RECENT DEVELOPMENTS IN POLYMER CHARACTERIZATION USING X-RAY DIFFRACTION

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An introduction to polymer structure and morphology will be followed by a brief review of the structural parameters that are commonly measured using X-ray scattering techniques. New measurement capabilities and their relevance for understanding the structural basis of performance will be discussed. Two techniques, microdiffraction and surface-enhanced scattering, two areas of investigation, crystallization kinetics and polymer deformation, and two examples of analysis of data, complete analysis of 2-D wide-angle pattern and analysis of 2-D small-angle X-ray scattering patterns in elliptical coordinates will be highlighted to illustrate the recent developments in polymer X-ray diffraction.

1. Introduction

The acknowledged versatility of polymeric materials, which are widely used in the form of plastics, films, coatings and fibers, arises from the complex structural organization in these materials. X-ray diffraction (XRD) has long been successfully used to study various aspects of these structures in semicrystalline polymers, which includes thermoplastics, thermoplastic elastomers and liquid crystalline polymers. While many of the well established methods for the determination of molecular structure, evaluation of crystallinity and analysis of texture, continue to be improved to enhance the speed and precision of these measurements, new techniques are also being continually introduced. With the availability of intense X-ray sources, high-speed detectors and faster methods of analyzing the data, it is now possible to examine the structure at higher spatial resolution and smaller time scales. For instance, it is possible to follow development of structure in a processing line, such as in spinning and drawing operations, or in extrusion of films with a time resolution of less than one second [1–4], or examine the structural inhomogeneities that introduced over distances of a few micrometers by the temperature and stress gradients that exist during processing [5–7]. These developments also permit combining XRD analysis with other characterization techniques such as thermal analysis [8], rheology, spectroscopy and microscopy [9]. We will discuss some of these developments that are useful in understanding the hierarchical structure and inhomogeneity in polymers, and the analyses of the 2-D data that are now commonly obtained during these measurements.

2. Structure in Semicrystalline Polymers

Polymers exhibit structural hierarchy at multiple length scales (Figure 1) [10, 11]. As a polymer is cooled from the melt, a fraction of the polymer chains (0.5 nm dia.) crystallizes into lamellae or small crystallites (10 nm in size), and another fraction remains amorphous as it freezes in its molten state. The organization of these crystals into the next level of hierarchy depends on the external constraints. In fibers, these lamellae are organized into fibrils (100 nm in length), which in turn form filaments (5 μm dia) that are then made into fibers (0.5 mm dia).

**Fig. 1.** A model for the hierarchical structure that is expected to be present in an oriented semicrystalline polymer.
In the absence of an orientational force, the lamellae organize into spherulites (1–10 μm in diameter). X-ray scattering can be used to obtain structural information at three length scales—1, 10 and 100 nm—using scattering at wide-, small- and ultra small-angles, respectively.

A continuum of structures between the extremes of what are generally regarded as amorphous and crystalline phases are present in a real polymer, and these entities have complex organization. But, a model that describes the semicrystalline polymers in terms of two phases, an average amorphous and an average crystalline phase, has been found to be adequate for many practical purposes. The fraction of the material that is crystalline, the crystallinity or crystalline index, is an important parameter in the two-phase model. Crystallinity can be determined from a wide-angle X-ray diffraction (WAXD) scan by comparing the area under the crystalline peaks to the total scattered intensity [12]. The accuracy and the precision of these measurements can be improved by drawing a proper base-line, using an appropriate amorphous template, and by carefully choosing the crystalline peaks [13, 14]. The disorder in the crystalline domains can be evaluated by measuring the crystallite sizes which are related to the radial widths Δ(2θ) of the reflections at a scattering angle 2θ by the Scherrer equation. In reality, there are two contributions to the width: one is the size and the other is the paracrystallinity or microstrain [15, 16]. A more detailed analysis based on the Warren-Averbach method is widely used in metals and ceramics, but less so in polymers [17]. The disorder in the crystalline domains is also reflected in the unit cell dimensions. But, calculation of the unit cell parameters requires an accurate measurement of the positions of many crystalline peaks, which can be difficult. Therefore, in practice, relative positions of selected crystalline peaks are used as accurate measures of the changes in unit cell parameters [18, 19].

Structures at length scales larger than a unit cell (~10 nm instead of ~1 nm) can be investigated using small-angle X-ray scattering (SAXS). The methodology for these analysis is now highly developed and can be found in any standard literature [9, 20–24]. While WAXD is used to study the orientation of the crystals, and the packing of the chains within these crystals, SAXS is used to study the electron density fluctuations that occur over larger distances as a result of structural inhomogeneities. SAXS is widely used to study the lamellar structure by measuring parameters such as lamellar spacing, height and diameter of the lamellar stacks, and thickness of the transition layer between the crystalline and amorphous domains. In the analysis of fibers, SAXS can provide information about the details of fibrillar morphology such as fibril diameter and orientation, and large scale inhomogeneity such as micropores and cracks. This information is somewhat similar to that obtained from a transmission electron micrograph, with one important difference: SAXS requires no sample preparation, and the data is averaged over the area (typically >0.1 mm²) of illumination. SAXS is also used for studying conformation, size and dynamics of polymers in solutions and in gels.

3. New Methods to Study Polymer Structure

The two-phase model for the polymer has been quite useful in providing a qualitative understanding of the polymer properties in terms of its structure, but is not adequate for quantitative prediction of the polymer properties. For this purpose, a detailed knowledge of the characteristics and distribution of soft (amorphous) and hard (crystalline) domains, and the interactions between these domains is necessary. New techniques that have been introduced during the past decade provide precisely this information. Some of these techniques will be discussed here.

3.1. Microbeam Diffraction

Microbeam diffraction, or microdiffraction, has been used in semiconductor industry for over 25 years [25]. It is now being used to examine polymeric materials. In most routine characterization of polymers, it is assumed that the structure is homogeneous. But, this is not always the case. Temperature gradients are present during injection molding, and both temperature and stress gradients are present during extrusion and drawing. These gradients introduce structural inhomogeneities that influence polymer performance. Even filaments that are only 10 μm in diameter show variations in orientation and density across the cross section [5, 26]. These structural gradients, and the changes in these gradients during deformation can now be studied at spatial resolutions as small as 1 μm using microbeam diffraction [26]. An example of the typical structural gradients present in a shown in Figure 2 [6]. This diffractogram was obtained from Kevlar® fiber with a 3 μm
diameter X-ray beam at the ESRF (European Synchrotron Radiation Facility) synchrotron source. The data show that the Herman's orientation function of the crystalline domains in this 12 μm diameter fiber increases from 0.955 at the center to 0.980 at the surface of the fiber. The higher orientation of the skin layer is obviously due to large shear stresses at the spinneret, extensional forces in the air-gap and the solidification in the coagulation bath. Such a structural gradient implies that the modulus decreases from the skin to core. It is interesting to note that these inhomogeneities gradually decrease and disappear under uniaxial stress.

Microbeam techniques have reached a level of sophistication that it is now possible to focus X-rays on a micron size crystal and follow the changes in the structure from one crystal to the next within a spherulite [27]. Figure 3 shows a series of hundred patterns registered from a
spherulite of Poly(hydroxybutarate). The photographs show the changes in texture as the beam was stepped in increments of 3 μm along the vertical line drawn in the polarized optical micrograph of the spherulite shown on the left. The three photographs in the foreground show the differences in the texture of three crystals 60 μm apart.

In other experiments, liquid crystal molecular alignment of the memory state in polymer dispersed liquid crystal (PDLC) used for light valves and displays has been investigated [28]. Microbeam diffraction, both SAXS and WAXD, has been used to measure the misalignment of the crystalline cellulose microfibrils with respect to the fiber axis from the azimuthal broadenings both of the equatorial small-angle scattering streak and of Bragg reflections, and the diffuse scattering on the layer lines and the equator of the fiber diffraction diagram is used to identify the presence of disordered cellulose between the cellulose microfibrils and of defects inside the crystals [29]. Microbeam diffraction is also useful in understanding the interfaces, for instance the morphology of transcristalline regions [30].

Although the experiments described above, and other to be described later, were carried out at synchrotron sources, it should be noted that it is possible to carry out somewhat less demanding, but equally important measurements using in-house facilities. Microfocus X-ray beams from glass capillaries are now used to examine areas as small as 50 μm using sealed or rotating anode generators.

3.2. Grazing Incidence Diffraction

Inhomogeneities in materials can be explored from an entirely different perspective using grazing incidence diffraction (GID), also known as glancing-angle diffraction or surface-enhanced scattering [31–33]. X-rays have a refractive index of slightly less than 1 in a solid and hence undergo total external reflection for angles of incidence (α) less than a critical angle αc which is typically 0.2°. This totally-reflected beam penetrates only the top 50 Å at the surface. A small fraction of this beam will be diffracted giving a weak diffraction pattern from the surface region alone. For α>αc, we get diffraction from layers below ~50 Å from the surface of the film. Comparison of the two scans shows how the effect of the surface on the polymer structure. By keeping the angle α (see inset to Figure 4) that the X-ray beam makes a with the sample surface small (~1°), it is possible to limit the penetration depth of the X-rays into the sample, thus reducing background scattering from the substrate or the bulk of the polymer. By varying α, one can change the penetration depth of the X-rays from several nm up to typically several 100 nm (determined by the absorption length). Depending on the length scale of the structure of interest, the exit angle can be either small (~10 nm structures, GISAXS) or large (0.1 nm structures, GIXRD). This technique is useful for studying skin-core structural gradients at the surfaces of flat samples at depths from a fraction of a μm to more than a millimeter, as well structures near the surface at depths as small as a few nm [34–36]. The glancing angle technique is especially well suited if the polymers are heavy absorbers, e.g., fluoropolymers, in which the penetration depth of X-rays is as little as 5 μm at even large incidence angles of 1°. In industrial laboratories, these measurements are useful in analyzing multilayer films and in measuring the changes from skin to core in injection molded plastics, for instance.
in assessing the performance and dimensional stability of engineering plastics.

The utility of this technique is illustrated in Figure 4 which shows GID scans obtained at several incidence angles (α) from a multilayer packaging film [32]. The peak at 2θ=23.4° in the first scan (α=0.25°) is due to the crystals of polyethylene (PE) at the surface of the top PE layer. The peak at 2θ=22.8° in the second scan (α=0.5°) is due to the PE crystals beneath the surface in the top PE layer. As α is increased further, we begin to see the 25° peak from the biaxially oriented nylon layer. These measurements clearly demonstrate the ability of the GID technique for examining the surfaces, interfaces as well as depth-profiling the structure in polymeric materials.

GID technique is useful in many areas that deal with surfaces and interfaces including paints and coatings, adhesives, polymer-based electronic devices, and biocompatible materials. GID is currently used extensively to study nanostructured surfaces and the structure at air-polymer and polymer-substrate interfaces in polymer films deposited onto a substrate. Examples include the use of GID to assess the structure of polymer blends at and below the surface [37], and the study of orientation, conformation and packing modes of the chains near a substrate [38].

3.3. Crystallization Kinetics

Crystallization kinetics in polymers has been traditionally investigated using optical microscopy. But recently XRD has been used to further elucidate the development of hierarchical structure in polymers. Whereas optical micrograph show the crystal nucleation events and growth usually at the level of spherulites and fibrils, XRD results can show the growth of structures at smaller length scale, i.e., lamellae and crystals. These data can help us in determining whether crystallization occurs via spinodal decomposition or by nucleation, reveal the presence of mesophases and different polymorphs that are typically formed under different cooling conditions, and enable the study of transformation from one crystalline polymorph to another due to external conditions such as heat and stress.

Figure 5 shows typical results of the investigation using combined small- and wide-angle X-ray scattering from polyethylene during isothermal crystallization [9]. The data show that during primary crystallization, both average long period (L) and lamellar thickness (l_c) decrease significantly. These values are much smaller, approximately linear with log time, and decrease over a longer period of time during secondary crystallization. The decrease in L and l_c is attributed to formation or insertion of thinner lamellae within existing stacks. Similar experi-

![Fig. 5. Evolution of lamellar parameters (long period (L), crystal thickness (l_c), amorphous layer thickness (l_a) and invariant (Q) and crystallinity (Φ_c) extracted from time-resolved 1D SAXS/WAXD study of PE isothermal crystallization at 115°C. Left panel is the model of that describes the data show on the right (courtesy of B. Hsiao, SUNY, Stony Brook).]
ments have been carried out to study the comonomers and plasticizers that slow the rate of crystallization, and nucleating agents as well prior mechanical history such as shear that increase the rate of crystallization [39].

Crystallization mechanism other than nucleation and growth are being investigated using X-ray techniques. It has been suspected for quite some time that crystallization in oriented amorphous polymers is somehow different than in unoriented polymers [40]. These modes of crystallization are now attributed to spinodal mechanisms [41], and are being intensely investigated. Some recent experiments on polymer melts quenched below the melting temperature, spinodal kinetics are observed in small-angle X-ray scattering before the emergence of Bragg peaks at wide angles [28, 42]. It is proposed that a coupling between density and secondary order parameters such as chain orientation gives rise to a liquid–liquid binodal buried within the equilibrium liquid–crystal coexistence region. Orientation can enhance the kinetic role of this hidden binodal [43].

3.4. Polymer Deformation

The macroscopic modulus in inorganic materials is about the same order of magnitude as that calculated from the crystal modulus. In these materials, when the macroscopic modulus is far less than the crystal modulus, the reasons are clearly understood in terms of defects, dislocations and other well studied structural features. In contrast, the macroscopic modulus in many polymers is only a small fraction (about 1/50) of the crystal modulus. Reasons for this large difference between the maximum achievable modulus (single chain property) and the observed modulus (bulk property) are not clearly understood. This and other related questions can be answered by studying the deformation of structures at various length scales as the polymer is deformed in situ. Many results have been published in this area [44–50]. The instrument of choice is usually a synchrotron [51], although interesting experiments can be carried out on in-house equipment as well. The usefulness is illustrated with an example below.

Figure 6 (left panel) is the combined wide- and small-angle X-ray pattern obtained from a poly(ethylene terephthalate) fiber. The origin is $x=50$ and $y=250$ pixels. The SAXS data near the origin extends to about $2.5\,\mu$ (10.0919 nm). Right panels: A sequence of SAXS patterns starting from (a) unstretched fiber, (b) at some initial load (b) at a load close to the breaking strength and (d) after removing the load. The x and y scales are given in pixels. 2θ (rad) = (distance in pixels from the origin) exp.0.0816/515.
tic deformation is minimal even though the fiber was taken close to the breaking strength of the fiber. The relaxed fibers have four reflections whereas the fibers under load have two reflections. This is attributed to the surface-normal of the lamellae being tilted with respect to the fiber axis in the relaxed fibers, and being oriented along the fiber-axis in the stretched fibers. The changes from the four-point in the SAXS pattern of the relaxed fiber to the two-points in the fibers under stress suggests that structures at 10–50 nm length scales undergo large scale, reversible reorganization under stress. The results have shown that while the single-chain modulus is ~200 GPa, as measured by the increase in the chain-axis repeat of the chains within the crystals, the modulus of the lamellar structures is ~5 GPa, same as that of the bulk polymeric fiber. This indicates that reorganization of crystallites, as evidenced by the tilting of the lamellae, could be one of the reasons for the fiber modulus being a small fraction of the chain-modulus in semicrystalline polymers.

3.5. Analysis of Diffraction Patterns

Least-squares analysis of the complete 1-D scan is now commonly used to obtain the relevant structural parameters such as crystallinity, crystallite size and unit cell dimensions [53]. Rietveld refinement is also used when high quality data is available and when the structure of the polymer is known [54, 55]. In addition to these two techniques, full-pattern analysis of the 2-D pattern also provides the most reliable structural parameters. Because polymers are disordered, and considering that proper analysis of even a 1-D scans is difficult, progress in analysis of the 2-D data from polymers has been slow.

One parameter that can be obtained only from 2-D analysis of the diffraction scans is the amorphous orientation. While crystalline orientation can be determined from 1-D azimuthal intensity distribution of the crystalline reflections, and expressed in terms of Herman's orientation function [12], the evaluation of amorphous orientation is not straightforward even in amorphous polymers. It might appear that in completely amorphous polymers, such as rubber or polycarbonate, the azimuthal width of amorphous halo, in analogy with the crystalline orientation, is a measure of amorphous orientation. But unlike the crystalline peaks, the amorphous halo has a large non-zero base-line (Figure 7a). This is attributable to a large fraction of unoriented amorphous chain segments. Note that this base-line drops as the fiber is drawn indicating that a large fraction of the amorphous chain segments are being oriented during the drawing process. To fully describe the amorphous orientation, we need two parameters: one is the width of the amorphous peak and the other is the ratio of the area of the amorphous peak above the base line to the entire amorphous intensity. The first parameter represents the degree of orientation of the oriented amorphous components \( f_{oa} \), and the second \( F_{oa} \) describes the fraction of the oriented amor-
phous phase [19, 56]. Such analysis can be efficiently accomplished by 2-D fitting of the crystalline reflections and amorphous halo [57, 58]. This is illustrated in Figures 6b and 6c that shows, respectively, the raw data and fitted data for an oriented amorphous PET [59]. These data were fitted using just two functions, one to account for the uniform base-line intensity from the unoriented amorphous, and the other to account for the Gaussian intensity distribution from the oriented amorphous segments. A similar 2-D analysis of the diffraction pattern from semicrystalline polymers, with both crystalline and amorphous reflections can be used to rapidly determine all the parameters that characterize the polymer structure such as crystalline and amorphous orientation, disorder, size, crystallinity and unit cell dimensions [58].

In analyzing the 2-D data in the small-angle region, one is faced with a new problem. The data cannot be described conveniently in either the Cartesian or the polar coordinates [60, 61]. A detailed investigation of the contours of the SAXS pattern has shown that, because of the manner in which the lamellar lattice is deformed, the small-angle data requires elliptical coordinates shown in Figure 8a. In the figure the lamellar reflections are overlaid on an elliptical $u$-$v$ coordinate system. This is equivalent to the Cartesian $x$-$y$ or polar $r$-$\theta$ coordinates. That the shape of the scattering is indeed elliptical can be seen in a plot of the $(L_\phi)^2$ vs. $\tan^2 \phi$,
which is straight line out to azimuthal angles 
\( \sim 70^\circ \) as predicted for an elliptical curve (Figure 8c) [61]. Here, \( \phi \) is the angle of a point along the maximum intensity contour line shown in figure (a), and \( L\phi \) is the Bragg-spacing corresponding to this point measured along the \( \gamma \)-axis. An example of the fit to the SAXS data from nylon \( \theta \) fibers is shown in Figures 8d and 8e [11]. This fit was achieved using just two functions, one to describe the lamellar reflections. In addition to rapid analysis of the data, such a procedure provides complete information on the lamellar organization such as the lamellar spacings (from the position of the reflections in \( \theta \)), the angle of tilt of the crystals with respect to the fiber-axis (from the azimuthal separation of the reflections), the diameter and the height of the lamellar stacks (from the width of the lamellar reflections), the Bragg-spacing corresponding to this point measured along the fiber-axis (from the azimuthal separation of the reflections in \( \phi \)- and \( \gamma \)-directions). Additional parameters concerning the fibrils and voids can be obtained from the equatorial streaks.

Acknowledgment
I wish to thank Dr. C. Riekel (ESRF) for giving permission to use Figures 2 and 3, and Prof. B. Hsiao for providing Figure 5.

References


