, attached to the optical microscope, was used in cold drawing the oriented polyvinyl chloride at a strain rate of 0.15 min⁻¹. Optical and strain measurements were made at room temperature after the test piece had been removed from the tensile machine. The material extended at elevated temperatures was cooled to below 30°C at constant length before removal from the machine.

As discussed in Chapter 2, the first stage strains were determined by measuring the relative displacement of small numbers of widely spaced lines drawn on the face of the strip, and by measuring changes in the width and thickness of the strips. Strains in stage 2 were measured from grids of dots which were printed on the oriented strip as described in Chapter 2. The grids of dots were also used to measure strains in stage 1 for test pieces extended at 50°C and room temperature. The spacings between the dots and the angle between the sides of the parallelogram were measured from micrographs. Accuracies were ±1% for the spacings and ±1° for the angles. The extension ratio, $R_2$, was used as a measure of the strain in stage 1, and the extension ratio, $R_t$, given by equation (2.1), was used for stage 2.

Optical measurements were made with polarized light transmitted through the test piece in the direction normal to its face,
using the Zeiss polarising microscope fitted with the Ehringhaus compensator. The extinction position could be located with respect to a reference line on the face to an accuracy of 0.4°. The extinction direction parallel to the direction of the larger of the two principal refractive indices in the plane of the sheet was indentified by locating the zero order fringe. For convenience this will be referred to as the major extinction direction. (It is assumed that, by the nature of the deformation, one of the principal axes of the indicatrix was always perpendicular to the face of the test piece.) By measuring the retardation and also the thickness of the test piece, the birefringence was calculated. For material extended in stage 1 the birefringence was measured to ±2% for the strip with \( R_z = 7.5 \). At smaller values of \( R_z \), this accuracy improved with decreasing \( R_z \). Measurements of birefringence after deformation in stage 2 were less accurate because of some non-uniformity in the material. The estimated accuracies will be mentioned, where necessary, in the following text.

5.2 Results

5.2.1 First Stage. Extension of the Unoriented Material

It was found that during the extension, the major extinction direction was always parallel to the tensile direction, \( O_2 \), and the birefringence was positive and increased from zero as the extension ratio increased. The variations of birefringence as a function of extension ratio for extension at room temperature, 50°C, 71°C and 90°C are shown in Figure 5.1. All the plotting symbols are measured values except for the square plotting symbols in Figure 5.1. These symbols will be referred to in Section 5.3.2.
5.2.2 Second Stage. Uniform Deformation of Oriented Material

The appearance of the test piece before and after extension in stage 2 is shown in Figure 5.2. The square grid of dots was printed on the material prior to the second stage extension such that one side of the square was parallel to Oz, the major extinction direction after the stage 1 extension, and the other was parallel to Ox. These axes are indicated in Figure 5.2(a). Also marked are the direction of extension, Ot, which was parallel to the sides of the test piece, and the angle $\lambda_o$, between Oz and the tensile axis.

After extension, the originally square grid of dots became a parallelogram. This is apparent from Figure 5.3(b) which shows the test piece in Figure 5.3(a) after it had been extended to an extension ratio, $R_t$, of 1.76. Oz was still defined to be parallel to the line of dots to which it was parallel prior to deformation. Since this line of dots rotated during the extension, Oz was inclined at an angle $\beta$ to the tensile axis, Ot, such that $\beta \neq \lambda_o$. The x-axis was defined to be in the plane of the dot pattern and still perpendicular to Oz. Since the original square deformed into a parallelogram, Ox was no longer parallel to the line of dots to which it was originally parallel prior to deformation. The major extinction direction, indicated by Oe, was no longer parallel to Oz after deformation but was inclined at an angle $\lambda$ to Ot such that $\lambda \neq \beta$.

Both the z-axis and the major extinction direction, Oe, rotated towards the tensile axis, Ot, with increasing extension. The extent of these changes of angle is shown in Figures 5.4 and 5.5. Here, $\lambda$, the angle between Oe and Ot, and $\beta$, the angle between Oz and Ot, are plotted as a function of $R_t$, the extension.
ratio measured in the tensile direction. Plots are given for various values of $\lambda_0$, and for various extension ratios, $R_z$, used to orient the material in stage 1. (The symbol $R_t$ is used only for extension in stage 2, whereas $R_z$ is used only for extensions in stage 1.)

It can be seen that the major extinction direction always deviated from the $z$-direction such that $\lambda < \beta$. In the majority of cases the angle of deviation, $\alpha = \beta - \lambda$, increased as $R_t$ increased. These results are reproduced as plots of $\alpha$ against $R_t$, in Figure 3.37. An exception to this was at $\lambda_0 = 45^\circ$ for $R_z = 1.5$, for which $\alpha$ increased up to a maximum value after which it decreased.

The influence of the orienting process, as represented by $R_z$, on the changes in the major extinction direction with $R_t$ can be seen by comparing the behaviour of test pieces of different $R_z$ but with the same value of $\lambda_0$. Both for $\lambda_0 = 45^\circ$ and for $\lambda_0 = 64^\circ$, as $R_t$ increased, the major extinction direction rotated towards the tensile axis less rapidly with larger $R_z$.

Not only did the value of $R_z$ influence the change in $\lambda$, but so also did the value of $\lambda_0$. This is best demonstrated by considering the extreme case at $\lambda_0 = 0^\circ$ and $\lambda_0 = 90^\circ$. The general observations can be described quite simply. For $\lambda_0 = 0^\circ$, the $z$ direction of the grid of dots and the major extinction direction were both initially parallel to the tensile axis and remained so during the subsequent extension. Thus, $\alpha$ remained constant and equal to zero. For $\lambda_0 = 90^\circ$, the $z$-direction and the major extinction direction were both initially perpendicular to the tensile axis. As a result of the deformation, the $z$-direction remained
perpendicular to this axis but the major extinction direction became parallel to the tensile axis. Thus, \( \alpha \) attained its maximum possible value of \( 90^\circ \). The behaviour at intermediate values of \( \lambda_o \) is illustrated in Figure 5.5.

Changes in the magnitude of the birefringence with extension ratio \( R_t \) are shown in Figures 5.6, 5.7 and 5.8. For this purpose, the deformation of unoriented material at \( 50^\circ C \) can be considered as deformation in stage 2 of material of extension ratio 1.0 prepared in stage 1. Birefringence results for \( \lambda_o = 45^\circ \) were not obtained since the test pieces were destroyed before birefringence measurements were made. It can be seen that for larger values of \( \lambda_o \), i.e. \( 56^\circ \) and \( 64^\circ \), there was an initial decrease in birefringence followed by an increase. At smaller angles, i.e. \( \lambda_o = 25^\circ \) and \( 0^\circ \), the birefringence increased at all stages of the deformation. In the case where there was an initial decrease in birefringence, a larger value of \( R_t \) was needed for the large value of \( R_z \) in order to bring the birefringence back to its initial value, corresponding to \( R_t = 1 \), as indicated by the broken lines in Figure 5.6. For test pieces at \( \lambda_o = 0^\circ \) and \( 25^\circ \), the birefringence measurements were accurate to \( \pm 2\% \), or better. At \( \lambda_o = 56^\circ \) and \( 64^\circ \), the birefringence measurements were accurate to \( \pm 3\% \) and \( \pm 4\% \) respectively. The uncertainties were larger at larger values of \( \lambda_o \) because there was a tendency for cracks to open up at large values of \( \lambda_o \), causing some non-uniformity in the deformation.

5.2.3 Second Stage. Cold Drawing of the Oriented Polyvinyl Chloride

All directions and angles referred to in this section are defined to be the same as in Section 5.2.2. As in the case of the
uniformly deformed test pieces, the extinction direction, $O_e$, and the $z$-axis rotated towards the tensile axis as a result of deformation. Again $\beta$ remained larger than $\lambda$. Since the extension ratio, $R_e$, varied as a function of $\lambda_o$, it is considered more suitable to plot the variation of $\lambda$ as a function of $\lambda_o$. Such plots are shown in Figure 5.9; the values of $R_e$ can be obtained by consulting Figure 3.35. No test pieces with grid of dots printed on them were used with values of $\lambda_o = 0^\circ$ and $\lambda_o = 90^\circ$. However, the experimental points at these values of $\lambda_o$ in Figure 5.9 were obtained from results for the cold draw test pieces discussed in Chapter 3. $\beta$ has not been plotted in Figure 5.9 but it decreased from $90^\circ$ at $\lambda_o = 90^\circ$ to $0^\circ$ at $\lambda_o = 0^\circ$, always remaining larger than $\lambda$.

Birefringence measurements were also made and these results are presented in Figure 5.10. It can be seen that the birefringence had a maximum at approximately $46^\circ$ for $R_z = 2.0$, and at approximately $35^\circ$ for $R_z = 2.6$.

5.3 Discussion

5.3.1 Qualitative Interpretation of Results

The following model of the structure of the polymer enables the results presented in Section 5.2 to be given a qualitative interpretation. If the material is considered to consist of a network structure of optically anisotropic units, the birefringence gives a qualitative measure of the degree to which these units are aligned. Thus, the unoriented material, in which the units are randomly aligned, has zero birefringence. It is as a consequence of the alignment of the units during extension that, in the stage 1 extension, the birefringence increased monotonically with
increasing extension ratio, $R_z$. Since the stage 2 extension was carried out on material prepared in stage 1, the stage 2 deformation involved the realignment of a network which was already aligned to some extent.

Using the above model it is possible to qualitatively account for some of the results presented in Section 5.2.2 for the uniform deformation of oriented polyvinyl chloride in stage 2. For instance, if the angle $\lambda_0$ was small it might reasonably be expected that the degree of alignment of the units would be improved by further extension. (This obviously must be so in the limiting case of $\lambda_0 = 0^\circ$.) This was indeed the case, since, for $\lambda_0 = 25^\circ$ and $\lambda_0 = 0^\circ$ in Figure 5.7, it can be seen that the birefringence increased with increasing extension ratio, $R_t$. At larger values of $\lambda_0$, one might expect that the process of realignment into the new tensile direction would, in the early stages, produce a reduction of the degree of alignment, but that the degree of alignment would eventually increase again as the units in the network continued to turn towards the new tensile direction. It might also be expected in this case that the higher the original degree of alignment (i.e. the greater $R_z$) the material would have to be extended further (i.e. the greater $R_t$) to regain the original degree of alignment. This latter point is most easily visualised by considering the simple case of $\lambda_0 = 90^\circ$. In fact extension at large angles to the original tensile direction caused the birefringence first to fall and then to increase again, as shown in Figure 5.8 for $\lambda_0 = 56^\circ$ and in Figure 5.6 for $\lambda_0 = 64^\circ$.

Figure 5.6 also shows that with the higher degree of initial alignment ($R_z = 7.5$ as against $R_z = 2.9$), a greater amount of extension was needed in the second stage ($R_t = 2.4$ as against
\( R_t = 1.6 \) to return to the initial value of birefringence, (i.e. the value at the end of stage 1).

Since the changes in optical anisotropy depend both upon the initial value of \( \lambda_0 \) and the extension ratio, \( R_t \), which was fixed by the natural draw ratio of the test piece, the results for the cold drawn test pieces are not easily discussed in terms of the above model.

As regards the observation that, on restretching the material, the major extinction direction did not remain parallel to a grid line on the material to which it was originally parallel, there is no requirement apparent in the model that the two directions should remain parallel. There is a distribution of directions of the units of the network and the major extinction direction is determined by some averaging process. It is not to be expected that this averaging process will determine a direction which at all stages of the extension is parallel to the same grid line. Brown, Duckett and Ward (1968b) have made this point that there is not a unique molecular direction in their discussion of deformation bands in polyethylene terephthalate, in which they observed deviations between extinction direction and reference line, these being parallel prior to deformation.

5.3.2 Optical Anisotropy and Strain History

In the same paper Brown, Duckett and Ward (1968b) put forward the hypothesis, which has also been stated by Saunders (private communication), that the state of optical anisotropy is a single-valued function of the state of strain, zero strain corresponding to the isotropic state. The principal axes of the indicatrix (Fresnel ellipsoid) will then have the same directions
as the principal axes of strain. The application of this hypothesis to the present results will now be considered.

The hypothesis has to do with the state of strain referred to the unoriented material as the zero state of strain. However, the square grid of dots used to measure strain in stage 2 was not printed on the material until it had already been strained to orient it. The first step, therefore, is to calculate what would be the pattern of dots which, if printed on the unoriented material, would, as a result of the extension applied in the first stage of the experiment, coincide with the square pattern actually printed.

Figures 5.11(a), (b) and (c) illustrate the situation respectively: (a) when the material was unoriented; (b) after the material had been extended in the first stage, but before it had been extended in the second stage; (c) after the material had been extended in the second stage. Figures 5.11(b) and (c) correspond with Figures 5.2(a) and (b). The positions of the dots in Figures 5.9(b) and (c) are the observed positions, but the positions of the dots in Figure 5.11(a) are inferred. It is evident from the results noted in Section 2.3 that the basis of the grid on the unoriented material, Figure 5.11(a), would have been a rectangle with sides along Ox and Oz of lengths \( a_1 \) and \( c_1 \) given by

\[ a_1 = a_2 R_x^{-1} \quad \text{and} \quad c_1 = c_2 R_z^{-1} \]

where \( a_2 = c_2 \), the length of the sides of the square as printed (Figure 5.11(b)). Thus it follows that

\[ a_1/c_1 = R_z R_x^{-1} \quad \text{(5.1)} \]

It was found experimentally that in the stage 1 extension \( R_x = R_y \) and \( R_x R_y R_z = 1 \). Thus \( R_x = R_z^{-\frac{1}{2}} \) and
Now \((a_1/c_1)\) can be calculated from observations made after the stage 2 extension, that is in the situation shown in Figure 5.2(b) and Figure 5.11(c), in the following way. In these two figures 0e is the major extinction direction. However, it is a consequence of the hypothesis put forward above that this direction coincides with one of the principal axes of strain. It can be shown that

\[
a_1/c_1 = (a_3/c_3) \left( \sin 2 \omega \cot 2 \alpha - \cos 2 \omega \right)^{\frac{1}{2}}.
\]  

Here \(a_3\) and \(c_3\) are the lengths of the sides of the parallelogram of dots (Figure 5.11(c)) which in the unoriented state of the material was the rectangle of sides \(a_1\) and \(c_1\) respectively, \(\omega\) is the angle between the sides of the parallelogram, and \(\alpha\) is the angle between the z-axis and the principal axis of strain identified with the major extinction direction. The derivation of equation (5.3) is straightforward (see Jaeger, 1962. The equation (5.3) is equation 19 on page 27 of Jaeger's book with the following substitutions: \(c_3/c_1\) for his \(a\); \((a_3/a_1) \cos \omega\) for his \(b\); zero for his \(c\); \((a_3/a_1) \sin \omega\) for his \(d\); \(\delta\) for his \(\alpha'\).)

All the quantities on the right hand side of equation (5.3) were measured so that \(a_1/c_1\) could be calculated and then substituted in equation (5.2) to give a calculated value of \(R_z\). If this hypothesis, that the optical anisotropy is a single-valued function of the state of strain, is correct, then the calculated value of \(R_z\) will be equal to the measured value. Furthermore, for a given measured value of \(R_z\), this agreement should be obtained irrespective of the extension ratio, \(R_e\), applied to the oriented material in stage 2 of this experiment.
These calculations were carried out for both the uniformly deformed and also cold drawn test pieces. The results for the uniformly deformed test pieces are shown in Figure 5.12. Figure 5.12 shows a plot of $R_z^2$ (calc.) against the measured extension ratio for the second stage, $R_e$, for a series of test pieces having various values of $R_z$ and $\lambda_0$. The limits associated with each experimental point indicate the maximum possible error in $R_z^2$ (calc.) arising from errors in $a_3$, $c_3$, $\omega$ and $\alpha$. Similar results are presented in Figure 5.13 for cold drawn test pieces. It can be seen that, contrary to the expectations based on the state-of-strain hypothesis, the calculated extension ratio was not constant.

In case this failure was due to the hypothesis not being valid in the stage 2 extension, a value of $R_z$ (calc.) was obtained by extrapolating to $R_e = 1$. This extrapolated value, $R_z^\star$, is compared with the measured extension ratio, $R_z$, over a range of values in Figure 5.14. The expectation of equality between the two quantities based on the hypothesis is not fulfilled, since the calculated values of extension ratio are very much lower than the measured value. For the material originally extended at 90°C the discrepancy between $R_z^\star$ and $R_z$ is greater than that for material originally extended at 71°C.

The failure of the hypothesis to account for the results presented here is in contrast to its success in Brown, Duckett and Ward's analysis of deformation bands in polyethylene terephthalate. It is thought that if the hypothesis fails to some extent in the second stage extension, as evidenced by the non-constancy of the calculated extension ratio shown in Figures 5.12 and 5.13, then this is allowed for by the extrapolation procedure. The reason for the continued failure is apparent in Figure 5.1.
figure shows that while the birefringence-extension ratio relationship was not very different at 50°C and at room temperature, it changed with increasing rapidity at higher temperatures. (This change may have been due to the increasing flexibility of the molecular chains with rising temperature in the neighbourhood of $T_g$.) That is, above 50°C the optical anisotropy-strain relationship became a rapidly varying function of temperature. However, in the calculation of $R_z$ (calc.) it was implicitly assumed that the optical anisotropy-strain relationships for the extensions in stage 1 and stage 2 were the same although one extension was carried out at 90°C and the other at 50°C, and in fact the relationships at these two temperatures were very different. This is the reason for the lack of agreement between the calculated and measured extension ratios for the stage 1 - stage 2 process.

From these considerations it can be postulated that $R^*$ is equal to the extension ratio that, if applied to the unoriented material, would produce the same state of optical anisotropy as was actually produced by the corresponding measured extension ratio applied at 71°C and 90°C. This inference is supported by the observations. For when the measured birefringence for the first stage extension at 90°C and 71°C is plotted in Figure 5.1 using the calculated value of extension ratio, $R^*$, rather than the measured value, $R_z$, (square plotting symbols) the results lie on or close to the curve for the measurements made in extending unoriented material at room temperature. Further comments will be made on these results in the light of results to be discussed in the following Chapter.
Figure 5.1 Graph showing the observed variation of birefringence with extension ratio, $R_z$, for extension carried out at the temperatures shown.
Optical micrograph of a test piece showing the grid of dots (a) as printed at the beginning of stage 2, and (b) after extension in stage 2 to extension ratio $R_t = 1.76$. Oz is parallel to the same line of dots before and after extension and Oz' is taken parallel to the major extinction direction (Oe). The tensile axis, Ot, was parallel to the edge of the test piece.
Figure 5.3 Graphs showing the variation of $\beta$ and $\lambda$ with extension ratio $R_t$ in the second stage extension at $50^\circ$C. The results are for different values of $R_z$ and $\lambda_0$.
Figure 5.6  Graphs showing the variation of the birefringence $\Delta n_{xx}$ with extension ratio $R_z$ in the second stage extension at 50°C. The results are for different values of $R_z$ and $\lambda_0$. 

Figure 5.7 

Figure 5.8
Figure 5.9 Graphs showing the variation of $\lambda$ and birefringence respectively, with $\lambda_0$ after extension in second stage at 20°C.

$\lambda$ (degrees)

$\lambda_0$ (degrees)

$R_z = 2.0$ $R_z = 2.6$

Birefringence $\times 10^3$

$R_z = 2.0$ $R_z = 2.6$

Figure 5.10
Figure 5.11 Diagram illustrating the change in dimensions of square forming the basis of the grid of dots which was printed on the test piece prior to extension in stage 2. (For details see the text.)
Figure 5.12 $R_z^3$ (calc) plotted against the measured extension ratio $R_t$ for test pieces extended at 50°C in stage 2. $R_z^3$ is obtained by extrapolating to $R_t = 1$. 

Extension Ratio, $R_t$
Figure 5.13 \( R_z^{3/2} \) (calc) plotted against the measured extension ratio for test pieces extended at 20°C in stage 2. \( R_z^{3/2} \) is obtained by extrapolating to \( R_t = 1 \).

\begin{align*}
R_z^{3/2} (\text{calc}) & \quad \text{Extension Ratio, } R_t \\
1.6 & \quad 2 \quad 3
\end{align*}
Figure 5.1b  $R_z^*$ plotted against the measured extension ratio $R_z$ for stage 1 extension at 71°C and 90°C.
In the previous chapter, a model was used which enabled a qualitative interpretation to be obtained for the results of an experimental investigation into the changes in the optical anisotropy of oriented polyvinyl chloride subjected to uniaxial tension. It is the object of the present chapter to use a more detailed form of this model in order to obtain a quantitative explanation of the observed behaviour. The model used will be one which was originally due to Kuhn and Grün (1942), and which has been used with some success by Ward and co-workers to account for the optical and mechanical anisotropy of some oriented polymers. It was applied to oriented polyethylene by Ward (1962), and to oriented polyethylene terephthalate by Pinnock and Ward (1964) and Ward (1967). Hennig (1967) has also used this model to account for the anisotropy in the thermal and mechanical properties of oriented polyvinyl chloride. The applications of this model so far published have been to the extension of an originally unoriented material, or to the extension in the original draw direction of a material already oriented by extrusion. In all of these applications, it was assumed that, during extension, the transverse contraction of the material perpendicular to the tensile axis was isotropic. This is not the case for the results presented in Chapter 5, and so, in the present chapter, the theory is developed so that it can be applied to cases where the transverse contraction is anisotropic. The theory has also been developed by Duckett, Richardson and Ward (unpublished) and applied to
deformation bands in oriented polyethylene terephthalate such as were described by Brown, Duckett, and Ward (1968b). Some of the results and discussion of this and the previous chapter have been reported elsewhere by Hargreaves and Rider (1969).

The following discussion is also of importance in any aggregate model which might be used to account for the yield stress anisotropy of oriented polymers as discussed in Section 4.4.

6.1 Theory

6.1.1 Outline of the Theory

Kuhn and Grün (1942) suggested two models in their paper, and it is the first of these which is adopted here in order to account for optical anisotropy changes during deformation at room temperature and 50°C. The material is considered to be an aggregate of rigid anisotropic uniaxial units, with each unit having transverse isotropy about its axis. The principal polarizabilities are the same for all units and remain constant throughout the deformation of the material. Throughout deformation the axis of the unit rotates so as to remain parallel to the line connecting a pair of points in the material, (affine deformation). The polarizability of the material in a given direction is taken to be the sum of the components of polarizability in that direction arising from all the units. Because of the rotation of the units, the sum is a function of the deformation. The refractive index is calculated from the polarizability. Hence, the extinction directions and the birefringence can be found.

6.1.2 Optical Anisotropy Due to a Distribution of Units

The material as used was in the form of a strip. Rectangular
Cartesian axes Ox, Oy, and Oz are considered, such that Ox and Oz are parallel to the face of the strip, as in Figure 6.1. The axis of a unit is denoted by $O\xi$, and the polarizabilities of the unit are $p_1$ parallel to $O\xi$ and $p_2$ in all directions perpendicular to $O\xi$. The direction of $O\xi$ relative to Ox, Oy, and Oz is defined by the polar angles $\theta$ and $\phi$, where $\theta$ is the angle between Oz and $O\xi$ and $\phi$ is the angle between Oy and the projection of $O\xi$ on the xy plane. The optical measurements were made with light transmitted parallel to Oy.

Let $p_{ij}$ be the components of the polarizability tensor of the unit referred to the axes Ox, Oy and Oz, where $i, j$ can be $x, y$ or $z$. Then

\[
\begin{align*}
    p_{xx} &= a_{11}^2 p_1 + a_{12}^2 p_2 + a_{13}^2 p_3 , \\
    p_{zz} &= a_{31}^2 p_1 + a_{32}^2 p_2 + a_{33}^2 p_3 , \\
    p_{xz} &= a_{11} a_{31} p_1 + a_{12} a_{32} p_2 + a_{13} a_{33} p_3 ,
\end{align*}
\]

where $a_{ij}$ are the direction cosines defining the direction of $O\xi$ relative to Ox, Oy, and Oz. It can be shown that

\[
a_{11}^2 + a_{12}^2 + a_{13}^2 = 1 ,
\]

(6.2)

and

\[
a_{31} a_{11} + a_{32} a_{12} + a_{33} a_{13} = 0 ,
\]

(see Nye (1957) Chapter II). Using equations (6.1) and (6.2), and the fact that $p_3 = p_2$, it can be shown that

\[
\begin{align*}
    p_{xx} &= p_2 + (p_1 - p_2) a_{11}^2 , \\
    p_{zz} &= p_2 + (p_1 - p_2) a_{31}^2 , \\
    p_{xz} &= (p_1 - p_2) a_{11} a_{31} .
\end{align*}
\]

(6.3)

The direction cosines $a_{ij}$ are given in terms of $\theta$ and $\phi$ by
Thus equation (6.3) reduces to

\[ p_{xx} = p_2 + (p_1 - p_2) \sin^2 \theta \sin^2 \phi , \]
\[ p_{zz} = p_2 + (p_1 - p_2) \cos^2 \theta , \]
\[ p_{xz} = (p_1 - p_2) \cos \theta \sin \theta \sin \phi . \]  

The polarizability due to all the units is found by averaging over the whole distribution. If this is done, equation (6.4) becomes

\[ p_{xx} = \bar{p}_2 + (\bar{p}_1 - \bar{p}_2) \sin^2 \theta \sin^2 \phi , \]
\[ p_{zz} = \bar{p}_2 + (\bar{p}_1 - \bar{p}_2) \cos^2 \theta , \]
\[ p_{xz} = (\bar{p}_1 - \bar{p}_2) \cos \theta \sin \theta \sin \phi , \]  

where the bar over the angular functions indicates that they should be averaged over the whole distribution.

Consider rectangular Cartesian axes Ox', Oz', and Oy' such that Oz' and Ox' are in the xz plane and Oz' makes an angle \( \gamma \) with Oz. Then the polarizability \( p_{zz}' \) along Oz' due to the units is given by

\[ p_{zz}' = p_{xx} \sin^2 \gamma + 2p_{xz} \sin \gamma \cos \gamma + p_{zz} \cos^2 \gamma . \]  

The maximum and minimum polarizabilities in the xz plane, and the directions in which they occur, are found by setting \( \frac{\partial p_{zz}}{\partial \gamma} = 0 \). This gives

\[ \tan 2\gamma_m = \frac{2p_{xz}}{p_{zz} - p_{xx}} \]  

and for the differences between maximum and minimum polarizabilities,

\[ \Delta p_{zz}' = \left[ p_{zz}' - p_{xx}' \right]^2 + 4 \left[ \frac{p_{xz}'}{p_{zz}'} \right]^2 \]  

(6.8)
It is assumed by the nature of the deformation that one of
the principal axes of polarizability will always be perpendicular
to the wide face of the specimen, and therefore will be parallel
to Oy. Equation (6.7), therefore, gives the directions of the
other two principal axes of polarizability, and these are the ob­
served extinction directions, since the observations were made
with the light travelling parallel to Oy. From equations (6.7)
and (6.5) it follows that

$$\tan 2 \gamma_m = \frac{2 \sin \theta \cos \theta \sin \phi}{\cos^2 \theta - \sin^2 \theta \sin^2 \phi}.$$  \hspace{1cm} (6.9)

For an isotropic material the refractive index is given in terms
of the polarisability per unit volume, p, by the Lorentz-Lorenz
equation:

$$(n^2 - 1) \left( \frac{n^2 + 2}{n^2 + 2} \right)^{-1} = \frac{4\pi}{3} p.$$  \hspace{1cm} (6.10)

For an anisotropic material with principal polarizabilities $p_1$ and
$p_2$ (not to be confused with the polarizability of the units re­
ferred to earlier), the Lorentz-Lorenz equation gives the follow­
ing relationship between the difference in principal refractive
indices, $\Delta n$, and the difference in polarizabilities, $\Delta p$,

$$\frac{(n_1^2 - 1)}{(n_1^2 + 2)} - \frac{(n_2^2 - 1)}{(n_2^2 + 2)} = \frac{4\pi}{3} (p_1 - p_2),$$  \hspace{1cm} (6.11)

(see Treloar (1946)).

It can then be shown that

$$\Delta n = \frac{4\pi}{3} N_o \frac{(n_1^2 + 2)(n_2^2 + 2)}{(n_1 + n_2)} \Delta p,$$  \hspace{1cm} (6.12)

(in c.g.s. units), where $N_o$ is the number of units per unit volume.

From equations (6.8) and (6.5) the differences in principal polar­
izabilities in the $zx$ plane is given by

$$\Delta p_{zx} = (p_1 - p_2) \left[ \frac{1}{\cos^2 \theta - \sin^2 \theta \sin^2 \phi} \right]^2,$$

$$+ 4 \left( \frac{\sin \theta \cos \theta \sin \phi}{\cos^2 \theta - \sin^2 \theta \sin^2 \phi} \right)^2 \frac{1}{2}.$$  \hspace{1cm} (6.13)
Therefore,
\[
\Delta n_{zx} = \Delta n_{\text{max}} \left[ \frac{(\cos^2 \theta - \sin^2 \theta \sin^2 \phi)^2}{(\cos \theta \cos \phi \sin \theta)^2} \right] \frac{1}{\phi},
\]
(6.14)

where
\[
\Delta n_{\text{max}} = \frac{2\pi}{9} \frac{(n^2 + 2)^2}{n} (p_1 - p_2),
\]
(6.15)

and \( n \) has been put in place of \( n_1 \) and \( n_2 \) in equation (6.11). This latter approximation is justified if the difference between \( n_1 \) and \( n_2 \) is small. Thus the birefringence, as measured using light transmitted perpendicular to the sheet, is given in terms of \( \Delta n_{\text{max}} \) and the averaged angular functions. In the case of perfect molecular alignment, when all the units are parallel, the birefringence would be equal to \( \Delta n_{\text{max}} \).

Using a similar approach to that above \( p_{yy} \) was found to be given by
\[
p_{yy} = p_2 + (p_1 - p_2) \sin^2 \theta \cos^2 \phi.
\]
(6.16)

Thus from equations (6.5), (6.6) and (6.12), in the particular case of \( \gamma = 0^\circ \), the birefringence measured using light transmitted along \( Ox \) is given by
\[
\Delta n_{zy} = \Delta n_{\text{max}} \left[ \cos^2 \theta - \sin^2 \theta \cos^2 \phi \right] \cos \theta.
\]
(6.17)

Use will be made of this and the other results at a later stage in this chapter.

6.1.3 Evaluation of the Distribution of Units

The bars over the angular functions in Section 6.1.2 signify that these quantities must be averaged. For this purpose the distribution function, \( p(\theta, \phi) \) for the directions of the axes of the units, \( O\xi \), must be known. Here, \( p(\theta, \phi) \) is the fractional
number of units per unit solid angle having polar angles $\theta$ and $
phi$, so that the fraction of units whose polar angles lie between $\theta$ and $\theta + \phi_0$, and $\phi$ and $\phi + \phi_1$ is $p(\theta,\phi) \sin \theta \, d\theta \, d\phi$, and

$$
\int_{0}^{2\pi} \int_{0}^{\pi} p(\theta,\phi) \sin \theta \, d\theta \, d\phi = 1 \quad (6.18)
$$

The angular functions are averaged thus:

$$
\bar{f}(\theta,\phi) = \int_{0}^{2\pi} \int_{0}^{\pi} f(\theta,\phi) \, p(\theta,\phi) \sin \theta \, d\theta \, d\phi \quad , \quad (6.19)
$$

where $\bar{f}(\theta,\phi)$ denotes the angular functions in equations (6.9), (6.14) and (6.17).

Kuhn and Grün (1942) and Ward (1962) assumed transverse isotropy of the material about the z-axis. In such a case

$p(0,\phi)$ is a function of $0$ only, so that $\sin \theta \cos \theta \sin \phi = 0$

and $\sin^2 \theta \sin^2 \phi = \frac{1}{2} \sin^2 \theta$. The angle $\gamma$ then has the values $0^\circ$ and $90^\circ$, and the expression for the birefringence as a function of $0$ becomes identical with that of Kuhn and Grün and of Ward.

In this theory deformation affects the extinction directions and birefringence through the distribution function $p(0,\phi)$. The relationship between the distribution functions before and after deformation is

$$
p_2(\theta_2,\phi_2) \sin \theta_2 \, d\theta_2 \, d\phi_2 = p_1(\theta_1,\phi_1) \sin \theta_1 \, d\theta_1 \, d\phi_1 \quad , \quad (6.20)
$$

where the suffixes 1 and 2 refer to the states before and after deformation. That is, all the units whose axes lay between $\theta_1$ and $\theta_1 + d\theta_1$ and $\phi_1$ and $\phi_1 + d\phi_1$ before deformation, lie between $\theta_2$ and $\theta_2 + d\theta_2$ and $\phi_2$ and $\phi_2 + d\phi_2$ after deformation.

From equation (6.18) it follows that
\begin{equation}
P_{2}(\theta_{2}, \phi_{2}) = \begin{bmatrix} p_{1}(\theta_{1}, \phi_{1}) \end{bmatrix} \left( \sin \frac{\theta_{1}}{\sin \theta_{2}} \right) J_{12}, \tag{6.21}
\end{equation}

where \( J_{12} \) is the Jacobian:

\[
J_{12} = \begin{vmatrix}
\frac{\partial \theta_{1}}{\partial \theta_{2}} & \frac{\partial \phi_{1}}{\partial \phi_{2}} \\
\frac{\partial \theta_{1}}{\partial \phi_{2}} & \frac{\partial \phi_{1}}{\partial \theta_{2}} \\
\frac{\partial \theta_{2}}{\partial \phi_{2}} & \frac{\partial \phi_{2}}{\partial \theta_{2}}
\end{vmatrix}.
\]

The assumption of affine deformation allows the relationships between \( \theta_{1}, \phi_{1}, \theta_{2} \) and \( \phi_{2} \) to be determined from measurements made on the lines or grid of dots printed on the specimens. If, therefore, the distribution function is known at some stage of the deformation, it can be calculated at other stages, and hence, the optical properties can be calculated. The determination of the birefringence also requires a knowledge of the quantity \( \Delta n_{\text{max}} \).

Provided that the deformation geometry is measured relative to the unoriented state, the distribution function in the deformed state can be found from equation (6.21); for, if the suffix 1 refers to the unoriented state, then \( p_{1} \) is independent of \( \theta_{1} \) and \( \phi_{1} \), and, as equation (6.18) shows, takes the value \( 1/4\pi \). It follows that the distribution function \( p_{2} \), and hence the optical anisotropy in the deformed state, are single valued functions of the state of strain, zero strain corresponding to the unoriented state. This is the hypothesis adopted in Chapter 5.

Suppose that the unoriented material is now extended in the direction of the \( z \)-axis (Figure 6.1) but in such a way that the contraction perpendicular to \( z \) is not isotropic, although the axes \( O_{x}, O_{y} \) and \( O_{z} \) are the principal axes of strain. The distribution function after such an extension, \( p_{2}(\theta_{2}, \phi_{2}) \), can be found as follows. Consider that before extension a line is drawn in the material from the origin \( O \) to the point \( (x_{1}, y_{1}, z_{1}) \). Using the same system of
polar angles as for the unit axis \( \theta_s \), the angles \( \theta_1 \) and \( \phi_1 \) for this line are given by

\[
\tan \theta_1 = \frac{(x_1^2 + y_1^2)^{1/2}}{z_1},
\]

(5.22)

\[
\tan \phi_1 = \frac{x_1}{y_1}.
\]

(6.23)

After extension the coordinates of the point become \((x_2, y_2, z_2)\) and the polar angles of the line become \(\theta_2\) and \(\phi_2\). The relations between these coordinates and angles are those of equations (6.22) and (6.23) with suffix 2 substituted for suffix 1. The relations between \(x_2, y_2, z_2\), and \(x_1, y_1, z_1\), can be written simply:

\[
x_2 = R_x x_1,
\]

\[
y_2 = R_y y_1,
\]

\[
z_2 = R_z z_1,
\]

(6.24)

where \(R_x\), \(R_y\), and \(R_z\) are the principal extension ratios, since \(x\), \(y\) and \(z\) axes are principal axes of strain. From equations (6.22), (6.23) and (6.24) it follows that

\[
\tan \theta_1 = \left(\frac{R_z}{R_y}\right) \left[\cos^2 \phi_2 + \left(\frac{R_y}{R_x}\right)^2 \sin^2 \phi_2\right]^{1/2} \tan \theta_2,
\]

(6.25)

and

\[
\tan \phi_1 = \left(\frac{R_y}{R_x}\right) \tan \phi_2.
\]

(6.26)

Because of the assumption of affine deformation, equations (6.25) and (6.26) can be taken to apply also to the polar angles of the units. By using these relationships in conjunction with equation (6.21) and by putting \(p_1(\theta_1, \phi_1) = 1/(4\pi)\), it can be shown that

\[
p_2(\theta_2, \phi_2) = \frac{R_x^2 R_y^2 R_z^2}{4\pi \left[\left(\frac{R_x^2 \cos^2 \theta_2 + R_y^2 \sin^2 \phi_2}{R_x^2} + \frac{R_y^2 \cos^2 \phi_2}{R_y^2}\right)^2 + \left(R_z^2 \sin^2 \phi_2\right)\right]^{3/2}}.
\]

(6.27)

The quantities \(R_x\), \(R_y\), and \(R_z\) can be obtained by measurement on the material; thus \(p_2(\theta_2, \phi_2)\) is determined.
Substitution in equations (6.19), (6.9), and (6.14) now allow $\gamma_m$ and $\Delta n_{zx}/\Delta n_{\text{max}}$ to be evaluated.

It is pointed out that it is not necessary in all cases to refer deformation to the unoriented state; indeed in some cases this would be impossible if an arbitrary form of distribution is chosen for $p_1(\theta_1, \phi_1)$ irrespective of the previous deformation history. Provided $p_1(\theta_1, \phi_1)$ is known, it is of no consequence whether it refers to an oriented or an unoriented state.

$p_2(\theta_2, \phi_2)$ can be found from equation (6.21) if the deformation in state 2 is measured relative to state 1.

### 6.1.4 Alternative Procedure for Averaging Angular Functions

As discussed in Section 6.1.3, the angular functions after deformation are averaged thus:

$$
\bar{f}_2(\theta_2, \phi_2) = \int_0^{2\pi} \int_0^\pi f_2(\theta_2, \phi_2) p_2(\theta_2, \phi_2) \sin \theta_2 \, d\theta_2 \, d\phi_2.
$$

(6.28)

In order to evaluate $\bar{f}_2(\theta_2, \phi_2)$ it is necessary to determine $p_2(\theta_2, \phi_2)$, the distribution after deformation. This can, however, be avoided by rewriting equation (6.28) in terms of $p_1(\theta_1, \phi_1)$ using equation (6.20) to give

$$
\bar{f}_2(\theta_2, \phi_2) = \int_0^{2\pi} \int_0^\pi f_2(\theta_2, \phi_2) p_1(\theta_1, \phi_1) \sin \theta_1 \, d\theta_1 \, d\phi_1.
$$

(6.29)

In order to evaluate the integral $f_2(\theta_2, \phi_2)$ must be expressed in terms of $\theta_1$ and $\phi_1$. This is possible since $\theta_2$ and $\phi_2$ are related to $\theta_1$ and $\phi_1$ through the geometry of deformation. Equation (6.29) can be rewritten in the form
This form of the equation is more convenient since the transformation of \( p_1(0_1, \phi_1) \) to \( p_2(0_2, \phi_2) \) in terms of the deformation geometry is often complicated and would have to be repeated for each particular form of \( p_1(0_1, \phi_1) \) chosen to describe the initial distribution of units. On the other hand, the transformation of \( f_2(\theta_2, \phi_2) \) to \( f_2(\theta_1, \phi_1) \), although complicated, is the same no matter what form is chosen for \( p_1(0_1, \phi_1) \) and provided the deformation is always described in the same way.

6.2 Application of the Theory to the Experimental Results

6.2.1 First Stage of Experiment

In the first stage of the experiment the polyvinyl chloride was initially unoriented. The tensile direction is taken to be along \( O_2z \). Measurements showed that \( R_x = R_y \) and \( R_x R_y R_z = 1 \). Thus \( R_x = R_y = R_z \). These are the conditions assumed by Kuhn and Grün (1942) and substitution for \( R_x \) and \( R_y \) in equation (6.27) shows that it reduces to their result, namely

\[
\begin{align*}
\frac{f_2(0_2, \phi_2)}{f_2(0_1, \phi_1)} & = \int_0^\pi \int_0^{2\pi} f_2(0_1, \phi_1) p_1(0_1, \phi_1) \sin \theta_1 \, d\theta_1 \, d\phi_1 \\
(6.30)
\end{align*}
\]

This is the distribution function at the end of stage 1. Substitution in equations (6.19) and (6.9) gives \( \gamma_m = 0^0 \) and \( 90^0 \) as was found experimentally. Substitution in equation (6.14) gives the birefringence:

\[
\Delta n_{zx} = \Delta n_{\text{max}} F(R_z) ,
(6.32a)
\]
where

\[
F(R_z) = \frac{2R_z^3 + 1}{2(R_z^3 - 1)} - \frac{3 R_z^3 \arctan (R_z^3 - 1)^{\frac{3}{2}}}{2(R_z^3 - 1)^{\frac{3}{2}}}. \quad (6.32b)
\]

This is the expression found by Kuhn and Grün (1942) and Ward (1962).

Even without a knowledge of \( \Delta n_{\text{max}} \) it is possible to test this expression by plotting measured values of \( \Delta n_{xx} \) against the corresponding values of \( F(R_z) \) calculated from the measured extension ratio, \( R_z \). The graph should give a straight line through the origin. \( \Delta n_{\text{max}} \) would then be obtained from the slope. Figure 6.2 shows the results of plotting this graph for material which was extended at room temperature, 50°C, 71°C and 90°C. Only the material extended at 71°C and 90°C was used in the second stage deformation. All the plotted points except those denoted by square plotting symbols are directly measured values. The square plotting symbols are plots of \( \Delta n \) against \( F(R_z) \), which was evaluated using the extrapolating procedure discussed in Section 5.3.2. The data in Figure 6.2 are those presented in Figure 5.1. Some of the results in Figure 5.1 for material of large values of \( R_z \), prepared at 71°C and 90°C, have not been included in Figure 6.2, in order that a suitable scale could be chosen to show up the curvature in the plot for material extended at 50°C.

The reason for the absence of measured values at small birefringences for room temperature deformation is that, under the conditions of the experiment, the material necked abruptly. Considering the experimental results alone, it cannot be said that the room temperature plot is linear. However, additional evidence for a linear plot is obtained from the square plotting symbols. Also, study of the curves for other temperatures shows that, as the temperature decreases, the plot becomes more nearly
linear. Thus, since the plot for material extended at 50°C is 
very nearly linear, it is reasonable to assume that the plot for 
material extended at room temperature is linear. The slope of 
the line gives $\Delta n_{\text{max}} = 7.2 \times 10^{-3}$. It may be noted that the plot 
is non-linear at 50°C, 71°C and 90°C so that the data for these 
temperatures cannot be fitted simply by choosing a different value 
of $\Delta n_{\text{max}}$.

It appears that the theory is adequate for deformation carried 
out at room temperature, and can therefore be applied to the material 
cold drawn at room temperature in the stage 2 deformation. It is 
also considered that the theory applies to deformation at 50°C, 
but, because of relaxation effects, the birefringence developed 
during extension is less than that which would be predicted by the 
theory. The discrepancy between the theory and experiment for 
material deformed at 50°C was not large, and so it is considered 
reasonable to apply the theory to the material uniformly deformed 
at 50°C in stage 2.

It is interesting to note that Hennig (1967) has applied the 
Kuhn and Grün rigid unit theory to the properties of linear 
thermal expansion, linear isothermal compressibility, and thermal 
conductivity in polyvinyl chloride which had been stretched to 
different extension ratios in the temperature range 90°C-120°C 
and then cooled to room temperature. He found that all three 
properties were well fitted by equations (6.32a) and (6.32b), 
where $\Delta n$ now stands for the differences in property measured 
parallel and perpendicular to the extension direction. It is 
not known why the theory applied at higher temperatures in Hennig's 
case and not in the present one.
It might be thought that the reason for the discrepancy between the theory and the experimental results for 71°C and 90°C in the present case is that at these temperatures the Kuhn and Grün rigid unit model is not appropriate, and that their second model ought to be adopted. In this second model the polymer was considered to consist of a network of chains connected together at cross-link points. Each network chain, i.e. that portion of the molecule between two cross-link points, is considered to contain a number of freely jointed rigid units, which are anisotropic. According to this second model it is the cross-link points which deform affinely and not the units. The distribution of the units is then found by statistical means. Roe and Krigbaum (1964) have shown that for low extension ratios the distribution function is given by

\[ p(0, \phi) = \frac{1}{4\pi} + \frac{1}{3N^2 \pi} (3 \cos^2 \theta - 1) \left( R_z^2 - \frac{1}{R_z} \right) \]  

(6.33)

where \( N \) is the number of random links per network chain. Equation (6.33) is not a function of \( \phi \) since in extending the unoriented material the deformation was assumed to be transversely isotropic. This theory also predicts the following relationship between the birefringence and extension ratio, \( R_z \):

\[ \Delta n_{zx} = \frac{\Delta n_{\text{max}}}{5N} \left( R_z^2 - \frac{1}{R_z} \right) \]  

(6.34)

where \( \Delta n_{\text{max}} \) is the birefringence of the rigid unit. The unit in this model is not necessarily the same as the rigid unit discussed with reference to the first model. However, it could be assumed that the value of \( \Delta n_{\text{max}} \) should be the same for each unit. For instance, in the second model the rigid unit would consist of a length of molecular chain. Similarly the unit of the first model could be considered as a length of molecular chain or a
region in which lengths of polymer chain are parallel. The existence of such structural units in glassy polymers has been suggested by Robertson and Joynson (1963) and Lebedev et al (1967). The optical anisotropy due to a region in which lengths of molecular chain are parallel would be the same as the optical anisotropy due to the individual chains, as suggested in deriving equation (6.14). Ward (1967) in considering the two models assumed that \( \Delta n_{\text{max}} \) was the same in each case. It is assumed, therefore, that \( \Delta n_{\text{max}} \) is equal to \( 7.2 \times 10^{-3} \) in the present case.

One drawback with equation (6.34) is that it gives a curve which is convex to the extension ratio axis, the birefringence increasing more rapidly as the extension ratio, \( R_z \), increases (see Treloar, 1958, p. 208, Figure 10.2, curve e). In contrast, the measured birefringence curves for polyvinyl chloride are concave to the extension ratio axis, tending towards a constant value as the extension ratio increases. Stein and Norris (1956) have shown that the theoretical birefringence can be made to reach a maximum value by modifying the theory to allow for the limited extensibility of the chains. The chains became fully extended when \( R_z = N^{\frac{1}{2}} \). Stein and Norris assumed that the birefringence curve remained convex to the extension ratio axis. The theory was further modified in such a way as to produce a curve concave to the extension ratio axis. The modification consisted of assuming that the network chains were not all of the same length but that there was a distribution of chain lengths, different chains becoming fully extended at different extension ratios. This approach is rather complicated and necessitates the assumption of some chain length distribution. It is not considered, therefore, that this approach is suitable for the present analysis.
The concave nature of birefringence against extension ratio curve can also be accounted for by relaxation effects. At the same time as they are being extended the molecules also tend to relax back to a random configuration. Thus, the birefringence would be less than that expected by an affine deformation model. This relaxation effect would also mean that when held at constant length at the stretching temperature, the birefringence in the strip would gradually decay with time. However, both Utsuo and Stein (1967) and Shindo, Read and Stein (1968) have found that the change of birefringence with time was negligible for material extended at 60°C and 80°C. On the basis of this evidence it is also assumed that relaxation effects are negligible for the polyvinyl chloride used here.

Another factor which might effect the birefringence vs. extension ratio curve is that the cross-linking of the network consists of physical entanglements which may undergo changes as a result of the deformation. It might be expected that such changes in cross-linking would occur as the molecules reached their maximum extension. An approximate method of evaluating the decrease in cross-linking, which is equivalent to an increase in $N$ in equations (6.33) and (6.34), is to fit the measured value of $\Delta n$ and $R_z$ to equation (6.34) with $\Delta n_{\max} = 7.2 \times 10^{-3}$, and hence evaluate $N$. Such results are reproduced in Table 6.1 for material of different extension ratios obtained by extension at 71°C and 90°C. Also evaluated is $N^{1/2}$ which can be seen to be close in value to $R_z$. This would be consistent with the cross-links being broken as the chains tend towards their maximum extensibility.

Bowden and Raha (private communication) have analysed the birefringence changes during extension of polystyrene on the
basis of a model in which cross-links are destroyed during ex-
tension. Although not using exactly the same equation, Bowden
and Raha found that the birefringence is related to the extension
ratio by
\[
\Delta n = \frac{\Delta n_{\text{max}}}{5} \frac{1}{N_0 \exp \left| k \left( R_z - 1 \right) \right|} \left( R_z^2 - \frac{1}{R_z} \right), \tag{6.35}
\]
where \(N_0\) is the number of units per network chain in the unde-
formed material and \(k\) is a constant. In fact this equation
could also be fitted to the results for polyvinyl chloride ex-
tended at room temperature (20°C), 50°C, 71°C, and 90°C. This
is apparent from the plots of \(\Delta n \left[ \Delta n \left( R_z^2 - \frac{1}{R_z} \right) \right]^{1/2}\) against \(R_z\)
shown in Figure 6.3. The points for extension at 20°C are not
actual experimental results but are plotted from results given
by equation (6.32), which gave good agreement with the actual
experimental results. It can be seen that all the plots are
linear. Values of \(N_0\) evaluated from the intercept at \(R_z = 1,\)
and assuming \(\Delta n_{\text{max}} = 7.2 \times 10^{-3}\), are given in Table 6.2, along
with the values of \(k\) for the different stretching temperatures.
It can be seen that \(N_0\) increased and \(k\) decreased with increasing
extension temperature. Although equation (6.35) fits the ob-
served birefringence, it is difficult to justify on physical grounds
its application to deformation below \(T_g\). Equation (6.35) is based
on the theory of rubber elasticity and involved evaluating the
statistical distribution of units in the network chain. Since
at temperatures below \(T_g\), i.e. room temperature and 50°C, the
number of units in the chain becomes close to unit, any statistics
on which equation (6.35) is based would no longer be valid. Neve-
theless, equation (6.35) is useful in that it accounts for the ob-
served variation of birefringence at temperatures both above and
below \(T_g\).
6.2.2 Second Stage of Experiment; Choice of Initial Distribution Function

As a result of the discussion presented in the previous section, it is intended to use Kuhn and Grün's first affine deformation model to describe the molecular re-orientation during the second stage extension at room temperature and 50°C. However, since this model does not apply during the stage 1 deformation, there still remains the problem of selecting an appropriate distribution function at the end of stage 1 and the beginning of stage 2.

The first distribution function to be chosen was that in equation (6.31), given by the Kuhn and Grün first model. This was because of the inference in Chapter 5, that, for any extension ratio, $R_z$, applied at 71°C or 90°C to the unoriented material, it is possible to find an equivalent extension ratio, $R^*_z$, which, if applied to the unoriented material at room temperature, would produce the same state of optical anisotropy. Thus, the distribution at the beginning of stage 2 was taken to be that in equation (6.31), with $R_z$ replaced by $R^*_z$. $R^*_z$ was evaluated by fitting the birefringence at the beginning of stage 2 to equation (6.32) with $\Delta n_{\text{max}} = 7.2 \times 10^{-3}$. This value of $R^*_z$, with the exception of that for the material with $R_z = 7.5$, would be very close to that obtained using the extrapolation procedure discussed in Chapter 5, since the latter results lie very close to the straight line in Figure 6.2. This distribution will be referred to as the Kuhn and Grün type 1 distribution.

Since the material used for the stage 2 deformation was originally extended in stage 1 at 71°C or 90°C, at which temperatures the material behaved in a rubbery manner, the Kuhn
and Grün second model might be considered to be the most suitable for evaluating the distribution function at the end of stage 1 and the beginning of stage 2. In this case, the distribution function would be as in equation (6.33). \( N \) was evaluated by fitting the measured values of \( \Delta n \) and \( R_z \) to equation (6.34), assuming that \( \Delta n_{\text{max}} = 7.2 \times 10^{-3} \). This value of \( N \) and the measured \( R_z \) were then used in equation (6.33) to give the distribution function. This distribution function will be referred to as the Kuhn and Grün type 2 distribution. A method essentially the same as this one has been used by Ward (1967) to account successfully for birefringence changes in oriented polyethylene terephthalate deformed in tension in the molecular alignment direction at room temperature after first being oriented by extrusion.

The Kuhn and Grün type 1 distribution function has been criticized by Gupta and Ward (1967). These authors have also used an empirical distribution function suggested by Raraty (1966), which they regarded as being rather more realistic and as giving a better fit to their polyethylene results. X-ray investigations by Gupta, Keller and Ward (1968) and NMR investigations by McBrierty and Ward (1968) have also shown the Raraty distribution to be the most appropriate for oriented polyethylene. Although there is no evidence to suggest that the Raraty distribution would be suitable for hot stretched polyvinyl chloride, calculations have also been carried out with this as the distribution function at the beginning of stage 2. The Raraty distribution takes the following form:

\[
p(\theta, \phi) = N \exp \left[ -\frac{1}{2} \frac{\tan^2 \theta}{\tan^2 \theta_0} \right],
\]

where \( N \) and \( \theta_0 \) are constants. \( N \) and \( \theta_0 \) were evaluated by fitting the measured birefringence of the starting material. This will be discussed in a later section.
The theory discussed in Section 6.1 will now be applied to the process of extension in the second stage of the experiment using the above distribution functions at the beginning of stage 2. It will be convenient to define the following states of the material:

state 1 - unoriented at the start of stage 1;
state 2 - oriented at the end of stage 1 and before extension in stage 2;
state 3 - re-oriented after extension in stage 2.

Suffixes 1, 2, and 3 will be used to correspond with these three states. The detailed application of the theory to each distribution function will be discussed in the following sections and the results will be discussed collectively in Section 6.3.

6.2.3 Second Stage of Experiment; Kuhn and Grün Type 1 Distribution

The distribution function to be used in this section will be that in equation (6.31), with $R_z$ replaced by $R_z^*$. In principle the simple way to calculate the extinction directions and birefringence after extension in stage 2 is in the following steps:

1. Calculate the distribution function $p_2(\theta_2, \phi_2)$ at the start of stage 2 by substituting $R_z^*$ for $R_z$ in equation (6.31).
2. Calculate the distribution function $p_3(\theta_3, \phi_3)$ after extension in stage 2 from $p_2(\theta_2, \phi_2)$ by using equation (6.21) with suffixes 3 and 2 replacing 2 and 1 respectively. The relationships between polar angles $\theta_3$, $\phi_3$, $\theta_2$ and $\phi_2$ are obtainable from measurements made on the grid of dots printed on the specimen at the start of stage 2.
3. Calculate the extinction directions and the birefringence from equations (6.9), (6.14), and (6.17).
In practice, however, this method involved a considerable amount of calculation in step (2) to obtain $p_3(0,\phi_3)$, because of the somewhat complex relationship between the angles. Therefore, an alternative method was adopted.

Since, in this particular case, the molecular re-orientation in the first and second stages of the experiment occur according to the Kuhn and Grün first model, use can be made of the result noted in Section 6.1.3, namely that the distribution function $p(0,\phi)$ is unique for a given state of strain, no matter how that strain was achieved. For calculation purposes, therefore, the material can be considered to have been taken direct from state 1 to state 3 in one (fictitious) deformation process, and the distribution function $p_3(0,\phi_3)$ can be obtained from equation (6.27). In this equation $R_x, R_y$ and $R_z$ are replaced by $R'_x, R'_y$ and $R'_z$, the principal extension ratios for the fictitious state 1-state 3 deformation. The principal axes of strain from this deformation will be denoted by $Ox', Oy'$ and $Oz'$, where $Oy'$ is perpendicular to the face of the sheet and therefore parallel to $Oy$, but $Ox'$ and $Oz'$ are not parallel to $Ox$ and $Oz$. Suffix 2 is replaced by suffix 3, and $\phi_3$ and $\phi_3$ are measured with respect to $Ox', Oy'$ and $Oz'$.

The evaluation of $R'_x, R'_y$, and $R'_z$ will now be described with the aid of the diagrams in Figure 6.4. A grid of dots was printed on the face of the specimen at the start of stage 2 (i.e. state 2), having a square basis with sides $c_2 = a_2$ (Figure 6.4(b)). One of the sides ($OC$) was arranged to be parallel to the tensile direction of the stage 1 extension, (the Oz direction of Section 6.2.1). State 2 is considered to have been produced from the unoriented state 1 by a transversely isotropic, constant volume extension of extension ratio $R^*_z$ in the z direction. Thus, in
state 1 the grid square would have been a rectangle of sides \( c_1^* \) in the z direction and \( a_1^* \) perpendicular to the z-direction given by

\[
a_1^* = a_2 \left( \frac{\hat{a}_2}{c_2^*} \right)^{\frac{1}{2}},
\]

\[
c_1^* = c_2 \left( \frac{\hat{a}_2}{c_2^*} \right)^{-1}.
\]

The grid basis became a parallelogram in state 3 (after the stage 2 extension) as illustrated in Figure 6.4(c), with sides \( c_3 \) and \( a_3 \), and angle \( \omega \) between the sides. The Oz axis is taken to be along the same line of dots as in state 2. \( R'_x, R'_y \) and \( R'_z \) are therefore the principal extension ratios of a deformation which converts the rectangle of Figure 6.4(a) to the parallelogram of Figure 6.4(c). It is then straightforward to show that

\[
(R'_x + R'_z)^2 = \left[ \frac{a_3}{a_1^*} \right]^2 + \left[ \frac{c_3}{c_1^*} \right]^2 + 2 \left[ \frac{a_3}{a_1^*} \frac{c_3}{c_1^*} \right] \sin \omega,
\]

\[
(R'_z - R'_x)^2 = \left[ \frac{a_3}{a_1^*} \right]^2 + \left[ \frac{c_3}{c_1^*} \right]^2 - 2 \left[ \frac{a_3}{a_1^*} \frac{c_3}{c_1^*} \right] \sin \omega,
\]

and that the principal axis of strain Oz' makes an angle \( \alpha \) with Oz given by

\[
\tan 2\alpha = \frac{\sin 2\omega}{\left[ \frac{a_1^*}{a_3} \frac{c_3}{c_1^*} \right]^2 + \cos 2\omega}.
\]

(See Jaegar (1962). These are his equations 19, 28 and 29 on pages 27 and 28 of his book with the following substitutions: \( c_3/c_1^* \) for his \( a \); \( (a_3/a_1^*) \cos \omega \) for his \( b \); zero for his \( c \); \( (a_3/a_1^*) \sin \omega \) for his \( d \); \( R'_z \) for his \( A \); \( R'_x \) for his \( B \); \( \alpha \) for his \( \alpha' \).)

By substitution of the measured values of \( a_2, c_2, a_3, c_3 \) and \( \omega \), and the derived values of \( \hat{a}_2 \) into equations (6.37), (6.38)
and \((6.39)\), the quantities \(R_x'\) and \(R_z'\) can be found. \(R_y'\) is obtained by using the fact that the deformation was at constant volume, so that \(\sum R_i' = 1\). Substitution in equation \((6.27)\) as described in the previous paragraph then gives the distribution function \(p_3(\theta_3, \phi_3)\) for the end of the second stage and the optical properties can be calculated. The extinction directions can be found with the aid of equations \((6.9)\) and \((6.19)\). The angle \(Y\) of equation \((6.9)\) is the angle between the extinction direction and the \(z'\) axis, which is one of the principal directions of strain for the fictitious state 1-state 3 deformation. The calculations show that in all cases \(Y = 0^\circ\) and \(90^\circ\), that is, the extinction directions coincide with the principal axes of strain \(Oz'\) and \(Ox'\) (as assumed in Chapter 5). By using equations \((6.37)\) and \((6.40)\), these directions can be located with respect to the line of dots \(Oz\), and hence with respect to the tensile axis (since the angle between \(Oz\) and the tensile axis was measured). Substitution of the measured values of \(c_3, a_3, c_2, a_2\) and \(\omega\), and of the derived values of \(R^*_z\), gives \(\alpha\), which is the angle between \(Oz\) and \(Oz'\). The birefringences were calculated with the aid of equations \((6.19)\), \((6.14)\) and \((6.17)\), putting for \(\Delta n_{\text{max}}\) the value of \(7.2 \times 10^{-3}\) obtained from the experimental results of stage 1. The results obtained will be discussed in more detail in a later section.

In order to check the results obtained using the above method, the birefringence, \(\Delta n_{xz'}\), and extinction directions were calculated by the method discussed in Section 6.1.4. In this case the angular functions were calculated from equation \((6.30)\) with suffix 2 replaced by 3 and the suffix 1 replaced by 2. \(p_2(\theta_2, \phi_2)\) was taken as equation \((6.31)\) with \(R^*_z\) replacing \(R_z\).
The terms \( f_3(\theta_2, \phi_2) \) were derived in terms of \( \theta_2, \phi_2, a_2, c_2, a_3, c_3 \) and \( \omega \). This first necessitated evaluating \( \theta_2 \) and \( \phi_2 \) in terms of \( \theta_3 \) and \( \phi_3 \). When the deformation is described by the grid of dots as shown in Figures 6.4(b) and 6.4(c) it can be shown that

\[
\tan \theta_2 = (\tan^2 \phi_3 + h^4 d^2)^{\frac{1}{2}} \left\{ \frac{d(\tan^2 \phi_3 + 1)^{\frac{1}{2}}}{a \tan \theta_3} - \frac{b \tan \phi_3}{a} \right\}^{-1},
\]

(6.41)

\[
\tan \phi_2 = \frac{\tan \phi_3}{h^2 d},
\]

(6.42)

where \( a = c_3/c_2, b = (a_3/a_2) \cos \omega, d = (a_3/a_2) \sin \omega \) and \( h = (c_3 a_3/c_2 a_2) \sin \omega \). \( a_2, c_2, a_3, c_3 \) and \( \omega \) were measured from the grid of dots. By suitably manipulating equations (6.41) and (6.42), the angular functions \( f_3(\theta_2, \phi_2) \) were found to be

\[
\cos^2 \theta_3 = \left[ \frac{(\tan^2 \phi_2 + 1)^{\frac{1}{2}}}{\tan \theta_2} + \frac{b \tan \phi_2}{a} \right]^2 \left[ \frac{(d^2 h^4 \tan^2 \phi_2 + 1)}{a^2 h^4} \right]^{-1},
\]

\[
\sin^2 \theta_3 \sin^2 \phi_3 = \frac{d^2 \tan^2 \phi_2}{a^2} \left[ \frac{(d^2 h^4 \tan^2 \phi_2 + 1)}{a^2 h^4} \right]^{-1},
\]

\[
\sin \theta_3 \cos \theta_3 \sin \phi_3 = \frac{d \tan \phi_2}{a} \left[ \frac{(\tan^2 \phi_2 + 1)^{\frac{1}{2}}}{\tan \theta_3} + \frac{b \tan \phi_2}{a} \right]^2 \left[ \frac{(d^2 h^4 \tan^2 \phi_2 + 1)}{a^2 h^4} \right]^{-1} \left[ \frac{(\tan^2 \phi_2 + 1)^{\frac{1}{2}}}{\tan \theta_3} + \frac{b \tan \phi_2}{a} \right]^2 \right\}^{-1}.
\]

(6.43)

From equations (6.43) and (6.30) with suffixes 1 and 2 replaced by 2 and 3 respectively \( f_3(\theta_3, \phi_3) \), and hence \( \Delta_n_{xx} \) and \( \gamma_m \), could be evaluated using equations (6.9) and (6.14).
6.2.4 Second Stage of Experiment; Kuhn and Grün Type 2 Distribution

In this section, it is intended to consider the second distribution function suggested by Kuhn and Grün, namely

\[ p_2(\theta_2, \phi_2) = \frac{1}{4\pi} + \frac{1}{8N\pi} (3 \cos^2 \theta_2 - 1) \left( R_z^2 - \frac{1}{R_z} \right). \quad (6.44) \]

Since \( p_2(\theta_2, \phi_2) \) in this equation is a function of \( \theta_2 \) only, it can only be used for material having transverse isotropy. This can be considered to be the case for the material in state 2 since the stage 1 deformation was transversely isotropic.

The extinction directions and birefringence after extension in stage 2 were calculated in the following steps: (1) the distribution function \( p_2(\theta_2, \phi_2) \) at the start of stage 2 was evaluated by fitting \( N \) to the measured birefringence and \( R_z \), as discussed in Section 6.2.2. (2) The angular functions were then averaged using equation (6.30), suffixes 2 and 1 replaced by 3 and 2 respectively, and equation (6.43). (3) From these averaged angular functions the values of \( \gamma_m \) and \( \Delta n_{2x} \) after deformation were evaluated using equations (6.9) and (6.14).

6.2.5 Second Stage of Experiment; Raraty Distribution

It was assumed in the previous two sections that the distribution function in state 2 was related in some way to the deformation in stage 1, whether this be actual or fictitious. It is now intended to consider the distribution in state 2 to be of the type suggested by Raraty, namely

\[ p_2(\theta_2, \phi_2) = N \exp \left( -\frac{\tan^2 \theta_2}{2 \tan^2 \theta_0} \right). \quad (6.45) \]

Since no affine deformation model would give a distribution of the form in equation (6.45), the parameters \( \theta_0 \) and \( N \), which define
the precise shape of the distribution, cannot be related to the prior deformation in stage 1, but must be fitted to some measured property such as the birefringence. This is essentially the same method as that used in evaluating $R_2^*$ and $N$ for the two Kuhn and Grün distributions.

The extinction direction and birefringence after extension in stage 2 were calculated in the following steps: (1) the distribution function $p_2(\theta_2, \phi_2)$ at the start of stage 2 was calculated by adjusting the constants $N$ and $\theta$ to fit the measured birefringence for state 2. (2) The distribution function $p_3(\theta_3, \phi_3)$ after extension in stage 2 was calculated using equation (6.21), with suffixes 3 and 2 replacing 2 and 1 respectively. The relationships between $\theta_3$, $\phi_3$, $\theta_2$ and $\phi_2$ were obtained from measurements on the grid of dots and are as shown in equations (6.41) and (6.42). (3) The extinction direction and birefringence, $\Delta n_{zx}$, were calculated, using $p_3(\theta_3, \phi_3)$, from equations (6.19), (6.9), and (6.14).

The birefringence for state 2 is given in terms of the averaged angular functions by equation (6.14). However, because of the transverse isotropy, $\sin \theta_2 \cos \theta_2 \sin \phi_2 = 0$ and $\sin^2 \theta_2 \sin^2 \phi_2 = 0.5 \sin^2 \theta_2$, and it can be shown that equation (6.14) reduces to

$$\Delta n_{zx} = 0.5 \Delta n_{\text{max}} (1 - 3 \cos^2 \theta_2) , \quad (6.46)$$

where

$$\cos^2 \theta_2 = \int_0^{2\pi} \int_0^\pi p_2(\theta_2, \phi_2) \cos^2 \theta_2 \sin \theta_2 \, d\theta_2 \, d\phi_2 . \quad (6.47)$$

Thus to fit the birefringence at stage 2, the Raraty distribution must be such that
There are two unknowns, \( N \) and \( \theta_o \), in equation (6.48), but one of these can be eliminated since \( p_2(\theta_2, \phi_2) \) must satisfy the following condition:

$$
\int_0^{2\pi} \int_0^{\pi} N \exp \left( -\frac{\tan^2 \theta_2}{2 \tan^2 \theta_o} \right) \cos^2 \theta_2 \sin \theta_2 \ d\theta_2 \ d\phi_2 = \frac{1}{3} \left( 1 - \frac{2\Delta n}{\Delta n_{\text{max}}} \right) .
$$

(6.48)

Dividing equation (6.48) by equation (6.49) gives

$$
\int_0^{2\pi} \int_0^{\pi} N \exp \left( -\frac{\tan^2 \theta_2}{2 \tan^2 \theta_o} \right) \sin \theta_2 \ d\theta_2 \ d\phi_2 = \frac{1}{3} \left( 1 - \frac{2\Delta n}{\Delta n_{\text{max}}} \right) .
$$

(6.49)

The only unknown in equation (6.50) is \( \theta_o \). From Table 1 given by Raraty (1966) it was possible to determine, within a 5° range, the value of \( \theta_o \) which satisfies equation (6.50). The left hand side of equation (6.50) was then computed for 0.2° steps in \( \theta_o \) within the 5° range, and the value of \( \theta_o \) was found which satisfied most closely equation (6.50). Using this value of \( \theta_o \), \( N \) was determined from equation (6.49). The distribution function, \( p_3(\theta_3, \phi_3) \), at the end of stage 2 was evaluated using equations (6.21), (6.41) and (6.42) to give

$$
p_3(\theta_3, \phi_3) = \frac{d^2 h^2}{a} N \exp \left[ -\frac{(\tan^2 \phi_3 + h^4 d^2)}{2 \tan^2 \theta_o} \right] \left\{ \frac{d (\tan^2 \phi_3 + 1)^{\frac{3}{2}}}{a \tan \theta_3} \right\}^2 \left[ \frac{b \tan \phi_3}{a} \right]^2 + \frac{(\tan^2 \phi_3 + 1)^{\frac{3}{2}} (1 + \tan^2 \theta_o)^{\frac{3}{2}}}{\tan^3 \theta_3}
$$

(6.51)
knowing $p_3(\theta_3, \phi_3)$, the averaged angular functions $\cos^2 \theta_3$, 
$\sin^2 \theta_3 \sin^2 \phi_3$, and $\sin \theta_3 \cos \theta_3 \sin \phi_3$ were evaluated, and hence 
the extinction direction and birefringence at the end of stage 2 
could be determined from equations (6.9) and (6.14).

A check on the above calculation was carried out using the 
procedure suggested in Section 6.1.4. The angular functions 
$f_3(\theta_3, \phi_3)$ were averaged using equation (6.30) with suffixes 1 
and 2 replaced by 2 and 3. $p_2(\theta_2, \phi_2)$ was evaluated as above, 
and the angular functions $f_3(\theta_2, \phi_2)$ were as in equation (6.43).

6.3 Results and Discussion

All stages of the calculations discussed in the previous 
sections were carried out using an ICL 1905 F computer. The 
integrals used in averaging the angular functions were evaluated, 
using Simpson's method, to an accuracy of ±0.1%. Since it was 
necessary to subtract the angular functions in calculating $\Delta n_{zx}$ 
or $\Delta n_{xy}$, accuracies of less than ±0.5% in the angular functions 
could, depending upon the relative magnitudes of the functions, 
give rise to large inaccuracies in the values of the birefringence. 
Because of the somewhat complicated nature of the equations, a 
number of checks were carried out on the programmes. Having 
evaluated the precise shape of the function at the beginning of 
stage 2 from the measured birefringence at the beginning of stage 
2, the condition of zero strain in stage 2, i.e. $a_2 = c_2 = a_3 = c_3$ 
and $\omega = 90^\circ$, was used in the programme. Under these circum-
stances the computed value of $\Delta n_{zx}$ should be the same as that 
used initially in determining the exact shape of the distribution 
function in state 2, and $\gamma_m = 0^\circ$; this was always found to be 
the case. Also, by using $\Delta n = 0$ in determining the distribution
function at the beginning of stage 2, all programmes should give
the same variation of birefringence with extension ratio as that
given by equation (6.32). All programmes were found to satisfy
this condition. In the case of the Raraty distribution when the
averaged angular functions were evaluated from the distribution
function at the end of stage 2, another useful check was to see
if \( p_3(\theta_3, \phi_3) \) satisfied equation (6.18). This condition was al­
ways satisfied to better than 0.1%. In addition, when \( y_m \) and
\( \Delta n_{zx} \) were evaluated by two different methods, the value of \( y_m \)
and \( \Delta n_{zx} \) were in agreement to within 0.5\(^\circ\) and 1\% respectively.
Dr. T. Hinton (private communication) has evaluated \( y_m \) and \( \Delta n_{zx} \)
for the Kuhn and Grün type 1 distribution using a numerical
method, and his results showed similar good agreement with those
evaluated using the above method.

The results of these calculations are shown in Figures 6.5
and 6.6 for test pieces extended at 50\(^\circ\)C in stage 2, and in
Figure 6.7 and 6.8 for test pieces extended at room temperature
in stage 2. \( y_m \) gave the angle between the extinction direction
and Oz, but since the angle between Oz and the tensile axis, Ot,
was measured, \( \lambda \) could be evaluated. \( \lambda \) is plotted as a function
of \( R_t \) and \( \lambda_o \) in Figures 6.5 and 6.7 respectively, for the three
distribution functions discussed in Section 6.2. Experimental
points are also plotted in these figures. The predicted values
of \( \Delta n_{zx} \) for the three distribution functions are plotted in Figures
6.6 and 6.8 along with the experimental points. Also shown is
\( \Delta n_{zy} \) which was only evaluated using the Kuhn and Grün type 1 dis­
tribution in stage 2.

It can be seen from Figures 6.5 and 6.7 that the different dis­
tribution functions gave the correct variation for \( \lambda \), but in all
cases the predicted values were smaller than those actually measured. The Kuhn and Grün type 1 distribution gave the closest agreement with experiment, and the Raraty distribution gave the largest discrepancy between experimental and predicted results; the results for the Kuhn and Grün type 2 distribution were intermediate between those for the Kuhn and Grün type 1 and Raraty distributions. It is as a consequence of the failure of the Kuhn and Grün type 1 distribution to account for the observed variation of $\lambda_0$, that the values of $R_z (\text{calc})$, calculated as discussed in Chapter 5, varied as a function of extension ratio, $R_t$. In Section 6.2.3 the calculated extinction direction was always found to be parallel to the principal axis of strain, $Oz'$. This result was independent of $R_t$. However, the determination of the angle $\alpha$ between $Oz'$ and the grid line, $Oz$, did require a knowledge of $R_t^*$ and the use of equation (6.40). Reference to Section 5.3.2 shows that $R_z (\text{calc})$ was obtained by the reverse of this route, starting from the assumption that the extinction direction and the principal axis of strain were parallel. Thus, the divergence between the measured and calculated values of $\lambda$ is directly related to the non-constancy of $R_z (\text{calc})$.

As far as the birefringence results in Figure 6.6 are concerned, the predicted results did not agree with the experimental results. For $\lambda_0 = 64^\circ$, $R_z = 2.9$ and 7.5, and $\lambda_0 = 56^\circ$, $R_z = 4.4$, the agreement is quite good for small values of $R_t$, but at large values of $R_t$, the discrepancy became progressively larger. For $\lambda_0 = 25^\circ$, $R_z = 4.4$, and $\lambda_0 = 0^\circ$, $R_z = 3.0$ and 1.0, the predicted and experimental results do not agree. With the exception of $\lambda_0 = 0^\circ$, $R_z = 3.0$, the Kuhn and Grün type 1 distribution gives the best agreement with the measured results in all cases. The
discrepancy between predicted and experimental results could be considered to arise from the fact that the Kuhn and Grün affine deformation model is not strictly applicable to deformation at 50°C. However, it is clear from the results for $\lambda_o = 0^\circ$, $R_z = 1.0$, that this would result in the predicted values of $\Delta n_{z\bar{x}}$ being larger than the predicted ones. This would account for the discrepancy at large values of $R_t$ for $\lambda_o = 64^\circ$, $R_z = 2.9$ and 7.5, and $\lambda_o = 56^\circ$, $R_z = 4.4$, but not for the discrepancy at $\lambda_o = 25^\circ$, $R_z = 4.4$, and $\lambda_o = 0^\circ$, $R_z = 3.0$, for which the predicted values of $\Delta n_{z\bar{x}}$ were smaller than the measured values. Another possibility is that the incorrect form of the distribution function was chosen. However, it is thought that any improvement in results in one case would only result in a greater discrepancy in another case if a new form of distribution function was used.

As far as the results in Figure 6.8 are concerned the Kuhn and Grun type 1 distribution gives the best agreement with experiment, but again there was some discrepancy between experimental and predicted results.

It can also be seen from Figure 6.6 that $\Delta n_{z\bar{y}}$ calculated using the Kuhn and Grün type 1 distribution increased with increasing values of $R_t$. This is not surprising since the thicknesses of the test pieces decreased as $R_t$ increased. Thus, units aligned out of the plane of the sheet tended to become aligned parallel to the sheet, and the birefringence, $\Delta n_{z\bar{y}}$, measured using light transmitted parallel to the plane of the sheet, would increase.

If the unit in the affine deformation model is considered to be either a length of molecular chain, or a region in which molecular chains are parallel, the value of $\Delta n_{\text{max}}$ can be related to the polarizability of the molecules using equation (6.15).
considering the polarizabilities of the bonds comprising the molecules, the polarizability of the molecules can be calculated, and hence compared with the value obtained for $\Delta n_{\text{max}}$, i.e. $7.2 \times 10^{-3}$. Rider (private communication) has carried out such a calculation using the values of polarizabilities given by Bunn (1961) (Table IX). He showed that, if during the extension the molecules became aligned in the extinction direction, then the oriented polyvinyl chloride would be negatively birefringent. This was not the case for the results discussed here. However, Rowell and Stein (1967) have pointed out that polarizability is affected by such factors as the size of the molecule, whether the molecule is in the vapour or solid phase, whether the solid phase is crystalline or amorphous, and the crystal structure of the solid phase. These differences were accounted for by the internal field effects due to the interaction between neighbouring molecules. Since the result quoted by Bunn (1961) for the polarizability of the C-Cl bond was that evaluated by Denbigh (1940) for low molecular weight compounds in the liquid state, this value, which was used by Rider, cannot be considered to be applicable to polyvinyl chloride in the solid state. Denbigh (1940) even found some discrepancy between the values of the polarizability of the C-Cl bond evaluated for two different low molecular weight compounds, CH$_3$Cl and CH Cl$_3$. The effect of changing the internal field on the birefringence of oriented polyvinyl chloride has also been indicated by the results of Andrews and Kazama (1968). In changing the temperature from approximately 0°C to -200°C they found that the birefringence decreased by approximately 35%. Such changes could not be accounted for by changes in molecular alignment since there would be little molecular motion at these temperatures. Thus the birefringence decrease can only be accounted for by
changes in internal field effects arising from the temperature change. It seems likely that any additives would also affect the polarizability of the molecules. In view of the above discussion the result obtained by Rider, that the birefringence of oriented polyvinyl chloride should be negative, cannot be considered applicable to the material used in these experiments. It was suggested in Chapter 2 that birefringence cannot be used to compare molecular alignment in Cobex and Vybak. This is because different amounts of additives might result in different molecular polarizabilities, giving rise to different values of $\Delta n_{\text{max}}$ for the two materials, and hence, for a given birefringence, the distribution function would be different for each material.

Although in evaluating $\gamma_m$ and $\Delta n_{zx}$ the distribution functions were used in averaging the angular functions, the different shapes of the functions before and after extension in stage 2 have not so far been considered. In Figures 6.9, 6.10, and 6.11 the section in the xz plane for each of the distribution functions is given for material with $R_z = 2.9$ and birefringence $1.34 \times 10^{-3}$, before and after extension at $50^\circ$C in stage 2 with $R_\varepsilon = 1.76$. The distributions before deformation are plots of equations (6.31), (6.33), and (6.36). The Raraty distribution after deformation is a plot of equation (6.51) with $\phi_3 = 90^\circ$. Equations (6.27), (6.38) and (6.39) were used in determining the shape of the Kuhn and Grün type 1 distribution function after deformation. Using equations (6.21), (6.41), (6.42), and (6.44) it can be shown that the Kuhn and Grün type 2 distribution takes the following form after deformation in stage 2:
\[ p_3(\theta_3, \phi_3) = \frac{d^2 h^2}{a} \left[ \frac{1}{4\pi} - \frac{1}{8\pi} (3F(\theta_3, \phi_3) - 1) (R_z^2 - R_z^{-1}) \right] \]
\[ x \frac{(\tan^2 \phi_3 + 1)^{\frac{3}{2}}}{\tan^3 \theta_3} \left( 1 + \tan^2 \theta_3 \right)^{\frac{3}{2}} \left[ \left( \frac{d(\tan^2 \phi_3 + 1)^{\frac{1}{2}}}{a \tan \theta_3} - \frac{b \tan \phi_3}{a} \right) \right]^{\frac{3}{2}} \]
\[ + \tan^2 \phi_3 + h^4 d^2 \right]^{\frac{3}{2}}, \]  

(6.52)

where

\[ F(\theta_3, \phi_3) = \left[ \left( \frac{d(\tan^2 \phi_3 + 1)^{\frac{1}{2}}}{a} - \frac{b \tan \phi_3}{a} \right) \right] \left[ (\tan^2 \phi_3 + h^4 d^2) \right]^{-1} \]

Equation (4.52) with \( \phi_3 = 90^\circ \) was used in plotting the Kuhn and Grün type 2 distribution after deformation in stage 2. It can be seen from Figures 6.9, 6.10, and 6.11 that, in going from the Kuhn and Grün type 1 distribution, through the type 2 distribution to the Raraty distribution, there is a gradual change in shape of the distribution prior to extension in stage 2. Both the maximum and minimum lengths of the radius vector become smaller, but at intermediate positions the radius vector increases in length. This progressive change in shape accounts for the result noted earlier that, as far as the predicted values of \( \lambda \) and \( \Delta n_{zx} \) are concerned, the behaviour of the Kuhn and Grün type 2 distribution was intermediate between that of the other two distributions.

It can be seen from Figure 6.9 that, for the Kuhn and Grün type 1 distribution, the distribution functions before and after extension in stage 2 are of a similar shape, although the size has changed. In each case the extinction direction coincides with the maximum of the distribution. (The extinction directions indicated in Figures 6.9, 6.10, and 6.11 are those predicted by
the theory for each distribution function.) These two results arise from the fact that the stage 1 and stage 2 deformations can be replaced by one fictitious deformation going from state 1 to state 3. Because of this, the distribution function is always of the form given by equation (6.27).

As far as the Raraty distribution is concerned, the distributions before and after extension (Figure 6.11) are of different shapes. In particular, two maxima have developed as a result of the extensions, and the extinction direction coincides with neither of these. (In referring to two maxima, a range of 180° only in θ is being considered.) However, the extinction direction is closest in direction to the larger of the two maxima. Since the initial distribution is symmetrical the extinction direction coincides with the maximum of the distribution in state 2. The relative magnitudes of the two maxima which develop during extension in stage 2 depend to some extent upon the value of $\lambda_0$. For instance, calculations have shown that at $\lambda_0 = 90^\circ$ two equal maxima develop, but at $\lambda_0 = 0^\circ$ there remains only one maximum. Because of the diffuse nature of the diffraction photographs, it was not possible to obtain X-ray evidence for the existence of two maxima in the distribution.

The behaviour of the Kuhn and Grün type 2 distribution is intermediate between the two other distributions. Again two maxima develop but the smaller one is not as well developed as the corresponding maximum for the Raraty distribution.

It has been stated by Gupta, Keller and Ward (1967) that the Kuhn and Grün type 1 distribution is elliptical in shape. However, it is clear from Figure 6.9 that this is not the case. Although the strain, to which the distribution function is related by the affine deformation model, can be described by the
strain ellipse, the distribution is not elliptical. Similarly
the Kuhn and Grün type 2 distribution function, although related
to the strain ellipse by a second affine deformation model, is
not elliptical.

In this Chapter it has been shown that the molecular re-
orientation during the extension of the unoriented polyvinyl chloride
at room temperature (20°C) can be accounted for by Kuhn and Grün's
first affine deformation model. In this model it is assumed
that the material consists of a large number of rigid anisotropic
units which undergo affine rotation during deformation. It was
found, by fitting equation (6.32) to the experimental results, that
this model predicts that the maximum birefringence which can be
achieved by extension, i.e. $\Delta n_{\text{max}}$, is equal to $7.2 \times 10^{-3}$. For
extension of unoriented material at temperatures above 20°C, the
fit between the results predicted by the affine deformation model
and those actually measured becomes progressively worse as the
extension temperature is increased. It was, however, considered
that the affine deformation model still gave a good approximation
to the behaviour of the material extended at 50°C.

The birefringence results for unoriented material extended at
various temperatures could be fitted to an equation, used by
Bowden and Raha (unpublished), which is based on molecular net-
work theory, but which allows the cross-link density to change
during deformation. This equation is particularly useful in
that it describes for the observed birefringence changes at
temperatures both above and below $T_g$.

As far as the extension of the oriented material in stage 2
is concerned, three different distribution functions were used
to describe the molecular orientation in state 2 before extension
in stage 2. Using the first Kuhn and Grün affine deformation model to describe the molecular re-orientation during extension in stage 2, it was found that the observed variation of birefringence was best fitted by using the Kuhn and Grün type 1 distribution in state 2. Although there was some discrepancy between predicted and experimental results, the theory did account for the salient features of the observed behaviour, in particular the observed minima in the birefringence for $\lambda_0 = 64^\circ$, $R_z = 2.9$ and $7.5$, and $\lambda_0 = 56^\circ$, $R_z = 4.4$. At small values of extension ratio, $R$, the agreement between theory and experiment was quite good for the curves which showed a minimum.

The result, that the birefringence changes during the deformation of unoriented polyvinyl chloride at room temperature can be accounted for by the Kuhn and Grün affine deformation model, suggests that the molecular alignment in this material would be described by the Kuhn and Grün type 1 distribution function. If this material had been subsequently retested at room temperature in stage 2, it is to be presumed that the agreement between theory and experiment would be good. Unfortunately insufficient Vybak was available to test this prediction. However, it was possible to extend Cobex strip at $50^\circ$C, and the strip was sufficiently wide for small test pieces, which were extended in stage 2 at room temperature, to be cut from it. Although no detailed results were obtained, rough calculations did indicate that the value of $R_z$ (calc), evaluated as discussed in Section 5.3.2, was close to that of $R_z$, the measured extension ratio in stage 1. This suggests that the theory would be able to predict quite accurately the observed variation of $\lambda$ during deformation, and also possibly the variation of birefringence. The good agreement between theory
and experiment achieved by Brown, Duckett and Ward (1968b) presumably arises from the fact that both stages of their experiment were carried out at the same temperature.

In view of the simple nature of the model and of the fact that deformation in stages 1 and 2 was carried out at different temperatures, the agreement between theory and experiment was quite satisfactory. The theory would presumably account for the observed optical anisotropy changes in deformation bands, as reported in Chapter 3.
Table 6.1

Values of $N$ and $N^\frac{1}{2}$ evaluated for Vybak having different values of $R_z$ and birefringence.

<table>
<thead>
<tr>
<th>$R_z$</th>
<th>Birefringence $\Delta n_{10}$</th>
<th>$N$</th>
<th>$N^\frac{1}{2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>0.38</td>
<td>6.0</td>
<td>2.5</td>
</tr>
<tr>
<td>2.9</td>
<td>1.34</td>
<td>8.7</td>
<td>2.9</td>
</tr>
<tr>
<td>3.0</td>
<td>1.4</td>
<td>9.0</td>
<td>3.0</td>
</tr>
<tr>
<td>4.4</td>
<td>1.93</td>
<td>14.3</td>
<td>3.8</td>
</tr>
<tr>
<td>5.0</td>
<td>2.1</td>
<td>17.0</td>
<td>4.2</td>
</tr>
<tr>
<td>7.5</td>
<td>2.42</td>
<td>34.0</td>
<td>5.9</td>
</tr>
</tbody>
</table>

Table 6.2

Values of $N_0$ and $k$ (as in equation (6.35)) evaluated for Vybak extended at different temperatures.

<table>
<thead>
<tr>
<th>Extension Temperature</th>
<th>$k$</th>
<th>$N_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C</td>
<td>0.55</td>
<td>0.93</td>
</tr>
<tr>
<td>50°C</td>
<td>0.47</td>
<td>1.25</td>
</tr>
<tr>
<td>71°C</td>
<td>0.33</td>
<td>1.97</td>
</tr>
<tr>
<td>90°C</td>
<td>0.32</td>
<td>4.7</td>
</tr>
</tbody>
</table>
Figure 6.1 Diagram indicating directions and angles used in the theory.
Figure 6.2  Plots of birefringence vs. $F(R_z)$ for extension of initially unoriented polyvinyl chloride at the temperatures indicated.
Figure 6.3 Plots of $\log_e \left[ \Delta n (R_z^2 - R_z^{-1})^{-1} \right]$ vs. $R_z$ for initially unoriented polyvinyl chloride extended at the temperatures indicated.
Figure 6.4  Diagram showing the change in dimensions of the initially square grid of dots printed on the test piece prior to deformation in stage 2. The various axes and angles referred to in the text are indicated.
Figure 6.5 Graphs comparing the theoretical and experimental results for $\lambda$ vs. $R_t$ for test pieces deformed at 50°C in stage 2. The different curves are for the three distribution functions used to describe the molecular alignment in state 2.
Figure 6.6  Graphs comparing the theoretical and experimental results for birefringence vs. $R_t$ for test pieces deformed at 50°C in stage 2. The different curves are for the three distribution functions used to describe the molecular alignment in state 2.
Figure 6.7  Graphs comparing the theoretical and experimental results for $\lambda$ vs. $\lambda_o$ for test pieces deformed at 20° in stage 2. The different curves are for the three distribution functions used to describe the molecular alignment in state 2.
Figure 6.8 Graphs comparing the theoretical and experimental results for birefringence vs. $\lambda_0$ for test pieces deformed at $20^\circ$C in stage 2. The different curves are for the three distribution functions used to describe the molecular alignment in state 2.
Figure 6.9  Section in the x-z plane of the Kuhn and Grün type 1 distribution for material with birefringence $1.34 \times 10^{-3}$ and $R_z = 2.9$. The two distributions are before and after deformation in stage 2 with $R_t = 1.4$. 
Figure 6.10 Section in the x-z plane of the Kuhn and Grün type 2 distribution for the material with birefringence $1.34 \times 10^{-3}$ and $R_z = 2.9$. The two distributions are before and after deformation in stage 2 with $R_t = 1.4$. 
Figure 6.11  Section in the x-z plane of the Raraty distribution for the material with birefringence $1.34 \times 10^{-3}$ and $R_z = 2.9$. The two distributions are before and after deformation in stage 2 with $R_t = 1.4$. 
In discussing the yielding and cold drawing behaviour of oriented polyvinyl chloride in Chapter 3, it was pointed out that in some circumstances the test pieces appeared to fracture prior to any yield point being detected. Also, in the case of cold drawing, no discussion of the ultimate mode of failure was given. In this Chapter it is intended to discuss the fracture results obtained from the test pieces used in obtaining the results in Chapter 3, and some additional results obtained for oriented Cobex will also be presented. In particular it will be shown that the development of stress whitening in the material has a significant effect upon the fracture behaviour.

7.1 Experimental

Some of the results presented in this Chapter were obtained from test pieces for which results have already been presented in Chapter 3. These test pieces, which had a gauge length of 6 mm and width 1.5 mm, were cut from sheets of oriented Vybak and were extended at an extension rate of 1 cm min\(^{-1}\), strain rate 1.7 min\(^{-1}\). These tests were carried out at room temperature (20 ± 2°C). Similar tests have also been carried out on Cobex. In this case test pieces having \(\lambda_0 = 0^\circ\) were deformed under the conditions discussed above, but some having a range of values of \(\lambda_0\) were deformed at a strain rate of 1.7 min\(^{-1}\) and at 35°C. In addition, some test pieces cut from sheets of Cobex and Vybak were extended, at room temperature, at a rate of 1.1 mm min\(^{-1}\), strain rate 0.18 min\(^{-1}\),
using the small tensile machine shown in Figure 2.3. Stages in
the deformation of these test pieces were observed microscopically.
Some test pieces having gauge length 12.5 mm and width 4.0 mm were
cut from sheets of Cobex such that $\lambda_o = 0^\circ$, and these were tested
at -82°C at an extension rate of 2 cm min$^{-1}$, strain rate 1.6 min$^{-1}$.

7.2 Results

In the following sections, the term fracture will be used with
reference to any separation of the test piece in which two new sur­
faces, the fracture surfaces, are formed, these surfaces originally
being in the interior of the test piece. Two different types of
fractures will be discussed. These are as follows:

1. Sudden fracture which occurred before any large amount of plastic
defformation had occurred, and for which the load recorded by the
load-extension curve dropped to zero with no prior warning.

2. Ductile fracture which occurred after a considerable amount of
plastic deformation had taken place by the propagation of a
running neck. In this case the load drop on the load-extension
curve was preceded by a decrease in slope of the load-extension
curve, and the progress of the fracture could be arrested by
stopping and reversing the tensile machine.

This fracture behaviour is discussed in more detail in the
following sections.

7.2.1 Sudden Fracture at $\lambda_o = 90^\circ$

In Section 3.2.1 it was reported that, for test pieces cut
from sheets of polyvinyl chloride which had not stress whitened,
failure occurred at an earlier stage in the test as the prior extension ratio increased. At prior extension ratio 3.3, this resulted in test pieces fracturing suddenly before a yield point could be detected on the load-extension curve. Measurement carried out on the test piece showed that the intersection of the fracture surface with the surface of the sheet test piece was parallel to the extinction direction. However, although the test piece had fractured suddenly before reaching the yield point, there was a region of plastic deformation in the vicinity of the fracture, suggesting that the test piece was close to its yield point when fracture occurred. The fracture, along with the associated region of plastic deformation, is shown in Figure 7.1. No further investigation of this type of behaviour at $\lambda_0 = 90^\circ$ has been carried out. However, the reader is reminded that, for Vybak, stress whitening supressed this tendency of the material to fracture (see Chapter 3).

7.2.2 Sudden Fracture at $\lambda_0 = 0^\circ$

In Section 3.2.2 it was noted that, for oriented Vybak at $\lambda_0 = 0^\circ$, the yield stress increased with increasing prior extension ratio up to an extension ratio of 3.7. Beyond this point the test pieces appeared to fracture before any yield point was reached, and the fracture stress decreased with increasing extension ratio (see Figure 3.5). This transition from yield to fracture coincided approximately with the development of stress whitening in the material, and so it was not clear whether this transition was associated with the stress whitening or just arose from the increase in extension ratio. Because insufficient Vybak was available this phenomenon could not be investigated further.
using this material. However, some investigations were carried out using Cobex which had been oriented by extension at 80°C. Test pieces having gauge length 6 mm and width 1.5 mm were cut from the sheet at $\lambda_0 = 0^\circ$, and they were tested in tension at room temperature ($20 \pm 2^\circ$C) at an extension ratio of 1 cm min$^{-1}$, strain rate 1.7 min$^{-1}$. $\lambda_0$ in fact ranged from $0^\circ$ to $1^\circ$, but this variation did not significantly affect the results to be presented in this section. The load-extension curves (Figure 7.2) for these test pieces showed a variation with extension ratio similar to that for Vybak at $\lambda_0 = 0^\circ$, as shown in Figure 3.1. The yield point, which was defined in the same manner as in Section 3.2.2, was easily detectable for extension ratios 1.8, 2.5, and 3.0. It was found that, for these extension ratios, the nominal yield stress increased with increasing extension ratio, as shown in Figure 7.3. However, no yield point was originally detectable for the test pieces at higher extension ratios, and so, the maximum recorded nominal stress was taken as a fracture stress, and is plotted as such in Figure 7.3. Extrapolation of the plot of nominal yield stress against extension ratio for extension ratios of 3.0 and below, indicated that the fracture stresses for extension ratios 3.5 and 3.7 were much larger than the yield stresses predicted by the extrapolation, suggesting that these test pieces had yielded prior to fracture. A closer study of the load-extension curve for extension ratio 3.5 showed that it was similar to that in Figure 7.2(c), but the change in slope between the two linear portions was very small and difficult to detect. The nominal yield stress evaluated from the intersection of these two linear portions was on the same curve as the nominal yield stress results at lower extension ratios. Another piece of evidence which suggested that the load-extension
curves of these test pieces at extension ratios 3.5 and 3.7 should show a yield point before fracture, was the tensile strain at fracture. This was determined from the extension recorded on the load-extension curve. For those pieces at low extension ratios which showed a definite yield point, the tensile strain at yield was approximately 10%. However, for those test pieces of extension ratios 3.5 and 3.7, the tensile strain at fracture was larger than this. In view of this, the yield point for these test pieces was taken to be at a tensile strain of 10%. In the case of the 3.5 extension ratio, the nominal yield stress evaluated in this way agreed with the value obtained from the intersection of the linear portions of the load-extension curve. For extension ratio 4.0, the tensile strain at fracture was approximately 10%, but at higher extension ratios, the tensile strain at fracture was less than this. The results for test pieces at extension ratio 4.0 and above were plotted as fracture stresses in Figure 7.3. Although there was some scatter in the fracture stress results, it is clear that the Cobex results presented in Figure 7.3 are similar to those for Vybak shown in Figure 3.5. The nominal yield stress increased with increasing extension ratio until fracture occurred before yielding, and the fracture stress then decreased with increasing extension ratio. It can be seen from Figure 7.3 that the behaviour of the polyvinyl chloride can be described by a fracture stress against extension ratio curves and a yield stress against extension ratio curve. Depending upon which stress is the smaller, the material will either yield or fracture. The point at which the yield-fracture transition occurs does appear to coincide with the development of pronounced stress whitening in the Cobex. At lower extension ratios some stress whitening was present but difficult to detect.
In the hope of moving the yield-fracture transition to lower extension ratios, i.e. away from the extension ratio at which stress whitening occurred, some tests were carried out on Cobex at -82°C. These tests were carried out using test pieces of gauge length 12.5 mm and width 4.0 mm which were extended at 20 mm min\(^{-1}\), strain rate 1.6 min\(^{-1}\). Because of the large temperature fluctuation in the environmental chamber at -82°C, satisfactory stress measurements were not obtained. It did appear, however, that, although the stress magnitudes were approximately doubled, the yield-fracture transition still coincided with the development of stress whitening in the material. One interesting result was that the unoriented material of extension ratio 1.0 fractured and did not yield, but the test piece of extension ratio 1.8 yielded. The yield stress at extension ratio 1.8 was larger than the fracture stress at extension ratio 1.0, but both were smaller than the fracture stress for extension ratio 4.0. In the vicinity of extension ratio 4.0 the fracture stress decreased with increasing extension ratio. These results suggest that, at low extension ratios, increasing molecular alignment has the effect of increasing both yield stress and fracture stress, but the fracture stress increases more rapidly, resulting in the fracture-yield transition between extension ratio 1.0 and extension ratio 1.8. However, at large extension ratios the situation was reversed in that there was a yield-fracture transition.

Although it is by no means certain, the results discussed above do indicate that the observed yield-fracture transition, and the associated decrease in fracture stress with increasing extension ratio, does seem to be associated with the development of stress whitening in the material during the initial
orienting process. However, it does not necessarily follow that the stress whitening, i.e. the presence of voids in the material, causes the yield-fracture transition. It may be that some other structural change, e.g. increasing molecular alignment, causes both the development of stress whitening and the yield-fracture transition. For instance, Andrews and Reed (1967) have shown that the development of stress whitening during the cold drawing of natural rubber is associated with the breaking of molecular chains. It could similarly be postulated that, during the extension of polyvinyl chloride at elevated temperatures, a stage is reached at which further extension cannot be achieved without the breaking of some molecular chains, and this gives rise to the development of voids in the material and the associated stress whitening. Similarly, it can be postulated that, when tested at room temperature, further extension of the test piece cannot be achieved without considerable breaking of molecular chains, but since the molecular mobility is much reduced at this temperature, this results in fracture of the material rather than yielding. It is presumed that the greater molecular mobility at the elevated temperature allowed the material to extend further rather than to fracture. Evidence that fracture involves the breaking of molecular chains has been presented by Regel et al (1966) and Zhurkov et al (1966). It is not surprising, using the above model, that at large extension ratios, the material should fracture rather than yield, but it is unexpected that the fracture stress should decrease with increasing extension ratio. However, if a considerable amount of molecular chain breaking does occur during the stress whitening at elevated temperatures, this might be effective in reducing the room temperature fracture
stress in that there are less molecular chains to break. The other possibility is that the voids in the material act as flaws, and that the increasing number of voids with increasing extension ratio causes the fracture stress to be reduced. Obviously further investigation of this behaviour is required. In particular it would be interesting to evaluate the molecular weight distribution at different extension ratios to see if there is any pronounced reduction in molecular weight associated with the development of stress whitening.

Although no detailed investigation has been carried out into the nature of the fracture surface, it was noted that the mode of fracture was different for test pieces deformed at room temperature and -82°C. In Figures 7.4 and 7.5 micrographs of test pieces fractured at the two temperatures are presented. At room temperature the fracture surface was normal to both the tensile axis and the molecular alignment direction (Figure 7.4). In some cases it was possible to detect, by virtue of the rotation of the extinction direction away from the tensile axis, a narrow band of plastically deformed material along each fracture edge. The fracture at -82°C was rather fibrous in that it tended to be inclined at a small angle to both the tensile axis and the molecular alignment direction. Typical fractures of this sort are shown in Figure 7.5. Cheatham and Dietz (1952) have previously observed this type of fracture in oriented polystyrene.

Andrews and Reed (unpublished) have investigated the deformation behaviour of oriented rubber tested in tension at temperatures below Tg. They observed, for \( \lambda_0 = 0^\circ \), that as the prior extension ratio increased, the yield point became less well defined in a manner similar to that observed for oriented
polyvinyl chloride, and the tensile strain at fracture also decreased. Thus, it would seem that oriented rubber would also show a yield-fracture transition as the extension ratio increased. It is not known if the fracture stress for rubber decreased with increasing extension ratio or if the rubber exhibited any stress whitening.

7.2.3 Ductile Fracture in the Neck

In discussing cold drawing in Chapter 3, no reference was made to the ultimate mode of failure of the cold drawn test pieces. It is intended to discuss in this and the next section this failure, which, since it occurred after considerable plastic deformation, will be referred to as ductile fracture. Usually those test pieces which were cut from strips of oriented polyvinyl chloride, which had not stress whitened, fractured within the necked region. Figure 7.6 shows the typical mode of failure under such circumstances. The micrographs in this figure show a test piece with \( \lambda_0 = 52^\circ \), extension ratio 2.6, which was deformed at room temperature and at a strain rate of 0.18 min\(^{-1}\), using the small tensile machine attached to the microscope. During the deformation, whilst the neck was propagating, a dark v-shaped region appeared at one edge of the test piece within the necked region, as indicated by the arrow in Figure 7.6(a). This region grew very slowly, the tip moving further into the test piece whilst the neck was still propagating. It is not known whether the dark appearance is due to geometrical effects arising from thickness change or to the material being opaque. Since the region is dark, there is still material present within this region and no separation
of the test piece has occurred. A stage was reached, shown in Figure 7.6(c), at which some separation did occur, and the fracture then propagated rapidly across the test piece, as shown in Figure 7.6(c) and Figure 7.6(d). This propagation of the fracture occurred much more rapidly than did the development of the dark v-shaped region. This mode of failure was observed for the majority of test pieces cut from sheets which had not stress whitened.

7.2.4 Ductile Fracture at the Neck Boundary

In contrast to the behaviour discussed above, the test pieces cut from sheets of stress whitened polyvinyl chloride (Vybak) of extension ratio 3.9, for which load-extension curves were presented in Figure 3.1, failed in a ductile manner at the boundary of the neck and not within the necked region. This ductile fracture, which had a very characteristic appearance, is shown in the micrograph in Figure 7.7. The most striking feature of this fracture is that the straight fracture edge, indicated by the arrow in Figure 7.7, is inclined at an angle to the tensile axis and is approximately at right angles to the extinction direction. In order to investigate further this mode of ductile fracture, a number of test pieces, having gauge length 6 mm and width 1.5 mm, were deformed, using the small tensile machine, at an extension rate of 1.1 mm min⁻¹, strain rate 0.18 min⁻¹, and stages in the progress of the fracture were observed microscopically. Since the test pieces did not always fracture before the neck had propagated throughout the gauge length, a notch was inserted in the test piece using a scalpel. This notch ensured that the deformation band formed at the notch, and ductile fracture
occurred as soon as the deformation band had formed. Successive stages in the development of the fracture are shown in Figure 7.8 for a test piece of extension ratio 3.9 with $\lambda_0 = 45^\circ$. It can be seen that, as the fracture progressed, the straight fracture edge propagated across the test piece and the neck boundary moved down the test piece, the fracture tip and the neck boundary meeting at a common point. The straight fracture edge appeared to be approximately at right angles to the extinction direction. In Figure 7.9 the ductile fracture is shown for both large and small values of $\lambda_0$, i.e. $\lambda_0 = 20^\circ$ and $80^\circ$, and again the extinction direction appeared to be approximately at right angles to the fracture edge. The ductile fracture is shown diagramatically in Figure 7.10. Since the micrographs referred to above indicated that the direction of the fracture edge AB depended upon $\lambda_0$, the angle $\theta$, between AB and the tensile axis, was measured in the sense shown in Figure 7.10. The angle $\theta$ is plotted as a function of $\lambda_0$ in Figure 7.11 for stress whitened polyvinyl chloride (Vybak) of different extension ratios. It can be seen that, although there was some scatter in the results, $\theta$ appeared to be linearly related to $\lambda_0$ in the same manner irrespective of extension ratio. The dashed curve in Figure 7.11 is that which would be expected if AB had been at right angles to the extinction direction. In fact the angle $(\theta - \lambda_0)$ ranged from $78^\circ$ to $85^\circ$ with decreasing $\lambda_0$. In view of this relationship between $\theta$ and $\lambda_0$ shown in Figure 7.11, a further investigation into this mode of ductile fracture was carried out on Cobex having a range of extension ratios prepared by extension at $80^\circ$C. Before discussing the results for Cobex, however, one further observation made on Vybak is worth reporting. In only one case was the type of ductile fracture discussed above observed in a test piece cut from oriented
material which showed no stress whitening. This was at $\lambda_0 = 52^\circ$ for extension ratio 3.0, and successive stages in the ductile fracture are shown in Figure 7.12. (Earlier stages in the deformation of the test piece are shown in Figure 3.26.) The interesting feature of this fracture is that $\theta$ is less than $90^\circ$, in contrast to results for stress whitened material for which $\theta$ was larger than $90^\circ$. Further investigation of this mode of fracture in material which had not stress whitened was carried out on Cobex.

Initially the Cobex test pieces, which were notched, were deformed at room temperature and at a strain rate of $0.18 \text{ min}^{-1}$ using the small tensile machine, but under these conditions the test pieces tended to fracture at the notch and parallel to the extinction direction. Because of this, test pieces had to be deformed at $35^\circ C$ in the environmental chamber using the E-type Tensometer. This caused the material to be more ductile in that deformation bands were formed at the notch. These tests were carried out on test pieces cut from sheets of different extension ratios, some of which were not stress whitened. Again the angle $\theta$ was measured for different values of $\lambda_0$ and different extension ratios. These results are reproduced in Figure 7.13 as plots of $\theta$ against extension ratio for different values of $\lambda_0$. The most striking feature of these results is that, at low extension ratios for a given $\lambda_0$, $\theta$ was constant and less than $90^\circ$. However, there was a discontinuity in the value of $\theta$, and at large extension ratios it was again approximately constant, but in this case it was larger than $90^\circ$. This sudden rise in the value of $\theta$ occurred in the vicinity of extension ratio 3.5, which corresponded to the extension ratio at which stress whitening started to develop. The
constancy of $\theta$ on either side of the discontinuity shows conclusively that the sudden change in behaviour arises from the effect of stress whitening in the material. $\theta$ before and after the discontinuity is plotted as a function of $\lambda_o$ in Figure 7.14. It can be seen that $\theta$ varied smoothly with $\lambda_o$, but $\theta$ for the stress whitened material did not reach such large values as those for Vybak in Figure 7.11.

Ductile fractures in Cobex which had not stress whitened are shown in the optical micrographs in Figure 7.15. These are for test pieces with $\lambda_o = 45^\circ$, extension ratio 2.5 and 3.0, for which $\theta$ was less than 90$^\circ$. In Figure 7.16 are shown ductile fractures in material which had stress whitened. For these test pieces $\theta$ was larger than 90$^\circ$. Because of the small depth of focus when using the optical microscope, the test piece in Figure 7.16(a) was studied using the scanning electron microscope, and two micrographs are shown in Figure 7.17. The small tongue of material protruding from the fracture surface in Figure 7.17(a) corresponds to the feature indicated by the arrow in Figure 7.16(a). The micrograph in Figure 7.17(b) was obtained looking into the fracture tip, B. The arrows indicate two features on the fracture surface which match up. Because one fracture surface is in the necked region, one of these features is more elongated than the other. No detailed study of the fracture surface has been carried out.

The observed deformation behaviour discussed in this section raises two important questions. Why does the value of $\theta$ remain constant on either side of the discontinuity as the extension ratio is varied? Secondly, why does the presence of voids in
the stress whitened material cause the value of $\theta$ to alter at the discontinuity? In fact the value of $\theta$ seems particularly sensitive to the presence of voids since reference to Figure 7.13 shows that the region in which $\theta$ varies, is between extension ratios 3.3 and 4.0, but the corresponding change in density shown in Figure 2.21 is less than 1%, indicating that the number of voids present was quite small.

The following theory is proposed to account for the observed variation of $\theta$ for the stress whitened material, and for the discontinuity of $\theta$ at the onset of stress whitening. The factors which affect $\theta$ are the rate at which the two surfaces separate at the point B in Figure 7.10, the rate of propagation of the neck boundary, and the angle $\gamma_1$ which the neck boundary makes with the tensile axis. The symbol $\gamma_1$ is used for this angle since the development of the neck arises from the movement apart of the boundaries of the type 1 band, and it is assumed that this boundary remains inclined at the same angle to the tensile axis during the subsequent deformation. Successive stages in the development of the ductile fracture are illustrated diagramatically in Figure 7.18.

In a given interval of time the surface AB extends by length $r$, B moving to B', and at the same time the band boundary moves through distance $D$, the point C on the boundary moving to B'. The direction of AB is defined by $\theta'$ which is equal to $180 - \theta$. It is clear from Figure 7.18 that the distances $r$ and $D$ are geometrically related through the angles $\theta'$ and $\gamma_1$, and since the deformation occurs in the same interval of time, the rates of change of $r$ and $D$ are related in the same way. It is easily shown that

$$\frac{dD}{dt} = \frac{dr}{dt} \left(\frac{\sin \theta'}{\tan \gamma_1} + \cos \theta'\right)$$

(7.1)
It is proposed that, for the stress whitened material, less energy is required to propagate the neck boundary than is required to produce new surface at the fracture. However, once the ductile fracture is initiated, it must continue to propagate. If the band boundary moves beyond the fracture tip B, the deformation would tend to spread across the test piece, but, since the drawing stress must remain constant, there would be a corresponding rise in load. This rise in load, however, would cause the fracture to propagate again, so that the tip of the ductile fracture remains at the band boundary. Since the ductile fracture, once it is initiated, must continue to propagate, it is proposed that it will do so such that the energy used in propagating the fracture is at a minimum. If it is considered that a certain amount of work is required to produce unit new surface at the fracture, then the condition of minimum energy corresponds to the minimum rate of propagation of the fracture. This obviously corresponds to a minimum in the rate of growth of AB i.e. dr/dt is at a minimum. In equation (7.1) it is clear that dr/dt depends upon dD/dt, θ', and γ₁. However, the rate of propagation of the neck boundary, dD/dt, is fixed by the extension rate and the natural draw ratio of the test piece, which depends upon the true stress-strain characteristics of the material. In addition γ₁ is fixed by the anisotropy of the material as discussed in Chapter 4. Thus, in equation (7.1) only θ' can be varied in order to obtain a minimum in dr/dt, and therefore, θ' is fixed if the condition that dr/dt should be a minimum is correct. Under these conditions θ' will in fact depend upon the value of γ₁. In order to check this hypothesis, the angle γ₁ was measured from the micrographs in Figures 7.7 and 7.9, and the value of θ' which gave a minimum in dr/dt was calculated.
The angle $\theta'$ was also measured from the micrographs in order to see if it agreed with the predicted value. These angles were measured using a protractor. In fact for the test piece in Figure 7.9(a) equation (7.1) predicted that $\theta'$ should be between $76.5^\circ$ and $78^\circ$, and the measured value of $\theta'$ was found to be $77.5^\circ$. Similarly for the test piece in Figure 7.7, the predicted value of $\theta'$ was between $56^\circ$ and $58^\circ$, and the actual measured value was $57.5^\circ$. For the test piece in Figure 7.9(b), the value of $\gamma_1$ could not be measured because the stress whitening caused the material to be opaque. However, this test piece was at $\lambda_\theta = 80^\circ$, extension ratio 3.9, and it was assumed that the value of $\gamma_1$ would be the same as that for the corresponding deformation band. Reference to Figure 3.16 suggests that, for this value of $\lambda_\theta$ and this extension ratio, $\gamma_1$ should be approximately $65^\circ$. Calculation using this value of $\gamma_1$ gave $\theta'$ to be between $23^\circ$ and $25^\circ$ which agrees favourably with the measured value, $20^\circ$. In view of the way in which the angles were measured, the agreement between theory and experiment is exceptionally good, confirming that ductile fracture proceeds such that minimum energy is used in propagating the fracture. This theory shows how the fracture direction is related to $\gamma_1$, and this accounts for the observed constancy of $\theta$ at large extension ratios. Comparison of the results for deformation band directions given in Figure 3.16, shows that at extension ratios 3.3 and 3.7, the change in extension ratio did not produce any significant change in $\gamma_1$. Thus for large extension ratios, $\gamma_1$ does not change, and so $\theta$ can be expected to remain constant, as observed.

As far as the material of small extension ratios is concerned the angle $\theta$ cannot be accounted for using this model. However, in this case it is proposed that the energy required to propagate the ductile fracture is less than that for the
propagation of the neck boundary. Thus, the ductile fracture will propagate such that the minimum amount of energy is used in propagating the band boundary. This would be satisfied if the band did not move, and thus AB would be parallel to the band boundary and $\theta = \gamma_1$. However, under these circumstances, the fracture produces no extension of the test piece, and thus, since the test piece is being extended by the tensile machine whilst the fracture is propagating, the fracture would have to occur very rapidly. If, however, it is proposed that the ductile fracture can propagate at only a finite and comparatively slow rate, then the neck boundary must propagate in order to accommodate the extension of the test piece. This would cause $\theta$ to be larger than $\gamma_1$, but not as large as the values for the stress whitened material. Without further investigation it is not clear how this model would give rise to the observed constancy of $\theta$ for the non-stress whitened material. However, the observed discontinuity in $\theta$ can be accounted for by the presence of stress whitening altering the relative ease with which ductile fracture and the neck boundary can propagate. In particular, the presence of stress whitening in the material favours the propagation of the band boundary rather than the ductile fracture, i.e. the stress whitening increases the ductility of the material. This would be consistent with the observation mentioned in an earlier section that, for test pieces deformed at $\lambda_0 = 90^\circ$, the presence of stress whitening tended to make the material more ductile.

Although this type of ductile fracture behaviour has not been previously reported in polymers, a similar type of behaviour has been observed in metals. Govila and Hull (1968)
deformed silicon iron single crystals in tension at 293 K and observed that two non-crystallographic localised shear bands, which were equally inclined on opposite sides of the tensile axis, were formed. A notch was formed at the point where these two bands intersected at the edge of the specimen. This notch propagated across the specimen before fracture occurred at the root of the notch. Although the above authors did not discuss this mode of deformation in any detail, Figure 5 of the above reference and Figure 17 given by Rogers (1968) suggest that the propagation of the notch was similar to the ductile fracture discussed in this section. It was thought that the propagation of the ductile fracture by the movement of two neck boundaries equally inclined on opposite sides of the tensile axis would have occurred in unoriented polyvinyl chloride. However, this was not observed since notched test pieces, which were cut from unoriented polyvinyl chloride, fractured suddenly at the notch. In oriented polymers, it was because only type 1 bands formed a running neck that the tip of the fracture B, propagated obliquely across the test piece.

7.3 Concluding Remarks

It has been shown in this Chapter that the development of stress whitening, i.e. the presence of voids, in the material caused a definite change in the ductile fracture behaviour. The observed transition from yield to fracture with increasing extension ratio for test pieces with $\lambda_o = 0^\circ$, although associated with the development of stress whitening, was not believed to be caused directly by the stress whitening. Instead, it is thought that both the stress whitening at elevated temperatures and the yield-fracture transition at room temperatures, arise from the
fact that a stage is reached at which further extension of the material cannot be achieved without considerable breaking of molecular chains. At room temperature this results in the fracture of the test piece, but because of the increased molecular mobility, the material can continue extending at elevated temperature, resulting in the development of stress whitening. The observed decrease in fracture stress with increasing extension ratio may arise from the fact that considerable molecular breakage at elevated temperatures results in a weakening of the material at room temperature.

The direction of the fracture edge in the stress whitened material has been related to the angle, \( \gamma_1 \), which the neck boundary makes with the tensile axis, through a theory which proposes that the minimum amount of energy is used in producing new surface at the fracture tip. The discontinuity in the fracture edge direction has been accounted for by proposing that the stress whitening, i.e. the presence of voids, increases the ductility of the material, this being consistent with results quoted in Chapter 3 for \( \lambda_0 = 90^\circ \). Any increase in ductility at \( \lambda_0 = 0^\circ \) would not be effective in preventing fracture since further extension could not be achieved without breakage of molecular chains.

In the future it would be interesting to determine whether the development of stress whitening is associated with a decrease in molecular weight. Also, further investigation is required to see if stress whitening is associated with an increase in ductility of the material. If this is the case, how is the increase in ductility brought about? This would involve evaluating in more detail the characteristics of the voids which produce the stress whitening.
Figure 7.1 Optical micrograph of a test piece at $\lambda_o = 90^\circ$, extension ratio 3.0 showing fracture edge and associated region of plastic deformation.
Figure 7.2 Load extension curves at $\lambda = 0^\circ$ for Cobex of different extension ratios.
Figure 7.3  Plots of yield stress and fracture stress vs. extension ratio for Cobex prepared by extension at 80°C.
Figure 7.4 Optical micrographs of test pieces, cut from sheets of Cobex of extension ratios (a) 3.7 and (b) 4.4 at $\lambda_0 = 0^\circ$, showing fracture when tested at 20°C.

Figure 7.5 Optical micrographs of test pieces, cut from sheets of Cobex of extension ratios (a) 2.6 and (b) 4.0 at $\lambda_0 = 0^\circ$, showing fracture when tested at -82°C.
Figure 7.6  Optical micrographs showing successive stages in the development of ductile fracture within the necked region.
Figure 7.7  Optical micrograph showing ductile fracture in a test piece with $\lambda_{0} = 49.5$, cut from a sheet of Vybak of extension ratio 3.7.

Figure 7.8  Optical micrograph showing successive stages in the development of ductile fracture in a test piece with $\lambda_{0} = 45^\circ$ cut from a sheet of Vybak of extension ratio 3.9.
Figure 7.9 Optical micrographs showing ductile fracture in stress whitened Vybak. The test pieces were cut from sheets of extension ratio 3.7 and 3.9 at (a) $\lambda_o = 20^\circ$ and (b) $\lambda_o = 80^\circ$, respectively.

Figure 7.10 Diagram illustrating the ductile fracture in stress whitened material and showing the sense in which $\theta$ and $\lambda_o$ were taken positive.
Figure 7.11 Variation of $\theta$ with $\lambda_0$ for ductile fracture in stress whitened Vybak of different extension ratios.
Figure 7.12 Optical micrographs showing successive stages of ductile fracture in non-stress whitened Vybak of extension ratio 3.0, with $\lambda_0 = 52^\circ$. 
Figure 7.13: Plots of $\theta$ vs. extension ratio for ductile fracture in Cobex at different values of $\lambda_0$. 

(a) $\lambda_0 = 35^\circ$

(b) $\lambda_0 = 45^\circ$
Figure 7.14 Variation of $\theta$ with $\lambda_0$ for ductile fracture in stress whitened and non stress whitened Cobex.
Figure 7.16 Optical micrographs of test pieces cut from Cobex with (a) $\lambda_o = 45^\circ$, extension ratio 3.0 and (b) $\lambda_o = 55^\circ$, extension ratio 2.5, showing ductile fracture such that $\theta < 90^\circ$.

Figure 7.16 Optical micrographs of test pieces cut from Cobex with (a) $\lambda_o = 35^\circ$, extension ratio 4.4 and (b) $\lambda_o = 45^\circ$, extension ratio 4.4, showing ductile fracture with $\theta > 90^\circ$. 
Figure 7.17 Scanning electron micrographs of the test piece shown in Figure 7.16(a).
Figure 7.18 Diagram illustrating successive stages in the development of the ductile fracture.
Some experiments were carried out on oriented polyethylene before those on oriented polyvinyl chloride in order to gain familiarity with the techniques and problems involved in the testing. Some interesting results were obtained, and, although they have not been investigated in great detail, they are considered to be of sufficient interest to be presented in this Chapter.

Previous investigations into the plastic deformation behaviour of oriented polyethylene have been carried out by Richard and Gaube (1956), Kurokawa and Ban (1964), Seto and Tajima (1966) and Keller and Rider (1966).

8.1 Experimental

Tensile tests were carried out at room temperature on test pieces of gauge length 10 mm and width 2.4 mm at an extension rate of 10 mm min\(^{-1}\), strain rate 1.0 min\(^{-1}\). The test pieces were cut from strips of oriented polyethylene at various values of \(\lambda_0\). These strips, which had been drawn at room temperature, were Rigidex 50, with extension ratio 10, Rigidex 2, with extension ratio 7.5, and Alkathene WNF15, with extension ratio 3.5. In addition, a few tests were carried out on Rigidex 2, with extension ratio 7.0, which had been annealed at various temperatures for 5 min in a silicone oil bath. The annealing temperatures were 60\(^\circ\)C, 80\(^\circ\)C, 100\(^\circ\)C, and 120\(^\circ\)C. No measurements were made of the changes in the dimensions of the material as a result of annealing. Birefringence measurements were not carried out on the polyethylene.
8.2.1 Yield Stress

The nominal yield stress was evaluated, as for oriented polyvinyl chloride, from the load at the yield point and the cross-sectional area of the test piece measured prior to deformation. The yield point was taken as the maximum on the load-extension curve after the initial load rise. Plots of nominal yield stress against $\lambda_0$ for Rigidex 2 and Rigidex 50, which had been drawn to extension ratios 10 and 7.5 respectively, are shown in Figure 8.1. It can be seen that the results are similar to those obtained by Keller and Rider (1966) for drawn polyethylene, both as regards the magnitudes of the yield stress and the position of the minimum yield stress, i.e. at $\lambda_0 = 55^\circ$. The results for the annealed polyethylene are also presented in Figure 8.1. It can be seen that the effect of annealing was to increase the yield stress, the yield stress for the material annealed at 120$^\circ$C being more than a factor of two greater than that for the unannealed material. For the Alkathene WNF 15 the yield stresses were lower than those for the high density polyethylene, and the minimum yield stress was at $\lambda_0 = 70^\circ$ (see Figure 8.2). These results will be discussed further in Section 8.3.

8.2.2 Deformation Bands

In the following discussion type 1 and type 2 bands are as defined for oriented polyvinyl chloride. In their investigation Keller and Rider (1966) did not observe type 1 deformation bands in drawn polyethylene tested at room temperature. However, in the material used in this investigation type 1 bands were observed for values of $\lambda_0$ less than approximately $70^\circ$. These bands appeared to be regions of highly localised shear in which the originally
slightly opaque material had become less opaque. Such a de-
formation band is shown in an advanced state of development in
Figure 8.3(a). Optical measurement of the bands indicated that
the c-axis direction (taken as the extinction direction) inside
the band was parallel to the band boundary, but the band boundary
was not parallel to the c-axis direction in the adjacent un-
deformed regions. Instead, the angle $\gamma_1$ was less than $\lambda$ (as a
result of the deformation $\lambda_0$ had decreased slightly and is,
therefore, referred to as $\lambda$) and the two angles differed by 4°
or less. At values of $\lambda_0$ below 30°, the phenomenon, which
Kurokawa and Ban (1964) referred to as slip off, was observed.
In this the test piece appeared to rupture by localised slip
on one plane in the test piece at the boundary of the band.
Such a test piece is shown in Figure 8.3(a). The planes on
which slip off occurred are indicated by the arrows in this
figure. This plane was not parallel to the c-axis inside or
outside the band; the angle between the slip off plane and the
c-axis direction outside the band could be as large as 11°. For
values of $\lambda_0$ between 30° and 70° the initially localised shear
spread throughout the test piece by the formation of an asymmetrical
neck, as shown in Figure 8.3(b). This behaviour was referred
to as draw off by Kurokawa and Ban (1964). Thus, the type 1
bands in drawn Rigidex 50 and Rigidex 2 behaved in a manner
similar to those observed by Kurokawa and Ban (1964).

Seto and Tajima (1966) have also observed type 1 bands
in oriented polyethylene deformed in tension, but they reported
that the c-axes inside and outside the band were equally inclined
on opposite sides of the band boundary. This certainly was not
the case for the deformation bands discussed above. In order
to investigate this further, an investigation into the c-axis directions, using the X-ray diffraction technique discussed in Section 2.1.4, was carried out on deformation bands in drawn and annealed, and drawn rolled and annealed polyethylene for which Keller and Rider (1966) presented band direction results. Typical photographs are shown in Figure 8.4. It can be seen that there is a split in the (110) reflection, the two adjacent arcs arising from the deformed and undeformed material inside and outside the band. By measuring the angular splitting of the arcs, and their position relative to the shadow of the reference wire, it was possible to evaluate the directions of the c-axes relative to the band boundary. It was in fact found that the c-axis was equally inclined on opposite sides of the band boundary. Typical values obtained for the angle between the boundary and the c-axis were 8° (Figure 8.4(a), 7°, (Figure 8.4(b), 6° and 4.5°. These results indicate that there are in fact two different kinds of type 1 bands which can form in oriented polyethylene. The type formed in drawn polyethylene appear to form by shear parallel to the c-axis direction and might correctly be referred to as slip bands. Those observed in drawn and annealed polyethylene appear to involve the kinking of molecular chains (see Figure 10(c) of Seto and Tajima (1966)) and might correctly be referred to as kink bands.

In order to investigate this further, tests were carried out on drawn polyethylene annealed at different temperatures. The annealing temperatures were 60°C, 80°C, 100°C and 120°C. Yield stress results for these test pieces have been presented in Figure 8.1. Deformation bands were formed in all test pieces except those cut from the unannealed material, and the angle $(\lambda - \gamma_1)$ was measured. $(\lambda - \gamma_1)$ is plotted as a function of
\[ \lambda \] in Figure 8.5. It can be seen that results for material annealed at 60°C and 30°C were the same, and so also were the results for material annealed at 100°C and 120°C. However, in going from 80°C to 100°C there has been a sudden increase in \((\lambda - \gamma_1)\). In those deformation bands formed in material annealed at 60°C and 80°C, the c-axis was parallel to the band boundary suggesting that these are in fact type 1 slip bands. Those observed in material annealed at 100°C and 120°C were thought to be the same as those observed by Keller and Rider (1966), suggesting that these are type 1 kink bands. Optical micrographs of deformation bands in material annealed at 80°C and 120°C are shown in Figure 8.6.

At values of \(\lambda_0\) above 70°, type 2 bands were observed to be formed in the drawn polyethylene. In Rigidex 50 the band was similar to that shown in Figure 10 of Keller and Rider (1966). In this case the deformation spread along the test piece by the movement apart of the boundaries of the type 2 band. As soon as these boundaries reached the shoulders of the test piece, a type 1 band developed within the deformed region and formed an asymmetrical neck. (At values of \(\lambda_0\) near 90° the test pieces fractured before a type 2 deformation band formed.) In Rigidex 2, the type 2 bands did not develop in the manner discussed above. Typical stages in the development of the type 2 bands in Rigidex 2 are shown in Figure 8.7. These micrographs are not of the same test piece but for test pieces having different values of \(\lambda_0\), as indicated in the figure caption. It can be seen that although a type 2 band did form initially, it did not spread along the test piece. Instead further bands formed in the same region and the test piece necked down (Figure 8.7(a), (b) and (c)).
In some cases the test pieces then fractured but for others, the neck propagated along the gauge length. A feature, which Rider (private communication) has previously observed and referred to as a fish tail, also developed ahead of the neck (Figure 8.7(d)). This feature has also been observed previously by Richard and Gaube (1955) (see their Figure 11).

In the low density polyethylene, type 1 bands were formed at values of \( \lambda_o \) below 70°. However, because the extinction direction was not well defined and because the band boundaries were not sharp, these could not be investigated in any detail. It was noted that the bands were regions of localised shear which propagated along the test piece by the formation of an asymmetrical neck. At values of \( \lambda_o \) above 70°, type 2 bands were formed and these propagated along the test piece by the movement of their boundaries. When there was sufficient re-oriented material between the boundaries, a type 1 band was formed. This developed into an asymmetrical neck but this necked region was always bounded by the boundaries of the type 2 band i.e. the type 2 band boundary moved ahead of the neck boundary, and both moved at the same rate.

8.3 Discussion

The results presented in the previous sections raised a number of questions which, because insufficient time was available could not be investigated further.

Comparison of the yield stress against \( \lambda \) curves for polyvinyl chloride, low density polyethylene, and high density polyethylene suggests that the value of \( \lambda_o \) at which the minimum yield stress occurs moves from 90° to 55° as the crystallinity of the material
increases. The degree of molecular alignment might be another factor which influences the yield stress behaviour. The high density polyethylene had better molecular alignment than the other two materials, but it is not known how the molecular alignment of the low density polyethylene compared with that of the polyvinyl chloride. A crystalline material with perfect molecular alignment might be expected to behave like a single crystal. The minimum yield stress would then occur at $\lambda_0 = 45^\circ$.

It would be worth investigating further whether two difference kinds of type 1 bands are formed in oriented polyethylene, and if so, by what mechanism. It might be that increasing the annealing temperature caused slip parallel to the c-axis to become progressively more difficult (this is indicated by the increase in yield stress) until a stage was reached at which some other deformation mechanism, i.e. kinking of molecular chains, occurred more readily than slip, thus causing a transition from type 1 slip bands to type 2 kink bands. It would also be interesting to see how the Hill theory (see Chapter 4) could be fitted to these results. The sudden change in the band directions would presumably result in a change in either the Hill theory parameters, or $a_{xx}$. An investigation of the structural changes which bring about this change would also be of interest.

Other investigations might be carried out on the different modes of development of type 2 bands for the different materials referred to in this thesis, and on the phenomenon of slip off in oriented high density polyethylene.
Figure 8.1: Plots of nominal yield stress vs. \( \lambda_0 \) for drawn, and drawn and annealed Rigidex (8.1), and for drawn Alkathene (8.2).
Figure 8.3 Optical micrographs showing (a) slip-off and (b) asymmetrical necking for type 1 bands.

Figure 8.4 Wide angle X-ray diffraction photographs from type 1 bands in drawn, rolled, and annealed high density polyethylene. The photographs show reflections arising from deformed and undeformed regions.
Figure 8.5  Plot of $(\lambda - \gamma_1)$ vs. $\lambda$ for drawn Rigidex 2 annealed at different temperatures.

![Graph showing plot of $(\lambda - \gamma_1)$ vs. $\lambda$ for drawn Rigidex 2 annealed at different temperatures.]

Figure 8.6  Optical micrographs showing type 1 deformation bands in drawn Rigidex 2 annealed at (a) 80°C and (b) 100°C.

![Optical micrographs showing type 1 deformation bands in drawn Rigidex 2 annealed at (a) 80°C and (b) 100°C.](image)
Figure 8.7  Optical micrographs showing stages in the development of type 2 bands in Rigidex 2.

\[ \lambda \cdot 85^\circ \quad a \quad \times 10 \]

\[ \lambda \cdot 89^\circ \quad b \]

\[ \lambda \cdot 88^\circ \quad c \]

\[ \lambda \cdot 82^\circ \quad d \quad \times 30 \]
The more important results which have been presented in this thesis can be summarised as follows:

1. At yield, the plastic deformation of oriented polyvinyl chloride was localised into deformation bands which were inclined at an angle, \( \gamma \), to the tensile axis. Two kinds of deformation bands were observed. Type 2 bands formed first at the maximum on the load-extension curve, but type 1 bands formed subsequently and developed into running necks. The effect of increasing molecular alignment was to cause an increase in anisotropy of the values of \( \gamma_1 \) and \( \gamma_2 \).

2. Both the nominal yield and drawing stresses showed increasing anisotropy with increasing molecular alignment, having maximum and minimum values at \( \lambda_0 = 0^\circ \) and \( 90^\circ \) respectively. However, both the true drawing stress and the tensile strain at yield showed little variation.

3. The yielding behaviour, both as regards yield stress and deformation band directions, has been accounted for by the Hill modification of the von Mises yield criterion, provided an internal stress acting in compression in the molecular alignment direction was taken into account. The internal stress was uniquely related to the birefringence, and was also equal to the true stress applied to the material during hot stretching.

4. As a result of deformation at different temperatures, optical anisotropy changes occurred in both initially unoriented and
initially oriented polyvinyl chloride. The birefringence changes for the unoriented material deformed at room temperature were fitted by the Kuhn and Grün first affine deformation model. As the extension temperature increased, the discrepancy between the results predicted by this model and the experimental results also increased. Fitting the model to the experimental results for unoriented polyvinyl chloride deformed at room temperature, led to the prediction that the maximum birefringence which can be achieved in polyvinyl chloride should be $7.2 \times 10^{-3}$. The model accounted qualitatively for the optical anisotropy changes during deformation, at room temperature and 50°C, of oriented polyvinyl chloride which had been initially oriented by extension at 71°C and 90°C. The best quantitative agreement was achieved if the molecular alignment in the oriented material was described by the Kuhn and Grün type 1 distribution function. Finally, the birefringence changes during the extension of unoriented polyvinyl chloride at temperatures both above and below $T_g$ could be fitted by an equation suggested by Bowden and Raha.

5. Stress whitening, which developed during extension at elevated temperatures and which was thought to arise from the formation of voids in the material, was found to be associated with changes in the room temperature deformation behaviour of the material. For test pieces at $\lambda_0 = 0^\circ$ there was a yield-fracture transition and a subsequent decrease in fracture stress with increasing extension ratio. It has been suggested that the stress whitening and the yield-fracture transition arise because a stage is reached at which further
extension cannot be achieved without breaking molecular chains. At $\lambda_o = 90^\circ$, the development of stress whitening is associated with an increase in ductility. An increase in ductility has also been used to account for the observed discontinuity in the ductile fracture behaviour. The ductile fracture direction has been related to the direction of the neck boundary through a theory which proposes that the minimum amount of energy is used in propagating the fracture.

6. Type 1 slip bands and type 1 kink bands have been observed in oriented high density polyethylene. The effect of annealing high density polyethylene was to cause an increase in yield stress, and at a particular annealing temperature, there was a transition from type 1 slip bands to type 1 kink bands. Results for high density and low density polyethylene suggest that crystallinity might affect the position of the minimum yield stress.

The following suggestions are made for possible future lines of investigation:

1. It is important to determine whether unoriented polymers yield according to a Coulomb criterion or pressure dependent von Mises criterion. If they yield according to the latter, the form of the pressure dependence should be evaluated and the directions of deformation bands formed in tension and compression should be accounted for. It would also be interesting to measure possible plastic volume changes.

2. If the Coulomb criterion is found to be the more appropriate, it should be applied to oriented polymers, as discussed in Chapter 4.
3. In extending the von Mises criterion to oriented polymers, use should be made of either the Hill theory modification or the critical strain criterion. A test of the critical strain criterion would be to measure strains at yield; this test is considered more direct than that suggested at the end of Chapter 4 and is not complicated by non-linear elastic effects.

4. It seems likely that all of the above criteria will require the inclusion of an internal stress effect. It would be worthwhile investigating what factors, e.g. crystallinity, influence the magnitude of the internal stress. The observed equality of the internal stress and the true stress during hot stretching should be investigated further in order to determine whether this agreement was fortuitous.

5. It would be interesting to see if the optical anisotropy changes of polyvinyl chloride deformed in a two stage process at room temperature can be accounted for by the Kuhn and Grün affine deformation model.

6. Further investigation should be carried out into the nature of the voids in stress whitened polyvinyl chloride and into the factors which cause them. It would be interesting to determine, by making molecular weight measurements or by using more sophisticated spectroscopic techniques, whether this is associated with the breaking of molecular chains.

7. It would be worthwhile investigating further the observed increase in ductility associated with stress whitening.

8. As far as oriented polyethylene is concerned, a thorough investigation is required into the various deformation
bands and their associated mode of deformation. It would be particularly interesting to determine what factors influence the formation of type 1 kink bands and type 1 slip bands.
Acknowledgements

I should like to thank

My supervisor, Dr. J. G. Rider, for suggesting this project and for his enthusiastic guidance and interest throughout the past three years;

The Science Research Council for providing financial support;

Mrs. Gillian Smith for writing and operating the computer programmes;

Dr. T. Hinton for many stimulating and interesting discussions;

My wife, Margaret, for her encouragement throughout the past three years, and for reading the draft of this thesis.

Miss Norma Draper for typing this thesis.
References


Bishop, J.F.W., and Hill, R., 1951a, Phil. Mag., 42, 414.

Bishop, J.F.W., and Hill, R., 1951b, Phil. Mag., 42, 1298.


Bunn, C.W., 1961, Chemical Crystallograph, O.U.P.


Dinnewell, A.E., 1969, Final Year Project Report, Department of Physics, University of Surrey.


Jaeger, J.C., 1960, Geol. Mag., 97, 6.


Kauffman, J.W., and George, W., 1951, J. Colloid Sci., 6, 450.


Kurokawa, M., and Ben, T., J. Appl. Polymer Sci., 8, 971.


Robertson, R.E., 1964, General Electric Research Laboratory Rept. No. 64-RL- (3580c).
Rogerts, H.C., 1968, Ductility, A.S.M.
Stein, R.S., and Norris, F.H., 1956, J. Polymer Sci., 1, 381.


Treloar, L.R.G., 1958, The Physics of Rubber Elasticity, O.U.P.


Vincent, P.I., 1960, Polymer, 1, 7.


