

*Polymer Science Library 8*

# X-RAY SCATTERING OF SYNTHETIC POLYMERS

*F.J. Baltá-Calleja*

*Instituto de Estructura de la Materia (CSIC), Serrano 119, E-28006 Madrid, Spain*

*C.G. Vonk*

*Formerly DSM Central Laboratory, Geleen, The Netherlands*



**ELSEVIER**

**Amsterdam — Oxford — New York — Tokyo 1989**

## CONTENTS

<i>Preface</i>	v
<i>Chapter 1</i>	
<b>The Theory of Coherent X-ray Scattering</b>	
1.1. Introduction	1
1.2. The scattering from one electron	2
1.3. The scattering from many electrons	3
1.4. Fourier transformation and reciprocal space	6
1.5. The Ewald sphere construction	7
1.6. The convolution operation	8
1.7. The Fourier transforms of convolutions and products of functions	12
1.8. General relations involving Fourier transforms	14
1.9. Diffraction by crystals	16
1.10. Powder patterns	23
1.11. Diffraction from non-crystalline substances	25
References	31
<i>Chapter 2</i>	
<b>Experimental Techniques</b>	
2.1. Properties of X-ray radiation	33
2.2. X-ray excitation	34
2.2.1. White radiation	34
2.2.2. Characteristic radiation	35
2.2.3. Sealed tubes	37
2.2.4. Rotating anode tubes	39
2.2.5. Synchrotron radiation.	40
2.2.5.1. Synchrotrons and storage rings	41
2.2.5.2. Intensity, polarization, time structure	42
2.2.5.3. Energy spectrum	44
2.2.5.4. Applications in synthetic polymers	46
2.3. Absorption of X-ray radiation	47
2.3.1. Absorption	47
2.3.2. Photoelectric effect	48
2.3.3. Scattering of X-rays	48
2.3.4. Absorption edges	49
2.3.5. Single and balanced filters	50
2.4. X-ray detection	51
2.4.1. Photographic films	51
2.4.2. Counters for X-ray detection	55
2.4.2.1. Gas counters	56
2.4.2.2. Scintillation counters	57
2.4.2.3. Solid state detectors	58

2.4.2.4. Pulse height discrimination	58
2.4.2.5. Use of crystal monochromators	60
2.4.2.6. Position sensitive counters (PSC)	61
2.5. Apparatus	66
2.5.1. Wide-angle techniques	66
2.5.1.1. Cameras	66
2.5.1.2. Diffractometer	72
2.5.1.3. Advanced technique for rapid recording of X-ray diffractograms	75
2.5.1.4. Energy dispersive diffractometer	76
2.5.2. Small-angle scattering techniques	78
2.5.2.1. Pinhole collimation	78
2.5.2.2. Focusing by reflection	82
2.5.2.3. Slit collimation	82
References	86

### Chapter 3

#### Lattice Constants

3.1. Introduction	89
3.2. Measurement of lattice constants by photographic methods	89
3.2.1. Debye-Scherrer camera	91
3.3. Measurement of lattice constants from diffractometer line profiles	92
3.3.1. Use of a flat specimen	94
3.3.2. Transparency error	95
3.3.3. Divergence of the primary beam	96
3.3.4. Specimen displacement	97
3.3.5. Calibration	98
3.4. Unit cell measurements in polymers	99
3.4.1. Variations with temperature (thermal expansion)	99
3.4.2. Effect of crystallization temperature	103
3.4.3. Effect of lateral chain defects	106
3.4.4. Effect of drawing	114
3.4.5. Effect of high pressure	118
3.5. Interpretation of unit cell variations	119
3.5.1. The incorporation of chain defects in polymer crystals	121
3.5.2. Effect of lamellar thickness on lattice constants	124
References	127

### Chapter 4

#### Line Breadth Measurements: Paracrystallinity

4.1. Introduction	129
4.2. Lattice distortions	130
4.3. Distortions of the first kind	132
4.4. The concept of paracrystal: distortions of the second kind	134
4.4.1. The paracrystalline lattice factor	138
4.4.2. Integral breadth	139
4.4.3. Intensity function	140

4.5.	Line broadening analysis	141
4.5.1.	Crystallite size	143
4.5.2.	Lattice disorder	143
4.5.3.	Separation of crystal size and lattice disorder broadening	145
4.5.4.	Applications to synthetic polymers	148
4.5.4.1.	$\delta\beta$ -versus-h plots	148
4.5.4.2.	Shape ellipsoid	151
4.6.	$\alpha^*$ -Relation: natural paracrystals	155
4.6.1.	Bearing lattice planes	158
4.6.2.	Origin of distortions of the 2nd kind in polymers	158
4.7.	Fourier transform methods	161
4.7.1.	The Warren-Averbach method	161
4.7.2.	Alternative Fourier techniques	162
4.7.3.	Truncation effect	164
4.7.4.	Examples	165
4.8.	Instrumental corrections	169
4.8.1.	Fourier method	169
4.8.2.	Reference methods	170
	References	172

## Chapter 5

### The X-ray Determination of the Crystallinity in Polymers

5.1.	Introduction	175
5.2.	Methods based on external comparison	176
5.2.1.	The method of Goppel and Arlman	176
5.2.2.	The method of Wakelin, Virgin and Crystal	177
5.2.3.	The method of Hermans and Weidinger	179
5.2.4.	The method of Hendus and Schnell	180
5.3.	Methods based on internal comparison	182
5.3.1.	Theoretical	182
5.3.2.	Some older methods	183
5.3.3.	Ruland's method	184
5.3.3.1.	Principles	184
5.3.3.2.	Computerization	187
5.3.3.3.	Practical aspects	192
5.3.3.4.	Anisotropic samples	195
5.3.3.5.	Incongruent phases	198
5.3.3.6.	General considerations	201
	References	203

## Chapter 6

### The X-ray Determination of the Orientation in Polymers

6.1.	Introduction	205
6.2.	Classification	206
6.3.	The X-ray registration of the orientation of crystallites	207
6.4.	Pole figures	211
6.5.	Specification of orientation	213
6.5.1.	Types of orientation	214

6.5.2. The degree of orientation	215
6.5.2.1. Uniaxial orientation	218
6.5.2.2. Biaxial orientation	223
6.5.2.3. Application to blown films of polyethylene	226
6.6. The interpretation of orientation phenomena	228
6.6.1. The pseudo-affine transformation approximation	228
6.6.2. Studies on the deformation of polyethylene	229
6.6.2.1. Twinning	230
6.6.2.2. Slip	233
6.6.3. Row orientation	236
References	239

## Chapter 7

### The Small-angle X-ray Scattering of Polymers

7.1. Introduction	241
7.2. Primary data treatment	242
7.2.1. Raw data correction	242
7.2.2. Background subtraction	242
7.2.3. Desmearing	244
7.2.4. Calculation of the correlation function	247
7.2.5. Calculation of absolute intensities	251
7.2.6. Calculation of the invariant	254
7.3. Two-phase structures	255
7.3.1. General	255
7.3.2. Determination of the specific surface	257
7.3.3. Determination of the width of the phase boundary	261
7.4. Particle scattering	266
7.5. Lamellar systems	270
7.5.1. The ideal lamellar model: simple analysis	271
7.5.2. The direct method	273
7.5.2.1. Properties of the intensity function at the lowest angles	278
7.5.2.2. Variations in lamellar thickness	280
7.5.2.3. Further improvements of the model	281
7.5.3. The correlation function approach	282
7.5.4. Deviations from the ideal lamellar model	288
7.6. The small-angle scattering of oriented polymers	294
7.6.1. Registration of two-dimensional X-ray patterns	294
7.6.2. General description of SAXS fibre patterns	296
7.6.3. Interpretation of fibre patterns in terms of models	298
7.6.3.1. Models based on continuous lamellar structures	299
7.6.3.2. Models based on microfibrils	300
References	304
Author Index	307
Subject Index	312