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Walter Wade Adams
University of Massachusetts Amherst

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AN ELECTRON MICROSCOPY AND X-RAY SCATTERING INVESTIGATION OF
THE DEFORMATION MORPHOLOGY OF SOLID STATE EXTRUDED FIBERS
AND MELT DRAWN FILMS OF POLYETHYLENE

A Dissertation Presented

By

WALTER WADE ADAMS

Submitted to the Graduate School of
The University of Massachusetts in partial fulfillment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

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Polymer Science and Engineering
AN ELECTRON MICROSCOPY AND X-RAY SCATTERING INVESTIGATION OF
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A Dissertation Presented

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Dedicated to
the Memory of
My Father
Walter Wilson Adams
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ABSTRACT


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The deformation morphology of high density polyethylene (PE) was been investigated by electron microscopy and x-ray scattering methods applied to oriented thin films and to solid-state extruded (SSE) fibers. PE was melt-drawn at 120°C and annealed to produce nearly perfectly chain axis oriented and planar textured thin film, which was deformed in situ at room temperature in a scanning transmission electron microscope. Deformation along c is initially accomodated by the interlamellar regions, which cavitate and form microfibers. At about 300% strain in the fibrils, strain-induced crystallization occurs. With increased deformation, the lamellar crystals deform by two clearly visualized chain slip systems: \{100\}, <001> and \{010\}, <001>. These c-axis shear processes were further distinguished as
fine slip or as block shear. Higher deformation causes more breakup of blocks by shear; when the block size is less than some critical nucleus size, the crystal "melts". Fibrillar crystals arise from crystallized amorphous material at high elongations, crystal blocks broken out of lamellae, and chains drawn out of lamellae and recrystallized.

For deformation 90° to c the lamellar crystals cleave on (0k0), and fibrils are pulled from connecting amorphous zones. Deformation at 45° to c results in a combination of the 0° and 90° processes.

The microstructure of SSE PE fibers was examined quantitatively using SAXS. By measuring absolute intensities using the ORNL two dimensional position sensitive detector, accurate values of the SAXS invariant for anisotropic samples were obtained, which coupled with wide angle x-ray scattering and thermal analysis, permitted determination of the noncrystalline component density. The effective crystalline phase density decreases by 1% (.999 to .990 g/cm³) from the unextruded billet compared to a 36 draw ratio extrudate while the noncrystalline phase density increases by 6% (.84 to .89 g/cm³), leading to a 63% decrease in the mean squared electron density fluctuation. The average axial crystallite length measured by WAXS increases with extrusion draw ratio while the SAXS long period decreases and weakens considerably. These results are consistent with a two phase model using deformation dependent effective densities, and support the Peterlin model of fiber microstructure.
TABLE OF CONTENTS

ACKNOWLEDGEMENTS ................................................. v
ABSTRACT .................................................................... viii
LIST OF TABLES .......................................................... xii
LIST OF ILLUSTRATIONS .............................................. xiii

Chapter

I. INTRODUCTION ......................................................... 1

1.1 Opening Remarks .................................................. 1
1.2 Organization of the Dissertation ................................. 2
1.3 Background .......................................................... 4

1.3.1 Solution Grown Single Crystals ......................... 4
1.3.2 Spherulitic Structure ........................................... 5
1.3.3 Macroscopic Deformation Analysis ...................... 6
1.3.4 Microfiber Model .............................................. 8
1.3.5 Tie Molecules and Links ..................................... 10
1.3.6 Spherulite Deformation Models ......................... 12
1.3.7 Composite Models ............................................ 13
1.3.8 Quantitative Approaches to the Study of Deformation 14

1.4 Conclusions ......................................................... 15

II. ELECTRON MICROSCOPY OF POLYETHYLENE ............. 16

2.1 Introduction ........................................................ 16
2.2 Conventional Transmission Electron Microscopy .......... 19
2.3 Operation of STEM for Radiation Sensitive Polymers .... 23
2.4 STEM Scanning Microdiffraction ............................... 30
2.5 STEM Dark Field of Crystalline Polymers .................. 37
2.6 Experimental Techniques ....................................... 45
2.7 Applications of CTEM Imaging ................................. 48
2.8 Ghost Images ....................................................... 48
2.9 Applications: STEM Imaging of Polyethylene .......... 57
2.10 Conclusions ....................................................... 73

III. DEFORMATION MORPHOLOGY OF MELT-DRAWN ORIENTED
THIN POLYETHYLENE FILMS ......................................... 76

3.1 Introduction ....................................................... 76
3.2 Background ....................................................... 78
3.3 Experimental Methods .......................................... 86
3.4 Results ............................................................ 92
# TABLE OF CONTENTS (Continued)

## Chapter III (continued)

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.4.1</td>
<td>Initial Microstructure</td>
<td>92</td>
</tr>
<tr>
<td>3.4.2</td>
<td>Deformation Parallel to C</td>
<td>95</td>
</tr>
<tr>
<td>3.4.3</td>
<td>AN Films</td>
<td>100</td>
</tr>
<tr>
<td>3.4.4</td>
<td>AD Films</td>
<td>113</td>
</tr>
<tr>
<td>3.4.5</td>
<td>Deformation Perpendicular to C</td>
<td>113</td>
</tr>
<tr>
<td>3.5</td>
<td>Discussion</td>
<td>122</td>
</tr>
<tr>
<td>3.5.1</td>
<td>&quot;Amorphous&quot; Fibers</td>
<td>122</td>
</tr>
<tr>
<td>3.5.2</td>
<td>Lamellar Deformation</td>
<td>124</td>
</tr>
<tr>
<td>3.5.3</td>
<td>Fold Plane</td>
<td>130</td>
</tr>
<tr>
<td>3.6</td>
<td>Conclusions</td>
<td>134</td>
</tr>
</tbody>
</table>

## IV. MICROSTRUCTURE OF HIGH MODULUS SOLID STATE EXTRUDED POLYETHYLENE: X-RAY SCATTERING STUDIES OF 12, 24 AND 36 EXTRUSION DRAW RATIO | 137 |

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Introduction</td>
<td>137</td>
</tr>
<tr>
<td>4.2</td>
<td>Background</td>
<td>139</td>
</tr>
<tr>
<td>4.3</td>
<td>Samples</td>
<td>143</td>
</tr>
<tr>
<td>4.4</td>
<td>Experimental Methods</td>
<td>145</td>
</tr>
<tr>
<td>4.4.1</td>
<td>Wide Angle X-ray Scattering</td>
<td>145</td>
</tr>
<tr>
<td>4.4.2</td>
<td>Small Angle X-ray Scattering</td>
<td>146</td>
</tr>
<tr>
<td>4.5</td>
<td>Results</td>
<td>152</td>
</tr>
<tr>
<td>4.5.1</td>
<td>Wide Angle X-ray Diffraction</td>
<td>152</td>
</tr>
<tr>
<td>4.5.2</td>
<td>Small Angle X-ray Scattering</td>
<td>156</td>
</tr>
<tr>
<td>4.6</td>
<td>Discussion</td>
<td>170</td>
</tr>
<tr>
<td>4.7</td>
<td>Conclusions</td>
<td>180</td>
</tr>
</tbody>
</table>

## V. CONCLUSIONS AND POSSIBLE EXTENSIONS | 182 |

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>Overview</td>
<td>182</td>
</tr>
<tr>
<td>5.2</td>
<td>Polymer Electron Microscopy</td>
<td>183</td>
</tr>
<tr>
<td>5.3</td>
<td>Deformation Microscopy of Thin Oriented Films</td>
<td>185</td>
</tr>
<tr>
<td>5.4</td>
<td>Microstructure of Solid State Extruded Polyethylene</td>
<td>186</td>
</tr>
<tr>
<td>5.5</td>
<td>Possible Extensions to This Work</td>
<td>188</td>
</tr>
<tr>
<td>5.5.1</td>
<td>Oriented Thin Film Studies</td>
<td>188</td>
</tr>
<tr>
<td>5.5.2</td>
<td>SAXS Studies of Solid State Extruded Polyethylene</td>
<td>191</td>
</tr>
</tbody>
</table>

REFERENCES ................................................. | 196 |
APPENDIX A .................................................. | 220 |
APPENDIX B .................................................. | 228 |
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Structure-Factors for Selected Polyethylene Reflections</td>
<td>46</td>
</tr>
<tr>
<td>4.1</td>
<td>Properties of Solid State Extruded Polyethylene Samples</td>
<td>144</td>
</tr>
<tr>
<td>4.2</td>
<td>WAXS Data</td>
<td>153</td>
</tr>
<tr>
<td>4.3</td>
<td>Comparison of Crystallite Sizes and Long Periods (Å)</td>
<td>158</td>
</tr>
<tr>
<td>4.4</td>
<td>Porod Law Ranges in q (Å⁻¹)</td>
<td>167</td>
</tr>
<tr>
<td>4.5</td>
<td>Anisotropic Porod Analysis</td>
<td>168</td>
</tr>
<tr>
<td>4.6</td>
<td>Mean Squared Electron Density Fluctuation and Effective Densities From Small Angle X-ray Scattering</td>
<td>171</td>
</tr>
</tbody>
</table>
LIST OF ILLUSTRATIONS

Figure

1.1 Typical engineering stress-strain curve of polyethylene showing the three stages of deformation ............. 7
1.2 Schematic diagram of spherulite deformation zone classification ................................................. 9
2.1 Optical configuration in the electron microscope for different imaging conditions ................................. 20
2.2 Schematic ray diagrams of CTEM diffraction geometries. (a) SAD - selected area diffraction, (b) MBD - microbeam diffraction ................................................................. 22
2.3 Schematic illustration of the basic components of a STEM (operating in bright field mode) ..................... 24
2.4 Bright field micrograph of overgrown polyethylene single crystal. The rectangular region at left center is lighter and lacks contrast because it was radiation damaged during focusing at high magnification ........... 29
2.5 (a) STEM convergent beam scanning micro-diffraction. A fine convergent beam of about 20 nm diameter is scanned over the sample. The area contributing to the diffraction pattern is determined by the area scanned ............. 32
2.5 (b) Scanning microarea diffraction pattern obtained from 100 nm x 100 nm area of a polyethylene crystal ........ 33
2.6 STEM microarea diffraction pattern from a polyethylene single crystal with beam stop tip for annular DF in position. The reflections are broad due to the large divergence of the incident beam .................. 38
2.7 (a) Schematic drawing of a uniformly bent crystal showing planes oriented properly for diffraction (s=0) and for non-diffraction (s<0, s>0). (b) Schematic of the diffraction condition: \( K_0 \) is the incident beam vector, \( K \) the diffracted beam vector, \( g \) is the reciprocal lattice vector for a particular reflection, and \( s \) is the deviation parameter .............................................................. 40
2.7 (c) Rocking curve (110) for a 300 A thick polyethylene single crystal .............................................. 41
2.8 Dark field efficiency for various crystal thicknesses as a function of the maximum deviation parameter .......... 44
2.9 (a) CTEM BF micrograph of a Marlex® thin film spherulite showing diffraction contrast banding. Light regions are spherulite boundaries ........................................... 49
2.9 (b) CTEM BF micrograph of less organized banding (arrowed) in a Hifax® film. (c) CTEM BF micrograph at higher magnification of the Hifax® film. Arrows point to several cross bend contours ..................... 50
LIST OF ILLUSTRATIONS (Continued)

Figure

2.10 (a) CTEM BF ghost image of oriented polyethylene film (underfocused). Circled regions are crystals oriented for other than (110)/(200) diffraction. (c) CTEM BF ghost image of oriented polyethylene film (overfocused). Circled regions show variation of image shift of (110)/(200) diffracting regions indicating variation of chain tilt angle .......................... 53

2.10 (b) Schematic of ghost image pattern expected for a single lamella oriented (h00) ......................... 54

2.11 Schematics of various STEM detector geometries and micro-diffraction patterns. (a) STEM BF (c) STEM n beam annular DF (e) STEM 002 annular DF .................. 58

2.11 Schematics of various STEM detector geometries and micro-diffraction patterns. (b) Micro-micro diffraction pattern of oriented Marlex® PE film (d) Micro-micro diffraction pattern for n beam annular DF (f) Micro-micro diffraction pattern for 002 annular DF .......................... 59

2.12 STEM n beam annular versus single beam dark field for two halves of the same single crystal. Spot size approximately 60 Å, beam divergence 3.7 x 10^{-3} radians. 62

2.13 (a) STEM n beam annular DF image showing 50 to 200 Å diameter diffracting microfibril crystallites within the microneck zone of a deformed spherulitic polyethylene film. (b) Enlargement of area in box in (a), showing 25 Å resolution from separation of microcrystallites 63

2.14 STEM n beam annular DF tilt series of oriented polyethylene lamellar film. TA indicates the tilt axis. (a) +1° tilt (b) 0° tilt and (c) -2° tilt .................. 65

2.15 (a) STEM BF image of spherulitic polyethylene films (b) STEM n beam annular DF image of same region as (a); (c) STEM 002 annular DF image of same region as (a) .......................... 66

2.16 (a) STEM n beam annular DF of a spherulitic Hifax® film. Amorphous regions are imaged grey by mass thickness contrast; (c) CTEM BF ghost image of spherulitic Hifax® film (overfocused). Amorphous regions are imaged dark by phase contrast .......................... 68

2.16 (b) Schematic of tilted lamellae and amorphous regions in thin film .................. 69

2.17 STEM n-beam annular DF micrograph of spherulitic Hifax® film containing symmetrically bent lamellae .......................... 71

3.1 Schematic of orientation induced crystallization [115]: (a) random coils, (b) chains oriented by (horizontal) stress, (c) crystallized oriented chains, (d) remaining
LIST OF ILLUSTRATIONS (Continued)

Figure

3.1 (Cont'd)
random coil chain segments available for epitaxial crystallization on fiber nuclei, (e) folded chain lamellar overgrowths, resulting in shish kebabs or fiber-platelet morphology ........................................... 79

3.2 Keller-Machin [128] row structure for uniaxial bulk samples (cylindrites), with ideal pole figures consistent with low and high stress cases (adapted from [119] and [129]) .......................................................... 81

3.3 Effect of strain-induced nucleation density on row structure morphology (a) low stress, sparsely arrayed fibrils with long, twisting overgrowths; (b) high stress, densely arrayed fibrils with impinged lamellae, adapted from Katti & Schultz [130] ........................................ 83

3.4 Keller-Machin [128] row structure model for thin films, with ideal pole figures for low and high stress cases (adapted from [119] and [129]) ........................................ 84

3.5 Photograph of the process of melt-drawing a thin oriented polyethylene film: (a) a bead of polymer solution (arrow) is placed on a hot glass plate, (b) after spreading the solution with a hot glass rod, the film (arrow) is drawn off the glass onto a roller ...................................................... 87

3.6 Photographs of the in situ deformation method: (a) elongation grid showing support layer of polyethylene and copper bars cut to allow unsupported deformation of a second layer of PE in narrow region at center; (b) an elongation grid mounted in the deformation holder, 13% strain in horizontal direction ........................................ 88

3.6 Photographs of the in situ deformation method: (c) close up of (b), showing how notched copper side bars have broken but support bars are intact, supporting a carbon film with a PE film on top .................................................. 89

3.7 Photograph of special adapter which allows deformed film in elongation holder to be coated with carbon in vacuum evaporator .......................................................... 91

3.8 Bright field CTEM micrographs of melt-drawn oriented thin PE film: (a) as-drawn (at 120°C), drawing direction vertical (arrow), inset (top right) optical transform of negative, inset (top left) selected area electron diffraction pattern showing high orientation, c-axis vertical .................................. 93

3.8 Bright field CTEM micrographs of melt-drawn oriented thin PE film: (b) annealed for two hours at 128°C, black regions are Bragg oriented diffracting lamellar crystals ............................................... 94
LIST OF ILLUSTRATIONS (Continued)

Figure

3.9 Schematic of oriented lamellar films with coordinate systems indicated for crystal axes and for film directions ................................................................. 96

3.10 CTEM bright field micrograph of annealed film deformed over a crack in supporting carbon film, deformation direction vertical (arrow). Top right is small angle electron diffraction pattern from this area, schematic of pattern lower right. Letters are explained in the text ................................................................. 97

3.11 Enlargement of deformed area similar to that of Figure 3.10. Carbon film (c) extends vertically to horizontal line marked by short arrow, deformation direction vertical. Right side is an enlargement of the area outlined by the box. The deformation of the film in this region increases from the bottom of the figure to the top, as one traverses the film towards the unsupported region ................................. 99

3.12 Series of CTEM bright field micrographs of annealed film at 0%, 39% and 340% elongation as measured by comparing the deformed long period (lamella repeat) to the initial long period .............................................. 101

3.13 Series of STEM n-beam annular dark field micrographs of annealed film; (a) 0%, 23%, 54%, 74% long period deformation, deformation direction vertical ......................... 102

3.13 Series of STEM n-beam annular dark field micrographs of annealed film; (b) 240% long period deformation, deformation direction vertical ................. 103

3.14 (a) CTEM bright field micrographs of deformed AN films. BS_{g} and BS_{b} refer to lamellae deformed by block shear, while FS indicates fine shear ............... 105

3.14 (b) CTEM bright field micrographs of deformed AN films. BS_{g} and BS_{b} refer to lamellae deformed by block shear, while FS indicates fine shear ............... 106

3.15 CTEM BF selected regions of deformed AN film. (a) lamella in center has sheared by combined block shear (h00) and fine shear (0k0), (b) block shear (h00) overlapping lamellae, (c) lamellae with fibers extending through along c, (d) Fresnel fringes due to defocus at edges of lamellae and at thickness differences in sheared lamellae ........................................... 107

3.16 (a) STEM DF images of deformed AN films showing Fine Shear (FS), Block Shear (BS) and many crystals in fiber areas (labeled c) ......................... 108
Figure

3.16  (b) STEM DF images of deformed AN films showing Fine Shear (FS), Block Shear (BS) and many crystals in fiber areas (labeled c) ........................................ 109

3.16  (c) STEM DF images of deformed AN films showing Fine Shear (FS), Block Shear (BS) and many crystals in fiber areas (labeled c) ........................................ 110

3.16  (d) STEM DF images of deformed AN films showing Fine Shear (FS), Block Shear (BS) and many crystals in fiber areas (labeled c) ........................................ 111

3.17  CTEM bright field micrograph (left) of unsupported annealed PE film deformed to about 300% strain. Right side is a similar area imaged by CTEM dark field using the 110, 200 reflections. Large arrow points to a lamellar crystal and the small arrows indicate small crystals in the oriented amorphous regions............. 112

3.18  CTEM bright field micrograph series of as-drawn film at 0%, 34% and 56% long period deformation parallel to c (arrow) .............................................................. 114

3.19  STEM n-beam annular dark field image series of as-drawn film, deformation vertical, at 0%, 50% and 90% long period strain .......................................................... 115

3.20  Deformation perpendicular to c-axis for AD film imaged by CTEM bright field. Arrows point out fibers spanning the cracks opened by crystal cleavage along b .............. 116

3.21  CTEM bright field series for AN films, deformation along TD, (a) shows fibers spanning small voids opened by crystal cleavage, (b) and (c) are at higher strains ... 118

3.22  STEM n-beam annular DF image of AN film deformed along TD. (a) region of relatively low deformation showing bands of voids and fibers along a line at about 45° to c .................................................................. 119

3.22  STEM n-beam annular DF image of AN film deformed along TD. (b) enlargement of region in box from (a), large arrows indicate (sharp) edge of cleaved crystal, small arrows point to fibers from amorphous regions bridging the void formed (black regions) ......................... 120

3.23  STEM n-beam annular dark field micrograph series of an annealed film deformed at a 45° angle to the c-axis direction. (a) is 0% strain, and (b), (c) and (d) are at increasing strain levels ................................. 121

3.24  Drawing showing the elongation of the rubber-like amorphous zones into fibers with increasing strain (a) 0% strain, (b) 100% amorphous strain, 20% long period
LIST OF ILLUSTRATIONS (Continued)

Figure

3.24 (Cont'd) strain, (c) 400% amorphous strain, 60% long period strain ........................................... 123

3.25 Drawing after Schultz [140] of the ultrastructure of deformation: (a) undeformed parallel lamellae, (b) separation of lamellae along c, (c) strain in amorphous regions sufficient to induce crystallization in the fibers, (d) beginnings of c-axis slip (fine slip shown), (e) block slip resulting in breakup of lamellae into large blocks, (f) fibrillar morphology with discrete microfibers containing some lamellar block crystals and strain induced fibrillar crystals ............... 125

3.26 Schematic diagrams illustrating different degrees of fineness of slip. (a) Fine slip. A displacement of one lattice vector has occurred on every other lattice plane in the crystal. The direction n is the normal to the surface of the crystal which has rotated relative to the chain axis c during deformation. (b) Coarse slip. The same total shear has been produced by a displacement of two lattice vectors on every fourth plane [141] .... 128

3.27 Schematic drawing of the block slip mechanisms, (1) undeformed lamellar block, (2) (h00), [002] slip producing long, thin sheared lamellae, (3) alternatively, (0k0), [002] slip producing stair step sheared lamellae, (4) combined shear modes leading to reduction of block crystal size. ................................. 129

3.28 Representations of (110),<001> slip system, not observed for these oriented films, (a) undeformed lamella, (b) wedge shaped slipped crystal ............................. 130

3.29 Schematic drawing of deformation perpendicular to c, i.e. parallel to b, showing the opening of small voids between fractured crystals. The crack is spanned by fibers formed from the amorphous interlamellar regions .... 132

4.1 Solid state extruded polyethylene billet removed from extrusion die (top) and extruded fiber, 36 EDR (bottom). .......................................................... 137

4.2 (a) Peterlin's model for cold drawn microfibrils [175], (b) Ward's model for hot drawn and solid state extruded fibers [32,36]. ............................................. 142

4.3 Schematic of the ORNL 10 meter small angle x-ray scattering machine. Variable detector positions for nominal 1,2 and 5 meter sample-to-detector distances are shown. Scattering vectors measured on the plane of the detector and the azimuthal angle \( \mu \) are shown at the 5 meter location (fiber direction vertical) ............ 148
LIST OF ILLUSTRATIONS (Continued)

Figure

4.4 Isointensity contour plot of the relative extent of the small angle scattering patterns for the 36 EDR sample. Interior contours are obtained at 5 meters sample-to-detector distance, outside contours at 1 meter, fiber direction vertical. .......................................................... 149

4.5 Wide angle x-ray flat film photographs of solid state extruded polyethylene of extrusion draw ratio (a) 1 (undeformed billet), (b) 12, (c) 24, (d) 36 ................................ 154

4.6 Microdensitometer iso-intensity contour plot of the flat film wide angle x-ray photographs from Figure 4.5, equatorial profiles only. ................................................................. 155

4.7 SAXS iso-intensity contour plots at 5 meter geometry for (a) initial billet, 1 EDR and (b) 12 EDR, (c) 24 EDR and (d) 36 EDR samples. Data are normalized for sample volume and incident beam intensity, outer contour at 16 counts, each inner contour increases by a factor of 2. Void scattering at the centers of the patterns was not included in the invariant calculations. Scattering vectors q1 and q2 and azimuthal angle µ are indicated on (b) .......................................................... 157

4.8 Plot of normalized intensity versus scattering angle q (Å⁻¹), meridional direction (µ = 0°). ................................. 159

4.9 Ratio of 4th to 3rd moment of microfibril radius distribution function, <R>, versus (EDR)⁻¹/₂. .......................... 161

4.10 Porod plots at three azimuthal angles (µ). Lines are least squares fits to Porod’s Law, equation (4.9). (a) 1 EDR (isotropic sample). ............................................................... 163

4.10 Porod plots at three azimuthal angles (µ). Lines are least squares fits to Porod’s Law, equation (4.9). (b) 12 EDR. .......................................................... 164

4.10 Porod plots at three azimuthal angles (µ). Lines are least squares fits to Porod’s Law, equation (4.9). (c) 24 EDR. .......................................................... 165

4.10 Porod plots at three azimuthal angles (µ). Lines are least squares fits to Porod’s Law, equation (4.9). (d) 36 EDR. .......................................................... 166

4.11 Iso-intensity contour plots for data taken at 1 meter geometry (fiber direction vertical). Round “holes” in centers are due to the use of a 4.6 cm diameter beam stop to block the interference peak, avoiding counter overflow during the long run times. (a) 1 EDR, (b) 12 EDR, (c) 24 EDR, (d) 36 EDR ......................... 169

B.1 Geometry and scattering angle relationships for the ORNL 10 meter small angle scattering system. ............. 231

B.2 Flow chart of program execution for invariant analysis. .................. 233
CHAPTER I
INTRODUCTION

1.1 Opening Remarks

Polymer deformation is important both as a means of imparting improved properties to a polymer and as a method used in the study of the microstructure of the polymer itself. The polymer producer often deforms the material to strengthen it; the polymer user very often relies on the material's resistance to deformation; the researcher utilizes polymer deformation to assist in the elucidation of microstructure and to correlate with other structural studies.

Deformation of polymers to produce high strength fibers has been used for many years commercially in the textile industry. The deformation morphology has been studied extensively, and the fiber structural models are reasonably developed. The transformation from the lamellar structure of a partially crystalline polymer to fibrillar structure is still not fully explained by any model. Despite an almost endless procession of technical papers concerning structure-property relations of polyethylene, there remains a clear lack of quantitative analysis of the deformation of polyethylene.

This dissertation is directed toward filling that gap - realizing that there have been many qualitative studies already, this research effort was directed toward quantitative morphological evaluation of
solid state extrusion as well as toward direct visualization of deformation ultrastructure. Two approaches were taken to address these two different yet related problems in polyethylene deformation morphology: the fibrillar microstructure of solid state extruded polyethylene was examined primarily by small angle x-ray scattering; melt-drawn oriented lamellar thin films were deformed in situ to allow electron microscopic examination of the deformation microstructure. Both approaches involved development of new techniques to be applied to new experimental situations, followed by extensive application of these new techniques along with conventional polymer morphological studies. The results of these investigations revealed new quantitative information about deformation processes in polyethylene. That quantitative approaches are critical has been emphasized by one of the great polymer physicists: "We have an inexhaustible variety of interplay between organized structure and disordered material. The full comprehension of it all requires the appreciation of the role played by the morphology with all its variety and subtlety" [1].

1.2 Organization of the Dissertation

The remainder of this chapter is a brief introduction to and review of polyethylene morphology and deformation morphology. The basic background material will be relevant to more specific discussions in later chapters. Chapter II is a detailed and extensive exposition of specific electron microscopy techniques for the study of polyethylene morphology. The chapter is not a comprehensive text on
conventional transmission electron microscopy on polymers, nor does it dwell on the myriad sample preparation methods employed in the field. Rather, it emphasizes the methods developed (especially in this laboratory) for scanning transmission electron microscopy of polyethylene, and provides several graphic illustrations of applications to both spherulitic and oriented thin films.

Chapter III contains the results of an extensive study of the deformation at room temperature of thin oriented polyethylene films, using the methods developed in Chapter II. The images presented in this chapter show several of the ultrastructural deformation processes which previously could only be inferred from global scattering methods or visualized poorly from replicated, stained, microtomed or otherwise adulterated specimens. These deformations include $c$-axis shear processes on planes perpendicular to the $a$ or $b$ axes, the transformation of lamellar crystals to fibrillar (crystalline) structure, the cleavage of lamellar crystals when deformed perpendicular to $c$, and complex deformation modes when the stress is applied obliquely.

Chapter IV is a morphological study by x-ray scattering of solid state extruded polyethylene high modulus fibers. The method developed for measurement of the small angle x-ray scattering invariant for an anisotropic fiber was used to calculate the density of the non-crystalline component. This data, coupled with wide angle x-ray scattering data, is important in helping choose among the possible microstructural models proposed for the process of solid state deformation of polyethylene.
Chapter V is a brief recapitulation of the dissertation, and suggests further studies and possible extensions to this work.

1.3 Background

Polyethylene is one of the most studied semi-crystalline polymers both in terms of its mechanical properties and its morphology. Following Keller's admonition from the opening remarks, in order to understand the properties of polyethylene, we must strive to understand its morphology. The commercial bulk polymer (high density polyethylene, HDPE) generally has a spherulitic microstructure, which can be varied to some extent as needed for strength, toughness, impact strength, or other requirements. In general, higher molecular weight (MW) or smaller MW distributions produce better impact strength and toughness. As the processing or annealing temperature increases, large spherulites can be formed which will produce lower strength than samples with small spherulites [2].

The spherulite is a radially symmetric structure which contains platelike crystals (lamellae) arranged with their long axis parallel to the radius. The crystals are typically several hundred angstroms thick, up to 0.1 microns wide, and many microns long. These folded chain lamellar crystals first inferred by Storks in 1928 [3] for gutta-percha and polyesters are apparently crystallographically identical to solution grown single crystals, whose first observation is usually credited to Keller [4] and others [5,6] in 1957.

1.3.1 Solution Grown Single Crystals. Polyethylene single crystals
are thin platelets which nucleate and grow into pyramidal forms (typically lozenge shaped), usually with four growth faces \([110]\). The chain axis is along \(c\), and the long polymer molecules fold repeatedly at the surface, producing \(\sim 100\) Å thick crystals (chain axis perpendicular or at a large angle to the surface) \([7]\).

The unit cell is orthorhombic \([8]\), and the polymer single crystals can exhibit many of the features of macroscopic single crystals, i.e. twinning, slip, dislocation defects, etc. If the concentration or crystallization temperature of the solution is raised, multilayers can develop, and ultimately hedrites or axialites, which are sheaf-like structures, can form \([9]\).

1.3.2 Spherulitic Structure. At 100% concentration (i.e. the bulk polymer crystallized from the melt) the single crystal layers grow radially from a nucleus region, with \(b\) directed along the radius and \(a\) and \(c\) rotating about \(b\) \([10]\). Electron diffraction patterns of polyethylene thin films have confirmed the twisted ribbon-like arrangement, and the twist of the lamellae often results in a banded appearance, either in crossed polar optical microscopy or in electron microscopy \([11]\), but the exact nature of the lamellar twist is still not clear \([12,13]\). A recent rationale by Keith \([14]\) for both s-shaped bent crystals and twisted crystals is based upon transient bending moments associated with unequal stresses at chain fold surfaces during crystallization. The stresses arise from over crowding of chain segments at the fold surface.

Although the crystal perfection of solution grown single crystals
is high, the structure of the lamellae in the spherulite is not well known. Mosaic blocks may exist, as claimed from x-ray line broadening analysis [15], and the lower density of spherulitic polyethylene compared to solution grown single crystals may be due partially to the presence of defects in the crystal cores.

Spherulitic polyethylene is usually considered to be a two phase system, consisting of lamellar crystals embedded in and intimately attached to an amorphous matrix. This amorphous component is primarily inter-lamellar and inter-spherulitic. It probably has some orientation due to its topological interconnectedness, i.e. a single random coil may crystallize in different lamellae, and the amorphous portions of that chain are thereby constrained, preventing truly random coil conformation. These entangled molecular segments can exist as loose loops, cilia, or tie molecules between lamellae or between spherulites [16]. Tie molecules can cluster and crystallize, forming intra-links and inter-links [17]. The spherulite must be considered as a composite in order to understand its mechanical properties, and the nature of the bonding between the filler (lamellar crystals) and the matrix (amorphous material) is very important.

1.3.3 Macroscopic Deformation Analysis. Polyethylene deformation can be classified into three regions by reference to the engineering stress-strain curve for a bulk sample (Figure 1.1). In region I, often called the linear region, the polymer deforms initially by elastic processes [18], perhaps up to a strain of 5%. At higher strains (5-60%), crystal twinning, chain tilt by fine shear parallel
Figure 1.1 Typical engineering stress-strain curve of polyethylene showing the three stages of deformation.
to the \( c \) axis, and orthorhombic to monoclinic phase transformation occurs [10]. By 60% strain, much of the material has been converted to monoclinic structure, which reverts back to orthorhombic with time after the applied stress is relaxed.

Region II begins at the yield point, where the process of micronecking [19] begins to propagate throughout the specimen at a constant load level. Lamellar crystals are transformed into microfibril bundles with the fiber axis along the direction of applied stress. Keith and Padden [20] observed that the transformation zone was very sharp and that the equatorial zone and polar boundaries of the spherulite deformed preferentially. The classification scheme [10] for the deformation regions is shown in Figure 1.2. The transformation zone propagates into the polar zone with increasing deformation [21]. In addition, crystal axis rotation occurs preferentially about \( b \) during micronecking.

Stage III of the deformation process occurs at a relatively high strain value, where the microfibril bundles are themselves deformed. The dominant mechanism here is sliding of microfibrils past one another longitudinally, followed by formation of longitudinal cracks and ultimately, by failure [22]. Some drawing and chain extension of the microfibrils can occur [23].

1.3.4 Microfiber Model. The model which has dominated thinking of the micronecking process is due to Peterlin [19,24]. The microfiber, approximately 200 A wide and 15-20 microns long, is envisioned to be formed by breaking of lamellae into blocks which are incorporated into
Figure 1.2 Schematic diagram of spherulite deformation zone classification.
the fibers. However, Petermann [25] in low temperature single crystal deformation studies, postulates thermal rearrangement and refolding in his "string-of-pearls" structure. The folded chain blocks alternate with noncrystalline regions, which contain some extended chains (tie molecules) connecting adjacent crystallites. Peterlin postulates that the modulus depends upon the number and distribution of taut tie molecules. The model has been extended to hot drawn material by adding the concept of crystalline bridges, or regions in the amorphous zones where the aligned taut tie molecules have crystallized [26]. All the current fiber models assume highly aligned crystals, with variations in defects, bridges, ties, and amorphous content. A general observation for fibrous polymers is that the initial modulus increases with the draw ratio [27], which has led to the production of ultra high modulus fibers by various high elongation methods [28-32].

1.3.5 Tie Molecules and Links. Tie molecules are formed during the crystallization process when portions of a random coil chain are crystallized into different regions of the same lamella, different lamellae, or different spherulites. The perfection of the crystal depends strongly upon the amount of undercooling. Regime I crystallization [33] (ΔT<16°C) involves lateral growth on a layer from a single nucleus, while Regime II (16<ΔT<23°C) growth causes multiple nucleation and growth on each layer. At still greater undercooling (ΔT>23°C), Regime III crystallization occurs where the growth kinetics increase such that the nucleation density is about the width of a single chain stem [34]. This means that for higher undercooling, it is likely that
more than one polymer molecule will be involved in the growth of a layer of crystal (lamella) [16,33]. Hence, the degree of undercooling will influence the number of tie molecules; as $\Delta T$ increases, the number increases. The effect of molecular weight and $\Delta T$ upon intraties has been estimated for single crystals by Ewers, Zachmann and Peterlin [35], and as MW increases, the number of chain ends decreases, and the number and length of ties increases.

For bulk samples, many authors have studied the effect of MW and MWD upon deformation, with conflicting results. Some report the attainable draw ratio increasing with increasing MW [36,37], while others show the opposite behavior [38,39]. Variations of crystallization conditions and large differences in MWD probably account for the discrepancies. Capaccio and Ward [39] in the early 1970's suggested that MWD and cooling rate controlled drawability, but more recent studies [40] have indicated that almost any HDPE sample can be highly drawn at an appropriate temperature and strain rate. Exceptions include ultra-high molecular weight PE (UHMW PE) and HDPE without the very low MW component. UHMW PE cannot be very highly drawn and undergoes brittle fracture; the reasons for this behavior are not well understood. By removing the longest chains from HDPE, Warner [41] showed that the crystallization rate was increased, which apparently compensated for the MW change effect, leaving the number of tie molecules and, hence, the draw ratio unchanged.

Keith and Padden [42] observed links directly by solvent extraction of paraffin which had been co-crystallized with polyethylene,
leaving the inter-links readily apparent. Tarin and Thomas [23,43] made an intensive study of the role of links in polyethylene deformation, exploring the inter-connectedness of the links and modeling the possible origins of the link junctions. Observations included the fact that low MW PE did not form stable structures upon deformation (a threshold MW effect, also observed by Warner [41]), and for higher MW PE, the attainable draw ratio increases as ΔT decreased.

Recent work by Grubb [44] and by Fischer and Ruland [45,46] has advanced the concept that the entanglement network, consisting of transient physical crosslinks due to entangled chains, determines the deformability of polymers. The solidification model of Fischer [47] for melt-crystallized polymers implies the formation of entanglements due to the interpenetration of molecules, and the deformation of such a network is resisted mainly by the chain segments between entanglements. Grubb envisions the entanglements in a fiber to be localized small defect regions along mostly continuous crystalline micro-fibers.

1.3.6 Spherulite Deformation Models. Affine deformation, originally applied to chain segments in rubber [48], is the standard by which all other deformation models are compared. Affine deformation means that the deformation suffered by each microscopic element in the structure is identical to the macroscopic deformation imposed upon the entire structure. Wilchinsky [49] applied this description to spherulites and found that it did not adequately explain crystallite orientation data. The non-affine theory he proposed (using multiple concentric
shells) has been examined by many researchers [50-52] who found that it too was inadequate to explain crystallite orientation, but others [21,53] showed that the overall spherulite shape closely conformed to the predicted shape. Kataoka [54] measured the deformed shapes of spherulites in both thin films (two-dimensional) and thick films (three-dimensional) and found that the elongation in the periphery of the spherulite was less than that of the sample, at variance with Wilchinsky. Van Aartsen and Stein [55] used an affine model to explain small angle light scattering observations, and Todo [56] observed affine deformation up to 60% by light scattering measurements. Variations in sample MW and MWD, sample preparation, and test conditions in these experiments likely account for the differences in the observed deformation processes.

1.3.7 Composite Models. Takayanagi [57] used a simple series-parallel model to calculate the effective modulus of semi-crystalline polymers, based upon anisotropic linear viscoelasticity. Halpin and Kardos [58] used the Halpin-Tsai [59] equations from chopped fiber composite theory to calculate the modulus, taking into account the shape of the crystals. Patel and Phillips [60] used a simple modification of the Halpin-Kardos theory to calculate the mechanical response of a bulk PE sample. Chow [61] calculated stress concentration factors from a more complete crystal shape factor and the volume fraction of filler. Pakula [62] used a Takayanagi element to calculate properties of two-dimensional spherulites.

A more elegant method is that of T.T. Wang [63], who used linear
elastic continuum mechanics to calculate properties of spherulitic polyethylene at three different structural levels: lamellae, spherulites and bulk.

1.3.8 Quantitative Approaches to the Study of Deformation. Quantitative methods for determining bulk mechanical properties are relatively straight-forward - overall moduli, stresses and strains can be measured with precision. Likewise, morphology can be assessed quantitatively by light and x-ray scattering, calorimetry, etc. These techniques all provide global averages; that is, a large portion of the entire bulk sample is used to give an average value of the measured quantity. But small scale information is important due to the often extreme inhomogeneity of the deformation. The literature contains many examples of qualitative micro-morphological investigations. One of the few quantitative investigations is that of Hay and Keller [21] using micro-x-ray diffraction.

To quantize deformation on a local scale, various workers have used scribed thin films [64], metal decoration [43,65,66] and gold markers [23]. These methods may affect the specimen deformation, and are limited in scale and accuracy. Lauterwasser and Kramer [67] recently developed a technique to measure micro-mechanical properties in thin amorphous polymer films, based upon the exponential decrease in intensity (due to scattering) of an electron beam passing through a film. Local draw ratios and volume fractions can be determined with high accuracy by this method, and its adaptation for use on semi-crystalline thin films provides a key technique needed for performing
This chapter presented an introduction to the dissertation problem, and a short review of polyethylene morphology as relevant background information. Because the dissertation addresses both global measures of deformation morphology (such as wide and small angle x-ray scattering) and local measures (such as electron microscopy), the review encompassed morphology from the level of the unit cell to macroscopic fibers. A thorough review of the subject is beyond the scope of this dissertation. For a more extensive bibliography of polyethylene deformation and microstructure, a recent dissertation by Gedde [69] is recommended.
CHAPTER II
ELECTRON MICROSCOPY OF POLYETHYLENE

2.1 Introduction

The use of electron microscopy in studies of the microstructure of polyethylene has been widespread. Examination of features from micron size to near atomic scale is possible with a conventional transmission electron microscope (CTEM), and the increasing application of new imaging techniques in scanning transmission electron microscopy (STEM) is routinely producing detailed microstructure analyses once considered impractical if not impossible. Typical morphological studies of polyethylene use global methods, such as x-ray or neutron scattering, to provide a statistical average of data from a bulk sample (usually ~ 1 mm³). Electron microscopy, however, can provide that same type of scattering data from a vastly smaller volume (a minimum of about 3 x 10⁶ nm³ for selected area electron diffraction in CTEM to 10⁵ nm³ for micro-micro electron diffraction from polyethylene in STEM for 100 KV and room temperature). In addition, an image can be obtained of the same region, and it is the comparison of that image (from a thin specimen) to the bulk material that is the central question in most polymer microscopy studies.

The two-phase nature of polyethylene makes the application of electron microscopy very useful for determining the size and shapes of
the crystallites, and the organization of lamellar crystals (dispersed in a noncrystalline phase) into higher order structures such as spherulites or oriented films. The use of crystalline diffraction contrast in images and electron diffraction from the crystallites provides the means to study the orientation and the internal structure of the crystals, provided the ever present problem of radiation sensitivity of the material can be overcome.

Grubb in a recent review article summarized the major properties of polymers which adversely affect electron microscopy [70]:

1. Polymers, like most organic materials, are highly sensitive to radiation damage so that the electron beam of the microscope can cause rapid chemical and physical changes in the specimen during observation, so much so that there is a complete loss of crystalline order.
2. Polymers are comprised of low atomic number material, scattering high energy electrons comparatively weakly so that image contrast is low.
3. Polymers are often soft and tough so that cutting ultra-thin sections for microscopy distorts or destroys their structure.
4. Polymers are insulators, so that electrostatic charging may occur in the electron beam.

To overcome these problems, electron microscopy studies of polyethylene have traditionally involved either replication or staining techniques. These methods have been employed because of the difficulty of preparing thin sections of polyethylene and because the polymer crystallinity is rapidly damaged by the electron beam at the current densities usually employed in conventional transmission electron microscopy [71]. This deterioration has two aspects: (1) loss of crystallinity and (2) sample distortion resulting from thinning of
lamellae in the chain axis direction and expansion in the normal directions. Therefore, electron damaged specimens do not convey an accurate image of the micromorphology. Staining, especially that involving chlorosulphonation [72] can prevent much of the distortion of the thin film during electron exposure (provided careful low intensity techniques are employed) and permits detailed examination of the local morphology primarily by use of mass thickness contrast. Staining techniques, along with replication and small angle scattering have been used to understand the effects of crystallization temperature, molecular weight, pressure and other intrinsic and extrinsic parameters on the micromorphology of polyethylene [73-75]. Chlorosulphonation, however, can itself lead to significant dimensional changes (a 30% shrinkage!) in the lamellar spacing of polypropylene [76]. Thus, the electron microscopic study of untreated crystalline thin films or sections in addition to permitting the observation of unaltered specimens, has advantages not realizable with treated or replicated specimens.

In summary, if a thin enough specimen can be obtained a high resolution image can also be obtained, except that the contrast will be low unless the material is stained, in which case the morphology may well be altered. If the material is crystalline, diffraction may provide sufficient contrast, but the crystallinity is destroyed by the very process of recording the image. Fortunately, the development of the STEM has provided a new tool for helping overcome some of these limitations and frustrations. The advantages of STEM techniques on
polyethylene have been demonstrated by Low et al. [77] as well as in papers from this laboratory [78-80]. This chapter will detail the use of STEM for studies of the microstructure of polyethylene, but the applicability of the techniques presented is general for other semicrystalline polymers as well. A basic review of conventional transmission electron microscopy techniques precedes more detailed presentations of scanning transmission electron microscopy methods, including microdiffraction and STEM dark field. Finally, numerous applications of the methods to thin oriented and unoriented polyethylene films are given. Much of this chapter has appeared in the literature [78-80] and, in fact, is the current culmination of a research effort directed towards development of electron microscopic methods to study the micro-morphology of polyethylene, beginning with the work of Thomas in the early 1970's [81-83], continuing with Tarin and Thomas [43,23], Sherman and Thomas [78], Sherman, Adams and Thomas [79], and Chacko, Adams and Thomas [80].

2.2 Conventional Transmission Electron Microscopy

Before proceeding to STEM methods, it is useful to define briefly conventional transmission electron microscopy methods. Figure 2.1 is a schematic of the CTEM imaging modes for bright field (BF), using the electrons transmitted through a thin specimen, and tilted-beam dark field (DF), imaging with diffracted electrons selected by the objective aperture. Contrast is enhanced in BF by blocking the scattered electrons with an objective aperture. The high contrast in DF is
Figure 2.1 Optical configuration in the electron microscope for different imaging conditions.
somewhat offset by the lower intensity levels, and the DF image is very sensitive to the sample-electron beam geometry. In fact, the observation of the diffraction pattern is absolutely necessary in order to specify the DF image conditions.

Selected area diffraction (SAD) geometry, the most commonly used CTEM diffraction method, is shown in Figure 2.2. Diffraction from a large diameter, parallel beam incident on the sample is limited by a field limiting aperture at the first image plane of the intermediate lens. The sample area from which the diffraction pattern is formed is determined by the SAD aperture size and by spherical aberration of the objective lens, which limits the minimum area to about an 0.2 micron diameter circle. Unfortunately, the sample sees the large incident beam, which is then mostly blocked by the SAD aperture, and areas adjacent to the one selected are radiation damaged.

Microbeam diffraction (MBD) is also possible with a CTEM by using a strongly excited first condenser lens and a very small second condenser lens aperture (typically 20 μm) to illuminate the sample with a fine parallel beam of electrons (see Fig. 2.2b). Since no field-limiting aperture is used, the spherical aberration of the objective lens does not play a role and the minimum diffraction area is the incident beam diameter (c. 250 nm). Because the incident beam only illuminates the area of interest, successive patterns may be obtained from adjacent areas. The only drawbacks are the 250 nm size limitation, the non-uniform intensity distribution across the illuminated area (approximately Gaussian), and lack of a precise means of
Figure 2.2 Schematic ray diagrams of CTEM diffraction geometries. 
(a) SAD - selected area diffraction, (b) MBD - micro-beam diffraction.
repositioning the beam to an adjacent area of interest.

An extensive literature exists on CTEM imaging, including many general textbooks. Applications to biological materials (usually very electron beam sensitive), metals and other beam resistant materials have been extensively developed, and applications to polymeric materials, though often lagging, are nevertheless considerable. Recent reviews by Grubb [70] and by Thomas [84] include many interesting applications of CTEM to polymers, as well as the newer techniques of STEM.

2.3 Operation of STEM for Radiation Sensitive Polymers

Figure 2.3 shows schematically the basic components of a STEM. The central feature is a highly focused beam of small diameter (10 to 60 Å for CTEM with a scanning attachment and as low as 2 Å for dedicated STEM) which is sequentially scanned over the thin specimen. The beam is focused onto the specimen by the strong prefied of the objective lens and the transmitted electrons are detected by a photomultiplier tube (PMT). In order to form the image, the amplified signal is displayed on a cathode ray tube (CRT) which is synchronized with the scan coil of the incident illumination. Image contrast arises from variations of the transmitted intensity. The magnification is set by the ratio of the area of the scan on the CRT to the area of the scan on the specimen. The bright field (BF) image is recorded by an on-axis disc detector. An annular detector outside the BF disc detector may be used with a second viewing CRT to provide simultaneous
Figure 2.3  Schematic illustration of the basic components of a STEM (operating in bright field mode).
BF and DF images. Also, the BF disc detector may be made effectively into an annular detector by blocking out the main transmitted beam with, for example, the diffraction beam stop. For crystalline specimens where a specific reflection is desired to form the DF image, the intermediate lens aperture (SAD aperture) can be used to block out all scattered intensity but the reflection of interest. Because the illumination in STEM is conical, the BF disc detector angle $\alpha$ should be equal to the illumination angle $\beta$ (see Figure 2.3).

STEM has been suggested to have an advantage over CTEM for two principal reasons: (1) the collection efficiency of scattered electrons is higher for STEM than for CTEM and (2) microarea diffraction patterns may be obtained without cumulative radiation damage to adjacent areas [85-87]. Specific comparison between STEM and CTEM depends precisely on the type of incident illumination, mode of image formation, type of image contrast and image resolution desired. Because the STEM image is collected point by point, the various kinds of transmitted electron signals can be processed in many possible ways permitting, for example, selected energy loss images for chemical mapping, elastic to inelastic scattering ratio images for atomic number contrast, etc. [88,89]. The approach in this chapter will be restricted to applications of STEM imaging of radiation sensitive crystalline polymers.

Since radiation damage is the limiting factor in electron microscopy of crystalline polymers, the main issue is to consider how to minimize the specimen damage to obtain a given amount of information
from the specimen [71,81]. The electron dose ($\phi_{\text{max}}$) that can be used to extract information before the sample is severely damaged (thereby making further information more noise than signal) depends only on the radiation physics and chemistry taking place in the sample [71]. This maximum level of damage which can be tolerated depends on what type of information is desired from the specimen. Diffraction contrast images and electron diffraction patterns depend on the crystallinity of the specimen. Because the long range crystalline order of the sample is destroyed with increasing electron dose, a limited number of scattered electrons can be used to obtain crystallographic information. By employing higher accelerating voltages [90] or by specimen cooling, $\phi_{\text{max}}$ may be increased [91]. High voltage does not result in any net improvement because although $\phi_{\text{max}}$ increases, the diffracted intensity per unit incident dose decreases by the same amount. Specimen cooling to cryotemperatures ($\sim 20^\circ\text{K}$) can result in an approximate 3X improvement of $\phi_{\text{max}}$ over room temperature for polymers which damage by crosslinking by reducing the mobility and hence the reactivity of the radicals which lead to crosslinking [91,92]. In addition to improving $\phi_{\text{max}}$, specimen cooling also increases the scattering efficiency by decreasing the loss of diffracted peak intensity due to thermal diffuse scattering (about 10% increase for polyethylene) [93].

The image resolution, $\delta$, is related to $\phi_{\text{max}}$ by the equation

$$\delta = \frac{\text{SNR}}{C[\phi_{\text{max}}]/q^{1/2}}$$  \hspace{1cm} (2.1)
where SNR is the signal to noise ratio sufficient to detect a signal in a noisy background (it is usually taken as at least 5 [94]), f is the utilization efficiency (i.e. the fraction of the electrons passing through the specimen which contribute to the image), q is the charge of an electron, and C is the image contrast [95]. Both f and C are imaging mode dependent. Because f and C are coupled as \( f^{1/2}C \), the most efficient use of the transmitted electrons (BF) does not necessarily provide the highest resolution [71,81].

The only way of improving resolution at a given specimen temperature is thus to increase f [85]. A STEM equipped with an annular detector can collect nearly all electrons scattered outside of the central beam. Optimum information extraction is achieved if all this signal is transferred without loss to the recording medium and if the information loss in the focusing/area selection/diffraction optics set up steps is negligible in comparison to the radiation damage which occurs during recording. The inherent image intensification, control of illumination location and magnification independent focus capabilities of STEM permit a very convenient and precise focusing/area selection/diffraction optics set up without significant radiation damage to the area of interest.

Image intensification is provided by the electronic contrast and brightness controls of the STEM detection system. The electronically manipulated image does not of course contain more information but is merely brighter than the unintensified image [81]. The lower limit at which an ideal image intensification system can be used for focusing
or area selection is limited by the statistical electron beam noise to about $1 \times 10^{-14}$ Amp cm$^{-2}$. This is a factor of 100 to 200 lower than the necessary current density required for minimum microscope phosphor screen brightness for unaided focusing/area selection by the dark adapted eye [96], provided image intensification does not introduce additional noise (commercial systems approach this ideal [97]). Only the specimen region viewed on the CRT is radiation damaged so that the selected area mode (a variable size reduced raster on the CRT) and variable beam scan speeds are quite useful as discussed in the following example. The specimen is first observed with a rapid scan at low magnification (hence low dose rate). A coarse focus and area selection are accomplished with only slight sample damage. A low quality BF micrograph of the area is taken for reference using the Polaroid camera. At this point the selected area mode is used to observe an area from the first selected region that does not contain the precise feature of interest but is sufficiently close so that focusing on this second region will give adequate focus for the desired area. Since focus is independent of magnification in STEM (which is not the case for CTEM) the image is focused for high resolution at a high magnification in the selected area mode with a slow scan speed to improve SNR for precise focus, damaging (severely) only a very small area. The magnification is then reduced and a full CRT scan is used to record a high resolution image from a nearby undamaged, in focus, selected area. Figure 2.4 is a BF micrograph taken of a polyethylene single crystal using this method (note the
Figure 2.4 Bright field micrograph of overgrown polyethylene single crystal. The rectangular region at left center is lighter and lacks contrast because it was radiation damaged during focusing at high magnification.
nondiffracting area which was damaged during selected area focusing).

2.4 STEM Scanning Microdiffraction

The normal STEM microdiffraction method uses the strongly excited objective lens to focus a fine electron probe on the sample (convergent beam diffraction). The diffraction pattern formed is then magnified by the lower half of the objective lens. The sample area producing the diffraction pattern is determined by the incident beam diameter, which is fixed by the objective and condenser lens settings. The technique is essentially the same as CTEM microbeam diffraction but with much smaller incident beam size due to the strong focusing action of the objective lens. Typical values for a tungsten hairpin filament source operated at 100 keV are 20 nm probe size with angular aperture of the convergent beam about $1 \times 10^{-3}$ rad ("Spot Mode" on the JEOL 100CX).

Another standard STEM microdiffraction method employs a rocking incident beam, with the sample positioned midway between the objective lens pole pieces such that a nearly parallel incident beam can be rocked about a point lying in the specimen plane. In this manner diffraction patterns have been obtained from 3 nm diameter metal crystals. This is approximately the theoretical minimum crystal size for a meaningful diffraction pattern of about 5 times the unit cell size [98]. The main obstacle to the successful application of microdiffraction to polymers is, again, radiation damage. The minimum polymer sample size which can form a useful diffraction pattern is
limited by the insufficient S/N statistics in the scattered peaks at low doses and destruction of the crystal by radiation damage at high doses. Experiments employing the two standard STEM microdiffraction techniques using a JEOL 100CX "TEMSCAN" with 20 nm electron probe and 12 nm thick polyethylene single crystals indicated severe radiation damage occurred before a diffraction pattern of the crystal could be obtained. To adopt STEM microdiffraction for radiation sensitive polymers the following procedure was developed (see Figure 2.5a) [78]: the microdiffractive mode of the STEM is selected and the optics are adjusted for the normal convergent beam diffraction pattern at 100,000X magnification. However, instead of operating in the spot scan mode (stationary beam) the selected-area frame scan mode is used. The selected-area scan is adjusted to scan a square area $W \, \text{cm} \times W \, \text{cm}$ on the CRT (corresponding to $W \times 10^2 \, \text{nm}$ by $W \times 10^2 \, \text{nm}$ on the sample). A scanning beam microarea diffraction pattern can thus be viewed on the fluorescent screen. Successive adjacent area scanning microarea diffraction patterns for mapping the specimen crystallography in the region of interest can be obtained routinely since the selected area scan mode can be adjusted to the desired size, shape and location on the sample with the incident beam off. By systematically varying the size of the scanned area and recording (using normal electron image plates) diffraction patterns at fixed incident beam current, it was determined that an area approximately 100 nm x 100 nm was the smallest area which could yield a "useful" pattern (see Figure 2.5b). The usefulness of a particular diffraction pattern will, of course, depend on
Figure 2.5 (a) STEM convergent beam scanning micro-diffraction. A fine convergent beam of about 20 nm diameter is scanned over the sample. The area contributing to the diffraction pattern is determined by the area scanned.
Figure 2.5  (b) Scanning microarea diffraction pattern obtained from 100 nm x 100 nm area of a polyethylene crystal.
what information is required. There will be a sacrifice of signal to noise ratio for smaller diffraction volumes. The criteria for a useful pattern will also depend on the radiation damage characteristics of the particular reflections of interest. Some reflections simply weaken and disappear as the crystal damages whereas others weaken, shift and broaden, eventually forming an amorphous halo.

The essential differences between microbeam diffraction (MBD) and scanning microbeam diffraction (SMD) are incident beam diameter and beam divergence. To compare MBD and SMD, it is necessary to assess the effect of beam divergence and diameter on the scattered peak intensity and peak width. To resolve a given reflection in an electron diffraction pattern requires both a sufficient signal/noise and a sufficiently narrow peak breadth.

The effect of beam divergence will be to decrease the diffracted intensity and to broaden the reflections. Assuming kinematical scattering, the scattered intensity will vary as

\[ I(s) \sim |F(hk\ell)|^2 \frac{\sin^2 \pi st}{\sin^2 \pi s} \quad (2.2) \]

where \( F(hk\ell) \) is the structure factor for the \((hk\ell)\) reflection, \( t \) is the crystal thickness parallel to the optic axis and \( s \) is the deviation of the \((hk\ell)\) planes of interest from the Bragg condition \((s=0)\).

An overestimate of the decrease in the diffracted intensity due to beam divergence can be made by assuming all incident electrons to have
a deviation from the Bragg condition equivalent to the beam divergence (e.g. $1 \times 10^{-3}$ rad). For the 110 reflection of a 12 nm thick polyethylene crystal, this amounts to less than a 1% decrease in the scattered intensity.

Neglecting radiation damage and paracrystalline line-broadening contributions, the observed peak width will be:

$$\delta \beta^2 = \delta \beta_D^2 + \delta \beta_\phi^2$$

(2.3)

where $\delta \beta_D$ is the broadening due to the beam diameter and $\delta \beta_\phi$ is the broadening due to beam divergence.

Beam divergence and beam diameter are in general inversely related - for the JEOL 100CX the beam divergence for a 100 nm beam is five times less than for the 20 nm beam. The contribution to the line broadening from beam size will usually be negligible in comparison to that from beam divergence. Therefore, for a given total area illuminated and total incident beam intensity the MDB pattern will exhibit sharper reflections because of the inherently lower divergence of a larger incident beam.

The scanning beam diffraction patterns obtained exhibit broadened diffraction spots typical of the convergent (stationary) beam technique. High order reflections can be observed out to the available limit of $2\theta$. The strong 110 and 200 polyethylene reflections are superimposed on an amorphous halo which grows as the crystal becomes damaged during the diffraction pattern exposure. Since the selected scan area can be electronically adjusted (with the beam off) to any
rectangular size and shape and as well accurately repositioned in two perpendicular directions on the sample, successive adjacent area scanning microdiffraction patterns can be obtained very routinely.

The conditions used for scanning microdiffraction are an incident beam diameter of 20 nm, incident beam current of approximately $5 \times 10^{-13}$ A, beam divergence of approximately $1 \times 10^{-3}$ rad (20 μm second condenser aperture), and the "rapid scan 2" mode which gives a beam velocity on the sample of $5 \times 10^{-3}$ cm sec$^{-1}$ horizontally and $1 \times 10^{-5}$ cm sec$^{-1}$ vertically (500 line scans/frame). The diffraction pattern fades in approximately 4 sec for these conditions. Assuming that the average current density can be approximated by the beam current divided by the area scanned, the total dose/cm$^2$ is $2 \times 10^{-2}$ coulomb cm$^{-2}$, which is in reasonable agreement with published values of the crystal lifetime dose for polyethylene at 100 keV at room temperature [71,99]. Calculations also show that for the beam current density employed ($\approx 0.16$ A cm$^{-2}$), sample temperature rise due to electron-beam heating should be negligible [100]. The only limitations of scanning microdiffraction are the maximum $2\theta$ allowed by the inner bore of the microscope column (for the JEOL 100CX, $2\theta_{\text{max}} = 3 \times 10^{-2}$ rad, i.e. reflections out to about 0.12 nm are obtainable), line broadening due to somewhat larger beam divergence than for MBD and the maximum scan distance along the sample due to inclination of the incident beam to the specimen surface as the beam scans across the sample.

The minimum sample volume for diffraction from a polyethylene single crystal at 100 keV and room temperature is, therefore,
approximately $10^5$ nm$^3$ (e.g. 100 nm x 100 nm x 12 nm). This is diffraction from about 4 million carbon atoms. The ultimate spatial resolution would be obtained by using a single crystal sample of maximum thickness. For polyethylene at 100 keV this single scattering thickness is on the order of 100 nm. Thus the minimum area for a useful microdiffraction pattern from a 100 nm thick polyethylene crystal is $10^3$ nm$^2$. For a polycrystalline (lamellar) film, the minimum area would be larger since the crystallinity is less than 100% and the orientation distribution of the crystallites places fewer at the Bragg condition.

2.5 STEM Dark Field of CrystallinePolymers

Inherent to all DF imaging is proper selection of the portion of the diffraction pattern which will be used to form the DF image. Such selection is possible by employing relatively low incident beam divergence so that discrete diffraction spots can be resolved in the diffraction pattern [101] (Figure 2.6), as discussed in the previous section.

There are several methods of obtaining STEM DF images. If all but one of the reflections are restricted (by the SAD aperture) from reaching the PMT detector, the conventional single beam DF image is obtained. Various types of multiple beam DF images are possible with STEM. In principle, such images could be obtained in CTEM, i.e. using the strioscopy technique where the main beam is blocked by a fine wire placed across the objective aperture, or by using hollow cone
Figure 2.6  STEM microarea diffraction pattern from a polyethylene single crystal with beam stop tip for annular DF in position. The reflections are broad due to the large divergence of the incident beam.
illumination. Besides being a very exacting technique, multiple beam CTEM DF imaging is resolution limited by spherical aberration and objective lens defocus image displacements [102]. Because STEM imaging is not so affected, the annular DF detector may be usefully employed to increase the utilization efficiency of the scattered signal. Although beam divergence is not normally important for CTEM DF imaging the rather large beam divergences encountered in STEM imaging must be considered.

As introduced in the previous section, beam divergence and beam diameter are inversely related. The beam divergence $\beta$ (defined as half the total angular width of the incident beam, see Figure 2.3) can typically vary from about $1 \times 10^{-3}$ radians for a 20 nm diameter beam (microdiffraction mode) to about $5 \times 10^{-2}$ radians for a 1 nm beam (high resolution imaging mode). The effect of increased beam divergence will be to decrease the diffracted intensity and to broaden the reflections. The DF image efficiency will of course depend on the diffracted intensity.

The diffraction or Bragg condition can be expressed as a vector equation:

$$\vec{K} - \vec{K}_0 = \vec{g}$$ (2.4)

where $\vec{K}_0$ and $\vec{K}$ are unit vectors of the incident and scattered beams and $\vec{g}$ is the reciprocal lattice vector of the operating reflection. Contrast arises from the local deviations of the lattice planes from the Bragg angle (see Figure 2.7a).
Figure 2.7  (a) Schematic drawing of a uniformly bent crystal showing planes oriented properly for diffraction (s=0) and for non-diffraction (s<0, s>0).  
(b) Schematic of the diffraction condition: \( K_0 \) is the incident beam vector, \( K \) the diffracted beam vector, \( g \) is the reciprocal lattice vector for a particular reflection, and \( s \) is the deviation parameter.
Figure 2.7 (c) Rocking curve (110) for a 300 Å thick polyethylene single crystal.
The relationship of \( s \) and the diffraction vector, \( q \) and the Ewald sphere can be seen in Figure 2.7b. The variation of diffracted intensity with misorientation from the Bragg condition, the so-called "rocking curve" given by equation (2.2), is illustrated in Figure 2.7c for the (110) reflection of a 300 A thick polyethylene crystal. The diffracted intensity falls to zero for less than one degree of misorientation. Strain fields cause displacements of the lattice planes and affect the local diffracted intensity accordingly. Specimen texture will cause overall displacements of arrays of crystals from the Bragg condition. By using different sets of diffracting planes (different \( g \) vectors) to form DF images of the same region, it is possible to map out the strength and symmetry of the displacement field and understand details of the defects or textures present.

The magnitude of \( s \) depends on the magnitude of the diffraction vector of the reflection used, \( q \), and the amount of divergence of the beam \( (s = q\beta) \). Since the STEM illumination is conical, there is a distribution of \( s \). If, as is usual, the second condenser aperture is evenly illuminated, this incident intensity distribution \( \rho(\beta) \) will be

\[
\rho(\beta) = \begin{cases} 
1 & \text{if } |\beta| < \beta^* \\
0 & \text{if } |\beta| \geq \beta^*. 
\end{cases}
\]

(2.5)

The scattered intensity of a reflection \( q \) with an incident beam divergence of \( \beta^* \) will be given by

\[
I_g(s^*) = \left| F_g \right|^2 \int_{-q\beta^*}^{q\beta^*} \rho(s) \frac{\sin^2 \pi st}{\sin^2 \pi s} ds.
\]

(2.6)
For a perfectly parallel incident beam ($\beta^* = 0$), the scattered intensity will be proportional to $t^2$. Figure 2.8 shows calculated curves of the scattering efficiency (defined as $I(s^*)/t^2$) as a function of the maximum deviation parameter $s^*$ for different crystal thicknesses. For the typical beam divergence range ($1 \times 10^{-3} < \beta < 5 \times 10^{-2}$ radians) the maximum deviation parameter varies from approximately $0.2$ to $1.0 \times 10^{-3}$ Å⁻¹. It is apparent that for thick crystals a significant portion of the possible Bragg scattered intensity could be lost. The beam divergence thus should be kept below about $5 \times 10^{-3}$ radians. This requires about a 20 μm diameter second condenser aperture (instead of the normal 100 μm) to yield a low divergence small diameter beam (although now of relatively low brightness - requiring increased gun brightness and decreased beam scan rates).

A large divergence can also be useful. For a very parallel illuminating beam, as in CTEM, Bragg diffraction is strong for only a limited tilt range of the crystal. STEM will image crystals in DF over a greater tilt range than CTEM, however, the images of the crystals will be somewhat less intense because of the larger beam divergence. On average more crystals will be imaged per unit area and the image will be less sensitive to tilt of the crystallites. It should be mentioned that when several diffracted beams contribute to the image, diffraction contrast image interpretation is rather complicated. The least efficient, tilted CTEM single beam dark field mode provides the easiest interpretation since both the diffraction vector $g$ and the deviation parameter $s$ are unique. The chief
Figure 2.8  Dark field efficiency for various crystal thicknesses as a function of the maximum deviation parameter.
advantages of DF are the high image contrast and the direct interpretation afforded diffraction contrast features in the image. The disadvantage (particularly for single beam DF) is the much lower diffracted intensity compared to the transmitted beam intensity.

For the BF image, the (kinematic) intensity can be expressed as

\[ I = I_0 - \sum Ig \]  

(2.7)

where \( I_0 \) is the incident intensity and the summation is over all the Bragg reflections active for the particular crystal orientation.

Table 2.1 presents calculated structure factors for the prominent PE reflections for 100 KeV electrons. The two strongest reflections are from the (110) and (200) planes. Therefore, regions of crystal with (00\( \ell \)) orientation, i.e. with the chain direction parallel to the beam, will generally appear darker in bright field than regions in any other orientation (assuming for comparison, equal film thickness of each region and all \( s_g = 0 \) for a particular crystal orientation).

2.6 Experimental Techniques

Thin spherulitic films of Marlex® 6003 (Mw = 200,000, MWD = 7-13) and Hifax® 1900, an ultra high molecular weight linear polyethylene (Mw = 2.0 \times 10^6, MWD = 4.6) were prepared for microscopy by the following method: a dilute solution of the polyethylene (0.2%) was prepared in previously filtered, dried xylene and drops of the hot solution were placed onto the surface of glycerol kept at 140°C.
<table>
<thead>
<tr>
<th>hkl</th>
<th>$2\theta$ mrad</th>
<th>$d_{hkl}$ (Å)</th>
<th>$F^2(A)^2$</th>
<th>$F^2/F^2_{110}$</th>
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</thead>
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<tr>
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<td>9</td>
<td>4.10</td>
<td>92.0</td>
<td>1.00</td>
</tr>
<tr>
<td>200</td>
<td>10</td>
<td>3.69</td>
<td>68.5</td>
<td>0.74</td>
</tr>
<tr>
<td>020</td>
<td>15</td>
<td>2.46</td>
<td>27.9</td>
<td>0.30</td>
</tr>
<tr>
<td>002</td>
<td>29</td>
<td>1.27</td>
<td>18.0</td>
<td>0.19</td>
</tr>
<tr>
<td>201</td>
<td>18</td>
<td>2.09</td>
<td>15.7</td>
<td>0.17</td>
</tr>
<tr>
<td>011</td>
<td>16</td>
<td>2.25</td>
<td>15.0</td>
<td>0.16</td>
</tr>
<tr>
<td>121</td>
<td>22</td>
<td>1.72</td>
<td>13.1</td>
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<tr>
<td>400</td>
<td>20</td>
<td>1.85</td>
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<td>0.14</td>
</tr>
<tr>
<td>031</td>
<td>27</td>
<td>1.38</td>
<td>11.0</td>
<td>0.12</td>
</tr>
<tr>
<td>310</td>
<td>17</td>
<td>2.20</td>
<td>10.1</td>
<td>0.11</td>
</tr>
</tbody>
</table>

*100 KeV electrons assuming scattering from 4 carbon and 8 hydrogen atoms per unit cell (see Appendix A for computer program).
After all the xylene had evaporated, the glycerol and polyethylene film were transferred to a Mettler FP-2 hot stage. The film was heated to 160°C for fifteen minutes and then rapidly (1°C/sec) cooled to 120°C. The crystallized thin films were then transferred onto distilled water, washed and then picked up on grids. At all stages of preparation, care was taken to avoid oxidation by using a nitrogen blanket.

Thin oriented films of the Marlex® and Hifax® polyethylenes were prepared by drawing from a thin molten layer of polymer on a glass surface maintained at 120°C following the method of Petermann [103]. When the film is drawn off the heated surface it simultaneously undergoes high deformation and rapid cooling, resulting in high orientation. Samples were subsequently annealed at 128°C for two hours and then lightly coated with evaporated carbon before examination.

CTEM and STEM of the thin polyethylene films were performed using a JEOL 100CX 'TEMSCAN'. For CTEM, micrographs of specimen areas with minimum electron damage were obtained by focusing on an area, translating to an adjacent area and recording the image on Kodak SO163 plates using approximately 60% of the crystal lifetime dose. DF imaging was obtained by tilting the incident beam so that the objective aperture selected the reflection of choice.

For STEM BF and DF imaging a 20 μm diameter second condenser aperture was used to limit incident beam divergence. Details of the STEM optics are given in section 2.9. Polaroid type 55 P/N film was
employed for recording.

2.7 Applications of CTEM Imaging

Figure 2.9a is a CTEM BF image showing diffraction contrast banding of polyethylene spherulites grown from the Marlex® polymer. Contrast arises from the alternating orientation of the lamellae with respect to the incident electron beam along the radial directions. Figure 2.9b shows similar diffraction contrast banding in a Hifax® thin film. In Figure 2.9c, also of the Hifax® polymer, the lamellae are particularly well defined whenever the crystal orientation is near (h00), i.e. the b and c axes lie in the plane of the film, normal to the electron beam direction. Such clear distinction of the lamellae in unstained, spherulitic films has not been noted in the literature. The good definition achieved in Hifax® is due to the relatively high amorphous content (~ 40% by DSC measurement) which lies predominantly between lamellae.

2.8 Ghost Images

A somewhat more novel CTEM diffraction contrast feature is that of bright field "ghost" images. Keller et al. [104] in an early study of polyethylene single crystals showed that such white diffraction images are seen whenever the objective lens is defocussed and no (or a large) limiting objective aperture is used. In a focussed BF image, spherical aberration causes the diffracted beam (dark field) images from a crystal to rejoin the unscattered beam (bright field) image with a
Figure 2.9  (a) CTEM BF micrograph of a Marlex® thin film spherulite showing diffraction contrast banding. Light regions are spherulite boundaries.
Figure 2.9  (b) CTEM BF micrograph of less organized banding (arrowed) in a Hifax® film.  
(c) CTEM BF micrograph at higher magnification of the Hifax® film.  Arrows point to several cross bend contours.
slight lateral shift given by \( \Delta x = C_s(2\theta)^3 \) (e.g. \( C_s = 6 \text{ mm}, \Delta x = 50 \text{ A} \) for a 110 PE reflection at 100 KV). This image defect in CTEM is of no consequence when a limiting objective aperture is employed, but it can be used to determine the \( C_s \) for a particular objective lens pole piece \[105\]. When a defocus \( \Delta f \) (in the object plane) is introduced, the various diffraction images shift by an additional amount given by \( \Delta f \cdot 2\theta \), in the direction of the respective operating \( g \) vectors. Note that further variation in \( \Delta x \) will occur in a field of view if the sample is tilted with respect to plane of focus. Thus, the total image shift for a dark field ghost image is given by

\[
\Delta x(r) = C_s(2\theta)^3 + \Delta f(r)2\theta
\]

(2.8)

where \( \Delta f(r) \) is the positional dependent defocus. In bright field ghost imaging, the simultaneous presence of bright and dark field images provides a real space method to determine the orientation of particular diffracting crystallites.

Care must be taken to correct objective lens astigmatism, since this will result in variable shift lengths of the diffraction images for different crystal orientation. In addition, if an objective aperture is used, it must be carefully centered, since one reflection of a Friedel pair may be blocked while the other forms a single diffraction image.

For example, consider a polyethylene lamella oriented such that the electron beam is normal to the \( b \) and \( c \) axes ((h00) orientation).
The diffraction pattern for such a crystal will be the \((0k\ell)\) reciprocal lattice. The three most prominent reflections in this section of reciprocal space are the \((020)\), \((011)\) and \((002)\). Each set of planes diffracting in the crystal will give rise to two ghost images (one each for \(\pm \) \(g\)) displaced exactly the same distance from the bright field image but in opposite directions. If the crystal is oriented such that the deviation parameter \(s_g\) is nearly zero for all three reflections, six ghost images will be produced. For a given \(\Delta f\), the image shifts will be in the approximate ratio of \(1 : 1.1 : 2\) (see Figure 2.10b). Since normally only a few crystals in a given field are diffracting simultaneously, ghost images provide a means to obtain selective local crystal orientation without the need for successive microarea electron diffraction patterns or sequential single beam DF images which are difficult to obtain for radiation sensitive crystals approaching the size of typical polymer lamellae. Since this real space crystallography method identifies the particular region of the crystal oriented for diffraction from a particular set of planes, crystal bending may be mapped by monitoring the positional variation in the diffracted intensity for the various ghost images.

It should be noted that the ghost image technique is essentially the same approach as the defocus multiple dark field image technique recently applied to polymers by Lovinger and Keith [106]. In this technique, the selected area diffraction pattern is spread into discs by defocussing of the intermediate lens. Each of the noncentral discs is a dark field image which corresponds to the particular Bragg
Figure 2.10  (a) CTEM BF ghost image of oriented polyethylene film (underfocused). Circled regions are crystals oriented for other than (110)/(200) diffraction. (c) CTEM BF ghost image of oriented polyethylene film (overfocused). Circled regions show variation of image shift of (110)/(200) diffracting regions indicating variation of chain tilt angle.
Figure 2.10  (b) Schematic of ghost image pattern expected for a single lamella oriented (h00).
reflection while the central disc is the bright field image. As is the case for ghost images, the image array provides simultaneous information rather than sequential which is beneficial for radiation sensitive polymers. Unfortunately, the multiple dark field images are also aberrated by the defocus employed. Ignoring radiation damage effects, the image resolution in both the ghost and multiple dark field image techniques is determined by the incident beam divergence combined with objective lens spherical aberration and more importantly image defocus. In order to sufficiently displace the various dark field images from the bright field images, a defocus equal to \( p/2\alpha \) is required where \( p \) is the center-to-center spacing of the image discs in the multiple dark field technique or the center-to-center image shift in the ghost image technique. The defocus limited resolution is given by \( \Delta f \Delta \alpha \), where \( \Delta \alpha \) is the incident beam divergence in radians. In the multiple DF technique, for 1 \( \mu \)m area discs (corresponding to the smallest practical SAD aperture) separated to just-touching, the required \( \Delta f \) is about \( 10^6 \) \AA. For a typical beam divergence of \( 10^{-4} \) radians, the divergence smearing resolution limit is about 100 \AA. For ghost images of lamellae, the necessary defocus can be much less since now only the individual object images need to be separated to just-touching. For 1000 \AA long lamellae, this would necessitate a defocus of about \( 10^5 \) \AA, improving the divergence limited resolution to about 10 \AA.

Figures 2.10a and 2.10c are BF CTEM ghost images of an oriented Marlex® film prepared following the method of Petermann [103].
Examination of the direction and magnitude of the image shift and the image intensity indicates only the (110) and (200) reflections produce readily visible ghost images. Distinction between these two reflections is difficult at the resolutions obtainable since their respective shift direction and magnitude and image intensity are very similar. Regions displaying symmetrical ghosts are oriented precisely symmetrically about the Bragg condition for \( \pm g_{hk\ell} \). Note that the width of the diffracting regions varies from 100 - 800 Å. While other planes do diffract (see circled regions), their ghost images are unfortunately imperceptible against the phase contrast background of alternating amorphous and crystalline lamellar regions. Occasionally the (110) and (200) ghost images are observed to shift at an angle to the BF image of the lamella (see circled regions in Figure 2.10c). Such nonparallel shifts indicate that the diffracting planes are inclined to the lamellar surface normal. Since the chain axis in PE is parallel to the (110) and (200) planes, the chains are therefore oblique to the lamellar surface normal. Chain obliquity is a common feature in polyethylene and has been measured in individual single crystals by DF CTEM tilt experiments [107] and an average value for the bulk can be deduced from x-ray diffraction methods and low frequency Raman spectroscopy [108].

Inspection of (110)/(200) ghost image shifts shows a variation in angle from 0° up to about 22°. This is direct evidence of the occurrence of variable chain inclination in a given oriented lamellar preparation. Voigt-Martín et al. [109] have also recently identified
the occurrence of different surface planes even within single lamella employing CTEM BF imaging of stained PE films. Such variation of chain tilt has important implications for the correct determination of the crystal core thickness, crystalline stem length and long period distributions obtained from models assuming constant chain obliquity for all lamellae.

It is also interesting to note the reversal of the phase contrast of the amorphous and crystalline regions in the overfocused image (Figure 2.10c) compared to the underfocused image (Figure 2.10a). Ongoing studies of phase contrast imaging employ the magnitude of the ghost image shifts to determine local values of specimen defocus [110].

2.9 Applications: STEM Imaging of Polyethylene

Imaging of radiation sensitive polymers is much easier with STEM primarily because of image intensification and higher collection efficiency of scattered electrons. Another advantageous feature that we demonstrate here is the flexibility of imaging. It is possible to vary the optical parameters of the STEM to permit novel DF imaging modes. Use of the sample z-axis lift and intermediate lens current control permits variation of the camera constant. In addition, the use of a modified beam stop tip and various SAD apertures effectively converts the photomultiplier tube detector into a number of detectors with differing geometry and size.

Figure 2.11a-f shows schematics of the optics and the resultant microdiffraction pattern intensity distribution at the detector
Figure 2.11 Schematics of various STEM detector geometries and microdiffraction patterns.  
(a) STEM BF  (c) STEM n beam annular DF  (e) STEM 002 annular DF
Figure 2.11  Schematics of various STEM detector geometries and microdiffraction patterns.  
(b) Micro-micro diffraction pattern of oriented Marlex® PE film  (d) Micro-micro diffraction pattern for θ beam annular DF  (f) Micro-micro diffraction pattern for 002 annular DF
(utilizing an oriented PE film) for some optical arrangements which can be utilized for BF and DF STEM. For BF, diffraction contrast is provided by blocking almost all the scattered electrons with an SAD aperture (see Figure 2.11a). For n-beam annular DF, the main beam is blocked by a modified beam stop and all other reflections out to some cutoff angle (determined by the SAD or column apertures) are collected (see Figures 2.11c and 2.11d). For example, in (110)/(200) annular DF, the main beam as well as all other reflections are blocked using the beam stop and a larger diameter SAD aperture. For (002) annular DF, the intermediate lens current is adjusted using the intermediate lens free lens control to decrease the camera constant so as to collapse all the inner reflections into the beam stop, effectively allowing only the (002) reflection and other higher angle, weaker reflections to form the image (see Figures 2.11e and 2.11f).

We have employed STEM DF technique in several ways. By simply blocking the main beam with the diffraction beam stop tip a DF image employing all excited reflections is produced (n-beam annular DF). This type of DF image is essentially the complement of the BF image. Depending on the orientation, it is possible for several reflections from the same crystal to contribute to that crystal's image, resulting in a higher SNR than for a single beam DF. The image intensity of a crystal will be proportional to the crystal thickness along the optic axis, the number of reflections contributing and their respective structure factors. The resolution improvement attainable depends on the square root of the intensity enhancement. For a polyethylene
crystal with the (hk0) reciprocal lattice orientation (a rather favorable situation for n beam imaging) the n beam image (n is about 20 beams) by structure factor calculation (room temperature, 100 kV) should be approximately 9 x more intense [111]. This would result in a 3 x improvement in resolution. Since single beam g_{110} DF resolution is estimated at about 40 Å for a 120 Å thick lamella [71,81], STEM annular n beam DF for this crystal orientation should yield a resolution of perhaps 15 Å - the same as the practical beam size limited resolution of a tungsten hairpin filament STEM.

An example of the intensity enhancement of an n beam annular DF image compared with a single beam DF image for a polyethylene single crystal is shown in Figure 2.12. By using the selected area mode the optics were adjusted so that the left half of the crystal was imaged by the annular DF mode and the right half was imaged using single beam g_{110} DF. Images of both halves were recorded under identical illumination conditions.

In order to demonstrate improved image resolution by STEM DF, some reliably known convenient scale (15 to 100 Å) high diffraction contrast objects must be present. The crystallite blocks in microfibrils represent such objects. Figure 2.13a is a STEM annular DF image of microfibrils within a microneck zone of a deformed spherulitic polyethylene film. The relatively undeformed regions on either side of the transformation zone are overexposed in this micrograph because of the greater sample thickness. Small 50 to 200 Å diameter crystallites alternate along the fibril axis with thin nondiffracting
Figure 2.12  STEM n beam annular versus single beam dark field for two halves of the same single crystal. Spot size approximately 60 A, beam divergence $3.7 \times 10^{-3}$ radians.
Figure 2.13  (a) STEM n beam annular DF image showing 50 to 200 A diameter diffracting microfibril crystallites within the microneck zone of a deformed spherulitic polyethylene film.  
(b) Enlargement of area in box in (a), showing 25 A resolution from separation of microcrystallites.
regions. In the enlargement (Figure 2.13b) the crystallites appear with rounded corners because of the approximately 15 Å incident beam diameter. Arrows point to adjacent diffracting crystallites separated by 25 Å.

A systematic STEM DF study of an oriented polyethylene (Marlex) film is shown in Figure 2.14a-c. These micrographs were taken at 10,000 x magnification and are part of a tilt series which includes 6 STEM DF images and 2 CTEM BF images. The 4 circular nondiffracting areas are from the regions used to obtain spot mode microdiffraction patterns. The tilt axis is shown in Figure 2.14a. Arrows point to selected lamellae which change their image intensity with angle of tilt.

Three consecutive STEM images from the same area of a Marlex spherulitic film utilizing the various optical modes are shown in Figure 2.15a-c. The BF and n-beam annular DF images are, as expected, complementary - the dark diffracting regions in the BF image (Figure 2.15a) corresponding to the bright diffracting regions in the DF image (Figure 2.15b). Dark regions in the DF image occur because such regions are either not at the Bragg condition for the reflection(s) employed or they are noncrystalline. Since in STEM annular DF, the entire azimuthal distribution of diffracted intensity of a reflection is employed, all azimuthal orientations of the lamellae at the Bragg angle will be imaged.

The single powder reflection annular DF image (Figure 2.15c) is much simpler in appearance, making for more straightforward image
Figure 2.14 STEM n beam annular DF tilt series of oriented polyethylene lamellar film. TA indicates the tilt axis. (a) +1° tilt (b) 0° tilt and (c) -2° tilt.
Figure 2.15
(a) STEM BF image of spherulitic polyethylene films (b) STEM n beam annular DF image of same region as (a); (c) STEM 002 annular DF image of same region as (a).
interpretation as compared to the n beam image since the chain axis reflection image shows only the thin lamellar crystals oriented with their chain axis in the plane of the specimen film. This technique is thus very suitable for studying the rotation and orientation of lamellae during deformation. Furthermore, one obtains a direct measure of the crystal thickness along the chain direction, which is useful to compare with that determined by small angle x-ray and laser Raman methods.

Figure 2.16a is an n-beam STEM annular DF micrograph of a region of a spherulitic Hifax® film containing stacks of long thin lamellae. The bright regions are due to diffraction from the (110) and (200) planes. In addition to the bright diffracting regions, there are long continuous dark regions parallel to and alternating with somewhat thinner regions of intermediate intensity (labeled A). Since the dark regions are locally co-linear with the bright diffracting regions, and become bright with appropriate specimen tilt, the dark regions represent crystalline lamellae not properly oriented to scatter into the region of reciprocal space selected by the annular detector (~ 0.2 Å⁻¹ to 0.3 Å⁻¹). The long, thin grey regions are proposed to be amorphous interlamellar zones, made visible from other nondiffracting crystalline regions by the high collection efficiency of the STEM annular detector for the amorphous halo (centered at .22 Å⁻¹).

It is interesting that most of the widths of the diffracting lamellae are greater than the widths of the dark nondiffracting lamellar regions. A possible explanation of this effect is shown
Figure 2.16 (a) STEM n beam annular DF of a spherulitic Hifax® film. Amorphous regions are imaged grey by mass thickness contrast; (c) CTEM BF ghost image of spherulitic Hifax® film (overfocused). Amorphous regions are imaged dark by phase contrast.
Figure 2.16 (b) Schematic of tilted lamellae and amorphous regions in thin film.
schematically in Figure 2.16b. The lamellae are depicted with a slight tilt with respect to the film plane such that the projected diffracting crystalline images are wider than the projected non-diffracting regions due to the intensity contribution of the intervening amorphous regions. Variation of lamellar width and tilt angle can account for side-by-side images of crystalline regions with no apparent interlamellar amorphous zone (see arrowed regions in Figure 2.16a).

Ghost image shifts from CTEM BF images (see Figure 2.16c) confirm the prominent diffracting regions as from the (110) and (200) planes. Furthermore, the phase contrast image nicely delineates the intervening amorphous regions (dark regions in this overfocused image) in those portions of the film having lamellar arrangements as in Figure 2.16c.

Figure 2.17 is a (110)/(200)/(020) annular DF micrograph illustrating cross or star bend contours. The origin of these contrast features can be understood assuming that the diffracting lamella is oriented exactly (00\%) at the position where the contours intersect and is approximately uniformly curved about this position (i.e. sections through the lamella appear as Figure 2.7a). Since a misorientation of greater than about 1° places the crystal out of the diffraction condition, uniform bending results in \( s = 0 \) conditions along radial sectors for the various \((hk\ell)\) reflections. The three strong ((110), (200) and (020)) reflections thus give rise to the multiple symmetric bend contours. Asymmetric bending of the lamella
Figure 2.17  STEM n-beam annular DF micrograph of spherulitic Hifax® film containing symmetrically bent lamellae.
results in distortion of the contours. The bright contours in Figure 2.17 have been labeled assuming the b axis is the growth direction (long dimension of lamellae). The measured angle between the assumed (110) and (200) contours of 60° compares favorably with the calculated value for symmetric bending of 56°, and the angle between the (200) and (020) contours is 95°, nearly the expected value of 90°. J.F. Revol et al. [112] have also noted the presence of "long curved streamers... frequently cross(ing) at a commonpoint" in BF CTEM images of annealed nascent polyethylene films. Examination of their Figure 7 in view of the present results indicates the "streamers" are (hk0) bend contours. One may estimate the curvature of the (002) oriented lamellae from the lateral extent of the bend contours and the angular width of the rocking curve assuming uniform bending. The approximate value is 0.01°/Å. This is of the same order of magnitude of curvature of the S-shaped polyethylene lamellae studied by Voigt-Martin et al. [74] and Bassett and Hodge [73].

These rather well defined CTEM and STEM diffraction contrast BF and DF images can also be examined to assess the size of any lamellar mosaic block substructure that may be present in these melt crystallized thin films. The mosaic block model of polymer lamellar crystals depicts a substructure on the order of 300 Å lateral extent with tilts between neighboring blocks of 0.6° to 11° to account for the observed x-ray diffraction line broadening [15]. The rocking curve of Figure 2.7c shows the expected variation of diffracted intensity as a function of tilt away from the Bragg condition. Considering
the size of the mosaic blocks and the large tilts associated with them, diffraction contrast microscopy should reveal their presence.

In BF, the diffracting blocks would appear as dark regions within the lamellae and in DF one would expect both black (nondiffracting) and white (diffracting) regions. From the present results it is evident that the lamellae in the spherulitic films are quite different from those in the oriented films in terms of a mosaic block substructure. In the spherulitic films, continuous (hk0) bend contour lengths range up to 4,000 Å, indicating long range perfection of the crystal lattice. However, in the oriented films one does observe the several micron long continuous lamellae to consist of much shorter (hk0) diffracting regions, ranging from 100 Å up to 1000 Å in length. Current line broadening measurements on stacks of the oriented films yields for example, an average crystallite size from the 110 peak of about 350 Å [113]. Direct visualization of the individual diffracting units by electron microscopy reveals the extremely wide distribution of crystallite sizes present.

2.10 Conclusions

Electron microscopy of radiation sensitive semicrystalline polymers presents a challenge which can be answered by careful conventional technique, by new applications of old techniques, and by application of new methods, both for CTEM and for STEM. This chapter has explored CTEM and STEM methods for crystalline diffraction contrast imaging of polyethylene.
CTEM bright field "ghost imaging" permits real space crystallography of the specimen and reveals the occurrence of variable chain inclination in oriented lamellar thin films. The added contrast due to defocus phase contrast also permits examination of the intercrystalline regions between crystalline lamellae.

The typical approach to CTEM DF imaging of radiation sensitive polymers is to focus in bright field, insert the objective aperture in the diffraction pattern, translate to an adjacent undamaged area and record the (single beam) DF image. The disadvantage of this approach is a low yield of useful micrographs due to focusing errors and blind selection of diffraction optics and specimen areas. This method is clearly difficult for performing systematic studies. Because of image intensification, control of illumination location and magnification independent focus, STEM operation for focusing, area selection and optics set up permits a high yield of systematic data.

STEM scanning microdiffraction allows useful diffraction patterns to be recorded from much smaller areas than for CTEM selected area diffraction, provided the incident beam divergence is limited by use of a small second condenser aperture. In addition, the use of the reduced raster scan mode permits mapping the specimen crystallography in the region of interest by adjusting the size and shape of the area scanned with the incident beam off.

STEM DF imaging may be done with one or more reflections. For efficient DF imaging of thin crystals, a small second condenser aperture should be employed so that the beam divergence is less than
5 x 10^{-3} \text{ radians}. Use of n beam annular DF allows investigation of crystalline species present only in small volume fractions. N beam annular DF is a high contrast complement to the BF image. Use of the entire azimuthal range of a single powder pattern reflection permits examination of crystal texture - in particular, images produced by chain axis reflections show the detailed arrangements of lamellae. By using more than one reflection to image a crystal, the DF image intensity and resolution are increased. In the most favorable cases, n beam DF imaging of PE single crystals will yield at most a 3X improvement in resolution, or for a given resolution, a 9X increased number of micrographs over single beam DF. N beam annular dark field scanning transmission electron microscopy is also useful for distinguishing between curved lamellae and mosaic blocks as well as for the direct imaging of the amorphous regions between lamellae.
CHAPTER III

DEFORMATION MORPHOLOGY OF MELT-DRAWN ORIENTED THIN POLYETHYLENE FILMS

3.1 Introduction

Most commercial polymeric products are oriented to some extent. The orientation is either desired (and necessary) as in high strength or high modulus fibers, or is unavoidable, as in injection-molded parts, where the flow of the polymer results in residual orientation even when an isotropic material is desired. The manner in which an oriented polymer deforms is usually quite different from the corresponding isotropic polymer, and the morphology both reflects and controls those differences. Even for an isotropic polymer (such as spherulitic polyethylene), the morphology of the deformation process can be heterogeneous and dependent upon orientation on a small scale, as discussed in Chapter I for the different zones of a deforming spherulite. A major problem in the elucidation of the deformation morphology of a semicrystalline polymer is the complexity of the process, primarily due to the hierarchy of structures present. An approach to the determination of the important morphological processes occurring during deformation is the simplification of either the process or of the morphology, or both. The study of a model system allows the examination of specific aspects of the deformation process.
by limiting the complexity of the morphology and hence its response to a specific stress condition.

This chapter reports the results of the deformation of such a model system. The production of a near-single crystal texture thin polyethylene film was made possible by modification [113] of Petermann's method [114] for preparation of thin fiber texture film. By using a higher molecular weight polyethylene and melt-drawing from a glass slide at a lower temperature (120°C) than did Petermann, an asymmetric fiber texture resulted, which upon annealing with free ends, gave a nearly perfectly chain axis oriented and planar textured film (uniplanar axial). This single crystal texture was ideal for in situ microscopic deformation studies, which revealed a variety of ultrastructural deformation processes from the application of modern electron microscopic methods (Chapter II). These deformation results are relevant to the current microstructural understanding of lamellar deformation in different regions of a spherulite, to the morphology of commercial extruded and blown films, and to specially prepared textured polymers, such as rolled and annealed films or capillary melt flow and solidification methods which can produce texture approaching that of a single crystal. Deformation microstructure, which had only been inferred previously from x-ray or mechanical tests, or poorly visualized in stained or replicated type microscopic studies, was clearly imaged in undamaged, unsupported films.
3.2 Background

A common feature in stress-crystallized polymers is the ordered stacking of lamellar crystals perpendicular to the stress direction, with fibrillar cores oriented parallel to the stress direction. This process is given schematically in Figure 3.1 [115], where long polymer chains in (a) are stretched by external influences to an oriented state (b), where they crystallize into extended chain fibers (c). If most of the chains are extended, then a strong, high modulus fibrous material is the result, as demonstrated by Pennings [116]. More commonly, however, many unextended parts of the chains are available which use the fibers as nuclei for epitaxial crystallization (d) leading to lamellar overgrowths (e). This is the composite fiber-platelet morphology, or shish-kebabs [115].

Orientation induced polymer crystallization historically dates back to rubber network stretching, and the examination of the morphology of stress crystallized rubber has been useful in the understanding of the more modern shish-kebabs [117]. The areas of flowing solution induced chain stretching [116], deformation of gel networks [118], and melt drawing [114] have all been very active in recent years, both scientifically and industrially, since these processes present opportunities for significant advancements in mechanical properties of commonly used polymers. As Keller has pointed out [115], the deformation of crystalline polymers is also related to the subject of oriented crystallization, since crystallization or recrystallization of oriented chains is operative in the deformation
Figure 3.1  Schematic of orientation induced crystallization [115]: (a) random coils, (b) chains oriented by (horizontal) stress, (c) crystallized oriented chains, (d) remaining random coil chain segments available for epitaxial crystallization on fiber nuclei, (e) folded chain lamellar overgrowths, resulting in shish kebabs or fiber-platelet morphology.
process.

Industrially, production of oriented polymeric materials is very important, and film blowing, extrusion, injection molding and fiber spinning are probably the most important examples of processes producing large quantities of oriented polymer from the melt [119].

The morphology of the film-blowing process has received considerable attention, beginning with the study of hot-extruded low density PE films by Holmes [120] using wide angle x-ray diffraction. Their conclusions were that the a axis of the PE unit cell tended to align along the extrusion direction (MD), and the c-axis tended to align perpendicular to MD. Keller [121] proposed an alternative morphology, called row orientation, in which the b-axis is perpendicular to MD and a and c have cylindrical symmetry about b. The two possible textures could not easily be distinguished by WAXS, and further studies [122] concluded that commercial processes produced textures very much a function of the processing conditions. Lindenmeyer [123] advanced the use of pole figures in texture studies to overcome the limitations of flat film x-ray techniques, and showed that previous studies had been, in fact, inconclusive about the c-axis orientation. A number of studies have now established the variability of crystallite orientation as a function of process conditions [124-127]. Two distinct types of orientation texture have emerged (Figure 3.2), termed high and low stress to reflect their origin. At low elongation rates (low stress), the nuclei (fibrils) are sparsely arrayed, and the lamellar overgrowths can extend far enough to twist, as is also seen for bulk quiescently
Figure 3.2  Keller-Machin [128] row structure for uniaxial bulk samples (cylindrites), with ideal pole figures consistent with low and high stress cases (adapted from [119] and [129]).
crystallized PE. For high rates of elongation (high stress), however, a more dense array of nuclei is produced (fibers), and the lamellar overgrowths impinge before growing long enough to twist (Figure 3.3). If the film formation process is constrained to two dimensions, i.e. a very thin film is formed, then it is possible to form a "single crystal" texture, as has been recently demonstrated by Yang and Thomas [113] (see Figure 3.4).

While electron microscopy studies can in principle provide quite detailed microstructural information - the key to any successful investigation is sample preparation. The preparation of thin films which are both suitable for electron microscopy and relevant to understanding some of the details of the deformation processes in semicrystalline polymers is a challenge. Early workers produced thin spherulitic films by quiescent recrystallization of an initial film of polymer made thin by solvent casting [20]. Such films when mounted on normal electron microscopy grids could then be deformed by hand permitting interesting although only qualitative observation of the deformation process, which due to the complexity of the film microstructure and uncontrolled mode of deformation was rather difficult to interpret [21].

In 1973 Petermann [114] found that he could produce well oriented thin films by drawing a thin film from a molten pool of PE on o-phosphoric acid (135-200°C). The films produced consist of well oriented periodic stacks of lamellae exhibiting a fiber texture with their \(c\) axis along the draw direction. Annealing at high temperatures
Figure 3.3 Effect of strain-induced nucleation density on row structure morphology (a) low stress, sparsely arrayed fibrils with long, twisting overgrowths; (b) high stress, densely arrayed fibrils with impinged lamellae, adapted from Katti & Schultz [130].
Figure 3.4 Keller-Machin [128] row structure model for thin films, with ideal pole figures for low and high stress cases (adapted from [119] and [129]).
for long times recrystallized the films with a {110} surface texture [114]. Fiber symmetry could be restored upon cold drawing. Hot stretching on the other hand produced films with a {200} surface texture [131]. Deformation studies were conducted by Petermann's group on such melt drawn thin films of various degrees of preorientation made possible by varying the melt temperature of the PE from which the film is drawn. Uniaxial deformation at 92°C produced a fibrillar morphology consisting of needle-like, micron long crystals for both highly oriented and poorly oriented precursor films. Upon annealing at high temperature the fibrillar material generated by deforming less oriented precursor film recrystallized into a periodic crystalline/noncrystalline structure whereas the more perfect needle material obtained from the highly oriented lamellar precursor film was stable with annealing. This was explained by invoking a molecular unfolding process for the well oriented material and a lamellar shear process for the less oriented material [132,133].

In order to produce more highly oriented films, Petermann employed melt drawing from a glass surface wherein the better adhesion of the polymer to the glass caused a shorter drawing zone as compared to the phosphoric acid surface (1 µm compared to 1 cm) [103]. These films were also found to display fiber symmetry but if formed by drawing just below the melting temperature, a significant (about 1/3) fraction of the material was present in the form of needle crystals in the as drawn films. Because of these microstructure differences, Petermann's melt drawn films (glass) deform quite differently than o-phosphoric
acid prepared material [134].

3.3 Experimental Methods

Thin oriented films of high density polyethylene (Marlex 6003, \(M_w = 2 \times 10^5, M_w/M_n = 3\)) were prepared by the method of Petermann [103], using techniques reported previously [113]. Films drawn from a glass slide at 120°C were used as-drawn (AD) or were annealed on glycerol for two hours at 128°C (AN) (Figure 3.5). After washing with distilled water, the films were placed upon specially fabricated elongation grids (Figure 3.6a). The electroformed copper grids, manufactured by the Buckbee-Mears Co., St. Paul, Minnesota, were softened by vacuum annealing at 700°C for 18 hours. A layer of PE film was placed on the grid, then a region (approximately 2 x 0.5 mm) of the film along with the supporting copper wire was removed by cutting with a razor. A second layer of the film was then placed on the grid in the desired orientation for deformation, typically parallel, perpendicular, or at a 45° angle to the film chain axis direction, c. Adhesion between the layers of PE and between the PE and copper grid allowed the deformation to occur in the unsupported area of gauge length approximately 0.5 mm.

In situ deformation was performed in an elongation sample holder (model SEH, see Figure 3.6b) on a JEOL 100CX Scanning Transmission Electron Microscope, operated at 100KV. Elongations of up to 150% at room temperature were possible with this method, limited by the catastrophic failure of the unsupported thin polymer film. The
Figure 3.5 Photograph of the process of melt-drawing a thin oriented polyethylene film: (a) a bead of polymer solution (arrow) is placed on a hot glass plate, (b) after spreading the solution with a hot glass rod, the film (arrow) is drawn off the glass onto a roller.
Figure 3.6  Photographs of the in situ deformation method: (a) elongation grid showing support layer of polyethylene and copper bars cut to allow unsupported deformation of a second layer of PE in narrow region at center; (b) an elongation grid mounted in the deformation holder, 13% strain in horizontal direction.
Figure 3.6 Photographs of the in situ deformation method: (c) close up of (b), showing how notched copper side bars have broken but support bars are intact, supporting a carbon film with a PE film on top.
deformation rate was 0.05 mm/min, with an 0.5 mm gauge length, which gives an 0.1 min⁻¹ initial strain rate.

Higher deformation was possible by placing a PE film onto a film of evaporated carbon previously placed on the deformation grid in a manner similar to Gohil and Petermann [133]. Deformation of the grid then produced cracks in the carbon perpendicular to the draw direction, over which the polyethylene film was readily drawn to several hundred percent (Figure 3.6c).

For most CTEM (BF) photographs, a thin layer of carbon was evaporated onto the deformed thin film in the deformation holder in order to prevent sample motion due to radiation damage (see Figure 3.7) while for STEM examinations the carbon was unnecessary. Phase contrast BF images were obtained by defocus of the objective lens [110,135,136]. In order to minimize radiation damage in CTEM, the focusing was carried out on an area, then the sample was translated to an adjacent undamaged area and the image recorded on Kodak SO-163 film using approximately 60% of the crystal lifetime.

STEM techniques were found to be particularly useful, including scanning micro area electron diffraction [78], and STEM n-beam annular dark field (DF) [79,80]. The high collection efficiency of scattered electrons and selectability of the region imaged was advantageous in observing the deformation in situ at successive intervals of increasing strain. For STEM DF, an area of interest was located at low magnification (10,000X or less), then careful focusing and intensity and contrast adjustment was performed at 50,000X, using the
Figure 3.7 Photograph of special adapter which allows deformed film in elongation holder to be coated with carbon in vacuum evaporator.
reduced raster mode to restrict (severe) radiation damage to a small area (typically ~ (0.5 μm)²). An image was then recorded (100 seconds) on Polaroid Type 55 P/N film at 40,000 instrumental magnification. Optical transforms from CTEM BF negatives were recorded on Polaroid Type 55 film, using a Polaron optical diffraction system. Spacings due to periodicity in the image were calibrated by a standard of known spacing. Small Angle Electron Scattering (SAES) patterns were recorded using the "High Dispersion Diffraction" mode on an area selected by the smallest intermediate lens aperture. In this mode, low beam divergence is achieved by use of a small second condenser lens aperture and minimum excitation of the second condenser lens. The intermediate lens and projector lens are adjusted for magnification of the diffraction pattern. The divergence of the beam under these conditions was estimated to be 1.5 x 10⁻⁵ radians, for a maximum resolvable spacing of 2500 Å. The camera constant was calibrated by a standard of known spacing (grating replica).

3.4 Results

3.4.1 Initial Microstructure. The initial microstructure of the thin oriented films was reported by Yang and Thomas [113]. Figure 3.8a shows a CTEM BF micrograph of an as-drawn film, indicating highly oriented lamellae imaged by defocus phase contrast. The arrow indicates the melt draw direction, and the electron diffraction pattern (top left inset) demonstrates that the films consist of oriented crystallites with c parallel to the draw direction. The dark patches are
Figure 3.8  Bright field CTEM micrographs of melt-drawn oriented thin PE film: (a) as-drawn (at 120°C), drawing direction vertical (arrow), inset (top right) optical transform of negative, inset (top left) selected area electron diffraction pattern showing high orientation, c-axis vertical.
Figure 3.8 Bright field CTEM micrographs of melt-drawn oriented thin PE film: (b) annealed for two hours at 128°C, black regions are Bragg oriented diffracting lamellar crystals.
crystals that are Bragg-oriented with respect to the incident electron beam. The lamellae are somewhat "wavy" in texture, with lengths of 0.2 to 0.5 μm, and with lamellar surface normals of up to +30° to the draw direction. The lamellar thickness (along c) is approximately 300 Å and the long period is about 450 Å. The lateral crystal size measures 250 Å (by WAXS and TEM DF). The film has uniplanar texture, with a preferentially perpendicular to the film surface, and b in the film plane and normal to the draw direction c (see Figure 3.9).

Upon unconstrained annealing (on the surface of glycerol) at 128°C for 2 hours, the film texture does not change, but the c-axis orientation improves, the long period increases slightly to 480 Å, and the crystal thickness (along c) increases significantly to about 370 Å. The lateral crystal size also greatly increases (to nearly 400 Å), and the degree of crystallinity (from DSC) increases from 0.67 to 0.82. After annealing, the lamellae are much straighter and longer, up to 10 μm (see Figure 3.8b). The average thickness of the intercrystalline region between adjacent lamellae decreases considerably (from 150 Å to 110 Å). No extended chain or needle crystals parallel to c were observed by electron microscopy or were evidenced by DSC for either AD or AN films.

3.4.2 Deformation Parallel to c. Figure 3.10 is a CTEM bright field micrograph of an annealed film deformed over a crack in carbon film, deformation direction given by the arrow. The lighter region in the center is unsupported and has been deformed to approximately 250% as calculated by measuring the average lamellar spacing and confirmed by
MD - MELT DRAWING DIRECTION (Machine Direction)
ND - NORMAL TO PLANE OF FILM DIRECTION
TD - TRANSVERSE DIRECTION

Figure 3.9 Schematic of oriented lamellar films with coordinate systems indicated for crystal axes and for film directions.
Figure 3.10 CTEM bright field micrograph of annealed film deformed over a crack in supporting carbon film, deformation direction vertical (arrow). Top right is small angle electron diffraction pattern from this area, schematic of pattern lower right. Letters are explained in the text.
optical transforms of the negative. The deformation zone extends into the area supported by the carbon film, and the deformation gradually decreases until, approximately 0.5 µm from the edge of the break, no deformation is observed. The PE has apparently been pulled away from its close contact with the carbon film. This region of uniformly changing deformation gives rise to a broad maximum along the draw direction (L') in the small angle electron scattering (SAES) pattern shown as the right top inset in Figure 3.10. The long period of the undeformed lamellar structure results in the sharp maximum marked L in the schematic (bottom right inset). The measured SAES long period of 461 Å agrees well with that measured by optical transform (499 Å) and by CTEM BF (480 Å). The lateral breadth of the long period spot is very narrow, indicating very wide lateral structures (lamellae). The broad maximum L' due to the deformed region includes spacings from about 550 Å to 2300 Å with a maximum at 900 Å. Other features in the SAES pattern to note include the horizontal streak (V) due both to the presence of long, narrow fibers and to voids parallel to the stretch direction, and the narrow vertical streak (E) due to scattering from the carbon film edge. These effects will be explored in more detail in a future publication [137].

A similar region of this type of deformation is shown enlarged in Figure 3.11. The overall deformation mode is more apparent, and consists of separation of lamellae along c with increasing deformation. The deformation occurs initially entirely in the interlamellar regions, which become thinner and cavitate to form fibers separated by
Figure 3.11 Enlargement of deformed area similar to that of Figure 3.10. Carbon film (c) extends vertically to horizontal line marked by short arrow, deformation direction vertical. Right side is an enlargement of the area outlined by the box. The deformation of the film in this region increases from the bottom of the figure to the top, as one traverses the film towards the unsupported region.
voids (craze). At higher strain levels (toward the top of the images), the lamellae begin to shear and deform, and ultimately an entirely fibrous morphology would result. These films, however, always fail catastrophically before the transformation to fibers is complete, unlike the films deformed at higher temperature by Petermann [133]. The deformation process will be detailed in the following sections separately for AD and AN films, beginning with the AN films which are considerably easier to visualize.

3.4.3 AN Films. In Figure 3.12 a series of CTEM bright field micrographs show progressive stages of deformation parallel to c, using the unsupported film deformation method for the 39% deformed sample and the carbon crack method for that with 340% deformation (based on the change from the initial sample long period). The dark regions are Bragg oriented crystals, the white regions oriented parallel to c in the deformed film micrographs are voids between the darker fibers connecting the separated lamellae. A similar series is shown in Figure 3.13 imaged by STEM n-beam annular dark field, where diffracting crystals are now white and the voids are black. At small strains, the change in the sample long period is due entirely to deformation in the amorphous zones, which cavitate and fibrillate due to the lateral constraint in the system. This is shown clearly at very high deformation (Figure 3.13b) where the average long period deformation is 240%. The crystal blocks in the lamellae do not deform or thin until the strain in the amorphous region reaches about 300%, at which point the crystal blocks begin to shear apart. Since these
Figure 3.12  Series of CTEM bright field micrographs of annealed film at 0%, 39% and 340% elongation as measured by comparing the deformed long period (lamella repeat) to the initial long period.
Figure 3.13 Series of STEM n-beam annular dark field micrographs of annealed film; (a) 0%, 23%, 54%, 74% long period deformation, deformation direction vertical.
Figure 3.13 Series of STEM n-beam annular dark field micrographs of annealed film; (b) 240% long period deformation, deformation direction vertical.
films are textured with \( c \) along the draw direction and \( b \) predominantly perpendicular to \( c \) in the plane of the film, \( c \)-axis shear on a plane perpendicular to \( b \) results in either a continuous "wavy" shear deformation (labeled FS for fine shear in Figures 3.14 and 3.16) or a stair step structure in the lamellae (labeled BS\(_b\) for block shear), while shear perpendicular to \( a \) results in thinner lamellae with mass thickness contrast due to overlapped crystals (labeled BS\(_a\) for block shear, also see Figure 3.15b). The intralamellar shear is seen to occur on two different slip systems: \( \{010\}, <001> \) and \( \{100\}, <001> \).

Other features to note are: thread-like structures extending transverse to \( c \), usually seen in the deformed amorphous regions (Figure 3.14b); dark diffracting crystalline regions in the oriented amorphous regions (Figure 3.14a and b), also seen as white spots in the STEM DF images (Figure 3.16a and b); crystals at edges of lamellae in DF images (Figure 3.16b); fibers apparently extending through (or over/under lamellae in Figure 3.15c.

Selected area diffraction patterns of undeformed and deformed films show that the crystallite orientation increases with deformation, and the breadth of the equatorial reflections increases, indicating a decrease in the lateral crystal size. A very small amount of the monoclinic crystal form for PE is observed, and the 002 reflection becomes weaker. A CTEM dark field image of an annealed film deformed to 300% is shown in Figure 3.17. The large white areas are lamellar crystals, but also visible are small crystals in many of the fibrillar regions. Although some of the crystals in the fibers are long and
Figure 3.14  (a) CTEM bright field micrographs of deformed AN films. \( BS_a \) and \( BS_b \) refer to lamellae deformed by block shear, while \( FS \) indicates fine shear.
Figure 3.14  (b) CTEM bright field micrographs of deformed AN films. BS\textsubscript{a} and BS\textsubscript{b} refer to lamellae deformed by block shear, while FS indicates fine shear.
Figure 3.15 CTEM BF selected regions of deformed AN film. (a) lamella in center has sheared by combined block shear (hU0) and fine shear (0k0), (b) block shear (h00) overlapping lamellae, (c) lamellae with fibers extending through along c, (d) Fresnel fringes due to defocus at edges of lamellae and at thickness differences in sheared lamellae.
Figure 3.16 (a) STEM DF images of deformed AN films showing Fine Shear (FS), Block Shear (BS) and many crystals in fiber areas (labeled c).
Figure 3.16 (b) STEM DF images of deformed AN films showing Fine Shear (FS), Block Shear (BS) and many crystals in fiber areas (labeled c).
Figure 3.16 (c) STEM DF images of deformed AN films showing Fine Shear (FS), Block Shear (BS) and many crystals in fiber areas (labeled c).
Figure 3.16 (d) STEM DF images of deformed AN films showing Fine Shear (FS), Block Shear (BS) and many crystals in fiber areas (labeled c).
Figure 3.17 CTEM bright field micrograph (left) of unsupported annealed PE film deformed to about 300% strain. Right side is a similar area imaged by CTEM dark field using the 110, 200 reflections. Large arrow points to a lamellar crystal and the small arrows indicate small crystals in the oriented amorphous regions.
narrow, most are more nearly equiaxial approximately 60 Å in size; a few fibers show a periodic arrangement along the fibers.

3.4.4 **AD Films.** Figure 3.18 shows a series of CTEM BF micrographs for the as-drawn films at successive stages of deformation. The deformation mode is similar to the AN films, and the lamellae are pulled apart along \( c \) with increasing strain, with the formation of connecting fibrils as the intercrystalline region is stretched. There are fewer voids found in the AD case, and they are smaller. The lamellar crystals begin to break up at lower strain levels than do the AN crystals, and the texture becomes much more "wavy" as the crystals shear, mostly by (010), \(<001>\) slip. The ease of crystal shear is apparent in Figure 3.19 as the large bright crystals easily seen in the STEM DF image at 0%, nearly all disappear into the mottled background at modest (~ 50%) deformation compared to the AN films. At 90% deformation, the film appears rather homogeneous without any recognizable lamellar structure retained. The image quality is much poorer due to the smaller crystal size, poorer quality of the crystals, and more diffuse separation between crystal and amorphous regions.

3.4.5 **Deformation Perpendicular to \( c \).** By placing the thin film on the deformation grid with the melt-drawing direction transversely oriented, it is possible to observe deformation perpendicular to \( c \), i.e. parallel to \( b \). Figure 3.20 is a CTEM BF image of an AD film showing this deformation, beginning with the point where a long thin crack (craze) begins to open along the \( b \) direction (lower part of
Figure 3.18 CTEM bright field micrograph series of as-drawn film at 0%, 34% and 56% long period deformation parallel to $c$ (arrow).
Figure 3.19 STEM n-beam annular dark field image series of as-drawn film, deformation vertical, at 0%, 50% and 90% long period strain.
Figure 3.20  Deformation perpendicular to c-axis for AD film imaged by CTEM bright field. Arrows point out fibers spanning the cracks opened by crystal cleavage along b.
image). The crack is spanned by fibrils in the deformation direction, and the fibrils almost always originate in the intercrystalline region. At higher deformation, the cracks open wider and then cross fibrils are extended, normally moving laterally from their origin point. As the strain increases, whole blocks and layers of lamellae are separated and incorporated into an increasingly complex fibrillar structure, which can include crystal blocks, strings of crystal blocks, and fibril-fibril junctions of several types. For the annealed film (AN), the deformation mode is very similar to the AD, as shown by Figures 3.21 and 3.22, CTEM BF and STEM DF images, respectively. Figure 3.21a clearly reveals that the fibers originate in the amorphous regions between crystalline lamellae. Voids which are one crystal thickness wide are visible in Figure 3.22b (marked by arrows), and the voids sometimes terminate abruptly at a diffracting crystal. The very small speckle is the grain of the Polaroid Type 55 films, while the larger round spots are due to the electron probe size used (approximately 50 Å). Figure 3.22a also shows the formation of voids and fibrils in the film along a direction about 45° to the deformation direction.

3.4.6 Deformation at 45° Angle to c. Deformation at 45° to the c-axis direction is shown in Figure 3.23. The film deforms by a combination of the two orthogonal deformation modes, and the lamellae are pulled apart as some voids and fibrils form parallel to c. The complexity of this mode of deformation, beginning to be obvious in Figure 3.23d, for a simple arrangement of lamellae, results in
Figure 3.21 CTEM bright field series for AN films, deformation along TD, (a) shows fibers spanning small voids opened by crystal cleavage, (b) and (c) are at higher strains.
Figure 3.22 STEM n-beam annular DF image of AN film deformed along TD. (b) enlargement of region in box from (a), large arrows indicate (sharp) edge of cleaved crystal, small arrows point to fibers from amorphous regions bridging the void formed (black regions).
Figure 3.23 STEM n-beam annular dark field micrograph series of an annealed film deformed at a 45° angle to the c-axis direction. (a) is 0% strain, and (b), (c) and (d) are at increasing strain levels.
different types of fibers as well as different types of broken crystal blocks and recrystallized material. This is but a small indication of the even more complex situation in the intermediate zone of a spherulite.

3.5 Discussion

3.5.1 "Amorphous" Fibers. An observation upon deforming the oriented lamellar films along the MD (c-axis) is that the deformation initially occurs entirely in the intercrystalline regions. The amorphous polymer between two adjoining lamellae behaves as a compliant rubber, becoming thinner in the ND and trying to become thinner in the TD as it is lengthened along the MD. This is depicted in Figure 3.24, where the initial deformation results in a thinner "film" between lamellae (Figure 3.24b), which can be seen in the low deformation areas in Figure 3.11. With further stretch, the lateral stress on the rubber becomes large enough to cause cavitation and fibrillation, and the thin rubber film becomes a craze as the oriented amorphous material forms fibrils (Figure 3.24c). These fibers differ in lateral size, probably due to different local levels of stress and differences in film thickness. With more deformation, the fibers become thinner until a strain of about 300-350% (in the fiber) is reached. At that point, the entangled non-crystalline chains have reached their elongational limit, which for HDPE has been estimated to be 370% [44]. More elongation would require bond breakage or a higher temperature in order to give the chains enough mobility to disentangle.
Figure 3.24 Drawing showing the elongation of the rubber-like amorphous zones into fibers with increasing strain (a) 0% strain, (b) 100% amorphous strain, 20% long period strain, (c) 400% amorphous strain, 60% long period strain.
The elongated "amorphous" fibers stress crystallize; the fibrillar crystal size is small (50-150 Å) and is limited both by the lateral size of the fibers and the very high undercooling (room temperature deformation). These fibrillar crystals can best be seen as white spots in the CTEM dark field image in Figure 3.17, examples marked by the small arrows distinguish them from the large lamellar crystals (large arrow). A periodic arrangement of these crystals in the fiber direction is occasionally seen.

Many voids are formed in this process, which results in an extremely (micro) porous membrane. The appearance of the film at low deformation is superficially similar to that of the "hard elastic" fibers (see [138] for a brief review), where small voids are opened by some reversible combination of fibrillation and elastic lamellar bending. At high deformation, the voids are considerably enlarged and elongated, giving rise (along with the fibers) to the lateral streak in the small angle electron scattering patterns. The low deformation fibrillation and voiding process was observed to be qualitatively reversible upon relaxation of the applied stress, but a quantitative study remains to be performed. Petermann [139] in his early studies with these type films also noted the resemblance to the "hard elastic" materials.

3.5.2 Lamellar Deformation. The annealed films deform parallel to $c$ in a manner much like that depicted by Schultz [140]. Figure 3.25 is a modification of his version of Peterlin's model, suitably oriented for the parallel deformation mode. Figure 3.25b shows lamellar
Figure 3.25 Drawing after Schultz [140] of the ultrastructure of deformation: (a) undeformed parallel lamellae, (b) separation of lamellae along c, (c) strain in amorphous regions sufficient to induce crystallization in the fibers, (d) beginnings of c-axis slip (fine slip shown), (e) block slip resulting in breakup of lamellae into large blocks, (f) fibrillar morphology with discrete microfibers containing some lamellar block crystals and strain induced fibrillar crystals.
separation at low draw, with all the strain accommodated in the amorphous zones. As discussed in 3.5.1, at higher strain some crystallization occurs in the extended noncrystalline fibers, shown in Figure 3.25c, resulting in strain hardening such that the adjoining crystals begin to deform. They can deform in several ways. The lowest energy crystalline response to a stress along c is c-axis slip \[141\]. Figure 3.25d and e show (only in 2 dimensions) both "block" slip and fine slip on planes perpendicular to b, leading ultimately to a fiber structure somewhat like Figure 3.25f. To Schultz's summary of the deformation process we can add two new items (2a), (3a) \[140\]:

1. First stage: Lamellar ribbons slip rigidly past each other. Clearly, the ribbons lying parallel to the tensile axis cannot do so and the deformation must be anisotropic within the spherulite. At this stage the strain is accommodated almost entirely by the interlamellar amorphous layer.

2. Second stage: Here the tie chains are highly extended and deformation occurs by the slip-tilting of the crystalline lamellae.
2a. Strain induced crystallization of oriented amorphous fibers increases the strain hardening of the process.

3. Third stage: Blocks of crystal are pulled out of the ribbons. The blocks are still attached to each other by tie chains.
3a. As block shear continues, portions of lamellae which are below a critical size (for the particular T[draw]) melt and contribute to strain softening (i.e. they become unstable with respect to the applied stress and chains are readily drawn).

4. Fourth stage: Both the blocks from crystal shear and strain induced crystallization become aligned along the tensile axis.

The shear processes have been inferred mostly from x-ray and mechanical property studies, and Bowden and Young \[141\] have
summarized the processes. On a molecular level, Figure 3.26 gives the basis for distinguishing the fineness of slip. Figure 3.26a is uniform fine slip, where every two chains are displaced one lattice vector along \( \mathbf{c} \). Coarser slip (referred to here as block slip) is shown in Figure 3.26b, with blocks of chains (4 shown) slipping by 2 lattice vectors to give the same total shear deformation as Figure 3.26a.

Block slip can be further distinguished by the plane of shear as either (h00) or (0k0). This difference is modeled in Figure 3.27 where (h00), \( \mathbf{c} \)-axis slip is seen in part 2, and (0k0), \( \mathbf{c} \)-axis slip is shown in part 3. Combinations are also possible, depicted in part 4 to produce successively smaller blocks. The actual slip systems are indeed recognizable in these highly textured films, as shown in Figure 3.16. Block slip is labeled BS with a subscript for the plane on which the shear operates. Fine shear is seen many places, and is selectively labeled as FS. CTEM BF images give exceptional detail for these slip systems, and Figure 3.14 gives examples of all 3 types of slip. Figure 3.15 is a selection of regions demonstrating these features. For example, (h00), \( \mathbf{c} \)-axis shear (BS\(_a\)) is manifested by a decrease in intensity in the regions of the lamellae that are displaced and no longer overlap (Figure 3.15a). In other words, the dark band in the center of the lamellae (parallel to \( \mathbf{b} \)) is indicative of the original thickness (along \( \mathbf{a} \)) of the lamellar crystal, and the lighter grey areas are thinner sheared portions of the crystal (Figure 3.15b). Thickness differences are accentuated by Fresnel fringes in Figure 3.15d where a dark line next to a white line at the edge of a lamellae
Figure 3.26  Schematic diagrams illustrating different degrees of fineness of slip. (a) Fine slip. A displacement of one lattice vector has occurred on every other lattice plane in the crystal. The direction \( n \) is the normal to the surface of the crystal which has rotated relative to the chain axis \( c \) during deformation. (b) Coarse slip. The same total shear has been produced by a displacement of two lattice vectors on every fourth plane [141].
Figure 3.27 Schematic drawing of the block slip mechanisms, (1) undeformed lamellar block, (2) (h00), [001] slip producing long, thin sheared lamellae, (3) alternatively, (0k0), [001] slip producing stair step sheared lamellae, (4) combined shear modes leading to reduction of block crystal size.
is due to objective lens defocus, the width and contrast of which varies due to the differences in thickness at this edge.

With increasing deformation, the sheared blocks can break up further by more slip, and/or folded chains can be directly pulled out. As the process continues to the point at which the crystal block size is less than a critical nucleus size for the particular drawing temperature, the crystal "melts" contributing to strain softening, concomitantly strain hardening occurs with recrystallization of the highly drawn chains in the fiber structure. A lamellar crystal in the final stages of block shearing is well visualized by STEM DF in Figure 3.16d.

3.5.3 Fold Plane. The fold plane in these lamellar crystals appears to be (100), an interpretation consistent with the slip systems identified, the shapes of the sheared lamellae observed and the ease of lateral film deformation and crystal cleavage. The uniformity in the BF contrast in the lamellae sheared in the (100) planes (Figure 3.15) favors an interpretation of "clean" crystal cleavage parallel to the (100) planes. If extensive (110) folding were present, c-axis slip would be more likely along (110) planes, which would result in crystals with wedge shapes and varying thickness, which was not observed for these films (Figure 3.28).

For shear in the (010) planes, both stairstep and continuous shapes were seen (Figure 3.16). If substantial (110) folding and hence shear on (110) were present, the edges of the sheared crystals would display tapered contrast profiles both in BF and in DF, which
were not observed. Indeed, the edges of the stairstep (block) sheared crystals were uniform and sharp in contrast.

Deformation perpendicular to $c$, i.e. along $b$, always resulted in sharply cleaved lamellar crystals (Figures 3.21, 3.22, 3.29). The clean edges observed are consistent with (100) folding, since (110) folding would likely result in wedge shaped crystal edges and the fracture surface would have to cut across molecular folds to cleave parallel to (010). There are other reports in the literature supporting (100) folding in melt crystallized polyethylene [142,143]. PE single crystals grown at high temperatures with (100) growth faces [144], and deformation of single crystals both have been used to infer that fold planes lie parallel to growth sector edges (e.g. the $bc$ plane for (100) folding). Preferential folding along (100) in bulk is reasonable, and the molecules would lie along the growth direction in spherulites. For a stress crystallized system, after row nucleation occurs along a fibrillar core, the growth direction is radially outward, but the two dimensional form of a thin film constrains crystal growth to the lateral direction (TD). The very long coherent lamellae seen, especially after annealing [113], give further evidence for this argument. Folding along (110) planes would produce boundaries at intervals of about 300 A for 500 A thick films. Crystallographic shear deformation on a specific slip system argues against significant amounts of random switchboard folding model for these textured melt crystallized films.
Figure 3.29  Schematic drawing of deformation perpendicular to $c$, i.e. parallel to $b$, showing the opening of small voids between fractured crystals. The crack is spanned by fibers formed from the amorphous interlamellar regions.
3.6 Conclusions

The study of the morphology of the deformation process for bulk spherulitic polymers is a challenge, complicated by the hierarchical morphology. The approach used in this chapter involved the study of a model system that allowed simplification of both the morphology and the deformation process. This simplification of the problem enabled the examination and elucidation of specific ultrastructural deformation processes which had heretofore only been partially inferred by indirect measurement or poorly visualized in stained or replicated type microscopy studies.

The system studied was near-single crystal texture thin polyethylene film made by modification of Petermann's method. The film was melt-drawn from a glass slide at 120° and annealed with free ends to give a nearly perfectly chain axis oriented and planar textured film (α perpendicular to the plane of the film; β perpendicular to c and in the plane of the film, parallel to the long dimension of the well formed lamellae). The films were deformed in situ at room temperature in a scanning transmission electron microscope.

At low strain, deformation along c is accomodated entirely by the interlamellar regions, which cavitate to form fibrils due to lateral constraint. At strains of about 300% in the fibrils, strain induced crystallization occurs which contributes to strain hardening of the system. With further deformation, the lamellar crystals deform by chain slip processes. Two slip systems were clearly visualized: \{110\},<001> and \{010\},<001>. The c-axis shear process was further
resolved into fine slip, resulting in inclined lamellar normals, due to small continuous chain slip increments on (010) planes, or block slip where large blocks shear on either the (100) or (010) planes. Further deformation causes more breakup of blocks by shear, with some pullout of folded chains. When the sheared block size becomes less than some critical nucleus size, the crystal "melts", which contributes to strain softening. Thus, in these films melting is seen to be a natural result of crystal shear processes while, at the same time, recrystallization in the drawn fibrils occurs. Both the blocks from crystal shear and strain induced crystallization become aligned along the tensile axis.

For deformation perpendicular to $c$ the lamellar crystals cleave easily along the (010) plane, the fibrils are formed from the connecting amorphous zones. Chain unfolding and crystal block cleavage both occur during the transformation to the drawn (fibrillar) structure. Deformation at 45° to $c$ results in a more complex combination of the processes occurring in deformation at 0° and 90° to $c$. The deformation processes are consistent with predominantly (100) chain folding.

Although generalization is tempered by the simplicity of this model texture, these deformation results are highly relevant to the current microstructural understanding of lamellar deformation in different regions of a spherulite, to the morphology of commercial extruded and blown films, and to specially prepared textured polymers,
such as rolled and annealed films or capillary melt flow and solidification methods which can produce texture approaching that of a single crystal.
CHAPTER IV
MICROSTRUCTURE OF HIGH MODULUS SOLID STATE EXTRUDED POLYETHYLENE:
X-RAY SCATTERING STUDIES OF 12, 24 AND 36 EXTRUSION DRAW RATIO

4.1 Introduction

The application of the solid state extrusion (SSE) (Figure 4.1) method to various thermoplastics has produced high modulus ultradrawn fibers and films with remarkable properties [145,146]. Samples produced by this technique, along with related methods such as hydrostatic extrusion, have been extensively studied (especially high density polyethylene) but the detailed microstructural picture is still not complete [147,148]. Recently Kanamoto [149] obtained an axial tensile modulus near that of the theoretical crystal modulus of polyethylene (222 GPa vs. 240-340 GPa [150,151]) by post drawing of a solid state extruded single crystal mat formed from ultrahigh molecular weight polyethylene. This achievement of properties by chain orientation and extrusion in the solid state reinforces the need for more thorough understanding of the process and the resultant morphology of the materials.

This chapter reports the results of a wide and small angle x-ray scattering study of the morphology of a series of solid state extruded polyethylene samples of extrusion draw ratio 1 (initial billet), 12, 24 and 36. This work was started by Dr. Edward S. Sherman in 1978,
Figure 4.1  Solid state extruded polyethylene billet removed from extrusion die (top) and extruded fiber, 36 EDR (bottom).
and preliminary results were reported in his dissertation [152]. These extended studies were performed partly in collaboration with Dr. Robert M. Briber (wide angle x-ray scattering line broadening analysis).

4.2 Background

Prior microstructural studies of the solid state extrusion process of polymers have revealed the nature of the initial deformation of spherulitic material into a highly oriented fibrillar texture [32,147, 153-158]. For linear polyethylene (PE), an extrusion draw ratio (EDR) of 6-12 is sufficient for the transformation which is accompanied by drastic changes in the birefringence, crystallite orientation, and long period, as well as tensile modulus and strength. For higher EDR, properties such as tensile modulus and axial crystallite size continue to change, while crystallite orientation, birefringence and noncrystalline chain mobility reach a plateau in the range of 15 EDR [32,159,160]. Changes in other properties are variable: for example the long period has been reported to either increase [157], decrease [146,154,155,158,160], or remain nearly constant [32], and its intensity decreases [32,147,154,160] or disappears altogether [161] with increasing EDR, depending upon the details of the extrusion process (pressure, temperature, extrusion rate, molecular weight).

Some models of the fibrillar structure which account for the increase in tensile modulus with increasing deformation rely heavily on the long period measured by small angle x-ray scattering [26,162]. It is therefore worthwhile to critically assess the small angle x-ray scattering from SSE fibers in view of the cited variable long period
behavior.

The variation of the SAXS intensity with increasing polymer deformation has included measures by visual estimation [162], peak height [163-165], peak area [166-169] and "intensity per unit volume" [147], none of which by themselves permit fundamental interpretation. The integrated intensity or invariant has seldom been measured, and then only by film or one-dimensional detector methods [170-174]. Since the small angle scattering from a fiber (or any other oriented system) is anisotropic, the proper integration of the scattered intensity requires two-dimensional digital recording which will also enable determination of other useful information, including macrolattice size and macrolattice distortion from the breadth of the long period peak(s), the anisotropy of the electron density fluctuations and the specific surface area between the crystalline and noncrystalline phases. In addition, the integrated intensity, placed on an absolute scale yields the mean squared electron density fluctuation which when coupled with data on degree of crystallinity and crystal density, allows the determination of the effective noncrystalline phase density, a parameter that should prove useful in understanding the deformation process during solid state extrusion and help distinguish among the proposed microstructural models.

Among the many models that have been proposed to describe the morphology of high modulus fibers, the two most notable at present are by Peterlin [175] and Ward [26]. These models have evolved from many previous ideas of the microstructure of fibers including Mark [176],
Staudinger [177], and Hess and Kiessig [178]. Figure 4.2a shows Peterlin's model, where the microfibril (C) [179] is the key microstructural feature governing mechanical properties. Microfibrils are typically ~ 200 Å wide and 15 - 20 μm long and consist of alternating crystal blocks and intercrystalline regions connected by taut tie molecules located primarily at the exterior of the microfibrils. Microfibrils are connected laterally by interfibrillar tie molecules (B) and axially by intrafibrillar tie molecules (A). The axial modulus is a function of the number of load bearing tie molecules that cross the noncrystalline regions to connect adjacent crystalline blocks along the microfiber.

Figure 4.2b shows Ward's [32,26] extension of Peterlin's model to include crystalline bridges formed from groups of crystallized taut tie molecules between the crystallites. The cross sectional area of the crystalline bridges is assumed to be considerably less than that of the individual microfibril. These structural models, while emphasizing highly oriented chains, disagree as to whether the high modulus arises from the reinforcement effect of long, narrow crystal bridges and extended chain crystal regions (Ward) or from the resistance of the (folded chain) crystals to unfolding as the taut tie molecules strain the crystals during deformation (Peterlin).

In an earlier study [180], electron microscopy was used to determine the microstructure of a series of solid state extruded polyethylene fibers. Microfibers composed of alternating crystalline and noncrystalline regions formed ribbon-like aggregates, and the axial
Figure 4.2  (a) Peterlin's model for cold drawn microfibrils [175], (b) Ward's model for hot drawn and solid state extruded fibers [32,36].
crystallite size increased with increasing extrusion draw ratio. In the 36 EDR sample, the crystal size distribution was broad, with a small component of very long crystals (1000 - 8000 Å). Aligned diffracting crystallite colonies observed in dark field images indicated coherence of sequences of adjacent crystallites along the fiber, imparted by needle crystals or thin crystalline bridges. At these high draw ratios, the tensile moduli of extruded materials is likely to be controlled by the size and amount of the long crystals and the number and type of bridges between shorter crystals.

In the present study small and wide angle x-ray scattering is employed to investigate the nature of the regions along the microfibers between the crystals, in particular, the noncrystalline phase density as well as the axial crystal coherence and fiber long period.

4.3 Samples

Details of the sample preparation by solid state extrusion were given previously [180]. Solid state extrusion was performed at 120°C and 2400 atmospheres pressure using a conical die of 20° semiangle. Sample designation and some properties are listed in Table 4.1. Reexamination of the higher molecular weight sample from the previous study revealed significant preferred orientation in the starting billet, making the final draw ratio uncertain. Only the lower molecular weight polyethylene (Alathon® 7050, M_w = 59,000, M_w/M_n = 3) will be considered here.
Table 4.1
Properties of Solid State Extruded Polyethylene Samples

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<tr>
<th>Extrusion Ratio</th>
<th>Draw Rate</th>
<th>Extrusion Rate</th>
<th>Tensile Modulus</th>
<th>DSC Degree of Crystallinity</th>
<th>Density g/cm³</th>
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<td>GPa</td>
<td>ϕc</td>
<td>− p</td>
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<td>40</td>
<td>83</td>
<td>0.975</td>
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</tr>
</tbody>
</table>
4.4 Experimental Methods

4.4.1 Wide Angle X-ray Scattering. Profiles of the (002) reflection were recorded using a Siemens D500 wide angle diffractometer employed in the symmetric transmission mode with Ni filtered CuKα radiation. The beam divergence was minimized for line broadening measurements with 0.1° incident beam slits and a 0.018° receiving slit so that a 1.5 mm thick hexamethylenetetramine standard had an integral breadth \( \Delta \beta_{\text{instr.}} \) of 0.13° for a reflection at \( 2\theta = 76.73° \).

The PE sample profiles were recorded over a \( 2\theta \) angular range of 5° starting from 73° at a rate of 0.1°/min. The count rate at the main peak was typically 150 counts/second. The background was found to be constant (~3-5 counts/sec) on both sides of the peak. The Rachinger correction was applied to remove the CuKα2 peak from the (002) profile [181]. Integral breadths, \( \Delta \beta_{\text{obs}} \), were calculated from the corrected profiles by

\[
\Delta \beta_{\text{obs}} = \frac{1}{I_{\text{max}}} \int I(2\theta)d(2\theta) \quad \text{(4.1)}
\]

where \( I_{\text{max}} \) is the maximum peak intensity.

The correction of the observed integral breadths for instrumental broadening depends on whether the peak shapes are Cauchy or Gaussian [182]. If the profiles are Cauchy:

\[
\Delta \beta_{\text{obs}} = \Delta \beta_{\text{L}} + \Delta \beta_{\text{instr.}} \quad \text{(4.2)}
\]

while for Gaussian profiles:
where $\Delta B_L$ is the broadening from the sample. Since the observed peaks are generally represented by a combination of Cauchy and Gaussian functions we have calculated the mean crystal size for both cases using the Scherrer equation:

$$\Delta B^2_{\text{obs}} = \Delta B^2_L + \Delta B^2_{\text{instr.}}$$  \hspace{1cm} (4.3)

where $K = 1.0$ for $00\ell$ reflections [183].

Precise measurement of the $(200)$, $(020)$ and $(002)$ d-spacing was made using the Kα1 peak after applying the Rachinger correction. Quartz was used to calibrate the $2\theta$ values.

Orientation measurements were made from microdensitometer traces (Optronics Photoscan P-2000) of flat film photographs made on a Statton type (Warhus) camera with CuKα radiation from an Elliot GX20 Rotating Anode Generator. The azimuthal angle of arcing where the intensity of a reflection decreased to half its maximum value was taken as a measure of orientation.

4.4.2 Small Angle X-ray Scattering

Small angle x-ray scattering was performed at the National Center for Small Angle Scattering Research (NCSASR) at Oak Ridge National Laboratories, Oak Ridge, Tennessee, using the 10-meter camera (details of this facility are given in [184]). The pinhole
collimation and two dimensional position sensitive detector makes this instrument useful for studying the anisotropic scattering from fibers. The CuKα x-ray source was monochromated by pyrolitic graphite in the incident beam. Incident beam intensity was calibrated with a series of nickel foils [185]. Specimen transmittance was measured by comparing the small angle scattering of a standard (Lupolen) to its scattering with the beam attenuated by the PE sample placed in front of the first collimation pinhole.

Extruded PE samples are visually transparent, indicating the absence of heterogeneities larger than about 0.1 microns (see Figure 4.1). Samples were trimmed to approximately 1 mm thickness and were greater than 1 mm wide so that the incident 1 mm x 1 mm x-ray beam was completely covered by sample. Data were collected at specimen to detector distances of 5.15 m, 2.20 m and 1.12 m encompassing a scattering vector range from 0.00122 to 0.488 Å⁻¹ (Figure 4.3). A comparison of the relative angular extent of the scattering patterns for the 36 EDR sample is shown in Figure 4.4. Data from the samples (mounted with the fiber direction vertical) was collected for a time sufficient to give ~ 3% counting statistical error after correction for electronic noise, parasitic scattering, and detector sensitivity.

The integrated intensity, or Porod invariant \(Q\) [186] is of the form

\[
Q = \text{Const.} \int_0^1 \int_0^1 I(q_1, q_2)q_1q_2dq_1dq_2
\] (4.5)
Figure 4.3 Schematic of the ORNL 10 meter small angle x-ray scattering machine. Variable detector positions for nominal 1, 2 and 5 meter sample-to-detector distances are shown. Scattering vectors measured on the plane of the detector and the azimuthal angle $\mu$ are shown at the 5 meter location (fiber direction vertical).
Figure 4.4  Isointensity contour plot of the relative extent of the small angle scattering patterns for the 36 EDR sample. Interior contours are obtained at 5 meters sample-to-detector distance, outside contours at 1 meter, fiber direction vertical.
assuming cylindrical symmetry about the fiber direction \( q_1 \). A computer program to perform this integration was written for use at ORNL [187]. The program "INVAR" is available at the ORNL NCSASR and is listed in Appendix B. The mean squared electron density fluctuation can be written:

\[
\langle (\rho - \bar{\rho})^2 \rangle = Q \frac{i_e N^2 t \lambda^3 I_0 a}{i_e N^2 t \lambda^3 I_0 a} ,
\]

(4.6)

where \( i_e \) is the Thomson cross-section of a free electron \((7.9 \times 10^{-26} \text{ cm}^2)\), \( N \) is Avogadro's number, specimen thickness is \( t \), \( a \) is the specimen-detector distance, and \( I_0 \) is the normalized total incident intensity measured in absolute units [188].

By subtracting from the measured scattered intensity the liquid scatter contribution \((F \lambda)\) arising from density fluctuations within each phase, the mean squared electron density fluctuation measured then arises only from the electron density difference between the phases, independent of the number of phases or the nature of the phase boundaries. For a semicrystalline polymer, the usual two-phase, sharp boundary approximation yields

\[
\langle (\rho - \bar{\rho})^2 \rangle = (\rho_c' - \rho_a')^2 \phi_c \phi_a ,
\]

(4.7)

where \( \phi_c \) and \( \phi_a \) are the volume fractions of the crystalline and noncrystalline phases, respectively. Note that \( \rho_c' \) and \( \rho_a' \) represent the actual average densities of the two phases for the particular deformation state. Thus, one anticipates the initial crystal density \( \rho_c \) to be reduced by defects to \( \rho_c' \) and the noncrystalline density
\( \rho_a \) to be increased by the drawing to \( \rho_a' \). As first shown by Fischer [171,189], combining an independent measure of \( \bar{p} \) (the bulk sample density) with an accurate measure of \( \rho_c' \) from wide angle x-ray scattering enables the value of \( \rho_a' \) to be determined:

\[
\rho_a' = \bar{p} - \frac{\langle (\rho - \bar{p})^2 \rangle}{(\rho_c' - \bar{p})}.
\] (4.8)

The accurate measurement of the liquid scattering (Fl) can be obtained by a Porod law analysis at high scattering angles. The dependence of the scattered intensity from oriented assemblies of anisotropic particles at large q is given by [190]:

\[
I(q,\mu) = \frac{K_p(\mu)}{q^4} + Fl(\mu).
\] (4.9)

Indicated in Figure 4.3 is the azimuthal angle \( \mu \), such that Fl(\( \mu \)) can be determined from plots of \( q^4 I \) versus \( q^4 \) at various azimuthal angles. Subtraction of the liquid scattering from the scattered intensity was performed by sectors (\( 0^\circ < \mu < 22.5^\circ \), \( 22.5^\circ < \mu < 67.5^\circ \), and \( 67.5^\circ < \mu < 90^\circ \)) assuming Fl(\( \mu \)) was independent of scattering angle within each sector.

Porod law analysis also gives Porod constants (\( K_p \)) from the intercepts on the \( q^4 I \) vs \( q^4 \) plots. \( K_p \) can be used for isotropic systems to give the surface-to-volume ratio [188], or for anisotropic systems, \( K_p(\mu) \) can be interpreted as relative sizes and shapes of oriented ellipsoids of revolution [190].
4.5 Results

4.5.1 Wide Angle X-ray Diffraction. The uncorrected integral breadths of the (002) reflections are given in Table 4.2. Since the observed peak profiles are neither Gaussian or Cauchy, calculated values of crystal size were made for both cases and are also listed in Table 4.2. Since there are no detectable higher order (002) reflections, no correction can be made for possible strain and paracrystalline line broadening contributions, and hence the values listed are lower bounds on crystal thickness. A strong increase in the axial crystal coherence length is observed with EDR, rising from 240 Å for the billet to 400 Å for the 36 EDR sample.

The (200), (020) and (002) spacings are also listed in Table 4.2. The effect of increasing draw ratio is to increase the a axis spacing with essentially no change in the dimensions of the b and c axes. The expansion of the a axis causes the unit cell density to drop by about 1% from the billet (.999 g/cm³) to the most highly drawn 36 EDR sample (.990 g/cm³).

The crystallite orientation increases with increasing draw ratio. Wide angle flat film x-ray diffraction patterns (see Figure 4.5) had half-angle azimuthal spreads of 17°, 6° and 5° for (110) for the 12, 24 and 36 EDR samples, respectively (see Figure 4.6). This increase in orientation agrees with earlier electron diffraction results [180] showing that the c-axis orientation increases greatly up to EDR 24 but only slightly thereafter. These values also agree with spectroscopic orientation data which gave chain axis misorientation angles of 17°,
Table 4.2
WAXS Data

<table>
<thead>
<tr>
<th>Extrusion Draw Ratio EDR</th>
<th>d_{200}</th>
<th>d_{020}</th>
<th>d_{002}</th>
<th>\rho_C</th>
<th>8002</th>
<th>002 \xi_C</th>
<th>Azimuthal Orientation Half-angle (110)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.707</td>
<td>2.471</td>
<td>1.273</td>
<td>.999</td>
<td>.529°</td>
<td>220-260</td>
<td>360°</td>
</tr>
<tr>
<td>12</td>
<td>3.717</td>
<td>2.469</td>
<td>1.272</td>
<td>.997</td>
<td>.426°</td>
<td>260-340</td>
<td>17°</td>
</tr>
<tr>
<td>24</td>
<td>3.726</td>
<td>2.467</td>
<td>1.272</td>
<td>.995</td>
<td>.448°</td>
<td>260-320</td>
<td>6°</td>
</tr>
<tr>
<td>36</td>
<td>3.735</td>
<td>2.471</td>
<td>1.273</td>
<td>.990</td>
<td>.357°</td>
<td>330-470</td>
<td>5°</td>
</tr>
</tbody>
</table>

* G = Gaussian profile, C = Cauchy profile
Figure 4.5  Wide angle x-ray flat film photographs of solid state extruded polyethylene of extrusion draw ratio (a) 1 (undeformed billet), (b) 12, (c) 24, (d) 36.
Figure 4.6  Microdensitometer isodensity contour plot of the flat film wide angle x-ray photographs from Figure 4.5, equatorial profiles only.
6° and <2° [191,192].

4.5.2 Small Angle X-ray Scattering. Figure 4.7 shows isointensity contour plots for the long geometry (sample-to-detector distance, 5.15 m) for all the extrudates. The data has been background corrected and normalized with respect to incident beam intensity and sample thickness. Contour line intervals are at multiples of $2^n$ counts, with the outside line representing 16 counts. All samples show a two point pattern of intensity on the meridian similar to that observed for conventionally drawn fibers [193,194]. The long period calculated by applying Bragg's law to the position of the peak intensity maximum is given in Table 4.3.

A plot (Figure 4.8) of the intensity vs 2θ along q1 enables the meridional integral breadth ($\Delta \beta_1$) to be obtained and is given by:

$$\Delta \beta_1 = \frac{2}{I(q_1^*,0)} \int_{q_1^*}^{\infty} I(q_1,0) dq_1. \tag{4.10}$$

Similarly, the average width of the microfibers may be measured from the integral breadth of the peak in the q2 direction by:

$$\Delta \beta_2 = \frac{1}{I(q_1^*,0)} \int_{-\infty}^{+\infty} I(q_1^*,q_2) dq_2 \tag{4.11}$$

where $q_1^*,0$ is the position of the intensity maximum. The integral breadths along q1 (5.1, 4.3 and 4.4 mrad for 12, 24, 36 EDR) are much smaller than along q2 (7, 10, 12 mrad for 12, 24, 36 EDR).

The contancy of integral breadth $\Delta \beta_1$ along the meridional direction
Figure 4.7 SAXS isointensity contour plots at 5 meter geometry for (a) initial billet, 1 EDR and (b) 12 EDR, (c) 24 EDR and (d) 36 EDR samples. Data are normalized for sample volume and incident beam intensity, outer contour at 16 counts, each inner contour increases by a factor of 2. Void scattering at the centers of the patterns was not included in the invariant calculations. Scattering vectors $q_1$ and $q_2$ and azimuthal angle $\mu$ are indicated on (b).
### Table 4.3

Comparison of Crystallite Sizes and Long Periods (Å)

<table>
<thead>
<tr>
<th>Draw Ratio EDR</th>
<th>( \lambda_C^{DF} )</th>
<th>( *\lambda_C^{002} )</th>
<th>( \lambda_{S}^{LAM**} )</th>
<th>( \lambda_{SAXS} )</th>
<th>( \lambda_C^{002}/\lambda_{SAXS} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>---</td>
<td>240</td>
<td>---</td>
<td>279***</td>
<td>0.86</td>
</tr>
<tr>
<td>12</td>
<td>270</td>
<td>300</td>
<td>230</td>
<td>349</td>
<td>0.86</td>
</tr>
<tr>
<td>24</td>
<td>270</td>
<td>290</td>
<td>175</td>
<td>266</td>
<td>1.09</td>
</tr>
<tr>
<td>36</td>
<td>390</td>
<td>400</td>
<td>150</td>
<td>237</td>
<td>1.69</td>
</tr>
</tbody>
</table>

* Values listed are mean of Cauchy and Gaussian values from Table 4.2

** From Reference [192]

*** Lorentz corrected long period
Figure 4.8 Plot of normalized intensity versus scattering angle $q$ ($\text{Å}^{-1}$), meridional direction ($\mu = 0^\circ$).
indicates little net change in the three contributing factors (size, size distribution and paracrystalline distortion) to macrolattice line breadth with deformation. The integral breadth of the SAXS peak perpendicular to the fibers, $\Delta \beta_2$, can be interpreted in terms of microfibril radii by equation (4.12):

$$<R> = \frac{0.52\lambda}{\Delta \beta_2}$$  \hspace{1cm} (4.12)

where $<R>$ is the ratio between the 4th and 3rd moments of the microfibril radius distribution function [195]. $\Delta \beta_2$ increases proportional to EDR, indicating a thinning of the microfibers ($<R>$ decreases from 103 to 80 to 64 A), which was also observed by bright field electron microscopy and wide angle x-ray diffraction. It is interesting to note that $<R>$ obeys Peterlin's [196] prediction that the diameter of the microfibers follows a $\lambda^{-1/2}$ dependence (Figure 4.9).

The evaluation of $<(\rho-\bar{\rho})^2>$ for an anisotropically scattering specimen requires considerably more effort than for an isotropic specimen. The two-dimensional integration (equation 4.5) requires data collection at the one, two and five meter geometries. Complete details of the invariant calculation using a two-dimensional position sensitive detector system for samples possessing cylindrically symmetric scattering patterns are presented elsewhere [187]. The main features pertinent here are the verification of the two-phase, sharp boundary approximation and the separation and subtraction of the orientation dependent density fluctuation scattering component.
Figure 4.9  Ratio of 4th to 3rd moment of microfibril radius distribution function, $\langle R \rangle$, versus $(EDR)^{-1/2}$. 
The assumption of sharp interfaces between phases which is inherent is equation (4.7), was experimentally verified by Porod plots. Figure 4.10 shows plots of $q^4I$ vs $q^4$ for all the samples. The straight line between the individual points is a least squares fit to the data by equation (4.9), so that $F_\lambda(\mu)$ is the slope and $K_p(\mu)$ is the intercept for each value of $\mu$. Porod's Law was found to be obeyed over the range of scattering angles from approximately $q = 0.2\ \text{Å}^{-1}$ ($2\theta = 2.8^\circ$) to $q = 0.3\ \text{Å}^{-1}$ ($2\theta = 4.2^\circ$) except for $\mu = 45^\circ$, where a linear fit was possible to $q = 0.42\ \text{Å}^{-1}$ ($2\theta = 5.9^\circ$), see Table 4.4.

Table 4.5 gives the values of the liquid-like scatter $F_\lambda(\mu)$ along the meridian ($\mu = 0^\circ$), at $45^\circ$ to the meridian and along the equator ($\mu = 90^\circ$). Significant anisotropy in $F_\lambda$ occurs, for example in the 36 EDR sample, the intensity at $90^\circ$ is nearly three times that at $0^\circ$, as can be clearly seen in the high angle regions of the iso-intensity plots in Figure 4.11.

The Porod constants $K_p(\mu)$ listed in Table 4.5 are also anisotropic. In addition, there are significant increases in $K_p$ at all EDR over the undrawn isotropic values. The anisotropy is the most pronounced for samples of 24 and 36 EDR, with an almost 2:1 ratio of the liquid scatter intensity along $\mu = 90^\circ$ versus $0^\circ$. The specific surface $(S/V)$ can be calculated for isotropic samples from the Porod constant by [186]

$$S/V = \frac{K_p}{2\pi \left< (\rho - \rho)^2 \right>} \quad (4.13)$$
Figure 4.10 Porod plots at three azimuthal angles ($\mu$). Lines are least squares fits to Porod's Law, equation (4.9).

(a) 1 EDR (isotropic sample).
Figure 4.10  Porod plots at three azimuthal angles ($\mu$). Lines are least squares fits to Porod's Law, equation (4.9). (b) 12 EDR.
Figure 4.10  Porod plots at three azimuthal angles (μ). Lines are least squares fits to Porod’s Law, equation (4.9).
(c) 24 EDR.
Figure 4.10  Porod plots at three azimuthal angles ($\mu$). Lines are least squares fits to Porod's Law, equation (4.9).
(d) 36 EDR.
<table>
<thead>
<tr>
<th>EDR</th>
<th>0°</th>
<th>45°</th>
<th>90°</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.193 - .329</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>12</td>
<td>.187 - .296</td>
<td>.236 - .427</td>
<td>.199 - .320</td>
</tr>
<tr>
<td>24</td>
<td>.211 - .308</td>
<td>.224 - .308</td>
<td>.211 - .308</td>
</tr>
<tr>
<td>36</td>
<td>.211 - .308</td>
<td>.295 - .416</td>
<td>.224 - .308</td>
</tr>
</tbody>
</table>
### Table 4.5

Anisotropic Porod Analysis

<table>
<thead>
<tr>
<th>Extrusion Draw Ratio</th>
<th>$F_{\mu}(\mu)$ (electrons$^2$/Å$^3$)</th>
<th>$10^5 K_p$ (electrons$^2$/Å$^7$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\mu$</td>
<td>$0^\circ$</td>
</tr>
<tr>
<td>1</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>0.12</td>
<td>0.12</td>
</tr>
<tr>
<td>24</td>
<td>0.069</td>
<td>0.091</td>
</tr>
<tr>
<td>36</td>
<td>0.064</td>
<td>0.093</td>
</tr>
</tbody>
</table>
Figure 4.11  Isointensity contour plots for data taken at 1 meter geometry (fiber direction vertical). Round "holes" in centers are due to the use of a 4.6 cm diameter beam stop to block the interference peak, avoiding counter overflow during the long run times. (a) 1 EDR, (b) 12 EDR, (c) 24 EDR, (d) 36 EDR.
The specific surface of the billet is $7.87 \times 10^{-3} \text{Å}^{-1}$. Measured values for the mean square electron density fluctuation are given in Table 4.6, along with the degree of crystallinity and effective crystal density used in equations (4.7) and (4.8) to calculate the effective noncrystalline region density.

4.6 Discussion

Previously, dark field electron microscopy was used to directly image the crystalline regions to investigate their distribution of sizes and shapes [180]. Two additional methods have now been applied to study crystal size and connectivity therefore permitting a test of the various morphological models for the structure of solid state extruded PE. Wide angle x-ray diffraction line breadth analysis measures the weight average axial crystal size from coherently scattering (002) lattice planes. Measurement of d-spacings by WAXS yields the crystalline phase density and WAXS azimuthal arcing gives the orientation of the crystalline regions. SAXS will reveal a long period if the crystals exist within periodic macrolattices but most importantly, SAXS permits calculation of the density difference between the crystalline and noncrystalline regions from the invariant. Both x-ray techniques average over several $(\text{mm})^3$ of bulk sample while electron microscopy is highly specific to relatively small fields of view (circa 10 $\mu$m in diameter) of thin regions of the detached microfibers. Although differing in moment (weight vs. number average) and sensitivity, a combined synthesis of the observed quantities
Table 4.6
Mean Squared Electron Density Fluctuation and Effective Densities
From Small Angle X-ray Scattering

<table>
<thead>
<tr>
<th>Extrusion Draw Ratio EDR</th>
<th>(\langle (\rho - \bar{\rho})^2 \rangle) (mole (e^-/cm^3))^2</th>
<th>(\phi_c)</th>
<th>(\rho_c) g/cm(^3)</th>
<th>(\rho_a) g/cm(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.43 x 10(^{-3})</td>
<td>.77</td>
<td>.999</td>
<td>.84</td>
</tr>
<tr>
<td>12</td>
<td>.673 x 10(^{-3})</td>
<td>.73</td>
<td>.997</td>
<td>.88</td>
</tr>
<tr>
<td>24</td>
<td>.668 x 10(^{-3})</td>
<td>.82</td>
<td>.995</td>
<td>.88</td>
</tr>
<tr>
<td>36</td>
<td>.529 x 10(^{-3})</td>
<td>.83</td>
<td>.990</td>
<td>.89</td>
</tr>
</tbody>
</table>
reveals important measures of crystal order and connectivity via the intervening noncrystalline regions.

The value of the long period for the undeformed billet, 279 Å (Lorentz corrected) is significantly less than for the 12 EDR material (349 Å) and is determined by the billet preparation conditions (temperature and pressure). Further drawing decreases L considerably, to 266 Å and 237 Å for 24 and 36 EDR, respectively. This decrease of L with increasing draw has been previously reported for SSE PE [146, 154,155,158,160] and is at variance with other reports where L is either not affected much by drawing [32] or even increases [157]. The initial increase in L (280 to 350 Å) is accompanied by a decrease of sample crystallinity from 77% to 73%. On further deformation the crystalline volume fraction increases to 83%.

The fluctuation scattering can be measured by determining the absolute small angle scattering intensity at high scattering angles. This weak scattering, arising from spatial and temporal density fluctuations in both the crystalline and amorphous phases, can be written for an oriented system as:

\[ F\delta(T,\mu) = \phi_a F\delta_a(T,\mu) + \phi_c F\delta_c(T,\mu) \]  

(4.14)

The magnitude of the fluctuation scattering is directly proportional to the amounts of the phases present. The measured value of the total electron density fluctuation for the undrawn billet, 0.14 e^2/Å^3, is 50% higher than a calculated value of 0.095 e^2/Å^3 using Ruland and Rathje's [197] values of 0.22 e^2/Å^3 for F\delta_a and 0.058
e²/Å³ for Fₚₑ and the measured sample ψₑ of 0.77. For the undrawn material, the density fluctuations are isotropic, due to both the Fₚₑ term (mostly from phonons) and to Fₚₐ (from defects), which are randomly oriented. However, Fₚₑ exhibits strong anisotropy for the extrudates. The temperature and orientation dependence of Fₚₑ for a drawn (λ = 4) high density polyethylene has been examined by Wiegand and Ruland [198]. They found that for this modestly drawn PE sample the anisotropy in Fₚₑ was essentially due to the oriented crystals. We find at 12 EDR, a weakly orientation dependent Fₚₑ. But by 24 EDR, the scattered intensity along the meridian is less than half that along the equator. This anisotropy in Fₚₑ is more pronounced at 36 EDR.

The specific surface calculated from the Porod constant for the initial billet, 7.87 x 10⁻³ Å⁻¹, is in agreement with the simple estimate of S/V based on the long period (2/L = 7.17 x 10⁻³ Å⁻¹) supporting the picture of a periodic lamellar structure for the undeformed billet. The calculated density for the initial undeformed polyethylene billet, 0.84 g/cm³, is reasonable, compared to estimates from dilatometric melt density extrapolations [172], and other previous SAXS measurements for polyethylene [171]. It is also consistent with the enthalpic degree of crystallinity, the wide angle x-ray crystal density, and the experimental bulk density for the billet (i.e. ρcalc = [(0.77)(.999) + (.23)(.84)] = .962 versus .965 measured]. For the extrudates, current theory does not provide a quantitative interpretation to the magnitude of Kₚ(μ) in terms of a surface to volume ratio. However, it is notable that the Porod constants for
\[ \mu = 90^\circ \] increase with draw ratio, consistent with the thinning of the microfibers.

The dark field crystal size and distribution, and the wide angle x-ray scattering average crystal size are model independent, and provide direct measures of the crystalline coherence. Both of these techniques provide lower limits to the actual average crystal sizes. The longitudinal acoustic mode determined average stem length \( l_c \) does not differentiate between extended chains in crystals or other all-trans chain sequences, such as taut tie molecules. This decrease in the SAXS interference peak intensity indicates the amount of periodic material has decreased and/or the density difference between the components has diminished. The mean squared electron density fluctuation, however, is model independent.

The data presented support a fiber microstructure that is two phase, and remains two phase with increasing deformation. New crystalline regions are formed during the deformation, as indicated by the increase in degree of crystallinity. The microfibers become axially longer and narrower, and are increasingly better oriented. The crystalline regions contain more defects with increasing deformation as evidenced by the decreased effective crystal density, \( \rho_c^* \). Lasch and Hsu have measured the average stem lengths for these three extrudates by Raman longitudinal acoustic mode (LAM) spectroscopy [191,192,199], using the LAM peak maximum. The number average stem length decreased from 230 Å to 150 Å for 12 and 36 EDR, respectively (Table 4.3), while the breadth of the LAM peak increased, indicating a
broadening of the distribution of stem lengths, including a tail of short stem lengths which has been associated with a substantial population of short chain extended segments. The decrease in the LAM stem length and the increase in the number of shorter stem lengths further indicates a substantial increase in the crystal defect content. The SAXS invariant decreases, but certainly does not vanish, even though the small angle scattering long period peak intensity along the meridian decreases by a factor of 8 measured by peak height or 12 by peak area. A more reliable measure of the SAXS behavior, rather than merely examining $\bar{I}$, is the mean squared electron density fluctuation, which is consistent in its decrease with EDR, with a 21% reduction from 12 to 36 EDR, and a 63% reduction from the initial billet material. The crystal size distribution (from dark field) becomes broader, and the crystals are arranged in an increasingly non-periodic manner.

Consideration must also be given to the limits of the measurement of small angle scattering. For polymer systems with large crystal sizes (400 Å or more), a portion of the scattered intensity due to large periodicities (if any) is not observable by many instruments, and consequently is not sampled by this technique.

By assuming a two phase system with sharp boundaries (the latter assumption is verified by Porod analysis), the desired values of the effective noncrystalline phase density, $\rho_a'$, are seen to initially increase from the unoriented amorphous density of 0.84 g/cm$^3$ to a value of 0.89 g/cm$^3$, which is reasonable for a partially oriented,
more densely packed noncrystalline arrangement of chains. This plateau in $\rho_a^1$ with EDR indicates that after initial formation of the oriented fiber structure further changes in the noncrystalline regions are not reflected in the density $\rho_a^1$.

In order to make further use of SAXS, some model must be assumed, such as a sharp interface two phase system, which is often used for semicrystalline polymers. Sharp interfaces are verifiable from a Porod analysis which is anisotropic for an oriented system. The subtraction of the fluctuation scattering from the total scattering allows the determination of the densities of the two phases (now each of uniform density). The two phase model itself is not directly verifiable, but provides a self consistent picture, yielding a direct measure of $\rho_a^1$ unavailable for anisotropic samples from any other technique. To further assess the nature of the amorphous phase it would be necessary to measure heat capacity, or use NMR or IR to probe the mobile chain fraction.

The leveling off of $\rho_a^1$ with EDR is in agreement with studies of the dependence of transport properties of drawn semicrystalline polymers with draw ratio. Williams and Peterlin [200] found that for linear polyethylene drawn at 60°C, the sorption and diffusion constants of methylene chloride dropped drastically between $\lambda = 8$ and 9, and then remained nearly constant up to $\lambda = 25$. Later studies [201] on low density polyethylene showed a similar trend, although the highest draw ratios obtained were $\lambda = 6$. Since the transport behavior is dominated by the amorphous phase, the techniques used are very
sensitive to the nature of the noncrystalline component. On drawing, the system is transformed from spherulitic-lamellar with a high permeability amorphous matrix to a fibrillar system containing a densified, lower permeability amorphous phase.

Transport properties (i.e. diffusion rate of small molecules), birefringence, infrared dichroism and thermal expansion all provide information about the noncrystalline component in high modulus polyethylene. It is well established that the noncrystalline chain orientation increases with draw ratio, reaching a plateau above about 12 EDR. Since crystallite orientation also does not increase significantly at high draw ratios, the continued increase in modulus does not correlate well with chain orientation in either phase.

Ito [159] examined the noncrystalline phase in solid state extruded polyethylene by nuclear magnetic resonance, and found for 12 EDR or lower, three relaxation times which were associated with rigid (crystal), intermediate and noncrystalline components. At EDR of 25 or larger, only the crystalline and noncrystalline components were observed. The constraint on the noncrystalline component increased rapidly up to 12 EDR and reached a plateau above 12 EDR, in parallel to the degree of orientation of the noncrystalline chains, measured by birefringence [154,202] and thermal expansion coefficient [202].

Peterlin's model explains the increase in modulus with increasing draw ratio on a molecular basis: fibers are composed of microfibers with axially alternating regions of crystalline (folded chain lamellar crystals) and noncrystalline chains. The crystals are connected by a
population of tie molecules running through the noncrystalline regions, and the tie molecules at the lateral edges of the microfibers are taut or even crystallized. Further drawing increases the number of taut tie molecules by decreasing the microfibril diameter through shearing and extension of the folded chains, thereby increasing modulus. One aspect of Peterlin's model is that the structure of the noncrystalline regions does not change significantly with draw at high draw ratios [196,203]. The decrease in segmental mobility and the increase in chain orientation, coupled with the initial densification of the noncrystalline phase up to 12 EDR and saturation above 12 EDR all lend support to Peterlin's two phase model. The molecular arrangement in the noncrystalline phase changes little at high draw ratios. The crystalline fraction is constant or increases slightly, reflecting conversion of folded chains to more extended chains which can crystallize. But the noncrystalline regions resist further densification so the system must respond to the applied stress by microfiber shear and/or crystal deformation.

The Ward model [26], like any series arrangement of structural elements, relies on the size estimate of a microstructural element from a global measurement technique (SAXS). However, when one of the critical parameters needed is based upon the long period, and in the situation when the intensity of the long period and hence the periodic fraction of the material is low, the validity of the model must be questioned.

An ideally periodic structure with single valued crystal and
noncrystal lengths would produce an interference peak (long period) that is completely representative of that structure. An assessment of the ideality of such a periodic model can be made from an inspection of the SAXS intensity (in the long period region) and of the crystal size distribution from electron microscopy and wide angle x-ray scattering. For the 12 EDR sample, which exhibits relatively strong SAXS long period intensity, the periodicity is good, and the breadth of the long period peak is indicative of a narrow macrolattice size distribution. The crystal size distribution is relatively narrow as measured from dark field electron microscopy, and a periodic model is reasonable. But at 36 EDR, such an ideal periodic structure is certainly nonrepresentative. Rather, there is a broader crystallite size distribution containing a small component of very long crystals (1000 - 8000 Å), with sequences of diffracting crystallites (colonies) indicating the presence of thin intercrystalline bridges [180].

In Ward's intercrystalline bridge model, the parameter \( p \) is defined as the "area fraction of intercrystalline bridge material which traverses the disordered layer" [26] and is determined by:

\[
p = \frac{\overline{\kappa} - \overline{L}}{\overline{\kappa} + \overline{L}}.
\] (4.15)

This definition is only useful for cases where \( \kappa / L > 1 \); otherwise \( p \) is either zero or negative. This limits the applicability of this model, and in the present case, Table 4.3 indicates that \( \overline{\kappa} / \overline{L} \) is less than one at 12 EDR and barely exceeds one at 24 EDR where the modulus
is already 27 GPa! At 36 EDR the Ward model might appear to be reasonable, but the long period scattering peak is very weak indicating a very small amount of periodic structure (some material recrystallized at large undercooling for the high pressure extrusion?). Models that rely on the long period as a fundamental parameter, particularly for quantitative prediction of mechanical properties, must be reconsidered with the view that the long period although easily determined is not always a truly meaningful or appropriate average measure of the microstructure.

4.7 Conclusions

The use of a two phase model for solid state extruded polyethylene fibers is justified if consideration is given to the effective densities \( \rho_c \) and \( \rho_a \) of the phases, which change with deformation. Use of non-perturbed density values for a deformed system is invalid. Effective densities can be obtained by careful application of wide and small angle x-ray scattering methods for anisotropic systems.

The average axial crystallite length (lower bounds) measured by wide angle x-ray scattering increases with extrusion draw ratio, while the SAXS invariant and long period decrease. The effective density of the noncrystalline component increases rapidly with draw ratio up to about 12, then remains constant (at .89 g/cm\(^3\)) with further draw to 36 EDR.

These extensive morphological observations involving both microscopy and x-ray techniques on a series of solid state extrudates
are fully consistent with the key features of the Peterlin model of fiber microstructure.
CHAPTER V

CONCLUSIONS AND POSSIBLE EXTENSIONS

5.1 Overview

The purpose of this dissertation research was to develop and apply new methods toward the better understanding of an old problem in polymer science: How does a semicrystalline polymer deform? The polymer of choice was one that has probably been studied more than any other - polyethylene. The methods used were chosen both for their anticipated power in morphological analysis, and because the author wanted to gain at least a modest level of understanding of their usefulness. The success achieved in the determination of useful microstructural quantities by small angle x-ray scattering or in direct visualization of the deformation process reflects perhaps a serendipitous combination of sample availability and preparation, the emergence of analytical methodology with obvious applicability to the problems at hand, and a collection of scientific enthusiasts capable of building upon prior successes. The extent to which this work has contributed to progress in polymer physics will only be judged in time, but the extent to which it has advanced the author's appreciation for all of polymer morphology is already realized.

This chapter recapitulates the conclusions reached in the previous three chapters. It will briefly review the significance of the
advances in scanning transmission electron microscopy for the examination of electron beam sensitive semi-crystalline polymer morphology, coupled with examples of the careful application of conventional transmission electron microscopy to examine the undamaged polymer microstructure. The use of STEM and CTEM in the study of deformation of thin oriented polyethylene films is extensively demonstrated, providing images which verify deformation mechanisms previously only imagined. Finally, the measurement of the noncrystalline phase density for deformed polyethylene was made possible by the careful application of analysis of the anisotropic small angle x-ray scattering using modern instrumentation, the result being strengthened support for the Peterlin model of fiber formation. Possible extensions of these studies are included as suggestions for future investigations.

5.2 Polymer Electron Microscopy

In Chapter II, conventional transmission electron microscopy was used to obtain bright field images of spherulitic and oriented polyethylene. The magnification limitations for CTEM for radiation sensitive polymers are somewhat balanced by its inherently higher resolution. The method of CTEM bright field "ghost imaging" permits real space crystallography of a crystalline polymer specimen and reveals the occurrence of variable chain inclination in oriented lamellar thin films. Improved image contrast due to objective lens defocus phase contrast also permits examination of the intercrystalline regions between crystalline lamellae.
The typical approach to CTEM dark field imaging of radiation sensitive polymers is to focus in bright field, set up the dark field imaging conditions, translate to an adjacent undamaged area and record the DF image. The disadvantage of this approach is a low yield of useful micrographs which makes systematic studies very difficult. Because of image intensification, control of illumination location and magnification independent focus, STEM operation for focusing, area selection and optics set up permits a high yield of systematic data.

STEM scanning microdiffraction allows useful diffraction patterns to be recorded from much smaller areas than for CTEM selected area diffraction, provided the incident beam divergence is limited by use of a small second condenser aperture. In addition, the use of the reduced raster scan mode permits mapping the specimen crystallography in the region of interest by adjusting the size and shape of the area scanned with the incident beam off.

STEM DF imaging may be done with one or more reflections. For efficient DF imaging of thin crystals, a small second condenser aperture should be employed. N beam annular DF is a high contrast complement to the BF image. Use of the entire azimuthal range of a single powder pattern reflection permits examination of crystal texture - in particular, images produced by chain axis reflections show the detailed arrangements of lamellae. By using more than one reflection to image a crystal, the DF image intensity and resolution are increased. In the most favorable cases, n beam DF imaging of PE single crystals will yield a 3X improvement in resolution, or for a
given resolution, a 9X increased number of micrographs over single beam DF. N beam annular dark field scanning transmission electron microscopy is also useful for distinguishing between curved lamellae and mosaic blocks as well as for the direct imaging of the amorphous regions between lamellae.

5.3 Deformation Microscopy of Thin Oriented Films

Chapter III uses the techniques from Chapter II in an extensive study of the deformation of oriented polyethylene thin films. Previous work on the study of oriented thin films was done by Petermann's group, and we are indebted to them for pioneering the development of sample preparation methods. The main contribution in this work has been to systematically and quantitatively extend Petermann's scouting effort. A most useful development was the discovery by Yang that uniplanar film texture could be produced by lower temperature sample preparation than had been used by Petermann. By preparing stacks of thin films, we were able to bring to bear on the problem not only the extensive use of CTEM, STEM DF, SAES, optical transforms and electron diffraction for thin films, but also other morphological probes for bulk averages, including wide and small angle x-ray scattering.

The unique crystal orientation present in the thin films made possible more quantitative observations, including the investigation in the present study of deformation at various angles to the chain axis and of the c-axis slip mechanism including the unequivocal
assignment of specific slip systems. For deformation parallel to the c-axis, the slip systems are identified as \{010\},<001> and \{100\},<001>. Shear on (010) could be further distinguished as fine slip (of individual or small groups of chains) or block slip (of large groups of chains). Deformation in a direction perpendicular to the chain axis (along b) initiates with crystal cleavage on (0k0) concomitant with formation of fibers from the interlamellar amorphous regions which are drawn out to span the opening crack. With higher deformation the fibers pull out both lamellar crystal blocks and amorphous material as they increase in length, and the interconnectedness of the system quickly produces a complicated network of joined fibers in all directions. Fibrillar crystals can be seen to arise from crystallized amorphous (fiber) material at high elongations, from crystal blocks broken out of lamellae, and from chains drawn out of lamellae and recrystallized.

The total deformation morphology picture which emerges from this work is applicable as a model system for bulk, unoriented (spherulitic) polyethylene, and is particularly relevant to commercial processes for oriented polyethylene, such as melt blown or extruded film.

5.4 Microstructure of Solid State Extruded Polyethylene

Chapter IV examined the microstructure of a series of solid state extruded polyethylene fibers by wide and small angle x-ray scattering. Absolute intensities were measured using the two dimensional position sensitive detector at the Oak Ridge National Laboratories 10 meter SAXS
machine, allowing accurate values of the small angle scattering invariant for anisotropic samples to be obtained. The determination of the invariant for an anisotropic system required considerable effort, involving lengthy measurements at three different scattering geometries. A computer program was written to perform the integrations. The invariant, coupled with wide angle x-ray scattering and DSC thermal analysis permitted determination of the density of the noncrystalline component.

The use of a two phase model for solid state extruded polyethylene is justified if consideration is given to the effective densities of the crystalline and noncrystalline phases, which change with deformation. Use of ideal density values for a deformed system is invalid. Effective densities can be obtained by careful application of wide and small angle x-ray scattering methods for anisotropic systems. The effective density of the crystalline phase decreases by 1% (.999 to .990 g/cm³) for the unextruded billet compared to a 36 draw ratio extrudate while the noncrystalline phase density increases by 5% (.84 to .89 g/cm³). These changes lead to an overall decrease in the mean squared electron density fluctuation of 63%. Estimates of microstructure changes based on other measures such as peak intensity or area under a long period peak can lead to large errors, since these measures have no physical significance. In fact, reliance on the long period as a fundamental parameter, particularly for quantitative prediction of mechanical properties, should be reconsidered with the view that the long period although easily determined is not
always a truly meaningful or appropriate average measure of the microstructure.

The average axial crystallite length (lower bound) measured by wide angle x-ray scattering increases with extrusion draw ratio while the SAXS long period decreases and weakens considerably. These extensive morphological observations (including consideration of previous electron microscopy results) are fully consistent with the key features of the Peterlin model of fiber microstructure.

5.5 Possible Extensions to This Work

In this section a few questions and possible experiments are proposed as guidance for future studies. Realizing that it is far easier to talk about doing an experiment than to actually perform a good experiment, this section will nevertheless try to stimulate further experimentation in the area of polyethylene morphology and morphological methods in polymer science.

5.5.1 Oriented Thin Film Studies. The opportunity for study of thin oriented films by electron microscopy and, at the same time, the examination of the identical morphology in the bulk from layers of the same films is a rare opportunity for the polymer morphologist. Yang's measurements of the long period and crystal size distributions by electron microscopy and small and wide angle x-ray scattering showed excellent agreement among the different techniques [113]. The work in this dissertation has established the deformation microstructure for
polyethylene thin films, but no work was done on deformed layered bulk samples. Most of the models for polymer deformation have emerged based on indirect evidence (mostly scattering methods), and these techniques and approaches are very well developed. Many detailed inferences, especially from SAXS, such as the diffuseness and curvature of crystal-amorphous boundaries, can be critically examined with the opportunity for visually comparing microscopic with scattering results.

Other comparisons would be interesting, such as an assessment of chain orientation and lamellar orientation as a function of deformation, using wide angle x-ray and electron diffraction, versus small angle electron and x-ray scattering. In these films, the chains are better oriented than the lamellar normals, which is a result of the strain induced crystallization process. Void and microfiber sizes can be quantified by small angle scattering as well, and compared to microscopic observations. For example, the dependence of the fiber cross-sectional radius on draw ratio (see Figure 4.9) can be determined to examine the ideality of the rubber-like nature of the amorphous phase.

The next logical step in this study is deformation at elevated and/or lower temperatures, above the alpha transition or below the glass transition. A hot/cold deformation stage would be necessary, and would have to be custom built. Preliminary studies by this author placing the deformation holder in an oven, showed that at temperatures above the alpha transition the lamellae break up at lower levels of
strain, in agreement with dynamic studies of the α transition [204]. Lamellar separation was more heterogeneous, resembling the "piled lamellae" structure seen in SEM studies of blown films [205]. At low temperature, the crystals should break up into larger blocks, and the amorphous chains would behave as a glass below their $T_g$ (circa-150°C). Confirmation or refutation of the "string of pearls" low temperature deformation structure reported by Petermann [25] would be of interest.

Relaxation and annealing studies in situ would be useful to assess the stability of the fibrillar crystals at various strain levels. Petermann found reversibility up to about 100% elongation in his needle crystal reinforced lamellar films. The films investigated here which do not contain such fibrillar crystals should be even more elastic. Would annealing in the deformed state cause retraction of the fibers or crystallization?

A study of the birefringence during deformation would be interesting, since at up to several hundred percent strain no changes occur in the lamellae, while large orientational changes take place in the amorphous regions. This should allow separation of the birefringence into the crystalline and amorphous components, and could even be performed dynamically (form birefringence may be a problem).

It might be possible to use these model film systems to study the diffusion of chain segments in a semicrystalline polymer in a manner analogous to recent work by Crist [206]. A mixture of high molecular weight polyethylene with deuterated low molecular weight PE could be formed into an oriented film by the Yang method. After annealing, the
expected location of most of the lower molecular weight material would be the amorphous zones between lamellae. If the radius of gyration could be measured over a period of time by SANS (providing that any particle-particle interference effects do not extend into the Guinier region), any net movement of the deuterated species should be observable as a change in the radius of gyration. Differences in the diffusion rate could be enhanced by sample temperature variations. These studies could be compared to couplementary studies using solid state NMR where the local environment of the deuterated species is monitored. The evaluation of $R_g$ by SANS for these films would itself be useful for the study of the degree of extension of the molecules during the oriented crystallization process.

Other interesting studies can be envisioned. A continuous process for melt drawing films could be designed using a film extruder to coat solution onto a hot roller, with a take-off reel to pull the film off the roller at controllable rates. Modification of the melt drawing process to produce "biaxial" texture could be done by bubble-blowing from the hot surface. Production of larger quantities of uniaxial or biaxial film would certainly allow more bulk morphology studies to be performed, as well as mechanical property determinations. These continuous processes might be well suited for other polymers as well, and the applicability of melt drawing to other polymers has been demonstrated [132,207,208]

5.5.2 SAXS Studies of Solid State Extruded Polyethylene. The determination of the SAXS invariant for an oriented polymer system using a
two dimensional position sensitive detector is a natural consequence of the application of new methods to old problems. Numerous experiments can be performed as a new experimental method becomes available for use. The use of a PSD makes the study of oriented materials quantitative; the addition of high powered radiation sources makes the speed of such measurements faster, perhaps even fast enough to permit dynamic studies. The day-long SAXS measurements at ORNL in this dissertation would be far faster at a synchrotron, for example, if the detectors to accommodate the high count rates with good spatial resolution become available. Preliminary dynamic invariant studies have already been made at ORNL [209], but the requirements for quality data for accurate invariant calculations exceed that presently possible in the ORNL dynamic system, in the opinion of this author.

To further take advantage of the quantitative data from a two dimensional PSD, a logical extension of this work is to perform a two dimensional correlation function calculation, in the manner of Vonk [210]. Theory is well developed for the correlation function approach to SAXS analysis [186,211], and the extension to anisotropic systems may provide measures of the anisotropy of the degree of crystallinity, the specific surface, the electron density difference between phases, the average long period, and transition zone profiles analogous to the one dimensional (isotropic) case [212]. The requirement for quality data will be severe; both the accuracy and extent of the scattering patterns available on the ORNL system should prove extremely useful for this approach.
Modifications to the anisotropic invariant procedures developed here should include: (1) use of smaller azimuthal angle (\(\mu\)) intervals in the Porod analysis to examine the orientation dependence of the fluctuation scattering more carefully; (2) investigations of the use of nonlinear fitting functions in the Porod analysis, using a generalized fitting analysis that would not necessarily weight by the fourth power of the scattering vector. Although Porod's Law was derived [186] as an approximation (first non-zero term of a series) for isotropic, randomly dispersed particles, it has been found to be obeyed for anisotropic cases as well [190]. Generalization of the curve fit analysis should lead to more easily recognized functional dependence for different geometrical variations of the scattering medium; (3) modifications to the analysis from (2) should allow subtraction of a liquid scatter contribution that is scattering angle dependent, in a manner similar to, but not limited by the extrapolation methods of Ruland [197,198]; (4) several improvements in the data collection process, including sensitivity correction, transmission factor measurements, and incident beam measurement, will be considered in another publication [187]; (5) modification of the analysis to include a third phase (such as voids) is straightforward. The mean squared electron density fluctuation is model independent but equation (7) can be expanded to include other density differences between more than two phases. This has been demonstrated by Wu [213] and Stein [209]. The actual sorting out of the density differences can be nontrivial, however.
A definitive test for the presence of the tie molecules (crystalline bridges?) connecting the crystalline regions along a microfiber is that of annealing. The amount of retraction of a SSE fiber during annealing will depend upon the amount of crystallized tie chains, which would melt (and retract) at lower temperatures presumably than the crystal fibrillar blocks. Force-temperature measurements coupled with quantitative SAXS measurements would help determine the quantity of crystalline bridges.

Further studies of the noncrystalline component would be interesting. For example, Peterlin's work [200,201] indicates that small molecule absorption by fibers decreased with drawing, and (as we confirm) that densification of the noncrystalline regions during drawing is the likely cause. Since the noncrystalline zones are probably oriented in SSE PE, mass transport should be anisotropic, with more absorption in the fiber direction than perpendicular to the fiber. Knowledge of the orientation of the noncrystalline component would be useful; this can perhaps be determined by NMR [159] or by birefingence [154,202].

Independent values of the noncrystalline orientation would be useful for reexamination of the fluctuation scattering. Are the defect-dependent fluctuations isotropic (as measured at \( \leq 4^\circ \) K, to freeze out the phonon scattering contribution), and can one separate the noncrystalline and crystal contributions? Samples for such investigations could include Kanamoto's [149] recent ultra-highly drawn SSE PE, which is nearly single crystal (by WAXS) with no detectable long period (by SAXS), or highly crystalline high pressure crystallized PE [214].
In terms of the current status of high modulus flexible chain polymers, Kanamoto's material [149] is very exciting. It would be very interesting to examine quantitatively by SAXS the noncrystalline density, if indeed any small angle scattering except that from voids is measureable. Since the degree of crystallinity is over 90%, the SAXS intensity will be very weak, and the quantitative SAXS experiment could only be performed on the ORNL machine.
REFERENCES


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APPENDIX A

POLYETHYLENE STRUCTURE FACTOR PROGRAM

The calculated structure factors listed in Table 2.1 were computed by the program PESF. This computer program is specific to polyethylene and uses the structural data reported by Kavesh and Schultz [215]. The space group used was Pna21, with a = 7.388 Å, b = 4.929 Å and c = 2.539 Å. The structure factor calculations follow their equation 14, using electron scattering factors interpolated from data of Hirsch et al. [216]. Relativistic corrections can be applied for electron energies from 20 to 200 KeV. An electron microscope camera constant can be input to calculate the distance on the film (in mm) from the direct beam to any of the calculated reflections. Output also includes the d-spacing in Å, 2θ in milliradians, and separate lists of the structure factor for carbon atoms only (FC), for hydrogen atoms only (FH), the total calculated structure factor (F), and the intensity (I = F²). X-ray structure factors can also be calculated, which requires the x-ray wavelength and sample-to-film distance. For x-rays, carbon scattering factors are from Cromer & Mann [217], and hydrogen scattering factors are from Stewart, Davidson and Simpson [218]. The 2θ output is in degrees.
PROGRAM PESF (INPUT, OUTPUT)

CALCULATES STRUCTURE FACTORS FOR POLYETHYLENE USING THE
STRUCTURAL DATA FROM: S. KAVESH AND J. M. SCHULTZ,

REAL H,K,L,KV

100 WRITE(1,901)
901 FORMAT ('POLYETHYLENE STRUCTURE FACTOR PROGRAM')
TP=2.0*3.1415926535
110 WRITE(1,902)
902 FORMAT ('INPUT H,K,L LIMITS, IE H,H, ETC :')
READ(1,*),ERR=110 IHMAX,IHMIN,IKMAX,IKMIN,ILMAX,ILMIN
120 WRITE(1,903)
903 FORMAT ('X-RAY (1) OR ELECTRON (0) DIFFRACTION?')
READ(1,*),ERR=120 IX
IF(IX .EQ. 1) GO TO 300

130 WRITE(1,904)
904 FORMAT ('INPUT ELECTRON KV :')
READ(1,*),ERR=130 KV
IF (KV .NE. 20.) GO TO 140
WAV=0.08588
GAMMA=1.0391
GO TO 200
140 IF (KV .NE. 40.) GO TO 150
WAV=0.06014
GAMMA=1.0783
GO TO 200
150 IF (KV .NE. 60.) GO TO 160
WAV=0.04865
GAMMA=1.1174
GO TO 200
160 IF (KV .NE. 80.) GO TO 170
WAV=0.04177
GAMMA=1.1565
GO TO 200
170 IF (KV .NE. 100.) GO TO 180
WAV=0.03702
GAMMA=1.1957
GO TO 200
180 IF (KV .NE. 200.) GO TO 190
WAV=0.02508
GAMMA=1.3915
GO TO 200
190 WRITE(1,905)
905 FORMAT ('KV INPUT IN ERROR, PLEASE REPEAT:')
GO TO 130
200 WRITE(1,906)
IF(DYN.EQ.0)
GAMMA=1.0
GO TO 400
C
300 GAMMA=1.0
310 WRITE(1,907)
907 FORMAT('INPUT WAVELENGTH (ANGSTOMS)')
READ(1,*,ERR=310) WAV
C
400 WRITE(1,908)
908 FORMAT('DO YOU WANT TO ELIMINATE SYSTEMATIC ABSENCES (YES=1):')
READ(1,*,ERR=400) ISYS
410 IF(IX.EQ.0) WRITE(1,909)
IF(IX.EQ.1) WRITE(1,910)
909 FORMAT('INPUT CAMERA CONSTANT (0. MEANS 460. MM)')
910 FORMAT('INPUT THE SAMPLE TO FILM DISTANCE (MM)')
READ(1,*,ERR=410) CONST
IF(CONST.EQ.0.) CONST=460.
C
A=7.388
B=4.929
C=2.539
X=0.041
Y=0.060
Z=0.250
500 WRITE(1,911)
911 FORMAT(///,2X,'H','S',K',S',L',S',D',S',2-THETA',S',DIST',S',FC',S',FH',S',F',S',F**2,/) DO 600 IH=IHMIN,IHMAX,1 DO 600 IK=IKMIN,IKMAX,1 DO 600 IL=ILMIN,ILMAX,1 IF(IH.EQ.0.AND.IK.EQ.0.AND.IL.EQ.0) GO TO 600 IF(ISYS.NE.1) GO TO 520 IF(IK.NE.0) GO TO 510 IF(MOD(IH,2).NE.0) GO TO 600
510 IF(IH.NE.0) GO TO 520 Kl=IK+IL IF(MOD(KL,2).NE.0) GO TO 600
520 H=FLOAT(IH)
K=FLOAT(IK)
L=FLOAT(IL)
DD=(H+H)/(A*A)+(K*K)/(B*B)+(L*L)/(C*C)
D=1.0/SQRT(DD)
TD=1./(2.*D)
TTH=2.*ASIN(WAV*TD)
IF(IX.EQ.1) TTH=TTH*360./TPI
IF(IX.EQ.0) TTH=TTH*1000.
CALL SCAT(TD,GAMMA,FC,FH,IX,IERR)
IF(IERR.NE.1) GO TO 530
WRITE (2,912) IH,IK,IL,TD
FORMAT(//,'HKL=',J13,','SIN THETA/LAMDA=,’F6.3,/)
GO TO 600

COS1=H*X-K*Y+Z*L
COS2=H*(0.5-X)+K*(0.5-Y)+L*(Z+0.5)
COS3=H*X+0.143*K*Y+L*Z
COS4=H*(X-0.03)+K*(-0.21-Y)+L*Z
COS5=H*(0.357-X)+K*(0.52-Y)+L*(Z+0.5)
COS6=H*(0.53-X)+K*(Y+0.29)+L*(Z+0.5)
FC1=2.*FC1*(COS(TPI*COS1)+COS(TPI*COS2))
FC2=2.*FH*(COS(TPI*COS3)+COS(TPI*COS4)+COS(TPI*COS5)+COS(TPI*COS6))
FHKL=FC1+FC2
F2HKL=FHKL**2
DUM2=WAV+TD
DUM1=2.*ASIN(DUM2))
TAN=SIN(DUM1)/COS(DUM1)
DIST=CONST*TAN
WRITE(1,913) IH,IK,IL,D,TTH,DIST,FC1,FC2,FHKL,F2HKL

END

C

SUBROUTINE SCAT(STL,GAMMA,C,H,IX,IERR)
DIMENSION FC(17),FH(17),STLC(17),FCX(17),FHX(17)
DATA FC/2.45,2.25,2.09,1.74,1.43,1.15,0.92,0.74,0.6,0.41,0.3,0.22,
+ 0.18,0.14,0.12,0.1,0.08/
DATA FH/0.529,0.508,0.453,0.382,0.311,0.249,0.199,0.160,0.131,
+ 0.089,0.064,0.048,0.037,0.029,0.024,0.02,0.017/
DATA FCX/6.0,5.752,5.115,4.321,3.569,2.954,2.496,2.172,1.949,1.68,
+ 1.536,1.425,1.322,1.218,1.113,1.011,0.913/
DATA FHX/0.997,0.946,0.813,0.643,0.479,0.342,0.251,0.184,0.136,0.1,
+ 0.93,0.037,0.019,0.012,0.009,0.008,0.008/
DATA STLC/0.0.05,0.1,0.15,0.2,0.25,0.3,0.35,0.4,0.5,0.6,0.7,0.8,
+ 0.9,1.0,1.1,1.2/
IF (STL .LE. 1.2) GO TO 100
WRITE(1,901)
FORMAT(‘THETA TOO LARGE FOR SCATTERING FACTOR SUBROUTINE’)

CONTINUE

C

912 WRITE (2,912) IH,IK,IL,TD
FORMAT(//,’HKL=’,J13,’SIN THETA/LAMDA=’,F6.3,/)
GO TO 600

530 COS1=H*X-K*Y+Z*L
COS2=H*(0.5-X)+K*(0.5-Y)+L*(Z+0.5)
COS3=H*X+0.143*K*Y+L*Z
COS4=H*(X-0.03)+K*(-0.21-Y)+L*Z
COS5=H*(0.357-X)+K*(0.52-Y)+L*(Z+0.5)
COS6=H*(0.53-X)+K*(Y+0.29)+L*(Z+0.5)
FC1=2.*FC1*(COS(TPI*COS1)+COS(TPI*COS2))
FC2=2.*FH*(COS(TPI*COS3)+COS(TPI*COS4)+COS(TPI*COS5)+COS(TPI*COS6))
FHKL=FC1+FC2
F2HKL=FHKL**2
DUM2=WAV+TD
DUM1=2.*ASIN(DUM2))
TAN=SIN(DUM1)/COS(DUM1)
DIST=CONST*TAN
WRITE(1,913) IH,IK,IL,D,TTH,DIST,FC1,FC2,FHKL,F2HKL

END

C

610 WRITE(1,914)
914 FORMAT(//,’REPEAT PROGRAM (YES=1):’)
READ(1,*,ERR=610) IYN
IF(IYN .EQ. 1) GO TO 100
STOP
END

C

SUBROUTINE SCAT(STL,GAMMA,C,H,IX,IERR)
DIMENSION FC(17),FH(17),STLC(17),FCX(17),FHX(17)
DATA FC/2.45,2.25,2.09,1.74,1.43,1.15,0.92,0.74,0.6,0.41,0.3,0.22,
+ 0.18,0.14,0.12,0.1,0.08/
DATA FH/0.529,0.508,0.453,0.382,0.311,0.249,0.199,0.160,0.131,
+ 0.089,0.064,0.048,0.037,0.029,0.024,0.02,0.017/
DATA FCX/6.0,5.752,5.115,4.321,3.569,2.954,2.496,2.172,1.949,1.68,
+ 1.536,1.425,1.322,1.218,1.113,1.011,0.913/
DATA FHX/0.997,0.946,0.813,0.643,0.479,0.342,0.251,0.184,0.136,0.1,
+ 0.93,0.037,0.019,0.012,0.009,0.008,0.008/
DATA STLC/0.0.05,0.1,0.15,0.2,0.25,0.3,0.35,0.4,0.5,0.6,0.7,0.8,
+ 0.9,1.0,1.1,1.2/
IF (STL .LE. 1.2) GO TO 100
WRITE(1,901)
FORMAT(‘THETA TOO LARGE FOR SCATTERING FACTOR SUBROUTINE’)
IERR=1
RETURN

100 DO 200 I=1,17
  IF(STL .EQ. STLC(I)) GO TO 110
  IF(STLC(I) .LT. STL) GO TO 200
  GO TO 130

110 IF(Ix .EQ. 1) GO TO 120
  C=FC(I)
  H=FH(I)
  GO TO 210

120 C=FCX(I)
  H=FHX(I)
  GO TO 210

130 II=I-1
  IF(Ix .EQ. 1) GO TO 140
  C=(FC(II+1)-FC(II))**((STL-STLC(II))/(STLC(II+1)-STLC(II)))
    + FC(II)
  H=(FH(II+1)-FH(II))**((STL-STLC(II))/(STLC(II+1)-STLC(II)))
    + FH(II)
  GO TO 210

140 C=(FCX(II+1)-FCX(II))**((STL-STLC(II))/(STLC(II+1)-STLC(II)))
    + FCX(II)
  H=(FHX(II+1)-FHX(II))**((STL-STLC(II))/(STLC(II+1)-STLC(II)))
    + FHX(II)
  GO TO 200

200 CONTINUE

210 CONTINUE
  C=C*GAMMA
  H=H*GAMMA
  IERR=0
  RETURN
END

C

FUNCTION ASIN(X)

C

TANG=X/SQRT(1.0-X**2)
ASIN=ATAN(TANG)
RETURN
END
## Example Calculations

### Polyethylene Structure Factor Program

**Input HKL limits, IE +H-M, etc:**

2 0 2 0

**X-ray (1) or electron (0) diffraction?**

0

**Input electron kv:**

100

Do you want relativistic corrections (NO=0, YES=1)?

0

Do you want to eliminate systematic absences (YES=1)?

1

**Input camera constant (°), means (Å, mm):**


<table>
<thead>
<tr>
<th>H</th>
<th>K</th>
<th>L</th>
<th>2-Theta</th>
<th>DIST</th>
<th>FC</th>
<th>FH</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>2</td>
<td>1.2788</td>
<td>29.16</td>
<td>13.6</td>
<td>-2.47</td>
<td>-1.40</td>
</tr>
<tr>
<td>0</td>
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**Repeat program (YES=1):**

0

### Polyethylene Structure Factor Program

**Input HKL limits, IE +H-M, etc:**

2 0 2 0

**X-ray (1) or electron (0) diffraction?**

1

**Input wavelength (Ångstroms):** 1.5417

Do you want to eliminate systematic absences (YES=1)?

YES

**Input the sample to film distance (mm):**

29.
REPEAT PROGRAM (YES=1):

1

POLYETHYLENE STRUCTURE FACTOR PROGRAM

INPUT H,K,L LIMITS, IE =+H,-K, ETC:

2 0 2 0

X-RAY (1) OR ELECTRON (0) DIFFRACTION?

0

INPUT ELECTRON KV:

100

DO YOU WANT RELATIVISTIC CORRECTIONS (NO=0, YES=1):

1

DO YOU WANT TO ELIMINATE SYSTEMATIC ABSENCES (YES=1):

1

INPUT CAMERA CONSTANT (0. MEANS 460. MM):

460.

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APPENDIX B
APPENDIX B

AN INVARIANT PROGRAM FOR THE ORNL 10 METER SAXS CAMERA

This FORTRAN program was written for use on the MODCOMP II computer system at the National Center for Small Angle Scattering Research, Oak Ridge National Laboratories, Oak Ridge, Tennessee. Before the execution of this program, execution of other preliminary programs is necessary to correct two-dimensional data from the 10 meter SAXS machine, as given in the ORNL instruction manual. A brief explanation of the units involved and nomenclature for the ORNL system is useful before describing the computer program.

Making no assumptions about the nature of the scattering material, i.e., particle shape, dispersity, or composition of the sample, the quantity measurable is the mean squared electron density fluctuation, \( (\rho - \bar{\rho})^2 \), often called the scattering power of the material [188]. This quantity is proportional to the integrated scattered intensity or Porod invariant \( Q \) [186,219]:

\[
(\rho - \bar{\rho})^2 = K Q, \tag{B.1}
\]

where \( Q \) is the scattered intensity measured over all angles, usually expressed in the form (for pinhole collimation)

\[
Q = \int_0^\infty m^2 I(m)dm. \tag{B.2}
\]
Following the nomenclature from Chapter IV of Alexander [188], \( m \) is the linear distance between the incident beam and the scattered beam in the plane of the detector (see Figure B.1). If \( 2\theta \) is the angular difference between the two beams, then \( m = 2a \sin \theta \), where \( a \) is the sample-to-detector distance, or for small angles, \( m = 2a\theta \). Other measures in the literature can be related to these definitions, such as: \( s = 2 \sin \theta / \lambda \), and \( q = 4\pi \sin \theta / \lambda \) where \( \lambda \) is the wavelength of the x-ray beam (\( \lambda \)) (note: \( q = k \) at ORNL NCSASR).

\( I(m) \) is the measured intensity at any scattering angle \( m \), in absolute units. This absolute intensity is the ratio of the observed scattered intensity \( P(m) \) to the intensity of the incident beam \( P_0 \):

\[
I(m) = \frac{P(m)}{P_0} T \varepsilon e^{-\mu t} \frac{\lambda_1^2 \lambda_2^2}{a^2}.
\]

(B.3)

An incident beam of intensity \( P_0 \) measured in the plane of the detector, per area of sample illuminated (counts per sec per cm\(^2\)), is scattered by a sample with scattering probability \( T \) (Thomson's cross-section per electron, \( 7.94 \times 10^{-26} \) cm\(^2\)) of volume \( t \lambda_1^2 \) (thickness \( t \) cm with area \( \lambda_1^2 \), cm\(^2\)) with attenuation factor \( e^{-\mu t} \) (\( \mu \) is the linear mass absorption coefficient in cm\(^{-1}\)). The scattered intensity, \( P(m) \), in e\(^2\) cts/sec is recorded by a detector element of solid angle \( \lambda_2^2/a^2 \) (cm\(^2\)/cm\(^2\)), and the units of \( I(m) \) are therefore e\(^2\)/cm\(^3\). The units of \( Q \) then are seen to be e\(^2\)cm after integrating \( I(m) \) over all \( m \), and in order to arrive at \((\rho-\sigma)^2\) in (mole e\(^-\) per cm\(^3\))^2, \( K \) in equation 1 contains \( 4\pi/\text{NA}^2 \lambda^3 \), where \( \text{NA} \) is Avogadro's number and \( \lambda \) is now the
Figure B.1 Geometry and scattering angle relationships for the ORNL 10 meter small angle scattering system.

\[
S = \frac{2 \sin \theta}{\lambda}
\]

\[
q = k = \frac{4 \pi \sin \theta}{\lambda}
\]

\[
m = 2 \alpha \sin \theta
\]
wavelength in cm.

The flow chart for the sequence of steps necessary to generate a proper invariant is given in Figure B.2. The program uses data stored in either the floating point memory (CAMAC) or in the data base. If the data is to be fetched from the data base, it should have already been corrected by program BKC for dark current, detector sensitivity, and background scattering. If the data is in the floating point memory, it is important to know whether or not the user has "renormalized" the data back to original data after CORRUN or DIFFER has divided by monitor counts over 1000. If CORRUN or DIFFER was executed without renormalization (i.e., not inserting a multiplicative constant equal to monitor counts/1000), the data have already been divided by MON/1000, the count time has been reduced similarly, and the data have been divided by the transmission coefficient. The questions regarding count time and transmission factor should then be answered "NO" and "YES" respectively.

The interactive questions are generally self-explanatory, but several deserve additional comment. Origin limits (MR2,MR1) are input in milliradians, e.g. 4,2 for 4 milliradians in the X or M2 direction and 2 milliradians in the Y or M1 direction. This establishes a rectangle of data 4 by 2 mrad centered at CX,CY which will be excluded from the integration. A reply of 0,0 will include all the data. For 5 meter geometry data these limits are used to exclude low angle void scattering. For 2 or 1 meter geometry data these limits are used to "splice" data by not including data to be used in the integral
Figure B.2. Flow chart of program execution for invariant analysis.
calculated at another geometry. The question concerning the low angle approximation should be answered yes (for 5 meter data) if you want to perform an ellipsoidal approximation for the excluded portion contribution to the invariant. This approximation calculates the volume of an oblate ellipsoid of revolution \( V = \frac{4}{3} \pi a^2 b \), \( b \) is in M1 or Y direction) of minor axis radius MR1 and major axis radius MR2. The intensity value in three adjoining cells on both sides of each axis (at + MR1 and + MR2) are averaged, then the low angle integrated intensity is calculated as \( \text{SUMLA} = (\text{volume of ellipsoid}) \times (I_{\text{average}}) \).

The high angle limits (in milliradians) are also required, and should always be used to eliminate the edges of the detector, at least. These limits can also be used to "splice" data sets together by selecting upper limits at one geometry equal to the lower limits of the next longer geometry.

Liquid scatter counts (fluctuation scattering) are input for three azimuthal angles: 0°, 45° and 90°. These values are obtained from Porod plots \( (k^4 I \text{ vs. } k^4, \text{ slope } = F_k) \) in the 1-meter geometry, although a reasonably good approximate value is the minimum value of the corrected intensity at the limit of the 2 meter geometry data. The liquid scatter correction must be scaled for the different geometry data sets. There is no provision at present for applying a liquid scatter correction with scattering angle dependence. Splice factors can be calculated with the program CMB (Combine). \( F_k(\mu) \) is subtracted from the measured intensity in sectors of \( 0^\circ \leq \mu \leq 22.5^\circ \), \( 22.5^\circ < \mu \leq 67.5^\circ \), and \( 67.5^\circ < \mu \leq 90^\circ \).
After FP is subtracted, the corrected intensity data are stored in the floating point array, thereby overwriting the uncorrected data. If data was fetched from the data base, the corrected data are placed in the floating point array for further calculations. The summations for the integrated intensity simply weight each cell intensity by the scattering vector magnitude S2 (line 198), and store the running total in SUM. This is printed as the integrated intensity. Several other totals are accumulated, including the number of negative cells ICELL (i.e. F2 was greater than I), the total integrated counts TOTAL (should match the value printed out by CORRUN or DIFFER), the low angle integrated intensity SUMLA, the number of cells in the integrated intensity ISUMCL, and the total counts minus liquid scatter counts TOTDAT.

Q is then given in line 250 by (SUM + SUMLA)/(IO*CT*TMM), with units of e²/cm. The mean-squared electron density fluctuation MSEDF is equal to KQ, where K = 1/(THOMSN x AVOGAD² x STH * DIST2 * LAMBDA³), with MSEDF in units of (mole e/cm³)². All variables are defined in the comment statements in the program.
C

!C

1

PROGRAM INVVAR
2

C

C GLOBAL COMMONS USED:
3 C DATA #EFCC #1004
4 C ONEDTA #ECB0 #258
5 C HEADER #EF00 #64
6 C CSL01 #EFCC #18
7 C
8 C

9 C

C*******************************************************************************
10 C** PROGRAM TO CALCULATE THE INTEGRATED INTENSITY (Q) AND THE MEAN ***
11 C** SQUARE ELECTRON DENSITY FLUCTUATION (HSDEF) FOR A CYLINDRI-
12 C** CALL SYMMETRIC SAXS PATTERN ABOUT M1 (H1=0.0 DEG). ***
13 C** THE LOW ANGLE INTENSITY IS APPROXIMATED AS A CONSTANT ***
14 C** INTEGRATED OVER THE VOLUME OF AN ELLIPSOID ABOUT M1 IF DESIRE D.***
15 C** ANISOTROPIC LIQUID SCATTER CORRECTION
16 C** REQUIRES THREE VALUES OF FL AT 0, 45, 90 DEG AZIMUTHAL ANGLE.
17 C** VERSION NOVEMBER 4, 1983
18 C** IMPORTANT VARIABLES:
19 C** C1 = COUNTING TIME (SEC)
20 C** TM = SAMPLE TRANSMISSION
21 C** STH= SAMPLE THICKNESS (CM)
22 C** CPCM=CHANNEL PER CM
23 C** DIST2 = SAMPLE-DETECTOR DISTANCE (CM)
24 C** XCH = NUMBER OF CHANNELS ALONG X
25 C** YCH = NUMBER OF CHANNELS ALONG Y
26 C** ICELL=NUMBER OF NEGATIVE CELLS
27 C** ID=INCIDENT BEAM INTENSITY (COUNTS PER SECOND)
28 C** MR1,MR2=Y,X LOW ANGLE LIMITS (MILLIRADIANS)
29 C** MR3,MR4=Y,X HIGH ANGLE LIMITS (MILLIRADIANS)
30 C** LAMBDA = XRAY WAVELENGTH (CM)
31 C** AVOGAD = AVOGADRO'S NUMBER
32 C** THOMSN = THOMSON'S NUMBER (CM**2)
33 C** CX = X CENTER OF PATTERN (CHANNELS)
34 C** CY = Y CENTER OF PATTERN (CHANNELS)
35 C** FLS(I) = LIQUID SCATTER COUNTS AT 0,45, AND 90 DEGREES H1
36 C** M1 = SCATTERING VECTOR MAGNITUDE IN Y
37 C** DIRECTION ON DETECTOR PLANE (CH)
38 C** M2 = SCATTERING VECTOR MAGNITUDE IN X
39 C** DIRECTION ON DETECTOR PLANE (CH)
40 C** SUM = M2 WEIGHTED INTEGRATED INTENSITY (CM CTS)
41 C** SULMA = LOW ANGLE INTEGRATED INTENSITY
42 C** ISUMCL = NUMBER OF CELLS IN INTEGRATED INTENSITY
43 C** Q = ABSOLUTE INTEGRATED INTENSITY (E**2 CM)
44 C** HSDEF = MEAN SQUARE ELECTRON DENSITY FLUCTUATIONS
45 C** (MOLE ELECTRONS/CM**3)**2
46 C*******************************************************************************
47 C
48 C
DIMENSION IDATA(64,64)
DIMENSION FINPT(3),FLS(3)
REAL 10, LAMBDA, KR1, KR2, MSED, X, LS, MU, M1, M2, M3, M4
INTEGER ANS(3), HEDREC(100), XCH, YCH
COMMON/DATA/IDUM1, IDUM2, M, N, IDATA
COMMON/HEADER/HEDREC
COMMON/MANAGE/MAXREC, MXWRDS, LU, IDEM
COMMON/CSEL/NGC, NRTC, NSMS, NSHM, NSBB01
EQUIVALENCE (HEDS, HEDREC(9))
EQUIVALENCE (CPM, HEDREC(68)), (IK, HEDREC(52)), (DIST2, HEDREC(62))
EQUIVALENCE (CX, HEDREC(42)), (CY, HEDREC(44)), (YCH, HEDREC(11))
EQUIVALENCE (XCH, HEDREC(12)), (CLME, HEDREC(36))
DEFINE FILE 21(12992, 200, L, NXTRC)

LU = 21
MAXREC = 12992
MXWRDS = 100
IDEM = 4100
PI = 4.0 * ATAN(1.0)
P0 = PI / 8.
P3 = PI * 3. / 8.
AVOGAD = 6.0228E23
LAMBDA = 1.5417E-08
THDISH = 7.94E-26

20 CONTINUE
WRITE(6,45)
45 FORMAT(///,1H,'---ANISOTROPIC INVARIANT PROGRAM'), //,
      1H, ' VERSION NOVEMBER 4, 1983', ///)
WRITE(6,40)
40 FORMAT(1H, 'TYPE "1" IF DATA TO BE FETCHED FROM DATA BASE', 
      1', ' & TYPE "2" IF DATA FROM FLOATING POINT CADAC STORAGE')
CALL FREEFM(5,1,FINPT)
ILOC = FINPT(1)
IF(ILOC.EQ.2) GO TO 50
WRITE(6,30)
30 FORMAT(///,1H, 'ENTER DATA SET SEQUENCE NO.')
CALL FREEFM(5,1,FINPT)
ISEQ = FINPT(1)
NERR = 0
CALL FETCH(ISEQ, NERR, MAXREC, MXWRDS, LU, IDEM)
IF(NERR .EQ. 0) GO TO 50
GO TO 20

50 ICELL = 0
CONVERT VARIABLES TO CENTIMETERS
CPCH = CPM * 10.0
DIST2 = DIST2 / 10.0
WRITE(6,60) HEDREC(1)
60 FORMAT(1H,'IN Variant ANALYSIS FOR :',16/
WRITE(6,70) (HEDREC(I),I=76,100)
70 FORMAT(10X,'TITLE : ',25A2)
IF(CX.NE.0..OR.CY.NE.0.) GO TO 75
WRITE(6,72)
72 FORMAT(1H,'CENTER THE PATTERN! ENTER CX,CY:')
CALL FREEFM(5,2,FINPT)
CX=FINPT(1)
CY=FINPT(2)
IF(CX.NE.0..OR.CY.NE.0.) GO TO 75
GO TO 295
75 WRITE(6,80) TH,CPCCH,DIST2,CX,CY
80 FORMAT(1H,'THE SAMPLE TRANSMISSION = ',11X,F8.3/
X' THE CHANNELS PER CM = ',15X,F8.2/
X' THE SAMPLE-DETECTOR DISTANCE IN CM = ',F8.2/
X' THE CENTER OF PATTERN : CX = ',F8.2/
X' CY = ',F8.2//)
CT=CTIME
WRITE(6,82) CT
82 FORMAT(1H,'THE COUNT TIME IN SECONDS = ',F8.1/,1H,'DO YOU WANT ?,
1?'TU CHANGE THIS? TYPE Y OR N...')
READ(5,230) ANS
IF(ANS(1).NE.'Y') GO TO 89
WRITE(6,84)
84 FORMAT(1H,'INPUT THE COUNT TIME IN SECONDS')
89 READ(5,85) CT
85 FORMAT(F8.1)
WRITE(6,90)
90 FORMAT(1H,'ENTER THE SPECIMEN THICKNESS IN CM')
CALL FREEFM(5,1,FINPT)
5TH = FINPT(1)
WRITE(6,110)
110 FORMAT(1H,'ENTER THE INCIDENT INTENSITY IN CPS')
CALL FREEFM(5,2,FINPT)
10 = FINPT(1)
WRITE(6,130)
130 FORMAT(1H,'ENTER THE ORIGIN LIMITS IN MRAD IN X & Y DIR.')
CALL FREEFM(5,2,FINPT)
MR2 = FINPT(1)
MR1 = FINPT(2)
ANS(1)='N'
ISW=0
WRITE(6,135)
135 FORMAT(1H,'APPROXIMATE THE LOW ANGLE INTENSITY?')
READ(5,230) ANS
230 FORMAT(3A1)
IF(ANS(1).EQ.'Y') ISW=1
WRITE(6,140)
140 FORMAT(1H , 'ENTER THE HIGH ANGLE LIMITS IN MRAD IN X & Y DIR.',)
CALL FREEFM(5,2,FINPT)
MR3=FINPT(1)
MR3=TAN(MR3/1000.)*DIST2
MR4=TAN(MR4/1000.)*DIST2
MR1 = TAN(MR1/1000.)*DIST2
MR2 = TAN(MR2/1000.)*DIST2
WRITE(6,150)
150 FORMAT(1H , 'ENTER THE LIQUID SCATTERING COUNTS:',
& 3 VALUES FROM FOKOD PLOT AT MU=0, 45, 90 DEC. ')
CALL FREEFM(5,3,FINPT)
FLS(1) = FINPT(1)
FLS(2) = FINPT(2)
FLS(3) = FINPT(3)
ICELL=0
SUM = 0.0
TOTAL = 0.0
ISUMCL=0
151 WRITE(6,150)
152 PRINT FORMAT(2F6.1)
153 DO 190 J=1,YCH
154 DO 180 I=1,XCH
155 X=FLOAT(I)
156 Y=FLOAT(J)
157 K2=ABS((CX-X)/CPCM)
158 K1=ABS((CY-Y)/CPCH)
159 IF(M1.EQ.0.0) M1=0.00001
160 MU=ATAN(M2/M1)
161 IF(MU.GT.0.8) GO TO 141
162 LS=FLS(1)
163 GO TO 145
164 141 IF(MU.GT.0.9) GO TO 142
165 LS=FLS(2)
166 GO TO 145
167 142 LS=FLS(3)
168 145 IF(IL0C.EQ.2) GO TO 155
169 C*** CALCULATE SUM OF ALL DATA POINTS AND PI*SUM**2 IGNORING DATA
170 C*** IN AN ELLIPSE ABOUT THE ORIGIN IF THE LOW ANGLE INTENSITY IS
171 C*** TO BE ESTIMATED (ISW=1) - OTHERWISE IGNORE A RECTANGLE
172 DO 190 J=1,YCH
173 DO 180 I=1,XCH
174 X=FLOAT(I)
175 Y=FLOAT(J)
176 K2=ABS((CX-X)/CPCH)
177 K1=ABS((CY-Y)/CPCH)
178 C*** CALCULATE SECTOR FOR LIQUID SCATTER CORRECTION
179 IF(M1.EQ.0.0) M1=0.00001
180 MU=ATAN(M2/M1)
181 IF(MU.GT.0.8) GO TO 141
182 LS=FLS(1)
183 GO TO 145
184 141 IF(MU.GT.0.9) GO TO 142
185 LS=FLS(2)
186 GO TO 145
187 142 LS=FLS(3)
188 C*** STORE LS CORRECTED DATA IN FLOATING POINT ARRAY
189 145 IF(IL0C.EQ.2) GO TO 155
```
184  RDAT=FLOAT(IDATA(I,J))-LS
185  CALL FPUT2(1,I,J,RDAT)
186  GO TO 156
187  155  RDAT=(FGET2(1,1,I,J))-LS
188  156  TOTAL=TOTAL+IDATA(I,J)
189  TOTDAT=TOTDAT+RDAT
190  IF(H1.GT.MR3.OR.M2.LT.MR4) GO TO 180
191    IF(ISW.EQ.1) GO TO 160
192    IF(H1.LT.MR1.AND.M2.LT.MR2) GO TO 180
193    LD TO 170
194  160  E=H1**2/MR1**2+H2**2/MR2**2
195    IF(E.LE.1.) GO TO 180
196  170  IF(RDAT.LT.0.0) ICELL=ICELL+1
197    SUM=SUM+PI*RDAT*M2
198  180  CONTINUE
200  190  CONTINUE
201  SUML=0.0
202    IF(ISW.EQ.0) GO TO 200
203  *** APPROXIMATE THE LOW ANGLE INTENSITY AS AN AVERAGE OF
204  *** THREE CELLS ON EACH SIDE OF THE X AXIS AND THREE ON
205  *** EACH SIDE OF THE Y AXIS TIMES THE VOLUME OF AN OBLATE
206  *** ELLIPSOID (CONSTANT VALUE APPROXIMATION)
207    I2=INT(CX)
208    IC11=INT(CY-MR1*CPCH+.5)
209    IC12=INT(CY+MR1*CPCH+.5)
210    DAT11 = FGET2(1,I2,IC11)
211    DAT12 = FGET2(1,I2+1,IC11)
212    DAT13 = FGET2(1,I2-1,IC11)
213    DAT14 = FGET2(1,I2,IC12)
214    DAT15 = FGET2(1,I2+1,IC12)
215    DAT16 = FGET2(1,I2-1,IC12)
217    I1=INT(CY)
218    IC21=INT(CX-MR2*CPCH+.5)
219    IC22=INT(CX+MR2*CPCH+.5)
220    DAT21 = FGET2(1,IC21,11)
221    DAT22 = FGET2(1,IC21,11+1)
222    DAT23 = FGET2(1,IC21,11-1)
223    DAT24 = FGET2(1,IC22,11)
224    DAT25 = FGET2(1,IC22,11+1)
225    DAT26 = FGET2(1,IC22,11-1)
227    SUMLA=4.*PI/3.*MR1**2*MR2*(DAT1+DAT2)/2.
```
228      200 WRITE(6,210) ICELL
229      210 FORMAT(//,IH,'THE NUMBER OF NEGATIVE CELLS = ',I5)
230      260 WRITE(6,270) TOTAL
231      270 FORMAT(//,IH,'THE TOTAL INTEGRATED COUNTS = ',E15.6)
232      280 WRITE(6,275) SUMLA, SUM, ISUMCL
233      290 FORMAT(//,IH,'THE LOW ANGLE INTENSITY = ',E15.6,
234          +/IH,'THE INTEGRATED INTENSITY = ',E15.6,
235          +/IH,'THE NUMBER OF CELLS IN INTEGRATED INTENSITY = ',I4)
236      300 WRITE(6,276) TOTAL
237      310 FORMAT(//,IH,' THE TOTAL(COUNTS-LS) = ',E15.6)
238      320 C*** CALCUATE Q AND MSEDF FROM THE SUM##2 OF THE DATA ARRAY C***
239      330 C*** COKKH, DIFFER, AND OTHERS HANDLING FLOATING POINT DATA
240      340 C*** DIVIDE BY THE TRANSMISSION FACTOR. OLD HKC PROGRAM DOES NOT...
241      350        TM=1M
242      360        IF(NCDS.NE.1) GO TO 279
243      370        WRITE(6,277)
244      380      277 FORMAT(1H,'ACCORDING TO THE HEADER RECORDS, YOUR DATA HAS',
245               1H,'PREVIOUSLY BEEN DIVIDED BY THE TRANSMISSION FACTOR...',
246               1H,'DO YOU AGREE? TYPE Y OR N... Y WILL RESULT IN DATA',
247               1H,'MUT BEING DIVIDED BY TM IN THIS PROGRAM."
248      390        READ(5,230) ANS
249      400        IF(ANS(1).EQ.1HY) TMH=1.0
250      410      279 W=(SUM+SUMLA)/(((10*CT)*TMH)
251      420        K=1./(THUMSN*AVOGAD**2*STHIDIST2*LAMBO**2)
252      430        MSEDF=K**2
253      440        WRITE(6,280) Q,MSEDF
254      450      280 FORMAT(1H,'THE TOTAL ABSOLUTE INTEGRATED INTENSITY W= ',12X,E12.4,
255               1X,CM', '/ THE MEAN SQUARED ELECTRON DENSITY FLUCTUATION = ',
256               1X,E12.4, ' HUES OF E**2/CM**2')
257      460        WRITE(6,290)
258      470      290 FORMAT(1H,'DO YOU WANT TO RE-ANALYZE THIS DATA FILE??)
259      480        READ(5,230) ANS
260      490        IF(ANS(1).EQ.'Y') GO TO 55
261      500      295 WRITE(6,300)
262      510      300 FORMAT(1H,'DO YOU WANT TO ANALYZE A NEW DATA FILE??)
263      520        READ(5,230) ANS
264      530        IF(ANS(1).EQ.'Y') GO TO 20
265      540        STOP
266      550        END
EXAMPLE CALCULATION

PROGRAM DIFFER RUNNING
VERSION D.00 APR 1982
SELECT FUNCTION
FET
TYPE IN SEQUENCE NUMBER
6645
SAMPLE RUN NUMBER = 6645
TITLE: PE1 SH-SH BBS
EMPTY BACKGROUND NUMBER = 6634
CADMIUM (OR DARK CURRENT) RUN NUMBER = 6630
SENSITIVITY RUN NUMBER = 26631
OK?
YES
EMPTY BACKGROUND RUN NUMBER = 6634
TITLE: BACKGROUND BBS SH-SH
CADMIUM (OR DK. CURRENT) BACKGROUND RUN NUMBER = 6630
TYPE IN RUN NUMBER FOR RUN "B":
6645
RUN B SEQUENCE NUMBER = 6645
TITLE: PE1 SH-SH BBS
CORRECT FOR DETECTOR SENSITIVITY?
YES
INPUT VALUE BELOW WHICH SENS. DATA WILL NOT BE USED - USUAL VALUE (500 - 750)
200.
SELECT FUNCTION
HED
(1) SEQ= 6645 (2) LENGTH= 41 (3) OWNER= ELT (4) SITE= 0
(5) = 6645 (6) NDATA= 0 (7) NOVF= 0
(8) Ncorr= 0 (9) NCD= 0 (10) IS= DF0
(11) MXD= 64 (12) NYD= 64
(13) ID= 4 (14) ID= 61 (15) J= 4 (16) J2= 61
(17) IU= 3 (18) ITIME(1)= 335 (19) ITIME(2)= 3426
(20) MONTH= 3 (21) DAY= 1 (22) YEAR= 82
(23) ITIME(6)= 100 (24) NSUB= 2
(25) NC= 6630 (26) INSENS= 26631 (27) NMFT= 6634
(28) NTL= 0 (29) NI= 0 (30) NF= 0 (31) IND= 0
(32) MON= 304349 (34) TOTAL= 9000000 (36) TIME= 59734.
(38) SCAL(4)= 0 (40) SCALAR(5)= 0
(42) XCENT= 33.07 (44) YCENT= 34.00
(46) ANGLE= 0.00 (48) KAPCON= 0.000000 (50) = 0.00
(52) TRAN= 0.4790 (54) ABST= 1.00 (56) WAVE= 1.54 (58) THICK= 1.0000
(60) DIST= 1620.00 (62) DIST= 1040.00 (64) R0= 1.00 (66) R1= 1.00
(68) DXCHAN= 0.324 (70) DYCHAN= 0.324 (72) RHOF= 1.0000 (74) APV= 1.00000
(76) TITLE= PE1 SH-SH BBS
ANY CHANGES? (Y OR N)
Y
INPUT THE NUMBER OF THE ITEM TO CHANGE:
54
NEW VALUE (F):
.0032357
ANY CHANGES? (Y OR N)
N
SELECT FUNCTION
DIF
TYPE IN VALUE OF DK CONSTANT (USUAL VALUE IS 0.5)
.5
DO YOU WANT ANGLE AND INTENSITY PRINTOUT?
NO
***** PROGRAM DIFFER RUNNING *****
RADIAL AVERAGE OF CORRECTED RUN FOR DIFFERENCE OF 6645
TITLE: PE1 SH-SH BBS
MINUS RUN NO. 6645
TITLE: PE1 SH-SH BBS
DATE: 1-MAR-1982
OWNER INITIALS: ELT
DATA CORRECTED FOR SENSITIVITY
DATA TAKEN AT A MONITOR = 304349. MONITORS
BUT NORMALIZED TO A MONITOR OF: 1000.
NORMALIZATION FACTORS:
RUN A: 0.00329 RUN B: 0.00329 EMPTY RUN: 0.00279
K CURRENT NORMALIZED TO TIMES OF RUN A AND RUN B
ORM. FACTORS FOR DK. CURRENT - RUN A: 0.00491 RUN B: 0.00491
DATA FOR RUN "A":
ABSOLUTE INTENSITY CONSTANT = 0.0033
PACKING DENSITY = 1.0000
TRANSMISSION = 0.4790 THICKNESS = 1.000
SCATTERING CENTERS/CUBIC ANGSTORMS = 1.000000
DATA FOR RUN "B":
ABSOLUTE INTENSITY CONSTANT = 1.0000
PACKING DENSITY = 1.0000
TRANSMISSION = 0.4790 THICKNESS = 1.000
SCATTERING CENTERS/CUBIC ANGSTORMS = 1.000000
KAPPA CORRECTION CONSTANT = 0.000000
SAMPLE CONSTANT FOR RUN "A": = 0.0016
SAMPLE CONSTANT FOR RUN "B": = 0.4790
DIX, DKY = 0.012095 0.012095
DK = 0.0002552 DK CONSTANT = 0.500
CENTER: IO = 33.07 J0 = 34.00
AVERAGED OVER I = 4 61 J = 4 61
PROGRAM CALCULATES FA*[I(A)-BA] - FB*[I(B)-BB],
I(A,B) ARE FIRST CORRECTED FOR BACKGROUND IN THE USUAL WAY
NOW YOU MUST INPUT FA,FB, AND BA, BB:
FIRST, TYPE IN FA AND FB:
1. 0.
INCOHERENT CORRECTION FOR RUNS "A" AND "B"
TYPE IN BA AND BB:
[INPUT 0.0 IF NO CORRECTION]
0. 0.
B: PATIENT - I AM WORKING ON IT!
TOTAL NUMBER = 3362
SUM = 15434712.0 ERROR = 6832.9
AVERAGE = 4590.930 WITH ERROR = 2.032
WHAT INITIAL AND FINAL POINT NUMBER?
1 100
NI = 1 NF = 59
SAVE IT?
NO
SELECT FUNCTION
EX
$
EXE IN A

--ANISOTROPIC IN Variant PROGRAM
VERSION NOVEMBER 4, 1983

TYPE "1" IF DATA TO BE FETCHED FROM DATA BASE
244

TYPE "2", IF DATA FROM FLOATING POINT CAMAC STORAGE
2
IN Variant Analysis For : 6645

TITLE : PEI SH-SH BBS
THE SAMPLE TRANSMISSION = 0.479
THE CHANNELS PER CM = 3.24
THE SAMPLE-DETECTOR DISTANCE IN CM = 104.00
THE CENTER OF PATTERN:
CX = 33.07
CY = 34.00

THE COUNT TIME IN SECONDS = 196.3
DO YOU WANT TO CHANGE THIS? TYPE Y OR N... Y
INPUT THE COUNT TIME IN SECONDS
59733.6
ENTER THE SPECIMEN THICKNESS IN CM
.211
ENTER THE INCIDENT INTENSITY IN CPS
2132000
ENTER THE ORIGIN LIMITS IN MRAD IN X & Y DIR.
245
24 24
APPROXIMATE THE LOW ANGLE INTENSITY?
N
ENTER THE HIGH ANGLE LIMITS IN MRAD IN X & Y DIR.
82 85
ENTER THE LIQUID SCATTERING COUNTS: 3 VALUES FROM POROD PLOT AT MU=0, 45, 90 DEG
1253 1820 3195

THE NUMBER OF NEGATIVE CELLS = 391
THE TOTAL INTEGRATED COUNTS = 0.147098E+08

THE LOW ANGLE INTENSITY = 0.0000000E+00
THE INTEGRATED INTENSITY = 0.5670373E+08
THE NUMBER OF CELLS IN INTEGRATED INTENSITY = 2846
THE TOTAL(COUNTS-LS) = 0.729704E+07

ACCORDING TO THE HEADER RECORDS, YOUR DATA HAS PREVIOUSLY BEEN DIVIDED BY THE TR
DO YOU AGREE? TYPE Y OR N... Y WILL RESULT IN DATA NOT BEING DIVIDED BY TM IN T
Y
THE TOTAL ABSOLUTE INTEGRATED INTENSITY Q = 0.4455E-03 CM
THE MEAN SQUARED ELECTRON DENSITY FLUCTUATION = 0.1924E-03 MOLES OF E**2/CM**6

DO YOU WANT TO RE-ANALYZE THIS DATA FILE?
N

DO YOU WANT TO ANALYZE A NEW DATA FILE?
N