4.5. Polymer crystallography

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4.5.1. Overview

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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).

references