

## 4.5. POLYMER CRYSTALLOGRAPHY

## 4.5.2.6.3. Patterson functions

In fibre diffraction, the conventional Patterson function cannot be calculated since the individual structure-factor intensities are not available. However, MacGillavry & Bruins (1948) showed that the *cylindrically averaged Patterson function* can be calculated from fibre diffraction data. Consider the function  $\hat{Q}(r, z)$  defined by

$$\hat{Q}(r, z) = \sum_{l=0}^{\infty} \int \varepsilon_l I_l(R) J_0(2\pi Rr) \cos(2\pi lz/c) 2\pi R \, dR, \quad (4.5.2.58)$$

where  $\varepsilon_l = 1$  for  $l = 0$  and 2 for  $l > 0$ , which can be calculated from the intensity distribution on a continuous fibre diffraction pattern. Using equations (4.5.2.7), (4.5.2.10), (4.5.2.17) and (4.5.2.58) shows that  $\hat{Q}(r, z)$  is the cylindrical average of the Patterson function,  $\hat{P}(r, \varphi, z)$ , of one molecule, *i.e.*

$$\hat{Q}(r, z) = (1/2\pi) \int_0^{2\pi} \hat{P}(r, \varphi, z) \, d\varphi. \quad (4.5.2.59)$$

The  $\hat{\phantom{P}}$  symbols on  $\hat{P}(r, \varphi, z)$  and  $\hat{Q}(r, z)$  indicate that these are Patterson functions of a single molecule, as distinct from the usual Patterson function of a crystal, which contains intermolecular interatomic vectors and is periodic with the same periodicity as the crystal.  $\hat{P}(r, \varphi, z)$  is periodic only along  $z$  and is therefore, strictly, a Patterson function along  $z$  and an auto-correlation function along  $x$  and  $y$  (Millane, 1990*b*). The cylindrically averaged Patterson contains information on interatomic separations along the axial direction and in the lateral plane, but no information on orientations of the vectors in the lateral plane.

For a polycrystalline system; consider the function  $Q(r, z)$  given by

$$Q(r, z) = \sum_l \sum_{h,k} R_{hk} I_l(R_{hk}) J_0(2\pi R_{hk}r) \cos(2\pi lz/c), \quad (4.5.2.60)$$

where the sums are over all the overlapped reflections  $I_l(R_{hk})$  on the diffraction pattern, given by equation (4.5.2.24). It is easily shown that  $Q(r, z)$  is related to the Patterson function  $P(r, \varphi, z)$  by

$$Q(r, z) = (1/2\pi) \int_0^{2\pi} P(r, \varphi, z) \, d\varphi, \quad (4.5.2.61)$$

where, in this case,  $P(r, \varphi, z)$  is the usual Patterson function (expressed in cylindrical polar coordinates), *i.e.* it contains all intermolecular (both intra- and inter-unit cell) interatomic vectors and has the same translational symmetry as the unit cell. The cylindrically averaged Patterson function for polycrystalline fibres therefore contains the same information as it does for noncrystalline fibres (*i.e.* no angular information in the lateral plane), except that it also contains information on intermolecular separations.

Low resolution and cylindrical averaging, in addition to the usual difficulties with interpretation of Patterson functions, has resulted in the cylindrically averaged Patterson function not playing a major role in structure determination by fibre diffraction. However, information provided by the cylindrically averaged Patterson function has, in a number of instances, been a useful component in fibre diffraction analyses. A good review of the application of Patterson functions in fibre diffraction is given by Stubbs (1987). Removing data from the low-resolution part (or all) of the equator when calculating the cylindrically averaged Patterson function removes the strong vectors related to axially

invariant (or cylindrically symmetric) parts of the map, and can aid interpretation (Namba *et al.*, 1980; Stubbs, 1987). It is also important when calculating cylindrically averaged Patterson functions to use data only at a resolution that is appropriate to the size and spacings of features one is looking for (Stubbs, 1987).

Cylindrically averaged Patterson functions were used in early applications of fibre diffraction analysis (Franklin & Gosling, 1953; Franklin & Klug, 1955). The intermolecular peaks that usually dominate in a cylindrically averaged Patterson function can help to define the locations of multiple molecules in the unit cell. Depending on the space-group symmetry, it is sometimes possible to calculate the complete three-dimensional Patterson function (or certain projections of it). This comes about because of the equivalence of the amplitudes of overlapping reflections in some high-symmetry space groups. The intensity of each reflection can then be determined and a full three-dimensional Patterson map calculated (Alexeev *et al.*, 1992). The only difficulty is that nonsystematic overlaps are often present, although these are usually relatively few in number and the intensity can be apportioned equally amongst them, the resulting errors usually being small relative to the level of detail present in the Patterson map. For lower space-group symmetries, it may not be possible to calculate a three-dimensional Patterson map, but it may be possible to calculate certain projections of the map. For example, if the overlapped  $hk0$  reflections have the same intensities, a projection of the Patterson map down the  $c$  axis can be calculated. Since such a projection is along the polymer axes, it gives the relative positions of the molecules in the  $ab$  plane. If the combined helix and space-group symmetry is high, an estimate of the electron density can be obtained by averaging appropriate copies of the three-dimensional Patterson function (Alexeev *et al.*, 1992).

## 4.5.2.6.4. Molecular model building

The majority of the structures determined by X-ray fibre diffraction analysis have been determined by molecular model building (Campbell Smith & Arnott, 1978; Arnott, 1980; Millane, 1988). Most applications of molecular model building have been to polycrystalline systems, although there have been a number of applications to noncrystalline systems (Park *et al.*, 1987; Millane *et al.*, 1988). The approach is to use spacings and symmetry information derived directly from the diffraction pattern, coupled with the primary structure and stereochemical information on the molecule under study, to construct models of all *kinds* of possible molecular or crystal structure. These models are each refined (optimized) against the diffraction data, as well as stereochemical restraints, to produce the best model of each kind. The optimized models can be compared using various figures of merit, and in favourable cases one model will be sufficiently superior to the remainder for it to represent unequivocally the correct structure. The principle of this approach is that by making use of stereochemical constraints, the molecular and crystal structure have few enough degrees of freedom that the parameter space has a sufficiently small number of local minima for these to be identified and individually examined to find the global minimum. The X-ray phases are therefore not determined explicitly.

There are three steps involved in structure determination by molecular model building: (1) construction of all possible molecular and crystal structure models, (2) refinement of each model against the X-ray data and stereochemical restraints, and (3) adjudication among the refined models. The overall procedure for determining polymer structures using molecular model building is summarized by the flow chart in Fig. 4.5.2.2, and is described below.

The helix symmetry of the molecule, or one of a few helix symmetries, can be determined as described in Section 4.5.2.6.2. Different kinds of molecular model may correspond to one of a few different helix symmetries, usually corresponding to different