

4.5. POLYMER CRYSTALLOGRAPHY

by the cylindrically projected reciprocal lattice (Finkenstadt & Millane, 1998).

The molecules are periodic and are therefore usually aligned with one of the unit-cell vectors. Since the z axis is defined as the fibre axis, it is usual in fibre diffraction to take the \mathbf{c} lattice vector as the unique axis and as the lattice vector parallel to the molecular axes. It is almost always the case that the fibre is rotationally disordered about the molecular axes, *i.e.* about \mathbf{c} . Consider first the case of a monoclinic unit cell ($\alpha = \beta = 90^\circ$) so that the reciprocal lattice is cylindrically projected about \mathbf{c}^* . The cylindrical coordinates of the projected reciprocal-lattice points are then given by

$$R_{hkl}^2 = h^2 a^{*2} + k^2 b^{*2} + 2hka^*b^* \cos \gamma^* \quad (4.5.2.21)$$

and

$$Z_{hkl} = lc^*, \quad (4.5.2.22)$$

so that R depends only on h and k , and Z depends only on l . Reflections with fixed h and k lie on straight *row lines*. Certain sets of distinct reciprocal-lattice points will have the same value of R_{hkl} and therefore superimpose in cylindrical projection. For example, for an orthorhombic system ($\gamma = 90^\circ$) the reciprocal-lattice points (hkl) , $(\bar{h}kl)$, $(h\bar{k}l)$ and $(\bar{h}\bar{k}l)$ superimpose. Furthermore, the crystallites in a fibre specimen are usually oriented randomly up and down so that the reciprocal-lattice points (hkl) and $(h\bar{k}l)$ superimpose, so that in the orthorhombic case eight reciprocal-lattice points superimpose. Also, as described below, reciprocal-lattice points that have similar values of R can effectively superimpose.

If the unit cell is either triclinic, or is monoclinic with $\alpha \neq 90^\circ$ or $\beta \neq 90^\circ$, then \mathbf{c}^* is inclined to \mathbf{c} and the Z axis, and the reciprocal lattice is not cylindrically projected about \mathbf{c}^* . Equation (4.5.2.22) for Z_{hkl} still applies, but the cylindrical radius is given by

$$R_{hkl}^2 = h^2 a^{*2} + k^2 b^{*2} + l^2 [c^{*2} - (1/c^2)] + 2hka^*b^* \cos \gamma^* + 2hla^*c^* \cos \beta^* + 2klb^*c^* \cos \alpha^* \quad (4.5.2.23)$$

and the row lines are curved (Finkenstadt & Millane, 1998).

The most complicated situation arises if the crystallites are rotationally disordered about an axis that is inclined to \mathbf{c} . Reciprocal space is then rotated about an axis that is inclined to the normal to the a^*b^* plane, R_{hkl} and Z_{hkl} are both functions of h , k and l , equation (4.5.2.23) does not apply, and reciprocal-lattice points for fixed l do not lie on layer lines of constant Z . Although this situation is rather unusual, it does occur (Daubeny *et al.*, 1954), and is described in detail by Finkenstadt & Millane (1998).

The observed fibre diffraction pattern consists of reflections at the projected reciprocal-lattice points whose intensities are equal to the sums of the intensities of the contributing structure factors. The observed intensity, denoted by $I_l(R_{hk})$, at a projected reciprocal-lattice point on the l th layer line and with $R = R_{hk}$ is therefore given by (assuming, for simplicity, a monoclinic system)

$$I_l(R_{hk}) = \sum_{h', k' \in \mathcal{S}(h, k)} |F_{h'k'l}|^2, \quad (4.5.2.24)$$

where $\mathcal{S}(h, k)$ denotes the set of indices (h', k') such that $R_{h'k'} = R_{hk}$. The number of independent reflections contributing in equation (4.5.2.24) depends on the space-group symmetry of the crystallites, because of either systematic absences or structure factors whose values are related.

The effect of a finite crystallite size is to smear what would otherwise be infinitely sharp reflections into broadened reflections of a finite size. If the average crystallite dimensions normal and parallel to the z axis are l_{lat} (*i.e.* in the 'lateral' direction) and l_{axial} (*i.e.* in the 'axial' direction), respectively, the profile of the reflection centred at $(R_{hk}, Z = l/c)$ can be written as (Fraser *et al.*, 1984; Millane & Arnott, 1986; Millane, 1989c)

$$I(R, Z) = I_l(R_{hk})S(R - R_{hk}, Z - l/c), \quad (4.5.2.25)$$

where the profile function $S(R, Z)$ can be approximated by

$$S(R, Z) = \exp[-\pi(l_{\text{lat}}^2 R^2 + l_{\text{axial}}^2 Z^2)]. \quad (4.5.2.26)$$

The effect of crystallite disorientation is to smear the reflections given by equation (4.5.2.26) about the origin of the projected reciprocal space. If the effects of disorientation dominate over those of crystallite size, then the profile of a reflection can be approximated by (Fraser *et al.*, 1984; Millane & Arnott, 1986; Millane, 1989c)

$$I(\rho, \sigma) \simeq \frac{I_l(R_{hk})}{2\pi\alpha_0 l_{\text{lat}} l_{\text{axial}} \rho} \times \exp\left(-\left[\frac{(\rho - \rho_{hkl})^2}{2\beta_\rho^2} + \frac{(\sigma - \sigma_{hkl})^2}{2\beta_\sigma^2}\right]\right), \quad (4.5.2.27)$$

where $(\rho_{hkl}, \sigma_{hkl})$ are the polar coordinates of the reflection,

$$\beta_\rho^2 = \frac{l_{\text{lat}}^2 l_{\text{axial}}^2}{2\pi(l_{\text{lat}}^2 \sin^2 \sigma_{hkl} + l_{\text{axial}}^2 \cos^2 \sigma_{hkl})} \quad (4.5.2.28)$$

and

$$\beta_\sigma^2 = \alpha_0 + \frac{l_{\text{lat}}^2 l_{\text{axial}}^2}{2\pi\rho_{hkl}^2 (l_{\text{axial}}^2 \sin^2 \sigma_{hkl} + l_{\text{lat}}^2 \cos^2 \sigma_{hkl})}. \quad (4.5.2.29)$$

Reflections that have similar enough (R, Z) coordinates overlap severely with each other and are also included in the sum in equation (4.5.2.24). This is quite common in practice because a number of sets of reflections may have similar values of R_{hk} .

4.5.2.4.3. Random copolymers

Random copolymers are made up of a small number of different *kinds* of monomer, whose sequence along the polymer chain is not regular, but is random, or partially random. A particularly interesting class are synthetic polymers such as copolyesters that form a variety of liquid-crystalline phases and have useful mechanical properties (Biswas & Blackwell, 1988a). The structures of these materials have been studied quite extensively using X-ray fibre diffraction analysis. Because the molecules do not have an average c repeat, their diffraction patterns do not consist of equally spaced layer lines. However, as a result of the small number of distinct spacings associated with the monomers, diffracted intensity is concentrated about layer lines, but these are irregularly spaced (along Z) and are *aperiodic*. Since the molecule is not periodic, the basic theory of diffraction by helical molecules described in Section 4.5.2.3.2 does not apply in this case. Cylindrically averaged diffraction from random copolymers is described here. Related approaches have been described independently by Hendricks & Teller (1942) and Blackwell *et al.* (1984). Hendricks & Teller (1942) considered the rather general problem of diffraction by layered structures made up of different kinds of layers, the probability of a layer at a

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particular level depending on the layers present at adjacent levels. This is a one-dimensional disordered structure that can be used to describe a random copolymer. Blackwell and co-workers have developed a similar theory in terms of a one-dimensional paracrystalline model (Hosemann & Bagchi, 1962) for diffraction by random copolymers (Blackwell *et al.*, 1984; Biswas & Blackwell, 1988a), and this is the theory described here.

Consider a random copolymer made up of monomer units (residues) of N different types. Since the disorder is along the length of the polymer, some of the main characteristics of diffraction from such a molecule can be elucidated by studying the diffraction along the meridian of the diffraction pattern. The meridional diffraction is the intensity of the Fourier transform of the polymer chain projected onto the z axis and averaged over all possible monomer sequences. The diffraction pattern depends on the monomer (molar) compositions, denoted by p_i , the statistics of the monomer sequence (described by the probability of the different possible monomer pairs in this model) and the Fourier transform of the monomer units. Development of this model shows that the meridional diffracted intensity $I(Z)$ can be written in the form (Blackwell *et al.*, 1984; Biswas & Blackwell, 1988a; Schneider *et al.*, 1991)

$$I(Z) = \sum_i p_i |F_i(Z)|^2 + 2 \sum_i \sum_{j \neq i} \Re\{F_i(Z)F_j^*(Z)T_{ij}(Z)\}, \quad (4.5.2.30)$$

where the summations are over the different monomer types and $F_i(Z)$ is the axial Fourier transform of the i th monomer unit (each referenced to a common origin). The $T_{ij}(Z)$ are most conveniently described by defining them as the ij th element of an $N \times N$ matrix \mathbf{T} , which is given by

$$\mathbf{T} = \frac{\mathbf{PMX}(Z)}{\mathbf{I} - \mathbf{MX}(Z)}, \quad (4.5.2.31)$$

where \mathbf{P} , \mathbf{M} , $\mathbf{X}(Z)$ and \mathbf{I} are $N \times N$ matrices. \mathbf{I} is the unit matrix and \mathbf{P} is a diagonal matrix with elements p_i . The elements M_{ij} of \mathbf{M} are the probabilities of forming ij monomer pairs and can be generated for different kinds of random sequence (*e.g.* chemical restrictions on the occurrence of particular monomer pairs, random chains, varying degrees of blockiness, tendency towards alternating sequences *etc.*) (Schneider *et al.*, 1991). The matrix $\mathbf{X}(Z)$ is diagonal with elements equal to $\langle \exp(i2\pi Z\zeta_i) \rangle$ where the ζ_i are the projected monomer lengths and the average is over all chain conformations.

Equation (4.5.2.30) can be used to calculate the meridional diffraction for a particular random copolymer. The most important result of such a calculation is that intensity maxima are spaced irregularly along the meridian. The positions of the maxima depend on the monomer proportions, the sequence statistics and the projected monomer lengths.

The full cylindrically averaged diffraction pattern, denoted by $I(R, Z)$, from a noncrystalline specimen containing oriented random copolymer chains can be calculated by replacing $F_i(Z)$ in equation (4.5.2.30) by $F_i(R, Z)$, *i.e.*

$$I(R, Z) = \sum_i p_i |F_i(R, Z)|^2 + 2 \sum_i \sum_{j \neq i} \Re\{F_i(R, Z)F_j^*(R, Z)T_{ij}(Z)\} \quad (4.5.2.32)$$

(Biswas & Blackwell, 1988a). Note that we write $I(R, Z)$ rather than $I_l(Z)$ since the pattern cannot be indexed on the basis of regularly spaced layer lines. The $F_i(R, Z)$ in equation (4.5.2.32) depend on the chain conformation, since this affects the range of monomer orientations and hence their average diffraction. Chivers & Blackwell (1985) have considered two extreme cases,

one corresponding to fixed conformations between monomers and the other corresponding to completely random conformations between monomers, and have derived expressions for the diffracted intensity in both cases. Equation (4.5.2.32) allows one to calculate the fibre diffraction pattern from an array of parallel random copolymers that exhibit no lateral ordering. The diffraction pattern consists of irregularly spaced layer lines whose spacings (in Z) are the same as those described above for the meridional maxima. Measurement of layer-line spacings and intensities and comparison with calculations based on the constituent monomers allows chain conformations to be estimated (Biswas & Blackwell, 1988a).

Diffraction patterns from liquid-crystalline random copolymers often contain sharp Bragg maxima on the layer lines. This indicates that, despite the random sequence and the possible dissimilarity of the component monomers, the chains are able to pack together in a regular way (Biswas & Blackwell, 1988b,c). Expressions that allow calculation of diffraction patterns for arrays of polymers with minimal registration, in which short, non-identical sequences form layers, have been derived (Biswas & Blackwell, 1988b,c). Calculation of diffracted intensities, coupled with molecular-mechanics modelling, allows chain conformations and packing to be investigated (Hofmann *et al.*, 1994).

4.5.2.4.4. Partially crystalline fibres

In this section we address disorder in the packing of the molecules in a polycrystalline fibre. The presence of disorder within the crystallites modifies the intensities of the Bragg reflections, as well as introducing continuous diffraction. The dominant effect, sometimes seen on fibre diffraction patterns (Stroud & Millane, 1995a), is for Bragg reflections to remain at low resolution but to be replaced by continuous diffraction at high resolution. There are two distinct cases to consider. The first is where the distortions at different lattice points in the crystallite are uncorrelated, and the second is where they are correlated.

Disorder within a crystallite in a polycrystalline fibre may consist of (1) deviations in the positions of the molecules (which are treated as rigid bodies) from their positions in a regular lattice, (2) rotations of the molecules about their molecular axes from their rotational positions in an ordered crystal, and (3) random orientations (up or down) of the molecules. The first of these is called *lattice disorder*, and the second and third are components of *substitution disorder*.

Uncorrelated disorder has been treated by a number of authors (Clark & Muus, 1962; Tanaka & Naya, 1969; Fraser & MacRae, 1973; Arnott, 1980). A rather complete model has been described by Millane & Stroud (1991) and Stroud & Millane (1995b), which is presented here. If the lattice and substitution disorders are independent, and the lattice and substitution distortions at different lattice sites are uncorrelated, then the cylindrically averaged layer-line intensities $I_l(R)$ diffracted from a fibre can be written as a sum of Bragg and diffuse (continuous) intensities (Tanaka & Naya, 1969):

$$I_l(R) = I_l^B(R) + I_l^D(R). \quad (4.5.2.33)$$

The profiles of the Bragg reflections are independent of the position of the reflection in reciprocal space. If the Cartesian components of the lattice distortions are independent, normally distributed, and the x and y components have equal variances, cylindrical averaging of the diffracted intensity can be performed analytically.

The lattice disorder consists of distortions of the two-dimensional lattice (in the lateral plane) into three-dimensional space, and in the *absence* of substitution disorder the Bragg component is given by (Stroud & Millane, 1995b)