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4.5. Polymer crystallography

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4.5.1. Overview (R. P. MILLANE AND D. L. DORSET)

Linear polymers from natural or synthetic sources are actually polydisperse aggregates of high-molecular-weight chains. Nevertheless, many of these essentially infinite-length molecules can be prepared as solid-state specimens that contain ordered molecular segments or crystalline inclusions (Vainshtein, 1966; Tadokoro, 1979; Mandelkern, 1989; Barham, 1993). In general, ordering can occur in a number of ways. Hence an oriented and/or somewhat ordered packing of chain segments might be found in a stretched fibre, or in the chain-folded arrangement of a lamellar crystallite. Lamellae themselves may exist as single plates or in the more complex array of a spherulite (Geil, 1963). Diffraction data can be obtained from these various kinds of specimens and used to determine molecular and crystal structures.

There are numerous reasons why crystallography of polymers is important. Although it may be possible to crystallize small constituent fragments of these large molecules and determine their crystal structures, one often wishes to study the intact (and biologically or functionally active) polymeric system. The molecular conformations and intermolecular interactions are determinants of parameters such as persistence length which affect, for example, solution conformations (random or worm-like coils) which determine viscosity. Molecular conformations also influence intermolecular interactions, which determine physical properties in gels and melts. Molecular conformations are, of course, of critical importance in many biological recognition processes. Knowledge of the stereochemical constraints that are placed on the molecular packing to maximize unit-cell density is particularly relevant to the fact that many linear molecules (as well as monodisperse substances with low molecular weight) can adopt several different allomorphic forms, depending on the crystallization conditions employed or the biological origin. Since different allomorphs can behave quite differently from one another, it is clear that the mode of chain packing is related to the bulk properties of the polymer (Grubb, 1993). The three-dimensional geometry of the chain packing obtained from a crystal structure analysis can be used to investigate other phenomena such as the possible inclusion of disordered material in *chain-fold* regions (Mandelkern, 1989; Lotz & Wittmann, 1993), the ordered interaction of crystallite sectors across grain boundaries where tight interactions are found between domains, or the specific interactions of polymer chains with another substance in a composite material (Lotz & Wittmann, 1993).

The two primary crystallographic techniques used for studying polymer structure are described in this chapter. The first is X-ray fibre diffraction analysis, described in Section 4.5.2; and the second is polymer electron crystallography, described in Section 4.5.3.

Crystallographic studies of polymers were first performed using X-ray diffraction from oriented fibre specimens. Early applications were to cellulose and DNA from the 1930s to the 1950s, and the technique has subsequently been applied to hundreds of biological and synthetic polymers (Arnott, 1980; Millane, 1988). This technique is now referred to as *X-ray fibre diffraction analysis*. In fact, fibre diffraction analysis can be employed not only for polymers, but for any system that can be oriented. Indeed, one of the first applications of the technique was to tobacco mosaic virus (Franklin, 1955). Fibre diffraction analysis has also utilized, in some cases, neutrons instead of X-rays (*e.g.* Stark *et al.*, 1988; Forsyth *et al.*, 1989). X-ray fibre diffraction analysis is particularly suitable for biological polymers that form natural fibrous superstructures and even for many synthetic polymers that exist in either a fibrous or a liquid-crystalline state. Fibre diffraction has played an important role in structural studies of polynucleotides, polysaccharides, polypeptides and polyesters, as well as rod-like helical viruses, bacteriophages, microtubules and muscle fibres (Arnott, 1980; French & Gardner, 1980; Hall, 1984; Millane, 1988; Atkins, 1989). The common, and unique, feature of these systems is that the molecules (or their aggregates) are randomly rotated about an axis of preferred orientation. As a result, the measured diffraction is the cylindrical average of that from a single molecule or aggregate. The challenge for the structural scientist, therefore, is that of structure determination from cylindrically averaged diffraction intensities. Since a wide range of types and degrees of order (or disorder) occur in fibrous specimens, as well as a wide range of sizes of the repeating units, a variety of methods are used for structure determination.

The second technique used for structural studies of polymers is *polymer electron crystallography*. This involves measuring electron intensity data from individual crystalline regions or lamellae in the diffraction plane of an electron microscope. This is possible because a narrow electron beam can be focused on a single thin microcrystal and because of the enhanced scattering cross section of matter for electrons. By tilting the specimen, three-dimensional diffraction intensities from a single microcrystal can be collected. This means that the unit-cell dimensions and symmetry can be obtained unambiguously in electron-diffraction experiments on individual chain-folded lamellae, and the data can be used for actual single-crystal structure determinations. One of the first informative electron-diffraction studies of crystalline polymer films was made by Storks (1938), who formulated the concept of chain folding in polymer lamellae. Among the first quantitative structure determinations from electron-diffraction intensities was that of Tatarinova & Vainshtein (1962) on the α form of poly-γ-methyl-L-glutamate. Quantitative interpretation of the intensity data may benefit from the assumption of *quasi-kinematical* scattering (Dorset, 1995*a*), as long as the proper constraints are placed on the experiment. Structure determination may then proceed using the traditional techniques of X-ray crystallography. While molecular-modelling approaches (in which atomic level molecular and crystal structure models are constructed and refined) have been employed with single-crystal electron-diffraction data (Brisse, 1989), the importance of *ab initio* structure determination has been established in recent years (Dorset, 1995*b*), demonstrating that no initial assumptions about the molecular geometry need be made before the determination is begun. In some cases too, high-resolution electron micrographs of the polymer crystal structure can be used as an additional means for determining crystallographic phases and/or to visualize lattice defects.

Each of the two techniques described above has its own advantages and disadvantages. While specimen disorder can limit the application of X-ray fibre diffraction analysis, polymer electron diffraction is limited to materials that can be be prepared as crystalline lamallae and that can withstand the high vacuum environment of an electron microscope (although the latter restriction can now be largely overcome by the use of low-temperature specimen holders and/or environmental chambers).

4.5.2. X-ray fibre diffraction analysis (R. P. MILLANE)

4.5.2.1. *Introduction*

X-ray fibre diffraction analysis is a collection of crystallographic techniques that are used to determine molecular and crystal structures of molecules, or molecular assemblies, that form specimens (often fibres) in which the molecules, assemblies or

crystallites are approximately parallel but not otherwise ordered (Arnott, 1980; French & Gardner, 1980; Hall, 1984; Vibert, 1987; Millane, 1988; Atkins, 1989; Stubbs, 1999). These are usually long, slender molecules and they are often inherently flexible, which usually precludes the formation of regular three-dimensional crystals suitable for conventional crystallographic analysis. X-ray fibre diffraction therefore provides a route for structure determination for certain kinds of specimens that cannot be crystallized. Although it may be possible to crystallize small *fragments* or *subunits* of these molecules, and determine the crystal structures of these, X-ray fibre diffraction provides a means for studying the intact, and often the biologically or functionally active, system. Fibre diffraction has played an important role in the determination of biopolymers such as polynucleotides, polysaccharides (both linear and branched), polypeptides and a wide variety of synthetic polymers (such as polyesters), as well as larger assemblies including rod-like helical viruses, bacteriophages, microtubules and muscle fibres (Arnott, 1980; Arnott & Mitra, 1984; Millane, 1990*c*; Squire & Vibert, 1987).

Specimens appropriate for fibre diffraction analysis exhibit rotational disorder (of the molecules, aggregates or crystallites) about a preferred axis, resulting in cylindrical averaging of the diffracted intensity in reciprocal space. Therefore, fibre diffraction analysis can be thought of as 'structure determination from cylindrically averaged diffraction intensities' (Millane, 1993). In a powder specimen the crystallites are completely (spherically) disordered, so that structure determination by fibre diffraction can be considered to be intermediate between structure determination from single crystals and from powders.

This section is a review of the theory and techniques of structure determination by X-ray fibre diffraction analysis. It includes descriptions of fibre specimens, the theory of diffraction by these specimens, intensity data collection and processing, and the variety of structure determination methods used for the various kinds of specimens studied by fibre diffraction. It does not include descriptions of specimen preparation (those can be found in the references given for specific systems), or of applications of X-ray diffraction to determining polymer morphology (*e.g.* particle or void sizes and shapes, texture, domain structure *etc.*).

4.5.2.2. *Fibre specimens*

A wide variety of kinds of fibre specimen exist. All exhibit preferred orientation; the variety results from variability in the degree of order (crystallinity) in the lateral plane (the plane perpendicular to the axis of preferred orientation). This leads to categorization of three kinds of fibre specimen: *noncrystalline fibres*, in which there is no order in the lateral plane; *polycrystalline fibres*, in which there is near-perfect crystallinity in the lateral plane; and *disordered fibres*, in which there is disorder either within the molecules or in their crystalline packing (or both). The kind of fibre specimen affects the kind of diffraction pattern obtained, the relationships between the molecular and crystal structures and the diffraction data, methods of data collection, and methods of structure determination.

Noncrystalline fibres are made up of a collection of molecules that are *oriented*. This means that there is a common axis in each molecule (referred to here as the *molecular axis*), the axes being parallel in the specimen. The direction of preferred orientation is called the *fibre axis*. The molecule itself is usually considered to be a rigid body. There is no other ordering within the specimen. The molecules are therefore randomly positioned in the lateral plane and are randomly rotated about their molecular axes. Furthermore, if the molecule does not have a twofold rotation axis normal to the molecular axis, then the molecular axis has a *direction* associated with it, and the molecular axes are oriented randomly parallel or antiparallel to each other. This is often called *directional disorder*, or the molecules are said to be oriented *randomly up and down*. The average length of the ordered molecular segments in a noncrystalline fibre is referred to as the *coherence length*.

Polycrystalline fibres are characterized by molecular segments packing together to form well ordered microcrystallites within the specimen. The crystallites effectively take the place of the molecules in a noncrystalline specimen as described above. The crystallites are oriented, and since the axis within each crystallite that is aligned parallel to those in other crystallites usually corresponds to the long axes of the constituent molecules, it is also referred to here as the molecular axis. The crystallites are randomly positioned in the lateral plane, randomly rotated about the molecular axis, and randomly oriented up or down. The size of the crystalline domains can be characterized by their average dimensions in the directions of the **a**, **b** and **c** unit-cell vectors. However, because of the rotational disorder of the crystallites, any differences between crystallite dimensions in different directions normal to the fibre axis tend to be smeared out in the diffraction pattern, and the crystallite size is usefully characterized by the average dimensions of the crystallites normal and parallel to the fibre axis.

The molecules or crystallites in a fibre specimen are not perfectly oriented, and the variation in inclinations of the molecular axes to the fibre axis is referred to as *disorientation*. Assuming that the orientation is axisymmetric, then it can be described by an *orientation density function* $\Omega(\alpha)$ such that $\Omega(\alpha)\,\mathrm{d}\omega$ is the fraction of molecules in an element of solid angle $\mathrm{d}\omega$ inclined at an angle α to the fibre axis. The exact form of $\Omega(\alpha)$ is generally not known for any particular fibre and it is often sufficient to assume a Gaussian orientation density function, so that

$$\Omega(\alpha) = \frac{1}{2\pi\alpha_0^2}\exp\left(-\frac{\alpha^2}{2\alpha_0^2}\right), \qquad (4.5.2.1)$$

where α_0 is a measure of the degree of disorientation.

Fibre specimens often exhibit various kinds of disorder. The disorder may be within the molecules or in their packing. Disorder affects the relationship between the molecular and crystal structure and the diffracted intensities. Disorder within the molecules may result from a degree of randomness in the chemical sequence of the molecule or from variability in the interactions between the units that make up the molecule. Such molecules may (at least in principle) form noncrystalline, polycrystalline or partially crystalline (described below) fibres. Disordered packing of molecules within crystallites can result from a variety of ways in which the molecules can interact with each other. Fibre specimens made up of disordered crystallites are referred to here as partially crystalline fibres.

4.5.2.3. *Diffraction by helical structures*

Molecules or assemblies studied by fibre diffraction are usually made up of a large number of identical, or nearly identical, residues, or subunits, that in an oriented specimen are distributed along an axis; this leads naturally to helical symmetry. Since a periodic structure with no helix symmetry can be treated as a onefold helix, the assumption of helix symmetry is not restrictive.

4.5.2.3.1. *Helix symmetry*

The presence of a unique axis about which there is rotational disorder means that it is convenient to use cylindrical polar coordinate systems in fibre diffraction. We denote by (r, φ, z) a cylindrical polar coordinate system in real space, in which the z axis is parallel to the molecular axes. The molecule is said to have u_v helix symmetry, where u and v are integers, if the electron density

references