X-ray Diffraction Methods

2.1 X-ray Radiation
2.2 Theoretical Background of Diffraction
2.3 X-ray Diffractometry
2.4 Wide Angle X-ray Diffraction and Scattering

• X-ray diffraction methods are the most effective methods for determining the crystal structure of materials. Diffraction methods can identify chemical compounds from their crystalline structure, not from their compositions of chemical elements.

• It means that the different compounds (or phases) that have the same composition can be identified. Diffraction methods include X-ray diffraction, electron diffraction and neutron diffraction. X-ray diffraction by crystals was discovered in 1912, and since then it has been the most extensively studied and used technique for materials characterization.

• This chapter introduces X-ray diffraction methods. The theoretical background of diffraction discussed in this chapter is also applied to other types of diffraction methods. X-ray diffraction methods can be classified into two types: spectroscopic and photographic.

• The spectroscopic technique known as the X-ray powder diffractometry, or simply X-ray diffractometry, is the most widely used diffraction method and the main technique discussed in this chapter.

• Photographic techniques are not widely used as diffractometry in modern laboratories. One reason is that spectroscopic methods can replace most photographic methods. However, photographic methods are used to determine unknown crystal structures. These methods will not be discussed in this chapter because they require extensive knowledge of crystallography.
2.4 Wide Angle X-ray Diffraction and Scattering
Wide angle X-ray diffraction (WAXD) or wide angle X-ray scattering (WAXS) is the technique that is commonly used to characterize crystalline structures of polymers and fibers. The technique uses monochromatic X-ray radiation to generate a transmission diffraction pattern of a specimen that does strongly absorb X-rays, such as organic or inorganic specimens containing light elements. Wide angle X-ray diffraction or scattering refers to X-ray diffraction with a diffraction angle $2\theta > 5^\circ$, distinguishing it from the technique of small angle X-ray scattering (SAXS) with $2\theta < 5^\circ$. SAXS will not be discussed in Chapter 2 because its complexity in theoretical treatment is beyond the scope of this book.
2.4 Wide Angle X-ray Diffraction and Scattering

2.4.1 Wide Angle Diffraction
2.4.2 Wide Angle Scattering
2.4.1 Wide Angle Diffraction

2.4.2 Wide Angle Scattering
Arrangement of WAXD

Figure 2.28 illustrates the optical arrangement of WAXD. The incident X-ray beam is formed after X-rays pass through a monochromator and a collimator (not shown in Figure 2.28). The highly monochromatic and parallel X-ray beam strikes a sample and generates a diffracted beam at angle $2\theta_i$ with respect to the transmitted beam. The diffracted beams are recorded as an image on a film or by an area detector that is placed at distance $D$ from the specimen and perpendicular to the incident beam direction. Usually, there is a beam-stop (made from lead) placed in front the transmitted beam to prevent beam from striking the film or area detector directly. Thus, WAXD is a photographic method, differing from the spectroscopic methods of diffractometry. Small angle scattering uses the same optical arrangement as WAXD, except that $D$ is longer in order to record scattering from small $2\theta$ angles.
The Bragg angle $\theta_i$ is determined by a simple geometric relationship:

$$\theta_i = \frac{1}{2} \tan^{-1} \frac{R_i}{D}$$

where $R_i$ is the distance between the transmitted beam and the diffracted beam on the recording film plane as shown in Figure 2.28. The $d$-spacing of the crystallographic plane generating diffraction is calculated according to Bragg’s Law:

$$d = \frac{\lambda}{2 \sin \left( \frac{\tan^{-1} \left( \frac{R_i}{D} \right)}{2} \right)}$$

The accuracy of $d$-spacing measurement relies on the measurement of $R$ and $D$. A reliable method for determining $D$ is to calculate it from Equation 2.18 with a known $d$-spacing of crystal, not from a direct measurement. $R_i$ is commonly obtained by measuring $2R_i$ on a film in order to avoid the problem of determining the center of transmitted beam on the film.
Preferential Orientation of Polymer Crystals

One of the main reasons for using WAXD for polymer analysis is that crystalline polymers are frequently presented in the form of fibers with preferential crystal orientation with respect to the fiber axis; for example, the $a$–$b$ crystallographic plane is perpendicular to the fiber axis that is along a vertical direction in Figure 2.28. WAXD analysis can readily reveal the preferential orientation of polymer crystals for a diffraction pattern recorded on the film.

Polyethersulfone (PES) fibers

Reciprocal Lattice of Fibrous Polymer Crystals

Figure 2.29 illustrates the generation of such a diffraction pattern of highly oriented polymer crystals using the Ewald sphere. The orientation of crystals with $a$–$b$ planes perpendicular to a fiber axis can be represented by the reciprocal lattice of the crystals with $c^*$ perpendicular to the incident beam. The $a$–$c$ or $b$–$c$ planes of crystals can be randomly oriented in the fiber. Collective reciprocal lattices of the crystals with alignment of $a$–$b$ plane normal along the fiber axis but with random orientation of $a$–$c$ and $b$–$c$ planes are equivalent to rotating the reciprocal lattices around the $c^*$ axis. These collective reciprocal lattices form a series of co-centered rings as shown in Figure 2.29.

Figure 2.29  A WAXD pattern of highly oriented polymer crystals with their reciprocal lattices and the Ewald sphere.
Diffraction by Fibrous Polymer Crystals

As illustrated in Figure 2.10, the intersections between rings of reciprocal lattices and the surface of the Ewald sphere generate diffraction. Consequently, the oriented crystals in fiber generate a diffraction pattern as shown in the film plane of Figure 2.29.

Figure 2.29  A WAXD pattern of highly oriented polymer crystals with their reciprocal lattices and the Ewald sphere.
Diffraction Pattern of Highly Oriented Polymer Crystals

The diffraction spots on the **equatorial plane** represent the diffraction of [hk0] planes. A line of diffraction spots above or below the equatorial plane should represent the diffraction of (hkl) planes or (hk|) planes, respectively. The diffraction principles of oriented crystals discussed here apply to all type of samples through which X-rays can be transmitted, even though the main applications of WAXD are for crystalline polymers and proteins (special types of polymers). The most famous application to proteins is probably the determination of the DNA double helix structure.

![Diagram of a WAXD pattern with the Ewald sphere, reciprocal lattice, and detector plane](image)

**Figure 2.29** A WAXD pattern of highly oriented polymer crystals with their reciprocal lattices and the Ewald sphere.
WAXD Pattern of Kevlar Fibers

Figure 2.30 shows an example of a WAXD pattern of Kevlar fibers. The fiber axis is perpendicular to the incident X-ray beam and aligned in the meridional plane. The [hkl] diffraction spots are mainly located on the meridional plane with high symmetry with respect to the equatorial plane.


https://nptel.ac.in/courses/116102006/2
WAXD Patterns of Kevlar Fibers during Stretching

RSC Adv., 2016, 6, 81552–81558

https://pubs.rsc.org/en/content/articlelanding/2016/ra/c6ra17671b/unauth#!divAbstract
https://pubs.rsc.org/en/content/articlepdf/2016/ra/c6ra17671b
WAXD Pattern of a Composite with UHMWPE and Ceramic Particulates

Figure 2.31 shows another example of WAXD pattern of a composite with ultra-high molecular weight polyethylene (UHMWPE) fibrils and nano-sized ceramic particulates. The composite sample has been mechanically drawn in order to increase alignment of UHMWPE fibrils. The composite sample is perpendicular to the incident beam but the fibrils are aligned with a drawing direction marked on the pattern. The WAXD pattern revealed the preferential orientation of UHMWPE crystals and the perfectly random orientation of ceramic particles. A digital area detector provides a high-contrast WAXD pattern as shown in Figure 2.31.

![Figure 2.31](image)

**Figure 2.31** A WAXD pattern of a composite sample containing ultra-high molecular weight polyethylene (PE) fibrils and nanoparticles of hydroxyapatite (HA). The arrow indicates the drawing direction in the composite sample.
2.4.1 Wide Angle Diffraction

2.4.2 Wide Angle Scattering
The terms ‘wide angle X-ray scattering’ and ‘wide angle X-ray diffraction’ are often used without clear distinction because there is little difference in their instrumentation. However, ‘scattering’ is a more general term than ‘diffraction’ that refers to constructive interference of scattered rays from crystallographic planes. Wide angle X-ray scattering (WAXS) is considered to be an appropriate technique for examining both crystalline and non-crystalline materials. WAXS is particularly useful for polymers because a non-crystalline (amorphous) structure is the common characteristic of polymers, even for crystalline polymers because they are not totally crystalline.
An amorphous material can generate a diffraction spectrum in a $2\theta$ range as shown schematically in Figure 2.32. For an amorphous polymer, sharp diffraction peaks are absent from its diffraction spectrum, only showing a wide halo peak. Although there is a lack of diffraction peaks from crystallographic planes, an amorphous polymer may exhibit scattering intensity variations because of fluctuations in electron density over a certain length scale.

The fluctuations in electron density of polymers result from heterogeneity of their mass and chemical distributions at a microscopic level. WAXS is used to detect microscopic features less than about 10 nm in length, compared with SAXS that is often used to examine microscopic features greater than about 50 nm.

**Figure 2.32** X-ray scattering by amorphous materials showing the difference in range of small angle and wide angle scattering.
WAXS and SAXS Scattering Intensity Curves

WAXS/SAXS patterns are typically represented as scattered intensity as a function of the magnitude of the scattering vector \( q = \frac{4 \pi \sin(\theta)}{\lambda} \). Here \( \theta \) is the angle between the incident X-ray beam and the detector measuring the scattered intensity, and \( \lambda \) is the wavelength of the X-rays.

Fig. 3 (a) Wide angle X-ray scattering (WAXS) of polyurethane 1, (b) small angle X-ray scattering (SAXS) of polyurethane 1.

https://www.researchgate.net/publication/298430141_An_adhesive_elastomeric_supramolecular_polyurethane_healable_at_body_temperature
WAXS is commonly *(not always)* presented with **scattering intensity curves** over a range of *scattering vector magnitude* as shown in Figure 2.33, or two-dimensional (2D) **scattering intensity maps** as shown in Figure 2.34. The scattering vector magnitude is equal to $4\pi (\sin \theta) \lambda^{-1}$. The scattering vector magnitude is approximately proportional to length of $R_i$ in Figure 2.28; however, it is independent of the distance between the sample and detector plane. We may interpret a WAXS curve or map as the scattering intensity variation along the radial direction in the detector plane (Figure 2.28).

(a) A WAXS diffraction pattern taken in an area with a diameter of 10 μm approximately to the left of the centre of a 400-μm diameter LC n-butanol droplet. The intense diffuse bands at the left top and right bottom correspond with a scattering vector $q = 1.7 \ \text{Å}^{-1}$. (b) WAXS scattering intensity in the range 0.4 to 1.8 Å$^{-1}$ for isotropic liquid at 140 K and LC at 145 K (corresponding to the data in (a)).

https://www.nature.com/articles/srep42439/figures/4
WAXS of PTFE

Figure 2.33 shows an example of WAXS curves for a polymer (polytetrafluoroethylene). It is a crystalline polymer at room temperature and its crystalline structure is revealed by the sharp peaks as shown by the dashed line in Figure 2.33.

Fig. 4. A typical Teflon 7C WAXS trace showing a strong crystalline peak superposed over an amorphous halo.

https://pdfs.semanticscholar.org/e329/33bfe947d94f2d719b53e61dced4700a6dc2.pdf
WAXS Profile of Ethylene–Propylene (EP) Copolymer

The polymer becomes an amorphous molten phase at elevated temperature; consequently, the peaks disappear and become a broad ‘hilly’ curve as shown by the solid line.

Fig. 2. Linear WAXD profile of the EP copolymer annealed at 160°C for 10 min and then quenched to room temperature to crystallize for several days.

Fig. 6. Linear WAXD profiles at different strains (0.0, 0.12, 0.25 and 0.38) for the same EP copolymer crystallized as that in Fig. 4.
Crystalline-amorphous Transition Revealed by WAXS

FIG. 1. Wide-angle x-ray scattering data measured for OTP for different temperatures above $T_g$. The corresponding data for a crystalline sample are shown in the inset.

Crystalline-amorphous Transition Revealed by WAXS
A WAXS diffraction pattern taken in an area with a diameter of 10 μm approximately to the left of the centre of a 400-μm diameter LC n-butanol droplet. The intense diffuse bands at the left top and right bottom correspond with a scattering vector $q = 1.7 \, \text{Å}^{-1}$. (b) WAXS scattering intensity in the range 0.4 to 1.8 Å$^{-1}$ for isotropic liquid at 140 K and LC at 145 K (corresponding to the data in (a)).

https://www.nature.com/articles/srep42439/figures/4
WAXS of Polyetheretherketone (PEEK)

Figure 2.34 shows an example of WAXS presentation with a 2D map (Figure 2.34a) and also scattering intensity curves along two perpendicular directions (Figure 2.34b). The WAXS intensities of extruded non-crystalline polyetheretherketone (PEEK) indicate a certain degree of microstructural alignment along the extrusion direction. The alignment is revealed by the difference in the scattering intensity at about 1.3 Å⁻¹ in equatorial and meridional directions. The difference is shown in both the intensity contours in the 2D map and the intensity curves along equatorial and meridional directions.

Figure 2.34 added

Jasmin Althaus; Hans Deyhle; Bert Müller; Oliver Bunk; Per Magnus Kristiansen, “Anisotropy in polyetheretherketone films”, J. of Nanophotonics, 6(1), 063510 (2012). https://doi.org/10.1117/1.JNP.6.063510
End of 2.4
Peak width is inversely related to crystal size; that is, **peak width increases with decreasing crystal particle size** $t$, as shown in Figure 2.21.

$$t = \frac{0.94 \lambda}{B \cos \theta_B}$$

**Figure 2.21** Change of peak line width with crystal size. (Reproduced with permission from R. Jenkins and R.L. Snyder, *Introduction to X-ray Powder Diffractometry*, John Wiley & Sons Inc., New York. © 1996 John Wiley & Sons Inc.)