4.5. POLYMER CRYSTALLOGRAPHY

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.*

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

$$(4.5.2.32)$$

(Biswas & Blackwell, 1988*a*). 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, 1988*a*).

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, 1988*b*,*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, 1988*b*,*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, 1995*a*), 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 (1995*b*), 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):

$$I_l(R) = I_l^B(R) + I_l^D(R). \tag{4.5.2.33}$$

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, 1995*b*)

$$I_l^B(R) = I_l(R_{hk})w_{\text{lattice}}(R_{hk}, l/c) \tag{4.5.2.34}$$

where $I_l(R_{hk})$ is given by equation (4.5.2.24), the *lattice disorder weight*, $w_{\text{lattice}}(R,Z)$, is given by

$$w_{\text{lattice}}(R,Z) = \exp[-4\pi^2(R^2\sigma_{\text{lat}}^2 + Z^2\sigma_{\text{axial}}^2)], \tag{4.5.2.35}$$

where σ_{lat}^2 and σ_{axial}^2 are the variances of the lattice distortions normal ('lateral') and parallel ('axial') to the z axis, respectively. The diffuse component is given by

$$I_l^D(R) = (1/A_{\text{cryst}})I_l(R)[1 - w_{\text{lattice}}(R, l/c)], \tag{4.5.2.36}$$

where $I_l(R)$ is given by equation (4.5.2.17) and A_{cryst} is the average cross-sectional area of the crystallites. Inspection of equations (4.5.2.34) and (4.5.2.36) shows that the effect of the lattice disorder is to weight the amplitudes of the Bragg reflections down with increasing R and l, and to introduce a continuous intensity component whose amplitude increases with R and Z. Furthermore, the amplitude of the diffuse component relative to the Bragg component is inversely proportional to A_{cryst}, and therefore is not significant unless the crystallites are small.

If substitution disorder is also present, then equation (4.5.2.33) still applies but equations (4.5.2.34) and (4.5.2.36) are replaced by

$$I_l^B(R) = \left| \sum_n w_{nl} G_{nl}^2(R_{hk}) \exp[in(\psi_{hk} + \pi/2)] \right|^2 w_{\text{lattice}}(R_{hk}, l/c)$$

$$(4.5.2.37)$$

and

$$I_l^D(R) = (1/A_{\text{cryst}}) \sum_n |G_{nl}(R)|^2 [1 - |w_{nl}|^2 w_{\text{lattice}}(R, l/c)], $$

$$(4.5.2.38)$$

respectively, where the *substitution disorder weight*, w_{nl}, is given by

$$w_{nl} = \int\limits_0^{c/u} \int\limits_0^{2\pi} p(\varphi, z) \exp[i(2\pi zl/c - n\varphi)]\, \mathrm{d}\varphi\, \mathrm{d}z. \tag{4.5.2.39}$$

In equation (4.5.2.39), $p(\varphi, z)$ is the probability density function (p.d.f.) that describes the substitution disorder, *i.e.* the p.d.f. for a molecule being rotated by φ about and translated by z along the

molecular axis relative to its position in the undistorted lattice. Inspection of equations (4.5.2.37) and (4.5.2.38) shows that the substitution disorder weights the different contributing Bessel terms differently. This can lead to quite complicated effects on the diffraction pattern for various kinds of substitution disorder, resulting in different distributions and amplitudes of Bragg and diffuse diffraction over the diffraction pattern (Stroud & Millane, 1995b). If one assumes either uniform or normal distributions for φ and z, then expressions can be obtained for the w_{nl} in terms of the variances of the distributions of φ and z (Stroud & Millane, 1995b). The cases where distortions in φ are correlated with distortions in z (e.g. 'screw disorder'), and directional (up and down) disorder, can also be accommodated. This model has been shown to be capable of predicting diffraction patterns which are in good agreement with those measured from some disordered polycrystalline fibres (Stroud & Millane, 1995a).

We consider now the case of correlated packing disorder. As a result of intermolecular contacts within a polycrystalline specimen, it is possible that distortions at one lattice site will affect the degree of distortion at neighbouring sites. Coupling between distortions at different lattice sites can be included in the model of disorder by allowing the distortions at different lattice sites to be correlated. The effect of correlated distortions on diffraction patterns is that the diffracted intensity does not separate into Bragg and diffuse components as it does in the case of uncorrelated distortions [equation (4.5.2.33)]. The intensity can be described as being diffuse on the whole diffraction pattern, with (often broad) maxima occurring at some of the reciprocal-lattice points, but with no significant maxima at other reciprocal-lattice points. The widths of the profiles of the maxima generally increase with increasing resolution, whereas the widths of the Bragg maxima resulting from uncorrelated disorder as described above are independent of resolution. A broadening of diffraction maxima with increasing resolution and blending into continuous diffraction is sometimes seen on diffraction patterns from polycrystalline fibres, indicating the presence of correlated disorder (Stroud & Millane, 1996b).

Correlated lattice disorder consists of correlated distortions of the two-dimensional lattice into three-dimensional space. A flexible model of crystalline disorder is that based on the perturbed lattice approach (Welberry et al., 1980). While formulating perturbed lattices with only nearest-neighbour interactions is complicated, a more tractable approach is to base the statistics on an imposed correlation field (de Graaf, 1989; Stroud & Millane, 1996a). This approach has been used to describe cylindrically averaged diffraction from polycrystalline fibres that contain correlated lattice disorder and uncorrelated substitution disorder (Stroud & Millane, 1996a,b), and is presented here.

To develop a flexible and tractable theory for diffraction from crystallites with correlated disorder, it is necessary to formulate the problem in real space. The size and shape of a crystallite in the xy (lateral) plane is described by a *shape function* $s_{\mathrm{lat}}(\mathbf{r})$, where $\mathbf{r}$ denotes the position vector in real space, which is equal to unity inside the crystallite and zero outside. The autocorrelation of the shape function, $t(\mathbf{r})$, is given by

$$t(\mathbf{r}) = \int s(\mathbf{r}')s(\mathbf{r} + \mathbf{r}')\,\mathrm{d}\mathbf{r}'. \qquad (4.5.2.40)$$

The correlations between the x components, and between the y components, of the distortions at any two lattice sites are taken to be identical. The correlations between distortion vectors are defined in terms of lateral, $\rho_{\mathrm{lat}}(\mathbf{r})$, and axial, $\rho_{\mathrm{axial}}(\mathbf{r})$, correlation fields such that the correlation coefficients between components of the distortions in the x (or y) and z directions, respectively, are equal to the correlation field evaluated for $\mathbf{r}$ equal to the inter-site vector. Various functional forms for the correlation fields are possible, but exponential correlation functions are usually used (Stroud & Millane, 1996a). If $t(\mathbf{r})$ and the correlation fields are circularly

symmetric, then cylindrical averaging of the diffracted intensity can be performed analytically.

For a polycrystalline fibre with correlated lattice disorder and uncorrelated substitution disorder, the diffracted intensity is given by (Stroud & Millane, 1996b)

$$
\begin{aligned}
I_l(R) = &\sum_{j,k} t(r_{jk})w_{\mathrm{lat}}(R, r_{jk})w_{\mathrm{axial}}(l/c, r_{jk}) \\
&\times \sum_{m,n} J_{n-m}(2\pi R r_{jk})\Re\{w_{ml}w_{nl}^* G_{ml}(R)G_{nl}^*(R) \\
&\times \exp[i(m-n)\varphi_{jk}]\}
\end{aligned} \qquad (4.5.2.41)
$$

where $r = |\mathbf{r}|$, the sum over (j,k) is over all the sites of the undistorted lattice within the region occupied by the autocorrelation function, (r_{jk}, φ_{jk}) are the polar coordinates of the lattice sites, and the lateral and axial lattice disorder weights are given by

$$w_{\mathrm{lat}}(R, r) = \exp\left(-4\pi^2 R^2 \sigma_{\mathrm{lat}}^2[1 - \rho_{\mathrm{lat}}(r)]\right) \qquad (4.5.2.42)$$

and

$$w_{\mathrm{axial}}(Z, r) = \exp\left(-4\pi^2 Z^2 \sigma_{\mathrm{axial}}^2[1 - \rho_{\mathrm{axial}}(r)]\right). \qquad (4.5.2.43)$$

Equation (4.5.2.41) is an expression for the continuous intensity distribution along the layer lines and does not separate into Bragg and continuous components as in the case of uncorrelated disorder. However, calculations using these expressions show that the continuous intensity is sharply peaked around the projected reciprocal-lattice points at low resolution, the peaks broadening with increasing resolution until they have the character of continuous diffraction at high resolution (Stroud & Millane, 1996a). This is consistent with the character of diffraction patterns from some disordered polycrystalline fibres. A detailed study of the effects of correlated disorder on fibre diffraction patterns, and analysis of such disorder, can be found in Stroud & Millane (1996a) and Stroud & Millane (1996b).

4.5.2.5. *Processing diffraction data*

Since the diffraction pattern from a fibre is two-dimensional, it can be collected with a single exposure of a stationary specimen. Diffraction data are collected either on film, which is subsequently scanned by a two-dimensional microdensitometer to obtain a digitized representation of the diffracted intensity, or using an electronic area detector (imaging plate, CCD camera, wire detector etc.) (Fraser et al., 1976; Namba, Yamashita & Vonderviszt, 1989; Lorenz & Holmes, 1993). We assume here that the diffraction pattern is recorded on a flat film (or detector) that is normal to the incident X-ray beam, although other film geometries are easily accommodated (Fraser et al., 1976). The fibre specimen is usually oriented with its axis normal to the incident X-ray beam, although, as is described below, it is sometimes tilted by a small angle to the normal in order to better access reciprocal space close to the meridian. The diffraction and camera geometry are shown in Fig. 4.5.2.1. Referring to this figure, P and S denote the intersections of the diffracted beam with the sphere of reflection and the film, respectively. The fibre, and therefore reciprocal space, is tilted by an angle β to the normal to the incident beam. The angles μ and χ define the direction of the diffracted beam and θ is the Bragg angle. Cartesian and polar coordinates on the film are denoted by (u, v) and (r, φ), respectively, and D denotes the film-to-specimen distance.

Inspection of Fig. 4.5.2.1 shows that the cylindrical (R, ψ, Z) and spherical (ρ, ψ, σ) polar coordinates in reciprocal space are related to μ and χ by

$$\rho = (1/\lambda)[2(1 - \cos\mu - \cos\chi)]^{1/2}, \qquad (4.5.2.44)$$

$$Z = (1/\lambda)[\sin\beta(1 - \cos\mu\cos\chi) + \cos\beta\sin\chi]^{1/2}, \qquad (4.5.2.45)$$